

**STUDY ON THE CHLORINE LOSS AND RICH IN
MARINE ATMOSPHERIC AEROSOLS
—RESULTS OF INVESTIGATION DURING THE CRUISE OF BOSEI-MARU—**

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1. INTRODUCTION

On a global basis, sea salt aerosol, produced from action of wind on sea surface, plays an important role in climate and atmospheric chemistry, because of its larger emission than all other natural and anthropogenic emissions together with the total flux being 3,300Tg/y in 2000 [1]. Chlorine loss is known as a major emission mechanism of chlorine species in atmospheric air [2]. The sea salt particles react with atmospheric gaseous substances such as SO₂, H₂SO₄ and HNO₃, and subsequently degas volatile HCl with formation of sulfates and nitrates [eg.3,4]. Reaction between O₃ and aqueous sea salt is alternative pathway of chlorine loss and release photochemically active Cl₂ in the air [5,6]. Newly formed sea-salt particles are transported to land where they chemically interact with air pollutants and influence the urban air quality. Conversely, air pollutants originated from anthropogenic emission sources disperse into the marine boundary layer and undergo chemical reaction with sea salt particles. Therefore, Cl/Na ratio in aerosol samples is a good indicator for the interaction between sea salt particles and urban air pollutants. Authors have conducted monitoring of marine atmospheric aerosol components in the Pacific Ocean, focusing on a change in Cl/Na ratio with air trajectory, chemistry with acid pollutants, local climate and so on, and found complicated atmospheric chemistry including chlorine loss and rich, as described below.

2. EXPERIMENTAL

2-1 Sampling methods

Marine atmospheric aerosol and gaseous samples were collected during the Pacific Ocean cruises of Tokai University education and research vessel, Bosei-maru between Shimizu, Japan and Brisbane, Australia from 15 February to 31 March, 2002 (Fig.1a) and between Shimizu, Japan and Papeete, Tahiti from 15 February to 31 March, 2003 (Fig.1b). Aerosol samples were collected using a low volume air sampler (Shibata SIP-32L) on a sheet of quartz fiber filter (Whatman QM-A, 47mmφ) for 24hours at a flow rate of 22-26L/min. The sample

inlet was set on radar mast, approximately 20 meters above deck and connected with silicone tube to the pump put in a deck cabin. Passive samplers, which employed sodium nitrite coated filter [7], was collocated near the sample inlet for the collection of ozone (O_3) with 24hours exposure to the air. Number of samples collected was 27 in 2002 and 25 in 2003. Samples apparently contaminated by a refuse incineration inside the vessel were eliminated before analysis.

2-2 Analytical methods

Water soluble components were extracted with 15 ml of ion-exchanged distilled water (DIW) by shaking for 2hours. The residue was washed by 10 ml of DIW for 30 min and the solution was added. The final solution was made up to 25 ml after filtration. Anionic components (F^- , Cl^- , NO_3^- , SO_4^{2-}) were determined by ion chromatography (Yokogawa Analytical Systems, IC200). Cationic components (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) were analyzed by atomic absorption spectrophotometer (Hitachi, Z-5300) with air-acetylene flame. Nitrate, produced from nitrite in the presence of O_3 , was extracted with 10ml of DIW and analyzed by ion chromatography for the determination of O_3 collected on the trapping filter of the passive sampler. Limit of detection was defined as 3 times the standard deviation of the blanks and resulted in $0.062\mu g/m^3$ (F^-), $0.061\mu g/m^3$ (Cl^-), $0.091\mu g/m^3$ (NO_3^-), $0.045\mu g/m^3$ (SO_4^{2-}), $0.082\mu g/m^3$ (Na^+), $0.0046\mu g/m^3$ (K^+), $0.0011\mu g/m^3$ (Ca^{2+}), $0.0042\mu g/m^3$ (Mg^{2+}) and 8ppb (O_3). Analytical error of Na/Cl ratio was 1 ± 0.01 (1.0% of RSD) for extracts from NaCl added filters ($n=5$). Back trajectory analysis was conducted to each sampling using National Oceanic and Atmospheric Administration (NOAA) HYSPLIT Model Ver.4.

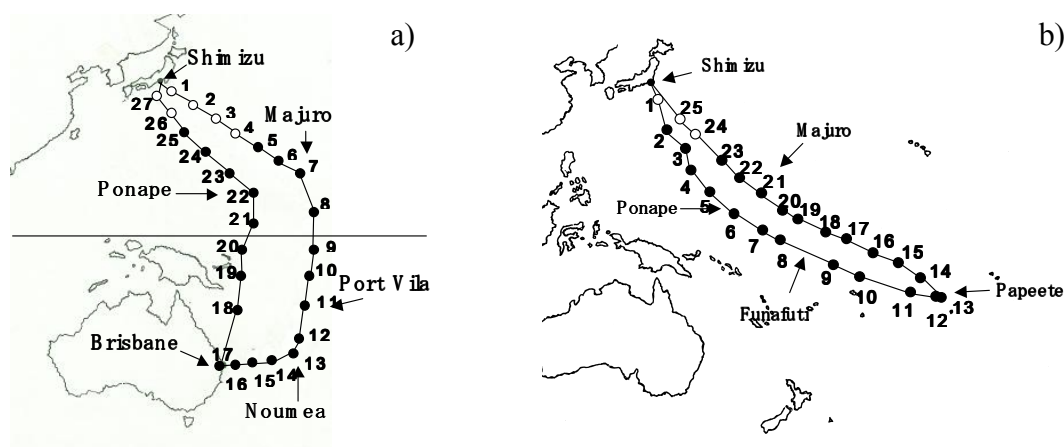


Fig.1 Sampling points of marine atmospheric air during the Pacific Ocean cruises of Tokai University education and research vessel, Bosei-maru (a) 15 Feb.-31 Mar., 2002, b) 15 Feb.-31 Mar., 2003). ● collection when air trajectory came from ocean, ○ collection when air trajectory came from land

3. RESULTS AND DISCUSSION

Mean atmospheric concentration of total suspended particles (TSP) was $25\mu\text{g}/\text{m}^3$ during the Pacific Ocean cruises in 2002 and 2003 with higher contents of Na^+ and Cl^- . Atmospheric mass concentrations of sea salt particles, sea salt sulfate(ss-SO_4^{2-}) and non sea salt sulfate (nss-SO_4^{2-}) were calculated from sea water composition considering that all the Na^+ in the aerosol is exclusively originated from sea salt spray. The mean concentration of sea salt particles resulted in $9.2\mu\text{g}/\text{m}^3$, contributing 30% of TSP. The contribution was approximately 2 times greater than that in coastal site in Japan. NO_3^- and SO_4^{2-} were significantly found as major components in the marine aerosol samples. According to calculations of eqs.(1) and (2) [8], 65% of sulfate originated from non sea salt sources such as marine biological activities, anthropogenic sulfur oxides transported from the land.

$$\text{Na}^+ \times 0.251 = \text{ss-SO}_4^{2-} \quad (1)$$

$$\text{total-SO}_4^{2-} - \text{ss-SO}_4^{2-} = \text{nss-SO}_4^{2-} \quad (2)$$

Figures 3 shows variation of Cl^-/Na^+ ratio in the marine atmospheric aerosol samples collected during the Pacific Ocean cruises. There was obvious volatilization of chlorine in the samples collected at offshore Japan, close to the land, when air trajectories came from eastern Asian continent and/or Japan Islands with lower Cl^-/Na^+ mole ratio than that in sea water (1.13). The Cl^-/Na^+ ratio decreased with an increase of nss-SO_4^{2-} concentration. Therefore, the chlorine loss was predominately caused by sulfur compounds following previous reactions.

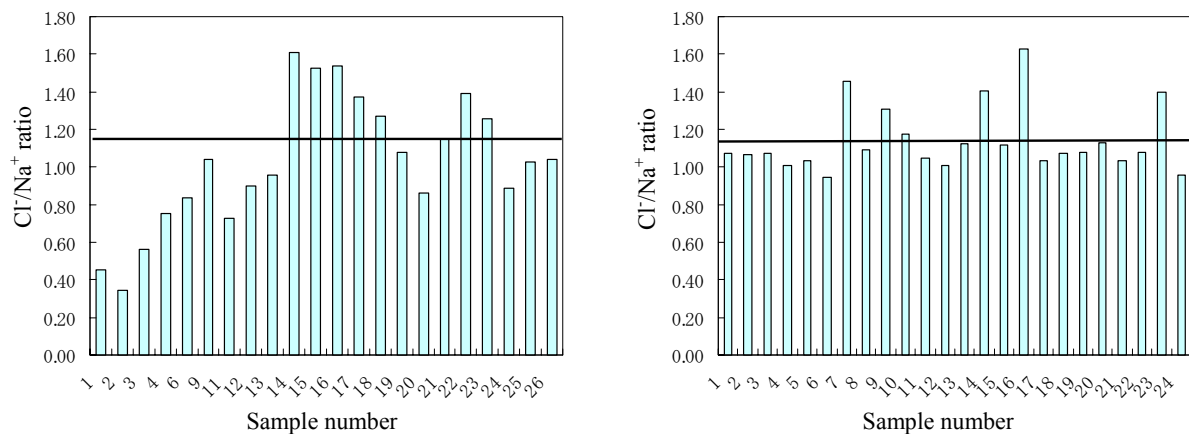


Fig.2 Variation of Cl^-/Na^+ ratio in the marine atmospheric aerosol samples collected during the Pacific Ocean cruises (a) 15 Feb.-31 Mar., 2002, b) 15 Feb.-31 Mar., 2003).

Possible contribution of ozone on the chlorine loss was also suggested in this monitoring. Figure 3 shows relationship between O_3 and $nss-SO_4^{2-}$ concentrations in marine atmosphere. Since the concentrations of $nss-SO_4^{2-}$ tended to increase with increase in the O_3 concentrations, Cl^-/Na^+ ratio decreased in high O_3 concentration regions (Figure 4). Atmospheric ozone should be considered as a potential cause of volatilization of chlorine because of its oxidizing activity of sulfur compounds and releasing potential of Cl_2 from aqueous sea salt aerosol initiated by photolysis of O_3 [5,6].

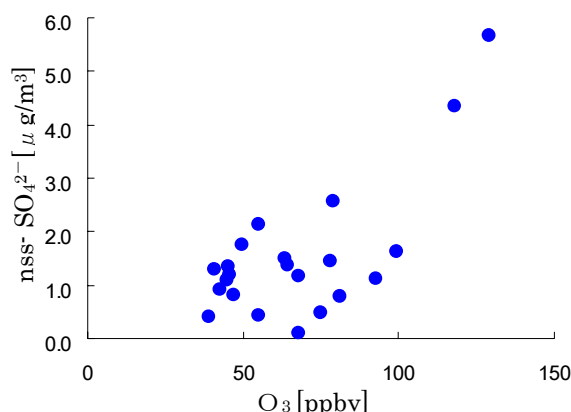


Fig.3 Relationship between atmospheric concentrations of $nss-SO_4^{2-}$ and O_3 concentration collected during the Pacific Ocean cruises of Bosei-maru (2003).

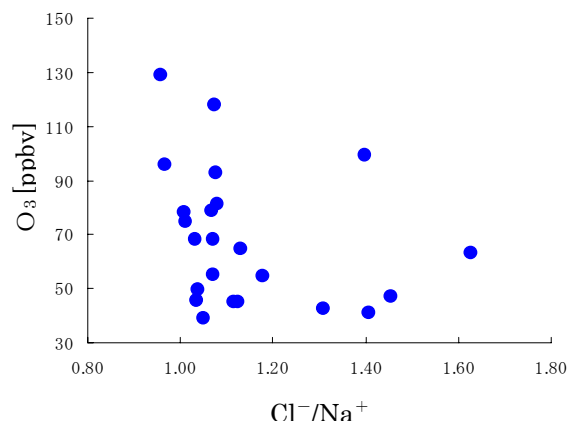


Fig.4 Relationship between atmospheric concentrations of O_3 and Cl^-/Na^+ ratio collected during the Pacific Ocean cruises of Bosei-maru (2003).

On the other hand, we found larger Cl^-/Na^+ ratio than that of sea water, which means enrichment of Chlorine, in several aerosol samples: 7 in 2002 and 6 in 2003. Excess amounts of Cl against sea water composition resulted in the range of 0.1-1.2 μmol per daily sample. Gabriel *et al.* [9] have reported an enrichment of bromide in marine aerosols affected by air masses having additional pollution-derived Br from organo-halogen additives in petrol. However, our results should be discriminated from Gabriel's cases, because most of samples had less influence of continental air pollutants according to air trajectories estimated by the on-line model and the crew had never released stuffs relating their life and ship maintenance outside the vessel. Then, we have to find the reason in the chemistry of sea salt particles.

Firstly, we thought the chlorine loss and rich were competitive. As can be seen in Figure 5, all of the chlorine enriched samples was observed when atmospheric concentrations of sea salt particles were low due to calm sea surface. Because the

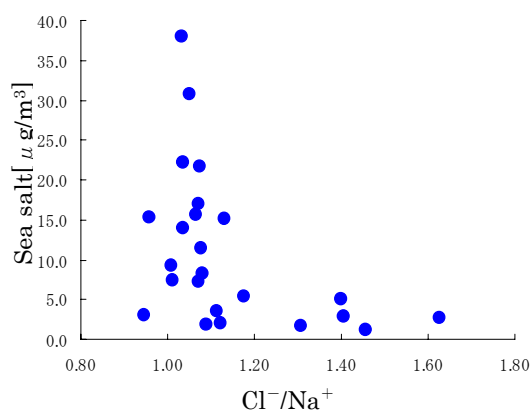


Fig.5 Relationship between atmospheric concentrations of sea salt and Cl^-/Na^+ ratio collected during the Pacific Ocean cruises of Bosei-maru (2003).

volatilization reaction of chlorine by H_2SO_4 is second order in NaCl , as noted in reaction (4), chlorine loss rate increases dramatically with Na^+ concentration. In figure 6, horizontal axis shows the volatilization rate of HCl expressed by a products of $[\text{Na}^+]^2$ and $[\text{nss-SO}_4^{2-}]$. It should be emphasized that the enrichment of chlorine can be found with relatively low volatilization rates. This leads us to have a look at weather condition during the samplings. Figure 7, showing a relationship between Cl^-/Na^+ ratio and irradiation intensity in the 2003 monitoring, suggests the enrichment of chlorine requires photo-induced reactions.

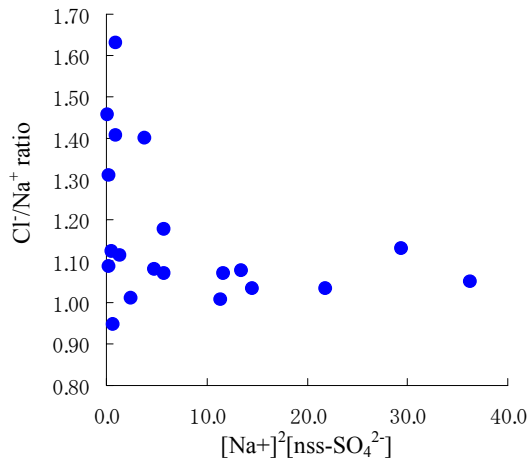


Fig.6 Relationship between Cl^-/Na^+ ratio and $[\text{Na}^+]^2[\text{nss-SO}_4^{2-}]$ collected during the Pacific Ocean cruises of Bosei-maru (2003).

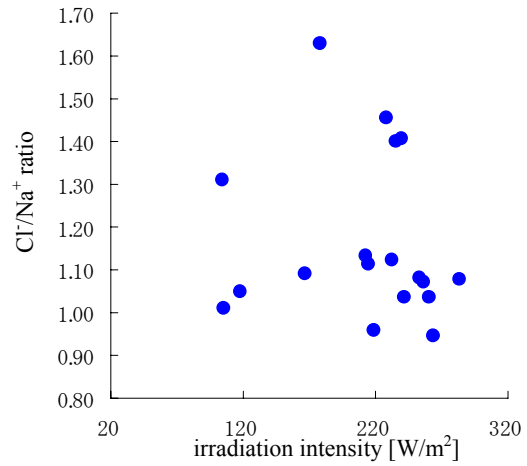


Fig.7 Relationship between Cl^-/Na^+ ratio and amount of insolation collected during the Pacific Ocean cruises of Bosei-maru (2003).

Then, the influence of Cl_2 generated from the aqueous sea salt particle was considered. Photolysis of O_3 produces OH radical which triggers release of Cl_2 from newly formed sea salt aerosols at their deliquescence point [5]. Enrichment of chlorine could be observed, if the Cl_2 molecules, having lower deposition rate than residual particles, were trapped on the filter with sea salt particles which survived from chlorine loss due to its lower concentration. Then, we estimated possible contamination of 330 ppt per day of Cl_2 , proposed by Spicer et al.[6], to assess the excess collection amount of Cl^- in each chlorine enriched aerosol sample by equation (5);

$$C = \frac{273 \times 2 \times 0.33 \times V}{22.4 \times (273 + t)} \quad (5)$$

where C is the estimated excess chlorine in μmol as Cl from 0.33ppb of Cl_2 , V is total sampling volume by the air sampler [m^3], t is average temperature at the sampling [$^\circ\text{C}$]. Table 1 shows comparison of the excess amount of Cl atoms in the marine aerosol samples between observed, C_0 and estimated, C . The observed excess amounts of Cl were equivalent

to ones originated from Cl_2 produced by ozone and aqueous sea salt particles. This result possibly shows justification of the hypothetical mechanism of chlorine rich mentioned above. However, a pathway from Cl_2 to Cl^- in final aerosol samples and fate of Na^+ attacked by radicals should be revealed in order to prove the hypothesis.

Table 1 Comparison of the excess amount of Cl species in the marine aerosol samples between observed, C_o and estimated, C .

2002			2003		
No	C_o [μmol]	C [μmol]	No	C_o [μmol]	C [μmol]
14	0.6	1.01	7	0.16	0.85
15	0.9	0.99	9	0.12	0.83
16	0.48	1.21	10	0.11	0.84
17	1.1	0.78	14	0.32	0.82
18	1.0	0.94	16	0.54	0.84
22	1.2	0.87	23	0.59	0.87
23	0.53	1.01			

4. CONCLUDING REMARKS

Chlorine loss and rich were found in marine atmospheric aerosol samples collected during the Pacific Ocean cruises in 2002 and 2003. We have considered a role of ozone in both chemistries, especially in the enrichment of chlorine as a trigger of generation of Cl_2 from aqueous sea salt particles. Although mechanism of the chlorine rich is not unknown, simple estimation showed possible contamination of Cl_2 in the chlorine enriched aerosol samples.

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REFERENCES

- [1] Intergovernmental Panel on Climate Change (IPCC), *Climate Change 2001-The Scientific Basis.*, edited by J. T. Houghton et al., pp.289-348, Cambridge Univ. Press, New York(2001)
- [2] Möller,D., *Tellus. Ser.B.*, 42, 254-262(1990) [3] Martens, C.S., Wesolowski, J.J., Harris,R.C., Karfer,R., *J. Geophys. Res.*, 78, 8778-8792(1973) [4] Pio,C.A., Lopes,D.A., *J. Geophys. Res.*, 103(D19), 25263-25272(1998) [5] Oum,K.W., Lakin,M.J., Dehean,D.O., Brauers,T., and Finlayson-Pitts,B.J., *Science.*, 279, 74-77(1998) [6] Spicer,C.W., Chapman,E.G., Finlayson-Pitts,B.J., Plastringe,R.A., Plastringe,R.A., Hubbe,J.M., Fast,J.D., and Berkowitz,C.M., *Nature.*, 394, 353-356(1998) [7] Koutrakis,P., Wolfson,J.M., Bunyaviroch,A., Froehlich,S.E., Hirano,K., Mulik,J., *Anal. Chem.*, 65, 209-214(1993) [8] Ohta,S., and Okita,T., *Atmos. Environ.*, 24A(4), 823-828 (1990) [9] Gabriel,R., von Glasow, R., Sander,R., Andrea,M.O. and Crutzen,P.J., *J. Geophys. Res.*, 107(D19), INX2/31/1-9(2002)