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## Roles of SO<sub>2</sub> oxidation in new particle formation events

He Meng<sup>1</sup>, Yujiao Zhu<sup>1</sup>, Greg J. Evans<sup>2</sup>, Cheol-Heon Jeong<sup>2</sup>, Xiaohong Yao<sup>1,2,\*</sup>

1. Key Lab of Marine Environmental Science and Ecology, Ministry of Education, Ocean University of China, Qingdao 266100, China. E-mail: [hemeng@ouc.edu.cn](mailto:hmeng@ouc.edu.cn)

2. Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, Toronto M5S 3E5, Canada

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### ABSTRACT

The oxidation of SO<sub>2</sub> is commonly regarded as a major driver for new particle formation (NPF) in the atmosphere. In this study, we explored the connection between measured mixing ratio of SO<sub>2</sub> and observed long-term (duration > 3 hr) and short-term (duration < 1.5 hr) NPF events at a semi-urban site in Toronto. Apparent NPF rates ( $J_{30}$ ) showed a moderate correlation with the concentration of sulfuric acid ([H<sub>2</sub>SO<sub>4</sub>]) calculated from the measured mixing ratio of SO<sub>2</sub> in long-term NPF events and some short-term NPF events (Category I) ( $R^2 = 0.66$ ). The exponent in the fitting line of  $J_{30} \sim [\text{H}_2\text{SO}_4]^n$  in these events was 1.6. It was also found that SO<sub>2</sub> mixing ratios varied a lot during long-term NPF events, leading to a significant variation of new particle counts. In the SO<sub>2</sub>-unexplained short-term NPF events (Category II), analysis showed that new particles were formed aloft and then mixed down to the ground level. Further calculation results showed that sulfuric acid oxidized from SO<sub>2</sub> probably made a negligible contribution to the growth of > 10 nm new particles.

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### Introduction

Atmospheric aerosol particles play critical roles affecting regional air quality and global radiative balance by directly scattering solar radiation (SR) and indirectly modifying cloud properties. Modeling results have suggested that a significant proportion of global cloud condensation nuclei in the mixed layer are secondary aerosols derived from nucleation (Merikanto et al., 2009; Yu and Luo, 2009). During the last three decades, nucleation followed by the growth of nucleated particles, conventionally referring as new particle formation (NPF) events, has been observed in a variety of environments and at different altitudes (Kulmala et al., 2004; Zhang et al., 2011; Gao et al., 2012; Wang et al., 2013). NPF events can occur over tens to hundreds of kilometers in the horizontal direction, while the start times and/or NPF rates generally exhibit spatial inhomogeneity (Wehner et al., 2007; Crippa and Pryor, 2013). What causes the spatial inhomogeneity

is still poorly understood. In the vertical direction, some studies suggested that NPF events started to occur in the troposphere (Rodríguez et al., 2009; Weber et al., 2003) while some studies proposed that NPF events occurred in the whole planetary boundary layer (Boulon et al., 2011; Karl et al., 2012). However, solid evidence is still non-existent to confirm whether new particles are formed at the surface layer mixing upwards (O'Dowd et al., 2009) or if nucleation occurs aloft then subsequently blends downwards (Siebert et al., 2004).

Several underlying mechanisms have been proposed to explain nucleation and subsequent growth of nucleated particles in the atmosphere (Kulmala and Kerminen, 2008; Luo and Yu, 2011; Kulmala et al., 2004, 2013). Gaseous sulfuric acid has been identified as a major driver to generate new particles in the ambient air because of its low vapor pressure, supported by good correlation between the measured nucleation rate and sulfuric acid concentration (Kuang et al., 2008;

\* Corresponding author. E-mail: [xhyao@ouc.edu.cn](mailto:xhyao@ouc.edu.cn) (Xiaohong Yao).

Sipilä et al., 2010). The theoretical nucleation rate  $J$  can be expressed as a function of the measured concentration of sulfuric acid with a power dependency of  $n$ , which is between 1 and 2, or even  $>2$  (Kulmala et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; Wang et al., 2011). Besides sulfuric acid, other compounds such as ammonia, oxidized organics and amines were thought to enhance atmospheric nucleation (Wang et al., 2010; Kirkby et al., 2011; Almeida et al., 2013), probably leading to  $n > 2$  or  $n < 1$ .

Moreover, a few studies quantified the role of  $\text{SO}_2$  oxidation in the growth of new particles (Boy et al., 2005; Smith et al., 2008; Yu, 2010). For example, some studies suggested that sulfuric acid condensation could be responsible for  $\sim 10\%$  of the new particle growth (Boy et al., 2005; Smith et al., 2008). The percentage was even higher in  $\text{SO}_2$ -rich cases, e.g., over 30% in Beijing as reported by Yue et al. (2010). Wehner et al. (2005) reported that the new particle growth up to 10–20 nm could be mainly explained by condensation of sulfuric acid. However, the role of  $\text{SO}_2$  oxidation in the growth of  $>10$  nm new particles is still controversial (Ahlm et al., 2012; Bzdek et al., 2012; Pierce et al., 2012).

In this study, we had made measurements including particle number size distributions, gaseous concentrations and particle chemical components during an intensive campaign from 17 to 28 August, 2007 in a mixed zoning urban area of Toronto, Canada ( $43^\circ 42' 33''\text{N}$ ,  $79^\circ 32' 36''\text{W}$ ). Several long-term NPF events (duration  $> 3$  hr) and tens of short-term NPF events (duration varying from several to dozens of minutes) were observed during the campaign and most of the short-term NPF events occurred concurrently with the long-term events in the same day. In this study, using these data, we conducted an in-depth analysis of these NPF events and tried to address the questions posed above.

## 1. Experimental

The sampling site was located in a parking lot near Highway 401 in Toronto (Yao et al., 2013). During the two week campaign in summer of 2007, particle number size distributions ranging from 5.6 to 560 nm in 32 size bins were measured by a Fast Mobility Particle Sizer (FMPS, in 1-sec resolution, TSI). Simultaneous measurements of particle chemical components in 15-min resolution were performed using a Gas Particle Ion Chromatograph (GP-IC, Dionex Corporation, Sunnyvale, CA). The mass concentration of  $\text{PM}_{2.5}$  was determined by a Thermo tapered element oscillating microbalance (TEOM, 1400AB) in 1-min resolution. Black carbon (BC) was measured by a multi-angle absorption photometer (MAAP, Thermo 5012) in 1-min resolution. Gas analyzers yielded mixing ratios of  $\text{SO}_2$  (TECO 43CTL),  $\text{NO}_x$  (TECO 42C) and  $\text{O}_3$  (TECO 49C) in 1-min resolution. The instruments were deployed on two mobile laboratories. The two mobile labs were parked side by side, 5 m apart. In the meantime, meteorological data was also obtained from the rooftop of a building (ca. 100 m from the labs) in 1-min resolution. SR was simultaneously measured in 5-min resolution. 1-min average data extracted from FMPS were used for analysis.

$(\text{NO}_2 + \text{O}_3)$  was used to quantify the photochemical activities instead of  $\text{O}_3$ , because of the titration reaction (Yao et al., 2010),  $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2$ . The increase of  $(\text{NO}_2 + \text{O}_3)$  in the mixing ratio

could not only be caused by photochemical activities but also due to vertical transport of  $\text{O}_3$  from the upper air to the ground level (Yao et al., 2010).

Gas-phase sulfuric acid concentration can be estimated from SR,  $\text{SO}_2$  concentration and a temperature dependent reaction constant (Mikkonen et al., 2011). This statistical proxy is as follows:

$$[\text{H}_2\text{SO}_4] = 0.186 \times (k \times 10^{12}) \times \text{SR} \times [\text{SO}_2]^{0.5} \quad (1)$$

where,  $k$  ( $\text{cm}^3/(\text{mol}\cdot\text{sec})$ ) is the temperature-dependent rate constant and is scaled by multiplying with  $10^{12}$  (Bzdek et al., 2012; Wu et al., 2013), SR ( $\text{W}/\text{m}^2$ ) is the solar radiation, and  $[\text{SO}_2]$  ( $\text{mol}/\text{cm}^3$ ) is the concentration of gas-phase  $\text{SO}_2$ . The  $k$  is given by Mikkonen et al. (2011):

$$k = B \times k_3 / (B + k_3) \times \exp\left\{k_4 \times \left[1 + \log_{10}(B/k_3)\right]^{-1}\right\} \quad (2)$$

where,  $[M]$  ( $\text{cm}^3/(\text{mol}\cdot\text{sec})$ ) is the density of the air,  $k_1 = 4 \times 10^{-31}$ ,  $k_2 = 3.3$ ,  $k_3 = 2 \times 10^{-12}$  and  $k_4 = -0.8$ .

The concentration of condensable vapor for particle growth from  $D_{p0}$  to  $D_p$  can be expressed by (Kulmala et al., 2001):

$$C = \rho \left\{ \frac{D_p^2 - D_{p0}^2}{2} + \left[ \frac{4}{3\alpha} - 0.623 \right] \lambda (D_p - D_{p0}) + 0.623 \lambda^2 \ln \frac{\lambda + D_p}{\lambda + D_{p0}} \right\} / \Delta t D m \quad (3)$$

here,  $C$  ( $\text{molecules}/\text{cm}^3$ ) is the condensable vapor concentration,  $\rho$  ( $\text{g}/\text{cm}^3$ ) is the particle density,  $D_{p0}$  and  $D_p$  (nm) are the particle diameters at the start and end of the particle growth respectively,  $\alpha$  is the mass accommodation coefficient (i.e., sticking probability),  $\lambda$  is the mean free path in nm,  $\Delta t$  (sec) is the time during particle growth from  $D_{p0}$  to  $D_p$ ,  $D$  ( $\text{cm}^2/\text{sec}$ ) is the diffusion coefficient of the condensing vapor, and  $m$  ( $\text{g}/\text{mol}$ ) is the molecular mass of condensable vapor.

In the atmospheric boundary layer, the relationship between the formation rate of 1 nm new particles and sulfuric acid concentration can be estimated as,  $J_1 \sim [\text{H}_2\text{SO}_4]^n$  (Kulmala et al., 2006; Riipinen et al., 2007). The corresponding semi-empirical expressions for  $J_1$  can be written as activation nucleation and kinetic nucleation models, respectively:

$$J_{1A} = A / [\text{H}_2\text{SO}_4], \quad (4)$$

or

$$J_{1K} = A / [\text{H}_2\text{SO}_4]^2, \quad (5)$$

where,  $A$  ( $\text{sec}^{-1}$ ) is the activation coefficient, between  $10^{-8}$  and  $10^{-6}$ , and  $K$  is the kinetic coefficient, ranging from  $10^{-14}$  to  $10^{-11}$   $\text{cm}^3/\text{sec}$  (Kuang et al., 2008; Nieminen et al., 2009; Wang et al., 2011). In this study, the widely adopted activation coefficient  $A = 1.7 \times 10^{-6} \text{sec}^{-1}$  and kinetic coefficient  $K = 5.7 \times 10^{-13} \text{cm}^3/\text{sec}$  were taken from Sihto et al. (2006), Riipinen et al. (2007), Paasonen et al. (2010) and Makkonen et al. (2014).

Apparent formation rates ( $J_{30}$ ) and growth rates (GR) of new particles were estimated based on Dal Maso et al. (2005) and Yao et al. (2010).

$$J_{30} = dN_{30}/dt + F_{\text{growth}} + F_{\text{coag}}, \quad (6)$$

where,  $N_{30}$  is the number concentration of the 5.6–30 nm particles during the initial 1–2 hr of new particle burst;  $F_{\text{growth}}$

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