

論文の内容の要旨

水圏生物科学 専攻

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論文題目 Impact of atmospheric reactive nitrogen compounds on marine biogeochemical cycles
over the Pacific Ocean
(太平洋における海洋大気中反応性窒素化合物の生物地球化学的
過程への影響)

Atmospheric reactive nitrogen (N) deposition can be important for marine biological activity over large remote areas of the oceans where N supply by deep nutrient rich water is small. Although recent studies have estimated impacts of atmospheric N inputs, there are still large uncertainties regarding the global atmospheric N cycle since most studies are based on the results of several models. The atmospheric N cycle over the oceans contains the most uncertain part because the validation of model output was primarily based on comparisons to terrestrial sampling sites. Moreover, because of rapid Asian economic growth, emissions of anthropogenic substances (e.g., nitrogen oxides; NO_x) from the Asian continent have significantly increased. Since the western North Pacific receives a large influx of mineral dust and pollution aerosol from the Asian continent through atmospheric transport, estimating deposition flux of atmospheric N and its impacts on biogeochemical cycles over the western North Pacific have become increasingly important.

Aerosol, rain and sea fog (only in the subarctic western North Pacific) samples were collected between 48°N and 55°S during the KH-08-2 (R/V *Hakuho Maru*, 29 July–17 September 2008, the subarctic and subtropical western North Pacific), the MR08-06 (R/V *Mirai*, 15 January–8 April 2009, the North and South Pacific) and the KT-09-5 (R/V *Tansei Maru*, 1 May–6 May 2009, the semi-pelagic western North Pacific) cruises conducted over the North and South Pacific Oceans, in order to estimate dry and wet deposition fluxes for atmospheric reactive N species, including ammonium (NH_4^+) and nitrate (NO_3^-), and evaluate their impact on marine biogeochemical cycle (Fig. 1).

Concentrations of NH_4^+ and NO_3^- in marine aerosols collected over the semi-pelagic western North Pacific Ocean varied from 59–182 nmol N m^{-3} and 13–86 nmol N m^{-3} , with averages of $117 \pm 42 \text{ nmol N m}^{-3}$ and $36 \pm 22 \text{ nmol N m}^{-3}$, respectively. Aerosol reactive N in our data was composed of ~77% NH_4^+ and 23% NO_3^- (median values for all data). Most NH_4^+ (~90%) was found in fine mode aerosols ($D_a < 2.5 \mu\text{m}$), suggesting that it was formed by gas-to-particle conversion. In contrast, NO_3^- (~55%) was predominantly found in coarse mode aerosols ($D_a > 2.5 \mu\text{m}$), indicating a chemical reaction between nitric acid gas ($\text{HNO}_{3(\text{g})}$) and sea-salt/crustal aerosol in the marine atmosphere. Both NH_4^+ and NO_3^- showed strong relationships with nss-SO_4^{2-} and nss-K^+ ($r = 0.73\text{--}0.96$), suggesting that fossil fuel combustion and biomass burning are significant sources of NH_4^+ and NO_3^- , and/or that they experienced similar transport and removal mechanisms. The estimates of fractions of atmospheric reactive N species derived from specific sources using the tracer species (nss-SO_4^{2-} , nss-K^+ , nss-Ca^{2+} and Na^+) revealed that 97–99% (mean 98%) of NH_4^+ and 78–88% (mean 84%) of NO_3^- were derived from agricultural activity and fossil fuel combustion, respectively. Mean dry deposition fluxes for NH_4^+ and NO_3^- were estimated to be $31 \pm 17 \mu\text{mol N m}^{-2} \text{ d}^{-1}$ and $33 \pm 17 \mu\text{mol N m}^{-2} \text{ d}^{-1}$, respectively. Although the mean concentration of NH_4^+ was 3 times higher than that of NO_3^- , dry deposition fluxes of both were approximately the same since fluxes to the ocean are dominated by the coarse mode, resulting in NO_3^- being deposited much more rapidly. Atmospheric bioavailable N deposition flux ($64 \pm 31 \mu\text{mol N m}^{-2} \text{ d}^{-1}$) was found to be maximally responsible for the carbon uptake of $420 \pm 210 \mu\text{mol C m}^{-2} \text{ d}^{-1}$ ($139\text{--}669 \mu\text{mol C m}^{-2} \text{ d}^{-1}$) by using the Redfield C/N ratio of 6.625, indicating that it can therefore support 0.05–1.5% of the primary production.

During the Leg 1 of KH-08-2 cruise, sea fog occurred predominantly when the dominant wind direction was southward and air temperature dropped to its dew point, indicating that the warm and humid air masses from the low and middle latitudes of the North Pacific passed over the cold sea surface of the northern North Pacific and they were cooled down to a saturation temperature, since the relatively cold sea surface temperature stabilizes the lower atmosphere, making a favorable condition for sea fog formation. Mean particle number densities during non sea fog events were $25 \pm 31 \text{ cm}^{-3}$ for aerosols in the range of $0.3 < D < 0.5 \mu\text{m}$, $2.6 \pm 3.0 \text{ cm}^{-3}$ for $0.5 < D < 1.0 \mu\text{m}$, $0.53 \pm 0.70 \text{ cm}^{-3}$ for $1.0 < D < 2.0 \mu\text{m}$, and $0.17 \pm 0.27 \text{ cm}^{-3}$ for $D > 2.0 \mu\text{m}$. In comparison, the mean particle number densities during sea fog events decreased by 4% (mean particle number density $24 \pm 20 \text{ cm}^{-3}$) for aerosols in the range of $0.3 < D < 0.5 \mu\text{m}$, 12% ($2.3 \pm 3.1 \text{ cm}^{-3}$) for $0.5 < D < 1.0 \mu\text{m}$, 55% ($0.24 \pm 0.52 \text{ cm}^{-3}$) for $1.0 < D < 2.0 \mu\text{m}$, and 78% ($0.038 \pm 0.091 \text{ cm}^{-3}$) for $D > 2.0 \mu\text{m}$. This result suggests that the growth of aerosol particles to liquid droplets leads to the acceleration of particle removal from the atmosphere, and that particles with diameters larger than $0.5 \mu\text{m}$ could act preferentially as condensation nuclei for sea fog droplets and were more efficiently scavenged by sea fog. The pH values of rain and fog water collected over the North Pacific varied from 3.4–5.9, whereas those of rainwater over the South Pacific ranged from 5.7–6.7. These results indicate strong influence of acidic substances in the northern hemisphere. Mean concentration of NO_3^- in fog water was approximately 6 times higher than that in rainwater, whereas those of NH_4^+ were almost similar in both fog water and rainwater. This result revealed that $\text{HNO}_{3(\text{g})}$ was scavenged more efficiently by fog water as well as NO_3^- in aerosols, and suggested that particle scavenging mechanisms between fog and rain are different (e.g. in-cloud scavenging, below-cloud scavenging and hygroscopic property).

Total concentrations of NH_4^+ and NO_3^- in bulk (fine + coarse) aerosols during the KH-08-2 and MR08-06 cruises varied from 0.93–12 nmol m^{-3} and 0.44–5.6 nmol m^{-3} , respectively. Aerosol reactive N in our data set was composed of ~68% NH_4^+ and ~32% NO_3^- (median values for all data), with ~81% and ~45% of each species being present on fine mode aerosol, respectively. The total NH_4^+ and NO_3^- concentrations showed similar trends, with higher concentrations in samples collected over the western North Pacific and lower values over the South Pacific. These distributions likely resulted from large terrestrial emission sources of N in the northern hemisphere, deposition during transport across the ocean, and the intertropical convergence zone (ITCZ) by which cross-equatorial transport is suppressed. Concentration of NH_4^+ (0.93–4.1 nmol m^{-3}) in aerosols collected over the South Pacific were a factor of 1.2–6.3 higher than the results of model study (0.65–0.78 nmol m^{-3} STP) calculated aerosol NH_4^+ concentrations without natural emissions in the South Pacific, suggesting that emissions of ammonia (NH_3) from the ocean could become a significant source of aerosol NH_4^+ in the South Pacific because NH_3 is emitted into the atmosphere from the ocean as a result of biological activity, and that much of observed aerosol NH_4^+ in the open ocean aerosols could be recycled oceanic NH_3 . Overall, NO_3^- mainly was found in coarse mode aerosols, while NH_4^+ was largely associated with the fine mode. Interestingly, $73 \pm 4.2\%$ of NO_3^- collected in the coast of Chile was found in fine mode aerosols, although it is known that NO_3^- in the marine atmosphere is predominantly associated with coarse mode aerosol, suggesting that NO_3^- accumulated in the coarse mode could have been removed more rapidly by dry or wet deposition during transport because of the larger particle size, and that NO_3^- could be produced by lightning in the free troposphere and by injection from the stratosphere because there are few chances to react with coarse mode sea-salt that is continuously supplied from the sea surface.

Concentrations of NH_4^+ and NO_3^- in rainwater during the KH-08-2 and MR08-06 ranged from 1.7–55 $\mu\text{mol L}^{-1}$ and 0.16–18 $\mu\text{mol L}^{-1}$, respectively. Reactive N in rainwater was composed of ~87% NH_4^+ and ~13% NO_3^- (median values for all data), suggesting that NH_4^+ is more abundant in rainwater collected over the North and South Pacific Ocean, and that it is a more important reactive N species supplied by wet deposition. A significant correlation ($r = 0.74$, $p < 0.05$, $n = 10$) between NH_4^+ and methanesulfonic acid (MSA) in rainwater samples collected over the South Pacific and the coast of Chile, where SeaWiFS satellite images revealed persistently high chlorophyll a levels because of upwelled sea water, suggesting that emissions of NH_3 from the ocean could become a significant source of NH_4^+ over the South Pacific.

The estimated dry deposition fluxes for atmospheric reactive N species varied from 0.55–7.8 $\mu\text{mol m}^{-2} \text{d}^{-1}$ for NH_4^+ to 0.22–8.6 $\mu\text{mol m}^{-2} \text{d}^{-1}$ for NO_3^- , contributing ~46% by NH_4^+ and ~54% by NO_3^- to the dry deposition flux for total reactive N (TRN, i.e. $\text{TRN} = \text{NH}_4^+ + \text{NO}_3^-$) (median values for all data). Wet deposition fluxes of atmospheric reactive N species varied from 3.5 to 119 $\mu\text{mol m}^{-2} \text{d}^{-1}$ for NH_4^+ and from 0.30 to 36 $\mu\text{mol m}^{-2} \text{d}^{-1}$ for NO_3^- , accounting for ~83% by NH_4^+ and ~17% by NO_3^- of TRN from wet deposition flux (median values for all data). While NO_3^- was the dominant reactive N species in dry deposition, reactive N supplied to surface waters by atmospheric wet deposition was predominantly by NH_4^+ (42–99% of the wet deposition fluxes for TRN). Total (dry + wet) mean deposition fluxes of atmospheric TRN in the Pacific Ocean from 48°N and 55°S were estimated to be 32–64 $\mu\text{mol m}^{-2} \text{d}^{-1}$, with 66–99% of this in the form of wet deposition, indicating that wet deposition plays an important role in the supply of atmospheric reactive N to the

Pacific Ocean compared to dry deposition, although the relative contributions are highly variable among regions. The total mean deposition fluxes of atmospheric reactive N over the Pacific Ocean were found to be maximally responsible for the carbon uptake of $210\text{--}420 \mu\text{mol C m}^{-2} \text{d}^{-1}$ in the Pacific Ocean, suggesting that reactive N deposited to the Pacific Ocean from the atmosphere can support 0.86–1.7% of the total primary production.

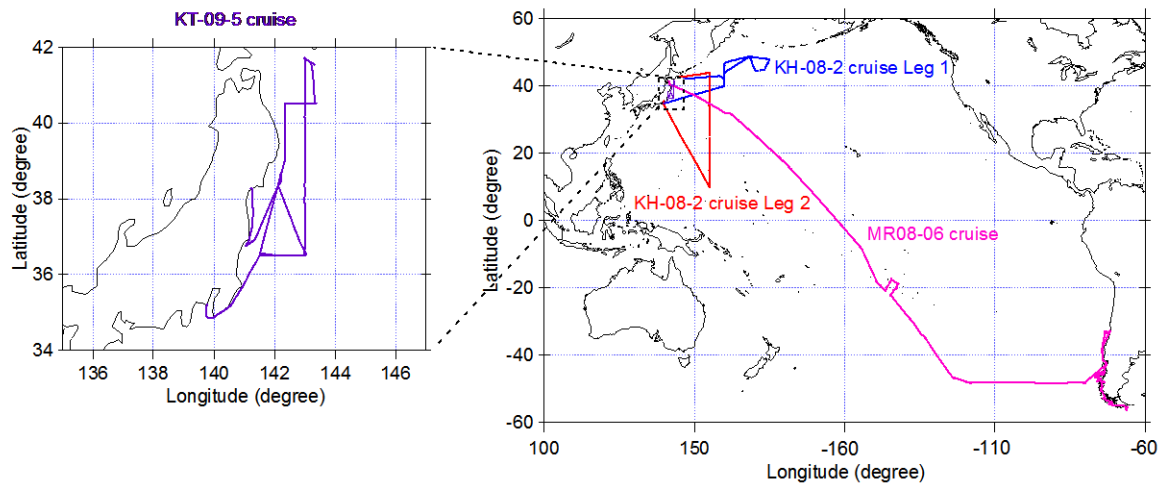


Fig. 1. Cruise tracks of the KH-08-2 (blue; Leg 1, red; Leg 2), the MR08-06 (pink) and the KT-09-5 (purple) cruises.