

# EFFECT OF COVERAGE BY FATTY ACIDS UPON CHLORINE LOSS FROM ATMOSPHERIC SEA SALT PARTICLES

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## 1. Introduction

Sea salt particles, produced by 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 [1]. The particles react with atmospheric gaseous substances such as  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , and subsequently degas volatile  $\text{HCl}$  with formation of sulfates and nitrates [eg.2,3]. Reaction between  $\text{O}_3$  and aqueous sea salt is alternative pathway of chlorine loss and release photochemically active  $\text{Cl}_2$  in the air [4]. Newly formed sea-salt particles are transported to land where they chemically interact with urban air pollutants and influence the air quality of coastal sites. Conversely, the pollutants in coastal cities disperse into the marine boundary layer and undergo chemical reaction with sea salt particles[5]. Therefore,  $\text{Cl}/\text{Na}$  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.* [6] recently provided experimental evidence using time-of-flight secondary ion mass spectrometry (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 ( $\text{C}_{16}$ ) and stearic acids ( $\text{C}_{18}$ ), originated from the decomposition of marine organisms, mainly phytoplankton [7,8]. While Cai and Griffin [5] 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.

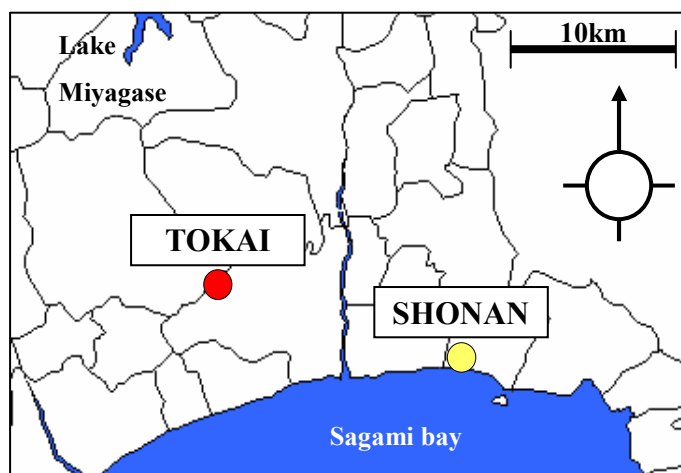
In this study, we have examined behavior of atmospheric sea salt particles in coastal sites in Kanagawa, Japan, and showed  $\text{HNO}_3$  was one of the dominant factors to the chlorine loss phenomena. Based on the results, the effect of coverage by fatty acids upon chlorine loss from a heterogeneous  $\text{NaCl}$  - $\text{HNO}_3$  reaction was investigated by laboratory experiments.

## 2. Experimental method

### 2.1. Air quality monitoring at coastal sites

Aerosol particles and gaseous components in the atmosphere were collected at the roof of the school buildings of Tokai University, Shonan campus (TOKAI :  $35^\circ 21' 45''$  N,  $139^\circ 16'$

36"E) and Shonan Institute of Technology (SHONAN : 35° 19' 14"N, 139° 27' 19"E). Figure 1 shows location of each site. Samplings were intensively carried out in following periods: 20 May – 30 July, 2002 (TOKAI site), 15 October – 17 December (TOKAI site), 2002 and 26 July – 26 August, 2003 (TOKAI and SHONAN sites),



excluding rainy-day samplings. Sampling duration was set 24 hours for each sampling. Figure 1. Sampling sites for the monitoring of coastal atmospheric contaminants (Shonan area, Kanagawa, Japan).

The aerosol samples were collected on quartz fiber filters (Whatman, QMA, 47mmφ) using low volume air sampler (Sibata, SIP-32L) at a flow rate of 28L/min for 24h duration. Sampling of HNO<sub>3</sub> and Cl<sub>2</sub> were made by absorbing into 1mM KOH-0.4mM NaHSO<sub>3</sub> solution in impinger, at 2.6L/min by electromagnetic air pump (Enomoto, MV-6005VP) for 24 hours. Passive samplers (Green Blue, HandySONOX) were deployed for the collection of HCl, NO<sub>2</sub> and SO<sub>2</sub>, using a triethanolamine impregnated filter as trapping media.

Water soluble anions in the aerosol samples were extracted into ion-exchanged deionized water and determined by Ion Chromatographic Analyzer (Yokogawa, IC200) with a Dionex, Ionpac AS9-HC separation column. Water soluble metal ions were determined by Polarized Zeeman Atomic Absorption Spectrophotometer (Hitachi, Z-5300). Gaseous components (HCl, NO<sub>2</sub>, SO<sub>2</sub>, HNO<sub>3</sub> and Cl<sub>2</sub>) were also determined by ion chromatography.

Atmospheric mass concentrations of sea salt particles, sea salt sulfate(ss-SO<sub>4</sub><sup>2-</sup>) and non sea salt sulfate (nss-SO<sub>4</sub><sup>2-</sup>) were calculated from sea water composition considering that the Na<sup>+</sup> in the aerosol is exclusively originated from sea salt spray.

## 2.2. Effect of fatty acids upon chlorine loss

Laboratory studies on the effect of organic layer upon chlorine loss from sea salt particles were carried out. Based on the results in section 3, HNO<sub>3</sub> was used as a gaseous reactant. According to the experimental results of Tervahattu *et al.*[6], sputtering in TOF-SIMS stripped palmitic acid which distributed on small particles and revealed the inner core of the sea-salt particles. Therefore, palmitic acid was employed for constructing the organic layer on NaCl dispersed on a cellulose fiber filter. The material was prepared stepwise as follows.

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. HNO<sub>3</sub> gas was generated from nitric acid solution kept at 25°C with bubbling N<sub>2</sub>. Air concentration of HNO<sub>3</sub> 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°C, at a flow rate 2.5L/min for 5 minutes. Relative humidity in the line was kept above the deliquescence point of NaCl (75%).

Breakthrough of HNO<sub>3</sub> and degassed Cl species were dissolved into 1mM KOH-0.4mM NaHSO<sub>3</sub> solution and determined by ion chromatography. Cl<sup>-</sup> residue and NO<sub>3</sub><sup>-</sup> fixed in the filters were extracted into ion-exchanged water and determined.

In this study, loss of chlorine from original NaCl was obtained as follows;

$$Cl \text{ loss}(\%) = \frac{Cl_V}{Cl_V + Cl_R} \times 100 \quad (1)$$

where  $Cl_V$  is amount of Cl (mol) volatilized from NaCl by HNO<sub>3</sub> and  $Cl_R$  is amount of Cl<sup>-</sup> (mol) found in the filter after HNO<sub>3</sub> gas exposure.

### 3. Result and Discussion

#### 3.1. Chlorine loss phenomenon

At Tokai site, mean atmospheric concentration of total suspended particles (TSP) was 22μg/m<sup>3</sup> in 2002 and sea salt particles contributed 15% of mass of TSP. Figure 2 shows mole concentration ratio of Cl<sup>-</sup>/Na<sup>+</sup> in the coastal aerosol samples. Chlorine loss is usually found in all season as the ratios of every sample were lower than that of sea water (1.13) with about

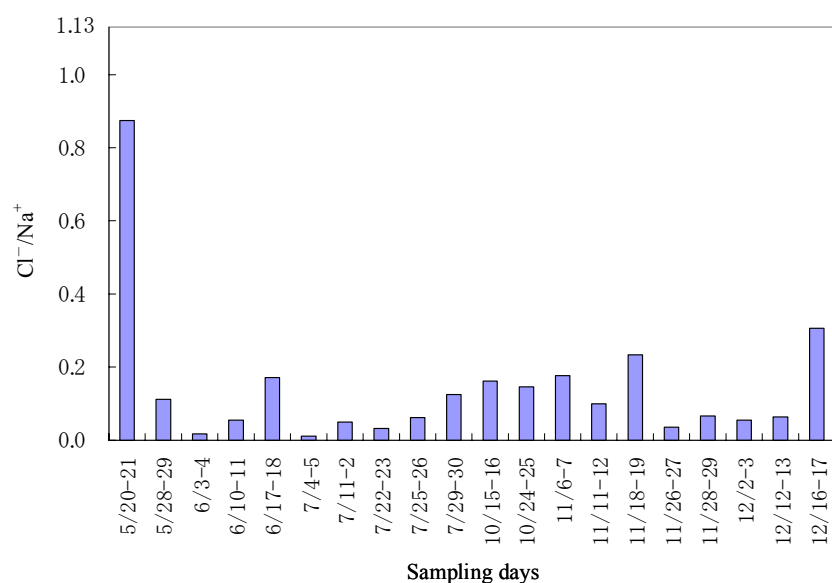


Figure 2. Variation of mole concentration ratios of Cl<sup>-</sup> and Na<sup>+</sup> in the coastal atmospheric aerosol samples collected at Shonan campus of Tokai University.

80% of volatilization percentage in average. Although variation of Cl<sup>-</sup>/Na<sup>+</sup> ratio was not correlated to those of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and nss-SO<sub>4</sub><sup>2-</sup> in aerosol samples, the ratio tended to decrease with an increase of atmospheric concentrations of HNO<sub>3</sub> as shown in Figure 3. Thus, we concluded that HNO<sub>3</sub> was the acid responsible for most of

the chlorine displacement from sea salt at this coastal area.

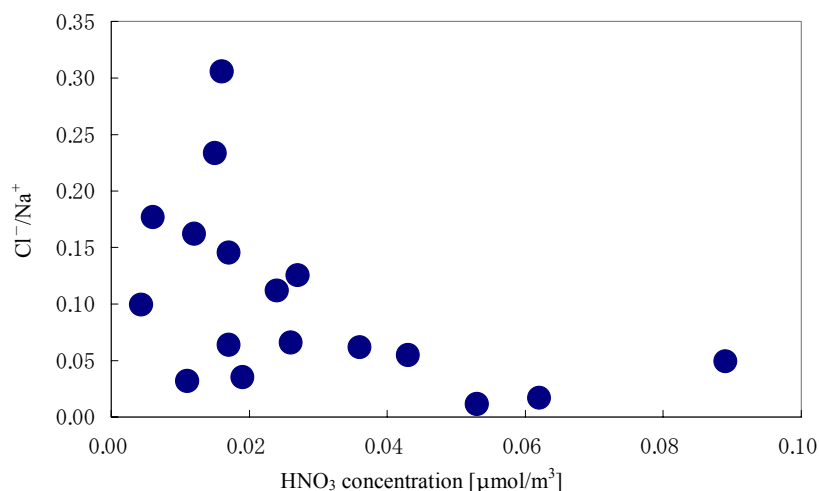


Figure 3. Relationship between mole concentration ratios of  $\text{Cl}^-$  and  $\text{Na}^+$  in aerosol samples and atmospheric concentrations of  $\text{HNO}_3$  collected at TOKAI and SHONAN.

### 3.2. Comparison of air quality

Figure 4 shows mean concentrations of ionic components in aerosol samples collected at TOKAI and SHONAN in summer 2003. Calculated atmospheric concentrations of sea salt particles were  $1.9\mu\text{g}/\text{m}^3$  (7.6% of TSP) at TOKAI and  $12\mu\text{g}/\text{m}^3$  (38%) at SHONAN. These reflect difference in distance from seashore between both sites. Chlorine loss percentages, calculated from concentrations of  $\text{Na}^+$ , resulted in 80% at TOKAI and 45% at SHONAN, respectively. Furthermore, concentrations of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  relative to those of  $\text{Na}^+$  were found higher in TOKAI samples. This suggests that volatilization of  $\text{Cl}^-$  occurs during

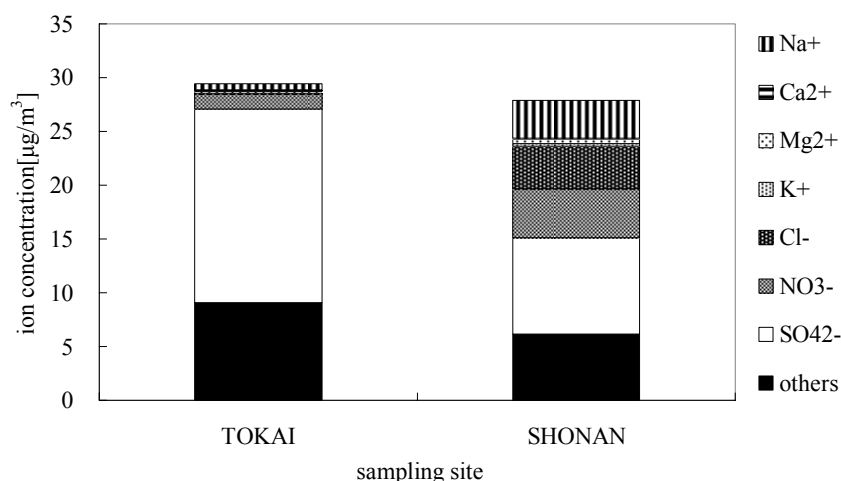


Figure 4. Comparison of atmospheric concentrations of water soluble ions collected at TOKAI (Tokai University) and SHONAN (Shonan Institute of Technology) (26 July – 26 August 2003,  $n=10$ ).

transport of air mass from seashore to inland, being attacked by acid pollutants with formation of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$ .

Back trajectory analysis was conducted for every sampling datum at each site. Air mass was typically transported from SHONAN to TOKAI during 28-29 July, 2003.

Then, both monitoring results on the days were singled out and compared in Figure 5. Lower concentrations of  $\text{Na}^+$  and  $\text{ss-SO}_4^{2-}$  originated from sea salt were found at Tokai site as expected. While apparent difference was not found in the concentrations of  $\text{NO}_2$ ,  $\text{SO}_2$  and  $\text{Cl}_2$ , concentrations of  $\text{HCl}$  and  $\text{HNO}_3$  in TOKAI were higher than those in SHONAN. These results suggest that  $\text{NaCl-HNO}_3$  reaction is the emission source of  $\text{HCl}$  in the local atmosphere, resulting in higher  $\text{NO}_3^-/\text{Na}^+$  ratio in the aerosol samples at TOKAI.

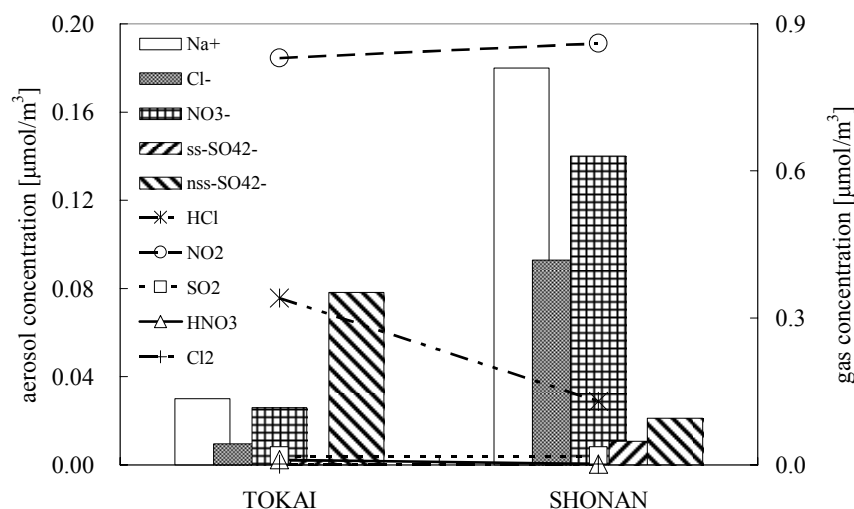


Figure 5. Comparison of concentrations of aerosols (water soluble ions) and gaseous substances, when air mass trajectories came from SHONAN to TOKAI (04:40 UTC 28 – 04:40 UTC 29 July 2003). Back trajectories were estimated by using HYSPLIT model Ver. 4, NOAA.

### 3.3. Effect of fatty acids upon chlorine loss

Figure 6 shows effect of addition of palmitic acid on the percentage of chlorine loss from  $\text{NaCl}$  impregnated filter. The horizontal axis shows ratio of total amount of  $\text{HNO}_3$  (mol) exposed to the filter and amount of  $\text{NaCl}$  (mol) supported in the filter. According to SEM images, mean particle size of  $\text{NaCl}$  was  $0.27\mu\text{m}$ . There found two apparent features. In a

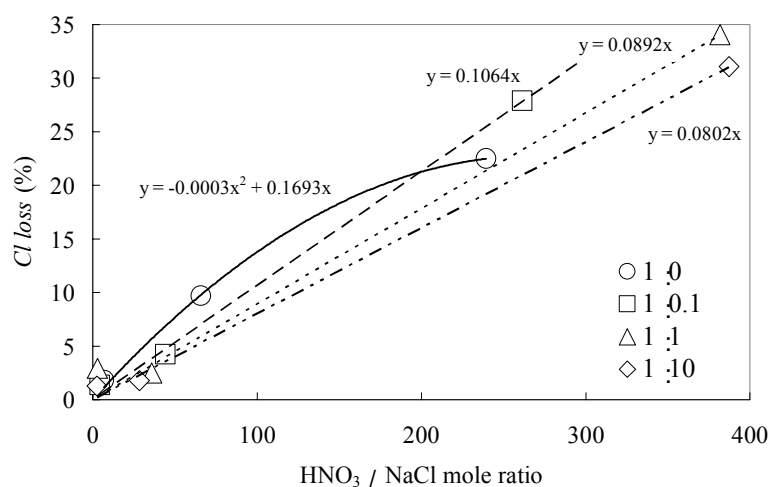


Figure 6. Plots of  $\text{Cl loss}$  against  $\text{HNO}_3/\text{NaCl}$  mole ratio. Legends show the proportion of  $\text{NaCl}$  to palmitic acid

relatively low  $\text{HNO}_3/\text{NaCl}$  region which is ordinary found in the ambient air, the chlorine loss percentage decreased with an increase of addition of palmitic acid. This means organic layer of palmitic acid prevents  $\text{NaCl}$  particles from being attacked by  $\text{HNO}_3$  depending on the coverage rate. On the other hand,

chlorine loss percentage of these covered samples proportionally increased with an increase in  $\text{HNO}_3/\text{NaCl}$ , even though it tended to become constant when NaCl was exclusively exposed by  $\text{HNO}_3$  at a deliquescence point of NaCl.

These results suggest that presence of water is important for chlorine loss from NaCl (sea salt). In the case of naked NaCl, deliquesced NaCl particle reacts with  $\text{HNO}_3$  in saturated aqueous solution. Then, the chlorine loss reaction rate,  $R_{\text{aqueous}}$ , is determined by activity of  $\text{HNO}_3$  and NaCl in the extremely high salinity water, resulting in saturation of chlorine loss percentage. In eq(2),  $\alpha$  is activity of NaCl and  $\text{HNO}_3$

$$R_{\text{aqueous}} = k\alpha_{\text{NaCl}}\alpha_{\text{HNO}_3} \quad (2)$$

On the other hand, hydrophobic palmitic acid, which once covers on NaCl particles, excludes water vapor from the surface of NaCl. Subsequently, interaction between  $\text{HNO}_3$  and NaCl become a heterogeneous solid-gas reaction and the rate is expressed as,

$$R_{\text{solid-gas}} = kP_{\text{HNO}_3} \quad (3)$$

where  $P$  is partial pressure of  $\text{HNO}_3$ . This means NaCl covered by palmitic acid keep on reacting with  $\text{HNO}_3$ .

#### 4. Conclusion

Laboratory studies were conducted on the effect of organic layer upon chlorine loss from sea salt particles, employing  $\text{HNO}_3$  as a gaseous reactant, based on the monitoring at coastal sites in Japan. The results showed, even though palmitic acid on the surface of NaCl particles works as diffusion barrier for  $\text{HNO}_3$ , they excludes water vapor due to their hydrophobic properties and makes NaCl keep on reaction with  $\text{HNO}_3$ . This suggests the presence of organic layer has a possible effect on the higher loss of chlorine (80%) in ambient air.

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