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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of biomass burning on surface water quality in Southeast Asia through atmospheric deposition: eutrophication modeling" *by* P. Sundarambal et al.

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Reviewer: Anonymous Referee #3

We appreciate the constructive feedback of the reviewer which helped to improve the quality of our journal article. Our detailed responses are as follows:

General comments I largely found this to be an enjoyable and informative paper. As with many types of ecological models the strength of this paper is not based on the certainty (or lack thereof) associated with the exact absolute output, but rather in demonstrating the potential importance of biomass burning on coastal ocean nutrients and algal growth. This work clearly establishes this as a plausible mechanism and now others can engage in more detailed field sampling to validate the results. This paper suffered from a lack of clearly stated methods. My sense was that the authors have this information but was just not clearly presented. Authors' response: We thank the reviewer for the encouraging comments. The method section is rewritten with improved clarity and better presentation.

Specific comments Introduction Comment 1: The case for a possible wide-ranging affect of large-scale biomass burning in areas of SEA on the eutrophication of coastal oceans is justified and clearly stated. A number of statements require literature citations, including page 7781-line 25, page 7782- line 2 and lines 4-15. Authors' response: References have been added as per reviewer's suggestion. In page 7781-line 25: Crutzen et al., 1979; 1985; Andreae et al., 1988; Crutzen and Andreae, 1990; Lobert et al., 1990; Qadri, 2001; In et al., 2007 have been included. In page 7782- line 2: Reference Sundarmbal et al., 2007; 2009 is inserted: A significant fraction of the N and P species entering coastal and estuarine ecosystems along Singapore and the 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 (Sundarambal et al., 2007; 2009). In page 7782- lines 4-15: References are inserted as follows: Water quality degradation is a worldwide subject of concern (Paerl, 1988; Smetacek et al., 1991; Watson et al., 1998; Selman, 2008). SEA surface waters receive a large nutrient supply of which a substantial portion is of anthropogenic origin (Chou, 1994; UNEP, 2000). Accelerated eutrophication and its subsequent effects such as nuisance algal blooms and reduced oxygen levels pose significant problems for coastal waters and aquatic ecosystems in SEA (Nixon, 1995; Azanza and Taylor, 2001; Selman, 2008). Algal blooms resulting from complex coupled physical/biological processes are steadily increasing in coastal waters (Pearl, 1988; Selman, 2008). No studies have investigated the responses of marine ecosystems to atmospheric deposition of nutrients due to episodic smoke haze events in SEA (Sundarambal et al., 2007; 2009; 2010b). 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 deposition of nutrients and marine phytoplankton blooms (Sundarambal et al., 2007). In order to examine the quantitative response of the pelagic food web to atmospheric N and P deposition events, a numerical modeling study is required (Sundarambal et al., 2010a; 2010c).

Smetacek, V., Bathmann, U., Nothig, E. M., and Scharek, R.: Coastal eutrophication: Causes and consequences, in: Ocean Margin processes in Global Change, edited by: Mantoura, R. C. F., Martin, J. M., and Wollast, R., John Wiley and Sons, Chichester, 251–279, 1991. Selman, M., Greenhalgh, S., Diaz, R., and Sugg, Z.: Eutrophication and Hypoxia in Coastal Areas: A Global Assessment of the State of Knowledge, WRI Policy Note, Water Quality: Eutrophication and Hypoxia No.1, Washington, DC 20002, 2008. Chou, L. M.: Marine environmental issues of Southeast Asia: state and development, Hydrobiologia, 285, 139-150, 1994. UNEP: Chia, L.S., and Kirkman H.: Overview of Land-Based Sources and Activities Affecting the Marine Environment in the East Asian Seas, UNEP/GPA Coordination Office & EAS/RCU, Regional Seas Report and Studies Series. 74 pp, 2000. Nixon, S. W.: Coastal marine eutrophication: A definition, social causes, and future concerns, 30 Ophelia, 41, 199–219, 1995. Azanza, R. V., and Taylor, F. J.: Are Pyrodinium blooms in the Southeast Asian region recurring and spreading? A view at the end of the millennium, Ambio, 30(6), 356-364, 2001. Paerl, H. W.: Nuisance phytoplankton blooms in coastal, estuarine and inland waters. Limnol. Oceanogr., 33, 823-847, 1988. Watson, R. T., Moss, R. H., and Ziny-

owera, M. C. (Eds.): The Regional Impacts of Climate Change: An Assessment of Vulnerability. Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK, 1998. Sundarambal, P., Balasubramanian, R., Karthikeyan, S., and Tkalich, P.: Atmospheric deposition of nutrients and its role on coastal eutrophication in Southeast Asia, in: Advances in Geosciences, Vol. 9: Solid Earth, Ocean Science and Atmospheric Science, edited by Chen, Y.-T., World Scientific Publishing Company, Singapore, 149–166, 2007. Sundarambal, P., Tkalich, P., and Balasubramanian, R.: Modeling the effect of atmospheric nitrogen deposition on marine phytoplankton at the Singapore Strait, Water Science and Technology, 61(4), 859-867, 2010a. Sundarambal, P., Balasubramanian, R., Tkalich, P., and He, J.: Impact of biomass burning on surface water quality in Southeast Asia through atmospheric deposition: Field observations, Atmospheric Chemistry Physics Discussion, 10, 7745–7778, 2010b. Sundarambal, P., Tkalich, P., and Balasubramanian, R.: Impact of biomass burning on surface water quality in Southeast Asia through atmospheric deposition: Eutrophication modeling, Atmospheric Chemistry Physics Discussion, 10, 7779–7818, 2010c.

Comment 2: Text regarding general modeling principles on page 7782 (lines 22-29) and page 7783 (lines 1-5) is unnecessary. Text on lines 15-22 from page 7783 is also not needed. Authors' response: The relevant text in the manuscript has been revised accordingly. The unnecessary contents/sentences are removed in the revised manuscript.

Materials and Methods Comment 3: A detailed, map with sampling sites and geographic features would be helpful. Were all wet and dry samples taken from the same location - did number of samples adequately cover the study period - how many hazy and no-hazy days were sampled? On page 7785 (line 10) how is a hazy day defined for dry deposition. Perhaps it is a matter of semantics, but values in Table 1 are not really deposition, they are aerosol concentrations. Dry deposition is of course modeled using those ambient air values. Is there an analytical distinction made between DON and PON? Should Tables 1&2 be in Methods or Results. Need a citation for the companion paper that is mentioned. Page 7785 (Lines 15-20) - How were deposition rates calculated and is the time period of a year (i.e. g/m2/yr) a full calendar year or the September-January sampling period? Again, it might be semantics, but the concentration data do not show a higher AD for dry fallout, of course it all depends on what actually is deposited in the water and what blows by. Authors' response: As per the reviewer's suggestion, a detailed map with sampling sites and geographic features is now included in the revised manuscript.

All wet and dry samples were taken from the same location at St. John's Island (SJI) (Refer to Fig. 2 in the companion paper of field observations) and the details of the sampling location, dry and wet sampling during hazy and no-hazy days, are explained in the companion paper on field observations (Sundarambal, P., Tkalich, P., Balasubramanian, R., and He, J: Impact of biomass burning on surface water quality in Southeast Asia through atmospheric deposition: field observations, Atmospheric Chemistry Physics Discussion, 10, 7745–7778, 2010). Altogether, total of 55 aerosol particulate samples and 21 rainwater samples (collected on event-to-event basis) were collected during the sampling period and number of samples selected for hazy and no-hazy days is given in Table 1 and Table 2 (as footnotes).

On page 7785 (line 10), a hazy day defined for dry deposition sample selection based on PSI (Pollutant Standards Index) measured by NEA, Singapore (the companion paper on field observations). We agree with reviewer that the values in Table 1 are aerosol concentrations. There is no analytical distinction made between DON and PON. Only dissolved nutrients were measured and modeled. Since the values in Tables 1&2 resulted from field observations and were used as input data for modeling, we thought it should be presented in the Methods section, not in the Results & Discussion section in the present modeling paper. The citation of the companion paper is provided in the revised manuscript.

Page 7785 (Lines 15-20): September-January was the sampling period; we agree with reviewer that deposition rates need to be calculated per day (i.e. g/m2/day) instead of

per year (i.e. g/m2/yr). The concentration data (Table 1) shows a higher AD during hazy days compared to those on non-hazy days.

Comment 4: Page 7785 (Lines 23-25) - I may have missed this but was the relationship between PSI and wet/dry concentrations established? Figure 1 shows PSI but text says ambient concentrations. Authors' response: The explanation of Figure 1 given in the text is rewritten for improving its clarity, and it provides relevant information correctly now. The relationship between PSI and dry or wet concentrations was established, but is not presented in the paper, therefore the related explanation is provided in the revised manuscript.

Comment 5: Bottom and page 7785 and top of 7786 - again, much of this may be better placed in results and even discussion (see Page 7786 Line 7-9). Not certain that the introduction to the model on Page 7786 (bottom of page) adds to the paper. Authors' response: Since the values in Tables 1 & 2 were obtained from field observations and wet deposition concentrations were used as input data for modeling, we thought it would be to appropriate to present this information in Methods, not in Results in the present modeling paper. So, we would like to retain these details in the same section as they are now.

Comment 6: This reviewer is not qualified to comment on the specific mathematics used in the NEUTRO Model. However, the expression for dry deposition modeling needs to be explained in more detail. Do the ambient concentrations change over long distances and how is this change accounted for? What about humidity, wind and water surface conditions. Is that state-of-the-art modeling for dry AD this simple? The Model Validation section on page 7791 appears to be limited. It was not discussed well and a single 24-hr validation data set does not seem adequate. Authors' response: The NEUTRO (Tkalich and Sundarambal, 2003; Sundarambal and Tkalich, under review) model is a water quality model developed for simulating the eutrophication dynamics of water in Singapore and surrounding regions. The Model NEUTRO takes into consideration tidal currents forcing, and associated advection, diffusion and settling of the admixture and suspended particles, as well as chemical and physical kinetic reactions of the diluted and suspended substances in the Singapore coastal waters (referring to kinetic equation in Tkalich and Sundarambal (2003), paper is attached herewith for your reference).

Please note that this study is focused on quantification of water soluble nutrients from dry atmospheric deposition (aerosol particulates) and wet atmospheric deposition (rainwater) which was utilized as atmospheric nutrient loading from deposition to a numerical eutrophication model in order to investigate its impact on coastal water quality. This work provides a scientific basis for more in-depth future studies in this region. In order to prove the hypothesis of contribution of atmospheric nutrients to coastal water eutrophication, it is necessary to model the eutrophication phenomeneon using important atmospheric water soluble nutrient loading conditions first. Water-soluble nutrients upon introduction into the water body undergo a complex physical (tidal forcing g, advection, diffusion, temperature and sunlight), chemical (chemical interaction between nitrogen, phosphorous and dissolved oxygen cycles) and biological processes (plankton (phytoplankton and zooplankton) dynamics).

The research is not dealt with development of dry atmospheric deposition modeling as our research objective is to simulate eutrophication contribution due to atmospheric nutrient deposition; the dry deposition estimation is discussed in detail in companion paper. The spatial distribution of ambient concentrations in Singapore doe not change significantly and the deposition of nutrients over the model domain is assumed as uniform. Based on the findings from the present research work, a local and regional long-term field monitoring program should be established to collect the representative temporal and spatial samples of dry atmospheric deposition and wet atmospheric deposition, as well as coastal water and offshore samples over the Singapore waters and Southeast Asia (SEA) region for measurement of nutrients and assessment of their impact on algal biomass. The day-to-day particle concentrations vary substantially in response to spatial and temporal changes of meteorological factors and of fire

activity (Thesis report, Sundarambal, P.: Estimation of the contribution of atmospheric deposition to coastal water eutrophication, Ph.D. Thesis, Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, 2009. and Fig 3 and 4 in the companion paper). We agree with reviewer that the state-of-the-art modeling for dry AD is not simple. In dry deposition, particle size, characteristics of surface water and temperature, the deposition velocity as provided in the literature was not simply used; the deposition velocity (Vs) calculation for the Singapore environment was based on the fundamental properties of aerosol particle characteristics, and atmospheric dynamics (meteorological conditions) as given in the supplementary material of the companion paper.

Please kindly note that the aim of the present study research focus is only to quantify the atmospheric deposition of nutrients (N and P species) and to estimate atmospheric nutrient fluxes by allowing a quantification of the relative contribution of atmospheric and ocean fluxes in the Singapore Strait and to assess the relative contribution of atmospheric nutrient deposition to coastal water eutrophication using the quantified nutrients data and the 3-D modeling program NEUTRO. The NEUTRO model is validated by comparing its prediction with field observations. NEUTRO's results were in close agreement with field measurements for 24 hrs hindcast (high resolution simulation) (Fig 3), baseline values (Thesis report, Sundarambal, P.: Estimation of the contribution of atmospheric deposition to coastal water eutrophication, Ph.D. Thesis, Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, 2009.) and monsoon related variations (Sundarambal and Tkalich, Submitted-a and unpublished reports in Tropical Marine Science Institute, National University of Singapore). The model is able to reproduce correctly general features in the Singapore waters by using verified kinetic coefficients and other model parameters (Tkalich and Sundarambal, 2003; Sundarambal and Tkalich, under review). The model performs well and is comparable to best-established modeling practices and standards in the region (Sundarambal and Tkalich, under review). The above-mentioned validation of the model is described in detail with references.

Sundarambal, P. and Tkalich, P.: Numerical 3-D water quality model (NEUTRO) for eutrophication and pollutant transport, Marine Environmental Research, under review, 2010. Sundarambal, P.: Estimation of the contribution of atmospheric deposition to coastal water eutrophication, Ph.D. Thesis, Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, 203 pp., 2009.

Comment 7: Page 7793, Lines 10-14 - I am confused as to whether this is for the sampling period of the entire year. Samples were only taken for part of the year. Does the 1.835 mg/L value for non-hazy, wet days come from Table 2? Authors' response: In the present paper, samples taken for part of the year (September-January) were utilized. The value for non-hazy, wet days comes from Table 2 and it is checked and revised for its correctness.

Comment 8: Again, I apologize if it is mentioned in the methods section, but what is the relationship between hazy and non-hazy and wet versus dry. Do you get all four of those combinations in the environment? Authors' response: It is discussed in the companion paper of field observations (Sundarambal, P., Tkalich, P., Balasubramanian, R., and He, J.: Impact of biomass burning on surface water quality in Southeast Asia through atmospheric deposition: field observations, Atmospheric Chemistry Physics Discussion, 10, 7745–7778, 2010.).

Results and Discussion Comment 9: Page 7794, Line 12 - Flux is not expressed as mg/L. Line 18 - be sure to call this a modeling experiment. What about discussing the possible contribution of TON as a source of DIN after TON is deposited in the water. Authors' response: We apologize for the mistake. Page 7794, Line 12 - refers to concentration not Flux. Line 18 – experiment is changed to modeling experiment in the revised manuscript.

The quantified water soluble organic nitrogen (ON) from the field measurement was also utilized to model the effect of atmospheric ON deposition on coastal waters. The possible contribution of TON as a source of DIN after TON is deposited in the water is

taken into account in the model kinetic equations (nutrient cycles in Tkalich and Sundarambal, 2003). The description of ON contribution to DIN is not estimated separately in this study and will be described elsewhere in future research.

Comment 10: Are results in Figure 4 supported by any bioassay experiments in the literature? What about sensitivity to P? Y-axis in Figure should be labeled phytoplankton biomass I believe. Does the phytoplankton respond to P once the steady state response to N occurs? Authors' response: Figure 4 shows the increase in the total mass of nitrate + nitrite in seawater proportional to the magnitude of the increment of atmospheric nitrite + nitrate fluxes into the model. Fig. 4 is not phytoplankton mass, so there is no need to get support from any bioassay experiments. A more detailed investigation will be made in a future study.

A similar variation of P in seawater was observed due to variation of atmospheric P deposition. Y-axis in the Figure should be labeled total mass of nitrate + nitrite in seawater, not phytoplankton biomass. Whenever the atmospheric nitrite + nitrate flux increased, similar increases in the phytoplankton concentration and total mass in the Singapore Strait were observed accordingly. The figure with the phytoplankton concentration and total mass of nitrate + nitrite in seawater due to various atmospheric nitrite + nitrate fluxes in the Singapore Strait is now included in the revised manuscript.

The model includes the growth kinetic equation of phytoplankton dynamics which are explained in Tkalich and Sundarambal (2003), and the phytoplankton responds to P depending on the nutrient limitation that occurred during the model computation.

Comment 11: Page 7795, Line 1 - what is the value for the phytoplankton biomass baseline. Line 11 - what are vertical fluxes? AD can be different since it enters the waterbody from the surface thereby maximizing the potential contact time with phytoplankton. Authors' response: Page 7795, Line 1 – It is nitrite + nitrate baseline concentration in seawater. The value for the phytoplankton biomass baseline is 0.02mg C/L (Table 3).

Line 11 – The vertical fluxes mentioned here are atmospheric depositions. In this study, the atmospheric nutrient deposition is taken as a uniform load over the water surface. The words "vertical" and "horizontal" before fluxes are removed from the text to avoid the confusion.

The NEUTRO model was run with conservative admixture assumption to assess the proportion of atmospheric nutrient fluxes by allowing a quantification of the relative contribution of atmospheric and ocean fluxes in the Singapore Strait.

Comment 12: Figure 5 - y-axis needs label. Is this nitate+nitrite? Text on page 7796 (Line 13) implies that Figure 5 represents wet AD. Is this true and if so what about dry deposition? If it is the combination of wet+dry that point should be made clear in the text and in the caption to Figure 5. A better distinction should be made between conservative and non-conservative admixture assumptions. Authors' response: We apologize for the unclear information. Yes, this is total mass of nitrate + nitrite concentration in seawater.

Yes, the text on page 7796 (Line 13) implies that Figure 5 represents wet AD. Also, in this study, we have modeled only wet atmospheric nutrient deposition, as it was clearly observed that wet atmospheric deposition is more dominant than dry atmospheric deposition (Sundarambal et al., 2010b).

Dry deposition is not included in this modeling test. It is not the combination of wet + dry and that point is made clear and has been amended accordingly in the text and in the caption to Figure 5 in the revised manuscript.

A better distinction is made between conservative and non-conservative admixture assumptions in the revised manuscript.

Comment 13: Page 7798 Section 3.5 Environmental Impacts - Notable results; however, others have found same thing in coastal waters and there this section needs to more fully discuss the Singapore results in light of that literature. Authors' response:

The Singapore results in light of other reports in the literature are discussed in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 7779, 2010.