# An estimation of ship-plume $SO_2$ lifetimes and OPEs using a photochemical/dynamic ship-plume model

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## ABSTRACT
A photochemical/dynamic ship-plume model, which can consider the ship-plume dynamics and ship-plume chemistry, simultaneously, was applied to estimate lifetimes of ship-plume $SO_2$ and OPEs were estimated for ITCT 2K2 (Intercontinental Transport and Chemical Transformation 2002) ship-plume case. In order to evaluate the performance of the model, the model-predicted mixing ratios of $SO_2$ and $H_2SO_4$ and model-estimated OPEs were compared with those observed. From the comparisons, it was found that the model-predicted and -estimated values were in reasonable agreement with those observed ($0.56 \leq R \leq 0.75$). The magnitude of ship-plume $SO_2$ lifetimes is mainly affected by two main factors: (i) the levels of in-plume hydroxyl radical (OH) and (ii) pH of sea-salt particles ($pH_{ss}$). The former is governed by stability conditions of marine boundary layer (MBL) when the ship-emitted $NO_x$ flux is fixed. The latter determines magnitude of aqueous-phase oxidation coefficients. Also, the magnitude of ship-plume OPE is mainly governed by stability conditions of MBL. According to multiple ship-plume photochemical/dynamic model simulations, the estimated $SO_2$ lifetimes and OPEs over the entire ship plumes ranged from 10.32 to 14.32 hrs and from 7.27 to 9.76 under moderately stable (E) and stable (F) MBL conditions. These values are clearly shorter than the background $SO_2$ lifetime of 23.2 hrs and background OPE of 33.50.

## INTRODUCTION
Recently, ship emissions have attracted increasing attention because it is becoming obvious that ship-emitted $NO_x$, $SO_2$ and particles can perturb the atmospheric photochemical cycles and global radiation budget significantly in the marine boundary layer (MBL). Based on Corbett and Koehler's estimation (2003), their $NO_x$ and $SO_2$ emissions contribute approximately ~21% and ~7% of the total global $NO_x$ and $SO_2$ emissions from fuel combustion. Although ship $SO_2$ emissions comprise ~7% of the global $SO_2$ emissions, it may produce significant amounts of non-sea-salt (nss) sulfate. The increased amount of nss-sulfate can further enhance the production of cloud condensation nuclei within the remote MBL, resulting in a negative global radiative forcing. In case of $NO_x$, it can greatly perturb atmospheric oxidation cycle within MBL. Several field observations also showed elevations of the ozone and OH levels in the MBL affected by ocean-going ship emissions. In this study, lifetimes of ship-plume $SO_2$ and OPEs were estimated using a ship-plume photochemical/dynamic model to investigate the characteristic of ship-plume chemistry and their environmental impact.

# ESTIMATION OF SHIP-PLUME SO2 LIFETIMES AND OPES

The full capability of the ship-plume photochemical/dynamic model was evaluated comprehensively using a data set from the ITCT 2K2 ship-plume measurements by comparing the model-predicted results with the aircraft-measured ship-plume concentrations of $SO_2$ and $H_2SO_4$. Then, ship-plume SO2 lifetimes and OPEs were estimated using a ship-plume photochemical/dynamic model.

## Model simulations

Detailed descriptions of the ship-plume photochemical/dynamic model have been reported elsewhere (Song et al., 2003a,b; Kim et al., 2009). Ship-plume model simulations were carried out for a case study – ITCT 2K2 ship-plume experiment. The simulation conditions, such as emission rates, meteorological parameters, aerosol-related parameters, and background gas and particulate species information, were obtained from the ITCT 2K2 observations, and are summarized in previous study.

### *$SO_2$ lifetimes*

The "instantaneous $SO_2$ lifetime ($\tau^i_{SO2}$)" is defined as the $SO_2$ concentration at a given point of time divided by the rate of $SO_2$ loss ($L^i_{SO2}$) at a given point of time:

$$L^i_{SO2} = k_{OH+SO2}[OH][SO_2] + k_{over,SO2}[SO_2] + \frac{v_{d,SO2}}{H}[SO_2] \quad (1)$$

$$\tau^i_{SO2} = \frac{[SO_2]}{L^i_{SO2}} = \frac{1}{k_{OH+SO2}[OH] + k_{over,SO2} + \frac{v_{d,SO2}}{H}} \quad (2)$$

However, $\tau^i_{SO2}$ represents the $SO_2$ lifetime only at the time of interest inside the ship plume. Cross-sectional averaged $\tau^i_{SO2}$ ($\overline{\tau^i_{SO2}}$) was therefore calculated to estimate an average of $\tau^i_{SO2}$ over a ship-plume cross-section:

$$\overline{\tau^i_{SO2}} = \int_{-2\sigma}^{+2\sigma}\int_{-2\sigma}^{+2\sigma} \tau^i_{SO2}(y,z)df_{SO2}(y)df_{SO2}(z) \quad (3)$$

Since, the $\overline{\tau^i_{SO2}}$ can only represent the $SO_2$ lifetime averaged over a cross-section at a given ship-plume travel time. The concept of "equivalent $SO_2$ lifetime ($\tau^{eq}_{SO2}$)" is

introduced to estimate the $SO_2$ lifetime throughout the entire volume of ship plumes, using the following formula (Kim et al., 2009):

$$\tau_{SO_2}^{eq} = \frac{\Delta t}{\int_{t}^{t+\Delta t} \frac{1}{\tau_{SO2}^{i}} dt} \text{ or } \frac{\Delta x}{\int_{x1}^{x2} \frac{1}{\tau_{SO2}^{i}} dx} \quad (4)$$

In this study, the values of $\tau_{SO_2}^{eq}$ were estimated from the plume transect A to H (i.e., $\Delta t$=140 min). Figure 1 shows the changes in $\tau_{SO2}^{eq}$ as a function of the $pH_{ss}$.

***Ship-plume OPEs***

The OPE can be defined as the number of ozone molecules produced per molecules of $NO_x$ oxidized:

$$OPE = \frac{F_{O3}}{L_{NOx}} \quad (5)$$

$$F_{O3} = \left(k_{HO2+NO}[HO_2] + k_{RO2+NO}[RO_2]\right)[NO] \quad (6)$$

$$\begin{aligned} L_{NOx} = {} & k_{OH+NO2}[OH][NO_2] + k_{NO3+DMS}[NO_3][DMS] + k_{mt,NO3}[NO_3] \\ & + 2k_{mt,N2O5}[N_2O_5] + k_{CH3CO3+NO2}[CH_3CO_3][NO_2] - (k_{PAN} + J_{PAN})[PAN] \end{aligned} \quad (7)$$

Figure 2 compared the two cross-section averaged instantaneous OPEs ($\overline{\text{OPE}^{\text{i}}}$) for the two MBL stability conditions. The model-estimated $\overline{\text{OPE}^{\text{i}}}$ show good agreements with observed OPEs ($0.61 \leq R \leq 0.75$). In this particular case (ITCT 2K2 ship-plume case) ship-plume OPEs exist between 7.53 and 9.77.

## SUMMARY

In this study, a ship-plume photochemical/dynamic model was applied for a better understanding of ship-plume sulfur and ozone chemistry. The simulation performance of ship-plume model was evaluated by comparisons with the data obtained from a ITCT 2K2 ship-plume experiment. Model-predicted concentrations of $SO_2$ and $H_2SO_4$, and -estimated OPEs show reasonable agreements with observations under moderately stable (E) and stable (F) ($0.56 \leq R \leq 0.75$) stability conditions. Within the entire plume, $\tau_{SO_2}^{eq}$ and equivalent OPEs ($\text{OPE}^{\text{eq}}$) were estimated for ITCT 2K2 ship-plume case. $\tau_{SO_2}^{eq}$ ranged from 10.32 hrs to 14.32 hrs and $\text{OPE}^{\text{eq}}$ exits between 7.73 to 9.77.

## ACKNOWLEDGEMENTS

This study was financially supported by Mid-Career Research Programme through the National Research Foundation of Korea (NRF) grant from the Ministry of Education, Science and Technology (MEST) (2010-0014058)

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## Figures

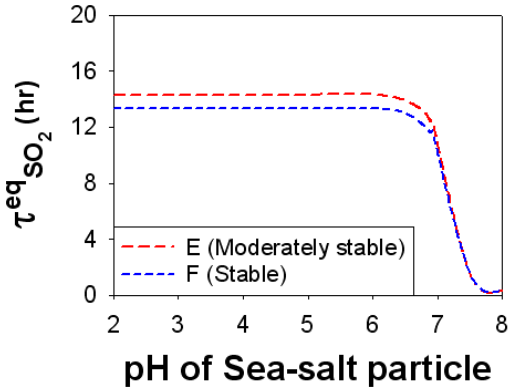


**Fig. 1.** Changes in equivalent $SO_2$ lifetimes with respect to $pH_{ss}$.

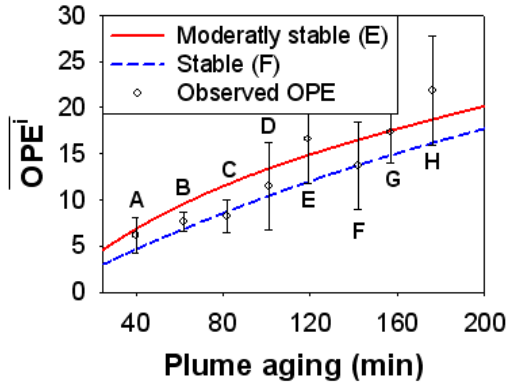


**Fig. 2.** Comparison between model-estimated cross-section averaged $OPE^i$ and observed OPEs.