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Interactive comment on "Isotopic composition of water-soluble nitrate in bulk atmospheric deposition at Dongsha Island: sources and implications of external N supply to the northern South China Sea" *by* J.-Y. T. Yang et al.

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Response

General comments Yang et al. monitored the concentrations of anions (nitrate and sulfate etc.) and cations (ammonium and calcium etc.), and analyzed the δ15N and δ18O-nitrate in the wet and dry depositions at the South China Sea (SCS) for four seasons, in order to investigate the sources of atmosphere Nr input and quantify its influence on marine N cycle of SCS. Although authors tried to show us potentially in-

teresting aspects (such as the impact of Typhoon on change in isotopic ratio of nitrate in wet and dry deposition) and to find out the source of wet and dry N deposition on ocean water using dual isotopic 15N-ratio, it is hard for me to recommend the publication of the manuscript in "Biogeosciences". The major problems are the insufficient supporting data to prove their hypotheses and the inconsistent results (such as exceptional case results (July 2010) showing opposite to their hypothesis). For example, they concluded "the major atmospheric Nr deposition was sourced from mainland China driven by the prevailing monsoon winds and occasionally by tropical cyclones". However, they showed us only one case of typhoon impact on nitrate and ammonium concentration and signal of delta 15N-nitrate, which is not enough data to support their opinion ands also is difficult to be statistically accepted. In addition, they did not explain why $\sim$0 per mil values in delta 15N-nitrate (which is indicative to lighting impact) was observed after typhoon phase 2 without observation of increase in nitrate concentrations. Secondly, they insisted that wet N deposition (such as precipitation) led to the increase in nitrate and ammonium concentrations, showing three cases. However, four cases did not follow their hypotheses (three precipitation event during July 2010, but no increase in inorganic N concentrations/ dramatically increase in nitrate concentrations during December 6th to 10th without precipitation impact). Thus, I suggest them to monitor for one more year to collect consistent data to support their hypotheses.

Response: We deeply appreciate the reviewer for his/her useful comments. Also we are sorry for our some misleading statements, leading to misunderstanding by the reviewer. First of all, such data set of atmospheric nitrogen deposition measurement on a remote island is invaluable, particularly since it was conducted on an offshore island, Dongsha Island, in the South China Sea, and with a finer time resolution (12-24 hrs) in different seasons. To our best understanding, this is the first hand dataset reporting the atmospheric nitrogen deposition to the South China Sea as well as its nitrogen isotope composition, where is the largest Chinese marginal sea, serving as the most important oceanic receptacle of atmospheric anthropogenic nitrogen. The operational practices of field experiment campaigns are not readily performed in terms of the logistics and

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transportation. This study would fill a critical data gap of nitrogen deposition over the world oceans. We might have overemphasized the typhoon case, as the reviewer has commented. However, after re-checking the north Pacific typhoon database, we found the other two rainfall events in July were likely influenced by typhoon's outer circulation (TOC) as well. Nevertheless, atmospheric nitrogen deposition fluxes did vary largely with time, region, wet/dry deposition processes, synoptic weather conditions and circulation patterns, and aerosol/gaseous nitrogen species of interest, and the variability might be amplified much more, particularly because our measurements were carried out in a so short time duration for each sample, as we emphasized above. This almost is a common phenomenon for atmospheric nitrogen deposition around the world. For example, Zhang et al. (2011; Nitrogen species in rainwater and aerosols of the Yellow and East China seas: Effects of the East Asian monsoon and anthropogenic emissions and relevance for the NW Pacific Ocean, GLOBAL BIOGEOCHEMICAL CYCLES 25, GB3020, doi:10.1029/2010GB003896) have reported data on wet deposition of reactive nitrogen (nitrate, ammonium, and organic nitrogen) for the Yellow Sea and East China Sea on a single rain even basis. The variability in concentrations and fluxes all could be up to three orders of magnitude or larger. Strayer et al. (2007; Influence of air mass origin on the wet deposition of nitrogen to Tampa Bay, FloridaâĂŤAn eight-year study, Atmospheric Environment 41, 4310–4322) reported wet deposition to Tampa Bay, which also showed such large variability for nitrogen species. Even for both NADP and EANET data sets, they also show vary large variability once the data are acquired on a daily/rain event basis. Moreover, the nitrate wet deposition fluxes contributed by the observed three typhoons actually behaved in two contrasting manners, with a large increase for the September typhoon but without increase for the two July typhoons. In fact, the co-variation in deposition flux and isotopic composition is not necessary since all the three typhoons didn't pass over the sampling site, Dongsha Island, of which the typhoon tracks are shown below (Fig. 1); among others, the two July typhoons crossed over the central part of South China Sea, south of Dongsha, and then made landfall on Hainan Island and Vietnam, and the September typhoon (Fanapi) made

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first landfall over eastern Taiwan and then second landfall on southern Fujian, tracked north of Dongsha all the time. As a result, the collected wet deposition samples all were caused by precipitating clouds of the typhoon's outer circulation, rather than its main circulation. Therefore the effects of tropical cyclones in terms of rainfall amount, rain composition, and in turn the deposition flux would be expected to be considerably complicated, perhaps largely event-dependent. Based on sequential rain samples, the precipitation chemistry and isotope signals have been found to show large inter- and intra-variability during the typhoon/hurricane event(s) (Mullaugh et al., 2013; Dynamics of the chemical composition of rainwater throughout Hurricane Irene, Atmos. Chem. Phys., 13, 2321–2330; Liotta et al., 2008; Isotopic composition of single rain events in the central Mediterranean, JGR 113, D16304, doi:10.1029/2008JD009996; Luo, 2001; The characterization of hydrogen ion concentration in sequential cumulative rainwater, Atmospheric Environment 35, 6219–6225). Wai et al. (2007; A dual site study of the rainwater chemistry within the Western Pacific region, J. Atmos. Chem. 57, 85–103) found that when typhoons bypassed Hong Kong, the resulting rain chemistry could vary with the typhoon paths. In order to being prevent from likely confusion with real typhoon rain, hereafter we call our typhoon rain samples as TOC rain samples. In summary, the TOC wet deposition may not necessarily lead to enhancement of nitrate flux, but the nitrate nitrogen isotope composition may change, corresponding to the change in predominant sources of nitrate. This result doesn't sound unreasonable; in contrast, it has also been observed previously. For example, Sakihama et al. (2008; Chemical characteristics of precipitation in Okinawa Island, Japan, Atmospheric Environment 42, 2320–2335) have observed that rain nitrate and ammonium concentrations largely decreased during typhoon periods, and annually, typhoons contributed only $\sim$10% of wet deposition of nitrate and ammonium. Fang et al. (2011; Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China, Atmos. Chem. Phys., 11, 1313–1325) have observed that lower δ15N ratios have been observed in summer in Guangzhou, South China, where is about 450 km northwest of our sampling island; it is noted that even negative val-

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ues were measured during heavy precipitation. The authors have attributed to natural sources such as lightning and soil emission, and further used -4.9 per mil as the fingerprint ratio of natural sources for estimating the relative contributions of anthropogenic and natural sources by employing a two end-member model. In our revised version, we add trajectories of the July typhoons into our sampling map for reference. Regarding the representative δ15N value of nitrate formed from lightning-induced NOx, we indeed referred to Morin et al. (2009), which has originally been cited in our manuscript, and cited a statement from there for reference, as below: "The δ15N of NOx produced by lightning processes [Schumann and Huntrieser, 2007] is assumed to be zero [Hoering, 1957] because of the very high temperatures prevailing during this process, most likely annihilating any isotopic fractionation." A much more negative ratio (-15 per mil) has been suggested by Moore (1977; The isotopic composition of ammonia, nitrogen dioxide and nitrate in the atmosphere, Atmospheric Environment 11, 1239-1243). In regards of spatial and temporal distribution of lightning NOx emission, based on a comprehensive review by Schumann and Huntrieser (2007; The global lightning-induced nitrogen oxides source, Atmos. Chem. Phys., 7, 3823–3907), the tropical regions and the summer have higher emission. Moreover, Lin (2012; Satellite constraint for emissions of nitrogen oxides from anthropogenic, lightning and soil sources over East China on a high-resolution grid, Atmos. Chem. Phys., 12, 2881–2898) specifically suggested that in summer contributions from natural sources combining soil emanation and lightning represent up to 30% of the NOx in the atmosphere in East China, which demonstrates the significance of lighting particularly during the episodic raining events. One more thing needed to be emphasized is most of our samples represent dry deposition samples rather than wet deposition, which may have caused confusion by the referee. We are also sorry for this, and thus we have clarified in our revised manuscript; please refer to it. We also give up the classification of Phase I and II in our old version for typhoon Fanapi. It is noted that the second rain event in July exactly shows a similar trend to that in September in dual isotopes yet no two separable phases. Accordingly, we have carefully revised our manuscript by considering the re-

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viewer's comments and suggestions and responded them point-to-point in details as follows. Also please refer to the revised manuscript.

Specific comments p. 9670 L1 to 5 You said that Typhoon phase 1 (no precipitation) caused to high level of nitrate during September 16th to 20th and the precipitation during Typhoon phase 2 caused to increase in the ammonium and nitrate concentrations. However, nitrate concentration was dramatically increased during December 6th to 12th without the Typhoon impact. So, what causes to this increase of nitrate concentrations during December 6th 12th? Also, you mentioned that precipitation (rain days) affected the nitrate and ammonium concentrations. However, in July 2010, there was no precipitation impact on the concentrations of nitrate and ammonium. Thus, it is still ambiguous how and why precipitation (rainy days or wet deposition) changed nitrate and ammonium concentrations because too many exceptional case (July 2012 and December 6th to 10th).

Response: It is our mistake. We should not classify the period between September 16 and 20 as Typhoon Phase 1 since the Typhoon Fanapi occupied somewhere far away from Dongsha Island by 1300 km (on September 17) to 500 km (on September 19). Tsai et al. (2011; Seasonal and rainfall-type variations in inorganic ions and dicarboxylic acids and acidity of wet deposition samples collected from subtropical East Asia, Atmospheric Environment 45, 3535-3547) have observed that in South Taiwan TOC rains had higher nitrate and ammonium concentrations than other types of rain. Along with isotope signatures, we have analyzed and add backward trajectories as supplementary materials in the revised manuscript in order to identify the likely source regions. As demonstrated by the two approaches, the two increasing cases in December could be attributed to long-range transport of pollutants from north China. Nevertheless, it is noticed that large variability of rain chemistry has well documented to be of rain-event dependence. Please refer to the revised manuscript in detailed revision.

p. 9672 L8-14 You mentioned that "Different trends are likely attributed to the sources of atm nitrate and their respective nitrogen imprints varying temporally from site to site".

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I think you need to explain which different source could make different temporal trends for 15N-nitrate between your study and other study because your research has mainly focused on the sources of atm nitrate.

Response: Thanks for the comment. In fact, we do have discussed the sources of nitrate deposition and also compared to other previous studies; please refer to Page 9674/Line 1-24 and Page 9675/Line 14 to Page 9676/Line 13 in old version. Besides, we will also strengthen the discussion utilizing results from air mass backward trajectory analyses. Moreover, in addition to source identification of nitrate deposition by analyzing the dual isotopes of nitrate, we indeed also aimed to present the atmospheric deposition of inorganic nitrogen deposition to the northern South China Sea as this would be the first hand data set for atmospheric nitrogen deposition of the South China Sea. Another objective is to discuss the biogeochemical implications for the northern South China Sea.

p. 9674 L18 I think that you need to supply the figures showing the relationship between nitrate and sulfate concentrations in bulk atmospheric depositions as supplementary materials because this correlation could support one of your hypotheses (Nitrate is derived from coral combustion).

Response: As suggested by the reviewer, we have added the correlation plot between nitrate and nss-sulfate in the supplementary materials. Thanks for the suggestion.

p.9675 L10 You mentioned that “Typhoon events caused to the increase in the level of nitrate concentrations and the isotopic ratio of 15N-nitrate was closed to N isotope signals derived from lightning”. However, during September 21st to 23rd (after typhoon), isotopic ration of 15N-nitrate was close to 0 per mil (which was identical to the 15Nnitrate produced by lighting), but there was no impact of typhoon and also no increase in nitrate concentrations. You need to explain why.

Response: It might be due to several causes. First, the lifetime of NOx and its resulting oxidation product, nitrate aerosols, in the troposphere could be as long as several

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days, thus likely prolonging the influence of lightning produced NOx and in turn showing ∼0 per mil. Second, the soil emission of NOx and N2O could be substantially enhanced after precipitation (Jaeglé et al., 2004; Satellite mapping of rain-induced nitric oxide emissions from soils, JGR 109, D21310, doi:10.1029/2004JD004787; Jaeglé et al., 2005; Global partitioning of NOx sources using satellite observations: Relative roles of fossil fuel combustion, biomass burning and soil emissions, Faraday Discuss., 130, 407–423; Zheng et al., 2000; Impacts of soil moisture on nitrous oxide emission from croplands: a case study on the rice-based agro-ecosystem in Southeast China, Chemosphere – Global Change Science 2, 207–224). Such natural NOx has been reported to have very negative values; for example, Li and Wang (2008; Nitrogen isotopic signature of soil-released nitric oxide (NO) after fertilizer application, Atmospheric Environment 42, 4747–4754) have measured -50‰ to -20‰ for the soil-released NO. We sincerely thank to the reviewer for his constructive comments. Accordingly, we have carefully revised our manuscript and made response. Please refer to them.

Interactive comment on Biogeosciences Discuss., 10, 9661, 2013.

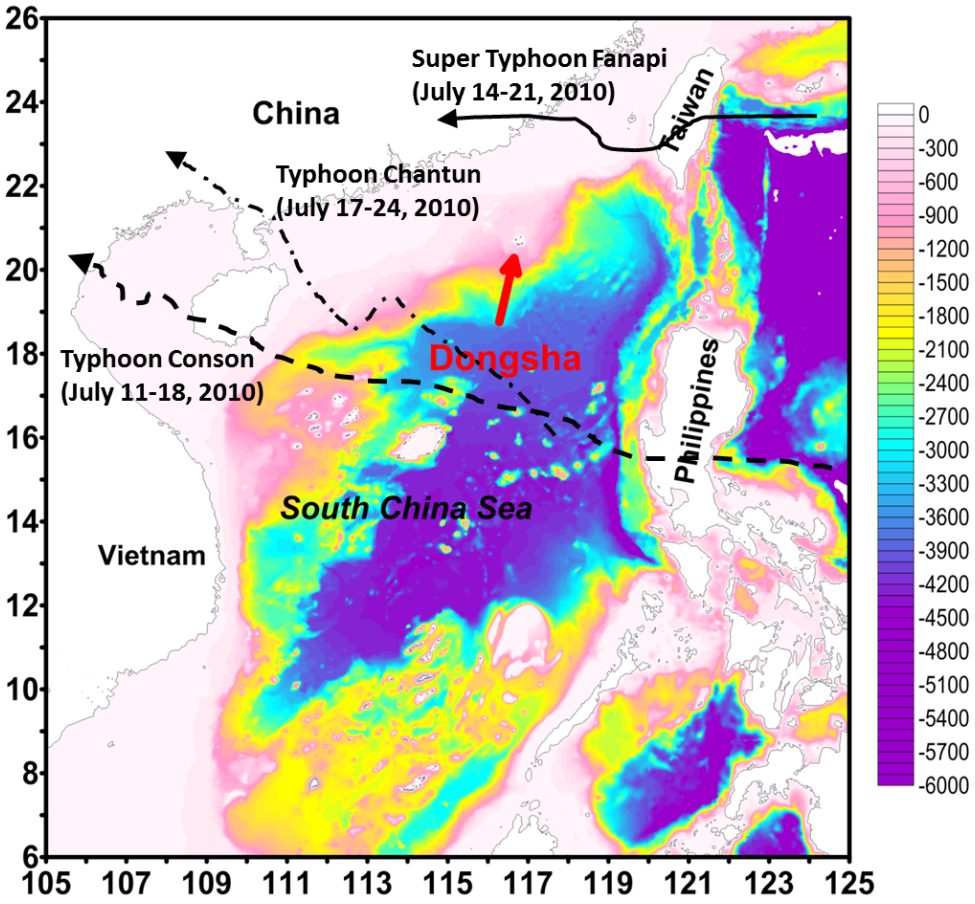

Fig. 1. The pathways of three typhoons in July and September of 2010