Study on Chlorine Loss of Atmospheric Sea Salt Particles in Coastal Area
（沿岸地域における大気中海塩粒子の塩素損失に関する研究）

3ASCM010　Akiyuki HIRANO
Supervisor　Prof. Yasuyuki MIURA
Dr. Yoshika SEKINE

1. Introduction

Sea salt particles, produced by the burst of bubble and the action of wind on the sea surface, play an important role in climate and atmospheric chemistry. Chlorine loss is known as a major emission source of chlorine species in atmospheric air. The particles react with atmospheric gaseous substances such as SO_2, H_2SO_4, HNO_3 and O_3, and subsequently degas volatile HCl and release photochemically active Cl_2 with formation of sulfates and nitrates [*e.g.* 1, 2]. Therefore, Cl/Na ratio in aerosol samples is a good indicator for the interaction between sea salt particles and air pollutants. On the other hand, Tervahattu *et al.* [3] recently provided experimental evidence using TOF-SIMS that some sea salt particles have a surface organic layer which is consistent with previously proposed theoretical models. This organic layer consists of non-volatile surfactants such as palmitic acids (C_{16}) and stearic acids (C_{18}), originated from the decomposition of marine organisms, mainly phytoplankton. While Cai and Griffin [4] have discussed the role of the organic layer on the formation of secondary organic aerosols, the effect on the chlorine loss has been still unknown. In this study, we have examined behavior of atmospheric sea salt particles in coastal sites in Kanagawa, Japan. Based on the results, the effect of coverage by fatty acids upon chlorine loss was investigated by laboratory experiments.

2. Experimental method

2.1. Air quality monitoring at coastal sites

Aerosol particles (Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, NO_3^- and SO_4^{2-}) and gaseous components (HCl, NO_2, SO_2 and HNO_3) in the atmosphere were collected at the roof of the school buildings of Tokai University, Shonan campus (TOKAI：35 ° 21’ 45” N, 139 ° 16’ 36”E) and Shonan Institute of Technology (SHONAN：35 ° 19’ 14”N, 139 ° 27’ 19”E). Samplings were intensively carried out in following periods: 20 May - 30 July, 2002 (TOKAI site), 15 October - 17 December 2002 (TOKAI site), 26 July - 26 August, 2003 (TOKAI and SHONAN sites) and 13 - 23 July, 2004 (SHONAN site), excluding rainy-day samplings. Sampling duration was set 24 hours for each sampling.

2.2. Effect of fatty acids upon chlorine loss

Firstly, 0.5mL of 2mM NaCl was dropped and impregnated on a cellulose fiber filter (Advantec, 51A, 47mmφ), and then dried in a vacuum desiccator. Secondly, 1mL of palmitic acid/methanol solution (0.1, 1 and 10mM) was added on the filter and dried. Based on the results in section 3, HNO_3 was used as a gaseous reactant. HNO_3 gas was generated from nitric acid solution kept at 25℃ with bubbling N_2. Air concentration of HNO_3 was controlled by dilution of nitric acid with water. The single prepared filter was set in a filter folder connected to the gas generator with silicone tubes. The gas was passed through the NaCl impregnated filter with and without palmitic acid, placed in a chamber at 30℃, at a flow rate 2.5L/min for 5 minutes. R.H. in the line was kept above the deliquescence point of NaCl (75%).

3. Result and Discussion

3.1. Chlorine loss phenomenon

At TOKAI site, mean atmospheric concentration of TSP was $25\mu g/m^3$ (Summer, 2002), $18\mu g/m^3$ (Winter, 2002) and $24\mu g/m^3$ (2003) and sea salt particles contributed 17%, 14% and 7.1% of mass of TSP, respectively. Chlorine loss was usually found in all season as the ratios of almost sample were lower than that of sea water (1.13) with about 90% of volatilization percentage in average. Although variation of Cl^-/Na^+ ratio was not correlated to those of NO_3^- and nss-SO_4^{2-} in aerosol samples, the ratio tended to decrease with an increase of atmospheric concentrations of HNO_3 as shown in Fig. 1. Thus, we concluded that HNO_3 was the acid responsible for most of the chlorine displacement from sea salt at this coastal area. At SHONAN site, mean TSP concentrations were $29\mu g/m^3$ (2003) and $19\mu g/m^3$ (2004) and contributions of sea salt particles were 41% and 23%, respectively. Such high percentages of sea salt reflect difference in distance from seashore between both sites. The relationship between Cl^-/Na^+ ratio and HNO_3 in SHONAN site tended to be similar to result of air quality monitoring at TOKAI site.

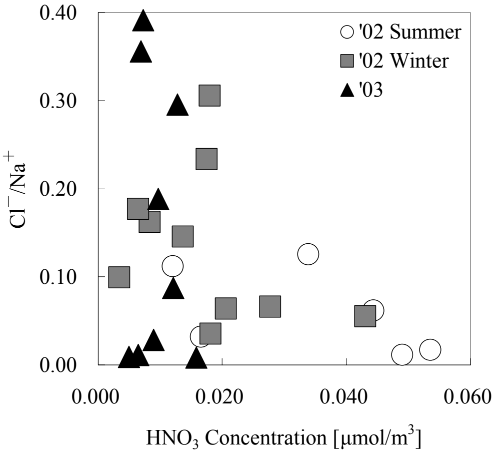

Fig. 1 Relationship between mole concentration ratios of Cl^- and Na^+ in aerosol samples and atmospheric concentrations of HNO_3 collected at TOKAI site.

3.2. Effect of fatty acids upon chlorine loss

Fig. 2 shows effect of addition of palmitic acid on the percentage of chlorine loss from NaCl impregnated filter. There found two apparent features. In a relatively low HNO_3/NaCl region, the chlorine loss percentage decreased with an increase of addition of palmitic acid. This means organic layer of palmitic acid prevents NaCl particles from being attacked by HNO_3 depending on the coverage rate. On the other hand, chlorine loss percentage of these covered samples proportionally increased with an increase in HNO_3/NaCl, even though it tended to become constant when NaCl was exclusively exposed to HNO_3 at a deliquescence point of NaCl. This suggests the presence of organic layer has a possible effect on the higher loss of chlorine (90%) in ambient air.

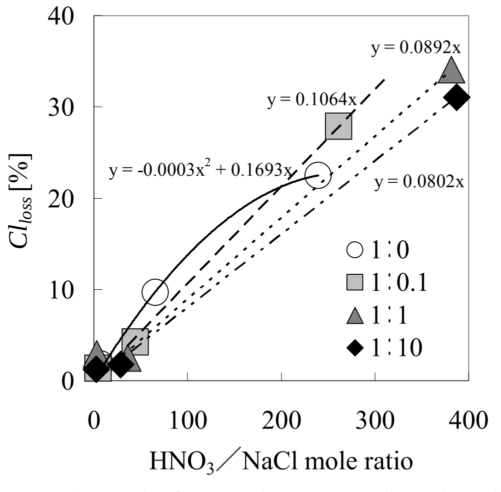

Fig. 2 Plots of Cl_{loss} against HNO_3/NaCl mole ratio. Legends show the proportion of NaCl to palmitic acid in mole.

Acknowledgement: Authors awfully thank Mr. Hiroo Nanba, Shonan Institute of technology and Mr. Junya Morita, Tokai University for their great helps in sampling site and analysis.

References: **[1]** Pio,C.A. and Lopes,D.A., *J.Geophys. Res.*, **103**(D19), 25263-25272(1998) **[2]** Oum,K.W. *et al.*, *Science*, **279**, 74-77(1998) **[3]** Tervahattu,H. *et al.*, *J.Geophys.Res.*, **107**(D16), ACH18.1-ACH18.7(2002) **[4]** Cai,X. and Griffin,R.J., *J.Geophys. Res.*, **108**(D15), AAC3.1-AAC3.14(2003)