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Long-term assessment of nitrogen deposition at remote EANET sites in Japan

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HIGHLIGHTS

- We assessed deposition of oxidized and reduced nitrogen from 2003 to 2012.
- We estimated dry deposition amounts by the inferential method.
- Dry deposition of oxidized nitrogen was mainly influenced by domestic emission sources.
- Reduced nitrogen deposition was mainly influenced by regional emission sources.
- Nitrogen deposition amounts remained high thorough the long period in Japanese remote area.

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ABSTRACT

Atmospheric emissions of reactive nitrogen have increased significantly on a global scale due to increases of the use of artificial fertilizer and the burning of fossil fuels. The Asian region has been identified as a high-risk area for nitrogen deposition effects on ecosystems. This paper describes a measurement-based assessment of nitrogen deposition carried out in cooperation with the Acid Deposition Monitoring Network in East Asia (EANET). The investigation aimed to understand the status and variability of dry, wet and total deposition of oxidized and reduced nitrogen over a 10-year period (2003–2012) at 8 remote sites in Japan (Rishiri, Tappi, Sado-seki, Happo, Oki, Yusuhara, Ogasawara and Hedo). Dry deposition amounts were estimated by the inferential method. All of the sites except Rishiri and Ogasawara had high mean annual total nitrogen deposition amounts of approximately 10 kg N ha^{-1} $year^{-1}$ or more, over the 10-year period. The high contribution of oxidized nitrogen deposition in the central area is mainly caused by domestic emissions, especially for dry deposition processes. An increase in reduced nitrogen deposition originating from regional emissions was found, and is likely to result in a subsequent increase in the total nitrogen deposition in Japan. Since neither a clear increasing nor decreasing trend in total nitrogen deposition was found at any site during the 10-year period, the nitrogen deposition amounts remained high thorough the long period in Japanese remote area. The spatial distribution of nitrogen deposition was found to be significant when uncertainties were accounted for.

1. Introduction

Human activities associated with food and energy consumption have caused a significant increase in reactive nitrogen emissions on a global scale, especially due to the use of artificial fertilizer and the burning of fossil fuels (Erisman et al., 2008; Galloway et al., 2008). The input of reactive nitrogen into the environment seriously influences the natural nitrogen cycle (Galloway et al., 2004). Bleeker et al. (2011) showed that nitrogen deposition was a growing issue for biodiversity in many parts of the world, particularly in Asia, and highlighted the importance of exploring the impacts at a regional or local scale. Vet et al. (2014) assessed the global distribution of deposition of major ions, including reactive nitrogen, and showed a large amount of nitrogen deposition in Asia, as well as in the United States and Europe, using output from global models. The same

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authors also carried out regional assessments of depositions utilizing monitoring networks across the world; however, there was lack of observations for dry deposition, except in North America, namely, by the Canadian Air and Precipitation Network (CAPMoN) and the Clean Air Status and Trends Network (CASTNET). It is therefore extremely important to carry out a measurement-based assessment of nitrogen deposition, including dry deposition, on regional or local scales in Asia, a region identified as a high-risk area for nitrogen deposition effects (Bleeker et al., 2011).

To estimate dry deposition, CAPMoN and CASTNET adopt indirect measurements using the so-called inferential method, which estimates dry depositions by multiplying measured concentrations by deposition velocities estimated using modeling techniques. Currently the inferential method is the most suitable technique for assessing long-term dry deposition at the regional scale, since direct measurements require highly sophisticated methods and instrumentation (Wesely and Hicks, 2000). The Acid Deposition Monitoring Network in East Asia (EANET) monitors dry deposition with the inferential method (EANET, 2010a) and estimates are available for sites in Japan. Endo et al. (2011) carried out a first attempt of dry deposition estimation by the inferential method and conducted an assessment of wet and dry deposition in Japan over a 5-year period from April 2003 using the EANET data. However there were large uncertainties related to the dry deposition estimates. In this study, we develop an assessment method that utilizes the data from EANET related to reactive nitrogen deposition, with the long-term aim of exploring the impact of nitrogen deposition on biodiversity in Asia. Using the latest knowledge on dry deposition estimation, we assess the spatial and temporal distribution of the dry, wet and total deposition of oxidized and reduced nitrogen based on the monitoring over a 10-year period, from 2003 to 2012, across remote Japanese areas.

2. Methodology

2.1. Site description

Eight remote Japanese EANET monitoring sites (Rishiri, Tappi, Sado-seki, Happo, Oki, Yusuhara, Ogasawara and Hedo) were used in the assessment (Fig. 1). According to the site criteria of EANET, remote sites are established to assess the background state of acid deposition, and should be located at a sufficient distance from significant stationary sources (such as urban areas, thermal power plants and large factories) and mobile sources (such as major highways, ports and railways) in ordered to minimize these influences (EANET, 2000). Geographic information for the 8 remote sites is shown in Table 1. The Rishiri, Sado-seki, Oki, Hedo and Ogasawara sites are located on islands. Happo and Ysuhara are located at high elevations. The main land use within a 10 km zone of all sites was forest. Although the percentage of forest around Rishiri was lower than for other sites (48%), when the shrub area (49%) was included as part of the forest surface, this increased to 97%.

2.2. Measurements of gas, particle and precipitation

The eight remote sites adopted a four-stage filter pack method for measurements of atmospheric concentrations of HNO_3, NH_3, particulate NO_3^- and NH_4^+ in total suspended particle (TSP) (EANET, 2013a). Sampling of the four-stage filter pack method was carried out biweekly at a constant flow rate of 2.0 L/min at Rishiri, Sado-seki and Ogasawara, and 1.0 L/min at other sites. The four-stage filter pack consists of a Teflon filter (Stage 1), Nylon filter (Stage 2), cellulose filter impregnated with K_2CO_3 (Stage 3) and cellulose filter impregnated with phosphoric acid (Stage 4). The particle

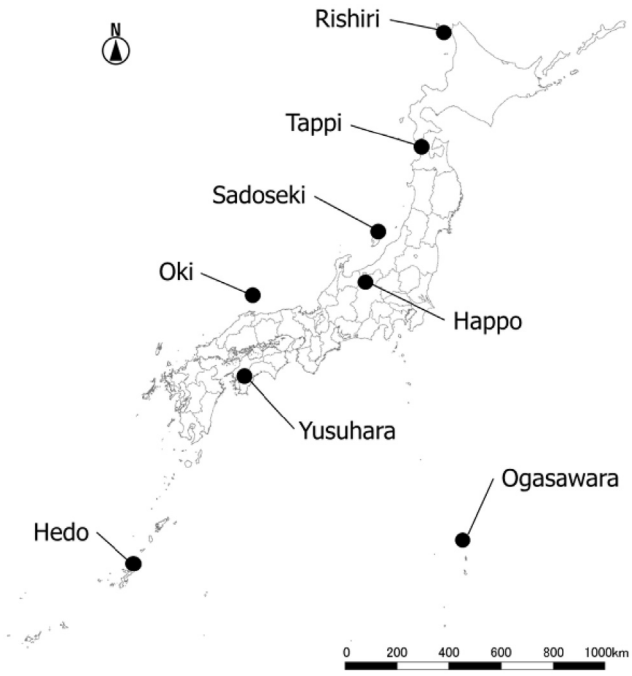

Fig. 1. Location of remote EANET sites used in this study.

components (NO_3^- and NH_4^+), HNO_3 and NH_3 were collected on the Stage 1, 2 and 4 stages, respectively. NH_3 collected on the Nylon filter (Stage 2) was also added to determine the concentration. Inorganic ions were extracted with deionized water from the filter samples, and then analyzed with ion chromatography.

A wet-only sampler was used to collect daily precipitation. Inorganic ions in the precipitation samples were also determined with ion chromatography (EANET, 2010b). All of the sites carried out meteorological observations of temperature, relative humidity, wind direction, wind speed, solar radiation and precipitation amount.

The inter-laboratory comparison activities (discussed in Section 3.3), site audit and data verification were conducted under the quality assurance/quality control program of EANET (EANET, 2000).

2.3. Estimation of deposition amount

2.3.1. Dry deposition

We use the inferential method to estimate dry deposition amounts. Dry depositions of HNO_3, NH_3, particle-NO_3^- and particle-NH_4^+ were taken into account for the total dry deposition. The inferential method estimates the dry deposition based on the following equation:

Table 1
Geographic information of the remote EANET sites used in this study.

site name	Latitude	Longitude	Elevation (m)	%-forest[a]
Rishiri	45°07′11″ N	141°12′33″ E	40	48
Tappi	41°15′06″ N	140°20′59″ E	106	93
Sado-seki	38°14′59″ N	138°24′00″ E	136	90
Happo	36°41′48″ N	137°47′53″ E	1850	75
Oki	36°17′19″ N	133°11′06″ E	90	91
Yusuhara	33°22′45″ N	132°56′05″ E	790	88
Hedo	26°51′58″ N	128°14′55″ E	60	83
Ogasawara	27°05′30″ N	142°12′58″ E	230	69

[a] %-forest means percentage of forest area within a 10 km zone of each site (except sea area).

$$F = -CV_d \quad (1)$$

where F is the dry deposition flux, C is the atmospheric concentration, and V_d is the deposition velocity. We applied the resistance model adopted by EANET (EANET, 2010a) to estimate V_d. The resistance model was developed by Matsuda (2008). V_d is calculated from the following equations:

$$V_d = (R_a + R_b + R_c)^{-1} \text{ for gas} \quad (2)$$

$$V_d = \left(R_a + V_{ds}^{-1}\right)^{-1} + V_g \text{ for particles} \quad (3)$$

where R_a is the aerodynamic resistance, R_b is the quasi-laminar layer resistance and R_c is the surface resistance, V_{ds} is the surface deposition velocity, and V_g is the gravitational settling velocity. For the R_a calculation based on parameterizations of Erisman and Draaijers (1995), we set the reference height to 10 m over the zero-plane displacement height. The R_c parameterization of Wesely (1989) for HNO_3 and NH_3 was used except for the outer surface resistance of NH_3. For the outer surface resistance of NH_3 the non-stomatal resistance of Smith et al. (2000) was used. The parameterization of V_{ds} for aerosol components followed Ruijgrok et al. (1997). This parameterization reproduced well the observed V_d of sulfate above forests in Japan (Matsuda et al., 2010, 2015).

For the V_d calculations, we used the parameters for forest surfaces because of the main land use around the sites mentioned above. Hourly data for wind speed, temperature, relative humidity, solar radiation and precipitation amount observed at the sites were used to calculate V_d. First, hourly V_d values were calculated from the hourly meteorological observations and then averaged to biweekly V_d values for adjusting to the time resolution of the concentrations. For V_d calculation, we assumed that atmospheric stability was neutral based on the sensitivity analysis of Fujimura et al. (2011, 2011) reported that the 2-week averages of V_d with and without diurnal variation of the atmospheric stability were about the same, as the averaged value of the atmospheric stability is close to neutral. Finally, we calculated the biweekly dry deposition values from Eq. (1).

We used the following criteria for the analysis: the biweekly dry deposition value was valid if at least 80% of the hourly meteorological values were available for the 2 weeks; the annual dry deposition value was valid if at least 80% of the biweekly dry deposition values were available for the year; and the 10-year dry deposition value was valid if at least 80% of the biweekly dry deposition values were available for the 10 years.

In some cases, NO_2 dry deposition needs to be included for the total dry deposition of oxidized nitrogen, if the contribution was significant (e.g., Shen et al., 2013). Based on NO_2 concentrations (about 1 ppb) and V_d of NO_2 (about 1% of V_d of HNO_3) in this study sites, we did not include the NO_2 dry deposition as in inferential estimation using regional networks in other studies (Meyers et al., 1991; Baumgardner et al., 2002).

2.3.2. Wet deposition

We estimated wet deposition amounts of NO_3^- and NH_4^+ from the concentrations in a rain sample multiplied by the precipitation amount during the sampling period measured by the standard rain gauge. Annual and monthly wet depositions were then calculated from the volume-weighted concentrations multiplied by the precipitation amounts. The wet deposition values for the monthly and annual period were valid if both the percent precipitation coverage length (PCL%) and the percent total precipitation (TP%) exceeded 80%. The 10-year wet deposition value was also valid if both PCL% and TP% exceeded 80% for the 10-year observation period. We note invalid dry and wet deposition data in the discussion.

3. Results and discussion

3.1. Spatial distribution

3.1.1. 10-Year average

Table 2 summarizes the 10-year averages of the concentrations and V_d of reactive nitrogen (i.e., HNO_3, NH_3, particle-NO_3^-, particle-NH_4^+, wet-NO_3^- and wet-NH_4^+) and precipitation during the period 2003 to 2012. The highest concentrations of HNO_3, NH_3, particle-NO_3^- or particle-NH_4^+ were found at Yusuhara or Hedo, and the second highest concentrations (with the exception of HNO_3) were found at Oki. Conversely, the lowest and the second lowest concentrations of these four components were found at Ogasawara, Rishiri or Happo. These sites are located in isolated areas: Ogasawara, Rishiri and Happo are the farthest sites from the Asian Continent; the northernmost and the highest sites, respectively. Overall, the concentrations were higher in western sites, and lower in the isolated sites. The concentrations of wet-NO_3^- and wet-NH_4^+ mostly depended on precipitation amounts; concentrations at sites with less than 1400 mm annual precipitation (Rishiri, Tappi, Sado-seki and Oki) were relatively high, while the other sites were low.

Estimated V_d values were in the range of those found in a previous study at the same sites (Endo et al., 2011). The distribution of V_d was similar to that of wind speed, especially for HNO_3 which is largely controlled by the aerodynamic resistance, therefore the large V_d of HNO_3 at Tappi and Sado-seki was caused by strong turbulence due to the local climate. Uncertainties of the measurements of concentration and the estimations of deposition velocity are discussed in Section 3.3.

Next, we summarize the deposition amounts of reactive nitrogen over the 10 years at the eight sites (Table 3). For dry deposition, we calculated the 10-year average from the total dry deposition amounts divided by the available sampling period. For wet deposition, we calculated the 10-year average value by averaging the 10 annual deposition values (that were previously calculated from volume-weighted concentrations) multiplied by annual total precipitation. Data completeness for all dry and wet deposition amounts during the 10-year period was over 80%, though, there were some years in which data completeness was under 80%. Uncertainties of the estimations of deposition amount are discussed in Section 3.3.

All of the sites except Ogasawara and Rishiri had high mean total annual nitrogen deposition amounts of approximately 10 kg N ha^{-1} $year^{-1}$ or more over the 10-year period. The ratios of dry deposition to total deposition (%-dry) were generally high at high deposition sites and low at low deposition sites. At the high deposition sites, dry deposition was a large contribution to the increase in total deposition, with the exceptions being Happo and Yusuahra, where %-dry was relatively low. This is possibly because high precipitation amounts over 2500 mm $year^{-1}$ at Happo and Yusuhara (Table 2) increased wet deposition and decreased dry deposition due to the scavenging effect of the precipitation. On the other hand, the ratios of reduced nitrogen to total nitrogen deposition (%-reduced) were mostly found to be lower at the high deposition sites, suggesting oxidized nitrogen deposition also contributed to the increase in total deposition. These results indicate that the spatial pattern of total nitrogen deposition is related to the distribution of dry and oxidized nitrogen deposition. Distribution of total nitrogen deposition is shown in Fig. 2, together with the range of the annual variability. The mean deposition amount and annual variability are low at Rishiri and Ogasawara, and high at the other sites. The high deposition sites are located in central regions of Japan, where

Table 2
10-year averages of concentrations and deposition velocities for reactive nitrogen and precipitation during the period from 2003 to 2012 at eight remote EANET sites in Japan.

	Dry				Wet	
	HNO_3	NH_3	$p\text{-}NO_3^-$	$p\text{-}NH_4^+$	NO_3^-	NH_4^+
	(nmol m^{-3})	(nmol m^{-3})	(nmol m^{-3})	(nmol m^{-3})	(μmol L^{-1})	(μmol L^{-1})
Rishiri (annual precipitation: 1015 mm)						
Concentration	2.8	16.0	10.5	24.6	14.0	17.6
V_d (cm s^{-1})	5.0	0.8	1.1	0.8	–	–
Tappi (annual precipitation: 1191 mm)						
Concentration	6.9	18.4	18.8	36.0	18.2	15.6
V_d (cm s^{-1})	9.4	0.8	2.2	1.7	–	–
Sado-seki (annual precipitation: 1234 mm)						
Concentration	10.2	25.5	14.7	31.4	18.4	15.9
V_d (cm s^{-1})	7.6	0.6	1.9	1.4	–	–
Happo (annual precipitation: 2532 mm)						
Concentration	10.4	15.5	3.7	29.0	8.6	8.7
V_d (cm s^{-1})	4.8	0.8	1.3	1.0	–	–
Oki (annual precipitation: 1339 mm)						
Concentration	7.2	32.4	21.0	52.6	19.9	14.9
V_d (cm s^{-1})	6.0	0.6	1.3	1.0	–	–
Yusuhara (annual precipitation: 2784 mm)						
Concentration	15.1	20.9	8.3	65.8	7.3	6.7
V_d (cm s^{-1})	2.9	0.8	0.6	0.4	–	–
Hedo (annual precipitation: 2069 mm)						
Concentration	3.6	43.7	21.5	38.4	8.0	10.8
V_d (cm s^{-1})	6.5	0.5	1.5	1.1	–	–
Ogasawara (annual precipitation: 1584 mm)						
Concentration	1.4	22.7	6.6	10.6	3.7	4.7
V_d (cm s^{-1})	2.2	0.7	0.4	0.3	–	–

Table 3
10-year averages of dry and wet depositions during the period from 2003 to 2012 at eight remote EANET sites in Japan.

Site name	Dry (kg N ha^{-1} $year^{-1}$)				Wet (kg N ha^{-1} $year^{-1}$)		%-dry	%-reduced	Total (kg N ha^{-1} $year^{-1}$)
	HNO_3	NH_3	$p\text{-}NO_3^-$	$p\text{-}NH_4^+$	NO_3^-	NH_4^+			
Rishiri	0.5	0.6	0.5	0.9	2.0	2.5	36	57	7.0
	(92)	(92)	(92)	(92)	(94)	(94)			
Tappi	2.3	0.6	1.8	2.5	3.0	2.6	56	45	12.9
	(83)	(80)	(82)	(82)	(88)	(88)			
Sado-seki	2.7	0.7	1.1	1.7	3.2	2.7	51	42	12.2
	(85)	(85)	(85)	(85)	(88)	(88)			
Happo	1.9	0.7	0.2	1.0	3.1	3.1	38	48	9.9
	(85)	(85)	(85)	(85)	(86)	(86)			
Oki	1.7	0.9	1.3	2.3	3.7	2.8	49	47	12.7
	(81)	(81)	(81)	(81)	(97)	(97)			
Yusuahra	2.0	0.7	0.2	1.3	2.9	2.6	44	47	9.7
	(90)	(90)	(90)	(90)	(95)	(95)			
Hedo	1.0	1.1	1.4	1.9	2.3	3.1	49	56	10.8
	(90)	(89)	(90)	(89)	(87)	(87)			
Ogasawara	0.1	0.7	0.1	0.1	0.8	1.1	37	64	3.0
	(82)	(81)	(81)	(81)	(95)	(95)			

( ): data completeness over the 10 years.
%-dry: percentage of dry deposition contribution to total nitrogen deposition.
%-reduced: percentage of reduced nitrogen deposition contribution to total nitrogen deposition.

domestic emissions are likely to have a greater influence than at the northernmost site (Rishiri) and the farthest site from continental Asia (Ogasawara). Therefore, it is likely that the high contribution of oxidized nitrogen deposition in the central area is mainly caused by domestic emissions, particularly for dry deposition.

3.1.2. Long-range transport of reactive nitrogen

Small islands have a geographical limitation on the size of local nitrogen emission sources. If the nitrogen deposition amount is larger than that emitted on the island, the excess deposition is considered to have originated from external sources. We estimated the deposition and local emission amounts for the four remote islands on which the Rishiri, Sado-seki, Oki and Ogasawara sites are located (Fig. 3). We did not estimate them for Okinawa Island (containing the Hedo site), since the island is quite large (more than 100,000 ha) and has large emission sources of nitrogen, unlike the other four islands. The emission amounts were estimated based on the 2010 emission inventory from the updated EAGrid2000-Japan (Fukui et al., 2014). In order to compare emissions and depositions, a representative value of emissions in kg N ha^{-1} $year^{-1}$ was estimated from the total emission amount of an island divided by the land area. Then, the ratio of the maximum value of grid emissions in an island was separately shown in the emission (Fig. 3). The nitrogen deposition at each site was assumed to be representative of the deposition across the entire island. Since the sum of forest and shrub areas accounted for more than 70% of the land use on all four islands, the dry deposition calculation used in this study (estimated for forest surfaces) was representative of the

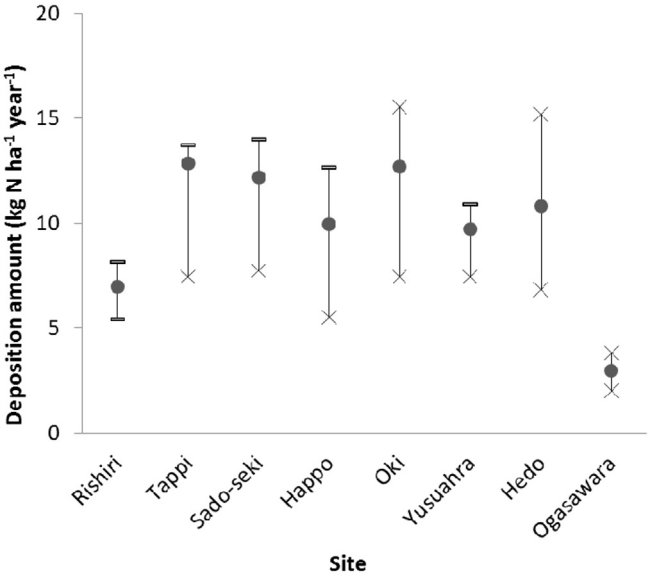

Fig. 2. Distribution of 10-year averages of total nitrogen deposition amount, and the maximum and minimum values (kg N $ha^{-1}year^{-1}$). Filled circles show the 10-year average of total nitrogen deposition, bars show the annual deposition over 80% of the completeness, crosses mean the annual deposition under 80% of the completeness for maximum and minimum values.

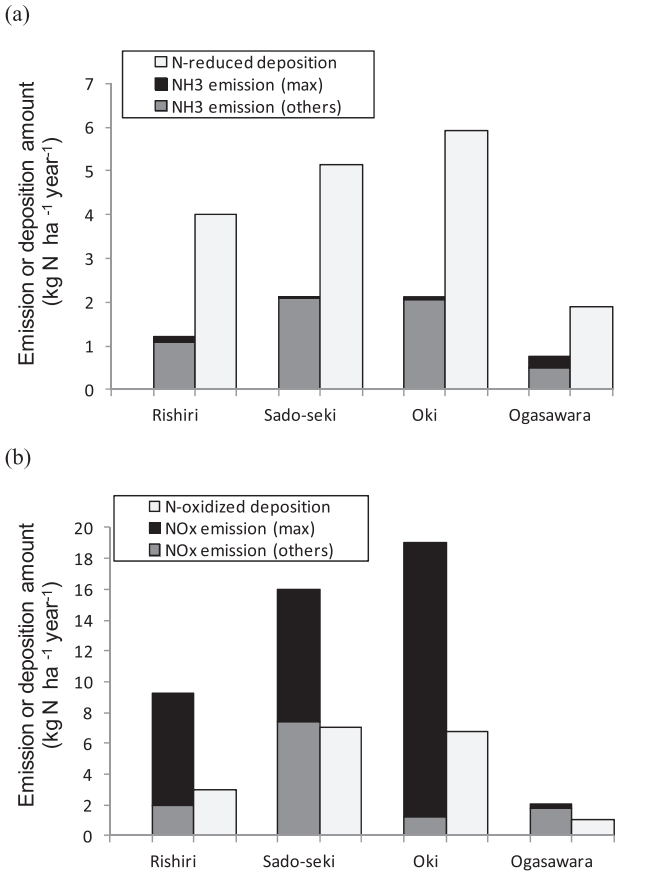

Fig. 3. Comparison between emissions and depositions for (a) reduced and (b) oxidized nitrogen at Rishiri, Sado-seki, Oki and Ogasawara (kg N ha^{-1} $year^{-1}$). Emission (max) and (others) show the ratio of the maximum value of grid emissions and total emission except the maximum value in an island, respectively.

average deposition across the islands.

Depositions of reduced nitrogen on the four island sites clearly exceeded the local NH_3 emissions (Fig. 3a). This result indicates that some of the reduced nitrogen depositions originated from outside sources. Although the total nitrogen depositions were low at Rishiri and Ogasawara, long-range transport of reduced nitrogen clearly contributed to the depositions at the two island sites, as well as at Sado-seki and Oki. This suggests that the reduced nitrogen deposition originating from regional emissions increased the level of total nitrogen deposition in Japan. This result is in accordance with Zhang et al. (2011) suggesting that the North China Plain located in the windward side of Japan exports a huge amount of reduced nitrogen. Whereas, depositions of oxidized nitrogen on the four islands were lower than their NO_x emissions. Since large portions of the total emissions were composed of emissions from limited areas (one grid; 1 km × 1 km) at Rishiri, Sado-seki and Oki (Fig. 3b), the depositions and emissions were not representative of the whole island. Therefore, we could not evaluate the oxidized nitrogen budget.

3.2. Temporal distribution

We estimated annual depositions of reactive nitrogen for each year and assessed the trends over 10 years (Fig. 4). All annual depositions are shown together with information on data completeness, which was less than 80% in some years (Fig. 4). No clear increasing or decreasing trends in the total nitrogen deposition were found at any of the sites from 2003 to 2012. Extremely low depositions were found in some sites, for example, Tappi in 2010, Sado-seki in 2003, Happo in 2010, Oki in 2003 and Hedo in 2003 and 2011, which is possibly due to low data completeness. For wet deposition, low data completeness can result in unrealistically high deposition values: for example, Hedo in 2012, in the case both low TP% and much valid data of higher concentration in the year. In order to determine the influence of precipitation variability on the deposition trends, correlations between the annual deposition and precipitation were estimated (Table 4). Since significant correlations between both total and wet depositions were found at Rishiri, Hedo and Ogasawara, the annual variability of precipitation was considered to be the dominant factor for nitrogen deposition. At the other sites, none of the measured variables were able to explain deposition trends (Fig. 4). According to the emission inventories for 2005 and 2010, NO_x and NH_3 emissions decreased by 28% and 5% in Japan (Fukui et al., 2014) and increased by 33.8% and 10.4% in China (Zhao et al., 2013), respectively. When considering deposition trends, the decrease in Japanese emissions were possibly offset by the increases in Chinese emissions. It means that nitrogen deposition amounts remained high thorough the long period in Japanese remote area.

3.3. Uncertainty

The dry and wet deposition amounts calculated in this study contain various uncertainties. One source of uncertainty is the monitoring network system. In order to evaluate the reproducibility among various laboratories analyzing the samples, the Network Center of EANET has been conducting the Inter-laboratory Comparison Project, as one of its QA/QC activities. This project has been carried out every year from 1998 for wet deposition and from 2005 for dry deposition. The Network Center prepared artificial rainwater samples for wet deposition and impregnated filters for dry deposition containing major ions, and distributed to the participating laboratories. For example, in 2012, values of NO_3^- and NH_4^+ in wet samples from eight laboratories assessed by the project

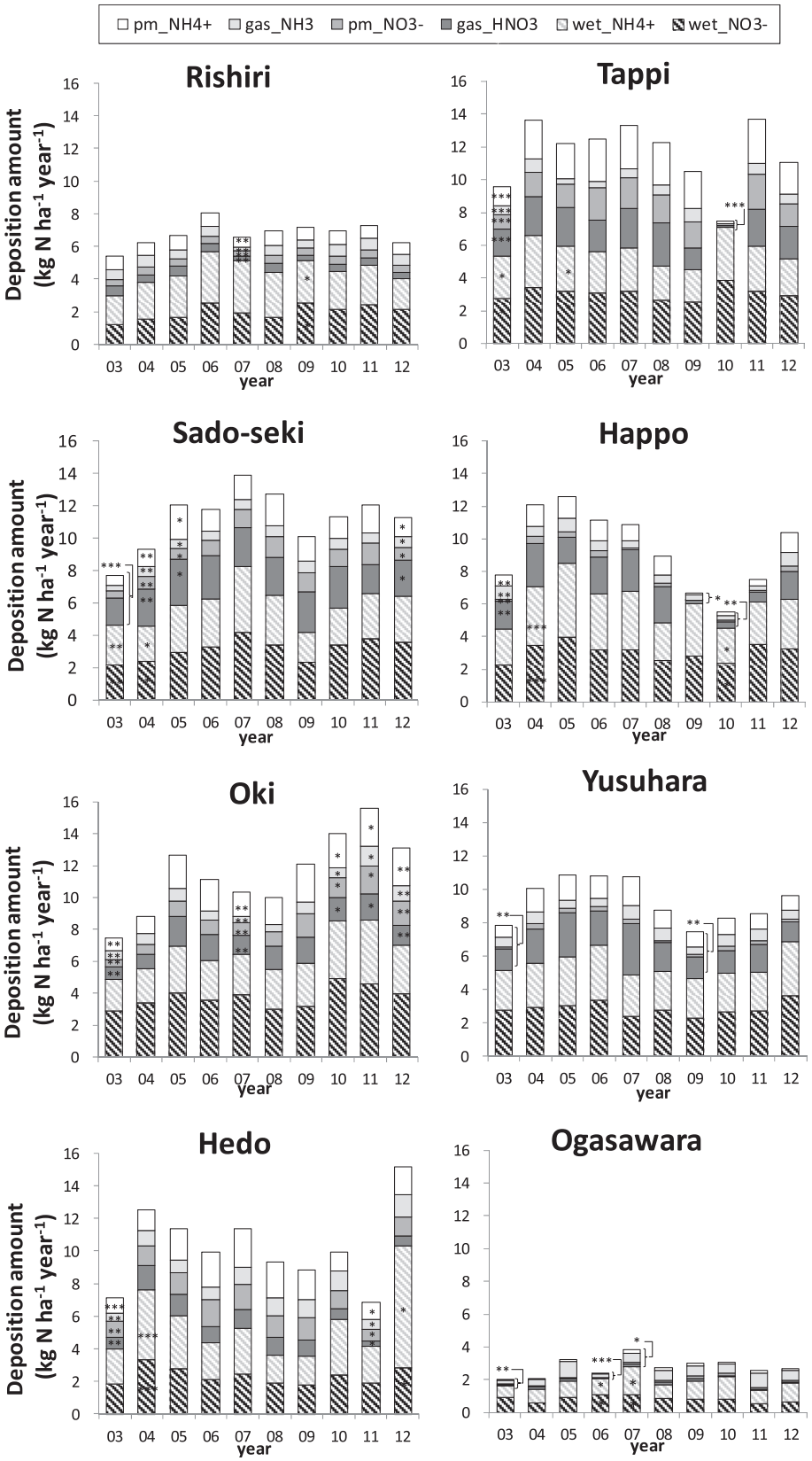

Fig. 4. Trends in the annual deposition of reactive nitrogen (kg N ha^{-1} $year^{-1}$). Data completeness of less than 80% are indicated (*: 80–70%, **: 70–60%, ***: <60%).

had differences in the range of 1.9–7.7%, and the values of NH_4^+ in dry samples had differences in the range of 6.7–8.7% (EANET, 2013b). Based on the project, the measurement values in this study are likely to include errors of less than 10% due to differences in precision between the laboratories.

Another source of uncertainty is the equipment used for dry

Table 4
Significance levels of correlation coefficients between annual precipitation amounts and total or wet deposition amounts of reactive nitrogen.

Data completeness	Deposition	Rishiri	Tappi	Sado -seki	Happo	Oki	Yusu-hara	Hedo	Ogasawara
>80%	Total	**							***
	Wet	*							***
>70%	Total	**						*	
	Wet	**	*					**	
>60%	Total	**						*	*
	Wet	**	*					**	

Significance levels: *, **, *** mean $\alpha < 0.1$, $\alpha < 0.05$, $\alpha < 0.01$, respectively.

deposition. The filter pack method has artifact effects, particularly due to volatilization of the sampled NH_4NO_3 particles. The effect strongly depends on temperature, and causes overestimation of gases (HNO_3 and NH_3) and underestimation of particles (NO_3^- and NH_4^+) during the warm season. Sickles and Shadwick (2008) reported that the overestimations and underestimations were found in summer but not found in other seasons, based on comparisons between a filter pack and a denuder sampling methodology. In order to evaluate the influence of the artifact effect on total nitrogen deposition, it was assumed that all gaseous HNO_3 and NH_3 collected in summer, from July to September, originated from the volatilization of particle-NH_4NO_3 collected on a PTFE filter during the samplings, and dry depositions were estimated under this assumption (Fig. 5). This means that the estimated depositions are the minimum deposition values, and therefore the true values probably lie between the sampled and minimum values shown in Fig. 5. The differences are estimated to be less than 5% for total deposition and 13% for dry deposition at all sites.

There was also uncertainty in the estimation of V_d. Fowler et al. (2009) showed that chemical transport models are able to estimate the dry deposition with uncertainties of the order of 50%, based on a review of ecosystem–atmosphere interaction studies. Uncertainties in dry deposition estimated by the inferential method are less than 50%, because they use observed concentrations and meteorological parameters. Takahashi et al. (2002) found the inferential method reproduced annual dry depositions of oxidized nitrogen with uncertainties of around 13%, when estimated by the throughfall/stemflow method in a Japanese cedar forest. Matsuda (2008) compared the friction velocity, a key factor used to estimate the V_d of HNO_3 largely controlled by R_a, inferred from meteorological parameters and directly measured by a 3D ultrasonic anemometer, and found a good agreement of within 10%. The estimated V_d also has an uncertainty associated with the topography of the area surrounding the sites, since remote EANET sites in Japan are often located in complex terrain, especially mountainous areas (e.g., Happo and Yusuhara). Weathers et al. (2006) showed large variations in depositions at the scale of mountainous areas (about 100–2000 km^2). On the other hand, Matsuda et al. (2015) suggested that complex terrain had no significant influence on the total flux of sulfate over a long time period (i.e. 2 weeks) at the scale of flux footprints (about 1–10 km^2) based on a comparison between the inferential method and the relaxed eddy accumulation method. Therefore the accuracies of the estimated depositions at Happo and Yusuhara are possibly constrained by the limited area around the sites. There were also uncertainties associated with the averaging strategy, which used biweekly mean concentrations and V_d, when the concentration and V_d have diurnal cycles. Hayashi et al. (2013) indicated an uncertainty of approximately 10% from a comparison between weekly mean flux of HNO_3, NH_3, particle-NO_3^- and particle-NH_4^+ estimated by the inferential method with and without day/night separation sampling using a similar type of EANET filter pack method. In addition, it should be noted that the resistance model used in this study did not include the emission process of NH_3 technically, although natural NH_3 flux shows bi-direction (Fowler et al., 2009).

From the discussions above, assuming the total uncertainties for

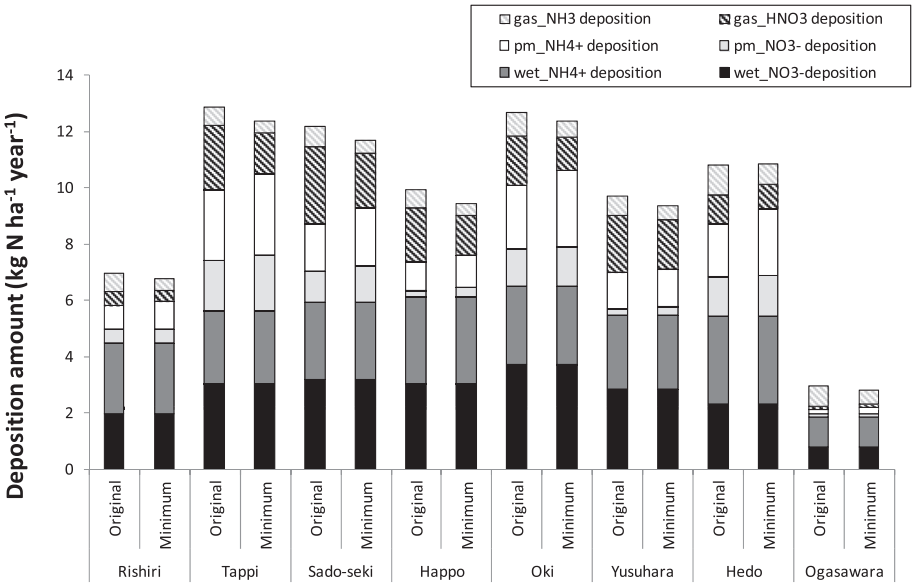

Fig. 5. Estimation of the artifact effect on total depositions. "Original" and "Minimum" show the original estimates in this study and the estimates under the assumption that all HNO_3 and NH_3 originated from the volatilization of NH_4NO_3 collected on the PTFE filters during the sampling from July to September, respectively.

the estimated wet and dry deposition in this study to be 10% and 10–50%, respectively, the uncertainty of the total nitrogen deposition (wet and dry) is estimated to be 10–30% for annual averaging. It is believed that these uncertainties do not have a significant influence on the conclusions presented on total nitrogen depositions and the spatial distributions in Section 3.1.

4. Conclusion

In order to understand the status and variability of nitrogen deposition, with the future aim of investigating the impact on biodiversity in Asia, we carried out a long-term assessment of deposition in remote Japanese areas, utilizing EANET data. We estimated dry, wet and total depositions of oxidized and reduced nitrogen based on observation data over a 10-year period (2003–2012) at eight remote sites. Concentrations of HNO_3, NH_3, particle-NO_3^- and particle-NH_4^+, and the wet depositions of NO_3^- and NH_4^+ were measured at each site by a four-stage filter pack method with biweekly sampling and a wet-only sampler with daily sampling, respectively. The inferential method was used to estimate the dry depositions, using parameterizations of V_d for forests.

We presented the 10-year average of the concentrations, precipitation, V_d, and dry and wet depositions for reactive nitrogen at each sites. The concentrations of gas and particle components were typically high in the western sites and low in the isolated sites. All of the sites except Rishiri and Ogasawara had high mean annual total nitrogen depositions of approximately 10 kg N ha^{-1} $year^{-1}$ or more over the 10-year study period. At the high deposition sites, dry deposition made a large contribution to the increase in total deposition. The large contribution of oxidized nitrogen deposition in the central area is mainly thought to be due to domestic emissions, especially for dry deposition processes. Long-range transport of reduced nitrogen had an impact on the total depositions, even in Rishiri and Ogasawara, since the depositions of reduced nitrogen clearly exceeded local emissions of NH_3 within the islands. The reduced nitrogen deposition originating from regional emissions probably increased the level of total nitrogen deposition in Japan.

No clear increasing or decreasing trends in total nitrogen deposition were found at any site over the 10-year study period. At Rishiri, Ogasawara and Hedo, the annual variability of precipitation was the dominant factor influencing the trend in nitrogen deposition. At the other sites, there was no common factor influencing deposition. The decrease in Japanese emissions was possibly offset by an increase in emissions from China. This means that nitrogen deposition amounts remained high thorough the long period in Japanese remote area.

Uncertainties associated with estimating depositions originate from inter-laboratory differences, the artifact effects of filter pack sampling, the estimation of V_d and the averaging strategy for the inferential method. These uncertainties do not have much influence on the total nitrogen depositions or the discussions on the spatial distributions. However, in order to assess distributions and trends in more detail, these uncertainties need to be reduced, especially for dry deposition, which requires further explanation of the observation methodologies.

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