

# STUDY ON THE CHLORINE LOSS AND RICH IN MARINE ATMOSPHERIC AEROSOLS

( 海洋大気エアロゾルの塩素損失及び濃縮に関する研究 )

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## 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<sup>1)</sup>. Chlorine loss is known as a major emission mechanism of chlorine species in atmospheric air<sup>2)</sup>. The sea salt particles react with atmospheric gaseous substances such as SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, and subsequently degas volatile HCl with formation of sulfates and nitrates<sup>3,4)</sup>. Reaction between O<sub>3</sub> and aqueous sea salt is alternative pathway of chlorine loss and release photochemically active Cl<sub>2</sub> in the air<sup>5,6)</sup>. 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.

## Experimental

**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 and between Shimizu, Japan and Papeete, Tahiti from 15 February to 31 March, 2003 (Fig.1). 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<sup>7)</sup>, was collocated near the sample inlet for the collection of ozone (O<sub>3</sub>) 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.

**Analytical methods:** Anionic components (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) were determined by ion chromatography (Yokogawa, IC200). Cationic components (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) were analyzed by atomic absorption spectrophotometer (Hitachi, Z-5300) with air-acetylene flame. Nitrate, produced from nitrite in the presence of O<sub>3</sub>, was analyzed by ion chromatography for the determination of O<sub>3</sub> collected on the trapping filter of the passive sampler. Analytical error of Na/Cl ratio was 1.0±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.

**Results and Discussion:** Mean atmospheric concentration of total suspended particles (TSP) was 25µg/m<sup>3</sup> during the Pacific Ocean cruises in 2003 with higher contents of Na<sup>+</sup> and Cl<sup>-</sup>. The mean concentration of sea salt

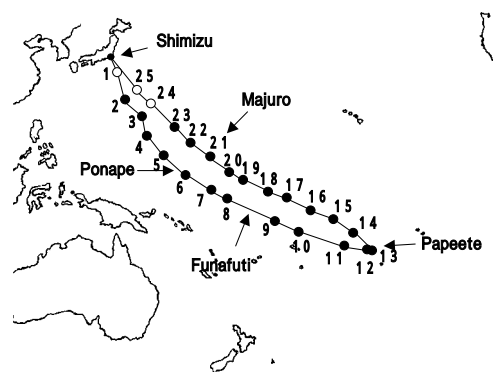


Fig.1 Sampling points of marine atmospheric air during the Pacific Ocean cruises of Tokai University education and research vessel, Bosei-maru (15 Feb.-31 Mar., 2003).

collection when air trajectory came from ocean, collection when air trajectory came from land

particles resulted in  $9.2\mu\text{g}/\text{m}^3$ , contributing 30% of TSP.  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were significantly found as major components in the marine aerosol samples. 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  $\text{Cl}/\text{Na}^+$  mole ratio than that in sea water (1.13). The  $\text{Cl}/\text{Na}^+$  ratio decreased with an increase of  $\text{nss-SO}_4^{2-}$  concentration. Therefore, the chlorine loss was predominately caused by sulfur compounds following previous reactions. Possible contribution of ozone on the chlorine loss was also suggested in this monitoring. Figure.2 shows relationship between  $\text{O}_3$  and  $\text{nss-SO}_4^{2-}$  concentrations in marine atmosphere. 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  $\text{Cl}_2$  from aqueous sea salt aerosol initiated by photolysis of  $\text{O}_3$ <sup>5,6</sup>. On the other hand, we found larger  $\text{Cl}/\text{Na}^+$  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 $\mu\text{mol}$  per daily sample. As can be seen in Figure 3, all of the chlorine enriched samples was observed when atmospheric concentrations of sea salt particles were low due to calm sea surface. This leads us to have a look at weather condition during the samplings. Figure 4, showing a relationship between  $\text{Cl}/\text{Na}^+$  ratio and irradiation intensity in the 2003 monitoring, suggests the enrichment of chlorine requires photo-induced reactions. Then, the influence of  $\text{Cl}_2$  generated from the aqueous sea salt particle was considered. Photolysis of  $\text{O}_3$  produces OH radical which triggers release of  $\text{Cl}_2$  from newly formed sea salt aerosols at their deliquescence point<sup>5</sup>. Enrichment of chlorine could be observed, if the  $\text{Cl}_2$  molecules, having lower deposition rate than residual particles, were trapped on the filter with sea salt particles that survived from chlorine loss due to its lower concentration. Then, we estimated possible contamination of 330 ppt per day of  $\text{Cl}_2$ <sup>6</sup>, to assess the excess collection amount of Cl in each chlorine enriched aerosol sample. The observed excess amounts of Cl were equivalent to ones originated from  $\text{Cl}_2$  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  $\text{Cl}_2$  to Cl in final aerosol samples and fate of  $\text{Na}^+$  attacked by radicals should be revealed in order to prove the hypothesis.

**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  $\text{Cl}_2$  from aqueous sea salt particles. Although mechanism of the chlorine rich is unknown, simple estimation showed possible contamination of  $\text{Cl}_2$  in the chlorine enriched aerosol samples.

**Acknowledgement and Reference:** Authors awfully thank Hiroaki MASUJIMA(JAMSTEC) and Pro.Morimasa TSUCHIYA(Tokai University) 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. *et al.*, *J. Geophys. Res.*, 78, 8778-8792(1973) 4) Pio,C.A. *et al.*, *J. Geophys. Res.*, 103(D19), 25263-25272(1998) 5) Oum,K.W. *et al.*, *Science.*, 279, 74-77(1998) 6) Spicer,C.W. *et al.*, *Nature.*, 394, 353-356(1998) 7) Koutrakis,P. *et al.*, *Anal. Chem.*, 65, 209-214(1993)

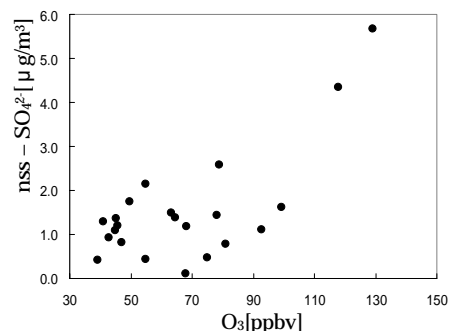


Fig.2 Relationship between atmospheric concentrations of  $\text{nss-SO}_4^{2-}$  and  $\text{O}_3$  concentration (2003)

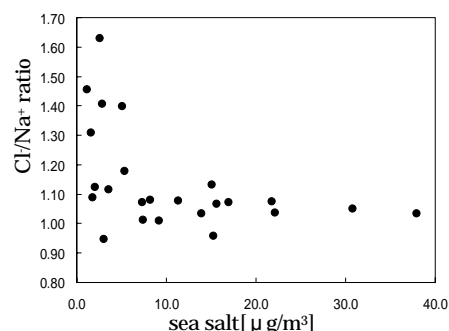


Fig.3 Relationship between atmospheric concentrations of sea salt and  $\text{Cl}/\text{Na}^+$  ratio (2003)

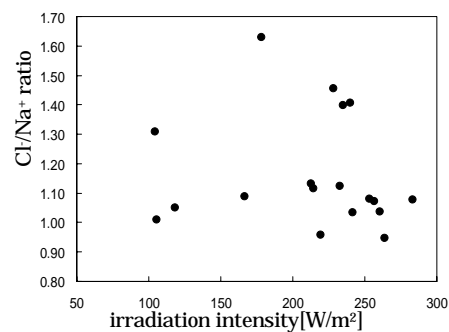


Fig.4 Relationship between  $\text{Cl}/\text{Na}^+$  ratio and amount of isolation (2003)