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Ship-borne observations of sea fog and rain chemistry over the North and South Pacific Ocean

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Abstract
Clouds, fogs, and rain can serve as useful integrators of both atmospheric aerosols and soluble trace gases. To better understand the chemical characteristics of sea fog and rain in the North and South Pacific Ocean, fog and rain were measured aboard the R/V ARAON in 2012 and 2014, respectively, as part of the Ship-borne Pole-to-Pole Observations (SHIPPO) project. The mean sea fog pH (3.59) was lower than the mean rain pH (4.54), reflecting greater inputs of non-sea-salt (nss)-SO_4^{2-}. For the collected rain, nss-Ca^{2+} and nss-Mg^{2+} from mineral dust particles were the major contributors to acidity neutralization. NO_3^- concentrations, which are derived from scavenging of gaseous nitric acid and aerosol nitrate, were higher than NH_4^+ concentrations, indicating that terrestrial and/or local anthropogenic NO_3^- sources outweighed contributions from anthropogenic or biological oceanic NH_3/NH_4^+ sources. The ratio of Cl^-/Na^+ in the sea fog was slightly lower than that in the sea water due to HCl volatilization from scavenged sea-salt particles. The ratio of NH_4^+/ nss-Ca^{2+} was lower in the rain than in the sea fog, revealing the influence of mineral dust particles at altitudes above the sea fog layer. The average sea fog water TOC concentration, 13.2 ppmC, was much higher than the measured TOC concentrations in marine fogs and clouds in other remote environments, likely due to continental influence; the TN and TOC concentrations in the fog water were much higher than those in the rain. The sea fog and rain chemical properties measured during research cruises like these enhance our understanding of wet deposition and cloud condensation nuclei sources and processes in the Pacific Ocean.

Keywords Sea fog · Rain composition · Marine aerosol chemical composition · North and South Pacific Ocean · Marine background aerosol

1 Introduction

The atmosphere is a host to diverse homogeneous and/or heterogeneous chemical reactions involving atmospheric gases and particles from natural (e.g., sea spray and soil) and anthropogenic (e.g., industrial emissions, fertilizer production, and biomass burning) sources. Fog and rain deposition contribute significantly to nutrient inputs to ecosystems, agriculture, and residential water supplies (Coble and Hart 2013; Dawson 1998; Ewing et al. 2009; Fenn et al. 2000), which can be either beneficial or deleterious, and to plant surface damage due to acidic rain and fog (Jacobson et al. 1989; Schaberg et al. 2000; Schemenauer 1986).

The atmospheric scavenging of water-soluble gases, including HNO_3, NH_3, and SO_2, by fogs is determined by the droplet composition, with the timescale for uptake depending on droplet size and growth rate (Aikawa et al. 2007). The chemical composition of fog and rain, which reflects both this scavenging of soluble gases and aerosol particle scavenging, varies with regional emission sources, atmospheric photochemistry, and fog liquid water content (LWC) (Collett et al. 2002; Kaul et al. 2011; van Pinxteren et al. 2005). Fog generally features higher ion concentrations than rain (e.g.,Igawa et al. 1998; Collett et al. 1991); thus, it has potentially greater ecosystem impacts through deposition.

Numerous studies have explored the chemical composition of fog in specific terrestrial and coastal locations, including coastal and inland California in the U.S. (Boris et al. 2018; Collett et al. 1990, 1999), the Po Valley in Italy (Fuzzi et al. 2002; Giulianelli et al. 2014), and the eastern Yellow Sea in Korea (Boris et al. 2016). A limited number of studies (e.g.,Watanabe et al. 2001; Sasakawa and Uematsu 2002; Straub et al. 2007; Benedict et al. 2012) have investigated the composition of clouds, fogs, and/or rain over the open ocean. Although organic compounds in fog and rain have historically received less scientific attention than inorganic compounds (Iavorivska et al. 2017; Herckes et al. 2013), the organic chemistry of fog and rain droplets is now recognized as a significant aspect of atmospheric chemistry (Chakraborty et al. 2016; Harris et al. 2013; Herckes et al. 2013; Kim et al. 2019).

The Ship-borne Pole-to-Pole Observations (SHIPPO) study was conducted in 2012 (Choi et al. 2017; Park and Rhee 2015) and 2014 (Kim et al. 2017) over the northern and southern Pacific Ocean, respectively. One of the study goals was to gain a better understanding of the chemical composition of sea fog and rain in the remote marine boundary layer. The sea fog and rain samples collected during these cruises were analyzed and compared to the fog and rain collected over marginal seas and coastal areas. Because fogs are good integrators of both aerosol particles and water soluble gases, measurements of their composition provide important insight into atmospheric pollution levels in key environments.

2 Methods

During the SHIPPO research cruises, the R/V ARAON ice breaker ship (Korea Polar Research Institute, Korea) participated in the measurement campaigns (1) from the Yellow Sea, through the East Sea (Sea of Japan), and to the western reaches of the North Pacific and Bering Sea from July 14–30, 2012 and (2) through the western Pacific Ocean from Christchurch, New Zealand to Gwangyang, South Korea from March 30–April 25, 2014 (Fig. 1). Twelve sea fog water samples were collected over the North Pacific, including seven samples (with 3–4 h durations) on 7/21, one sample on 7/22, one sample on 7/23, and three samples (with 3–4 h durations) on 7/24. Fog was not encountered during the South Pacific cruise. Five and eight rain samples were collected over the North and South Pacific, respectively. Choi et al. (2017) described the SHIPPO fog and rain sampling locations as 'clean ocean,' implying reduced influence of anthropogenic emission sources.

During the campaign sea fog water was collected with a compact version of the Caltech Active Strand Cloudwater Collector (CASCC2; Demoz et al. 1996). The CASCC2 collects fog/cloud drops by drawing droplet-laden air at 5.8 m^3/min over six banks of 508 μm diameter Teflon strands. Drops are collected via inertial impaction on the strands; the instrument features a 50% size cut droplet

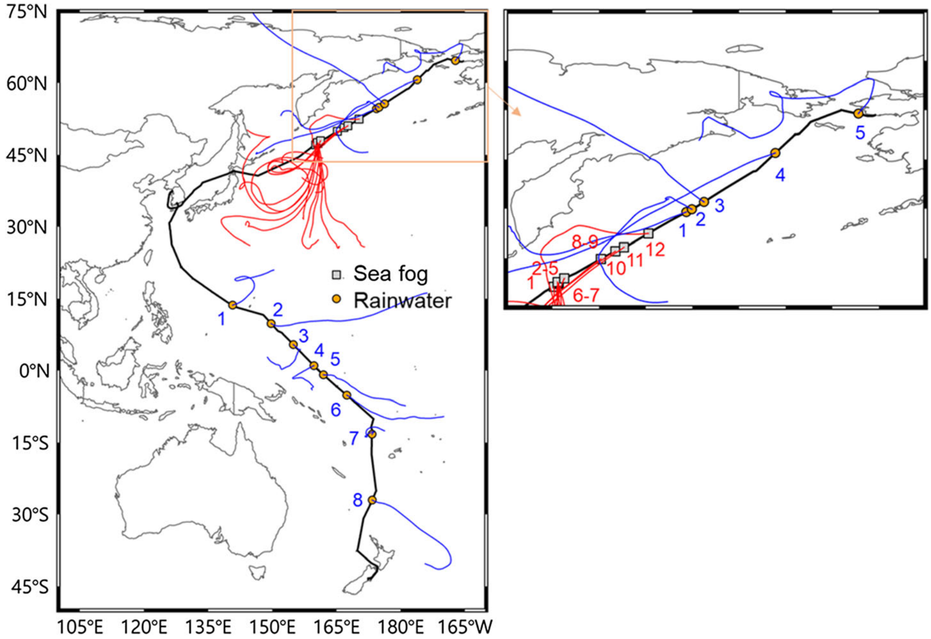

Fig. 1 Sea fog and rain sampling points on the ship-tracks during the two research cruises. The squares and circles indicated the collection sites for sea fog and rain. The inset figure indicates the detailed collection points in 2012. Five-day backward trajectories of air masses were computed with the HYSPLIT model for each measurement location. The red (sea fog) and blue lines (rain) represent backward trajectories arriving along the cruise track at 1000 m above sea level

diameter of 3.5 μm. The collected drops coalesce and are carried by gravity and aerodynamic drag downward through a Teflon collection trough and sample tube into a polyethylene sample bottle. Rain samples were collected using a simple gravity-fed funnel, 20 cm in diameter, connected to a 1000 mL bottle. Prior to each fog or rain event, collector blanks were acquired by rinsing with deionized water for cleaning. Wind direction was monitored onboard the ship to avoid collection of sea fog and rain samples contaminated by ship stack exhaust.

The collected sea fog and rain samples were analyzed for pH on-site using an Orion portable pH meter and a combination pH microelectrode (Thermo Fisher Scientific, USA) calibrated with pH 4 and 7 buffers; sample aliquots were prepared for later major ion concentration analysis at Colorado State University. The fog and rain samples were analyzed for three anions (NO_3^-, SO_4^{2-}, and Cl^-) and five cations (NH_4^+, Na^+, K^+, ca.$^{2+}$, and Mg^{2+}) using a dual-channel ion chromatograph (DX-500, Dionex, USA). Anions were analyzed using a Dionex AG4A-SC/AS4A-SC column pair and ASRS-ULTRA II suppressor with an eluent consisting of 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$; cations were analyzed using a Dionex CG-12/CS-12 column pair and CSRS-ULTRA II suppressor with a 20 mM methanesulfonic acid eluent. Sea salt contributions, including sea salt (ss)-Cl^-, ss-SO_4^{2-}, ss-K^+, and ss-Ca^{2+} were calculated using the following formulae: ss-$Cl^- = 1.8 \times Na^+$, ss-$Mg^{2+} = 0.12 \times Na^+$, ss-$K^+ = 0.036 \times Na^+$, ss-$Ca^{2+} = 0.038 \times Na^+$, and ss-$SO_4^{2-} = 0.252 \times Na^+$ (Terzi et al. 2010). Aliquots of a subset of samples were prepared for subsequent total organic carbon (TOC) and total nitrogen (TN) analysis. TOC and TN concentrations were analyzed at Colorado State University using a Shimadzu Model 5000A TOC analyzer.

Concentrations measured in collected field blanks were used to determine minimum detection limits (MDLs) (Nieman et al. 1998) and sample precision was determined from replicate sample analysis. The MDL (μN) and precision (relative standard deviation, %) for the major ion components (NO_3^-, SO_4^{2-}, NH_4^+) were 0.11 (0.35%), 0.18 (0.43%), and 0.18 (0.29%), respectively. The MDLs and precision values were 0.63 (1.1%), 0.23 (0.35%), 0.21 (4.1%), 0.44 (2.2%), and 0.35 (4.4%) for the minor ion components (Cl^-, Na^+, K^+, Mg^{2+}, and ca.$^{2+}$), respectively. The TOC and TN MDL and precision values were 0.10 ppmC (1.1%) and 0.03 ppmN (4.9%), respectively.

3 Results and discussion

3.1 Chemical composition of sea fog water (from the western North Pacific) and rain (from the Bering Sea and eastern South Pacific)

Sea salt components, including Na^+, ss-Cl^-, ss-SO_4^{2-}, ss-K^+, and ss-Ca^{2+} accounted for 59% of the total ionic molar concentration in the sea fog water and 83% in the rain, suggesting that sea salt emissions dominated the water-soluble composition of the marine boundary layer (Table 1). The fraction of sea salt-derived ionic components was lower in the sea fog than in the rain due to much higher amounts of nss-SO_4^{2-} in the sea fog. Na^+ and ss-Cl^- were the most abundant components in rain (Toyonaga and Zhang 2017), although the fractional contributions of other components varied depending on measurement location.

The ratio of Cl^-/Na^+ was lower in the sea fog (0.78) than in the sea water (1.17), which, as reported in Keene et al. 1986; Collett et al. 2002, can arise from depletion of Cl^- due to HCl volatilization from sea-salt particles (Table 2). Sea salt particles can be acidified via HNO_3

Table 1 Mean and standard deviation of ionic components concentrations[a], total organic carbon (TOC)[b] and total nitrogen (TN)[c] in sea fog and rain from the North Pacific and South Pacific Ocean

	North Pacific		South Pacific
	Sea fog	Rain	Rain
pH	3.59 ± 0.24	4.54 ± 0.54	-
Cl^-	104.2 ± 54.0	234.9 ± 271.2	109.7 ± 99.3
NO_3^-	35.8 ± 10.1	15.0 ± 1.3	7.28 ± 2.98
SO_4^{2-}	396.3 ± 133.5	49.4 ± 19.0	12.4 ± 5.0
Na^+	133.8 ± 59.0	187.4 ± 205.7	82.7 ± 100.4
NH_4^+	129.3 ± 62.1	2.46 ± 2.70	0.57 ± 0.97
K^{2+}	27.0 ± 21.4	4.20 ± 4.15	3.36 ± 4.37
Mg^{2+}	33.5 ± 14.5	46.1 ± 50.6	9.73 ± 11.0
Ca^{2+}	46.9 ± 23.4	13.6 ± 8.7	5.20 ± 3.31
TOC	13.2 ± 5.0	0.58 ± 0.28	0.83 ± 0.30
TN	3.27 ± 1.31	0.07 ± 0.03	0.28 ± 0.03
nss-SO_4^-	380.1 ± 133.8	26.8 ± 24.1	4.29 ± 2.43
nss-Cl^-	-	18.0 ± 34.9	16.6 ± 9.4
nss-K^+	24.2 ± 21.0	0.28 ± 0.27	1.61 ± 3.53
nss-Mg^{2+}	18.3 ± 7.9	24.8 ± 27.3	0.43 ± 0.28
nss-Ca^{2+}	43.9 ± 22.3	9.49 ± 4.90	3.39 ± 1.66
ss-SO_4^{2-}	16.1 ± 7.1	22.6 ± 24.8	10.0 ± 12.1
ss-Cl^-	-	216.9 ± 240.1	93.1 ± 117.2
ss-K^+	2.83 ± 1.25	3.97 ± 4.35	1.75 ± 2.13
ss-Mg^{2+}	15.2 ± 6.7	21.3 ± 23.4	9.39 ± 11.4
ss-Ca^{2+}	2.92 ± 1.29	4.08 ± 4.48	1.80 ± 2.19

[a] μN; [b] ppmC; [c] ppmN

Table 2 The ratio between two ionic components for sea fog and rain collected in the North Pacific and South Pacific Ocean

	North Pacific Ocean		South Pacific Ocean	Sea water [a]
	Sea fog	Rain	Rain	
Cl^-/Na^+	0.78	1.25	1.33	1.17
K^+/Na^+	0.20	0.02	0.04	0.02
Mg^{2+}/Na^+	0.25	0.25	0.12	0.23
Ca^{2+}/Na^+	0.35	0.07	0.06	0.04
SO_4^{2-}/Na^+	2.96	0.26	0.15	0.12
nss-SO_4^{2-}/Na^+	2.84	0.14	0.05	-
NO_3^-/Na^+	0.27	0.08	0.09	-
NH_4^+/Na^+	0.97	0.01	0.01	-
NO_3^-/nss-SO_4^{2-}	0.09	0.56	1.69	-
NH_4^+/nss-Ca^{2+}	2.94	0.26	0.17	-
NH_4^+/nss-Mg^{2+}	7.08	0.10	1.33	-

[a] Keene et al. (1986)

and/or H_2SO_4 uptake or production and then act as sea fog condensation nuclei (Andreae and Crutzen 1997; Raja et al. 2008; Jung et al. 2013). In contrast, the ratio of Cl^-/Na^+ was slightly higher in the rain than in the sea water. Previous studies have reported that volcanic ash, anthropogenic, and biomass burning aerosols can contribute to excess droplet HCl, resulting in high Cl^-/Na^+ ratios (Fu et al. 2017; Gioda et al. 2011; Jung et al. 2013). The ratios of NH_4^+/nss-Ca^{2+} in the rain averaged 0.26 for the North Pacific and 0.17 for the South Pacific. Sea fog ratios of these species in the North Pacific were lower, suggesting possible influence of transported mineral dust particles (e.g., $CaCO_3$) scavenged at altitudes above the sea fog layer. By the same token, the ratios of minor ionic components (e.g., K^+, Mg^{2+}, and ca.$^{2+}$) to Na^+ were similar to or slightly higher than those in the sea water, indicating likely contributions of biomass burning and/or mineral dust aerosols from continental sources (Luo et al. 2016). Choi et al. (2017) also reported that biomass burning occurred nearby the Tsugaru Strait during the same cruise in 2012.

Herckes et al. (2013) provide an overview of prior reports of fog/cloud TOC measured in locations around the globe. In general, highly polluted urban fogs under lower planetary boundary layers typically feature the highest TOC concentrations, as fogs formed overnight are exposed to more concentrated pollutants. High TOC concentrations in continental clouds have also been reported under strong influence from biomass burning emissions (Desyaterik et al. 2013; Herckes et al. 2013). In contrast, lower fog TOC concentrations are often reported in remote locations with deeper planetary boundary layers, under which emissions are readily diluted. Some of the lowest TOC concentrations have been reported for marine stratocumulus clouds sampled in the eastern Pacific Ocean (Straub et al. 2007; Benedict et al. 2012; Herckes et al. 2013). The sea fog TOC concentrations found in the SHIPPO cruises and in previous studies are summarized in Fig. 2, where broad variations in TOC concentrations are apparent between the measurement sites. The mean sea fog TOC concentration in this cruise was 13.2 ppmC, lower than the average values measured in Gosan (33.7 ppmC; Decesari et al. 2005) and Baengnyeong Island (17 ppmC; Boris et al. 2016) in Korea and Mount Tai in China (~ 16 ppmC; Shen 2011), but much higher than the average values found in tropical mountain clouds affected by

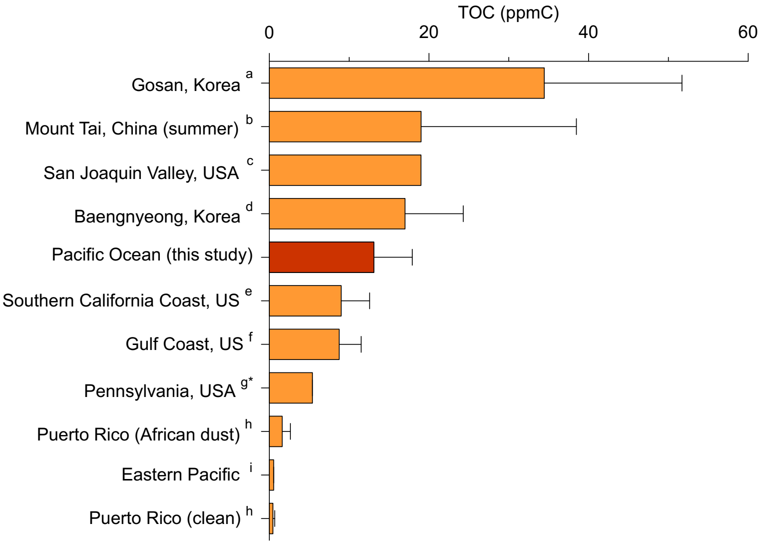

Fig. 2 TOC concentrations (ppmC) from sea fog observed in this study compared with other locations. The subscript from a to h indicated as follow; Decesari et al. (2005)[a], Shen (2011)[b], Collett et al. (1999)[c], Boris et al. (2016)[d], Boris et al. (2018)[e], Raja et al. (2008)[f], Straub et al. (2012)[g], Reyes-Rodríguez et al. (2009)[h], Straub et al. (2007)[j], * indicated the dissolved organic carbon (DOC) concentration

clean air masses from the Atlantic Ocean (0.45 ppmC; Reyes-Rodríguez et al. 2009) or in eastern Pacific stratocumulus clouds (Straub et al. 2007; Benedict et al. 2012). The SHIPPO cruise sea fog backward trajectories indicate that the relevant air masses originated not only from open marine areas but also from continental regions, suggesting significant influence by longer range transport from continental anthropogenic sources, especially biomass burning at the Tsugaru Strait (Choi et al. 2017).

The mean TOC concentrations in the rain collected in this study from the North and South Pacific Ocean were 0.58 and 0.83 ppmC, respectively, which are much lower than those in the sea fog due to smaller dilution of the collected particles and gases in cloud (Gioda et al. 2008). Iavorivska et al. (2016) reported TOC concentrations of 1.05 ppmC in rain from Australia/New Zealand, similar to values from the South Pacific in this study; however, reported TOC concentrations from the Pacific region (1.16 ppmC) are higher than those measured here in the North Pacific (average 0.58 ppmC); the measurement locations in the literature were closer to continental land masses and associated sources than the rain sampling locations in this study (see Fig. 3 in Iavorivska et al. 2016 and Fig. 1).

The sea fog TN concentrations, which averaged 3.1 ppm, were also higher than those in the rain (0.07 and 0.28 ppm). The mean rain TN concentration was similar to levels observed in Puerto Rico (0.27 ppm), New Guinea, and Costa Rica (0.2 ppm), but lower than those in other tropical montane regions influenced by human activity, such as concentrations of 0.6 and 0.9 ppm found in Colombia and Venezuela, respectively (Eklund et al. 1997; Gioda et al. 2008; Veneklaas 1990). The decreased N levels at less-impacted sites probably reflect minimal fire activity, low anthropogenic inputs, and clean air masses (Gioda et al. 2008). By the same token, the TN concentrations in the current study were lower over the North Pacific Ocean, which is further from continental Asian sources, than over the South Pacific Ocean.

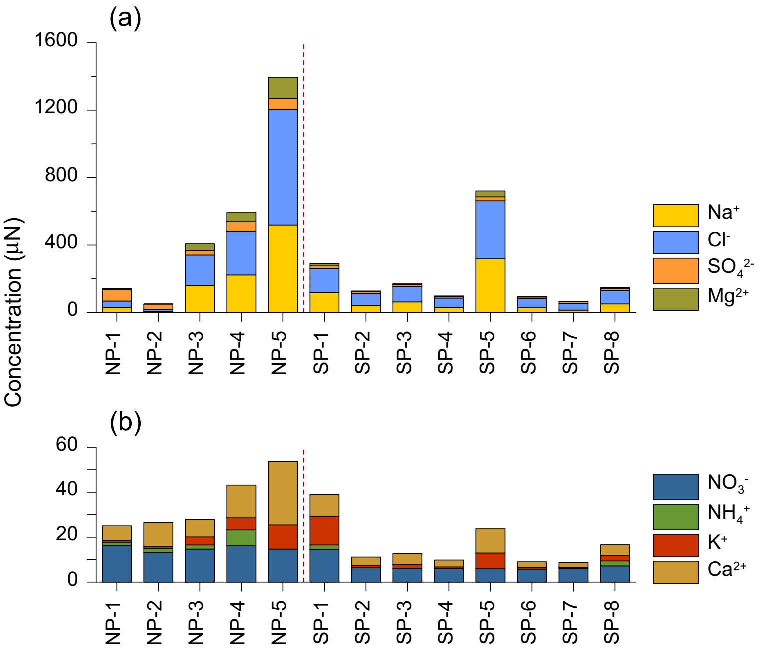

Fig. 3 The concentration of ionic component from rain collected in the North Pacific (NP) and South Pacific (SP) Ocean. Concentrations of trace species are enlarged in the lower panel

3.2 The pH of sea fog and rain in the Bering Sea

The sea fog and rain samples collected over the Bering Sea were acidic, with average pH values of 3.59 ± 0.24 (1σ) and 4.54 ± 0.54, respectively. Several acidic (e.g., HNO_3, HCl, and H_2SO_4) and basic (e.g., NH_3 and $CaCO_3$) compounds (Millet et al. 1996; Jung et al. 2013) contribute to sea fog and rain pH values. The sea fog pH was lower than the rain pH due to enhanced nss-SO_4^{2-} concentrations in the sea fog (see Table 1). The mean nss-Cl^- concentration in the rain from the North Pacific fell between the nss-SO_4^{2-} and NO_3^- concentrations, suggesting a potential importance of HCl in producing acidity (Table 1). It should be noted that the pH (4.3) calculated for the rain just from nss-Cl^-, nss-SO_4^{2-}, and NO_3^- concentrations in Table 1 was slightly lower than observed (4.54 on average), indicating 4.9% neutralization of the acidic compounds on average. The relatively low (< 1) NH_4^+/nss-Ca^{2+} and NH_4^+/nss-Mg^{2+} ratios suggest that nss-Ca^{2+} and nss-Mg^{2+} were the major contributors to rain acidity neutralization, as discussed earlier.

The nss-SO_4^{2-} was the dominant acidic species in the sea fog measured in the SHIPPO North Pacific cruise (Table 1). Previous studies reported higher NO_3^-/nss-SO_4^{2-} mole equivalent ratios (0.57 and 0.54) and higher pH values (4.12 and 4.00) in similar Pacific Ocean sea fog observations (Sasakawa and Uematsu 2002, 2005; Jung et al. 2013) (Table 3). The lower NO_3^-/nss-SO_4^{2-} ratio in our study indicates a larger nss-SO_4^{2-} contribution to the decreased sea fog pH (3.59). Higher sea fog nss-SO_4^{2-} concentrations, in comparison to rain, may have derived from marine biological activity (Sasakawa and Uematsu 2002), as the mean concentrations of methanesulfonic acid (MSA) and nss-SO_4^{2-} are generally higher in sea fog than in rain (Jung et al. 2013). Choi et al. (2017) reported higher MSA concentrations, using a High Resolution Time of Flight Aerosol Mass Spectrometer (AMS), on the same SHIPPO North

Table 3 Mean pH values and mean concentrations of ionic components (μN) in rain and sea fog reported in this study and referenced data for comparison

	Region	Periods	pH	nss-SO_4^{2-}	NO_3^-	NH_4^+	nss-Ca^{2+}	Na^+	Cl^-
Rain	North Pacific[a]	2012	4.5	27	15	2.5	9.5	187	235
	South Pacific	2014	-	4.3	7.3	0.6	3.4	83	110
	Reihoku-shiki, Japan[b]	1996–2003	-	30	13	14	8.5	77	91
	Rishiri, Japan	2000–2007	-	34	-	-	-	192	-
	Hedo, Japan	2000–2007	-	16	-	-	-	399	-
	Western North Pacific Ocean[c]	2008	4.1	5.5	7.9	25	380	580	1100
	Puerto Rico[d]	2004–2007	5.3	24*	5.4	3.7	14*	114	113
	Northwestern North Pacific[e]	1998	7.0	54	26	67	125	-	-
	Sea of Okhotsk		7.1	60	6.8	6.1	191	-	-
	Sea of Japan		7.2	45	40	29	279	-	-
	South Pacific[f]	2009	6.2	-	1.0	9.7	-	-	-
Sea fog	North Pacific[a]	2012	3.6	380	36	129	44	134	104
	Western North Pacific Ocean[c]	2008	4.2	72	50	22	4.6	390	400
	Puerto Rico[d]	2004–2007	5.5	83	29	20	69	418	433
	Northwestern North Pacific[e]	1998	4.2	82	25	25	28	-	-
	Sea of Okhotsk		3.0	1000	42	45	6.7	-	-
	Sea of Japan		2.8	870	1400	340	15	-	-

The subscript from a to h indicated as follow; [a] This study, [b] Toyonaga and Zhang (2017), [c] Jung et al. (2013), [d] Gioda et al. (2011), [e] Sasakawa and Uematsu (2002), [f] Jung et al. (2011). * indicated the total ion concentration

Pacific cruise in regions where sea fog was sampled. Several pathways can be important in the aqueous oxidation of dissolved sulfur dioxide to sulfate, including mechanisms involving organic radicals, H_2O_2, O_3, and O_2 (catalyzed by trace metals). Oxidation rates for each of the three pathways were not calculated, as the required oxidant analyses were not performed during the sea fog observations in this study. Under alkaline environments, in which ozone is an important aqueous S(IV) oxidant, variations in pH within the droplet population can result in faster sulfate production rates than expected based on average fog droplet properties (Collett et al. 1994; Benedict et al. 2012). However, in this region, which featured acidic conditions and sea fog pH values as low as 3.5, H_2O_2 oxidation is assumed to be the dominant sulfate oxidation pathway (Benedict et al. 2012; Shen et al. 2012).

3.3 The chemical characteristics of rain collected during the cruise

The chemical composition of the collected rain varied distinctly over the ship track (Fig. 3). The mean concentrations of Na^+ and Cl^- in the rain in the North Pacific were 2.3 times and 2.1 times higher than those in the South Pacific, respectively (Table 1). Higher wind speeds occurred over the North Pacific (9.1 ± 2.3 m/s) than the South Pacific (7.0 ± 3.0 m/s); aerosol sea-salt concentrations in the air are generally increased under high wind speeds (Parungo et al. 1986; Jung et al. 2011) due to increased surface roughness and attendant sea spray generation. Total ion concentrations increased dramatically as the ship approached Alaska on the North Pacific cruise, due to a combination of sea salt (Na^+ and Cl^-) and crustal ion components (Ca^{2+} and Mg^{2+}); the latter, among other minor components, indicates increasing continental influence.

NO_3^- and NH_4^+ concentrations, interestingly, did not vary significantly over either the North or South Pacific Ocean cruise tracks. In the North Pacific Ocean, the mean concentrations of NO_3^- and NH_4^+ were 15.0 ± 1.3 μN (13.2–16.3 μN) and 2.5 ± 2.7 μN (1.5–7.1 μN), respectively. Jung et al. (2011) reported lower mean concentrations of NO_3^-, at 7.8 μN (1.2–18 μN), and higher NH_4^+ concentrations, at 25 μN (4.1–55 μN), in the subarctic western North Pacific (Table 3). Moreover, the mean NO_3^- and NH_4^+ concentrations were 2.1 times and 4.4 times higher in the North Pacific Ocean than in the South Pacific Ocean, respectively, where NO_3^- concentrations ranged from 5.8 to 14.6 μN and NH_4^+ concentrations from 0.3 to 2.3 μN (see Table 1). Typically, the inorganic N concentration in rain varies with location, regional natural and/or anthropogenic emissions, meteorological conditions and biogenic gases (including DMS and NH_3) which are emitted from biological activity in open-ocean biota (Parungo et al. 1986) and sea bird colonies (Paulot et al. 2015). Therefore, it is not surprising that the fractional contributions of NO_3^- and NH_4^+ to total inorganic N in this study differ from those in Jung et al. (2011), the differences with this study probably reflect the more pronounced influence of terrestrial and/or local anthropogenic sources of NO_3^- due to transport above the marine boundary layer. Moreover, NH_4^+ in this study may also have derived from continental sources than biogenic sources. This tendency is more pronounced in the North Pacific Ocean where the backward trajectories were mainly passed through the continental region (see Fig. 1).

4 Summary and conclusions

During two research cruises, the R/V ARAON ice breaker ship collected sea fog and rain while cruising over the North Pacific and western South Pacific Ocean in 2012 and 2014, respectively. The nss-SO_4^{2-} concentrations were much higher in the sea fog than in the rain. Due to depletion of Cl^- via volatilization of HCl from sea salt particles, the ratio of Cl^-/Na^+ was slightly lower in the sea fog than in the sea water. The ratio of NH_4^+/nss-Ca^{2+} was lower in the rain than in the sea fog, indicating the influence of mineral dust particle scavenging (e.g., $CaCO_3$) at altitudes above the sea fog layer; associated transport of HCl and K^+ from fossil fuel combustion and/or biomass burning and Mg^{2+} and ca.$^{2+}$ from continental crustal sources also appeared to have influenced the rain composition. TOC concentrations in the collected sea fog varied widely; the mean TOC concentration of the fog samples in this study was 13.2 ± 5.0 ppmC, lower than that observed at polluted marine sites in Korea and China, but much higher than that measured in cleaner air masses over the Atlantic Ocean and eastern Pacific. Rain from the North and South Pacific Ocean contained the average TOC concentrations of 0.58 ± 0.28 and 0.83 ± 0.30 ppmC, respectively. The rain TOC over the South Pacific Ocean is similar to values measured in Australia/New Zealand; however, those in the North Pacific Ocean were lower than TOC values reported elsewhere in the Pacific region, likely due to differences in proximity to continents. TN concentrations were higher in the sea fog than in the rain, for which the TN concentration range was similar to those measured in previous studies.

The average sea fog pH (3.59 ± 0.24) was lower than that in the rain (4.54 ± 0.54) due to higher fog water nss-SO_4^{2-} concentrations, which are likely to be derived largely from marine biological activity and H_2O_2 aqueous oxidation of SO_2. For the rain, the relatively low NH_4^+/nss-Ca^{2+} and NH_4^+/nss-Mg^{2+} ratios suggest that nss-Ca^{2+} and nss-Mg^{2+} were the dominant contributors to the neutralization of rain acidity. The mean concentrations of Na^+ and Cl^- in the rain in the North Pacific were 2.3 times and 2.1 times higher than those in the South Pacific, respectively, likely due to higher wind speeds in the North Pacific that increased sea spray aerosol generation. The mean concentrations of NO_3^- and NH_4^+ in the North Pacific Ocean were 15.0 ± 1.3 μN (13.2 to 16.3 μN) and 2.46 ± 2.70 μN (1.5 to 7.1 μN), respectively, the inverse of the relative contribution patterns seen in prior work. This difference may stem from a pronounced influence of terrestrial and/or local anthropogenic NO_3^- sources and less abundant local emissions of NH_4^+ from open-ocean biological activity, which produces DMS and NH_3. The sea fog and rain chemical properties measured during these and other research cruises enhance our understanding of wet deposition and cloud condensation nuclei processing and sources in remote marine areas in the North and South Pacific Ocean.

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