九州西岸域における総観気象パターン別の降水化学

Rainwater Chemistry Associated with Synoptic Weather at the Southwestern Coast of Japan

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熊本県立大学　大学院　環境共生学研究科

大気環境学研究室

豊永　悟史

要　旨

降水は地球上の物質循環を考えるうえで重要なプロセスである。雲粒と雨粒は大気中のガスや粒子を吸収し、除去する。雲水に溶解したガスや粒子は化学変化を経て、別の物質を形成する。また、降水によって海域にもたらされるイオン成分が海洋生態系の進化と維持に重要な役割を果たしていることが近年の研究で明らかになってきている。特に東アジアでは、人為的な汚染物質の排出量の増加に伴い、陸域や海域における湿性沈着フラックスが増加しており、これが東シナ海の生物生産の増加に寄与している可能性が指摘されている。

総観規模で見れば、東シナ海の降水は主に温帯低気圧、停滞前線、台風の 3 種類の気象パターンによってもたらされる。これらの気象パターンは雲を作り出す気団の由来や熱力学的な性質が異なっていることから、降水の化学的性状が異なっていると推測される。長期間の観測データを用いた過去の降水化学や湿性沈着フラックスに関する研究は数多く存在する。しかし、そのほとんどは年や月単位の平均値を用いて評価されており、総観気象パターンとの関連性やその影響については十分な検討がされていないのが現状である。そのため、東シナ海において降水中のイオン変動を左右する要因は十分に解明されておらず、正確な月・季節・年変動の解釈も困難な状況にある。

本研究では、熊本県天草西岸域に設置されている苓北志岐大気汚染常時監視測定局 (32°30′N, 130°03′E; 5 m asl) における 1996-2003 年の降水中イオン濃度の観測データを用いて、温帯低気圧、停滞前線、台風による降水化学の特徴を解析し、それらがイオン成分濃度の年変動や月変動、湿性沈着フラックスに与える影響を検証した。

総観気象パターンによる降水化学の違いを調べるために、パターン別のイオン成分濃度を解析した。温帯低気圧による降水中の nss-SO_4^{2-}、NO_3^-、NH_4^+、nss-Ca^{2+}、Na^+、Cl^-の 8 年間の平均濃度はそれぞれ 32.1±8.8、14.4±3.7、15.3±3.5、8.3±3.4、68.6±33.1、80.9±40.9 μeq l^{-1} であった。対照的に、停滞前線による降水中の濃度はそれぞれ 18.2±7.5、8.1±3.1、9.9±4.2、4.4±2.7、24.9±6.2、30.2±6.9 μeq l^{-1} と低い値であった。台風による降水（全 11 事例）中の Na^+と Cl^-の濃度はそれぞれ 227.7±518.3 と 275.6±619.4 μeq l^{-1} であり、全イオン濃度の 79.2%を占めていた。後方流跡線と統計手法を用いた解析により、温帯低気圧と停滞前線による降水中イオンの濃度差は、気団の由来と化学プロセスの違いにより生じていることが示唆された。年間の全降水中の平均イオン濃度は温帯低気圧と停滞前線による降水によって主に決定されていた。停滞前線による降水量の年変動データを用いた試算から、停滞前線による降水量の年変動が年間の全降水中の平均イオ

ン濃度に強く影響しうることが示された。これらの結果は、降水化学の地域差の要因推定や正確な将来予測のためには、降水タイプを考慮する必要があることを示している。

各総観気象パターンは季節ごとに発生頻度が明確に異なる。この季節性が、イオン成分濃度の月変動に与える影響を調べるために、月平均イオン濃度を解析した。温帯低気圧による降水が優占する 11-5 月の nss-SO_4^{2-}、NO_3^-、NH_4^+、nss-Ca^{2+}、Na^+、Cl^- の月平均濃度はそれぞれ 25.1-57.8、9.9-25.0、11.3-31.4、5.5-18.7、24.2-154.9、30.0-178.5 µeq l^{-1} であった。停滞前線による降水が優占する 6-7 月の月平均濃度はそれぞれ 14.4-20.7、7.2-9.5、7.7-12.9、4.1-6.8、21.7-33.6、26.4-40.5 µeq l^{-1} であった。台風による降水が生じる 8-9 月の Na^+、Cl^-の月平均濃度は 97.7-105.3、116.8-122.9 µeq l^{-1} と高い値を示し、他のイオン濃度は低い値を示した。これらの結果は、降水をもたらす総観気象パターンの違いが、降水中イオン濃度の月変動を決定づけていることを示している。各季節の特徴は次のようにまとめられる。晩秋から初春にかけて、降水中イオン濃度は高く、変動が大きい。これに比べて、梅雨の時期は、濃度が低く、変動も小さい。夏から秋にかけては、台風の影響を受けるため、Na^+と Cl^-濃度が高く、他のイオン濃度は低い。

総観気象パターンが湿性沈着フラックスに与える影響を調べるために、各パターンによりもたらされた湿性沈着フラックスを定量的に解析した。陸域由来イオンである nss-SO_4^{2-}、NO_3^-、NH_4^+、nss-Ca^{2+}の平均フラックスはそれぞれ 37.6±7.3、16.3±4.2、19.0±3.4、9.6±4.8 meq m^{-2} yr^{-1}、海域由来イオンの Na^+と Cl^-ではそれぞれ 97.0±38.2 と 115.2±48.2 meq m^{-2} yr^{-1} であった。陸域由来イオンについて、温帯低気圧の寄与はほぼ全ての年で 50%以上を占めていた。これらのイオンについては、停滞前線の寄与も認められたが、基本的に温帯低気圧の寄与に比べて小さい傾向を示した。特に、海の栄養塩として重要な窒素化合物（NO_3^-、NH_4^+）は温帯低気圧の寄与が支配的であった。Na^+と Cl^-についても温帯低気圧の寄与が最も大きかったが、これらのイオンの濃度が極めて高い台風も一定の寄与を示した。以上の結果は、東シナ海地域の湿性沈着は温帯低気圧の寄与が支配的であることと、より詳細な経年変化及び地域差の解明のためには総観気象パターンを考慮する必要があることを示している。

本研究によって、総観気象パターンに依存して降水中のイオン成分濃度が異なっており、各パターンの年変動や季節変動が平均のイオン成分濃度を決定づけていることが示された。これは、湿性沈着フラックスについても同じであり、栄養塩である窒素化合物の供給に温帯低気圧が特に重要な役割を果たしていることが示された。

Abstract

Rain is one of major processes driving the physical, chemical and biological evolutions in the earth system. Airborne matters including aerosol particles and gaseous species are involved into cloud droplets, and consequently into rainwater via absorption and adsorption in the atmosphere. Parts of the species in cloud and rain droplets could be converted into other forms via chemical reactions. Except those released back into the atmosphere after the evaporation of cloud droplets, other species in cloud droplets will finally be removed from the atmosphere via wet deposition, i.e. rainout. It has been proved that the input of nutrients via rain to the ocean and island surfaces plays a crucial role in sustaining the development of marine ecosystems. Recent studies have shown that the rapid growth of anthropogenic emissions in the Asian continent leads to an increase of wet deposition fluxes of many ionic species, and a growth of wet deposition-induced primary production in the East China Sea. Elucidating the variations of rainwater chemistry and the fluxes of major ionic species into sea water will largely benefit our understandings on the linkage between the low troposphere and the upper sea surface.

On synoptic scales, rain in the East China Sea is usually generated by three types of weather: cyclones, stationary fronts and typhoons. The ionic composition and chemistry of the cloud water and the rainwater are expected to be different according to the types in the context of the clouds' thermodynamic structure and the sources of the particulates and gases associated with the clouds. Unfortunately, the association of ionic compositions in the rainwater with the weather types has rarely been carefully determined, and the dependence of rainwater chemistry on synoptic weather has not been clarified. Many vague points remain in the explanation of the rainwater chemistry over the East China Sea, and the elucidation of the monthly, seasonal, and annual variations with long-term records lacks accuracies.

In this study, the rainwater chemistry associated with nss-SO_4^{2-}, NO_3^-, NH_4^+, nss-Ca^{2+}, Na^+ and Cl^- and the wet deposition fluxes of these ions at the southwestern coast of Japan were discussed. The records of the ionic concentrations in the rainwater collected in every rain episode at the Reihoku-shiki Observatory (32°30′N, 130°03′E; 5 m asl), a coastal site in the East China Sea, in eight years from 1996 to 2003 were applied. The purposes of this study are (1) to clarify the rainwater chemistry according the rain types on synoptic scales; (2) to quantify ionic fluxes to the sea surface water by different rain types; and (3) to characterize the seasonal and annual variations of the rainwater chemistry and the fluxes over the East China Sea.

The eight-year mean concentrations of Na^+, Cl^-, nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+} in

cyclone-associated rainwater were 68.6±33.1, 80.9±40.9, 32.1±8.8, 14.4±3.7, 15.3±3.5 and 8.3±3.4 μeq l^{-1}, respectively. In contrast, the respective concentrations of these ions in stationary front-associated rainwater were 24.9±6.2, 30.2±6.9, 18.2±7.5, 8.1±3.1, 9.9±4.2 and 4.4±2.7 μeq l^{-1}. In typhoon-associated rainwater (11 cases in total), the concentrations of Na^+ and Cl^- were 227.7±518.3 μeq/L and 275.6±619.4 μeq l^{-1}, respectively, together constituting 79.2% of the ion content. Backward trajectories and statistical analyses revealed that differences in ion concentration between cyclone- and stationary front-associated rainwater were due to the different origins of and chemical processes in the air parcels. The yearly mean ion concentrations in total rainwater were dominated by cyclone- and stationary front-associated rain. A simple estimation according to rainfall variation by stationary front showed the variation could cause significant change of ion concentrations.

Monthly variation of rainwater chemistry showed a clear dependence on the rain types. In the period November-May when rain was mainly caused by cyclones, the monthly mean concentrations of nss-SO_4^{2-}, NO_3^-, NH_4^+, nss-Ca^{2+}, Na^+ and Cl^- over the eight years were 25.1-57.8, 9.9-25.0, 11.3-31.4, 5.5-18.7, 24.2-154.9 and 30.0-178.5 μeq l^{-1}, respectively. In June and July when rain was mainly caused by stationary fronts, i.e. Meiyu fronts, the concentrations were 14.4-20.7, 7.2-9.5, 7.7-12.9, 4.1-6.8, 21.7-33.6 and 26.4-40.5 μeq l^{-1}, respectively. In August and September when typhoons contributed substantial rainfall, the respective concentrations of Na^+ and Cl^- were as high as 97.7-105.3 and 116.8-122.9 μeq l^{-1}, while the concentrations of other ions were low. These results indicate a large variation of monthly rainwater chemistry, which is basically dependent on the synoptic weather patterns causing rain. From later autumn to early spring, rain contains ions in high concentration and large variation ranges. In the Meiyu season, rain contains less ions which vary in a range much smaller than that in later autumn-early spring. In summer and autumn, the concentrations are low, except Na^+ and Cl^- which can be large due to typhoons' contribution.

There is also a close dependence of wet deposition fluxes of the ions on the rain types. 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 meq m^{-2} yr^{-1}, and those of Na^+ and Cl^-, the major ions in sea water, were 97.0±38.2 and 115.2±48.2 meq m^{-2} 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 rainwater 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. In particular, cyclone-associated rain plays a crucial role in the input of nitrogen compounds via wet deposition of NO_3^- and NH_4^+, which are important nutrients for micro-bioactivities in sea surface water. All of these results suggest that the consideration of the distinctiveness of rain types is essential for an accurate evaluation of ions in rainwater, a meaningful inter-comparison between regions, and a more confident projection of future scenarios of rainwater chemistry over the East China Sea areas.

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Chapter 1

General Introduction

1.1 Chemistry associated with rain and the role in the ecosystems

Clouds and subsequent rain are important processes and play substantial roles in in the physical/chemical/biological cycles on the Earth. Clouds occurred under the conditions when the relative humidity (RH) of the air parcels increases and exceeds 100%. The increase of RH is usually the result of cooling of a moist air parcel (Barry and Chorley, 2003). Isobaric cooling and adiabatic cooling are two principle mechanisms of these cooling. Isobaric cooling is the cooling of an air parcel under constant pressure, which is usually caused by horizontal movement of an air mass from colder land to warmer ocean area or radiative losses of energy due to fog. Adiabatic cooling is the cooling of an air parcel through ascending current. Ascending of an air parcel causes its pressure decreases, the parcel expands, and its temperature decreased due to the loss of its internal energy.

During these processes, liquid droplets are formed via condensation on hygroscopic particles, which are called cloud condensation nuclei (CCN) (Seinfeld and Pandis, 2006). The minimum CCN particle diameter is 0.05-0.14 µm and large ones could be larger than 10 µm. CCN number concentrations vary from fewer than 100 cm^{-3} in remote marine regions to many thousand cm^{-3} in polluted urban areas (Andrea, 2009). There are two kinds of CCN particles according to their origin processes: primary particles and secondary particles. Primary particles are emitted directly as particles, such as soot, mineral dust and sea salt. Secondary particles are formed in the atmosphere by gas-to-particle conversion processes, such as sulfate, nitrate, and secondary organic and inorganic aerosols, which are mainly formed from SO_2, NO_X and volatile organic compounds (VOCs). Primary and secondary components could be internally mixed in a particle, such as particles having partial soot cores and sulfate shells (Li *et al.*, 2016).

After a cloud droplet is formed, it can absorb gaseous species and coagulated with other particles, which usually result in the growth of particles in size in addition to the variation of components. This process is the so-called “in cloud scavenging” of chemical species. The average lifetime of CCN is about 1 week, so that, on average, CCN will experience 5-10 cloud activation per cloud evaporation cycle. Finally, CCN will be removed from the cloud as precipitation. Particles and gases in the air below clouds can be removed by raindrops and snowdrops until reaching to the surface. This process is so-called “below cloud scavenging” of chemical species.

In-cloud and below-cloud scavenging maintain the concentration of atmospheric gases and aerosols (Galy-Lacaux *et al.*, 2009). The cloud water and rainwater are also important for transformation pathway of chemical species. Dissolved gaseous species in the cloud water and rainwater can be oxidized into salts, while particles can be reformed and ions can be converted into other forms in cloud droplets via chemical reactions (Seinfeld and

Pandis, 2006; Fig. 1.1).

In general, major ions in the rainwater are SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, Na^+ and Cl^-. SO_4^{2-} and NO_3^- are mainly derived from anthropogenic emissions through oxidation of gaseous SO_2 and NO_X, and are major acids in rainwater (Barth, 1994; Fujita *et al*., 2000). SO_2 is also emitted from volcano (Kitayama *et al*., 2010). SO_2 can be oxidized into SO_4^{2-} by gas-phase oxidation through the reaction with OH radical. Gas phase SO_4^{2-} in the atmosphere can be absorbed into cloud water and rainwater. SO_2 can also be oxidized into SO_4^{2-} by liquid phase reactions with H_2O_2 and O_3 after dissolved into cloud water and rainwater. Liquid phase reactions are usually more efficient than gas phase reactions for SO_2 oxidation (Khoder, 2002). NO_X can be oxidized into NO_3^- by gas-phase oxidation through the reaction with OH radical (Khoder, 2002; Russell *et al*., 1986). Gas phase NO_3^- can dissolve into cloud water and rainwater.

NH_4^+ and Ca^{2+} are the major bases which can neutralize acidic materials in rainwater. NH_4^+ is mainly derived from gaseous NH_3, which is emitted from both anthropogenic and natural sources, such as livestocks and soil emissions (Aneja *et al*., 2001). Gaseous NH_3 can dissolve into cloud water and rainwater in a direct way, and also can be absorbed via particulate phase of $(NH_4)_2SO_4$ and NH_4NO_3. Ca^{2+} is mainly derived from natural sources, such as soil, frequently in the form of particulate $CaCO_3$. In East Asia, desert dust is one of the largest sources of Ca^{2+}, and can cause significant increase of pH in the rainwater in spring (Wang *et al*., 2002). Na^+ and Cl^- are mainly derived from sea salts, and Cl^- is also from industrial emission as HCl in urban areas (Lightowlers *et al*., 1988; Seto *et al*., 2007).

The composition of fresh sea salt reflects the composition of seawater. After emitted in to the air from sea surface, sea salt particles can be modified in composition by reactions on the surface of the particles (Jacob, 1999). For example, sodium chloride reacts with nitric acid to produce $NaNO_3$ on the particles (Pio and Lopes, 1998). Particles in the atmosphere may change by collisions with other particles to produce particles mixed with multiple components. For example, dust-sea salt mixture particles can be frequently encountered in the spring at the areas of the southwestern Japan when Asian dust appear there in spring. Those particles can act as CCN to be involved into cloud droplets. In case, the cloud produce rain, the ion components will be dropped onto the surface with rain droplets. When the rain droplets drop out cloud bases and were settling to the surface, they can absorb gaseous and particulate matters in the below-cloud air, called below-cloud scavenging, (Seinfeld and Pandis, 2006). All of these processes result in the change of ion composition in the rainwater, and the ions were bring to the surface by rainwater, which is called wet deposition.

As mentioned previously, the wet deposition of ions to surface also play substantial roles in biological and physical cycles on the earth. Input of acid substances and nutrients to land surfaces could cause acidification of soils and excess enrichment of nutrient (Pan *et al*., 2013; Wright *et al*., 1995). On the other hand, nutrients to the open ocean can enhance the primary production by phytoplankton, and contribute to the conservation and evolution of marine ecosystems. This is also crucial for the climate changes with regard to its long-term effect, because 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 (Galloway *et al*., 2008; Jickells, 1995, 2006).

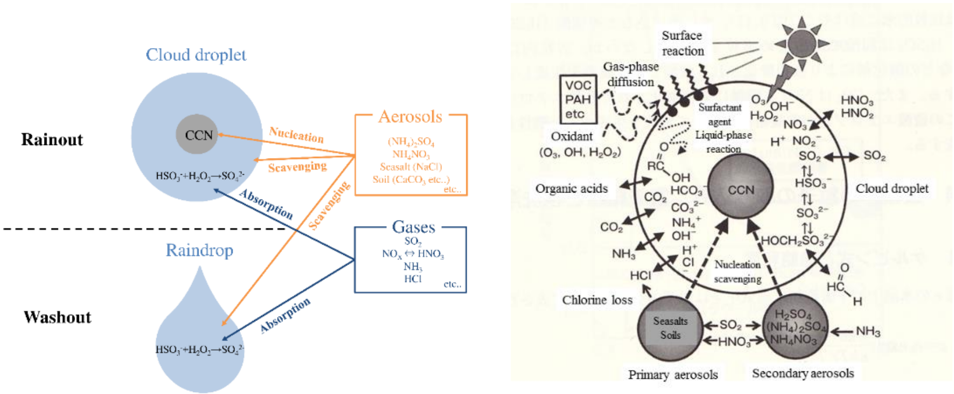

Fig. 1.1 Interaction of gas-aerosol-cloud and chemical processes associated with cloud droplets in the air (right panel was adapted from Fujita *et al.*, 2014).

1.2 Spatial and temporal variation of rainwater ions

Previous studies have shown long-term variations of ionic concentrations in rainwater and reported that the ionic composition could be significantly different upon locations (Vet *et al.*, 2014; Fig. 1.2). Temporal variation of rainwater chemistry has been discussed with long-term records of ions the rainwater.

The temporal change of anthropogenic ions in rainwater was observed in the North America, Europe and East Asia. For example, Keene *et al*. (2014) reported that the concentration of nss-SO_4^{2-} in rainwater at Bermuda, the island in the North Atlantic Ocean, significantly decreased from 1989-1997 to 2006-2009 due to the reduction of SO_2 emission in the North American continent. Tørseth *et al*. (2012) reported that a 80% reduction of nss-SO_4^{2-} in the precipitation from 1980 to 2009 due to 73% decrease of sulfur dioxide and sulfate. Yang *et al*. (2012) reported that the acidity of precipitation in Beijing, China, had been enhanced due to the increase of the regional transport and reinforced conversion of precursors and secondary particles. Fujita (2013) reported that ratio of NO_3^- to nss-SO_4^{2-} in western Japan increased during 1980s to 1990s, and the ratio in 2000-2007 was relatively stable, and after that the ratio increased again. They concluded that these trends were likely associated with the anthropogenic emission in China. Another major factor discussed in those studies and many previous reports is rainfall. Usually, rainfall amounts and ion concentrations are inversely proportional due to the dilution effect of rainwater (Huang *et al.*, 2009). For example, Seto *et al.* (2002) found that the effect of rainfall was significant on the annual variation of the concentrations of nss-Ca^{2+}, NH_4^+, NO_3^- and nss-SO_4^{2-} in the rainwater over Japan. These studies suggested that temporal trends of precursor emissions and rainfalls are the major factors affecting the ion concentration in rainwater.

Spatial variations of rainwater chemistry in several regions over the world have been discussed. In Europe, the concentration of nss-SO_4^{2-} in the rainwater in 2009 was high in Siberia and eastern Europe, and the concentration of NO_3^- was high in populated area and was associated with the emission from traffics or power plants (Tørseth *et al.*, 2012). In the North America, Barrie and Hales (1984) found that the maximum concentrations of SO_4^{2-} and NO_3^- in the rainwater occurred in south of the great lake region, near maximum anthropogenic emissions of sulfur and nitrogen oxides in 1980. It was also found that NH_4^+ maximum occurred in north central US, where there were many livestock feedlots. Moreover, Lehmann *et al.* (2005) reported that significant decrease of sulfate in the rainwater and significant increase of ammonium in the rainwater over the US, and significant increase of nitrate in the west central US and decrease in the northeastern US from 1885 to 2002. They concluded that these increase and decrease partly reflected changes in emissions, and pointed out that atmospheric chemical transformations and weather patterns should play a role in these trends. In Africa, chemical loading in rainwater presents a maximum in the dry savanna, middle in the wet savanna, and minimum in the forest, which was associated with the gradient of terrigenous sources, and wet deposition fluxes showed an opposite trend to the rainfall intensity (Galy-Lacaux *et al.*, 2009). In East Asia, the rainwater acidity increased as the distance from the Asian continent increased, due to relatively large reduction of base ions compared with acid ions (Fujita *et al.*, 2000). This result suggested that long-range transport of the ions in rainwater was the controlling factor of the rainwater chemistry over the East Asia. However, the mechanisms of the transportation and the detailed cause of the spatial variation were not clear (Fujita *et al.* 2000). Vet *et al.* (2014) reported that global concentrations and depositions of sulfur and nitrogen were characterized with levels generally high near emission sources, in addition to rainfall intensity.

These previous studies suggested that temporal and spatial variations of the precursor emissions and the rainfalls are major factors causing temporal and spatial variations of the ion concentrations in the rainwater. Ions in cloud water and rainwater, and wet deposition fluxes to the surface are determined by multiple processes and factors, i.e. emissions of substances to the air, histories of cloud producing air parcels, nuclei of cloud droplet formation, and the absorption and adsorption of gases and aerosols by the droplets. These processes and factors are generally governed by the thermodynamic motion of air parcels producing the clouds or rainwater (Barry and Chorley, 2003; Bethan *et al.*, 1998). In particular, weather patterns play a key role in regional transport, rainfall intensity, and chemical processes of ions (Jacob, 1999; Seinfeld and Pandis, 2006). Weather patterns associated with rain should be considered for accurate and detailed clarification of rainwater chemistry.

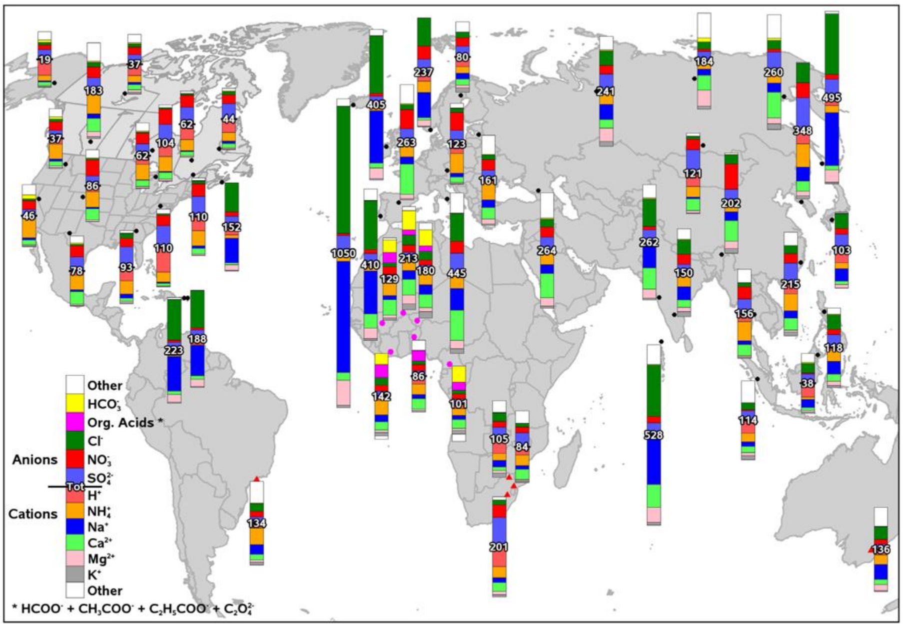

Fig. 1.2 Spatial distribution of the concentrations of major ions in rainwater over the world in 2005-2007 (Vet *et al.*, 2014).

1.3 Wet deposition fluxes to the seawater

The input of nutrients via atmospheric wet deposition 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 nutrients enhance the primary production by phytoplankton and fertilize the bioactivities in coastal and open sea water, which is crucial for climate changes with regard to the long-term effect on the exchange of greenhouse gases between the atmosphere and the ocean. The activation of phytoplankton in sea surface water can significantly enhance the uptake of carbon dioxide and modifies the balance between the atmosphere and the ocean (Galloway *et al.*, 2008; Jickells, 1995, 2006). Accurate evaluation of the wet deposition fluxes and clarifying the reasons/mechnisms of the variation of the fluxes are thus important for uncovering the underlying mechanisms and accurate future projection.

The fluxes are usually estimated from records obtained by short-term ship measurements (Baker *et al.*, 2010; Zhang *et al.*, 2011), long-term field observations on lands, such as coastal or island sites (Zhang *et al.*, 2007b) and numerical models (Uno *et al.*, 2007; Zhao *et al.*, 2015). For example, Baker *et al.* (2010) estimated the input of inorganic nitrogen over the Atlantic Ocean based on the data obtained by ship measurement. They found that the fluxes in the North Atlantic Ocean were higher than that in the Southern Atlantic Ocean and concluded that the gradient was due to large anthropogenic emission of nitrogen to the Northern Hemisphere. Jung *et al.* (2011) estimated the input flux of inorganic nitrogen to the North Pacific Ocean was 34 μmol m^{-2} d^{-1} and the flux to the South Pacific Ocean was 45 μmol m^{-2} d^{-1}, which was calculated from short-term (two-three month) ship observation. These values were much higher than the fluxes estimated by Duce *et al.* (1991), who estimated the fluxes by a calculation with extrapolating land-based observations around the Pacific Ocean. Jung *et al.* (2011) concluded that the difference of the estimated fluxes was caused by the difference of rainfall intensity at land and ocean areas, and long-term monitoring of atmospheric nitrogen was necessary in order to properly estimate the fluxes to the Pacific Ocean. Zhao *et al.* (2015) investigated the nitrogen deposition fluxes by using numerical models and found that seasonality of the fluxes was closely dependent on the meteorological conditions, which was largely dominated by the East Asian monsoon and by variations of nitrogen emissions.

A global assessment of wet deposition fluxes by Vet *et al.* (2014) revealed that East Asia and its marginal seas were the region with largest wet deposition flux of anthropogenic substances (Fig. 1.3), and the fluxes were in increasing trend unlike other regions such as the North America. Other recent studies also have pointed out an increase of deposition flux of anthropogenic substances in the marine and terrestrial areas of the East Asia (Kuribayashi *et al.*, 2012; Morino *et al.*, 2011; Vet *et al.*, 2014). In particular, nitrogen compounds, such as NO_3^- and NH_4^+, have been studied with special attention due to their enhancement of ocean fertilization (Jickells, 2006; Zhang *et al.*, 2011). Zhang *et al.* (2004) reported that new production induced by atmospheric wet deposition was comparable to the production induced by land-source input in the mid-shelf of the East China Sea, with the results estimated by incubation data at laboratory and field measurement data. The rainwater chemistry around the East China Sea area is becoming a big concern in recent years.

Long-range transport of the terrigenous substances from the land to the ocean areas and rainfall intensity are governed by synoptic weather pattern in principle (Barry and Chorley, 2003; Vogel *et al*., 2016). The evaluation of the fluxes according to weather patterns will be beneficial both to comparison studies based on different observation methods and to the validation of model simulation results.

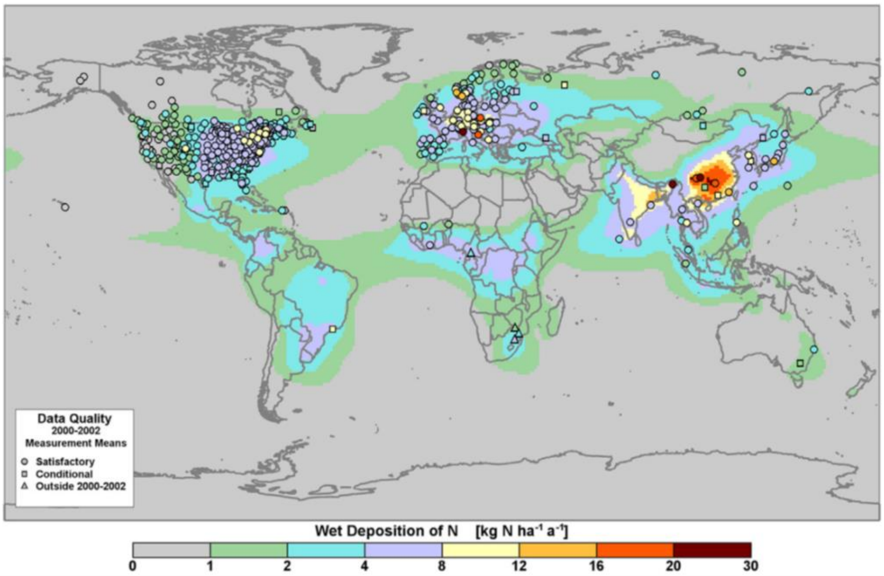

Fig. 1.3 Measurement-model wet deposition of N (Vet *et al*., 2014). Measurement values represent 3-year averages (2000-2002) of N; model results represent 2001 N values.

1.4 Synoptic weather pattern causing rain over the East China Sea

On synoptic scales, rain over the East China Sea is usually caused by cyclones, Meiyu fronts (i.e. stationary fronts) and typhoons. Thermodynamic properties of air parcels in these weather patterns are different and have distinctive seasonal characteristics. Cyclones are low-pressure systems generated initially by the southward intrusion of cold polar air in the Euro-Asian continent and move eastward in the mid-latitude westerly winds (Barry and Chorley, 2003).

A cyclone usually has a cold front, and sometimes also has a warm front after moving away from the Asian continent. Cyclone-associated rain, which is from clouds along fronts, can be observed in every month throughout a year. Meiyu fronts, also called Baiu fronts in Japanese, are stationary fronts. They are the boundaries between warm and humid tropical Pacific air in the south and cold and dry air in the north, when the tropical air expands northward under the prevention of the cold air. The fronts bring long-term and large rainfall over the East Asia, usually in June and July, i.e., late spring to early summer (Zhou *et al*., 2004). Typhoons are strong low-pressure systems in northwestern Pacific. They are initially generated in 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 short-term and extremely heavy rain in July–September, i.e., summer to early fall. These three types of weather are typical meteorological phenomena causing rain not only in the East China Sea, but also over the mid-latitude oceans and land in the East Asia (Barry and Chorley, 2003).

The mechanisms of cloud formation in these weather types 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.

1.5 History and current status of studies on the rainwater chemistry over the East China Sea

In the East Asia, studies on rainwater chemistry have been conducted in the scope of agricultural chemistry, meteorology, geochemistry and environmental sciences (Fujita, 2002). Acid rain is one of the largest concerns in the East Asia on the background of industrialization of East Asian countries after 1980's. Long-term and nation-wide monitoring of acid rain were conducted in many countries including China, Korea and Japan (Chung *et al.*, 1996; Okuda *et al.*, 2005; Pan *et al.*, 2012, 2013; Tu *et al.*, 2005).

The Acid Deposition Monitoring Network in East Asia (EANET) was established as cooperative regional initiative to promote efforts for environmental sustainability and the protection of human health over the East Asia (EANET, 2006). Sampling, measurements and quality controls at each sites of EANET were conducted by unified procedures which were established on the basis of the mannual used in Japanese nation-wide monitoring networks (Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia, 2000a, 2000b). EANET studies revealed that acid rain had been observed over the East Asia (EANET, 2006; 2011), and the largest acidic ion was sulphuric acid. The studies also revealed that spatial variation of pH in the rainwater was caused by variation of amount of basic ions rather than that of acid ions. Recent studies suggested that rapid growth of NO_X emission and reduction of SO_2 emission caused the recent changes of ion composition in the rainwater in China, and other countries in downwind areas (Fujita, 2013; Yang *et al*., 2012). In Japan, local governments also have conducted their own researches on acid rain monitoring since 1980’s. The research activities are being carried out in the same ways as the EANET, and have obtained long-term data over the Japan.

Wet deposition fluxes of nutrients to the East China Sea have been investigated by ship measurements (Zhang *et al*., 2011), measurements on island or coastal area (Zhang *et al*., 2007b), and numerical models (Uno *et al*., 2007). The investigations were motivated by the increasing concern on nutrient input to the ocean via atmospheric wet deposition and the possible subseque3nces to the ocean ecology in recent years (Duce *et al*., 2008). Zhang *et al*. (2007b) reported that the amount of inorganic nitrogen by wet deposition was greater than that by dry deposition, and the input amount via atmospheric deposition was comparable with the amount via river. Zhang *et al*. (2011) reported that the nitrogen species in the rainwater over the East China Sea were mainly originated from continental emissions of the East Asia, and found a strong gradient of wet deposition fluxes from the East Asia to the interior of the North Pacific Ocean. They pointed out the gradient possibly reflected changes in emission sources and chemical reactions, in rainfall and scavenging, and in air mass trajectory. Uno *et al.*, (2007) reported that wet and dry deposition fluxes in 2000s was three times higher than the fluxes in 1980s, corresponding with increased NO_X emissions.

Those studies strongly suggest that anthropogenic emission in East Asian continent changes the chemical composition of rainwater and subsequent wet deposition fluxes of nutrients. However, ion chemistry in the rainwater and the wet deposition fluxes associated with rain types have not quantitatively discussed. Lack of the investigation on the differences and the similarities of ions in rainwater relevant to synoptic weather patterns masks the underlying mechanisms of rainwater chemistry in the East China Sea area.

1.6 Purpose of this study

In this study, ion concentrations in rainwater and wet deposition fluxes to the surface collected at a coastal site on the southwestern Japanese coast in every rain episode over eight years from 1996 to 2003 were used to investigate the similarities and differences between the rain types of cyclones, stationary fronts and typhoons, and the respective contributions of these rain types to the integral characteristics of the rainwater chemistry over the areas. The purposes of this study are to explore the dependence of rainwater chemistry on the synoptic rain types of cyclones, stationary fronts and typhoons, and to address the importance of considering synoptic weather types for an accurate elucidation of rainwater chemistry (Fig.1.4).

In Chapter 2, sampling and measurement method, quality control of the data and rain type classification methods are described. In Chapter 3, rainfalls associated with cyclones, stationary fronts, typhoons over the eight years are illustrated. In Chapter 4, similarities and differences between the rain types, and the causes of the differences are discussed. In Chapter 5, the association of monthly variation of ion concentrations with the rain types is discussed. In Chapter 6, the dependence of wet deposition fluxes of the ions on the rain types, and the contribution of each type to the total fluxes are discussed.

An accurate quantification of rainwater chemistry according to rain types will benefit to the understanding of more detail chemical processes of rainwater ions based on field observations and model studies, to the understanding of the association of rainwater chemistry with emission and chemical processes, and to a more confident future projection and a convincible investigation of the roles of wet deposition in the air-sea interactions.

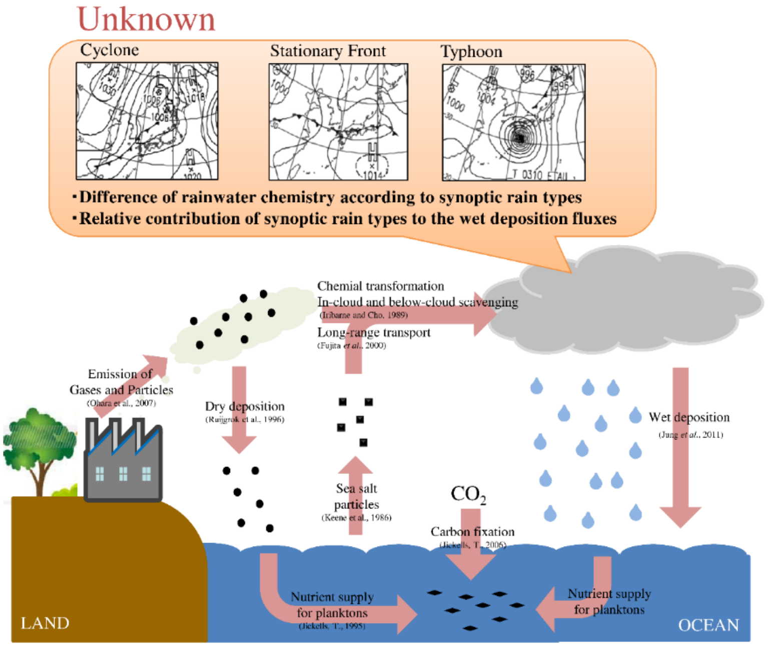

Fig. 1.4 Schematic diagrams of known and unknown parts of rainwater chemistry in the environment.

Chapter 2.

Material and Method

2.1. Dataset and measurement

Ionic concentrations, pH, and electrical conductivity (EC) of rainwater collected at several air pollution monitoring observatories in Kumamoto prefecture have been routinely measured by the Kumamoto Prefectural Institute of Public Health and Environmental Science since 1988 (Ogata *et al.*, 2004). In this study, data on ions in the rainwater, which was collected at the Reihoku-shiki Observatory during every rain episode over eight years from 1996 to 2003, were applied. The observatory is located at a coastal area on Amakusa Island, with the East China Sea approximately 400 m to its west and 1.7 km to its north (32°30′N, 130°03′E; 5 m asl; Fig. 2.1).

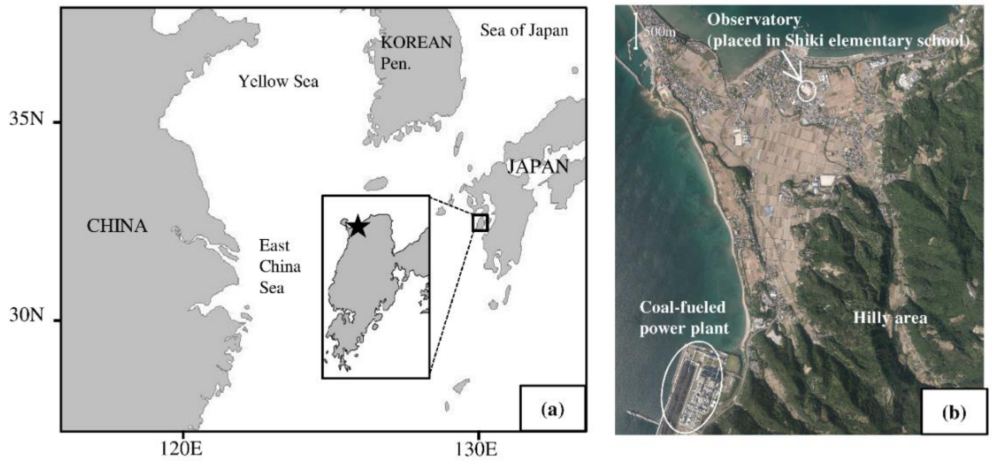

Fig. 2.1. A map showing rainwater sampling location ((a) Reihoku-shiki Observatory; marked with a star) and an aerial picture of a sampling site (b). The photo was issued by the Geospatial Information Authority of Japan.

At this location, rain is usually caused by synoptic weather changes. Local orographic and surface heating-derived short-term rain events such as thunderstorms rarely occur. Around the site, there are no anthropogenic sources of air pollutants that might considerably influence the ambient air. A coal-fueled power plant is located at 3.1 km to its south. Emissions from the plant is strictly controlled and monitored according to the guidelines of the national regulations. The average concentrations of SO_2 and NO_2 observed at the site of the rainwater collection, which is the nearest official observatory, in the period April 1996-March 2004 were 3.0-4.0 ppbv (Environmental Conservation Division of the Kumamoto Prefectural Government, 2004). The ion composition of rainwater collected at this site is dominated by particles and gaseous species loaded and transported by air parcels whose movement is governed by synoptic weather. Therefore, this site is a suitable place for the evaluation of ion chemistry dependence on synoptic weather over the East China Sea.

An auto-sampler for atmospheric wet-dry deposition was set up on the roof of the observatory (approximately 3 m above the ground) (US-750, Ogasawara Keiki Co., Meguro, Tokyo, Japan; Fig. 2.2). The hole for rainwater collection was set to automatically uncover when rain started and be covered when rain stopped. Rainwater was collected into a plastic bottle. Basically, the end of a rain event was judged by a non-rain period more than 4 hours. After that, a plastic bottle was manually replaced to a new bottle in the day time. After the replacement, the sample was rapidly sent to the institute for analysis.

Fig. 2.2. A picture showing an auto atmospheric wet-dry sampler (US-750, Ogasawara Keiki Seisakusho).

Collected rainwater samples were divided for measurements after filtration. 4 ml of sample were used for pH and 4 ml of sample for EC measurements. The remains were used for ionic composition measurements (Fig.2.3). The pH of the rainwater was measured with a pH meter (HM-60V, DKK-TOA Corp., Shinjuku, Tokyo), and the electric conductivity (EC) with a conductivity meter (CM-60S, DKK-TOA Corp., Shinjuku, Tokyo). Eight ions, including Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-}, which are usually the major ions in the rainwater, were quantified using ion chromatographs (Dionex 4040i and DX-500, Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA). The H^+ concentration was calculated from the pH. These procedures are described in detail in the *Technical Manual for Wet Deposition Monitoring in East Asia* (Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia, 2000a).

Data during 1996-2003 were used in this study. The rainwater collection and ion concentration analysis were operated according to the same protocol during this period. Rainwater was not collected in every rain episode anymore after 2003. The dataset enables a statistical investigation of rainwater according to the synoptic weather types.

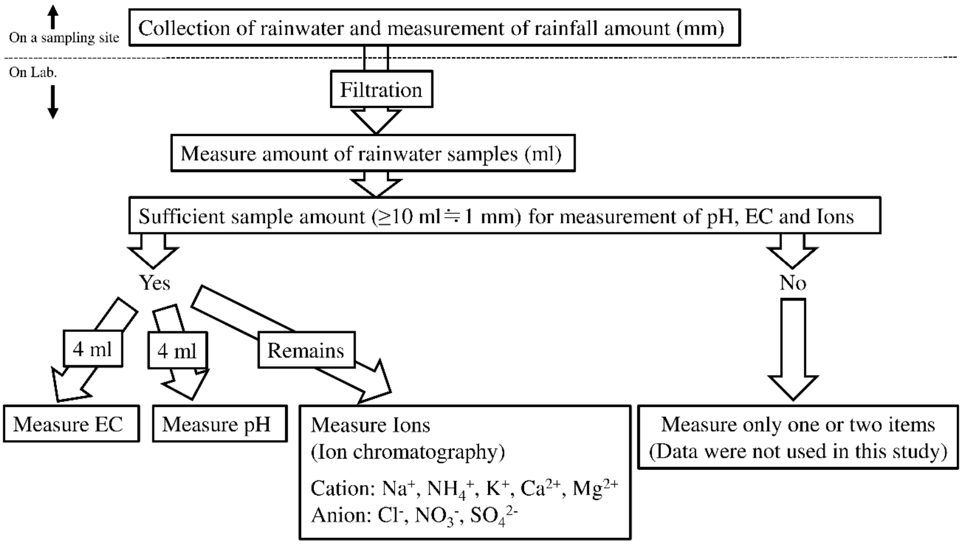

Fig. 2.3. Flow chart of sampling and chemical analysis of pH, EC and ions in rainwater.

2.2. Data screening and quality control

The analysis accuracy of the measurements by Kumamoto Prefectural Institute of Public-Health and Environmental Science has been managed by quality control project of Environmental Laboratories Association of Japan since 2002 (Aikawa *et al.*, 2005).

Data quality was evaluated based on the ion balance, the comparison of the measured EC and the calculated EC, and the rainfall amount for each sample. The criteria of ion balance were defined by each of the three certain ranges for ion concentration. The ion balance, i.e. the ratio of the difference between the measured cations and anions to the sum of the measured cations and anions, was limited to the range of ±30% in cases when the total ion concentration was less than 50 μeq l^{-1}.

The index for the comparison of the measured EC and the calculated EC was defined by each of the three certain ranges of the measured EC. For example, the ratio of the difference between the measured and the calculated EC to the sum of the measured and calculated EC was limited to the range of ±20% in the cases when the measured EC was less than 0.5 mS m^{-1}. These criteria are described in the *Quality Assurance/Quality Control Program for Wet Deposition Monitoring in East Asia* (Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia, 2000b). The criteria have been widely used in studies of rainwater chemistry, especially in East Asia. Screened data are statistically meaningful, and comparable with numerous previous studies. Extreme events may be excluded by the screening. In this study, only a small number of data were excluded, as described below. Besides the above operation for data quality control, samples collected when the rainfall less than 1 mm were also excluded from the analysis because of the insufficient amount to ensure the quality of the analysis results.

With above screening, 56 samples were excluded by the screening and the ion concentrations of 348 samples were used in the subsequent statistical analysis. The rainfall by excluded samples (N=56) was less than 10% of the total rainfall by all samples (N=404).

2.3. Rain type classification

Rainwater samples were classified into 4 groups according to the weather on synoptic scales causing the rain: cyclone (Cy), stationary front (SF), typhoon (Ty), and “Other”. The weather information including surface weather charts and also the variations of precipitation, temperature, pressure, relative humidity, wind speed and direction at a time resolution of one hour is publically opened by the Japan Meteorological Agency. Examples of surface weather charts for Cy rain, SF rain and Ty rain are illustrated in Fig. 2.3. The charts were from the *Annual for Meteorology* (*Kishounenkan*; issued by Japan Meteorological Agency) and homepages (http://www.jma.go.jp/jma/index.html; accessed on 3 Aug. 2014).

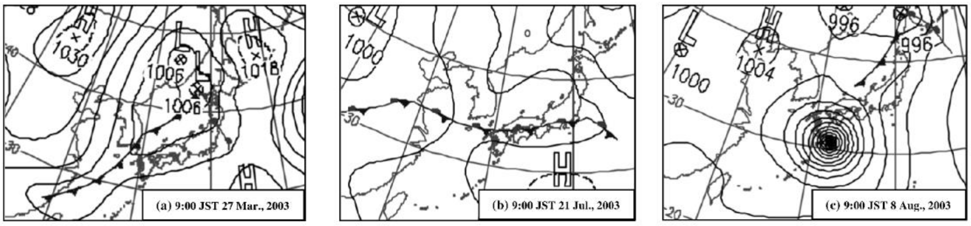

Fig. 2.4. Representative surface weather charts of the cyclones (a), stationary fronts (b) and typhoons (c). The weather charts were issued by the Japan Meteorological Agency.

Cy was the rain type caused by low-pressure systems moving eastward from the Asian continent to the Pacific Ocean (Fig. 2.4a). Cyclones moving out from the Asian continent in the westerlies are usually composed of cold fronts. Sometimes they also have warm fronts. Along the fronts, clouds are produced vigorously due to the intrusion of postfrontal cold air (cold fronts) and the ascending of warm air over cold air (warm fronts). The clouds can cause precipitation lasting several hours in a range of hundreds even more than one thousand kilometres. There are another two patterns of precipitation caused by the meet of cold and dry air with warm and humid air but there were no clear cold fronts over the East China Sea. One is the coupling of cold and dry high-pressure systems over the continent and the warm and humid low-pressure systems over the northwest Pacific, which occurs only in winter and usually result in raining or seldom snowing at Kumamoto areas. Another is the occurrence of low pressure troughs before or after extratropical cyclones. The troughs are similar to cyclones but are too weak to generate cold fronts. The precipitation in these two patterns is usually small. The time scale, the space scale and the intensity of such rain events are similar to those of cyclones. In this study, the precipitation of the two patterns was categorized into the group of the Cy rain type. These weather patterns were observed throughout a year around at the study site, and most frequently observed in spring and winter (Fig. 2.5).

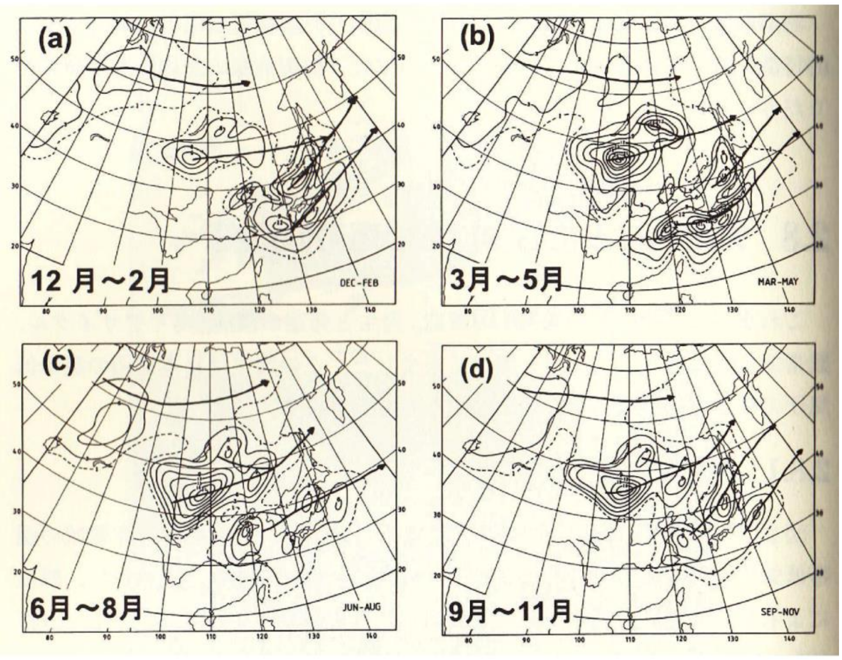

Fig. 2.5. Seasonal average of extratropical cyclone genesis frequency and pathway in thirteen years (1958-1987) (Ogura, 1999).

SF is a rain type associated with stationary fronts, most of which were Meiyu fronts. The rain is generated along the boundary between the warm and humid Pacific tropical air and the cold and dry air in the north in late spring when warm tropical air intends to expand northward under the prevention of the cold air (Fig. 2.4b). The fronts stay around the study site in late spring to early summer, which is also called the “Meiyu” season in this area, and move to northern part of East Asia in mid-summer, due to growth of Pacific anticyclone (Fig. 2.6). Such fronts bring long-term and large amount of rainfall in the mid-latitude and subtropical region over the East Asia, such as the study site and Okinawa, and they rarely cause rain in high latitude areas such as Hokkaido.

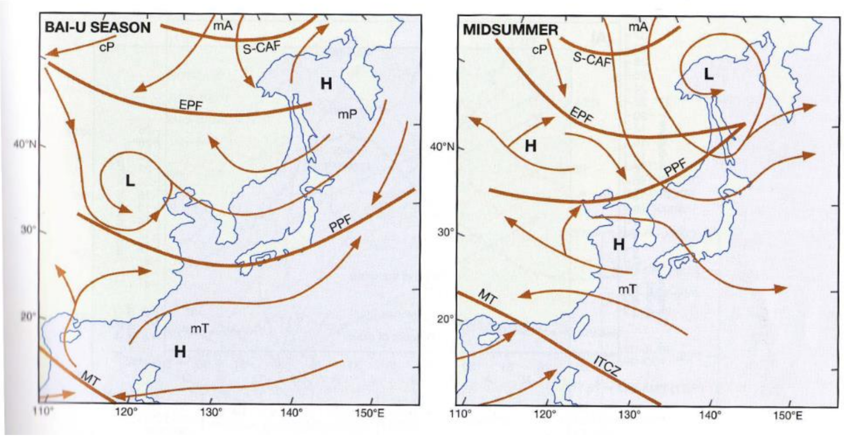

Fig. 2.6. Schematic surface circulation and frontal locations. PPF indicated Meiyu fronts (Barry and Chorley, 2003).

Ty is a rain type caused by typhoons. In summer, adiabatic air parcels near the Pacific tropical areas ascend due to temperature difference between aloft air and sea surface and form weak cyclones (low-pressure systems). The low-pressure systems develop to typhoons and intensify over the tropical and subtropical marine areas to produce rain clouds via continuous supply of water vapour from the sea surface by strong updraft. Typhoon paths over East Asia vary according to seasons, and some typhoons arrive at and pass the East China Sea, causing extremely heavy rain and strong wind in a short time usually in late summer (Fig. 2.7).

The remains were grouped into the rain type of “Other”. There were a few cases of thunderstorm rains, which were also categorized into this group.

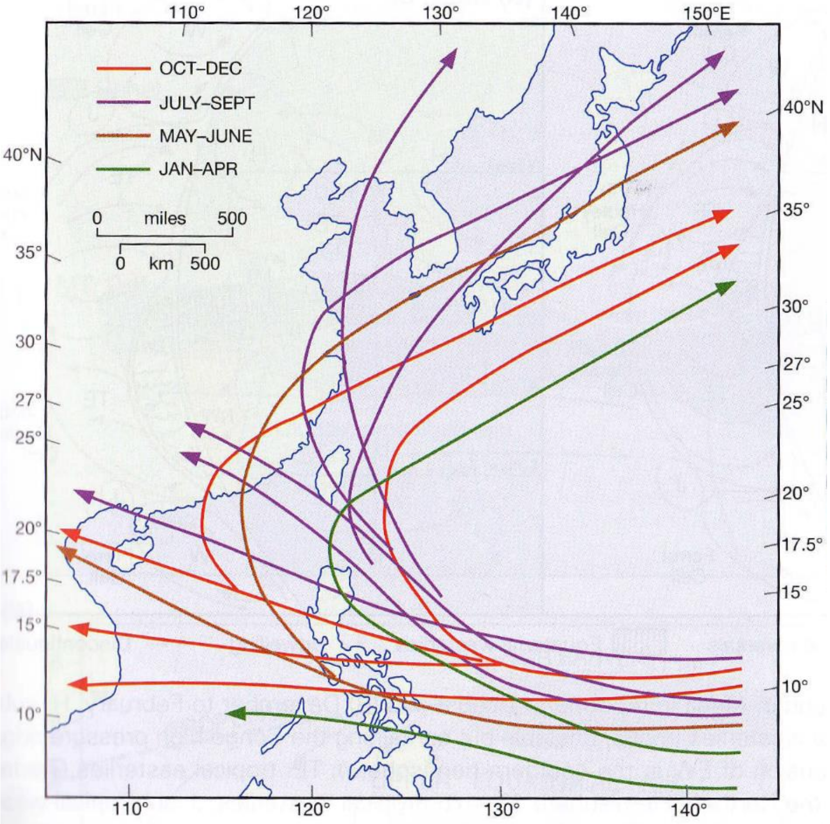

Fig. 2.7. Typhoon paths over East Asia during January to April, May to June, July to September and October to December (Barry and Chorley, 2003).

2.4. Statistical analyses

The eight-year concentration and annual mean concentration of one or multiple ions for one or all rain types were compiled into the "volume-weighted mean" (VWM) concentrations (Tiwari *et al.*, 2016). The VWM was calculated with

$$\mathrm{VWM} = \frac{\sum_{i=1}^{n} C_i P_i}{\sum_{i=1}^{n} P_i}$$

where C_i was the concentration of a specific ion in the *i*th sample (in μeq l^{-1}), P_i was the amount of rainwater for the rain episode (in liter) and *n* was the number of samples. If not mentioned, average concentration values are shown in the VWM in this paper.

Monthly mean concentration of ions in rainwater was also compiled into the VWM concentration of each month over the eight years. If there were less than three samples for a rain type in a certain month over the eight years, the monthly mean concentration was treated as "not available" (N.A.). The relative contribution of each rain type to the ions in the total rainwater in a certain period was evaluated according to ion deposition fluxes to the surface.

Fluxes of ions to the surface by rain were calculated with the concentration of one or multiple ions in the rainwater multiplied by the amount of the rainfall. 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.

The wet deposition flux of an ion (F_a) in the jth year was calculated with

$$F_{aj} = \sum_{i=1}^{n} C_{ji} P_{ji}$$

where C_{ji} was the concentration of the specific ion of the ith sample (in meq l^{-1}) in the jth year, P_{ij} was the amount of rainwater for the rain episode (in mm, i.e. liter per square meter).

The monthly flux of an ion of a rain type was the summation of the fluxes in all episodes of the rain type in a month, and the mean flux was the mean of the eight one-month integrated values.

The wet deposition flux of an ion (F_a) in the jth month was calculated with

$$F_{aj} = \sum_{i=1}^{n} C_{ji} P_{ji}$$

where C_{ji} was the concentration of the specific ion of the ith sample (in meq l^{-1}) in the jth month over the eight-years, P_{ij} was the amount of rainwater for the rain episode (in mm, i.e. liter per square meter).

Non-sea salt fractions of SO_4^{2-} (nss-SO_4^{2-}) and Ca^{2+} (nss-Ca^{2+}) were estimated with Na^+ as the conservative tracer for sea salt (Keene *et al.*, 1986), which was calculated with

$[\text{nss-}SO_4^{2-}] = [SO_4^{2-}] - ([SO_4^{2-}]/[Na^+])_{\text{seawater}}*[Na^+]$

$[\text{nss-}Ca^{2+}] = [Ca^{2+}] - ([Ca^{2+}]/[Na^+])_{\text{seawater}}*[Na^+]$

where $([SO_4^{2-}]/[Na^+])_{\text{seawater}}$ and $([Ca^{2+}]/[Na^+])_{\text{seawater}}$ were the equivalent concentration rations of seawater components. The method was applied in many previous studies (e.g. EANET, 2006) and has been proved to be an effective approach. The estimated fractions could be comparable with these studies.

A Kruskal Wallis test was conducted to examine the significance of differences in the eight-year VWM concentrations of six ion species in the Cy, SF and Ty rainwater. A multiple regression analysis was used to investigate relationships between rainwater acidity and the concentrations of ions. The multiple regression equation can be stated as follows:

$$[H^+]=a[NO_3^-]+b[nss\text{-}SO_4^{2-}]+c[NH_4^+]+d[nss\text{-}Ca^{2+}]+e$$

where *a*, *b*, *c* and *d* were referred to as partial regression coefficients and *e* was a constant term. The concentrations of ions were normalized by their mean concentrations in the calculation. Positive/negative values of partial regression coefficients indicate the ion species acting as acid/base, and its absolute values show the relative contribution of the ions species to the acidification/neutralization.

All statistical analyses were conducted using the software Ekuseru-Tokei 2012 (Social Survey Research Information Co., Ltd., Tokyo, Japan).

Chapter 3

Rain at Reihoku-shiki Observatory in the Eight Years

3.1 Introduction

Over the East Asia, rain on synoptic scale mainly caused by three types of weather: cyclones (Cy), Meiyu fronts (Stationary fronts; SF), and typhoons (Ty). Cyclones are low-pressure systems which are initially generated by southeastward outbreaks of cold polar air in the Asian continent and move eastward in the mid-latitude westerlies (Barry and Chorley, 2003). Meiyu fronts (also called Baiu fronts) are stationary fronts. They are generated along the boundary between warm and humid Pacific tropical air and cold and dry air in the north usually in June and July (Zhou *et al.*, 2004). Typhoons (also called tropical cyclones) are strong low-pressure systems that are initially generated in the tropical Pacific areas and intensify as they move to the middle latitude areas in summer (Su *et al.*, 2012). These three types of weather are typical and constant meteorological phenomena causing rain not only in the East China Sea, but also over the mid-latitude oceans and land in the East Asia (Barry and Chorley, 2003). In this chapter, annual and monthly characteristics of rainfall by Cy, SF, Ty rain in the eight years were described.

3.2 Cy rain

The annual rainfall amount by Cy rain was over 400 mm, which occupied 25-55% of total rainfall (Fig. 3.1a) and the frequency of Cy rain was 54-80% of total rain events in the eight years (Fig. 3.1b). Annual rainfall was the lowest in 1999 (419 mm), and was the highest in 2000 (1044 mm), although the rainfall frequency in 1999 and 2000 was similar (61% and 66%). The monthly mean rainfall amount and the frequency of Cy rain had a clear seasonality, which was at high levels in winter to spring and at low levels in summer and fall (Fig. 3.2). Largest monthly rainfall amount was observed in April (126 mm), which contributed 98% of the total rainfall. Smallest rainfall amount was observed in September (4 mm), which occupied only 3% of the total rainfall. This trend was similar to that of rainfall frequency, which was at the highest level in March and April (97%), and at the lowest level in September (8%). These results suggest that the annual rainfall variation was correlated with the rainfall variation of each events, while the monthly rainfall variation was dependent on the frequency of Cy rain. Cy rain usually leads to short-term (few hours) rainfall, and, sometimes, cause large rainfall lasting a day (Berry *et al*., 2011; Ogura, 1999).

3.3. SF rain

Annual rainfall amount by SF rain was more than 500 mm except for 2000 and 2002, although the frequency of SF rain was relatively stable and ranged in 9-22% (Fig. 3.1). High monthly mean rainfall by SF rain was 260 mm in June and 173 mm in July, and the frequencies in the two months were 55% and 44%, respectively (Fig. 3.2). SF rain was also observed in August-November, although the rainfall amount and frequency were relatively low. These results suggest that the variation of annual rainfall by SF rain was determined by the rain in June and July, because the months were Meiyu season (Zhou *et al*. 2004). SF rain events lasting few days to several weeks, and could cause numerous rainfall by an event (Barry and Chorley, 2003).

3.4. Ty rain

Annual rainfall by Ty rain was varied and ranged in 0-250mm, which occupied 0-15% of total rainfall (Fig. 3.1). The annual variation of rainfall by Ty rain was strongly dependent on the variation of each Ty rain events, because there were a few of Ty rain events in a year, which frequency was lower than 5%. Ty rain only observed in June-September, and monthly rainfall was 8-35mm (Fig. 3.2).

3.5 Summary

In the eight years, the annual mean rainfall was 1684±281 mm, in which 723±208 mm was caused by Cy, 557±231 mm by SF, 92±80 mm by Ty, and 312±181 mm by Other type rains. Therefore, Cy was the major type of rain, followed by SF in annual rainfall. Ty occupied a small fraction in annual rainfall. These rain types showed clear seasonal dependence. Cy was observed throughout a year, although the rainfall amount and frequency was high in winter-spring and low in summer-fall. SF was observed mainly in Meiyu season (June and July). Ty was observed only in June-September and showed episodic occurrence.

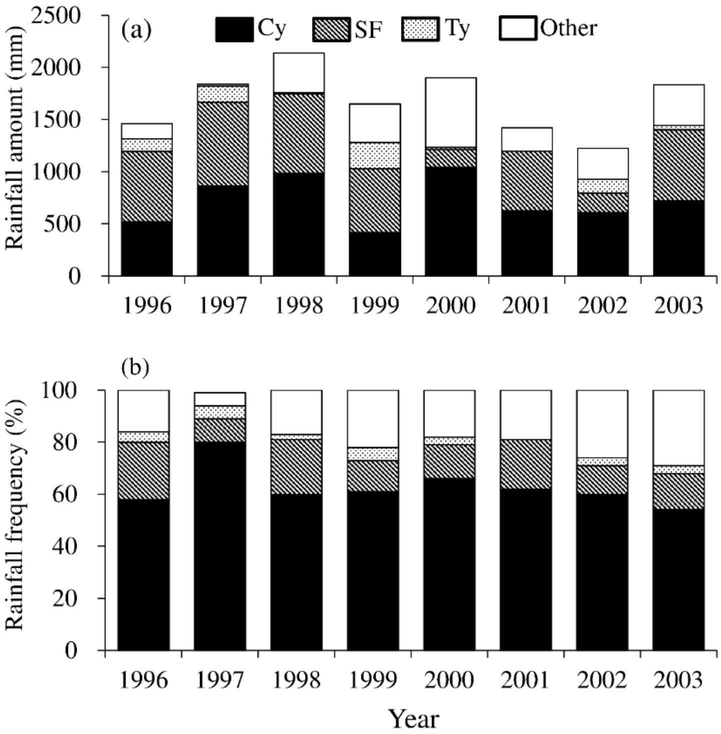

Fig. 3.1. Annual rainfall amount (a) and rainfall frequency (b) by Cy, SF, Ty and Other.

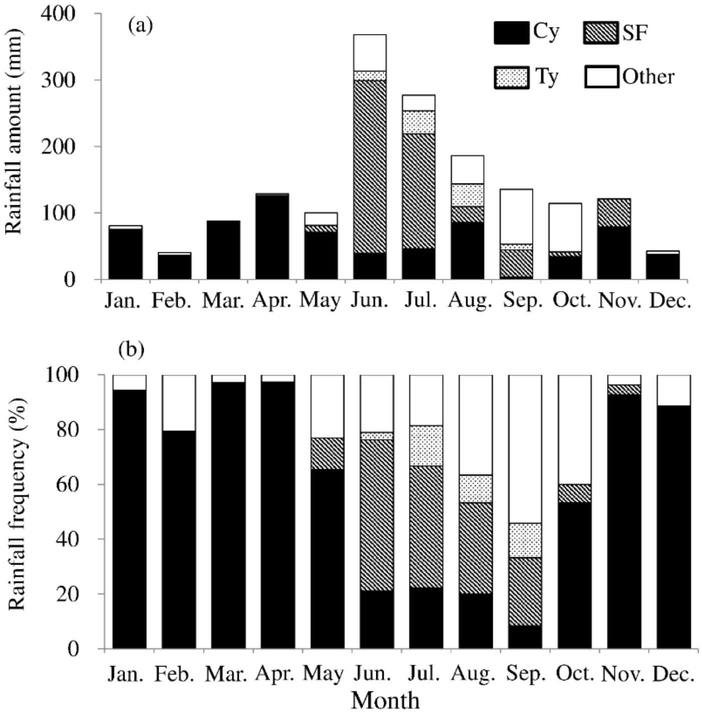

Fig. 3.2. Monthly mean rainfall amount (a) and rainfall frequency (b) by Cy, SF, Ty and Other.

Chapter 4

Chemical Characteristics of Rainwater Associated with Cyclones, Typhoons and Stationary Fronts

4.1. Introduction

Cloud water is an efficient medium for the transformation of airborne species. Dissolved gaseous species can be oxidized into salts, while particles can be reformed and ions can be converted into other forms in cloud droplets via chemical reactions (Seinfeld and Pandis, 2006). Rain is the major process by which gaseous species and aerosol particles are removed from the atmosphere, and wet deposition has been proved to stimulate the primary production in the open ocean (Duce *et al.*, 2008).

Previous studies have shown long-term yearly variations in ionic concentrations in rainwater (e.g., Mamane and Gottlieb, 1995), and the ionic composition could be significantly different upon locations (Vet *et al.*, 2014). Ions and their concentrations in cloud droplets and rain droplets are determined by multiple processes and factors. They are derived from the nuclei of cloud droplet formation, and the absorption and adsorption of gases and aerosols by the droplets. Reactions and conversions inside droplets can change their forms when the droplets are floating in the air within clouds or when they drop to the surface as rain drops. Therefore, the chemistry and ions in rainwater are closely associated not only with the ambient environment of clouds but also with the formation, evolution and settling of rain droplets, which are generally governed or regulated by the thermodynamic motion of air parcels (Barry and Chorley, 2003; Bethan *et al.*, 1998).

As mentioned previously, on synoptic scales, precipitation in the areas of the East China Sea usually occurs under three types of weather: cyclones, Meiyu fronts, and typhoons. Cyclones are low-pressure systems which are initially generated by southeastward outbreaks of cold polar air in the Asian continent and move eastward in the mid-latitude westerlies. They are composed of cold fronts. Sometimes, they also have warm fronts when they move out of the continent. Meiyu fronts (also called Baiu fronts) are stationary fronts. They are generated along the boundary between warm and humid Pacific tropical air and cold and dry air in the north usually in June and July, when warm tropical air tends to expand northward under the prevention of the cold air (Zhou *et al.*, 2004). Typhoons (also called tropical cyclones) are strong low-pressure systems that are initially generated in the tropical Pacific areas and intensify as they move to the middle latitude areas in summer (Su *et al.*, 2012). Some typhoons arrive at and pass the East China Sea, causing extremely heavy rains and strong winds. These three types of weather are typical and constant meteorological phenomena causing rain not only in the East China Sea, but also over the mid-latitude oceans and land in the East Asia (Barry and Chorley, 2003).

The ionic composition and chemistry of the cloud water and the rainwater are expected to be different according to the types in the context of the clouds' thermodynamic nature and the sources of the particulates and gases associated with the clouds. In fact, there were significant differences in ion chemistry of rainwater according to regions of the world. However, these differences have been usually evaluated on an integrated basis, i.e., annual, seasonal, or monthly averages of all rain types without consideration of their association with weather types (EANET, 2011; Zhang *et al.*, 2015). Differences in ion chemistry of rainwater associated with weather types have rarely been considered, and the dependence of rainwater chemistry on synoptic weather has not been carefully clarified (e.g. Seto *et al.*, 2002). For example, Fujita (2013) suggested recent changes of rainwater chemistry at remote sites of southwestern Japan were possibly corresponding to changes of precursor emission at East Asian continent. However, the results are integral characteristics of multiple rain types in certain periods such as months or seasons, and the factors or processes leading to the results are not clear due to the lack of an investigation on the respective contributions of different rain types.

In this study, ion concentrations in rainwater collected at the site on the southwestern Japanese coast in every rain episode over eight years from 1996 to 2003 were used to investigate the similarities and differences between the rain types of cyclones, stationary fronts and typhoons, and the respective contributions of these rain types to integral characteristics of the rainwater chemistry. The purposes of this study are to show the dependence of ion concentrations on types of weather on synoptic scales, and to address the cause of the difference and the importance of considering synoptic weather types for an accurate elucidation of rainwater chemistry and for meaningful inter-comparisons between regions.

4.2. Treatment of ion concentrations

The concentration of one or multiple ions in a given period and for one or all rain types was compiled into the "volume-weighted mean" (VWM) concentration (Tiwari *et al.*, 2016). Non-sea salt fractions of SO_4^{2-} (nss-SO_4^{2-}) and Ca^{2+} (nss-Ca^{2+}) were estimated with Na^+ as the conservative tracer for sea salt (Keene *et al.*, 1986). Details of sample collection, analyses, data screening and data processing are described in Chapter 2.

4.3. Result

4.3.1. Eight year average

The mean concentration of the total ionic species in the total rainwater, including all rain types, over the eight years was 230.8±81.9 μeq l^{-1} (Fig. 4.1). The most abundant two species were Na^+ and Cl^-. They constituted 58.2% of the total ion content. Nss-SO_4^{2-},

NO_3^- and NH_4^+ constituted 10.6%, 4.7% and 5.2% of the total ions, respectively. Nss-Ca^{2+}, which was regarded as being derived mainly from mineral particles, constituted 3.0% of the total ions. These six ions contributed 86.2% of the total ion content. The concentration of other ions, including $Mg^{2+}$and K^+, was low.

The eight-year mean concentration of total ions was 270.1 μeq l^{-1} in the Cy rainwater, 118.8 μeq l^{-1} in the SF rainwater and 635.7 μeq l^{-1} in the Ty rainwater. The mean concentration of each ion species in the Cy rainwater was significantly higher than the concentration in the SF rainwater ($p<0.05$). However, the ionic composition, i.e., the relative contribution of different ions to the total ion content, by the Cy rainwater was similar to that by the SF rainwater. The ionic composition over the eight years, on average, was dominated by rain of Cy and SF. The fraction of Na^+ and Cl^- in total rainwater from Ty was small because of the smaller amount of Ty rain relative to Cy and SF rain.

In the Cy rainwater, the mean concentration of Na^+ was 68.6±33.1 μeq l^{-1} and that of Cl^- was 80.9±40.9 μeq l^{-1}. They were the major ionic components and constituted 55.3% of total ions on average in this type of rain. Nss-SO_4^{2-} constituted a fraction of 11.9%. NO_3^-, NH_4^+ and nss-Ca^{2+} constituted 5.3%, 5.7% and 3.1%, respectively. The concentration of these ions was higher than their average in the total rainwater by approximately 11-12% for Na^+ and Cl^-; 26-32% for nss-SO_4^{2-}, NH_4^+ and NO_3^-; and 19% for nss-Ca^{2+}.

In the SF rainwater, Na^+ and Cl^- constituted 46.4% of the total ion content, on average. Nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+} accounted for 15.3%, 6.8%, 8.3% and 3.7%, respectively.

The ionic composition of the Ty rainwater was very different from those of the Cy rainwater and the SF rainwater. The concentration of total ions in the Ty rainwater was remarkably high, mainly due to Na^+ and Cl^-. The mean concentrations of Na^+ and Cl^- were 227.7 and 275.6 μeq l^{-1}, respectively. They constituted 79.2% of the total ion content on average in this type of rain. These figures were significantly larger than those in the SF rainwater ($p<0.05$). The figures were also larger than the mean ionic concentrations in the Cy and total rainwater. In contrast, the concentrations of the anthropogenic ions, including nss-SO_4^{2-}, NO_3^- and NH_4^+, were much lower than those in the Cy rainwater ($p<0.05$), and the concentrations were also lower than that in the SF and the total rainwater. The concentration of nss-Ca^{2+} was also lower than that in the Cy, SF and total rainwater.

In addition, VWM pH in the rainwater was very different according to rain types. VWM pH in the total rainwater of all rain types was 4.9±0.1, and that in the Cy, SF and Ty rainwater was 4.7±0.1, 5.0±0.2 and 5.1±0.3, respectively. Frequency distribution of pH values are apparently different (Fig. 4.2). The pH of approximately 23% and 52% of

Cy and SF rainwater samples were higher than or equal to 5.0. For Ty rainwater, the pH in 10 out of 11 samples was higher than or close to 5.0.

In summary, the concentrations of nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+} in the Cy rainwater were higher than those in other types of rainwater. Na^+ and Cl^- concentrations were extremely high in the Ty rainwater. The pH of Cy rainwater was lower than that of SF and Ty rainwater.

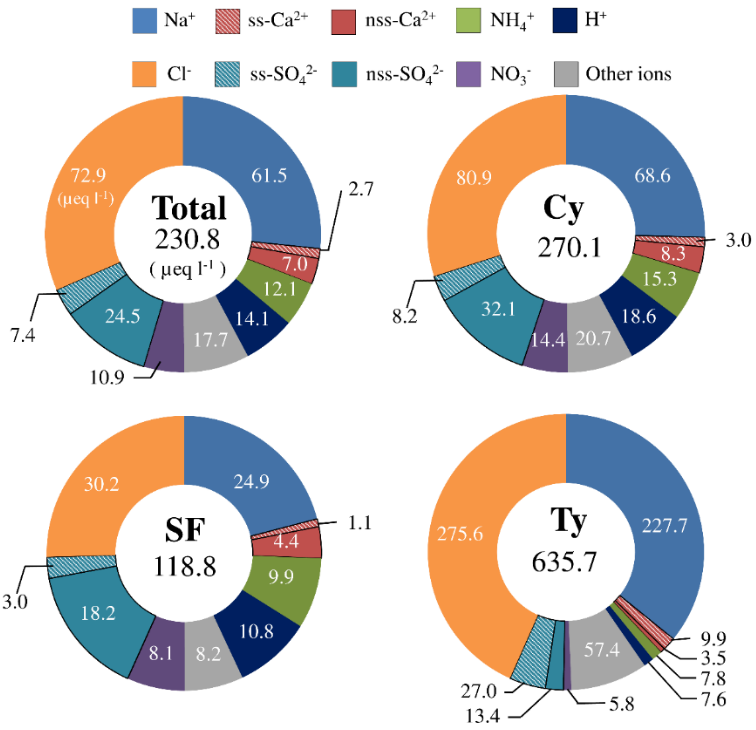

Fig. 4.1. Eight-year mean concentration of ions in the rainwater associated with cyclone (Cy), stationary front (SF), and typhoon (Ty), and the mean values in total rainwater of all rain types, including the three aforementioned types and “Other” (Total).

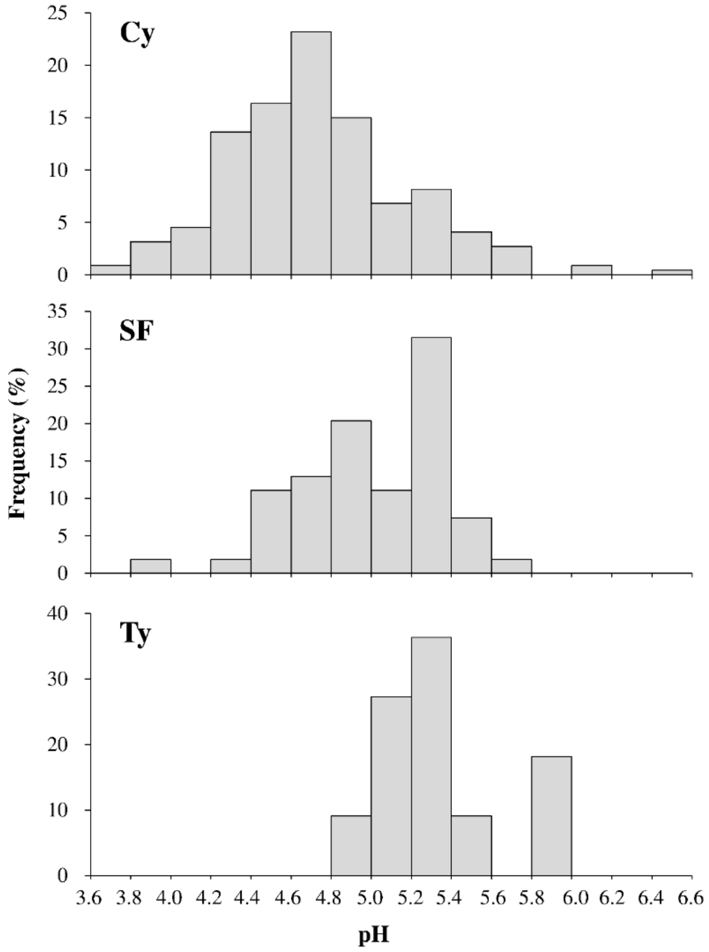

Fig. 4.2. Frequency distribution of pH in the rainwater associated with Cy (top), SF (middle) and Ty (bottom).

4.3.2. Yearly variations

The annual mean concentration of all ions in the total rainwater varied from year to year within a small range. Na^+ and Cl^- dominated this variation and contributed more than half of the total ions in all years (Fig. 4.3). The remaining ions were as follows (in decreasing order): nss-SO_4^{2-}, NH_4^+ or NO_3^-, and nss-Ca^{2+}, in almost all years. This order was the same as that of the mean ion concentrations in the eight years.

The annual mean concentrations of Na^+ and Cl^- in the total rainwater were the largest in 1996 (115.8 and 144.2 µeq l^{-1}, respectively). The respective concentrations decreased to 33.1 and 38.2 µeq l^{-1} until 2000. The concentration of Na^+ increased slightly to 36.4, and that of Cl^- to 41.1 µeq l^{-1} in 2001. In the following two years, the two ions were at high levels compared with other years except for 1996. The variation of the annual mean concentrations of nss-SO_4^{2-}, NO_3^- and NH_4^+ in the total rainwater was similar to that of Na^+ and Cl^-. In 1996, the concentrations were high and then decreased in 1999. In 2000 and 2001, the concentrations were slightly higher than in 1999. In later years, the concentrations were higher than or comparable to those in 1996.

The variation of the annual mean nss-Ca^{2+} concentration of the total rainwater was different from that of other ions. It increased gradually, except in 1996 when the concentration was 8.7 μeq l^{-1}. In 1997, it was 2.9 μeq l^{-1}. From 1997 to 2000, the concentration of nss-Ca^{2+} was approximately at a constant level. The concentration in 1999 increased slightly. From 2001 to 2003, the concentration was at a higher level compared with previous years, and it reached the highest concentration, 11.4 μeq l^{-1}, in 2003.

In the Cy rainwater, Na^+ and Cl^- were the most abundant ions, followed by nss-SO_4^{2-}, NH_4^+ or NO_3^-, and nss-Ca^{2+}, which is the same as the annual mean concentrations of the total rainwater. However, the nss-Ca^{2+} concentration was comparable to those of NO_3^- and NH_4^+ in some years, e.g., 1999. Variations of Na^+ and Cl^- had no clear trends. Their concentrations were large in 1996, 1999, 2002, and 2003. In other years, their concentrations were small. The concentrations of nss-SO_4^{2-}, NO_3^- and NH_4^+ decreased between 1996 and 1998, and then were approximately stable until 2001. Relatively high concentrations were also observed in 1999. The respective concentrations in 2002 were largest during the eight years and decreased again in 2003. Nss-Ca^{2+} was at very high levels in 1996 and 1999. However, in 1997 and 1998, it was low. After 1999, the concentration increased. Therefore, ions in the Cy rainwater showed a random-like variation, although they were at a high level compared to the annual mean values of the total rainwater.

In the SF rainwater, the rank order of ionic concentrations was similar to that of the mean values of the total rainwater. However, nss-SO_4^{2-} was higher than or comparable to Na^+ and Cl^- in 1996, 2002 and 2003 (Fig. 4.3). The annual concentrations of nss-SO_4^{2-}, NO_3^- and NH_4^+ gradually increased, except in 1996, and were highest in 2003. The concentration of nss-Ca^{2+} increased between 1997 and 2001, decreased in 2002, and was the highest in 2003.The concentrations of Na^+ and Cl^- showed increase and decrease in every two years and were approximately stable in comparison with other ions. Relatively high respective concentrations were observed in 1997, 1999, 2001, and 2003, but they were all lower than those in the Cy rainwater in all years.

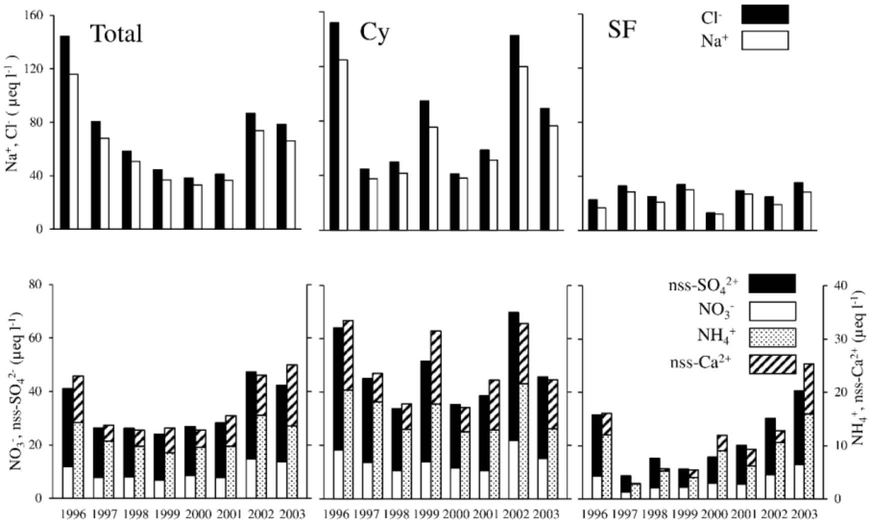

Fig. 4.3. Annual mean concentrations of ions in the total rainwater of all rain types (left) and in the rainwater associated with Cy (middle) and SF (right). Upper panels show the concentrations of Na^+ and Cl^-. Lower panels show the concentrations of nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+}.

4.4. Discussion

In this section, the differences of chemical characteristics of rainwater between rain types (Cy, SF, Ty) according to ion concentration are discussed in subsection 4.4.1. Reasons for the differences associated with pH are discussed with statistical analyses in subsection 4.4.2. Annual variation of mean ion concentrations associated with the rain types are discussed in subsection 4.4.3.

4.4.1. Differences in ion concentrations

The mean ionic concentration of nss-SO_4^{2-}, which was mainly contributed by long-range transported sulfur compounds, in the total rainwater was similar to those obtained at Goto, a remote site in the East China Sea, and at Shengsi, a coastal site of China (Table 4.1), suggesting the representativeness of the present results for synoptic-scale rain in this area. The concentration of NO_3^- in the present study was very low and close to that observed at remote sites in Japan, 6.1-16.2 μeq l^{-1} (Acid Deposition and Oxidant Research Center and Japan Environmental Sanitation Center, 2004). In contrast, the concentration of NO_3^- in the urban areas of cities like Tokyo (Okuda *et al.*, 2005) was influenced by local emissions and could be as high as 30.5 μeq l^{-1}, which is approximately 3 times higher than the concentration at the site of the present study.

The rainwater of Cy was abundant in nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+}, in addition to Na^+ and Cl^-. The concentrations of these ions in the SF rainwater were lower, although they were much larger than the concentrations in the remote marine atmosphere (Galloway *et al.*, 1982; Carrillo *et al.*, 2002). The eight-year mean concentrations of NO_3^- and NH_4^+ in the Cy rainwater were 1.8 and 1.5 times higher than those in the SF rainwater in this study. This result was similar to the results of a study conducted in Taiwan (approximately 1,400 km southwest from the present study site), where the concentrations of NO_3^- and NH_4^+ in cyclone-associated rainwater were 1.9-2.6 and 1.5-2.1 times higher than those in Meiyu front-associated rainwater (the SF rainwater in this study), and the abundance of the salts was attributed to the influence of anthropogenic emissions in upwind areas, i.e., the Asian continent (Chang *et al.*, 2005).

The abundance of anthropogenic pollutants in prefrontal air and the presence of desert dust in postfrontal air are the distinctive characteristics of the spatial distribution of air pollutants within cyclones moving out of the Asian continent, especially in spring (Zhang *et al.*, 2005, 2006). Abundant anthropogenic pollutants of gaseous species and particulates were also detected in postfrontal air in some cases around Japan (e.g., Kaneyasu *et al.*, 2000). In general, postfrontal air pushes the prefrontal air to ascend and produce clouds along the cold front of a cyclone, which results in the entrainment of pollutants into cloud droplets. Rain droplets can also adopt below-cloud particles and gaseous species. All of these processes can lead to the abundance of terrigenous ions in Cy rainwater. This is also supported by the analysis of the backward trajectories of the air parcels (Fig. 4.4a), which shows that the pathways of the air masses for Cy rain were frequently from the Asian continent.

Furthermore, results of chemical transport model revealed the influence of the long-range transport of anthropogenic substances in an episodic case of Cy rain. On December, 19-20, 2003 high sulfate and nitrate in the Cy rainwater was observed. In this case, the rainfall was 1 mm, in which the concentration of nss-SO_4^{2-} was 273 μeq l^{-1} and the concentration of NO_3^- was 179 μeq l^{-1}. The weather charts in this period showed the strong winter pressure pattern (Fig. 4.5a), which caused intrusion of cold continental air from the west as shown by the backward trajectories (Fig. 4.5b). Distribution of sulfate particles simulated by Chemical Weather Forecasting System (CFORS; Uno *et al.*, 2003) illustrated sulfate particles transported from Asian continent to the East China Sea (Fig. 4.5c), which must have resulted in high sulfate concentration in the rainwater via in-cloud and below-cloud scavenging.

In the case of SF rain, the cold and dry air in the north was stagnant and gradually influenced by air pollutants from the Asian continent and local areas (Kaneyasu *et al.*, 2005). Maritime warm air was abundant in Na^+ and Cl^- but contained less anthropogenic pollutants (Moreno *et al.*, 2013). The trajectory analysis confirmed that the air mass producing the rain clouds in the SF cases was frequently from the south or southwest, i.e., the ocean (Fig. 4.4b). The movement of these air parcels was much slower than the air parcels in the Cy cases. In addition to the dilution effects of the continuous long-term rain associated with SF, the concentration of pollutants in the cold and dry air was expected to be lower than in the air of the Cy cases because SF rain usually lasts longer than does Cy rain.

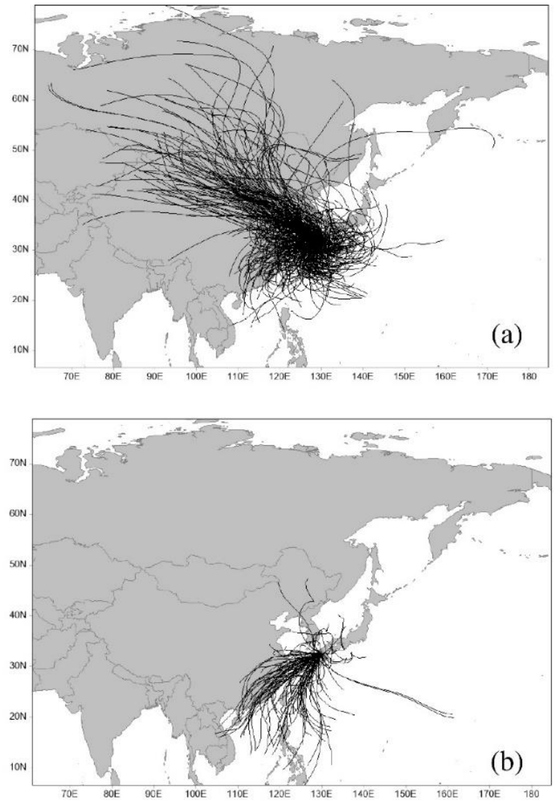

Fig. 4.4. 72-h back trajectories arriving at the sampling site (altitude of start point: 1,500m). Every trajectory was calculated from the start and end time of each case for Cy (a) and SF (b) rain. The trajectories were calculated with the on-line NOAA-HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT.php).

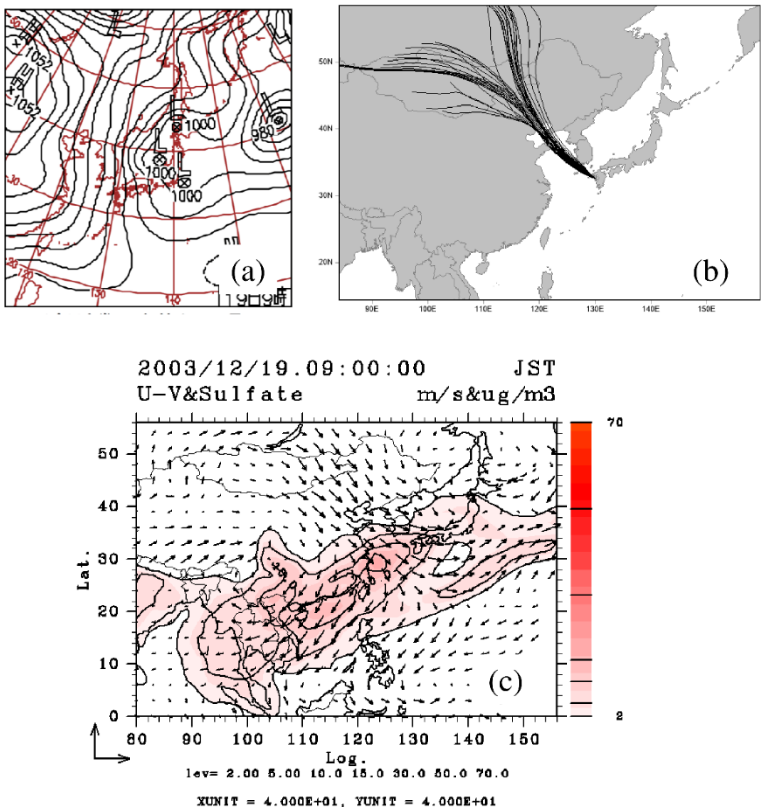

Fig. 4.5. A weather chart (a), back trajectories (b) and distribution of sulfate simulated by CFORS (c). (a) and (c) represent the weather chart and the distribution of sulfate at 9:00AM (JST), December 19, 2003. (c) represent 72-h back trajectories arriving at the sampling site (altitude of start point: 1,500m), started at every 1h during rain (7:00AM, 19-3:00AM, 20, December, 2003). The trajectories were calculated with the on-line NOAA-HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT.php).

Table 4.1. VWM concentrations (in µeq l^{-1}) of ions in the rainwater of the present study and at sites in China and Japan.

Country	Site name		Site type	Period	Ion concentration										
					Cl^-	SO_4^{2-}	nss-SO_4^{2-}	NO_3^-	Na^+	Ca^{2+}	nss-Ca^{2+}	NH_4^+	K^+	Mg^{2+}	H^+
Japan	Reihoku-shiki[a]	Total[*]	Remote	1996-2003	72.9±32.8	31.9±8.2	24.5±5.8	10.9±2.9	61.5±25.7	9.7±3.6	7.0±2.9	12.1±2.4	3.0±0.7	14.7±6.2	14.1±2.9
		Cy[*]			80.9±40.9	40.3±12.6	32.1±8.8	14.4±3.7	68.6±33.1	11.3± 4.7	8.3±3.4	15.3±3.5	4.1±1.0	16.6±8.1	18.6±5.2
		SF[*]			30.2± 6.9	21.2±7.4	18.2±7.5	8.1±3.1	24.9±6.2	5.5±2.8	4.4±2.7	9.9±4.2	1.7±0.5	6.5±1.8	10.8±4.2
		Ty[**]			275.6±619.4	40.4±56.9	13.4±23.5	5.8±24.5	227.7±518.3	13.4±27.9	3.5±18.8	7.8±21.0	6.3±11.3	51.1±117.7	7.6±2.9
Japan	Rishiri[b]		Remote	1996-2002	164.5	46.2	28.0	13.2	155.3	17.4	10.8	21.5	4.6	34.8	13.1
Japan	Oki[b]		Remote	1996-2002	406.0	67.7	25.7	16.2	350.4	23.8	8.8	16.9	10.5	77.8	17.5
Japan	Tsushima[b]		Remote	1996-2002	67.7	37.0	29.7	14.6	60.5	10.7	8.1	19.1	2.9	14.8	15.4
Japan	Goto[b]		Remote	1996-2002	153.1	41.6	25.9	12.3	129.7	14.1	8.6	15.4	3.9	29.9	13.7
Japan	Hedo[b]		Remote	2000-2001	371.6	50.7	12.3	6.1	329.8	15.8	2.4	6.1	6.7	72.0	8.9
China	Qianliyan[c]		CSC[***]	2000-2001	329.0	126.0	89.7	41.1	301.0	97.3	84.1	63.6	16.6	74.0	15.5
China	Shengsi[c]		CSC[***]	2000-2001	148.0	41.6	27.0	21.0	121.0	25.3	20.0	34.3	6.8	33.1	31.7
Japan	Tokyo[cd]		Urban	1990-2002	55.2	50.2	-	30.5	37.0	24.9	-	40.4	2.9	11.5	29.9
China	Beijing[de]		Urban	2001-2005	34.9	314.0	-	106.0	22.5	209.0	-	236.0	13.8	48.4	1.0
China	Guangzhou[f]		Urban	2001-2005	21.0	202.0	-	52.0	18.0	131.0	-	66.0	9.0	9.0	32.0

[a]This study, [b]Acid Deposition and Oxidant Research Center and Japan Environmental Sanitation Center (2004), [c]Zhang *et al.* (2007a), [d]Okuda *et al.* (2005), [e]Yang *et al.* (2012), [f]Huang *et al.* (2009).

[*] (VWM concentration)±(Standard deviation of annual VWM concentration) [**] (VWM concentration)±(Standard deviation of ion concentration in all samples (11 cases)) [***]Coastal site of China

4.4.2. Differences in chemical reaction associated with pH

The pH value was lower in Cy rainwater compared with SF rainwater. pH in rainwater depends on the difference between acid and base concentrations. Following Tsuruta (1989), we used [NO_3^-+nss-SO_4^{2-}] as acidifying potential (AP) and [NH_4^++nss-Ca^{2+}] as neutralizing potential (NP). According to the eight-year mean, the difference between AP and NP was 22.9 μeq l^{-1} for Cy rainwater and 12.0 μeq l^{-1} for SF rainwater (Fig. 4.1). This indicates that the higher abundance of acid species in Cy rainwater in comparison with SF rainwater was the major reason for the difference of pH.

A multiple regression analysis was conducted to quantitatively evaluate the contribution of each ion to the pH in Cy and SF rainwater. In the calculation, H^+ was selected as the variable dependent on NO_3^-, nss-SO_4^{2-}, NH_4^+, nss-Ca^{2+}, i.e., the major acid and base species at the area of our study site (EANET, 2006). The multiple regression equation can be stated as follows:

$$[H^+]=a[NO_3^-]+b[nss\text{-}SO_4^{2-}]+c[NH_4^+]+d[nss\text{-}Ca^{2+}]+e$$

In the equation, *a*, *b*, *c* and *d* are referred to as partial regression coefficients and *e* is a constant term. The concentrations of ions are normalized by their mean concentrations in the calculation. Positive/negative values of partial regression coefficients indicate the ion species acting as acid/base, and its absolute values show the relative contribution of the ions species for acidification/neutralization.

For acidification, nss-SO_4^{2-} was the most important contributor in both Cy and SF rainwater (Table 4.2). For neutralization, nss-Ca^{2+} was the most important contributor in the Cy rainwater, and NH_4^+ was the one in the SF rainwater. These results indicate different neutralization processes in the Cy and SF rainwater. The apparently different pH in the rainwater of Cy and SF also suggested there should have been a difference of oxidation processes. This is because the processes associated with sulfur chemistry in aqueous phase are critically pH dependent. The oxidation by H_2O_2 is predominant at pH<5 and the oxidation by O_3 becomes important at pH≥5 (Seinfeld and Pandis, 2006).

Consequently, the oxidation in Cy rainwater was expected to be dominated by H_2O_2-associated processes, and the oxidation via O_3-associated processes in SF rainwater, in contrast, was expected to be more important in addition to H_2O_2. This was also supported by the fact that SF rain and its associated air parcels moved slower and lasted longer than Cy rain, because H_2O_2 was quickly depleted by the production of sulfate and the oxidation by O_3 was more efficient in the slow moving clouds (Iribarne and Cho, 1989). This possible difference of oxidation processes is an important subject in future studies and needs to be investigated carefully for a deep understanding of the rain chemistry in different rain types.

In addition to the possible difference in oxidation processes, there were possible differences in H_2O_2 concentration between the rain types. Hatakeyama and Akatsuka (2014) reported that the average concentration of gaseous H_2O_2 at a background site in the East China Sea was 0.98-1.02 ppbv under the influence of continental air masses and was 0.39 ppbv under the influence of oceanic air masses, indicating the difference of H_2O_2 concentration in the air masses inducing Cy and SF rain. There is limited data of H_2O_2 in the rainwater around Japan (Watanabe *et al.*, 2001; 2006; 2009), which insufficient for quantitative discussion.

Furthermore, the ratios of sulfate and nitrate in the Cy rainwater and the SF rainwater were apparently different. The ratio of nss-SO_4^{2-} to NO_3^- in June and July, when SF rain occurred, was higher in the Cy rainwater than in the SF rainwater by a factor of 2.2 (Fig. 4.6). This is likely and partly due to the difference of the concentration of precursor gaseous SO_2 and NO_x. In addition, the concentration of gaseous H_2O_2 in continental air masses relative to that in oceanic air masses was 2.5-2.6 times higher according to Hatakeyama and Akatsuka (2014). Therefore, the production of sulfate and nitrate via H_2O_2 oxidation could, to a large extent, explain the difference of the ratio of nss-SO_4^{2-} to NO_3^- between the two types of rainwater. The eight-year mean concentration of nss-SO_4^{2-} in the Cy rainwater was approximately two times higher than that in the SF rainwater (Fig. 4.1). This difference of nss-SO_4^{2-} concentration should also be partly due to the different H_2O_2 concentration, besides the adsorption of particulate matter or precursor gases by cloud and rain droplets. These results further indicate the difference of dominant chemical processes, i.e., acid/base reaction and oxidation, in Cy and SF rainwater.

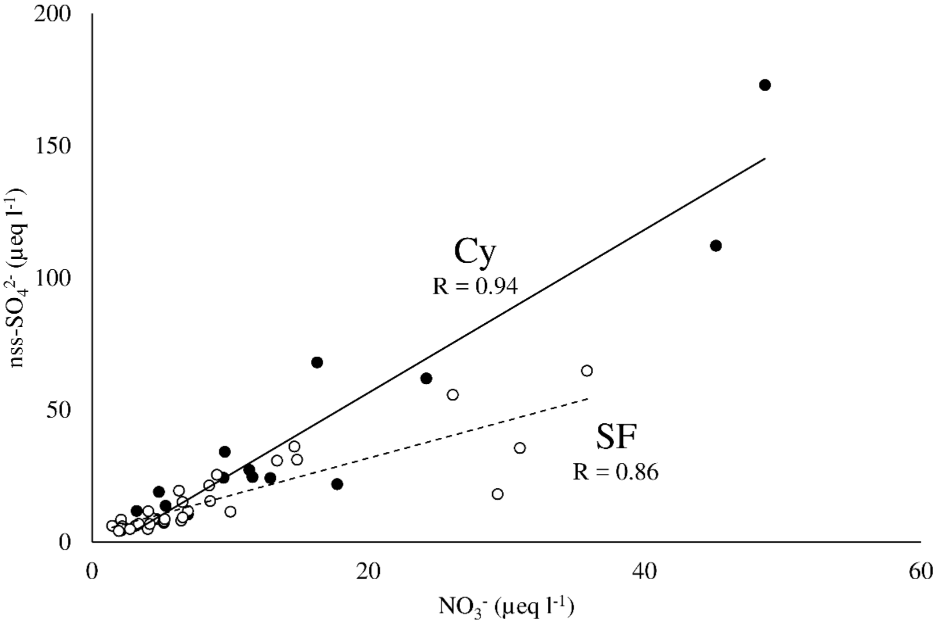

Fig. 4.6. nss-SO_4^{2-} vs. NO_3^- concentrations (in μeq l^{-1}) in the rainwater associated with Cy and SF in June and July over the eight years. Closed and open circles indicate the cases of Cy and SF, respectively. The linear regressions for Cy and SF rainwater are illustrated with solid and dashed lines, respectively.

Table 4.2. Partial regression coefficients of the standardized concentration of NO_3^-, nss-SO_4^{2-}, NH_4^+, and nss-Ca^{2+} in the Cy and SF rainwater acidity at the study site.

Rain types	NO_3^-	nss-SO_4^{2-}	NH_4^+	nss-Ca^{2+}	Constant	Multiple correlation coefficient
	a	*b*	*c*	*d*	*e*	
Cy rain	0.5561	0.9226	-0.2203	-0.4467	0.1883	0.839
SF rain	0.7888	1.3584	-0.8246	-0.5618	0.2393	0.926

The multiple regression equation: $[H^+]=a[NO_3^-]+b[nss\text{-}SO_4^{2-}]+c[NH_4^+]+d[nss\text{-}Ca^{2+}]+e$

4.4.3. Dominance of cyclones, stationary fronts and typhoons in the annual variation of rainwater chemistry

The annual mean concentrations of anthropogenic and soil-derived ions (nss-SO_4^{2-}, NO_3^-, NH_4^+, nss-Ca^{2+}) in the total rainwater were intermediate between those in Cy and SF rainwater (Fig. 4.1), because the total rainwater in each year was mainly contributed by Cy and SF weather and the contribution from Ty rain was small. This is consistent with that the mean concentrations of Na^+ and Cl^- in the total rainwater were much smaller than those in the Ty rainwater. The mean concentrations of Na^+ and Cl^-, and consequently the mean concentrations of sea salt-derived SO_4^{2-} and Ca^{2+}, in the total rainwater were actually close to those in the Cy rainwater. It must be noticed that this result was dependent on the respective contributions of Cy, Ty and SF rain.

Moreover, the trends of the annual mean concentrations of nss-SO_4^{2-}, NO_3^- and NH_4^+ in the total rainwater were similar to the trends in the Cy rainwater, and the variations can be explained by the ion concentrations and rainfall amounts of Cy and SF. The change of the annual mean concentration of nss-Ca^{2+} in the total rainwater from 2000 to 2002 was similar to that in the Cy rainwater but different from that in the SF rainwater. In contrast, in 2003, the mean concentration of nss-Ca^{2+} in the total rainwater was higher than that in the Cy rainwater and in the SF rainwater. This was caused by a single rain event during June 18-20, 2003, which was affected by a Ty and a SF and lead to 153 mm rainfall, approximately 8% of the total rainfall for the year. In that case, nss-Ca^{2+} was approximately four times higher than that in the Cy rainwater and SF rainwater during the year. This episodic event also led to a higher mean concentration of nss-Ca^{2+} in the total rainwater for that year compared to other years.

The annual mean concentrations of Na^+ and Cl^- were closely associated with Ty rain in some years, besides Cy and SF rain. High concentrations in the total rainwater in 1996 and 1997 were caused by the high concentrations in Ty rain, which contributed 49% and 54% of the ions in terms of fluxes (Toyonaga and Zhang, 2016). The concentrations were relatively low in 1998-2001, when the contribution of Ty rain to the ions was less than 10%. The relatively high concentrations in 2002 were due to the high concentrations in Cy rainwater and small total rainfall in the year, and those in 2003 were mainly caused by Ty rain, which contributed 19% of the ions. Therefore, the annual mean concentrations of maritime ions in the total rainwater were determined by Cy rainwater and SF rainwater and were episodically influenced by Ty rainwater.

In summary, the trend of annual mean concentrations of the terrigenous ions (nss-SO_4^{2-}, NO_3^-, NH_4^+, nss-Ca^{2+}) was determined mainly by ions from the Cy and SF rain, and the trend of Na^+ and Cl^- were episodically and largely influenced by Ty in some years, although they were dominated by the contribution of Cy and SF rain.

These results highlight the need to investigate rainwater chemistry according to the rain types associated with synoptic weather, to more accurately quantify the conversions and chemical reactions enclosed in cloud processes. Rainwater chemistry has been frequently studied and discussed with annually or seasonally integrated records, without consideration of its association with synoptic weather (e.g., Yang *et al.*, 2012). Those studies provided useful information on the long-term variation of ion concentrations in rainwater, but did not show compelling evidence to elucidate the variation in certain season or in comparison with other sites. For example, Takahashi and Fujita (2000) compared the annual average concentrations of NO_3^- and nss-SO_4^{2-} in precipitation in western Japan with NO_x and SO_2 emissions during the period 1987-1996 and concluded that the significant increase of NO_3^- in precipitation was due to the growth of NO_x emissions in East Asia. According to our results, the ratio of monthly mean NO_3^- to that of nss-SO_4^{2-} in the total rainwater in August over the eight years was 0.40, the ratio in Ty rainwater was 0.23, and the ratio in non-Ty rainwater was 0.46. Therefore, Ty rainwater at the present site caused changes of ion compositions in summer, suggesting the importance to consider rain types in order to understand the rainwater chemistry.

4.4.4. Implication for future projections and inter-comparisons between different geographic regions

The reduction of cyclone-associated rainfall and the increase of stationary front- and typhoon-associated rainfall have been projected in the IPCC report (Christensen and Kanikicharla, 2013). The changes of rainfall contributed by different rain types will lead to the variation of ions' chemistry in the base of annual rainwater. According to the record of Japan Meteorological Agency, the relative rainfall, i.e. ratio of rainfall in a certain year with average annual rainfall, in the Meiyu season varied from 32% to 185% during the period 1951-2015 (http://www.data.jma.go.jp/fcd/yoho/baiu/kako_baiu04.html, Date accessed 1 July 2016). Based on these data and the eight-year mean ion concentrations of this study, it is estimated that the rates of Na^+, Cl^-, nss-SO_4^{2-}, NO_3^-, NH_4^+, nss-Ca^{2+} and H^+ in the total rainwater varied in the ranges of -14%-17%, -13%-16%, -5%-9%, -4%-10%, -3%-7%, -8%-11%, and -4%-9%, respectively, suggesting that the changes of relative contribution by different rain types could significantly affect the annual mean concentration of ions in rainwater. Yoshizaki *et al.* (2005) estimated that rainfall by Meiyu fronts, i.e. stationary fronts, would increase from the present by approximately 30% untill

2080-2099. With this increase, it is estimated that the concentration of Na^+ and Cl^- will decrease 6%, that of nss-SO_4^{2-}, NO_3^-, NH_4^+ and H^+ will decrease 1%, and that of nss-Ca^{2+} will decrease 4%, if other conditions would not change.

The consideration of rain types in the present study is also crucial for the inter-comparisons of rainwater chemistry between different geographic regions. For example, rainwater collected at Rishiri, an island located in the northern part of the Sea of Japan, had higher anthropogenic ion concentrations than the mean ion concentrations in the total rainwater in the present study (Table 4.1). The mean concentrations of nss-SO_4^{2-} and NO_3^- at Rishiri were 28.0 and 13.2 μeq l^{-1}, respectively (Acid Deposition and Oxidant Research Center and Japan Environmental Sanitation Center, 2004), which are the levels between the total rainwater and the Cy rainwater of the present study. This is because the major type of rain at Rishiri was Cy, and that location was rarely affected by SF and Ty rain (Berry *et al.*, 2011; Kimura, 1970).

In contrast, the cape Hedo at Okinawa located approximately 1300 km to the south of the present study site, had higher Na^+ and Cl^- concentrations and lower anthropogenic ions (Table 3.1). Other than SF, Okinawa is more frequently affected by typhoons than the site of the present study, in addition to the fact that the observatory is very close to the sea. Ty contributed more than 30% of total rainfall there in a year (Sakihama *et al.*, 2008), which was comparable to the SF rainfall at the present study site. The annual mean concentrations of Na^+ and Cl^- in the total rainwater at Hedo, compared to the concentrations at sites like the present study, should be larger and the concentrations of ions mainly contributed by anthropogenic emissions should be smaller. These results further support that quantifying ions in rainwater according to rain types is critical to an accurate elucidation of rainwater chemistry and essential for meaningful inter-comparisons between regions.

4.5. Conclusions

Concentrations of Na^+, Cl^-, nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+} in the rainwater of a site on the southwestern Japanese coast over eight years were investigated according to the rain types of Cy, SF and Ty. The compositions and concentrations of the rainwater had distinctive characteristics corresponding to the rain types. Cy rainwater was abundant in terrigenous ions, i.e., nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+}. SF rainwater was relatively clean compared to Cy rainwater, although the relative composition was similar to that of Cy rainwater. Ty rainwater was extremely abundant in Na^+ and Cl^-. These differences were due to the different histories of the air parcels associated with the rains and the differences in chemical processes, i.e., acid/base reaction and oxidation by H_2O_2.

For terrigenous ions, nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+}, the mean concentrations and year-to-year variations were determined by Cy rainwater and SF rainwater in each year. The annual mean concentrations of Na^+ and Cl^- were episodically and largely influenced by Ty rainwater in years with more Ty passage, although they were dominated by the contribution of Cy and SF rain. These results indicate a close dependence of rainwater chemistry on synoptic weather patterns. A simple estimation with SF rain records suggested that the rainwater chemistry in an annual base could be significantly changed due to the variation of rainfall contributed by different rain types. Therefore, the lack of awareness of this dependence may impede an accurate elucidation of the presence of ions in rainwater due to primary emissions and chemical processes, and a more confident projection of future rainwater chemistry, and a meaningful inter-comparison between different geographical regions.

Chapter 5

Monthly Characteristics of Rainwater Chemistry

5.1. Introduction

Rain plays a crucial role in the chemical transformation and the removal of airborne species in the atmosphere and links various variations and evolutions on the Earth (Seinfeld and Pandis, 2006). The presence of ions such as sulfate and nitrate in rainwater and cloud water is a consequence of multiple processes and factors, including the emission and dispersal of air pollutants, chemical conversions in the air, thermodynamic properties of air parcels, and microphysical variations of cloud and rain droplets (Easter and Luecken, 1988; Iribarne and Cho, 1989). The input of ion species to ocean area via wet deposition is one of the key processes to drive the evolution and conservation of the marine ecosystems in the open ocean (Duce *et al*., 2008).

We have confirmed that the rainwater chemistry is different according to the rain types on synoptic scales because the thermodynamic mechanisms of the cloud formation are different. Seasonal variations of the rainwater chemistry over the East China Sea should be closely dependent on the predominant rain types in different months or seasons. In particular, typhoons and Meiyu fronts do not occur in every season or month. Monthly or seasonal variation of ions in rainwater, and wet deposition fluxes at lands and ocean areas have been well studied with long-term records. The studies are usually discussed with an integrated base of records while seasonal characteristics have rarely been carefully examined according to rain types in a quantitative manner (e.g. Pan *et al*., 2013; Yang *et al*., 2012).

In this chapter, seasonal characteristics of the concentrations of four terrigenous-origin ions (SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+}) and two marine-origin ions (Na^+ and Cl^-) in the rainwater at the coastal site are examined. The records of the 348 rain episodes over the eight years from 1996 to 2003 are applied. The major purposes are to demonstrate the association of the monthly variation of the rainwater chemistry with rain types causing the rain, and to provide accurate information for the inter-comparisons and the elucidation of rainwater chemistry.

5.2. Treatment of monthly ion concentrations

Monthly mean concentration of ions in rainwater was compiled into the “volume-weighted mean” concentration (Galy-Lacaux *et al.*, 2009) of each month over the eight years. If there were less than three samples for a rain type in a certain month over the eight years, the monthly mean concentration was treated as “not available” (N.A.). The relative contribution of each rain type to the ions in the total rainwater in a certain period was evaluated according to ion deposition fluxes to the surface. The fluxes were calculated with the concentration of one or multiple ions in the rainwater multiplied by the amount of the rainfall. The monthly flux of an ion of a rain type was the summation of the fluxes in all episodes of the rain type in a month, and the mean flux was the mean of the eight one-month integrated values. Non-sea salt fractions of SO_4^{2-} (nss-SO_4^{2-}) and Ca^{2+} (nss-Ca^{2+}) were estimated with Na^+ as the conservative tracer for sea salt (Keene *et al.*, 1986). The concentration and the flux of sea salt fractions of SO_4^{2-} and Ca^{2+} will not be described or discussed, because of their small contributions.

5.3. Results

Monthly mean concentrations of nss-SO_4^{2-}, NO_3^-, NH_4^+, nss-Ca^{2+}, Na^+ and Cl^- over the eight-years in total rainwater were 14.4-57.8, 7.2-25.0, 7.7-31.4, 2.3-18.7, 21.7-154.9 and 26.4-178.5 µeq l^{-1}, respectively (Table 5.1). The concentrations of nss-SO_4^{2-}, NO_3^- and NH_4^+ were the highest in February and the lowest in June. The concentration of nss-Ca^{2+} was the highest in February and the lowest in August. The concentrations of Na^+ and Cl^- were the highest in January, the lowest in June, and relatively high in August and September. These trends were closely associated with the dominant rain types, which will be discussed in details.

In November-May, the monthly mean concentrations of terrigenous ions, i.e., nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+}, in total rainwater were 25.1-57.8, 9.9-25.0, 11.3-31.4 and 5.5-18.7 µeq l^{-1}, respectively. The concentrations of marine-origin ions, Na^+ and Cl^-, were 24.2-154.9 and 30.0-178.5 µeq l^{-1}. The concentrations of all these ions were higher in November-May than the concentrations in other months, except for in August and September, and were actually very close to the concentrations in Cy rainwater. Monthly mean rainfall by Cy was more than 30 mm, which occupied 65-100% of monthly total rainfall (Fig. 5.1). Cy rain contributed more than 60% to the fluxes of the six ions in these months (Fig. 5.2). Therefore, the ions in the total rainwater in November-May were dominated by Cy rain.

In June and July, the monthly mean concentrations of nss-SO_4^{2-}, NO_3^-, NH_4^+, nss-Ca^{2+}, Na^+ and Cl^- in total rainwater were 14.4-20.7, 7.2-9.5, 7.7-12.9, 4.1-6.8, 21.7-33.6 and 26.4-40.5 µeq l^{-1}, respectively. The concentrations were relatively lower than those in November-May. This result was mainly due to the large rainfall by SF in June and July. The rainfall by SF was 260 mm in June and 173 mm in July. Each of these constituted more than 60% of the total rainfall in the months (Fig. 5.1). For this reason, SF rain contributed 35-75% of the fluxes of the six ions in the two months (Fig. 5.2). In addition, the concentrations of the six ions in the Cy rainwater in the two months were lower than those in November-May, and were close to the concentrations in the SF rainwater.

In August and September, Ty rain substantially contributed to marine-origin ions Na^+ and Cl^- in total rainwater. It was estimated that more than 60% in the fluxes of the two ions in the two months were from Ty rain (Fig. 5.2). This was due to the extreme abundance of the two ions in Ty rainwater. It is found that the concentrations of the two ions in Ty rainwater were 10-43 times the concentrations in Cy and SF rainwater. The concentrations were large enough to significantly influence the rainwater chemistry in the two months although the rainfall caused by Ty was 8-34 mm $month^{-1}$ and occupied only 6-18% of the total rainfall (Fig. 5.1). Ty rain also caused rainfall of 35 mm in July, which occupying 13% of the total rainfall in the month. However, the relative contribution of Ty rain to the fluxes of Na^+ and Cl^- was low in July, because of the dominant contribution by SF rain. In October, the rainfall and the ions were dominated by the rain type of Other. These cases were frequently associated with multiple rain types, because the month is a transition period from fall to winter.

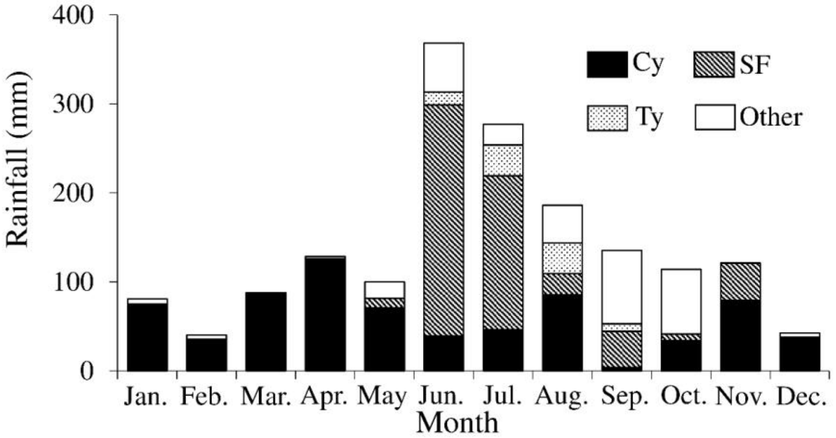

Fig. 5.1. Monthly mean rainfall by Cy, SF, Ty and Other over the eight years.

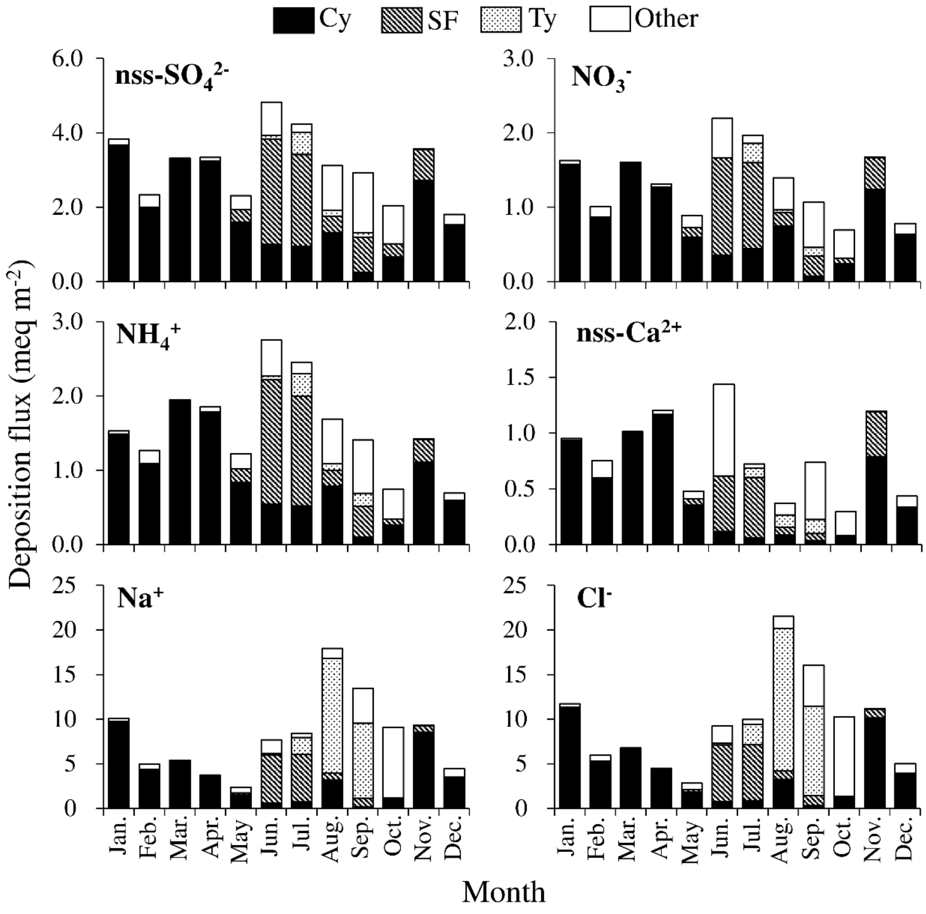

Fig. 5.2. Monthly mean wet deposition fluxes of the six ions by Cy, SF, Ty rain and Other over the eight years.

Table 5.1. Monthly mean concentrations (in μeq l^{-1}) of ions in the rainwater at the study site and at remote sites in Japan.

Site name	Ion species	Rain	Month											
(Period)	(μeq l^{-1})	type	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
Reihoku-shiki[a]	Nss-SO_4^{2-}	Total	45.8	57.8	37.4	25.1	26.3	14.4	20.7	20.6	21.4	20.7	29.1	43.4
(1996-2003)		Cy	46.7	55.8	37.3	24.9	27.1	25.4	23.0	15.4	-	20.6	38.6	39.9
		SF	-	-	-	-	29.1	12.3	21.4	20.2	23.0	-	-	-
		Ty	-	-	-	-	-	-	19.3	5.7	15.2	-	-	-
	NO_3^-	Total	19.3	25.0	18.7	10.3	9.9	7.2	9.5	8.3	8.2	8.2	14.6	20.7
		Cy	19.8	24.3	18.7	10.2	10.1	9.0	10.3	8.7	-	8.5	19.3	18.1
		SF	-	-	-	-	10.6	5.7	9.8	7.9	6.6	-	-	-
		Ty	-	-	-	-	-	-	8.8	1.3	13.8	-	-	-
	NH_4^+	Total	17.6	31.4	21.2	13.5	12.5	7.7	12.9	10.1	10.4	8.6	11.3	16.4
		Cy	18.0	30.5	21.1	13.3	12.4	13.9	13.0	9.2	-	8.3	15.5	15.4
		SF	-	-	-	-	14.2	7.1	14.2	8.3	10.2	-	-	-
		Ty	-	-	-	-	-	-	9.9	3.4	20.7	-	-	-
	Nss-Ca^{2+}	Total	10.0	18.7	11.4	8.6	5.5	6.8	4.1	2.3	6.4	4.8	11.8	11.0
		Cy	10.4	16.7	11.4	8.5	6.2	3.0	2.0	1.0	-	2.6	14.2	8.7
		SF	-	-	-	-	4.8	1.9	5.3	3.7	1.5	-	-	-
		Ty	-	-	-	-	-	-	2.7	3.7	15.1	-	-	-
	Na^+	Total	154.9	123.4	58.1	29.0	24.2	21.7	33.6	97.7	105.3	75.2	70.2	135.4
		Cy	159.6	122.3	58.1	29.3	24.2	16.0	13.9	37.1	-	31.6	126.4	115.8
		SF	-	-	-	-	16.4	19.5	34.7	40.8	23.2	-	-	-
		Ty	-	-	-	-	-	-	54.3	423.3	1004.2	-	-	-
	Cl^-	Total	178.5	148.1	72.5	34.7	30.0	26.4	40.5	116.8	122.9	85.5	85.5	152.3
		Cy	184.2	147.9	72.6	35.0	31.3	20.5	16.9	38.0	-	35.9	151.5	129.2
		SF	-	-	-	-	16.8	23.5	41.3	49.3	27.8	-	-	-
		Ty	-	-	-	-	-	-	67.5	513.5	1195.7	-	-	-
Rishiri[b]	Nss-SO_4^{2-}	Total	31.5	67.3	55.9	40.0	44.6	33.8	34.6	14.4	6.1	13.0	30.6	32.9
(2000-2007)	Na^+	Total	238.1	394.4	194.4	104.6	28.5	75.5	18.6	22.3	39.2	241.2	515.4	425.5
Hedo[b]	Nss-SO_4^{2-}	Total	17.8	28.9	37.1	19.8	14.0	10.8	12.2	4.6	3.3	15.3	12.4	18.1
(2000-2007)	Na^+	Total	352.1	233.9	219.9	67.8	64.5	71.7	423.4	2218.3	297.1	347.3	163.6	329.5

[a] This study, [b] Calculated from the data available from EANET homepage (Network Center for EANET, 2014).

-: Not available (N.A.)

5.4. Discussion

The above results indicate the remarkable seasonal characteristics of rainwater chemistry due to changes of the predominant rain types in different months or seasons. This is naturally acceptable because of the distinctive nature of rainwater chemistry in different rain types (Toyonaga and Zhang, 2016). Besides the changes of the predominant rain types and the respective frequency of different type, the variation of ion concentrations in Cy rainwater was also an important factor influencing the monthly variation of rainwater chemistry in the total rainwater. Terrigenous ions SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+} in Cy rainwater were closely associated with rainfall and emission amount of precursors.

To further evaluate the effect of the rainfall and the precursor emission on the ion concentrations, a simple regression analysis was conducted for the monthly rainfall and the fluxes by Cy rain in four seasons, i.e. winter (Dec.-Feb.), spring (Mar.-May), summer (Jun.-Aug.), fall (Sep.-Nov.). The regression equation is

$$\mathrm{Y} = a\mathrm{X} + b$$

where Y is monthly wet deposition fluxes and X is the total rainfall in a month during a season, a is the slope, and b is the intercept.

There were strong correlations (R>0.6) in all seasons between the monthly fluxes of anthropogenic ions (nss-SO_4^{2-}, NO_3^- and NH_4^+) and rainfall by Cy, indicating the rainfall is a factor influencing the fluxes of the ions (Table 5.2). Slopes, a, in the case of nss-SO_4^{2-} and NO_3^- were the highest in winter and the lowest in summer. The slopes corresponded to the loading of ions per unit rainfall, which could be interpreted as the strength of the emissions influence. Cy rain was mainly affected by continental air masses. The seasonal trend of the slopes should be corresponded to precursor gases and particulate matter emissions at Asian continent (Fujita *et al.*, 2000; Seto and Hara, 2006). The seasonal characteristics of nss-SO_4^{2-} and NO_3^- variations were consistent with the concentration of precursor gases (SO_2 and NO_X) and particulate SO_4^{2-} and NO_3^- in the air in China, which is high in winter and low in summer (Meng *et al.*, 2009; Pan *et al.*, 2013, 2012).

The slope in the case of NH_4^+ was the highest in spring and the lowest in fall. The precursor gas of NH_3 in China is high in summer and low in fall or winter (Meng *et al.*, 2010). However, particulate NH_4^+ is higher in winter or spring than in other seasons in China (Cao *et al.*, 2009; Meng *et al.*, 2014). Therefore, NH_4^+ in the Cy rainwater might be more closely associated with particulate NH_4^+ from China than the precursor gas NH_3.

There was no clear correlation between the flux of nss-Ca^{2+} and the rainfall in any season. This was mainly attributed to the fact that the rainfall of Cy rain with extreme high concentration of nss-Ca^{2+} was usually small. It is likely such Cy rain is the consequence of the influence by Asian dust (Seto *et al*., 2007; Toyonaga and Zhang, 2016). Asian dust-related rain is frequently observed in spring (Kawamura and Hara, 2006; Seto *et al*., 2004), and the flux of nss-Ca^{2+} observed in spring was high (Fig. 5.2).

The annual fluxes by Cy rain showed a year-by-year variation which is characterized by the influence of the anthropogenic emissions from the Asian continent because this type of rain is more significantly influenced by continental air than other types of rain (Toyonaga and Zhang, 2016). Therefore, the emission trend of anthropogenic pollutants in China should also be an important factor to influence the seasonal and annual variation of the chemistry in Cy rainwater, which is actually easily expected.

The seasonal variation of rainwater chemistry at other sites could also be interpreted as the consequence of seasonal changes of dominant rain types. For example, the variation of monthly mean concentration of Na^{+} and nss-SO_4^{2-} in the rainwater collected at Rishiri, the island located in the northern part of the Sea of Japan, was similar to the variation in the Cy rainwater at the site of this study (Table 5.1). This is consistent with the fact that the major type of rain at Rishiri is Cy rain, and the fact that Rishiri is rarely affected by SF and Ty rain (Berry *et al*., 2011; Kimura, 1970).

In contrast, the variation of monthly mean concentrations of the ions at Hedo, the north cape of Okinawa located approximately 1,300 km to the south from the site of this study, was similar to the variation in the total rainwater at the site of this study (Table 5.1). Moreover, in July-September, the concentration of Na^{+} was much larger than, and the concentration of nss-SO_4^{2-} was much smaller than those at the site of this study (Table 5.1). This was due to the more frequent typhoon at Okinawa than at the site of this study, besides Cy and SF rain (Sakihama and Tokuyama, 2005).

Therefore, quantifying ions in rainwater according to rain types is important for a meaningful inter-comparison of the seasonal variations at different geographic regions, and is essential for accurate understandings of the correlation between rain type and rainwater chemistry.

Table 5.2. Coefficients of the regression analysis between the monthly wet deposition fluxes and rainfall caused by Cy.

	Slope	*Intercept*	*Correlation coefficients*
	a	*b*	*R*
($nss\text{-}SO_4^{2-}$)			
Winter	0.0324	0.8636	0.78
Spring	0.0218	0.6412	0.73
Summer	0.0167	0.4571	0.89
Fall	0.0223	0.5062	0.74
(NO_3^-)			
Winter	0.0124	0.4521	0.73
Spring	0.0104	0.1676	0.72
Summer	0.0080	0.0717	0.96
Fall	0.0082	0.3008	0.62
(NH_4^+)			
Winter	0.0116	0.5295	0.65
Spring	0.0126	0.3218	0.71
Summer	0.0094	0.2148	0.84
Fall	0.0089	0.2184	0.67
($nss\text{-}Ca^{2+}$)			
Winter	0.0043	0.4510	0.40
Spring	0.0052	0.3551	0.44
Summer	0.0008	0.1038	0.37
Fall	0.0029	0.2790	0.30

Regression equation: $Y=aX+b$

Y: monthly deposition fluxes (meq m^{-2}), X: monthly rainfall (mm)

5.4. Summary

The monthly variation of rainwater chemistry of four terrigenous-origin ions (nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+}) and two marine-origin ions (Na^+ and Cl^-) at a coastal site in southwestern Japan was investigated with the records of 348 rain episodes over eight years according to the rain types of Cy, SF and Ty. Monthly mean concentrations of the ions in November-May, when the rain was mainly caused by Cy, were higher than the concentrations in June and July, when the rain was mainly caused by SF. In August and September, the concentrations of marine-origin ions were relatively high due to the contribution by Ty rain. Since Cy rain is a type of rain stimulated by continentally origin air, the monthly variation of the chemistry in Cy rainwater should be associated with the variation of the emission of air pollutants in China, in addition to the variation of rainfall. Comparison analysis with other sites suggested that the difference of seasonal variations of ion concentrations at the present site from those at Hedo of Okinawa and Rishiri of the Sea of Japan were due to the different seasonal dominance of the rain types depending on the regions. These results indicate that the monthly variation of the rainwater chemistry was closely associated with the variation of contribution by the rain types.

Chapter 6

Wet Deposition Fluxes of Ions Contributed by Cyclone-, Stationary Front- and Typhoon-associated rains

6.1. 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 (Kuribayashi *et al.*, 2012; Morino *et al.*, 2011; Vet *et al.*, 2014), and the increase of wet deposition-induced production in the East China Sea (Zhang *et al.*, 2007b; 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. 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, consequently, their wet deposition fluxes are expected to have distinctive characteristics of the weather types.

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 (Jickells, 2006; Zhang *et al.*, 2011). 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 at the 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. As mentioned previously, cyclones, stationary fronts and typhoons are the synoptic weather systems causing rain over the East China Sea. 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.

6.2. Treatment of wet deposition fluxes

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.

6.3. Result and discussions

The average rainfall amount per year over the eight years was 1684±281 mm, in which Cy, SF, Ty and Other constituted 43±9% (frequency: 63±7%), 33±13% (15±5%), 5±5% (4±1%), and 19±9% (18±7%), respectively (Fig. 6.1). 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.

6.3.1. Average flux

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 meq m^{-2} yr^{-1}, respectively (Fig. 6.1). The contributions by different types of rain to the flux of an ion differed with the types. Cy contributed 22.2±3.5 meq m^{-2} yr^{-1} to nss-SO_4^{2-}, 9.7±2.1 meq m^{-2} yr^{-1} to NO_3^-, 11.1±2.6 meq m^{-2} yr^{-1} to NH_4^+, and 5.6±0.8 meq m^{-2} 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 meq m^{-2} 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 meq m^{-2} 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 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 the two 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 (Kaneyasu *et al.*, 2000; Zhang *et al.*, 2005). 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. 6.1). 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.

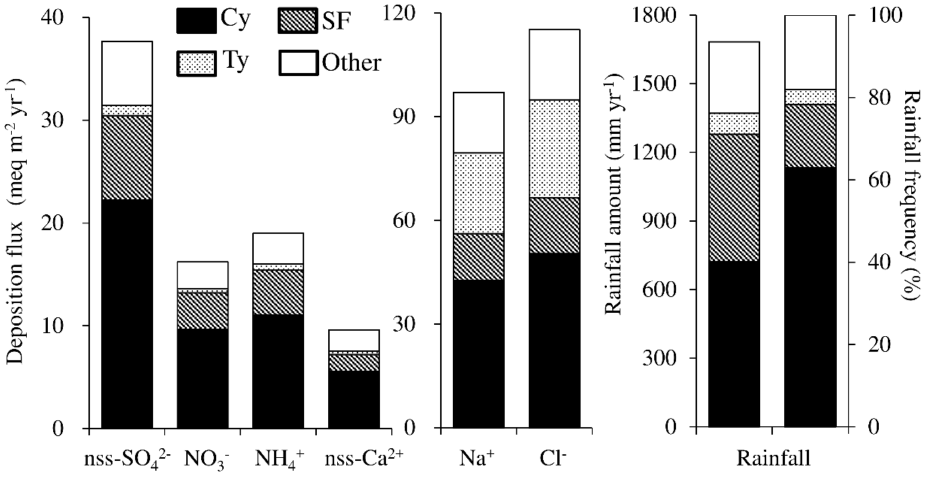

Fig. 6.1. Average wet deposition fluxes of ions, annual rainfall amount and frequency caused by Cy, SF, Ty and Other.

6.3.2. 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. 6.2). 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 that, the fluxes increased. The variation was similar to that of the portions contributed by Ty. However, in some years, the portion by Ty was 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 cases 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. Further 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 a stationary front and a 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 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 (EANET, 2006; Vet *et al.*, 2014). 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. 6.3). Weak positive relationship was confirmed between SF rain and the fluxes (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.

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. 6.3). The negative correlation was actually 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 concentrations 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 northwest 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).

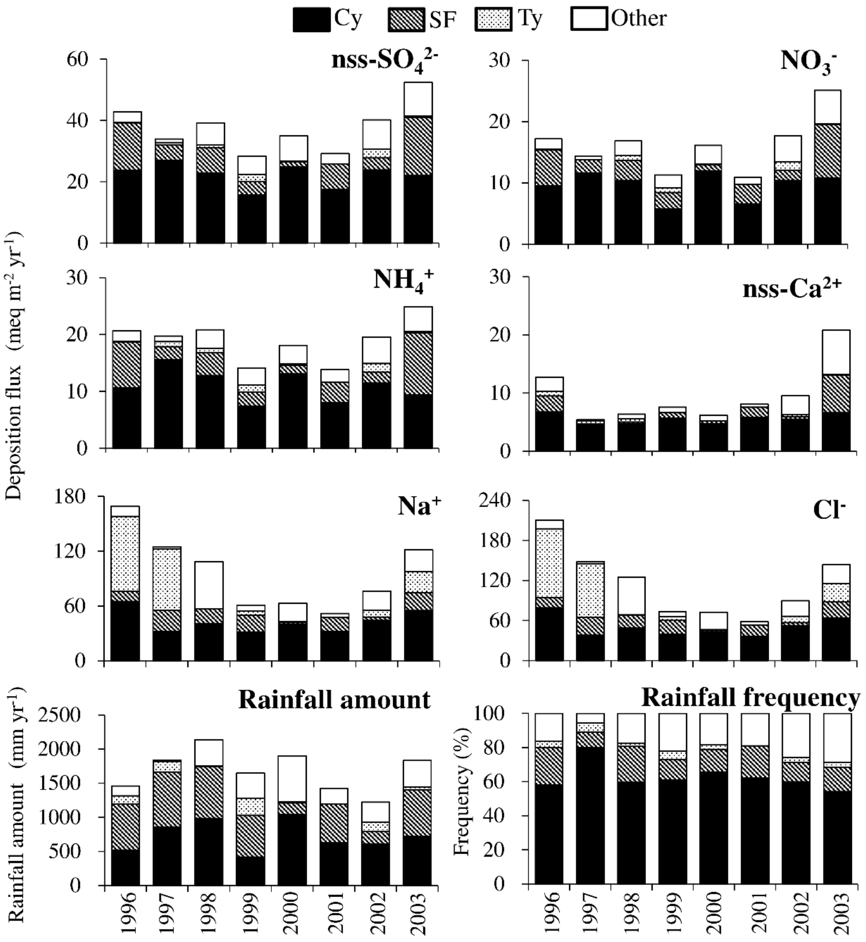

Fig. 6.2. Year-by-year variation of annual wet deposition fluxes of ions, rainfall amount and frequency caused by Cy, SF, Ty and Other.

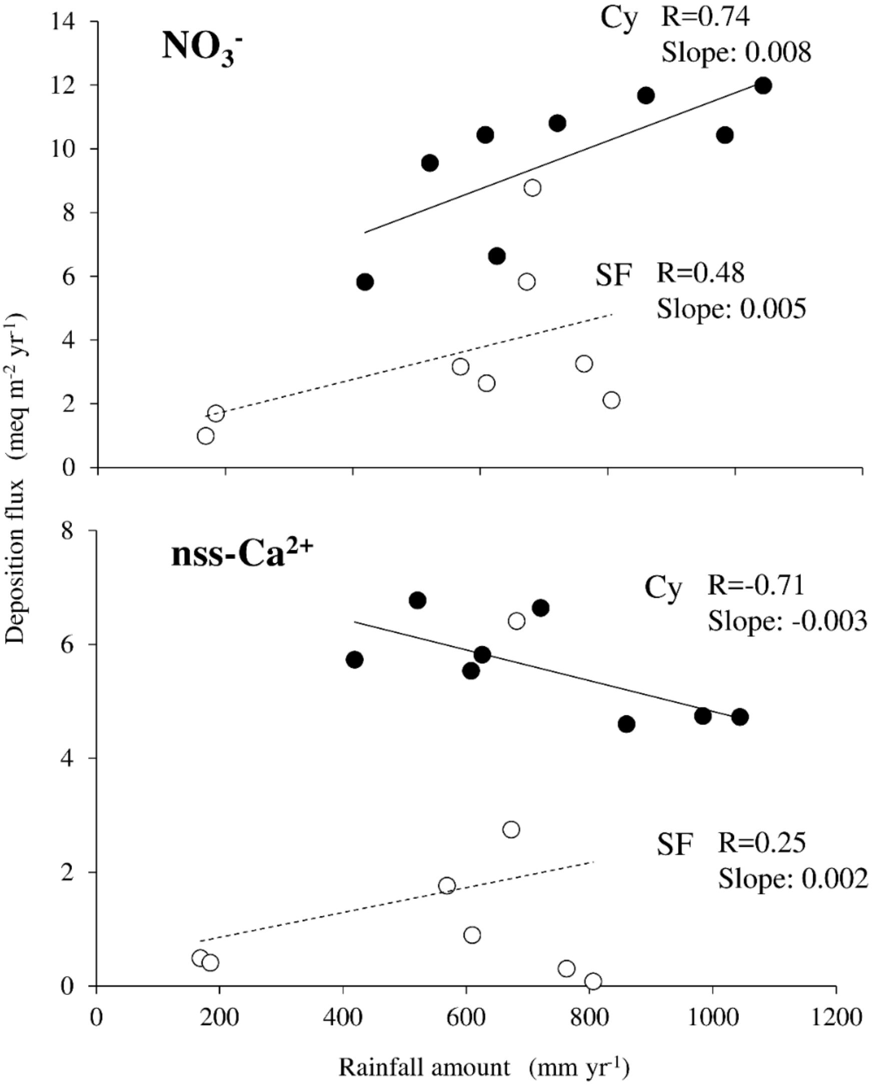

Fig. 6.3. Annual wet deposition fluxes of NO_3^- (upper) and nss-Ca^{2+} (lower) vs. annual rainfall amounts caused by Cy and SF. Closed and open circles indicate the cases of Cy and SF, respectively. Linear regressions are marked by solid and dashed lines with the slope and correlation coefficient (R).

6.3.3. Flux of nitrogen compounds and its dominant rain types

The average wet deposition flux of the nitrogen compounds, i.e. NO_3^- and NH_4^+, was 35.3 meq m^{-2} 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 6.1). The fluxes at ocean areas, including the Pacific, the Atlantic and the Indian Ocean, were 2.1-10.1 meq m^{-2} yr^{-1} (Baker *et al.*, 2010; Duce *et al.*, 1991). Therefore, the East China Sea is actually the region with large 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.*, 2007b), and the cause has been attributed to the emission of relevant compounds and precursor gases in the continent, particularly in China (Uno *et al.*, 2007; Vet *et al.*, 2014). The present results show that the contribution by SF, Ty and Other together to the flux was approximately 14.5 meq m^{-2} 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 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 (Baker *et al.*, 2010; Morino *et al.*, 2011; Zhang *et al.*, 2011). 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 meq m^{-2} yr^{-1} (Table 6.1) (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 meq m^{-2} 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 meq m^{-2} 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 (Kaneyasu *et al.*, 2000; Zhang *et al.*, 2005). 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 a constant role in the air-sea interaction in the sea areas.

Table 6.1. Wet deposition fluxes of nitrogen compounds (NO_3^-+NH_4^+) around the East China Sea and to the ocean area.

Site		Deposition flux (meq m^{-2} yr^{-1})	Rainfall amount (mm)	Period
Reihoku-shiki[a]	All rain types	35.3	1684	1996-2003
	Cy	20.8	723	1996-2003
	SF	7.9	557	1996-2003
	Ty	1.0	92	1996-2003
	Other	5.6	312	1996-2003
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

[a] This study, [b]EANET (2006), [c]Duce *et al.* (1991), [d]Baker *et al.* (2010).

6.4. 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 southwestern 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 including 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 usually lower than that by Cy in a year. 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 convincible investigation of their roles in the air-sea interactions.

Appendix Chapter 6

Table 6.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-}	All rain types	42.8	34.0	39.2	28.3	35.1	29.2	40.2	52.4	37.6	7.3
(meq m^{-2} yr^{-1})	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^-	All rain types	17.2	14.4	17.0	11.4	16.2	11.0	17.7	25.2	16.3	4.2
(meq m^{-2} yr^{-1})	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^+	All rain types	20.7	19.8	20.9	14.0	18.1	13.8	19.6	24.9	19.0	3.4
(meq m^{-2} yr^{-1})	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+}	All rain types	12.8	5.4	6.4	7.6	6.2	8.1	9.5	20.8	9.6	4.8
(meq m^{-2} yr^{-1})	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^+	All rain types	169.2	125.0	108.4	60.9	63.0	51.8	76.3	121.4	97.0	38.2
(meq m^{-2} yr^{-1})	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^-	All rain types	210.6	148.2	124.9	73.5	72.5	58.3	89.7	143.9	115.2	48.2
(meq m^{-2} yr^{-1})	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

Chapter 7

Summary

In this study, eight-year records of the concentrations of Na^+, Cl^-, nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+} in the rainwater of a site on the southwestern Japanese coast were investigated according to the rain types of Cy, SF and Ty. Similarities and differences of ion concentrations according to the rain types and their causes, association of monthly variation of the concentration with the rain types, and dependence of wet deposition fluxes on the rain types were examined.

The compositions and concentrations of the rainwater had distinctive characteristics corresponding to the rain types. Cy rainwater was abundant in terrigenous ions, i.e., nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+}. SF rainwater was relatively clean compared to Cy rainwater, although the relative composition was similar to that of Cy rainwater. Ty rainwater was extremely abundant in Na^+ and Cl^-. These differences were due to the different histories of the air parcels associated with the rains and the differences in chemical processes, i.e., acid/base reaction and oxidation by H_2O_2. The annual mean concentrations of nss-SO_4^{2-}, NO_3^-, NH_4^+ and nss-Ca^{2+} were determined by Cy and SF rainwater in each year. The annual mean concentrations of Na^+ and Cl^- were episodically and largely influenced by Ty rainwater. A simple estimation with SF rain records suggested that the rainwater chemistry in an annual base could be significantly changed due to the variation of rainfall contributed by different rain types.

Monthly mean concentrations of ions in November-May, when the rain was mainly caused by Cy, were higher than the concentrations in June and July, when the rain was mainly caused by SF. In August and September, the concentrations of marine-origin ions were relatively high due to the contribution by Ty rain. The monthly variation of the chemistry in Cy rainwater should be closely associated with the variation of the emission of air pollutants in China, in addition to the variation of rainfall, because Cy rain was induced by continentally origin cold and dry air.

The wet deposition fluxes of 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 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. The variations of the annual fluxes of Na^+ and Cl^- were caused by Ty 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 ions in the rainwater according to rain types is critical to an accurate elucidation of rainwater chemistry and their variations, and is also essential for meaningful comparisons of temporal and spatial variations between different areas over the world. Simple comparisons with integrated ion concentrations in rainwater may mask the real similarities and differences in the rainwater chemistry between geographically different regions. Furthermore, it is also important for accurately understanding the association of rainwater chemistry with emission, chemical processes, and for a more confident future projection and a convincible investigation of their roles in the air-sea interactions.

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