Atmos. Chem. Phys. Discuss., 10, 7745–7778, 2010
www.atmos-chem-phys-discuss.net/10/7745/2010/

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Impact of biomass burning on surface water quality in Southeast Asia through atmospheric deposition: field observations

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Received: 27 February 2010 – Accepted: 12 March 2010 – Published: 25 March 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Atmospheric nutrients have recently gained attention as a significant additional source of new nitrogen (N) and phosphorus (P) loading to the ocean. The effect of atmospheric N on marine productivity depends on the biological availability of both inorganic and organic N and P forms. During October 2006, the regional smoke haze episode in Southeast Asia (SEA) that resulted from uncontrolled forest fires in Sumatra and Borneo blanketed large tracts of the region. In this work, we determined the composition of nutrients in aerosols and rainwater during haze and non-haze periods to assess their impacts on aquatic ecosystem in SEA for the first time. We compared atmospheric dry and wet deposition of N and P species in aerosol and rainwater in Singapore between haze and non haze periods. Air mass back trajectories showed that large-scale forest and peat fires in Sumatra and Kalimantan were a significant source of atmospheric nutrients to aquatic environments in Singapore and SEA region on hazy days. It was observed that the average concentrations of nutrients increased approximately by a factor of 3 to 8 on hazy days when compared with non-hazy days. The mean dry atmospheric fluxes (g/m^2/year) of TN and TP observed during hazy and non-hazy days were 4.77±0.775 and 0.3±0.082, and 0.91±0.471 and 0.046±0.01, respectively. The mean wet deposition fluxes (g/m^2/year) of TN and TP were 12.2±3.53 and 0.726 ±0.074, and 2.71±0.989 and 0.144 ±0.06 for hazy and non-hazy days, respectively. The occurrences of higher concentrations of nutrients from atmospheric deposition during smoke haze episodes may have adverse consequences on receiving aquatic ecosystems with cascading impacts on water quality.

1 Introduction

Nutrient enrichment of aquatic ecosystems results in higher biological productivity, and can lead to undesirable effects including algal blooms and depletion of oxygen in the water. The process of eutrophication usually occurs naturally and gradually, but is

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greatly enhanced by various human activities. A significant source of nutrients to aquatic ecosystems is atmospheric deposition, either as "wet atmospheric deposition (WAD)" or as "dry atmospheric deposition (DAD)" (Fig. 1 and see auxiliary material for more details). Atmospheric inputs of nutrients (nitrogen (N), phosphorus (P) species and iron) have been hypothesized to play an important role in the chemical and biological dynamics of open oceans and aquatic ecosystems although delivered as a diffuse flux in contrast to localized river inputs (Menzel and Spaeth, 1962; Duce, 1986; Duce et al., 1991; Prospero et al., 1996; Spokes et al., 2000; Whitall et al., 2003). The role of atmospheric inputs as an annual source of nutrients to the euphotic zone has been recently evaluated (Duce, 1986; Duce et al., 1991; Hasager, 2003; Duce et al., 2008). Nitrogen is an essential nutrient in terrestrial and marine ecosystems. Increasing quantities of atmospheric anthropogenic fixed nitrogen entering the open ocean could account for up to about a third of the ocean's external (non-recycled) nitrogen supply and up to 3% of the annual new marine biological production (Duce et al., 2008).

Biomass burning is an important source of nutrients and numerous trace elements, especially in Southeast Asia (SEA), where the smoke haze phenomenon is a major and recurring problem (Balasubramanian et al., 1999, 2003; Zhong et al., 2001; Balasubramanian and Qian, 2004). To date, estimates of atmospheric nutrient transport in SEA have been deficient in several ways. Due to recurring forest and peat fires in SEA on a large scale and the abundant rainfall in this tropical region, DAD and WAD of nutrients to the ocean surface might be significant. More complete knowledge of atmospheric nutrient transport is needed if the role of atmospheric deposition in anthropogenic nutrient enrichment is to be understood. Atmospheric fluxes of nutrients could contribute a substantial fraction of dissolved N or P species to the euphotic zone, and enhance primary production, when nutrients are limited, leading to eutrophication. Despite the frequent occurrence of smoke haze episodes in SEA, no systematic field studies have been conducted yet to fully understand the impact of particulate emissions from forest fires on water quality. Atmospheric inputs are a key component in water quality

models and pollution loading budgets. Currently, limited experimental datasets on atmospheric deposition of N and P nutrient species exist for tropical ecosystems in the SEA Region. It is therefore important to quantify the levels of macro-nutrients such as N and P species, derived from atmospheric deposition as they have significant effects on aquatic and terrestrial ecosystems.

The effects of nutrient deposition on food web structure and ecological function influence how other toxic substances are processed by the ecosystem, how they bioaccumulate, and ultimately how they impact fish, wildlife, and humans. Considering that these atmospherically deposited nutrients are generated largely by human activities, it is clear that solutions must involve greater recognition, monitoring, and ultimately, regulation of this increasingly significant source of environmental pollution. In this study, significant observational data have been collected to characterize both DAD and WAD of nutrients such as inorganic and organic forms of N and P during non-hazy and hazy days. The objective of this study is to estimate DAD and WAD fluxes of N and P species during hazy and non-hazy days to coastal waters in Singapore.

2 Materials and methods

2.1 Experimental

2.1.1 Sampling location

Singapore is a small island with total land area of 710 km^2 located at latitudes 1°06′ N and 1°24′ N and longitudes 103°24′ E and 104°24′ E, 137 km north of the equator (Fig. 2). It is highly urbanized and industrialized with small water resources and limited ocean environment around the island. Because of its geographical location, its climate is characterized by uniform temperature and pressure, high humidity and abundant rainfall. Singapore has two main seasons, the Northeast Monsoon (NEM) (November to March) and the Southwest Monsoon (SWM) season (June to September), sepa-

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rated by two relatively shorter inter-monsoon (IM) periods (April to May and October, respectively). The ambient air temperature ranges from 21.1 to 35.1 °C, and the annual average rainfall is 2136 mm. The population of Singapore is 4.99 millions (Singapore Department of Statistics, 2009). Southwest (SW) and Northeast (NE) winds occur in the coastal area periodically and the maximum wind speeds range from 5 m/s to 10 m/s. Both aerosol and rainwater samples were collected at the Tropical Marine Science Institute in St. John's Island (SJI), Singapore (Fig. 2). This island is geographically located at the latitude of 1°13′10″ North of the Equator and the longitude of 103°50′54″ East of the Prime Meridian on the Map of Singapore. There are no industrial sources close to the sampling site. This sampling station in SJI was selected as it is near the open coastal area in southern part of Singapore and does not have local pollution sources. Except regional hazy days, the air is free from major air pollution. In this study, the DAD and WAD samples collected at the SJI station during hazy and non-hazy days were analyzed.

2.2 Sample collections

Aerosol particulate samples were collected using a High Volume Air Sampler (model 3800 AFC: HI-Q Environmental Products Company, USA). Air flow was maintained at 40 SCFM (Standard Cubic Feet per Minute) by an automatic air flow control device. Particulate samples were collected every 24 h three times a week at the sampling location mainly during dry weather conditions. The total suspended particulate (TSP) samples were collected on 20.3×25.4 cm size Whatman QM-A Quartz air-sampling filters for water soluble ionic and nutrients analysis. The filters were conditioned in a dry box at 30% relative humidity and 25 °C temperature for 24 h prior to and after air sampling; pre- and post-sampling weights were used to obtain the particulate mass collected on the filters. TSP had been widely measured in the past and present for the characterizations of its elemental composition and nutrients in aerosol for estimation of dry deposition fluxes (Caruso et al., 1981; Herut et al., 1999; Duarte et al., 2006; Chen et al., 2007; Ayars and Gao, 2007). The mass concentration of TSP ($\mu g/m^3$)

was calculated from the collected mass of particulates (μg) divided by the volume of air passed through the filter (m^3) during sampling period. Filters were then weighed using a MC5 microbalance (Sartorius AG, Goettingen, Germany) with the lowest readability of 0.0001 mg. The balance was regularly checked with NIST-traceable standard calibrated weights. The particulate filters were stored in a refrigerator at 4 °C until extraction for sample analysis.

The rainwater samples were collected by using an automated wet only rainwater sampler (Ecotech Model 200: Ecotech Pty Ltd, Australia) at the sampling location. Rainwater samples were transferred from the sampler to pre-cleaned high-density polyethylene (HDPE) bottles after the rain event and immediately filtered using 0.45 µm nylon membrane filters and refrigerated at 4 °C for sample analysis. Rainfall with <1 mm was not taken into account, firstly for analytical convenience, and secondly because even when the nutrient concentration was high, such events yielded low or negligible nutrient loads. Daily rainfall amounts and other meteorological parameters were obtained during the sampling period from September 2006 through January 2007 using an automated weather station at the Department of Geography, National University of Singapore (NUS). Altogether, 55 aerosol particulate samples and 21 rainwater samples (collected on event-to-event basis) were collected during the sampling period, and the results obtained from this field study are presented in this paper.

2.2.1 Reagents and standards

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

SRM 1648 (Urban Particulate Matter), obtained from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), was used for validation of the meth-

ods for both N and P species analysis. This standard consists of natural atmospheric particulate matter collected at an urban location, and is certified for its major, minor, and traces inorganic constituents.

For organic nitrogen, nitrogen standards were prepared from ethylenediaminetetraacetic acid (EDTA), urea, and glycine by dissolving appropriate amounts in ultra pure water so as to have a stock solution of 1000 mg N/L. EDTA-based standard nitrogen solution was used for optimization of microwave-assisted persulfate oxidation (Karthikeyan et al., 2009a). The other two reagents were used to check the robustness of the optimized procedure.

2.2.2 Sample processing and analysis

The aerosol particulate and rainwater samples were analyzed to characterize atmospheric wet and dry nutrient deposition as per the protocol developed in our laboratory (Sundarambal et al., 2006). The atmospheric nutrients analyzed in this study 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). A portion of filter samples (1/4 or 1/8th part of total filter area) was extracted with 20 or 50 ml Milli-Q water (Millipore) in an ultrasonic bath for l h. The filter extracts from the ultrasonic bath were cooled to ambient temperature. The solution was then filtered through a 0.45 µm polytetrafluoroethylene (PTFE) membrane syringe filter. Rainwater samples were taken after filtration for laboratory analysis. The rainwater and aerosol particulate samples were analyzed for the ionic species by ion chromatography (IC) (Model ICS-2000; Dionex Corporation) using a cation column and an anion column. Total nitrogen and total phosphorus were analyzed according to our standard laboratory procedure (Karthikeyan et al., 2005a, b; Sundarambal et al., 2006; Karthikeyan and Balasubramanian, 2006; Karthikeyan et al., 2007, 2009a, b).

2.3 Deposition flux calculations

2.3.1 Dry deposition

DAD is a slow, but continuous flux of airborne contaminants to an underlying surface. DAD fluxes (F_{dry} in g/m^2/year) were calculated from the product of dry deposition velocity (V_d in cm/s) and measured concentrations of nutrient species ($C_{aerosol}$ in µg/m^3), as shown in Eq. (1) with unit conversion factor of 0.31536.

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

Deposition velocity, V_d, may be viewed as the velocity at which pollutant gases and aerosols existing at a given atmospheric concentration are deposited to the Earth's surface. Processes that control V_d include gravitational settling, impaction, and diffusion. These processes all act simultaneously and are all affected by many variables including particle size, wind speed, relative humidity, and sea surface roughness. The term V_d is the result of many processes (for a full explanation see, e.g. Seinfeld and Pandis, 2006), and it is thus very difficult to determine V_d. However, the calculation of F_{dry} is usually carried out using V_d reported in the literature for many elements including nutrients (see e.g. Sehmel, 1980; Slinn and Slinn, 1980; William, 1982; Joffre, 1988; Dulac et al., 1989; Migon et al., 1991, 2001; Duce et al., 1991; Prospero et al. 1996; Nielsen et al., 1996; Zhuang et al., 1999; Spokes et al., 2000; Qi et al., 2005; Seinfeld and Pandis, 2006; Zhang et al., 2007). DAD fluxes were calculated using species-specific V_d since the nutrients are known to be associated with different particle fractions. The calculation of V_d is based on a simple parameterization of experimental meteorological measurements to determine atmospheric transport characteristics (Slinn, 1982; Zhang et al., 2001). The values of V_d estimated were 1.2 and 0.6 cm/s for nitrate and ammonium, respectively and 2 cm/s for phosphate, 1.2 cm/s for TN and ON and 2 cm/s for TP and OP, which are consistent with results reported in the literature (Duce et al., 1991; Prospero et al., 1996; Spokes et al., 2000; Herut et al.,

2002, Poor et al., 2006). These estimates result in an uncertainty of a factor of 2–3 in the calculated fluxes (Duce et al., 1991).

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

$$V_d = \frac{1}{R_a + R_b + R_a R_b v_s} + v_s \quad (2)$$

where v_s is the gravitational settling velocity (which is a function of particle size, density, and viscosity) (Seinfeld and Pandis, 2006), R_a is aerodynamic resistance refers to turbulent transport from the free atmosphere down to the receptor surface (R_a=9/[$u\sigma_\theta^2$], which is a function of wind speed, u and standard deviation of wind speed, σ_θ; Yamartino, 1984; Turner, 1986) and R_b is quasi laminar layer resistance (which is a function of particle size, Brownian diffusion, interception and impaction; R_b on water surface is given by van den Berg et al., 2000). Both R_a and R_b are site specific and are determined to a large extent by atmospheric properties. The formula used for V_d calculation is given in the supplementary material http://www.atmos-chem-phys-discuss.net/10/7745/2010/acpd-10-7745-2010-supplement.pdf. Metrological parameters such as ambient temperature (K) of 300.8±0.6 and 299.7±0.7, wind speed (m/s) of 1.3±0.49 and 1.0±0.32, and standard deviation of wind direction σ_θ (rad) of 0.773 and 0.513 were measured in the sampling location during October 2006 and November 2006, respectively. In SEA atmospheric environment, a majority of aerosols observed in the size range of 0.1–20 µm by the optical counter (Clark and Kremer, 2005) was in the fine mode (<1 µm). Dominance of fine particles is typical for biomass burning plumes as observed, for example, in Brazil (Reid and Hobbs, 1998). Both the mass and number concentrations were elevated across the entire size range on hazy days, and the

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

2.3.2 Wet deposition

WAD involves the removal of atmospheric substances within clouds and below the cloud base mainly by precipitation (Pryor and Barthelmie, 2000). Wet deposition fluxes (F_{wet} in g/m^2/year) were calculated from the product of precipitation rate (P in m) and measured concentrations of nutrient species (C_{rain} in mg/l) by the following Eq. (3):

$$F_{wet} = C_{rain} P \quad (3)$$

Precipitation rate is the analogous term describing the velocity that pollutants incorporated into precipitation and existing at a given liquid concentrations are deposited. Although intense fires burnt during dry periods when rainfall amounts were unusually low, precipitation samples were collected and analyzed during the 2006 haze episodes. The cumulative total of rain events during the time interval may be expressed as the sum of all events. The cumulative total precipitation of 48 mm, 250.8 mm and 495.2 mm was measured during October, November and December 2006, respectively. In this study, the total precipitation by summing the above-mentioned three cumulative total precipitation amounts was used for wet atmospheric flux calculation. Annual precipitation rate during the year 2006 was 2294.6 mm and the average precipitation rate was 203.1±126.5 mm/month. The deposition fluxes may show short term variations, rendering the quantification of the annual atmospheric input of nutrients into the sea

very difficult. Baeyens et al. (1990) described a method which allows estimation of the annual wet deposition flux of dissolved ions without measuring all rain events. When one rain event was sampled in several steps (sequential sampling), a nice, smooth dilution profile was obtained (Xianren and Baeyens, 1990) and the concentration decreased gradually with the volume of rainfall. Moy et al. (1994) found that slow air circulation coincided with a high concentration of pollutant gases in the atmosphere. If high precipitation occurred at this time period, more removal of pollutants from the atmosphere followed by their high concentrations would be observed in the rain water measurement. As reported by Migon et al., 1991, the number of rain events has a greater influence on flux than the intensity of the rain. It was observed in our study that, after long dry periods (typically several days), nutrient concentrations in rainwater were systematically higher than monthly mean concentrations, regardless the intensity of the rain event.

3 Results and discussion

3.1 Smoke haze episode

A higher level of TSP was found in Singapore during the 2006 smoke haze event (maximum TSP~140 µg/m^3) as compared to that measured during the 1997–1998 haze events (maximum TSP~110 µg/m^3) (Balasubramanian et al., 1999) caused by prolonged forest fires in the nearby provinces of Indonesia. The smoke haze originated from hundreds of bush, forest and peat fires across Sumatra and Borneo (National Environment Agency (NEA), Singapore). The prevailing southerly to southwesterly winds transported the smoke haze directly from southern Sumatra towards the Malacca Straits, peninsular Malaysia and Singapore; the smoke haze was also influenced by the prevailing southeasterly winds from Kalimantan to Singapore. The PSI (Pollutant Standards Index) measured by NEA, Singapore and the API (Air Pollution Index) by DOE (Department of Environment), Malaysia are indicators of the prevailing

air quality in Singapore and Malaysia, respectively. The air quality categories based on PSI or API and the general health effects associated with different categories of air quality are summarized as follows: PSI or API up to 50: Good; 51–100: Moderate; 101–200: Unhealthy; 201–300: Very Unhealthy; >300: Hazardous. The Total Suspended Particulates (TSP) measured in this study, PSI and API (2006 API data from http://en.wikipedia.org/wiki/2006_Southeast_Asian_haze) (Fig. 3) show the pattern of air pollution in Singapore and Malaysia [Locations (Latitude and Longitude): George Town (5°25′00″ N 100°19′00″ E), Johor Bahru (1°29′00″ N 103°44′00″ E), Kuala Lumpur (3°8′00″ N 101°42′00″ E), Kuantan (3°49′00″ N 103°20′00″ E) and Kuching (1°33′00″ N 110°25′00″ E)], moderate and unhealthy air quality during October 2006 and the overall air pollution load coming onto aquatic ecosystem in and around Singapore during haze events. Kuching, the capital of the East Malaysian state of Sarawak, is the largest city near Kalimantan (Borneo) where extensive forest fires took place. These islands are situated around Singapore from southeast (SE) to southwest (SW).

The areas of forest fires ranged from several hundred kilometers to about 2000 km from Singapore. Figure 3 shows that day-to-day particle concentrations vary substantially in response to spatial and temporal changes of meteorological factors, such as wind conditions and intermediate rainfall, and of fire activity. The particle concentration exhibited a distinct rise and high fluctuation during October. After mid-November, it decreased and remained at the background level. The air quality in Singapore during October 2006 was either moderate or unhealthy. Figure 3a also shows that day-to-day particle concentrations varied substantially in Singapore in response to spatial and temporal changes of meteorological factors such as wind conditions (Fig. 4a) and intermediate rainfall (Fig. 3b), and of fire activity and intensity (hotspots in Fig. 4). The highest 3-h PSI (150) recorded during this haze episode occurred on 7 October 2006 (NEA, Singapore).

The extreme smoke haze episodes that occurred on 7, 15, 17 and 20 October 2006 were selected for DAD estimation during hazy days and the 16 samples collected from

13 November 2006 to 4 January 2007 were selected for non-hazy days. The range of TSP was 99–138 µg/m^3 and 18–31 µg/m^3, respectively, during hazy and non-hazy days; the range of PSI was 92–119 and 25–47 during hazy and non-hazy days, respectively. The arithmetic means of TSP and PSI during hazy days were 113±17 µg/m^3 and 102±12, respectively while those during non-hazy days were 24±5 µg/m^3 and 35±7, respectively. The air quality reached the unhealthy range (PSI >100) on 3 days with the highest value being 128 (24 h average PSI) on 7 October 2006.

To investigate the possible sources of particulate air pollution and to assess the recent history and transport pathways of air masses before reaching the monitoring station in SJI, air mass back trajectories were constructed at 3 different heights 40, 100 and 500 m for a 5-days period using NOAA/ARL Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT; Draxler and Rholph, 2003). The 2006 smoke haze event, caused by continued uncontrolled burning from "slash and burn" cultivation in Indonesia, affected several countries in the SEA region and beyond such as Malaysia, Singapore, southern Thailand (see Fig. 4a), and as far as Saipan (Source: saipantribune.com on 5 October 2006). The fires originated mostly in Kalimantan, the Indonesian part of Borneo, and in Sumatra. The 5-days backward trajectories of air masses arriving in the SJI sampling station on three representative days 7, 17 and 20 October 2006 (SWM) and the representative smoke haze extent map in SEA are shown in Fig. 4a–d, respectively. The PSI during these three sampling days was 128, 92 and 102, respectively. During periods of active and intense biomass burning in Sumatra and Borneo, spells of moderate to dense smoke haze could be expected in the vicinity of the larger fire/hotspot clusters in the affected areas (see Fig. 4). The HYSPLIT model calculation results showed that the air mass was transported from different source areas to Singapore across the Indian Ocean at lower altitudes.

During the first haze event (Fig. 4a) one air mass traveled from Australia land origin at a higher altitude of 2000 m and others from Indian Ocean origin at a low attitude through Sumatra, Java Sea and areas impacted by fires evidenced by the extent of smoke haze in SEA map by NEA, Singapore. The PM concentration was largely dependent on the

direction of the prevailing winds (with southeasterly to southwesterly winds favoring the transport of haze towards Singapore), the fire activity (its location and intensity) and El Niño/Southern Oscillation (ENSO) (its effect on rainfall, atmospheric stability and convective activity). The monsoon transition (movement of airstream boundaries) shifted the wind pattern towards Peninsular Malaysia. It created convergence zones near Singapore and induced subsidence in the area as well (Koe et al., 2001). The local effects of land and sea breezes also contributed to the enhancement of PM concentration in Singapore, particularly during the transition period (Koe et al., 2001). During the other two haze events (Fig. 4b–c), the air mass mostly originated from Kalimantan and the surrounding areas. The air masses might contain mostly particulate matter and other air pollutants originating from biomass burning compared to that originated from other air pollution.

3.2 Atmospheric nutrient deposition

3.2.1 Dry deposition

The range, mean, median, geometric mean, range and standard deviation of the concentration of soluble inorganic and organic nutrients (N and P species) obtained from TSP samples during hazy and non-hazy days in Singapore are shown in Table 1. The baseline concentration of nutrients in Singapore seawater was referred from Tkalich and Sundarambal (2003). The range of concentrations of N species during hazy days was in the order of 10.1–14.9 $\mu g/m^3$ for TN, 5.15–8.16 $\mu g/m^3$ for ON, 2.28–6.36 $\mu g/m^3$ for NO_3+NO_2, and 1.53–2.43 $\mu g/m^3$ for NH_4. The range of concentrations of N species during non-hazy days was in the order of 1.31–3.84 $\mu g/m^3$ for TN, 0.43–2.5 $\mu g/m^3$ for ON, 0.41–1.51 $\mu g/m^3$ for NO_3+NO_2, and 0.01–1.6 $\mu g/m^3$ for NH_4. The high ratio of nutrients between hazy and non-hazy day (Fig. 7) shows that smoke haze episodes provided a significant source of nutrients to the coastal water in Singapore and SEA. The order of occurrences of N and P species in terms of ratios between those observed during hazy and non-hazy days was NH_4 >NO_3+NO_2 >TN>ON and OP>TP>PO_4,

respectively. The arithmetic mean of P species in aerosol were 0.48±0.13 μg/m^3 for TP, 0.38±0.16 μg/m^3 for OP and 0.09±0.07 μg/m^3 for PO_4 during hazy days and 0.07±0.02 μg/m^3 for TP, 0.05±0.02 μg/m^3 for OP and 0.02±0.01 μg/m^3 for PO_4 during non-hazy days.

DAD fluxes of N and P species were calculated from the field observations of DAD nutrients concentration (Table 1) using the Eq. (1) in Sect. 2.3.1. Figure 5 shows the DAD fluxes of N and P species during hazy and non-hazy days. The annual DAD fluxes of reactive (NO_2+NO_3)–N estimated into the coastal waters of Singapore were 1.61±0.724 g/m^2/year and 0.303±0.102 g/m^2/year during hazy days and non-hazy days, respectively. The annual DAD fluxes of reactive PO_4-P estimated into the coastal waters of Singapore were 0.059±0.042 g/m^2/year during hazy days and 0.014±0.006 g/m^2/year during non-hazy days. The mean (and range) DAD fluxes (g/m^2/year) of TN, NH_4 and ON were 4.78 (3.83–5.66), 0.362 (0.29–0.46) and 2.44 (1.95–3.09), respectively during the hazy period. The mean (and range) DAD fluxes (g/m^2/year) of TP and OP were 0.3 (0.222–0.413) and 0.242 (0.178–0.386), respectively during the hazy period. The mean (and range) DAD fluxes (g/m^2/year) of TN and TP species observed during the non-hazy period were 0.91 (0.497–1.46) for TN and 0.046 (0.023–0.056) for TP. The contribution of DAD nutrients followed the order TN>NO_2+NO_3 >ON>NH_4 for N species and TP>OP>PO_4 for P species with respect to their concentrations and fluxes.

3.2.2 Wet deposition

The concentration of nutrients (N and P species) in rainwater was obtained from the laboratory IC analysis during hazy and non-hazy days. Rainwater samples (3 rain events) were selected based on PSI from 15 to 21 October 2006 for hazy days and rainwater samples (3 rain events) from 11 November 2006 to 23 December 2006 for non-hazy days. The range of PSI during hazy and non-hazy days was 81–93 and 35–39, respectively. The range of wet deposition concentrations of N species

during hazy days was in the order of 11.8–20.4 mg/l for TN, 3.21–10.5 mg/l for ON, 7.78–9.48 mg/l for NO_3+ NO_2, and 0.77–1.19 mg/l for NH_4. The range of WAD concentrations of N species during non-hazy days was in the order of 2.38–4.79 mg/l for TN, 1.3–2.52 mg/l for ON, 1.03–2.24 mg/l for NO_3+ NO_2, and 0.03–0.39 mg/l for NH_4. On an event basis, the minimum and the maximum wet deposition fluxes of macro-nutrients were highly variable. The arithmetic mean of P species was 0.91±0.09 mg/l for TP, 0.65±0.29 mg/l for OP and 0.26±0.2 mg/l for PO_4 for hazy days and 0.18±0.08 mg/l for TP, 0.15±0.09 mg/l for OP and 0.03±0.01 mg/l for PO_4 for non-hazy days. The reported concentrations of NH_4 and NO_3 in rainwater were 0.312 mg/l and 1.041 mg/l during 1997 to 1998 in Singapore (Balasubramanian et al., 2001), and 0.247 mg/l and 1.232 mg/l, respectively during 1996 to 1997 in Malaysia (Ayers et al., 2002). The concentration levels of nutrients such as ammonium, nitrate and phosphorous spikes from biomass burning have been already reported (Lobert et al., 1990; Crutzen and Andreae, 1990; Mayewski et al., 1993, 1997; Kondo et al., 2004; Mahowald et al., 2005, 2008). The contribution of WAD of nutrients followed the order TN>NO_2+NO_3 >ON>NH_4 for N species and TP>OP>PO_4 for P species with respect to their concentrations and fluxes. The order of occurrences of WAD for N and P species in terms of ratios between those observed during hazy and non-hazy days was similar to DAD for N species and P species (PO_4 >TP>OP), respectively (Fig. 7). The mean concentrations of atmospheric aerosol and rainwater were comparable to the fluxes from land-based sources such as wastewater treatment plants (TN=2.13 mg/l and TP=0.17 mg/l) and rivers (NH_4=0.16 mg/l, NO_2+NO_3=0.34 mg/l and PO_4=0.14 mg/l) (DHI, 2004) in the Singapore coastal waters.

The magnitude of wet deposition fluxes depends on precipitation rate. In this study, the precipitation rate of 794 mm and cumulative rainfall amount of rain events during the study period of October 2006 to December 2006, were used for wet deposition flux estimation. A similar pattern of nutrient concentrations was observed in rainwater and seawater (Fig. 6a). Figure 6b shows the atmospheric fluxes of N and P species calculated based on the field measurements of wet deposition during hazy and non-

hazy days from October 2006 to December 2006 in Singapore. The annual mean wet deposition fluxes of reactive (NO_2+NO_3)–N and PO_4–P into the Singapore coastal waters were estimated to be 6.86±0.672 g/m^2/year and 0.207±0.161 g/m^2/year during hazy days, and to be 1.23±0.496 g/m^2/year and 0.027±0.008 g/m^2/year during non-hazy days, respectively. The annual mean wet deposition fluxes (g/m^2/year) of ammonium observed were 0.746±0.178 during hazy days and 0.122±0.165 during non-hazy days. Nominal annual average wet deposition fluxes (g/m^2/year) published elsewhere in SEA for NH_4 and NO_3 were 0.718 and 3.607 in Malaysia during 1993–1998 (Ayers et al., 1999, 2002), 1.383 and 1.74 in Indonesia during 1992 and 1996 (Gillett et al., 2000) and 0.079 and 0.308 in Australia (Ayers and Yeung, 1996). The annual mean wet deposition fluxes of TN and TP in g/m^2/year were 12.2±3.53 and 0.726±0.074, and 2.71±0.989 and 0.144±0.06 for hazy and non-hazy days, respectively. This observation is comparable to those made earlier for dry and wet atmospheric nitrogen fluxes during non-hazy days in Singapore (Karthikeyan et al., 2009a). The observed organic N and P annual mean wet deposition fluxes in g/m^2/year were 4.62±3.23 and 0.52±0.234 during hazy and 1.36±0.554 and 0.117±0.068 non-hazy days. The higher amount of WAD fluxes (about 3 times) was obtained when annual precipitation rate (2136 mm) was used instead of precipitation rate (794 mm) during the study period from October 2006 to December 2006. This ultimate WAD flux might be applied as a constant uniform load coming from the atmosphere over the coastal water in the study area for an eutrophication modelling study to understand their impact and effects on water quality. The ratio of haze to non-haze nutrients concentrations for aerosol and rainwater (Fig. 7) clearly shows that atmospheric deposition contributes a larger proportion of nutrients into coastal waters of SEA during smoke haze events. Concentrations of most ions in rainwater were higher during periods of intense biomass fires and the resultant haze than during periods when there were no significant forest fires. Since WAD and DAD contribute different forms of nutrients at different rates, the availability, stoichiometry, and nutrient loads from atmospheric sources would vary greatly with the rate and timing of precipitation. The haze events that have plagued

SEA are likely to affect atmospheric fluxes of nutrients and other pollutants into aquatic systems. Atmospheric deposition in Singapore and surrounding countries appears to provide considerable fluxes of nutrients of environmental concern and it may thus play an important role in the coastal eutrophication.

3.3 Implications and outlook

In this study, tropical marine atmospheric deposition of nutrients (N and P species) in aerosol and rainwater during smoke haze due to biomass burning and during non hazy period was quantified for the coastal water of the SEA region. Our findings indicate that atmospheric deposition can be a significant source of nutrients to ecosystems. The concentrations of nutrients (N and P species) in aerosol and rainwater were higher during haze episodes than during the non-haze period, and the increasing pollution load in air and rain may have negative consequences on receiving ecosystems. During hazy and non-hazy days, the order of occurrences of N and P species was NH_4 >NO_3+NO_2 >TN>ON and OP>TP>PO_4, respectively. It was observed that the average concentrations of nutrients increased approximately between a factor of 3 and 8 on hazy days when compared with non-hazy days. The high ratio of nutrients between hazy and non-hazy days shows that smoke haze episodes provided a significant source of nutrients to the coastal water in Singapore and SEA. The quantified nutrient fluxes from atmospheric deposition provided a baseline to study the possible ecosystem responses to atmospheric nutrient inputs into the water surface. These quantitative and qualitative aspects of atmospheric nutrient sources may promote biotic changes now apparent in estuarine and coastal waters with cascading impacts on water quality, and trophic and biogeochemical alterations (i.e., algal blooms, hypoxia, food web, and fisheries habitat disruption). Air mass back trajectories showed that large-scale forest fires in Sumatra and Kalimantan were a significant atmospheric nutrient source to aquatic environment in SEA region and Singapore's coastal water quality degradation during haze episodes.

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This study attempted to fill the knowledge gaps in the area of atmospheric deposition of N and P species in SEA in terms of field measurements and observations, especially during hazy and non-hazy days, as nutrient deposition is important to biogeochemical cycling. Because of increased biomass fires and reduced dispersion, the regional smoke haze events in SEA generally occur during the SWM period in ENSO years. The burning activities usually cease by October/November when the gradually interspersing northern monsoon brings abundant rainfall. Since the occurrence of these fires is centered on the dry tropics and mostly limited to dry seasons, their regional and seasonal impact is even more conspicuous. The low incidence of rain during the fire season enhances the atmospheric lifetime of the pyrogenic pollutants, increasing the potential for pollutant buildup during periods of recirculation and stagnation and for long range transport. Established monitoring sites at Singapore coastal waters would be a good start to address the impacts of atmospheric deposition of nutrients onto coastal water in SEA. The information presented in this paper advances scientific knowledge in issues related to atmospheric deposition of pollutants, particularly nutrients, to coastal waters of SEA.

In conclusion, we find that biomass burning in and around SEA act as highly significant sources of nutrients (both inorganic and organic N and P species) through atmospheric deposition to the regional surface water such as estuarine, coastal waters and the open ocean during haze episodes. Atmospheric deposition fluxes of nutrients could contribute a substantial fraction of dissolved N or P species to the euphotic zone and may be available for primary production when they are nutrient-limited. The quantified atmospheric deposition fluxes of nutrients provide a baseline to study the possible ecosystem responses to atmospheric nutrient inputs into the water surface. Hence, to test hypothesized effects of atmospheric inputs in these systems and to enhance our understanding of the interactions of physical, chemical, and biological processes controlling surface water ecosystems, eutrophication modeling study is needed and results obtained from the modeling work are presented in a companion paper.

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Acknowledgement. This research is a part of the main author's PhD research. We would like to thank Karthikeyan Sathrugnan for technical guidance in laboratory analysis, the Division of Environmental Science and Engineering for providing laboratory facilities, and Tropical Marine Science Institute, National University of Singapore for the financial and technical support. One of the authors, Rajasekhar Balasubramanian, gratefully acknowledges the support from the Singapore-Delft Water Alliance (SDWA). The research presented in this work was carried out as part of the SDWA's research programme (R-264-001-013-272). We are grateful to Serena Teo, Tan Koh Siang, Lim Chin Sing and their group for sample collections at Tropical Marine Science Institute in St. John's Island (SJI), Singapore.

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Table 1. Concentration of nutrients (N and P species) (μg/m^3) in aerosol during hazy and non-hazy days and in seawater.

Sample	Nutrients	Period	n	Mean	Median	GeoMean	SD	Min	Max
Aerosol	TN	Haze	4	12.6	12.7	12.5	2.05	10.1	14.9
Aerosol		Non-Haze	16	2.40	2.34	2.29	1.25	1.31	3.84
seawater			*	0.1129					
Aerosol	NH_4	Haze	4	1.92	1.85	1.89	0.38	1.53	2.43
Aerosol		Non-Haze	16	0.28	0.12	0.09	0.41	0.01	1.60
seawater			*	0.0133					
Aerosol	NO_3+NO_2	Haze	4	4.25	4.05	3.93	1.91	2.28	6.63
Aerosol		Non-Haze	16	0.80	0.77	0.76	0.27	0.41	1.51
seawater			*	0.02					
Aerosol	ON	Haze	4	6.44	6.23	6.35	1.29	5.14	8.16
Aerosol		Non-Haze	16	1.49	1.40	1.35	0.61	0.43	2.50
seawater			*	0.0796					
Aerosol	TP	Haze	4	0.48	0.45	0.46	0.13	0.35	0.65
Aerosol		Non-Haze	16	0.07	0.08	0.07	0.02	0.04	0.09
seawater			*	0.0251					
Aerosol	PO_4	Haze	4	0.09	0.07	0.08	0.07	0.04	0.19
Aerosol		Non-Haze	16	0.02	0.02	0.02	0.01	0.01	0.04
seawater			*	0.0116					
Aerosol	OP	Haze	4	0.38	0.32	0.36	0.16	0.28	0.61
Aerosol		Non-Haze	16	0.05	0.05	0.04	0.02	0.002	0.07
seawater			*	0.0135					

Note: * Seawater baseline (unit: mg/l) (Derived from Sundarambal and Tkalich, 2003).

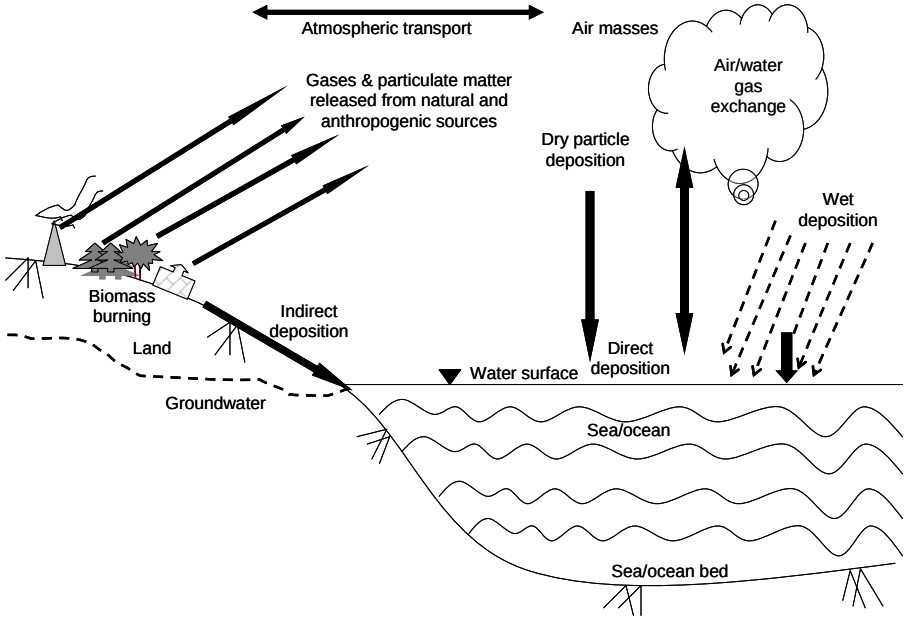

Fig. 1. A schematic illustration of atmospheric deposition processes.

Fig. 2. Sampling location (SJI) in Singapore.

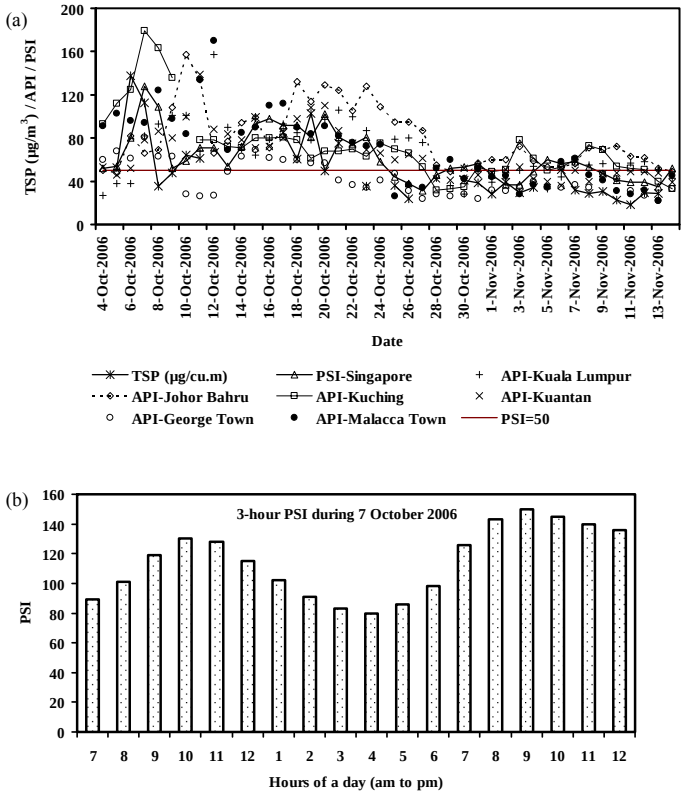

Fig. 3. **(a)** Total Suspended Particulates (TSP), Pollutant Standards Index (PSI) (Data from NEA, Singapore) and Air pollution index (API) (Data from DOE, Malaysia) from October 2006 to November 2006; **(b)** 3-h PSI on 7 October 2006; **(c)** Percentage of normal rainfall distribution in SEA during September 2006 (NEA, Singapore). Note: PSI or API<50 (Good); 51–100 (Moderate); 101–200 (Unhealthy); 201–300 (Very Unhealthy); >300 (Hazardous).

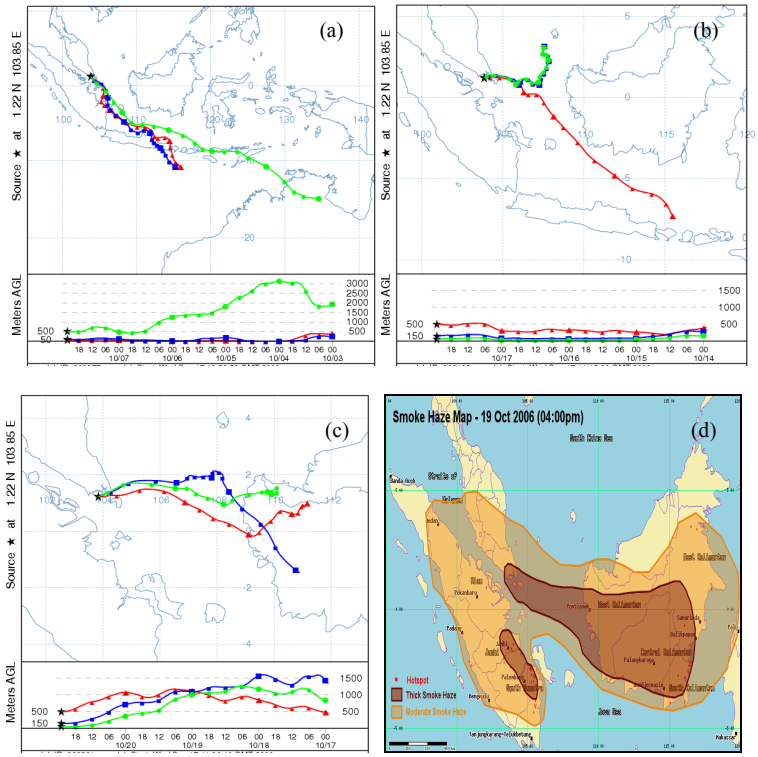

Fig. 4. Back trajectories of air masses for starting altitude of 500 m, 100 m, and 40 m above ground level (AGL) calculated from NOAA HY-SPLIT model for the sampling site in SJI and the extent of the smoke haze in SEA due to forest fires in Indonesia (courtesy: NEA, Singapore) **(a)** 7 October 2006; **(b)** 17 October 2006; **(c)** 20 October 2006 and **(d)** the representative regional haze map.

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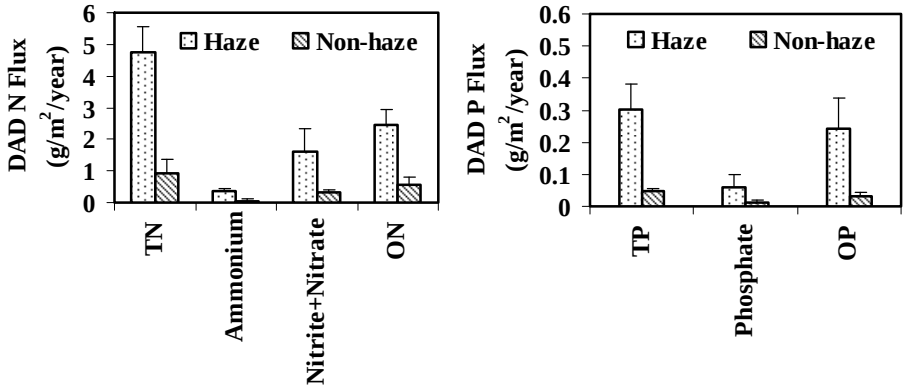

Fig. 5. Fluxes of nutrients (N and P species) in DAD during hazy and non-hazy days.

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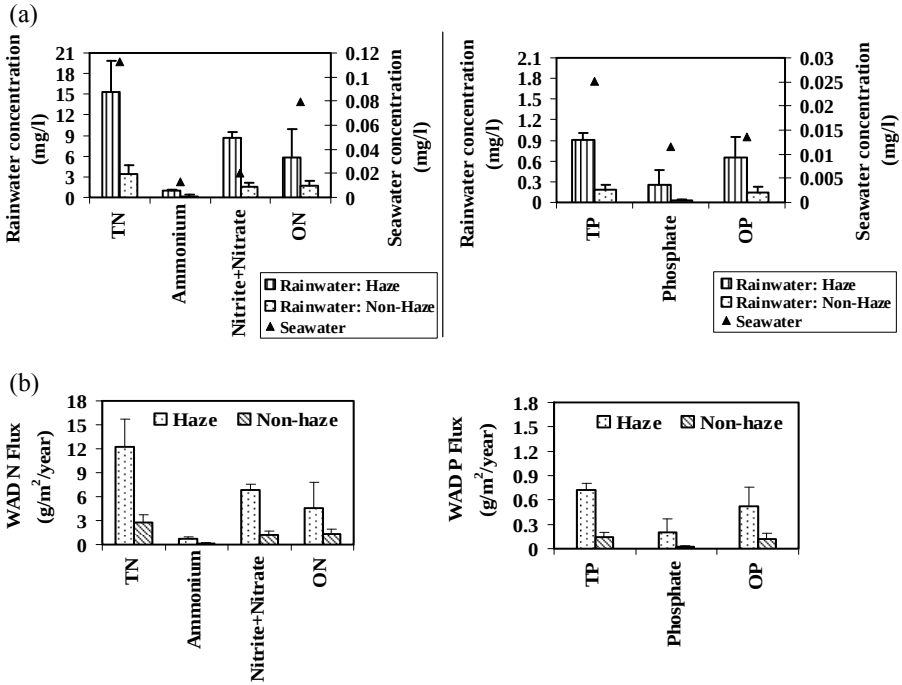

Fig. 6. (a) Concentration of nutrients (N and P species) in rainwater during hazy and non-hazy days and seawater; **(b)** Fluxes of nutrients (N and P species) in WAD during hazy and non-hazy days.

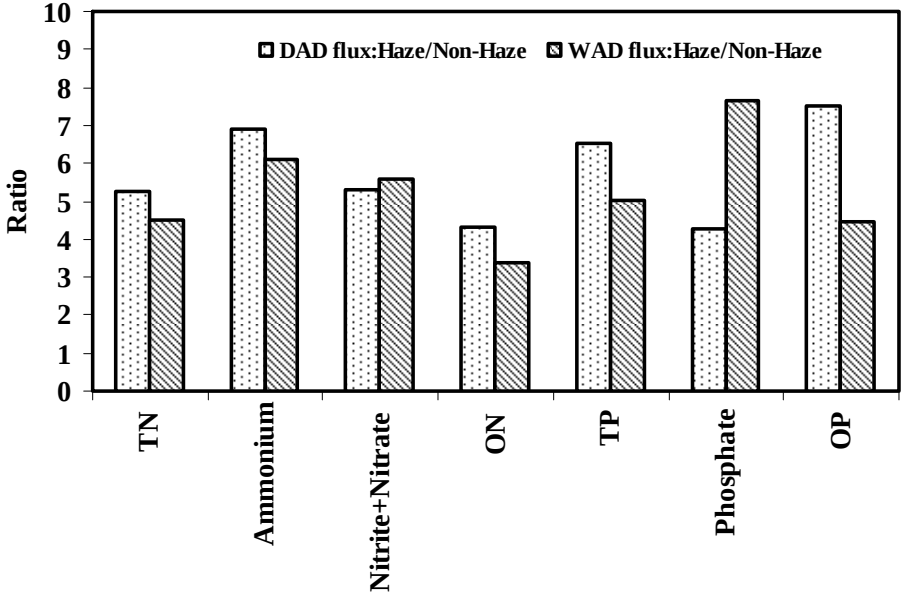

Fig. 7. Ratio of hazy to non-hazy days fluxes of N and P species in DAD and WAD during 2006 haze episodes, SEA.