



Wet Deposition Fluxes of Ions Contributed by Cyclone-, Stationary Front- and Typhoon-associated Rains at the Southwestern Japan Coast

Satoshi Toyonaga^{1,2)} and Daizhou Zhang^{1)*}

¹⁾Faculty of Environmental and Symbiotic Science, Prefectural University of Kumamoto, Kumamoto, Japan

²⁾Kumamoto Prefectural Institute of Public-Health and Environmental Science, Kumamoto, Japan

*Corresponding author. Tel: +81-96-312-6712, E-mail: dzzhang@pu-kumamoto.ac.jp

ABSTRACT

Wet deposition fluxes of ions at a coastal site in southwestern Japan in the period 1996-2003 were investigated to quantify the respective contributions of cyclone-, stationary front- and typhoon-associated rains. On average, the deposition fluxes of terrigenous-origin ions, nss-SO_4^{2-} , NO_3^- , NH_4^+ and nss-Ca^{2+} were 37.6 ± 7.3 , 16.3 ± 4.2 , 19.0 ± 3.4 and 9.6 ± 4.8 $\text{meq m}^{-2} \text{yr}^{-1}$, and those of Na^+ and Cl^- , the major ions in sea water, were 97.0 ± 38.2 and 115.2 ± 48.2 $\text{meq m}^{-2} \text{yr}^{-1}$, respectively. Cyclone-associated rain constituted more than 50% of the fluxes of the terrigenous ions in almost all years. Stationary front-associated rain also contributed significantly, although the contribution was lower than the contribution by Cyclone-associated rain in almost all years. In particular, the wet deposition flux of nitrogen compounds of NO_3^- and NH_4^+ , which are important nutrients for micro-bioactivities in sea surface water, was dominated by cyclone-associated rain. Due to the extreme abundance of Na^+ and Cl^- in the rain-water of typhoons, the fluxes of Na^+ and Cl^- were contributed substantially by typhoons in years with typhoons' passage although cyclones were still the largest contributor to the fluxes. These results indicate the dominance of cyclones in the wet deposition to the East China Sea areas and the necessity to take rain types into account for a more accurate elucidation of the temporal and spatial variation of the wet deposition.

Key words: Wet deposition, Synoptic weather, East China Sea, Nitrogen compounds, Annual fluxes

1. INTRODUCTION

Atmospheric wet deposition of ionic species as the input of nutrients is one of the key processes driving

the evolution and development of the ecosystems in the open ocean (Barile and Lapointe, 2005; Paerl and Fogel, 1994). The input enhances the primary production by phytoplankton and fertilizes the bioactivities in coastal and open sea water (Galloway *et al.*, 2008; Jickells, 1995). Since the activation of phytoplankton in sea surface water significantly affects the uptake of carbon dioxide and modifies the balance between the atmosphere and the ocean, the wet deposition is consequently crucial for the climate changes with regard to its long-term effect (Jickells, 2006). An accurate quantification of the wet deposition will thus benefit to understand more detail deposition process based on field observations and model studies.

Recent studies have revealed an increase of deposition flux of anthropogenic substances in the marine and terrestrial areas of East Asia (Vet *et al.*, 2014; Kuribayashi *et al.*, 2012; Morino *et al.*, 2011), and the increase of wet deposition-induced production in the East China Sea (Zhang *et al.*, 2007; Zhang *et al.*, 2004). On synoptic scales, precipitations in the East China Sea are usually caused by three types of weather: cyclones, Meiyu fronts (i.e. stationary fronts), and typhoons. Cyclones are low pressure systems generated initially by pulse south-eastward outbreak of cold polar air in the Asian continent. Each cyclone is usually composed a cold front, and sometimes also has a warm front. Along the fronts, clouds are produced and cause rains that last usually for hours but less one day in a range of hundreds even more than one thousand kilometers. Meiyu fronts are stationary fronts and generated usually in June and July when warm tropical air intends to expand northward under the prevention of the cold air in the north. The fronts bring long-term and large amount of rainfall in East Asia (Zhou *et al.*, 2004). Typhoons are strong low-pressure systems which are initially generated at the tropical ocean areas and move to the middle latitude areas (Su *et al.*, 2012). Some typhoons arrive at and pass the East China Sea causing extremely heavy rain and strong wind in a time frame from a few hours

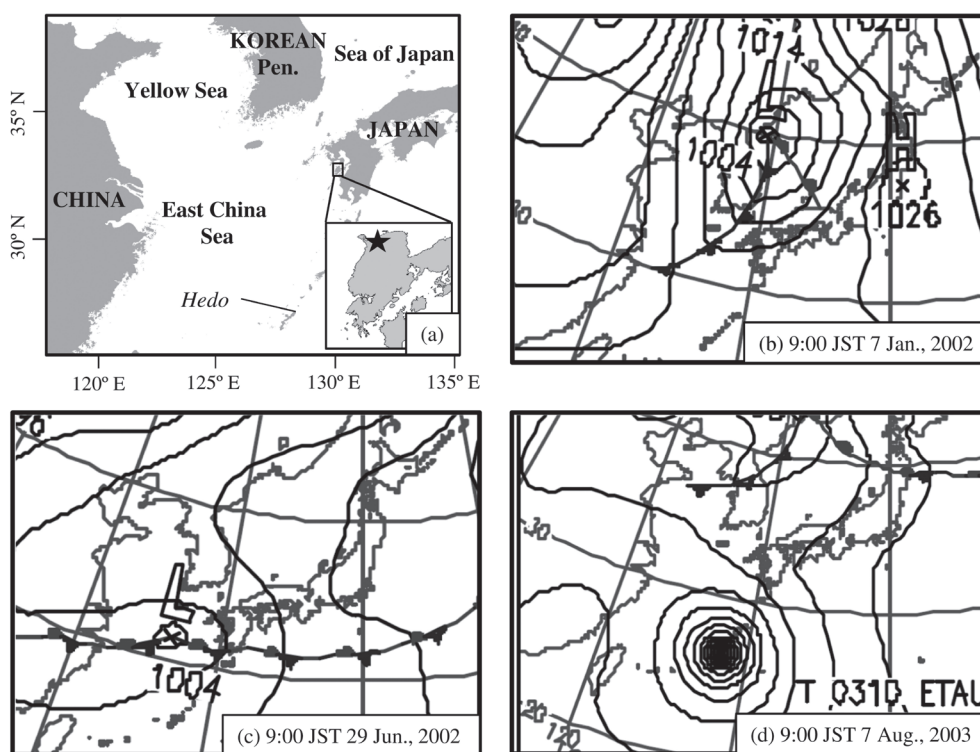


Fig. 1. Rainwater sampling location ((a) Reihoku-shiki Observatory; marked with a star) and representative surface weather charts of the cyclones (b), stationary fronts (c), typhoons (d). The weather charts were issued by the Japan Meteorological Agency.

to one day, usually in late summer.

The mechanisms of cloud formation in these processes differ with each other. Ions in cloud water are from particles and gaseous species in the air parcels relevant to the cloud formation, and ions in rainwater are also changed by below-cloud washout. Regarding these facts, the composition and concentration of ions in rainwaters and their wet deposition fluxes are expected to have distinctive characteristics of the weather types that cause the rain.

Wet deposition at land and ocean areas has been well studied with long-term records, but they were usually in an integrated base, i.e., annual, seasonal or monthly average (e.g. Pan *et al.*, 2012; Seto *et al.*, 2004), or were short-term measurements focusing on one or multiple rain cases (e.g. Sasakawa and Uematsu, 2002). Specifically, nitrogen compounds, such as NO_3^- and NH_4^+ , have been studied with special attention due to their enhancement of ocean fertilization (Zhang *et al.*, 2011; Jickells, 2006). Wet deposition of such ions has rarely been investigated in the point of view of its dependence on weather types. In this study, the wet deposition fluxes of ions to the East China Sea were investigated with the ions' concentration in the rainwater col-

lected at a coastal site. The ions included non-sea salt sulfate (nss-SO_4^{2-}), NO_3^- , NH_4^+ , and non-sea salt calcium (nss-Ca^{2+}), which were terrigenous-origin ions, and Na^+ and Cl^- , which were the major ions in sea water. Cyclones, stationary fronts and typhoons are the synoptic weather systems causing rain over the East China Sea. They usually move from the ocean side to the observatory. Thus, we consider that the records of wet deposition fluxes caused by these weather systems at the coastal site are suitable to the evaluation of the flux of each rain type to the ocean area. The purposes of this study are to explore the dependence of the fluxes of different ions on the weather types of rain formation, to evaluate the contribution of each type of rain to the total wet deposition fluxes, and to quantify the importance of individual rain types in the input of ionic nutrients into the ocean area.

2. MATERIALS AND METHODS

The data used in this study are the concentrations of SO_4^{2-} , NO_3^- , NH_4^+ , Ca^{2+} , Na^+ and Cl^- in the rainwater of each rain episode at the Reihoku-shiki Observa-

tory (32°30'N, 130°03'E; 5 m above sea level; Fig. 1) from January 1996 to December 2003. The observatory is located on the western coast of Amakusa island in the southwestern Japan with the East China Sea approximately 400 meters to its west and 1.4 km to its south. Rain around the observatory is mainly caused by cyclones, stationary fronts, and typhoons, i.e. by weather phenomena on synoptic scales. Other types of rain such as thunderstorms rarely occurred. The data were obtained in a campaign which was by Kumamoto prefectural government conducted to monitor the rainwater acidity in Kumamoto prefecture (Ogata *et al.*, 2004). Rainwater collection and the ion composition analysis were carried out by the atmospheric division of Kumamoto Prefectural Institute of Public-Health and Environmental Science. An auto atmospheric wet-dry deposition sampler (US-750, Ogasawara Keiki Seisakusho) was set up on the roof of the Reihoku-Shiki Observatory (about 3 m above the ground). The hole for rainwater collection was automatically opened when it started to rain and was covered when the rain stopped. For each time of raining, one sample was obtained. After the rain, the sample was saved in a plastic bottle, and rapidly sent to the institute via express delivery services and stored in a refrigerator (approximately 5°C) until analysis. In addition to the concentration of ions, the pH and electric conductivity (EC) of each rainwater sample were measured. The operation procedures of sample collection, reservation and analyses are described in detail in the Technical Manual for Wet Deposition Monitoring in East Asia (2000), which is available from the EANET homepage (<http://www.eanet.asia/product/manual/prev/techwet.pdf>; accessed on 4 Sep. 2014). In total, 404 rainwater samples were obtained in the period, from which ion concentrations of 348 samples were used for the flux investigation of this study after the quality control screening according to the Quality Assurance/Quality Control Program for Wet Deposition Monitoring in East Asia (2000), which is available from the EANET homepage (<http://www.eanet.asia/product/qaqc/qaqcwet.pdf>; accessed on 4 Sep. 2014).

Rainwater samples were classified into 4 groups: cyclone (Cy), stationary front (SF), typhoon (Ty), and "Other", based on the weather information and surface weather charts issued by the Japan Meteorological Agency (Fig. 1). The charts were available from the Annual for Meteorology (Kishounenkan; issued by Japan Meteorological Agency) and homepages (<http://www.data.jma.go.jp/fcd/yoho/hibiten/index.html>; accessed on 3 Aug. 2014). Cy was the rain type caused by low-pressure systems moving eastward from the Asian continent to the Pacific Ocean, and usually associated with cold fronts around the observation area. SF

was the rain type associated with stationary fronts, most of which were Meiyu fronts. Ty was the rain type caused by typhoons. The remains were grouped into "Other". There were a few cases of thunderstorm rains, which were also categorized into the group "Other".

The wet deposition flux of certain ion in one rain episode was calculated with the concentration of the ion in the rainwater multiplied by the rainwater amount. The annual flux of an ion of a rain type was the summation of the fluxes in all episodes of the rain type in one year, from January to December, and the average flux was the average of the eight one-year integrated values. The annual flux of an ion was the sum of the ion's annual fluxes of all rain types. Non-sea salt fractions of Ca^{2+} (nss- Ca^{2+}) and SO_4^{2-} (nss- SO_4^{2-}) were estimated with Na^+ as the conservative tracer of sea salt (Keene *et al.*, 1986). The fluxes of the sea salt fractions of SO_4^{2-} and Ca^{2+} will not be described and discussed in this paper, because of their small contributions to the total fluxes.

3. RESULTS AND DISCUSSION

The average rainfall amount per year over the eight years was 1684 ± 281 mm, in which Cy, SF, Ty and Other constituted $43 \pm 9\%$ (frequency: $63 \pm 7\%$), $33 \pm 13\%$ ($15 \pm 5\%$), $5 \pm 5\%$ ($4 \pm 1\%$), and $19 \pm 9\%$ ($18 \pm 7\%$), respectively (Fig. 2). Cy was the predominant rain type in terms of rainfall amount and frequency, and SF rain was in the second place. The rainfall amount and the frequency of Ty rain in all years were much lower than those of other rain types.

3.1 Average Fluxes

The average deposition fluxes of nss- SO_4^{2-} , NO_3^- , NH_4^+ , nss- Ca^{2+} , Na^+ and Cl^- by all types of rain (i.e., sum of the annual fluxes by the rainwater of Cy, SF, Ty and Other) over the eight years were 37.6 ± 7.3 , 16.3 ± 4.2 , 19.0 ± 3.4 , 9.6 ± 4.8 , 97.0 ± 38.2 , and 115.2 ± 48.2 $\text{meq m}^{-2} \text{yr}^{-1}$, respectively (Fig. 2). The contributions by different types of rain to the flux of an ion differed with the types. Cy contributed 22.2 ± 3.5 $\text{meq m}^{-2} \text{yr}^{-1}$ to nss- SO_4^{2-} , 9.7 ± 2.1 $\text{meq m}^{-2} \text{yr}^{-1}$ to NO_3^- , 11.1 ± 2.6 $\text{meq m}^{-2} \text{yr}^{-1}$ to NH_4^+ , and 5.6 ± 0.8 $\text{meq m}^{-2} \text{yr}^{-1}$ to nss- Ca^{2+} , which were 58-60% of the average deposition fluxes of the respective ions. The fluxes of nss- SO_4^{2-} , NO_3^- , NH_4^+ and nss- Ca^{2+} caused by SF were 8.2 ± 5.6 , 3.6 ± 2.4 , 4.3 ± 3.2 , 1.6 ± 2.0 $\text{meq m}^{-2} \text{yr}^{-1}$, respectively and the contribution was 17-23%. The fluxes of the terrigenous ions caused by Ty were 1.0 ± 1.0 , 0.4 ± 0.5 , 0.6 ± 0.5 and 0.3 ± 0.3 $\text{meq m}^{-2} \text{yr}^{-1}$, respectively and the constitution to any of the ions was less than 4%.

Na^+ and Cl^- , i.e. the major ions in sea water, were

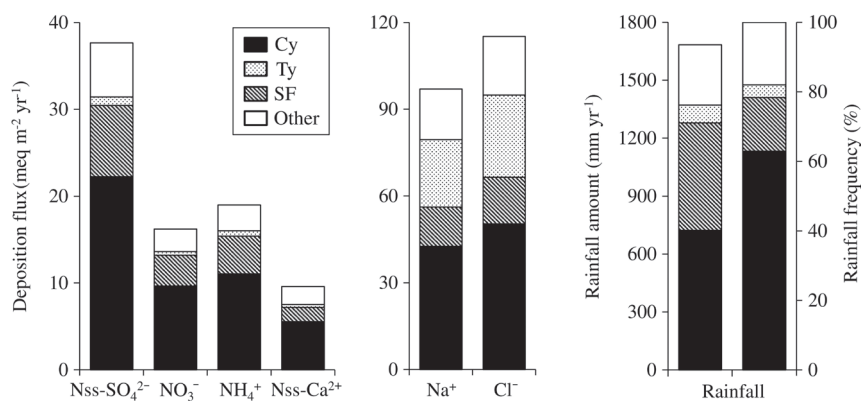


Fig. 2. Average wet deposition fluxes of ions, annual rainfall amount and frequency caused by Cy, SF, Ty and Other.

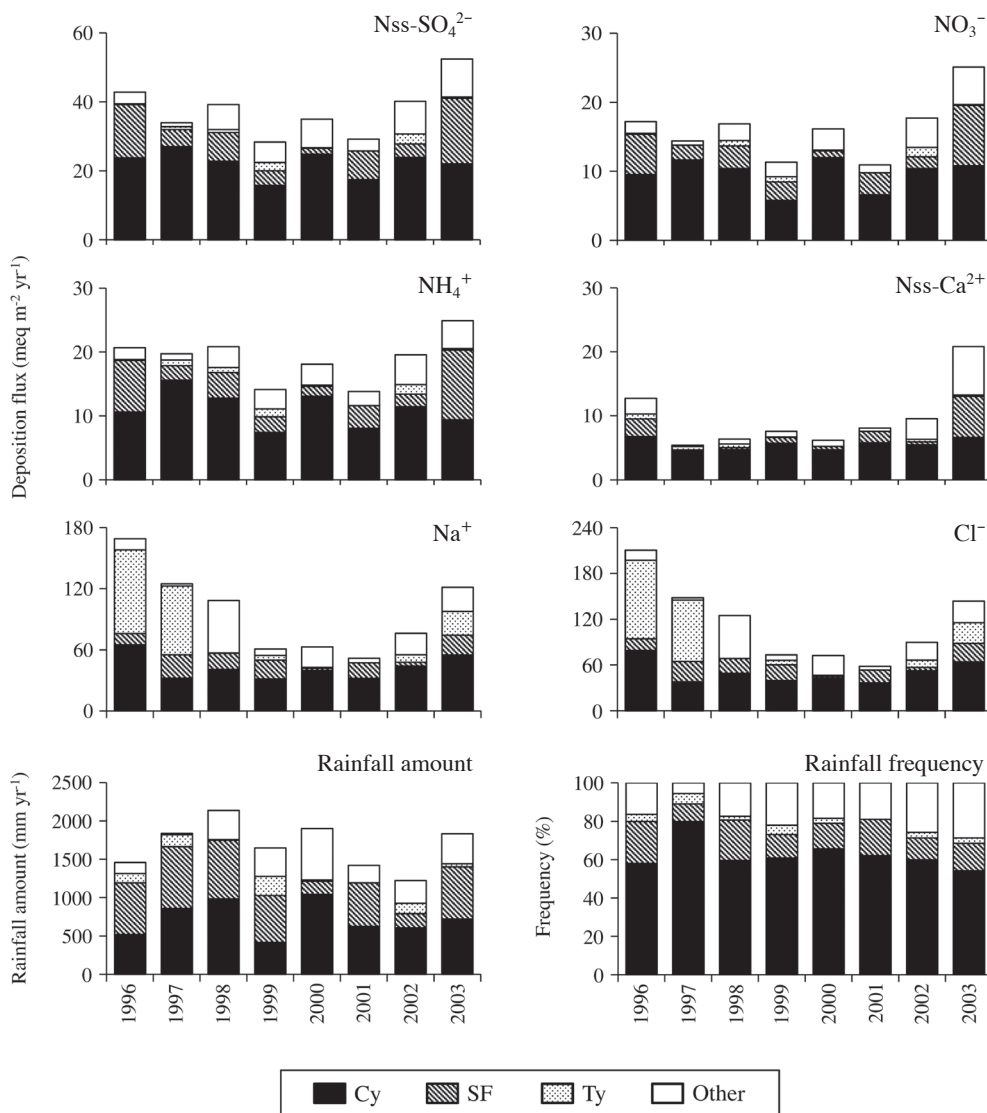


Fig. 3. Year-by-year variation of annual wet deposition fluxes of ions, rainfall amount and frequency caused by Cy, SF, Ty and Other.

extremely abundant in Ty rainwater and the contribution of Ty to the wet deposition fluxes of the two ions was not small, with 24% to the flux of Na^+ and 25% to the flux of Cl^- . Cy contributed approximately 44% to the fluxes of both ions, while SF approximately 14%. These results revealed that Cy type of rain was the largest contributor to the fluxes of all ions. The terrigenous ions nss-SO_4^{2-} , NO_3^- , NH_4^+ and nss-Ca^{2+} were dominated by Cy, and the contributions of Ty were small. Na^+ and Cl^- were substantially contributed by Ty, in addition to the predominant contribution by Cy.

The results were consistent with the characteristics of the rain types. It has been proved that cyclone-associated air masses around Japan were abundant in anthropogenic pollutants and mineral dust from the Asian continents (Zhang *et al.*, 2005; Kaneyasu *et al.*, 2000). Stationary front-associated air masses were affected by both continental air mass and maritime air mass, and were expected to be less abundant in anthropogenic pollutants and mineral dust (Zhou *et al.*, 2004). Moreover, the annual rainfall of Cy was larger than that of SF (Fig. 2). Therefore, the fluxes by Cy were higher than that by SF. Typhoons are strong low-pressure systems initially generated by tropical maritime air masses (Su *et al.*, 2012). As a consequence, the Ty rainwater is extremely abundant in sea salt components (Sakihama and Tokuyama, 2005) and it could significantly contribute to the fluxes of Na^+ and Cl^- , although the rainfall in a year was much less than that of Cy and SF.

3.2 Variations over the Eight Years

The year-by-year variations of the annual fluxes, sum of the fluxes from January to December in a year, of nss-SO_4^{2-} , NO_3^- and NH_4^+ did not have clear trends (Fig. 3). There were likely two-year repeats of increase and decrease from 1996 to 2002. However, the fluxes of the ions in 2003 were the largest in the eight years. Cy contributed more than 50% to the flux of each ion in most of the years, and the trends of these ions caused by Cy were similar to the variations caused by all rain types together. The portion contributed by SF was small and less than 30% in years except for 1996 (up to 39%) and 2003 (up to 44%). Ty's contribution constituted less than 10% in all years.

The year-by-year variation of the annual flux of nss-Ca^{2+} was different from those of nss-SO_4^{2-} , NO_3^- and NH_4^+ . The flux was high in 1996 and 2003, although it was low and did not change largely in the period 1997-2002. This variation was similar to the variation of the portion contributed by SF. The portion by Cy was approximately stable and was more than 30% of the total nss-Ca^{2+} flux in all years.

The annual fluxes of Na^+ and Cl^- were high in 1996 and 1997, and then they decreased until 2001. After

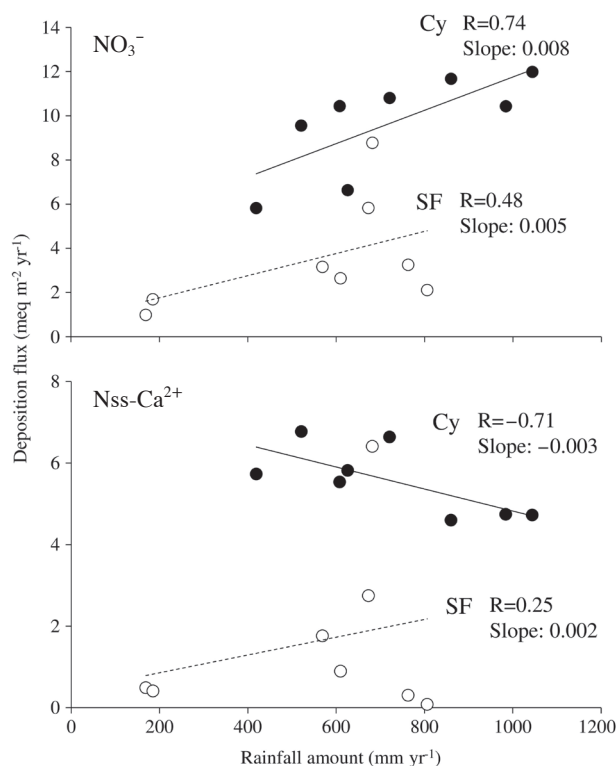


Fig. 4. Annual wet deposition fluxes of NO_3^- (upper) and nss-Ca^{2+} (lower) vs. annual rainfall amounts caused by Cy and SF. Closed and open circles indicate the cases of Cy and SF, respectively. Linear regressions are marked by solid and dashed lines with the slope and correlation coefficient (R).

that, the fluxes increased. The variation was similar to that of the portions contributed by Ty. But in some years, the portions by Ty were smaller than 10%. Variations of Na^+ and Cl^- fluxes caused by Cy rain were different from the variations caused by all rain types together, and the portions by SF were less than or close to 30% in all years.

Therefore, Cy was the largest contributor to the annual fluxes of the six ions. In details, the variation of the fluxes of nss-SO_4^{2-} , NO_3^- , NH_4^+ was mainly governed by Cy. SF substantially contributed to variation of the flux of nss-Ca^{2+} , and, in some years, episodic Ty could largely contribute to the amount and variation of the fluxes of Na^+ and Cl^- . Temporal variation of wet deposition flux has been usually studied and discussed by annually-, seasonally- or monthly-integrated data (e.g. Fowler *et al.*, 2007; Lehmann *et al.*, 2005). Those studies provided useful information on the long-term variation of wet deposition fluxes but did not explain the mechanisms for the variation. The results of the present study indicate that the fluxes by different types of rain need to be carefully investigated in order to accurately elucidate the long-term variations of the

fluxes. In addition, some single rain case significantly contributed to the annual fluxes. For example, high annual fluxes of nss-Ca^{2+} in 2003 was actually caused by two SF cases and one Other case. Detail analyses revealed that the SF cases were abundant in nss-Ca^{2+} due to the influence of continental air masses for a long duration. The Other case was a complex case which was affected by both stationary front and typhoon, and brought large rainfall with large amount of nss-Ca^{2+} . The flux of nss-Ca^{2+} caused by the three cases was 10.6 meq m^{-2} , which was corresponding to approximately half of the annual fluxes by all rain types in 2003. These results indicate that extreme rainfall events such as these should be treated carefully in discussing the temporal variation of the fluxes.

The rainfall and the ionic concentrations in rainwater are the factors determining the fluxes and their variations (Vet *et al.*, 2014; EANET, 2006). To evaluate the relationship between rainfall and the fluxes, regression analysis was conducted. There was an approximately positive relationship between the annual fluxes of terrigenous-origin ions such as NO_3^- and the annual rainfall caused by Cy ($R=0.74$, Slope=0.008) (Fig. 4). Weak positive relationship existed for SF rain ($R=0.48$, Slope=0.005). This is because Cy and SF were the major types of rainfall contributors and the concentrations of the ions in the rainwater of Cy and SF were larger than in other types of rain (Toyonaga and Zhang, 2016). In contrast, the annual fluxes of nss-Ca^{2+} caused by Cy were negatively correlated with the annual rainfall caused by Cy ($R=-0.71$, Slope=-0.003) (Fig. 4). Detailed analyses revealed that the negative correlation was due to the extremely high concentration of nss-Ca^{2+} and low rainfall of the Cy in spring when the Cy was influenced by Asian dust, which could also be confirmed in spring rain cases around the East China Sea in previous studies (e.g. Seto *et al.*, 2007). An exception is the Ty type of rain which had very high con-

centrations of Na^+ and Cl^- , but Ty had limited influence on the annual fluxes and the year-by-year variation. Typhoons are episodic phenomena in the north-west Pacific areas and several typhoons may arrive at and pass the East China Sea every summer (Ho *et al.*, 2004). At a place of more frequent typhoons' passage, such as the areas in the south of Okinawa, Ty's influence on ion fluxes would be more serious (Sakihama and Tokuyama, 2005).

3.3 Flux of Nitrogen Compounds and Its Dominant Rain Type

The average wet deposition flux of the nitrogen compounds, i.e. NO_3^- and NH_4^+ , was $35.3 \text{ meq m}^{-2} \text{ yr}^{-1}$ at the site of the present study. It is in the level similar to those observed at remote islands, such as Hedo of Okinawa (EANET, 2006) (Table 1). The fluxes at ocean areas, including the Pacific, the Atlantic and the Indian Ocean, were $2.1-10.1 \text{ meq m}^{-2} \text{ yr}^{-1}$ (Baker *et al.*, 2010; Duce *et al.*, 1991). Therefore, the East China Sea is actually the region with largest wet deposition flux of nitrogen compounds. Several previous studies have reported the large wet deposition fluxes of ions at the East China Sea areas (e.g. Zhang *et al.*, 2007), and the cause has been attributed to the emission of relevant compounds and precursor gases in the continent, particularly in China (Vet *et al.*, 2014; Uno *et al.*, 2007). The present results show that the contribution by SF, Ty and Other together to the flux was approximately $14.5 \text{ meq m}^{-2} \text{ yr}^{-1}$, which is close to the maximum at ocean areas. This suggests that the major contributor of the extreme large flux at the East China Sea areas was Cy rain. The increase or decrease of Cy rainfall in a year could largely influence the annual flux of nitrogen compounds to the ocean areas, in addition to the change of emission.

The above results also suggest the necessity of taking into account the synoptic weather types for an accurate

Table 1. Wet deposition fluxes of nitrogen compounds ($\text{NO}_3^- + \text{NH}_4^+$) around the East China Sea and to the ocean area.

| Site | Deposition flux ($\text{meq m}^{-2} \text{ yr}^{-1}$) | Rainfall amount (mm) | Period |
|----------------------------------|---|----------------------|-----------|
| Reihoku-shiki ^a | All rain types | 35.3 | 1684 |
| | Cy | 20.8 | 723 |
| | SF | 7.9 | 557 |
| | Ty | 1.0 | 92 |
| | Other | 5.6 | 312 |
| Hedo ^b | 37.5 | 2047 | 2000-2004 |
| North Pacific Ocean ^c | 5.9 | — | 1981-1987 |
| South Pacific Ocean ^c | 2.4 | — | 1981-1987 |
| Atlantic Ocean ^d | 9.2 | — | 2000-2005 |
| North Indian Ocean ^c | 10.1 | — | 1979-1980 |
| South Indian Ocean ^c | 2.1 | — | 1980-1986 |

^aThis study, ^bEANET (2006), ^cDuce *et al.* (1991), ^dBaker *et al.* (2010).

interpretation of wet deposition fluxes and their comparison with other areas. It has been reported that westerlies and meteorological conditions, such as the strength of cyclones, significantly influence the transport of air pollutants from the Asian continent and their deposition via rain (Morino *et al.*, 2011; Zhang *et al.*, 2011; Baker *et al.*, 2010). The results of the present study strongly indicate that the ignorance of the differences that were caused by individual types of rain masked the underlying variations with rain types. This was also supported by a comparison between the sites where frequency of typhoon's passage was apparently different. The flux at Hedo of Okinawa Island, where typhoons pass more frequently and is also influenced by SF every year, was $37.5 \text{ meq m}^{-2} \text{ yr}^{-1}$ (Table 1) (EANET, 2006). Sakihama *et al.* (2008) reported that the annual deposition flux of nitrogen compounds caused by typhoon-associated rain (i.e. as the Ty rain of the present study) constituted approximately 10% of the total flux in Okinawa Island. According to these values, the flux of nitrogen compounds by non-Ty rainwater at Hedo should have been approximately $33.8 \text{ meq m}^{-2} \text{ yr}^{-1}$. This is very close to the annual flux at the present study site after the extraction of the contribution by Ty, which was $34.3 \text{ meq m}^{-2} \text{ yr}^{-1}$. Therefore, the wet deposition fluxes of nitrogen compounds to the ocean caused by Cy and SF at different sites in the East China Sea were approximately similar and the differences of the fluxes between the sites were mainly due to Ty.

These results indicate Cy was the most important rain type for nitrogen compound supply to the East China Sea from the air in the point of view of long-term effects. Cyclones occur at the intrusion of cold polar air from northwest or west, and move eastward in the mid-latitude westerly wind flows (Barry and Chorley, 2003). The postfrontal or prefrontal air is abundant in terrigenous substances or anthropogenic pollutants in recent years (Zhang *et al.*, 2005; Kaneyasu *et al.*, 2000). As discussed in section 3.1, these characteristics were consistent with the fact that the fluxes of nitrogen compounds by Cy were larger than the fluxes by SF and Ty, because SF and Ty rains are mainly affected by maritime air and contain less anthropogenic air masses compared to Cy rain. Regarding the fact that cyclones are typical and constant meteorological phenomena causing rain in the East China Sea, the supply by Cy is common, and can play an constant role in the air-sea interaction in the sea areas.

4. SUMMARY

The wet deposition fluxes of nss-SO_4^{2-} , NO_3^- , NH_4^+ , nss-Ca^{2+} , Na^+ and Cl^- at a coastal site in the south-

western Japan were investigated according to the types of rain caused by Cy, SF and Ty. The contributions of individual rain types to the fluxes differed with ions. The deposition fluxes of terrigenous ions, nss-SO_4^{2-} , NO_3^- , NH_4^+ and nss-Ca^{2+} , were dominated by Cy. The fluxes were also significantly contributed by SF, although the contribution was lower than that by Cy in most cases. Ty contributed substantially to the fluxes of Na^+ and Cl^- , while Cy was still the largest contributor. The year-by-year variation of the annual fluxes of nss-SO_4^{2-} , NO_3^- and NH_4^+ were governed by Cy, while the variation of nss-Ca^{2+} flux was dependent on SF. Due to its episodic occurrence and the high concentration of Na^+ and Cl^- in its rainwater, Ty caused large variations of the annual fluxes of the two ions in some years. The fact that the East China Sea had the largest deposition flux of nitrogen compounds is the consequence of the input by Cy. All of these results indicate that quantifying wet deposition fluxes according to rain types is critical to an accurate elucidation of the fluxes and their variations, and is also essential for meaningful comparisons of temporal and spatial variations and for a convincing investigation of their roles in the air-sea interactions.

ACKNOWLEDGEMENT

We thank the Kumamoto Prefecture and the Kumamoto Prefectural Institute of Public-Health and Environmental Science for providing the long-term record. This study was promoted under the program of the Contributions of the Prefectural University of Kumamoto to the Local Environment Studies and also as a part of the JSPS-NSFC joint research program of 2013-2015. We also thank Prof. J. Morrow for his assistance in the word and grammar editing, and the two anonymous reviewers for their helpful comments.

REFERENCES

- Baker, A.R., Lesworth, T., Adams, C., Jickells, T.D., Ganzeveld, L. (2010) Estimation of atmospheric nutrient inputs to the Atlantic Ocean from 50°N to 50°S based on large-scale field sampling: Fixed nitrogen and dry deposition of phosphorus. *Global Biogeochemical Cycles* 24, GB3006.
- Barile, P.J., Lapointe, B.E. (2005) Atmospheric nitrogen deposition from a remote source enriches macroalgae in coral reef ecosystems near Green Turtle Cay, Abaco, Bahamas. *Marine Pollution Bulletin* 50, 1262-1272.
- Barry, R., Chorley, R. (2003) Mid-latitude synoptic and

- mesoscale systems, In *Atmosphere, Weather and Climate* (Barry, R. and Chorley, R. Eds), Routledge, London, pp. 226-268.
- Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Buat-Menard, P., Hicks, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W., Galloway, J.N., Hansen, L., Jickells, T.D., Knap, A.H., Reinhardt, K.H., Schneider, B., Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R., Zhou, M. (1991) The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 5, 193-259.
- EANET (2006) Periodic Report on the State of Acid Deposition in East Asia Part I: Regional Assessment.
- Fowler, D., Smith, R., Muller, J., Cape, J.N., Sutton, M., Erisman, J.W., Fagerli, H. (2007) Long term trends in sulphur and nitrogen deposition in Europe and the cause of non-linearities. *Water, Air, Soil Pollution Focus* 7, 41-47.
- Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., Sutton, M.A. (2008) Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. *Science* 320, 889-892.
- Ho, C.H., Baik, J.J., Kim, J.H., Gong, D.Y., Sui, C.H. (2004) Interdecadal changes in summertime typhoon tracks. *Journal of Climate* 17, 1767-1776.
- Jickells, T. (1995) Atmospheric inputs of metals and nutrients to the oceans: their magnitude and effects. *Marine Chemistry* 48, 199-214.
- Jickells, T. (2006) The role of air-sea exchange in the marine nitrogen cycle. *Biogeosciences* 3, 271-280.
- Kaneyasu, N., Takeuchi, K., Hayashi, M., Fujita, S., Uno, I., Sasaki, H. (2000) Outflow patterns of pollutants from East Asia to the North Pacific in the winter monsoon. *Journal of Geophysical Research* 105, 17361-17377.
- Keene, W.C., Pszenny, A.A.P., Galloway, J.N., Hawley, M.E. (1986) Sea-salt corrections and interpretation of constituent ratios in marine precipitation. *Journal of Geophysical Research* 91, 6647-6658.
- Kuribayashi, M., Ohara, T., Morino, Y., Uno, I., Kurokawa, J.I., Hara, H. (2012) Long-term trends of sulfur deposition in East Asia during 1981-2005. *Atmospheric Environment* 59, 461-475.
- Lehmann, C.M.B., Bowersox, V.C., Larson, S.M. (2005) Spatial and temporal trends of precipitation chemistry in the United States, 1985-2002. *Environmental Pollution* 135, 347-361.
- Morino, Y., Ohara, T., Kurokawa, J., Kuribayashi, M., Uno, I., Hara, H. (2011) Temporal variations of nitrogen wet deposition across Japan from 1989 to 2008. *Journal of Geophysical Research* 116, D06307.
- Ogata, K., Yano, H., Ueno, K. (2004) Long-term monitoring of acid deposition in Kumamoto prefecture. *Annual Report of Kumamoto Prefectural Institute of Public Health and Environmental Science* 34, 71-76. (in Japanese)
- Paerl, H.W., Fogel, M.L. (1994) Isotopic characterization of atmospheric nitrogen inputs as sources of enhanced primary production in coastal Atlantic Ocean waters. *Marine Biology* 119, 635-645.
- Pan, Y.P., Wang, Y.S., Tang, G.Q., Wu, D. (2012) Wet and dry deposition of atmospheric nitrogen at ten sites in Northern China. *Atmospheric Chemistry and Physics* 12, 6515-6535.
- Sakihama, H., Tokuyama, A. (2005) Effect of typhoon on chemical composition of rainwater in Okinawa Island, Japan. *Atmospheric Environment* 39, 2879-2888.
- Sakihama, H., Ishiki, M., Tokuyama, A. (2008) Chemical characteristics of precipitation in Okinawa Island, Japan. *Atmospheric Environment* 42, 2320-2335.
- Sasakawa, M., Uematsu, M. (2002) Chemical composition of aerosol, sea fog, and rainwater in the marine boundary layer of the northwestern North Pacific and its marginal seas. *Journal of Geophysical Research* 107, 4783.
- Seto, S., Hara, H., Sato, M., Noguchi, I., Tonooka, Y. (2004) Annual and seasonal trends of wet deposition in Japan. *Atmospheric Environment* 38, 3543-3556.
- Seto, S., Sato, M., Tatano, T., Kusakari, T., Hara, H. (2007) Spatial distribution and source identification of wet deposition at remote EANET sites in Japan. *Atmospheric Environment* 41, 9386-9396.
- Su, S.H., Kuo, H.C., Hsu, L.H., Yang, Y.T. (2012) Temporal and spatial characteristics of typhoon extreme rainfall in Taiwan. *Journal of Meteorological Society of Japan* 90, 721-736.
- Toyonaga, S., Zhang, D. (2016) Chemical characteristics of rainwater associated with synoptic weather: eight-year record at a coastal site in southwestern Japan. *Aerosol and Air Quality Research* (in submission).
- Uno, I., Uematsu, M., Hara, Y., He, Y.J., Ohara, T., Mori, A., Kamaya, T., Murano, K., Sadanaga, Y., Bandow, H. (2007) Numerical study of the atmospheric input of anthropogenic total nitrate to the marginal seas in the western North Pacific region. *Geophysical Research Letters* 34, L17817.
- Vet, R., Artz, R.S., Carou, S., Shaw, M., Ro, C.U., Aas, W., Baker, A., Bowersox, V.C., Dentener, F., Galy-Lacaux, C., Hou, A., Pienaar, J.J., Gillett, R., Forti, M.C., Gromov, S., Hara, H., Khodzher, T., Mahowald, N.M., Nickovic, S., Rao, P.S.P., Reid, N.W. (2014) A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. *Atmospheric Environment* 93, 3-100.
- Zhang, D., Iwasaka, Y., Shi, G., Zang, J., Hu, M., Li, C. (2005) Separated status of the natural dust plume and polluted air masses in an Asian dust storm event at coastal areas of China. *Journal of Geophysical Research* 110, D06302.
- Zhang, G., Zhang, J., Liu, S. (2007) Characterization of nutrients in the atmospheric wet and dry deposition observed at the two monitoring sites over Yellow Sea and East China Sea. *Journal of Atmospheric Chemistry* 57, 41-57.

- Zhang, J., Zou, L., Wu, Y., Lin, Y.A. (2004) Atmospheric wet deposition and changes in phytoplankton biomass in the surface ocean. *Geophysical Research Letters* 31, L11310.
- Zhang, J., Zhang, G.S., Bi, Y.F., Liu, S.M. (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.
- Zhou, Y., Gao, S., Shen, S.S.P. (2004) A diagnostic study of formation and structures of the Meiyu front system over East Asia. *Journal of Meteorological Society of Japan* 82, 1565-1576.

(Received 7 September 2015, revised 13 January 2016, accepted 30 March 2016)

Table A1. Annual and eight-year average wet deposition fluxes of ions.

| | Rain type | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 | Average | S.D. |
|--|----------------|-------|-------|-------|------|------|------|------|-------|---------|------|
| Nss-SO ₄ ²⁻ (meq m ⁻² yr ⁻¹) | All rain types | 42.8 | 34.0 | 39.2 | 28.3 | 35.1 | 29.2 | 40.2 | 52.4 | 37.6 | 7.3 |
| | Cy | 23.8 | 27.1 | 22.8 | 15.8 | 24.9 | 17.5 | 23.9 | 22.1 | 22.2 | 3.5 |
| | SF | 15.4 | 4.9 | 8.4 | 4.2 | 1.7 | 8.3 | 3.9 | 18.9 | 8.2 | 5.6 |
| | Ty | 0.2 | 0.9 | 0.8 | 2.4 | 0.2 | — | 2.9 | 0.4 | 1.0 | 1.0 |
| | Other | 3.4 | 1.1 | 7.2 | 5.9 | 8.3 | 3.4 | 9.5 | 11.0 | 6.2 | 3.2 |
| NO ₃ ⁻ (meq m ⁻² yr ⁻¹) | All rain types | 17.2 | 14.4 | 17.0 | 11.4 | 16.2 | 11.0 | 17.7 | 25.2 | 16.3 | 4.2 |
| | Cy | 9.6 | 11.7 | 10.4 | 5.8 | 12.0 | 6.6 | 10.4 | 10.8 | 9.7 | 2.1 |
| | SF | 5.8 | 2.1 | 3.3 | 2.6 | 1.0 | 3.2 | 1.7 | 8.8 | 3.6 | 2.4 |
| | Ty | 0.1 | 0.0 | 0.8 | 0.8 | 0.1 | — | 1.3 | 0.1 | 0.4 | 0.5 |
| | Other | 1.7 | 0.6 | 2.5 | 2.2 | 3.1 | 1.2 | 4.3 | 5.5 | 2.6 | 1.5 |
| NH ₄ ⁺ (meq m ⁻² yr ⁻¹) | All rain types | 20.7 | 19.8 | 20.9 | 14.0 | 18.1 | 13.8 | 19.6 | 24.9 | 19.0 | 3.4 |
| | Cy | 10.6 | 15.6 | 12.8 | 7.4 | 13.1 | 8.1 | 11.5 | 9.4 | 11.1 | 2.6 |
| | SF | 8.1 | 2.3 | 4.0 | 2.4 | 1.5 | 3.5 | 2.0 | 10.9 | 4.3 | 3.2 |
| | Ty | 0.1 | 0.9 | 0.8 | 1.2 | 0.2 | — | 1.5 | 0.2 | 0.6 | 0.5 |
| | Other | 1.9 | 1.0 | 3.3 | 3.0 | 3.3 | 2.2 | 4.6 | 4.4 | 3.0 | 1.1 |
| Nss-Ca ²⁺ (meq m ⁻² yr ⁻¹) | All rain types | 12.8 | 5.4 | 6.4 | 7.6 | 6.2 | 8.1 | 9.5 | 20.8 | 9.6 | 4.8 |
| | Cy | 6.8 | 4.6 | 4.7 | 5.7 | 4.7 | 5.8 | 5.5 | 6.6 | 5.6 | 0.8 |
| | SF | 2.7 | 0.1 | 0.3 | 0.9 | 0.5 | 1.8 | 0.4 | 6.4 | 1.6 | 2.0 |
| | Ty | 0.8 | 0.5 | 0.6 | 0.1 | 0.0 | — | 0.4 | 0.2 | 0.3 | 0.3 |
| | Other | 2.5 | 0.2 | 0.8 | 0.9 | 1.0 | 0.5 | 3.2 | 7.6 | 2.1 | 2.3 |
| Na ⁺ (meq m ⁻² yr ⁻¹) | All rain types | 169.2 | 125.0 | 108.4 | 60.9 | 63.0 | 51.8 | 76.3 | 121.4 | 97.0 | 38.2 |
| | Cy | 64.9 | 32.4 | 40.9 | 31.6 | 39.8 | 32.1 | 44.3 | 55.1 | 42.6 | 11.2 |
| | SF | 11.2 | 22.9 | 15.8 | 18.4 | 2.0 | 15.3 | 3.5 | 19.3 | 13.6 | 7.0 |
| | Ty | 82.1 | 67.5 | 0.3 | 4.7 | 1.0 | — | 7.4 | 23.4 | 23.3 | 30.8 |
| | Other | 11.0 | 2.2 | 51.4 | 6.2 | 20.2 | 4.4 | 21.1 | 23.6 | 17.5 | 14.9 |
| Cl ⁻ (meq m ⁻² yr ⁻¹) | All rain types | 210.6 | 148.2 | 124.9 | 73.5 | 72.5 | 58.3 | 89.7 | 143.9 | 115.2 | 48.2 |
| | Cy | 79.1 | 38.4 | 49.2 | 39.7 | 43.1 | 36.7 | 52.6 | 64.2 | 50.4 | 13.8 |
| | SF | 15.3 | 26.5 | 19.1 | 20.7 | 2.2 | 16.6 | 4.6 | 24.1 | 16.1 | 8.1 |
| | Ty | 102.9 | 80.3 | 0.4 | 5.7 | 1.1 | — | 9.3 | 27.3 | 28.4 | 37.9 |
| | Other | 13.3 | 3.0 | 56.2 | 7.4 | 26.1 | 5.0 | 23.2 | 28.3 | 20.3 | 16.4 |