Atmospheric Environment 98 (2014) 655–664

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Comparative analysis of new particle formation events in less and severely polluted urban atmosphere

Yujiao Zhu [a], Kelly Sabaliauskas [b], Xiaohuan Liu [a], He Meng [a], Huiwang Gao [a], Cheol-Heon Jeong [b], Greg J. Evans [b], Xiaohong Yao [a, b, *]

[a] Key Lab of Marine Environmental Science and Ecology, Ministry of Education, Ocean University of China, Qingdao 266100, China
[b] Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, 200 College Street, Toronto, Ontario, Canada

HIGHLIGHTS

- New particles can grow to be larger in more polluted atmosphere.
- Organics apparently dominated the growth of new particles below 50 nm.
- NH_4NO_3 played an important role in growing new particles over 50 nm.

ARTICLE INFO

Article history:
Received 10 March 2014
Received in revised form
18 July 2014
Accepted 15 September 2014
Available online 16 September 2014

Keywords:
Nucleation
Particle growth
NH_4NO_3
SOA
Cloud condensation nuclei

ABSTRACT

In this paper, we conducted a comparative study of new particle formation (NPF) events occurring between Qingdao and Toronto during spring. The extent of air pollution in Qingdao was much severer than that in Toronto, but the occurrence frequency of NPF events in Qingdao (41%) was almost same as that (42%) in Toronto. The geometric median diameter of new particles ($D_{pg,1}$) increased up to >40 nm in 15 days out of the total 16 NPF days in Qingdao, the $D_{pg,1}$ at least in eight days increased up to >60 nm and even reached >80 nm in two days. Two-stage growth was generally observed in these eight NPF events. The first-stage growth occurred in daytime and it was likely associated with formation of secondary organic aerosol (SOA) on basis of the modeling results. The second-stage growth was generally observed at nighttime when the modeling results showed increases of NH_4^+ and NO_3^- in concentration together with SOA, implying that NH_4NO_3 possibly played a role in the growth. In Toronto, the maximum $D_{pg,1}$ of the observed new particles in all 13 NPF events was less than 50 nm. A slight second-stage growth of new particles was observed only in four days when either the increase of NH_4^+ and NO_3^- in concentration or the increase of relative humidity occurred. The NPF events in Toronto less likely had a significant contribution to cloud condensation nuclei due to the small size of the observed new particles.

1. Introduction

Ultrafine particles (<100 nm) account for about 80% of the total atmospheric particles in number concentration (Kulmala and Kerminen, 2008; Kumar et al., 2010; Sabaliauskas et al., 2012). Including primary emissions from a variety of anthropogenic and natural sources, nucleation is also one of the important sources of ultrafine particles in the atmosphere (Spracklen et al., 2006; Holmes, 2007; Kulmala and Kerminen, 2008; Yu, 2010). The freshly nucleated particles can grow from about 1 nm to a full variety of sizes and can directly or indirectly impact the earth's radiation balance, depending on the size and chemical composition (Kulmala et al., 2004; Spracklen et al., 2010; Luo and Yu, 2011; Seinfeld and Pandis, 2012). It has been reported that the contribution of <50 nm particles to cloud condensation nuclei (CCN) was negligible because they need unrealistic supersaturation to be activated (Dusek et al., 2006; Seinfeld and Pandis, 2012). Some studies also showed that particles larger than 80 nm can be activated as CCN at moderate atmospheric supersaturation (Dusek et al., 2006; Petters and Kreidenweis, 2007).

Nucleation with sequential growth of nucleated particles in the atmosphere is conventionally referred as a new particle formation (NPF) event (Dal Maso et al., 2005). NPF events have been observed at a large number of sites all over the world (Kulmala et al., 2004), but the probability of the growth of new particles to CCN sizes and

* Corresponding author. Key Lab of Marine Environmental Science and Ecology, Ministry of Education, Ocean University of China, Qingdao 266100, China
E-mail address: xhyao@ouc.edu.cn (X. Yao).

http://dx.doi.org/10.1016/j.atmosenv.2014.09.043
1352-2310/

their impact on the climate have great uncertainties. For example, Pierce et al. (2012) observed NPF events in a forested mountain valley, in which there was 10–25% probability for new particles growing to CCN sizes in the first two days. A 10-years observation of NPF events in a Finnish forest showed that NPF could increase aerosol number concentrations for particles as large as 80 nm especially in summer and autumn when the particle growth rates were fastest (Asmi et al., 2011). A few modeling results also showed the great uncertainty (1–80%) for the climate effect of new particles, depending on locations and supersaturations (Kuang et al., 2009; Spracklen et al., 2008; Luo and Yu, 2011).

NPF is affected by several environmental factors such as gas-phase vapors, temperature, humidity and the pre-existing particles (Kulmala and Kerminen, 2008; Zhang et al., 2009; Yao and Zhang, 2011; Bzdek et al., 2012). Gaseous sulfuric acid, ammonia, amines and other organic species have been proposed to increase nucleation rates by orders of magnitude (Zhang et al., 2011). On the other hand, high surface concentrations of preexisting particles can lower formation rate and growth rate of new particles, sometimes even inhibit the occurrence of NPF events (Kulmala et al., 2005). Including the formation rate, the net increase of new particles in number concentration during NPF events is also related to the duration of the new particle concentration reaching the maximum value. However, studies on how preexisting particles affect the duration are rare.

In the past five years, we have performed a few of observations in different atmospheric environments. We found a large difference of the maximum size of grown new particles between Qingdao and Toronto, i.e., new particles more frequently grew over 60 nm in Qingdao, while they were hardly to grow over 50 nm in Toronto. We presented comparative analyses of NPF events observed in the two cities in order to address two important issues, i.e., 1) what are the similarity and difference of NPF events between severely polluted and less polluted atmospheric environments? 2) which chemicals determine the growth of new particles from 40-50 nm to larger sizes?

2. Methodology

The sampling site in Qingdao is located in the campus of the Ocean University of China (OUC) (36°09′37″N, 120°29′44″E, Fig. 1a–d), which is ~7 km away from the coastline of the Yellow Sea and ~10 km away from the centre of urban areas. A Fast Mobility Particle Sizer (FMPS, TSI Model 3091) was set up on the fifth floor of an academic building in OUC, providing the number-based size distribution of atmospheric particles over the range of 5.6–560 nm in 32 channels in 1-s time resolution (Liu et al., 2014). An identical FMPS was used for sampling at a roadside site at College street in downtown Toronto, Canada (43°39′39″N, 79°23′43″W, Fig. 1e–h, Sabaliauskas et al., 2012). Details of samplings and meteorological conditions of the two sites were given in Supporting Information.

NPF events usually had highest frequency in spring because of favorable temperature (T), relative humidity (RH) and solar radiation to produce sulfuric acid from the photochemical oxidation of SO_2 (Kulmala et al., 2004; Sabaliauskas et al., 2012). Thus, NPF events in spring at the two sites, i.e., from 23 April to 31 May 2010 in Qingdao, China and from 1 May to 31 May 2009 in Toronto, Canada were selected for a comparison. During the sampling period in Toronto, the semi-continuous measurement of SO_4^{2-}, NO_3^- and NH_4^+ in $PM_{2.5}$ were also made using a Dionex Gas Particle Ion Chromatograph (GP-IC) at the site (Yao et al., 2011). No particle chemical composition data were available during the sampling period in Qingdao. Alternatively, the U.S. EPA Community Multi-scale Air Quality Model (CMAQ v4.7.1; Byun and Ching, 1999) was used to simulate temporal variations of gases and particulate species during NPF events in Qingdao. According to our recent measurements in Qingdao (see Supporting Information), we found that the concentrations of SO_4^{2-}, NO_3^- and NH_4^+ in $PM_{2.5}$ modeled by the CMAQ showed a reasonable agreement with the observations (Fig. S2a–c).

NPF events are identified on basis of the criteria proposed by Dal Maso et al. (2005), i.e., 1) a new mode of particles (<30 nm) must be observed, 2) the mode must prevail over a time span of hours; 3) the new mode must show signs of growth. Particle apparent formation rates are calculated using the method provided by Dal Maso et al. (2005).

$$J = \mathrm{d}N_{<30\ \mathrm{nm}} \Big/ \mathrm{d}t + F_{\mathrm{growth}} + F_{\mathrm{coag}} \quad (1)$$

where $N_{<30\ \mathrm{nm}}$ is the concentration of the nucleation mode particles with the diameter <30 nm during the initial 1–2 h of new particle burst; F_{growth} is assumed to be zero because newly formed particles rarely grow over 30 nm during the initial 1–2 h; F_{coag} is the sum of particle–particle inter- and hetero-coagulation rate calculated as Yao et al. (2005).

A multi log-normal distribution function is used to fit these aerosol particle size distributions (Whitby, 1978), which can be expressed mathematically as below:

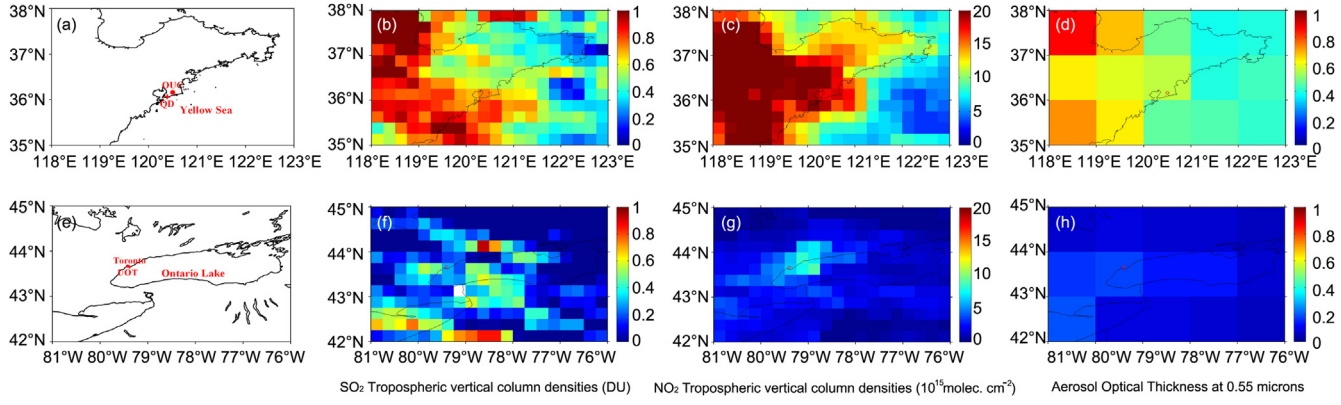

Fig. 1. Maps and satellite data of SO_2, NO_2 and AOD over Qingdao and Toronto. (b–d, averaged satellite value of SO_2, NO_2, and AOD during April and May in Qingdao; f–h, monthly averaged satellite value of SO_2, NO_2, and AOD in May in Toronto.)