Modeling Study on Behavior of Particulate Chlorine in the Marine Atmosphere

（海洋大気における粒子状塩素の挙動に関するモデル研究）

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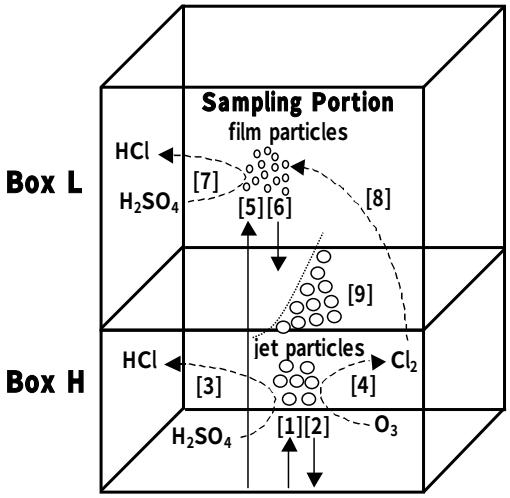
1.Introduction

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[1)]. On the other hand, chlorine rich phenomenon, which means the molar concentration ratio of Cl/Na in atmospheric marine aerosols becomes grater than that in sea water has been found in the monitoring of marine atmospheric aerosol components during the Pacific Ocean cruises of Tokai University education and research vessel, Bosei-maru in 2002 and 2003[2)]. The report mentioned a possible reason for the chlorine rich phenomenon: interactions between chlorine gas (Cl_2)[3), 4)] generated by the photochemical reaction of ozone and liquid sea salt particles in the marine atmosphere. Then, author has developed a simulation model which describes behavior of particulate chlorine in the marine atmosphere, to discuss mechanism of the chlorine rich.

2.Model Description

2.1. Hypothesis on the Chlorine Rich

A possible pathway of chlorine rich was assumed as follows. (1) Among two kinds of sea salt particles (jet particle and film particle) emitted from the surface of the sea, only film particles in fine mode are transported to the vicinity of the sampling portion of the Bosei-maru (radar mast located at about 20m above from the surface of the sea), without any attacks by acidic constituents. (2) In a high humidity area near the surface of the sea, Cl_2 is generated from the jet particles in coarse mode by the photochemical reaction with ozone. (3) Cl_2 generated in the high humidity area is uptaken into the film particles in the low humidity area, and causes chlorine rich in aerosol samples collected. In the low humidity area, generation of Cl_2 is not considered because film particles are dry.



[1]: jet particles emission, [2]: jet particles deposition, [3]: chlorine loss on jet particles with HCl generation, [4]: chlorine loss on jet particles with Cl_2 generation, [5]: film particles emission, [6]: film particles deposition, [7]: chlorine loss on film particles with HCl generation, [8]: uptake of Cl_2 in film particles, [9]: concentration distribution of jet particles by turbulent diffusion

Fig.1　Structure of the simulation model.

2.2. Method

Two boxes (high humidity area (box H) and low humidity area (box L)) were set in a vertical direction as shown in Figure 1. Horizontal boxes were not considered because horizontal flux of sea salt particles could be constant. Molar concentrations of particulate Cl and Na in each box were calculated based on the mass balances

considering various processes such as emission of sea salt particles, deposition of sea salt particles, chlorine loss reaction, and uptake of Cl_2 in film particles and so on. The simulation was conducted for each sampling condition of the Pacific Ocean cruses of Bosei-maru, as follows. (1) Calculations of molar concentrations of particulate Cl and Na in box H ($C_{Cl\_(H)}$, $C_{Na\_(H)}$) (2) Calculations of molar concentrations of particulate Cl and Na in box L ($C_{Cl\_(L)}$, $C_{Na\_(L)}$) using $C_{Cl\_(H)}$ and $C_{Na\_(H)}$ (3) $C_{Cl\_(L)}$ / $C_{Na\_(L)}$ were calculated and compared with observed values (If $C_{Cl\_(L)}$ / $C_{Na\_(L)}$ > 1.13 - 1.18, it is chlorine rich.).

2.3.Modeling Formula

$$\frac{dC_{Cl\_(H)}}{dt}V_{(H)} = E_{Cl\_j} - D_{Cl\_j} - L(HCl)_j - L(Cl_2) \quad ①$$

$$\frac{dC_{Cl\_f}}{dt}V_{(L)} = E_{Cl\_f} - D_{Cl\_f} - L(HCl)_f + U \quad ②$$

$$C_{Cl\_(L)} = C_{Cl\_f} + C_{Cl\_(H)\_diff} \quad ③$$

$$\frac{dC_{Na\_(H)}}{dt}V_{(H)} = E_{Na\_j} - D_{Na\_j} \quad ④$$

$$\frac{dC_{Na\_f}}{dt}V_{(L)} = E_{Na\_f} - D_{Na\_f} \quad ⑤$$

$$C_{Na\_(L)} = C_{Na\_f} + C_{Na\_(H)\_diff} \quad ⑥$$

C: particulate concentration (μmol/m^3), t: time (s), V: box volume (m^3), E: emission flux (μmol/s), D: deposition flux (μmol/s), $L(HCl)$: chlorine loss flux by HCl generation (μmol/s), $L(Cl_2)$: chlorine loss flux by Cl_2 generation (μmol/s), U: uptake of Cl_2 flux (μmol/s)　Subscripts: (H): box H, (L): box L, Cl: chlorine, Na: sodium, j: jet particle, f: film particle, diff: Transport by turbulent diffusion

3.Result and Discussion

Figure 2 shows the simulation results on Cl/Na ratios in marine atmospheric aerosol samples, comparing with observed values in 2002. The calculated Cl/Na ratio roughly showed a similar variation to that of observed and chlorine rich was reproduced in some samples. Therefore, this shows uptake of Cl_2 in sea salt particles is possible mechanism of the chlorine rich phenomenon in the marine atmosphere.

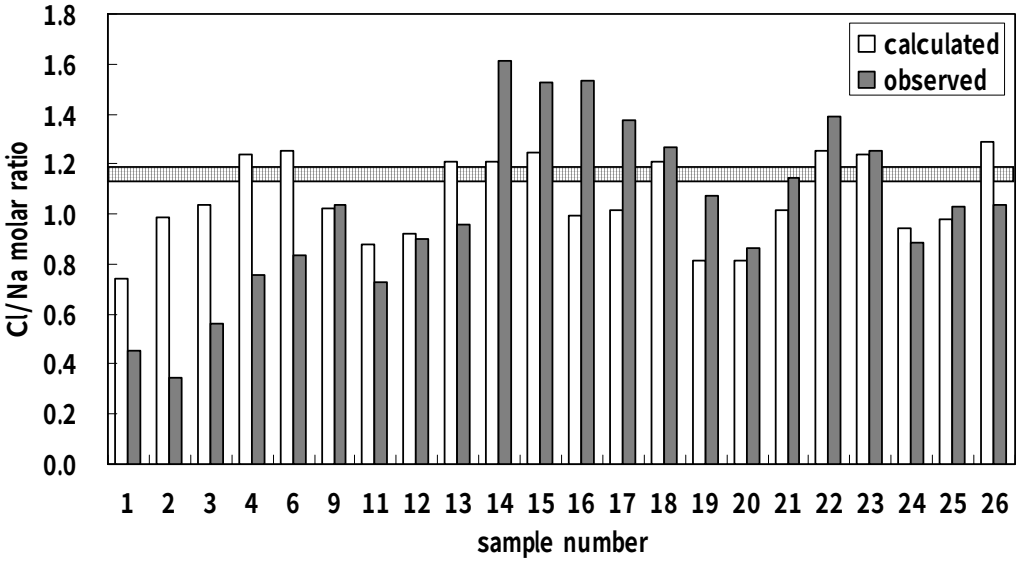


Fig.2　Simulated Cl/Na molar ratio by the model comparing with observed value of the Pacific Ocean cruses of Bosei-maru in 2002[2] (Cl/Na in sea water was indicated with a netted zone).

References: 1) Pio, C. A. *et al.*: *J. Geophys. Res.*, **103**(D19), 25263-25272(1998)　2) Matsuo, T., *et al.*: *Proc. of World Clean Air and Environ. Protect. Congress and Exhibition*, 232, 1-6(2004)　3) Oum, K. W., *et al.*: *Science*, **279**(5347), 74-77(1998)　4) Spicer, C. W., *et al.*: *Nature*, **394**(6691), 353-356(1998)