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

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Abstract

A numerical modeling approach is proposed for the assessment of the nutrient loading of coastal waters from atmospheric sources. The 3-D eutrophication model NEUTRO was enhanced to simulate the spatial distribution and temporal variations of nutrients, planktons and dissolved oxygen due to atmospheric nutrient loadings. It was found that nutrient loading from the atmospheric wet and dry deposition was remarkable during hazy days, the contribution being between 2 and 8 times that of non-hazy days; the smoke haze was due to biomass burning in the Southeast Asian region as discussed in a companion paper on field observations. Atmospheric nutrient loads during hazy days can lead to anthropogenic eutrophication and chemical contamination. The importance of regional smoke haze events in relation to non-hazy days to atmospheric nutrient deposition in terms of their biological responses in the coastal water of the Singapore region was investigated. The percentage increases of surface water nutrients due to atmospheric deposition during non-hazy and hazy days from seawater baseline were estimated. Model computations showed that atmospheric fluxes might account for up to 17–88% of total mass of nitrate nitrogen in the water column during hazy days and 4 to 24% during non-hazy days, which might be a relatively significant contribution into regional eutrophication. The results obtained from the modeling study could be used for a better understanding of the energy flow through the marine food web, exploring various possible scenarios concerning the atmospheric deposition of nutrients onto the coastal zone and studying their impacts on water quality.

1 Introduction

Increasing population, industrialization and agricultural activities will increase the atmospheric deposition (AD) of a wide variety of fixed and organic nitrogen (N) and phosphorous (P) species to both the pelagic and coastal oceans (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). 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 is an important source of limiting nutrients to the ocean, potentially stimulating oceanic biota. This will 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 has been particularly intense in years when the weather has been noticeably dry due to the effects of the *El Niño* phenomenon. By far the main source of forest fires caused by small holders and plantation owners has been Indonesia. The smoke from the forest fires has not only caused widespread air pollution in Indonesia itself but also in neighboring countries, resulting in what is termed as transboundary air pollution (Balasubramanian et al., 1999; Muraleedharan et al., 2000; Balasubramanian et al., 2001). The regional smoke haze events in Southeast Asia (SEA) generally occur during the southwest monsoon (SWM) period in *El Niño*-years, because of increased fire, favorable atmospheric conditions and wind directions. The burning activities usually cease by October/November when the gradually interspersing northern monsoon brings abundant rainfall.

The haze events, arising from forest fires modulated by El Nio Southern Oscillation (ENSO), have plagued SEA, and are likely to affect atmospheric fluxes of nutrients and other pollutants into aquatic systems. Despite its episodic nature, it is important in determining haze nutrient composition and its impacts on aquatic ecosystem which so far has not been studied in SEA. Most of local knowledge regarding contamination due to forest fires (biomass burning) originates from earlier studies conducted elsewhere, at various parts of the world (e.g., The United States, Australia, Brazil, Mexico, Africa). However, the results of these studies are of little use in assessing the environmental impacts of the resulting pollution since their main objective was to quantify the flux to the atmosphere of various trace gases such as CO_2, CH_4, and N_2O from biomass burning. A significant fraction of the N and P species entering coastal and estuarine

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ecosystems along the Singapore and surrounding countries arises from atmospheric deposition; however, the exact role of atmospherically derived nitrogen in the decline of the health of coastal, estuarine, and inland waters is still uncertain.

Water quality degradation is a worldwide object of concern. SEA surface waters receive a large nutrient supply of which a substantial portion is of anthropogenic origin. 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. Algal blooms resulting from complex coupled physical/biological processes are steadily increasing in coastal waters. No studies have investigated the responses of marine ecosystems to atmospheric deposition of nutrients due to episodic haze events in SEA. It is therefore necessary 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. In order to examine the quantitative response of the pelagic food web to atmospheric N and P deposition events, numerical modeling study is required. Water quality impact assessment of pollution sources (point and distributed) onto the aquatic ecosystem can be obtained using numerical models. Accordingly, the present study is embarked on quantifying the distribution of nutrients from atmospheric deposition on coastal water and their contribution to the coastal eutrophication. The model provides a convenient tool for testing hypotheses about the processes, otherwise not fully understood from direct measurements.

The need for water quality management tools has arisen as a result of increased eutrophication of coastal waters throughout the world. Water quality modeling is one of the most common approaches used to study the various processes involved that lead to the rapid degradation of the ecosystems. Recent increases in computing power have made the modeling of higher spatial dimensionality (i.e. 2-dimensional (D) and 3-D models) possible. The combination of a fine-resolution grid, sophisticated numerical schemes, and a complex ecological model present a serious computational challenge that can only be met with the use of state-of-the-art high-performance computer systems. Besides the advection-diffusion redistribution, a series of terms for the biochemical interactions between non-conservative quantities is considered. Many models for the description of the trophic and biochemical evolution in lakes, reservoir and marine environment have been developed in the past (Orlob, 1983; Thomann and Muller, 1987; Chapra, 1997) and in the last few years (Angelini and Petrere, 2000). The impacts of atmospheric N and P species deposition fluxes on the Singapore coastal water quality are 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 and dissolved oxygen in the water column due to nutrient loadings from point and distributed sources. NEUTRO is enhanced to predict the fate of nutrient transport and to assess the water quality changes that could result from atmospherically deposited nutrient loading during hazy and non-hazy days in Singapore waters.

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. There are two steps involved in the application of the model. In the first step, data on atmospheric nutrient fluxes and baseline concentration of diluted nutrients in the water column are utilized to explore possible scenarios allowing qualitative and quantitative understanding of the relative importance of atmospheric and ocean nutrient fluxes in this region. In the second step, the model is used to study spatial and temporal variability of eutrophication rate in the Singapore Strait due to changes in nutrient fluxes from atmospheric deposition in the model domain.

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2 Materials and methods

2.1 Study area

Singapore is a very environment conscious smallest country in Southeast Asia with total land area of 710 km^2. The country is immediately north of the Equator and positioned off the southern edge of the Malay Peninsula between Malaysia and Indonesia. 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. The port of Singapore, one of the world's busiest in terms of shipping tonnage, is a key component of Singapore's prosperity and economic health. Tourism is an important sector of Singapore's economy. During the Northeast Monsoon (NEM), northeast winds prevail, whereas southeast/southwest winds prevail during the SWM season. There is often haze from August to October due to bush fires in neighboring Indonesia. In general, dry weather is the result of lack of convection or stable atmosphere which prevents the development of rain-bearing clouds. Generally, Singapore is frequently affected by transboundary pollution from land, air and water of neighboring countries. Such a unique combination requires an efficient management of coastal environment.

2.2 Data

The study of atmospheric (dry and wet) deposition was carried out at St. Johns Island (SJI, latitude 1°13′10″ North and longitude 103°50′54″ East) in Singapore to estimate the AD nutrient fluxes during the recent 2006 SEA smoke haze episodes and non-haze days onto the coastal water. The nutrients from atmospheric deposition were quantified by analyzing dry deposition (55 number of aerosol samples) and wet deposition (21 number of rainwater samples) samples collected by the field monitoring during September 2006 to January 2007 using developed laboratory protocols (as in Sundarambal et al., 2006, 2009; Karthikeyan et al., 2009). The above sampling period includes both hazy days during 2006 SEA haze episode and non-hazy days. The types of nutrients identified from atmospheric wet and dry nutrient depositions were N species such as ammonium (NH_4), nitrate (NO_3), nitrite (NO_2), total nitrogen (TN) and organic nitrogen (ON), and P species such as phosphate (PO_4), total phosphorous (TP) and organic phosphorous (OP). More details can be found in the companion paper on field observations.

The 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 Table 1 and 2 and their detailed atmospheric deposition flux calculations can be found in the companion paper on field observations. The concentration of nutrients in Table 2 was selected based on Pollutant Standards Index (PSI, ranging 81–93 during haze and 35–39 during non-hazy days; NEA, Singapore) for wet atmospheric deposition. From the field measurement of nutrient concentrations from AD, it was evident that there was higher nutrient input into surface water during the haze period as compared to clear or non-haze period. The quantified wet atmospheric flux of inorganic nitrogen was 3.92 and 18.5 g/m^2/year into coastal waters during non-hazy and hazy days. On an event basis, the minimum and the maximum wet deposition fluxes of macro-nutrients were highly variable. The ratio of haze and non-haze concentrations for dry and wet AD clearly shows that AD contributes a larger proportion of nutrients into coastal waters during haze events.

About 14 seawater samples were also collected during 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. From the regression studies, a correlation between concentrations of nutrients in the atmosphere and in seawater was observed, indicating the significance of the atmospheric input of nutrients into the coastal waters of Singapore. The measured concentration range of parameters (in terms of minimum-maximum) was: phytoplankton (0.018–0.172 mgC/l), NH_4 (0.003–0.027 mg/l), NO_2+NO_3 (0.006–0.027 mg/l), TN (0.037–0.199 mg/l), PO_4 (0.005–0.015 mg/l) and TP (0.028–0.035 mg/l) while PSI was in the range of 23–109 during the sampling period. 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 1 shows the relationship between atmospheric depositions and seawater quality at the surface and also the relationship between phytoplankton and TN in seawater. Average baseline concentrations of nutrients in Singapore seawater (see Table 2, derived from Tkalich and Sundarambal, 2003) were used to estimate model kinetics. 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.

2.3 The concept of the model

Contaminant inputs into a coastal system are naturally subjected to physical and biogeochemical processes that effect the concentration of the contaminant in the water column. A substance or property whose concentration depends solely on physical transport and dilution is said to be a "conservative" substance. Most contaminants are non-conservative. Therefore, their distributions are subject to other processes in addition to physical transport including: biological uptake and release; chemical transformations; and interaction with the atmosphere. If the physical transport and mixing of a contaminant in a parcel of water can be estimated, the difference in concentration distribution 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 seawaters and adjacent water bodies, such as the Malacca Strait, South China Sea and Java Sea. Simulation of the ambient concentration of admixture 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

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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, 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 are 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 simulates long-term physical circulation and nutrient dynamics in Singapore seawater and surrounding seas. This model provides information on nutrient concentrations, primary production and dissolved oxygen necessary to estimate large-scale ecological effects.

The modeled nutrients consist of ammonium-nitrogen, nitrate-nitrogen (NO_2+NO_3), phosphate, organic nitrogen, organic phosphorus, total nitrogen and total phosphorous. Detailed NEUTRO model description and eutrophication kinetics are given in Tkalich and Sundarambal, 2003. For the present study, NEUTRO is enhanced in its capability to address the atmospheric input of macronutrients. The enhanced model (Sundarambal et al., 2006) is subsequently utilized to investigate the fate of atmospherically deposited nutrients in the water column, and its impact on water quality and aquatic ecosystems (Sundarambal et al., 2010). The present model can simulate the fate of transport of nutrients from point source (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

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transport; and physical, chemical, and biological transformation. Consider the coordinate system with x- and y- coordinates in the horizontal plane and the z- coordinate in the vertical plane. The 3-D transport equation is described as follows:

$$\frac{\partial C_j}{\partial t}+\frac{\partial C_j U}{\partial x}+\frac{\partial C_j V}{\partial y}+\frac{\partial C_j\left(W-w_j\right)}{\partial z}-\frac{\partial}{\partial x}\left[E_x\frac{\partial C_j}{\partial x}\right]-\frac{\partial}{\partial y}\left[E_y\frac{\partial C_j}{\partial y}\right]-\frac{\partial}{\partial z}\left[E_z\frac{\partial C_j}{\partial z}\right]$$

$$=\frac{Q\left(S_j-C_j\right)}{\Delta h\Delta x\Delta y}+R_j \qquad (1)$$

where C_j=concentration of jth pollutant (mg/l); S_j=contamination of the liquid source with jth pollutant (mg/l); Q=discharge of the source (m^3/sec); R_j=chemical reaction terms, corresponding to the interaction equations for jth state variable (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 jth pollutant at initial time, C_j^B is the baseline concentration of jth state variable obtained from field measurements; w_j=settling velocity of jth pollutant; U, V, W=tidal current in x-, y-, and z- directions respectively. The values of U, V, and W, E_x, E_y and E_z are computed using the 3-D hydrodynamic model (TMH, Pang and Tkalich, 2004) and are used as input to NEUTRO. Values of concentration (C_j) are computed at the nodes of a 3-D grid at different instances of time using transport equation. The missing element of atmospheric input of macronutrients was included in NEUTRO to explain anomalies in primary production. The enhanced model was utilized to investigate the fate of atmospherically deposited pollutants (nutrients) in Singapore and surrounding seawater in this study. The new atmospheric flux (F) in the model is quantified by source term $F=QS_j$ in the transport equation. The wet deposition flux (F) in the model is calculated by *precipitation* × *surface area*× *concentration* (S_j) of AD species and the dry deposition flux (F) by *settling velocity of AD species* × *surface area* × *concentration*

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(S_j) of AD species.

2.3.2 Marine Hydrodynamic Model (TMH)

A 3-D free surface primitive equation coastal ocean model Marine Hydrodynamic Model (TMH), developed at the Tropical Marine Science Institute, National University of Singapore, has been 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). 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. The mean tidal range is about 2.2 m and the maximum range is up to 3 m during spring tides. The hydrodynamic and water quality processes in Singapore coastal zone were discussed by Chan et al. (2006) and Sundarambal et al. (2008). In this study, a typical SWM covering a 5 days spring tide period from 30 June 2003 to 5 July 2003 was used for model simulation. 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.

2.4 Model setup, Forcing data and initial conditions

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). The bathymetry of the Singapore seawater and the model domain are shown in Fig. 2. Domain size, current velocities and free surface dynamics for NEUTRO were obtained using a semi-implicit sigma-coordinate hydrodynamic model (TMH) (Pang and Tkalich, 2004) having 500 m horizontal resolution and 10 vertical sigma layers. In water quality model, a horizontal grid of 500 m×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,

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20, 40, 60, 80 and 120 m was used. The mean concentrations of nutrients in Singapore seawater were taken from Tkalich and Sundarambal (2003) as model baseline. Generally, the water column is well mixed in Singapore and Johor Straits due to intensive tidal currents. The initial condition of each state variable is 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 surface water were obtained based on field monitoring and laboratory methods of nutrient analysis (as in Sundarambal et al., 2006, 2009). The open boundaries for the water quality modeling are 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 carries nutrients and other contaminants with them (i.e. transboundary fluxes).

2.5 Model calibration

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) are used to estimate kinetic coefficients by means of iterative model runs through the comparison of model predictions with baseline concentrations. The chosen values of the coefficients (Tkalich and Sundarambal, 2003) have to keep the state variables at quasi steady-state concentrations (baseline) under the fixed nutrient load conditions. The calibrated model is used to predict the water quality with an independent set of data as a part of validation exercise for model evaluation. Test runs show that NEUTRO reproduces the cycles of phytoplankton and nutrient concentrations with a good accuracy (Sundarambal et al., 2008).

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2.6 Model Validation

Validation of any numerical model is a quite complicated process. There are two standard ways to validate it either by comparing model results with analytical solutions or by comparing model results with measurements, or both. Comparison with measurements is preferable because it can verify the governing equations of the model as well as the approximated numerical solution of the equations. The model was simulated for the period from 18 March 2002, 12:00 p.m. to 19 March 2002, 12:00 p.m. for 24-h hindcast to compare with field measurement data at a monitoring location in the East Johor Strait. The computed concentration of state variables were in close agreement with field measurements (Fig. 3). The absolute error between predicted and observed Dissolved Oxygen (DO) was −0.5 mg/l. The negative and positive error occurs when the predicted values of model are higher and lower than the observed values respectively.

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 measures 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 (X) from its baseline (X) upon an increase of atmospheric nitrite + nitrate load input (Y) from its initial base load (Y) at every simulation time step as follows:

$$\frac{Y+\Delta Y}{Y} \times 100\% = \frac{X+\Delta X}{X} . 100\% \qquad (2)$$

2.8 Modeling approach

A mass balance modeling approach was carried out to predict nutrient fate and transport in the coastal water that could result from the varying atmospherically deposited nutrient loading conditions. The atmospherically deposited nutrients were assumed to be deposited uniformly onto water surface and spatially distributed by the action of tidal currents. IIn this modeling study, N and P species from AD were considered. Once N or P was deposited onto water surface, it was 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 planktons due to AD were computed. At any given location and at any given 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 various mixing 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 only the advection term is significant. The typical hydrodynamic forcing from TMH (Pang and Tkalich, 2004) was utilized to compute the changes in water column nutrients and planktons due to atmospheric wet deposition (uniform loads over the domain) along with system boundary conditions.

In this study, two numerical experiments were carried out as follows. At the first set of numerical experiments, the model was run for verification of mass conservation of nitrate-nitrogen and to understand relative importance of atmospheric (vertical) fluxes in the region as compared with lateral (horizontal) fluxes via ocean boundaries. The enhanced NEUTRO model was run for three cases (Case I to III), considering: (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 is run in a conservative mode (without kinetic exchange) for three cases, noted as below:

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

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

Case III: $C_j^0 = 0$, $B_j \neq 0$, $S_{j\mathrm{WD}} \neq 0$; 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 at ocean boundaries (B_j), atmospheric WD ($S_{j\mathrm{WD}}$) for hazy days and non-hazy days, and initial concentration in water column (C_j^0) were taken as 0.02 mg/l, 8.64 mg/l for hazy days and 1.835 mg/l for non-hazy days, and 0 mg/l, respectively, and the annual average rainfall in the model region was 2136 mm.

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 ($S_{j\mathrm{WD}} \times 2136$), ocean boundary conditions (C_j^B) for model state variables including N and P species, phytoplankton (0.02 mgC/l), zooplankton (0.0279 g/m^3) and DO (5.4 mg/l) used in the model are shown in Table 3.

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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 is that the atmospheric input is an important external source of nutrients, supporting significant fraction of excessive productivity in the region. Simulation of the effects of potential changes in atmospheric deposition on seawater/coastal water quality was provided through the analysis of modeling results with implemented fluxes of atmospheric nutrients quantified using field measurements. The sensitivity analysis and the application of NEUTRO to model the fate of atmospheric deposition fluxes of nitrogen in the water column are discussed in the following sections.

3.1 Sensitivity analysis

The values of typical wet atmospheric nitrite + nitrate flux estimates varied between 1.03–2.24 mg/l and 7.78–9.48 mg/l during non-haze and haze periods, respectively. Therefore, a sensitivity analysis on atmospheric deposition was conducted using nitrite + nitrate concentrations at different extremes. For sensitivity study, the calibrated model was analyzed for its response to an increase in nitrogen fluxes due to wet atmospheric deposition. An experiment was considered to investigate the increase in nitrite + 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 nitrite + nitrate concentration (C) from the atmosphere at 1 mg/l, 10 mg/l, 50 mg/l and 100 mg/l using four different model runs. The variation of atmospheric nitrite + nitrate fluxes into the model shows the increase in the total mass proportional to the magnitude of the increment (Fig. 4). In each model run, the total mass increased gradually during the initial model simulation period until a steady state condition was reached. The percentage increase in mass due to various atmospheric nitrite + nitrate

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fluxes from its baseline was in the order of 0.01%, 0.13%, 0.63% and 1.26% for nitrite + nitrate concentration of 1 mg/l, 10 mg/l, 50 mg/l and 100 mg/l, respectively from atmospheric deposition (Fi. 4). An area is said to be sensitive to atmospheric nutrient fluxes and has a higher risk of becoming eutrophic, when the phytoplankton concentration is increased disproportionately. Increased atmospheric nutrient fluxes, even as much as 100 times above the typical atmospheric nitrogen flux, could cause eutrophication in nearshore waters of Singapore and surrounding waters and also areas where tidal action is low.

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 (vertical) fluxes during haze and non-haze period in the region as compared with lateral (horizontal) fluxes via ocean boundaries, NEUTRO was run initially in a conservative mode (without eutrophication kinetics) (see Sect. 2.8). In this study, the concentration of nitrite + nitrate nitrogen at ocean boundaries (B_j), atmospheric wet deposition (WD) ($S_{j\mathrm{WD}}$) for haze period and non-haze periods, and the initial concentration in water column (C_j^0) were taken as 0.02 mg/l, 8.64 mg/l, 1.835 mg/l and 0 mg/l, respectively; and the annual average rainfall in the model region was taken as 2136 mm (Table 3). For this study, the enhanced model for atmospheric nutrient loading during haze and non-haze periods 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 (g) against simulation time (days) for Cases I–III for non-haze and haze periods is shown in Fig. 5. As there was an exchange of flux at open boundary, the model mass gradually accumulated into the computational domain until it reached the quasi-steady state condition. Total percentage of flux (%) from Case III is given by sum of boundary flux (%) from Case I and AD flux (%) from Case II. The

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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 was reached (Fig. 5). 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 III combines 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 nitrite + nitrate nitrogen during non-haze period might account for 4 to 24% (Fig. 5a) of total mass of nitrite + nitrate nitrogen in water column. During the haze period, it was observed that wet atmospheric fluxes of nitrite + nitrate nitrogen contributed about 17 to 88% (mean ∼72%) of total nitrite + nitrate nitrogen mass into the water column (Fig. 5b), which is a notable contribution into regional eutrophication. The percentage increase of nitrite + nitrate nitrogen concentration was 2 to 30% (mean ∼15%) during the non-haze period and 5 to 111% (mean ∼70%) during haze period.

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. The results were obtained from 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 model calculates the nutrient flux by using concentration and precipi-

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tation (wet deposition). The nutrients were transported to the water column, as well as spatially distributed by the action of tidal currents following the atmospheric deposition onto the water surface.

Computations showed that atmospheric fluxes might account for an increase of nitrite + nitrate nitrogen concentration in water column in the range of 1–16% (mean ~9.3%) and 5–76% (mean ~45%) during non-haze and haze periods, respectively. The spatial distributions of surface water concentration of nitrite + nitrate, ammonium and organic nitrogen from their baseline due to atmospheric nitrite + nitrate nitrogen deposition during haze and non-haze periods are shown in Fig. 6a1–a2, b1–b2 and c1–c2, respectively. The baseline concentrations of nitrite + nitrate, ammonium and organic nitrogen were taken as 0.02 mg/l, 0.0133 mg/l and 0.0796 mg/l, respectively. It was observed that the water surface at a shallow depth had a higher concentration of nitrite + nitrate nitrogen due to accumulation and reduced tidal mixing along the coastal areas in comparison to baseline data. It was also observed that the water surface at a deeper layer of water column, and the one far away from the coastal areas were 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 occurs after long dry period during hazy days, an episodic AD wet deposition with high N concentration can occur. Episodic wet deposition event with nitrate-nitrogen (C_{WD}) concentration of 34.6 mg/l occurred during October/November 2006 onto water surface and the computed absolute change of nitrate-nitrogen concentration of maximum 1 mg/l from baseline (0.02 mg/l) due to the assumed episodic wet deposition event (Sundarambal et al., 2010). The absolute difference (increase) of surface water phosphate and organic phosphorous concentrations from baseline due to the atmospheric wet deposition during haze and non-haze periods is shown in Figs. 6a1–a2 and 7a1–a2, respectively. With the estimated nutrient load from wet AD, the computed concentrations of N and P species changed considerably from the baseline value at a selected location in Singapore Strait (Table 4).

3.4 Contribution to Eutrophication

Algal growth in the marine environment is N-limited in the short term, in contrast to the P-limited freshwater system (Smetacek et al., 1991), an increase in N:P ratios can potentially have profound impacts on the phytoplankton community, not only in terms of increasing algal abundance but also by altering the relative abundance of species present (Jickells, 1998). The model computed absolute difference in spatial surface concentration distribution of phytoplankton (Fig. 8 and Table 5) indicated that the nitrite + nitrate species provide the necessary nutrient for low nutrient zone, but the biological response time is slow, as nitrogen is not a limiting nutrient for high nutrient zone. Only external (to the ocean) sources of N that reach the surface mixed layer can affect the steady-state balance of the biologically mediated flux of CO_2 across the air-sea interface. The open ocean sources of external N such as biological N_2 fixation and atmospheric deposition 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) (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 need in extensive research and management of nutrients. Atmospheric deposition has been shown to contribute an increasing fraction of the overall nitrogen and phosphorus load. The atmospheric inorganic input is furthermore directly consumable by the algae, which is only true for parts of the river runoff. Pollutants accumulate in the air and can then be advected over marine areas with associated high dry deposition; if rainfall occurs at the time, particularly high depositions can occur (Spokes et al., 1993, 2000). Once the atmospheric nutrients enter surface seawater, the chemical form of the dissolved iron may be altered, thus changing its solubility, retention in the euphotic zone, and bioavailability. The impact of nutrient-enriched atmospheric inputs is enhanced under oligotrophic conditions. The resulting 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. 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). 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).

4 Implications and outlook

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. 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 this numerical modeling approach. The importance of regional smoke episodic events, hazy days in relation to non-hazy days, to atmospheric nutrient deposition in terms of their biological responses in the coastal water of the Singapore region was investigated. It was found that nutrient loading onto the coastal and estuarine ecosystems of the Singapore and surrounding countries from the atmospheric wet and dry deposition during hazy days was remarkable, the contribution being between 2 and 8 times that of non-hazy days. Model computations showed that atmospheric fluxes might account for considerable percentage of total nitrogen mass found in the water column of the Singapore Strait. The percentage increase in computed phytoplankton concentration from its baseline was ranging from ∼0.01 to 1.11 and its average percentage change was 0.63±0.31 due to the nitrite + nitrate nitrogen deposition event during hazy days. The results of the present study depict that the impacts of nitrogen species through AD onto the coastal region are more significant than phosphorus species.

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It was observed that the atmosphere is a potentially significant source of “new” nitrogen on yearly time scales in the coastal waters of Singapore and surrounding areas, but not a dominant and comparable to point sources such as sewage outfall, which is a source of new nitrogen on yearly time scales in these areas. The information presented in this paper advances scientific knowledge in issues related to AD of pollutants, particularly nutrients, to surface 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 highlights the importance of addressing the issues of eutrophication in Singapore that the atmosphere is clearly the dominant source of “new’ nutrients (N and P species) in the surface waters of Singapore and surrounding areas. Establishing field monitoring sites and conducting modeling study pertaining to Singapore coastal waters would be a good start to address the impacts of atmospheric deposition of nutrients onto surface water in Singapore and surrounding waters, and SEA. This research shows 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.

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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): Haze[a]				Dry deposition (µg/m^3): Non-Haze[b]			
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	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

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

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):Haze[b]				Wet deposition (mg/l):Non-Haze[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	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

Note: [a] seawater baseline (Sundarambal and Tkalich, 2003); [b] Wet deposition: Haze period (3 rain events) samples from 15 to 21 October 2006 (unit: mg/l); [c] Wet deposition: Non-Haze period (3 rain events) samples from 11 November 2006 to 23 December 2006 (unit: mg/l); NO_3+NO_2=nitrate + nitrite.

Table 3. Model inputs parameters and their values.

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

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

Parameters (units)	WQ 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 (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 (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

Table 5. The percentage increase of surface water concentration of plankton and dissolved oxygen (DO) from baseline during non-haze and haze period.

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

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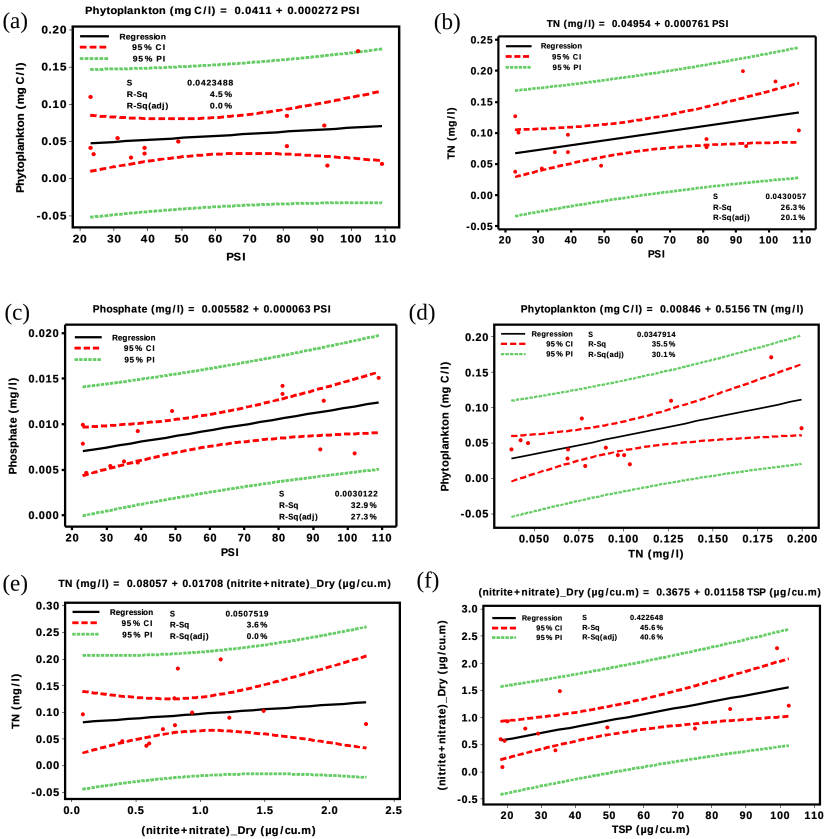

Fig. 1. Relationship between Pollutant Standards Index (PSI) and seawater parameters **(a)** phytoplankton, **(b)** TN and **(c)** phosphate; **(d)** the relationship between phytoplankton and TN in seawater; and the relationship of nitrite + nitrate from dry atmospheric deposition with **(e)** TN in seawater and **(f)** TSP. Note: Dry – Dry atmospheric deposition

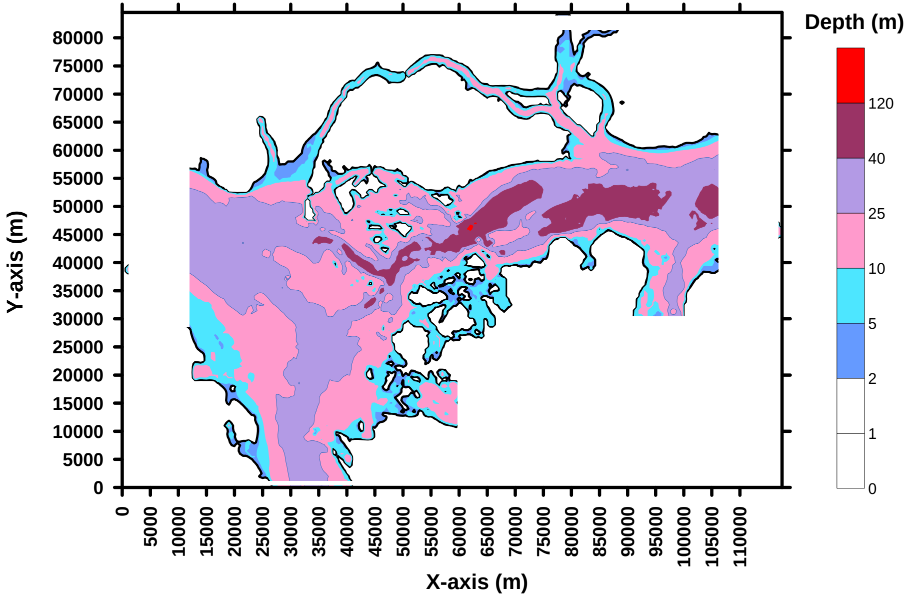

Fig. 2. Bathymetry of Singapore seawaters and NEUTRO model domain.

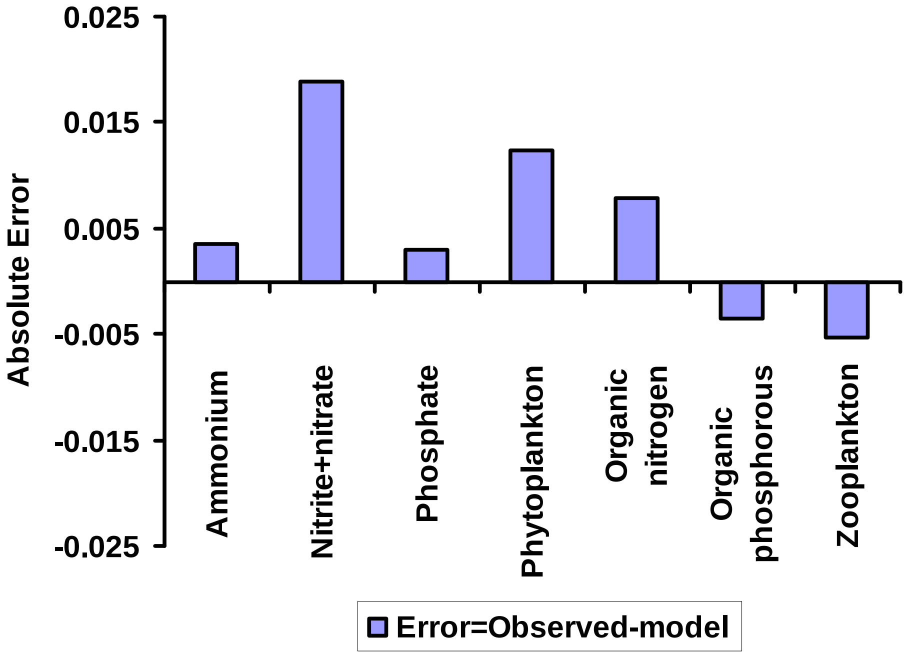

Fig. 3. Absolute Error diagram of model results from field observation. Note: Parameters (Units): Ammonium (mg/l), nitrite + nitrate (mg/l), phosphate (mg/l), phytoplankton (mgC/l), organic nitrogen (mg/l), organic phosphorous (mg/l) and zooplankton (g/m^3).

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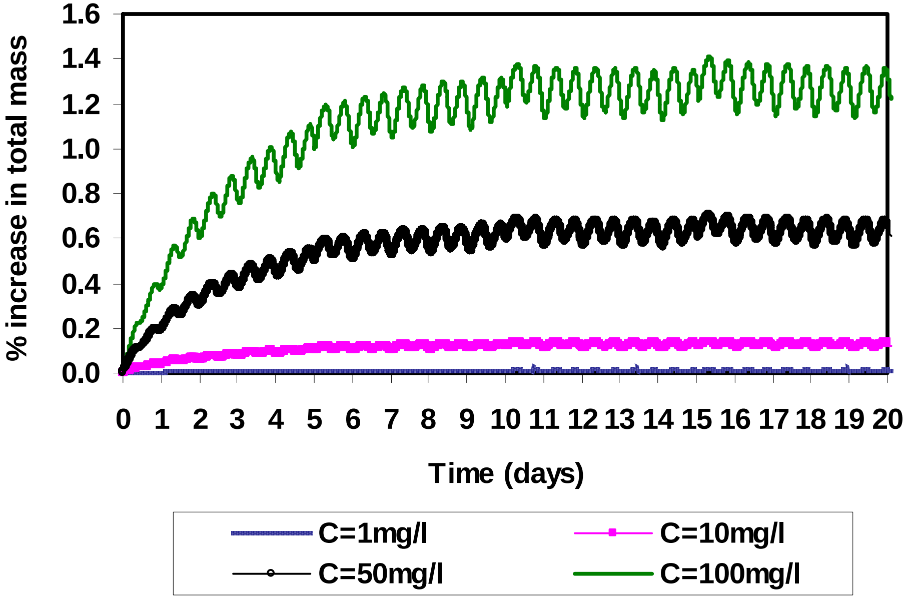

Fig. 4. The percentage increase in total mass from its baseline due to various atmospheric nitrite + nitrate fluxes in the Singapore Strait.

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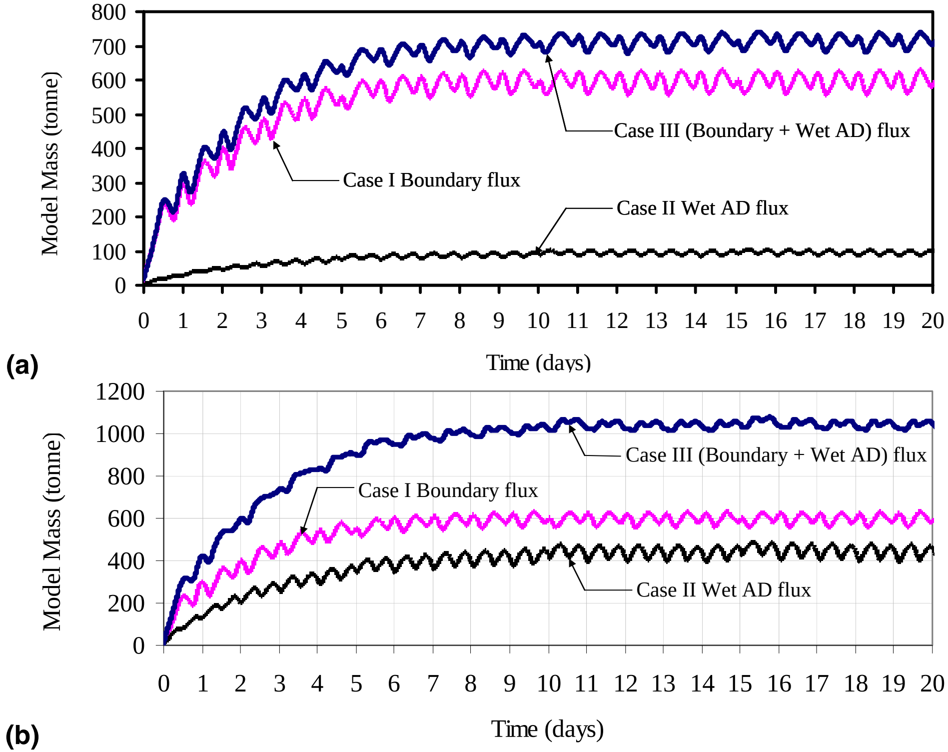

Fig. 5. Increase of nutrient mass in the Singapore Strait due to atmospheric fluxes during **(a)** non-haze period and **(b)** haze period. Note: Mass due to the total flux (Case III)=Mass due to boundary fluxes from the ocean (Case I) + Mass due to atmospheric deposition (AD) fluxes (Case II).

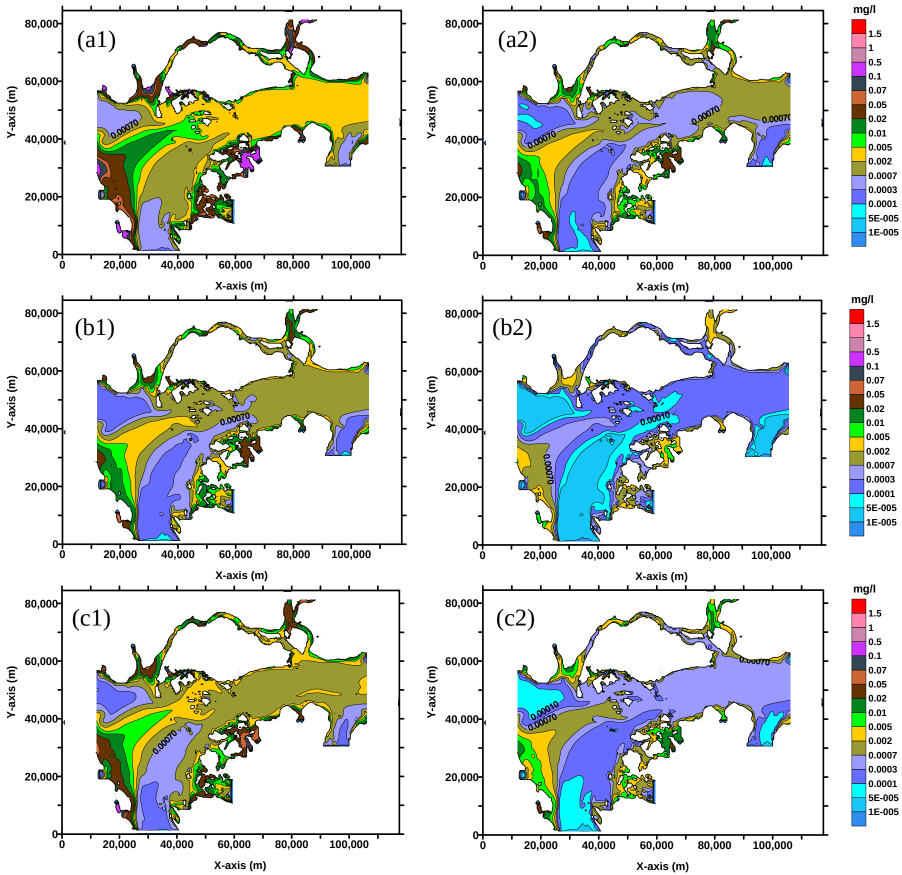

Fig. 6. The absolute change of **(a)** nitrite + nitrate, **(b)** ammonium and **(c)** organic nitrogen concentration at surface water from baseline due to the atmospheric wet deposition during (1) hazy and (2) non-hazy days.

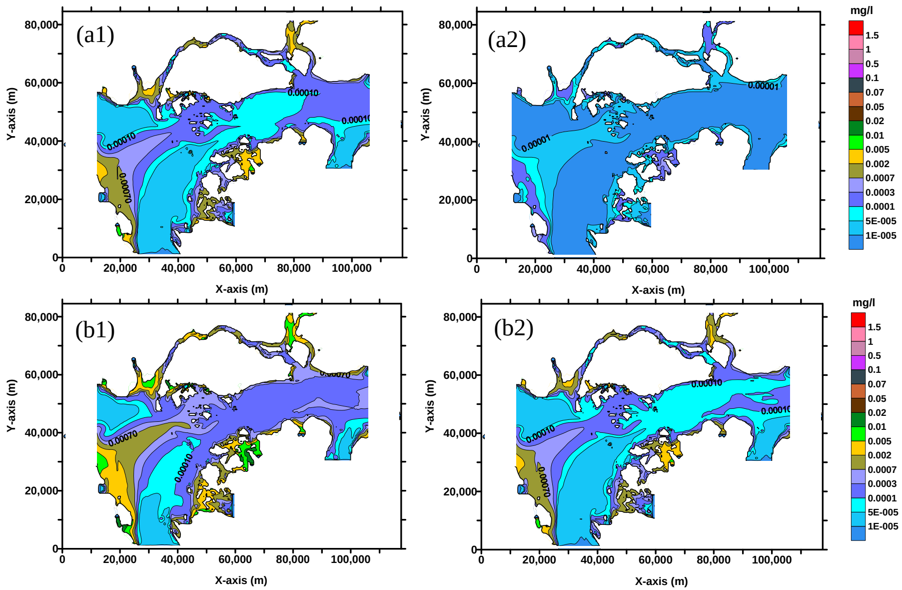

Fig. 7. The absolute change of **(a)** phosphate and **(b)** organic phosphorous concentration at surface water from baseline due to the atmospheric wet deposition during (1) hazy and (2) non-hazy days.

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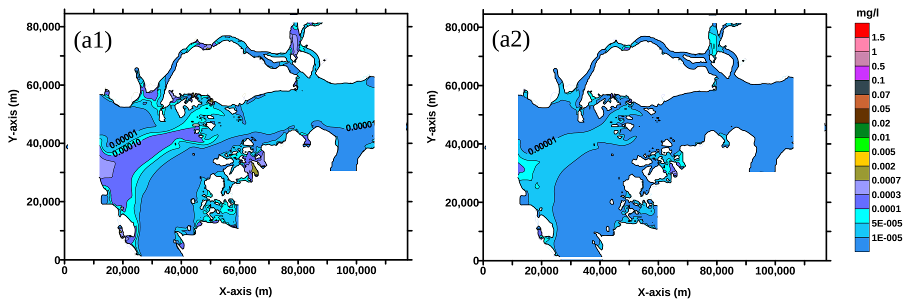

Fig. 8. The absolute change of phytoplankton concentration at surface water from baseline due to the atmospheric wet deposition during **(a1)** hazy and **(a2)** non-hazy days.