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New particle formation and growth at a suburban site and a background site in Hong Kong

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HIGHLIGHTS

- Regional transport elevated the concentration of nanoparticles in Hong Kong.
- Cluster activation theory explained most new particle formation events in Hong Kong.
- Ozonolysis of α-pinene contributed to formation and growth of nucleation mode particles.

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ABSTRACT

Atmospheric nanoparticles have great impacts on human health and global climate change. The number concentrations and size distributions of nanoparticles in the size range of 5.5–350.4 nm were detected at a background site and a suburban site in Hong Kong from summer to winter in 2011 and in autumn of 2013, respectively. Significantly higher particle number concentrations in all modes were observed at the suburban site ($p < 0.05$) during the sampling periods, possibly due to stronger primary emissions/regional transport and more intensive new particle formation (NPF). Particle number concentrations were much enhanced under northerly winds at both sites, resulting from regional transport of Aitken and accumulation mode particles, enhanced local NPF and occasionally low condensation sink. NPF was mainly limited by the precursors of condensable vapors and oxidative capacity of the atmosphere at the background site and the suburban site, respectively. In most cases, the formation rate of 5.5 nm particles was a function of sulfuric acid vapor to the power of 1.32 ± 0.34 at the background site and 0.81 ± 0.31 at the suburban site, abiding by the cluster activation theory. However, ozonolysis of monoterpenes (particularly α-pinene) might also drive NPF, particularly in the afternoon. These reactions also contributed to the growth of nucleation mode particles, which was largely explained by sulfuric acid vapor (73.6 ± 10% at the background site and 60.4 ± 9.8% at the suburban site). In contrast, the oxidations of isoprene, β-pinene and aromatics (particularly xylenes and trimethylbenzenes) were found to participate in the growth of Aitken mode particles.

1. Introduction

Nanoparticles (with aerodynamic diameter <350 nm) are ubiquitous in the atmosphere, and they interact with global climate change and pose harm to human health (Seaton et al., 1995; Seinfeld and Pandis, 2016). Combustion processes, such as vehicular exhaust and biomass burning, have been identified as the direct sources of nanoparticles (Petters et al., 2009; Ronkko et al., 2007, 2017). New particle formation (NPF) is a widely recognized source of secondary nanoparticles in atmosphere, spanning from the clean afforested areas in Europe to the highly polluted cities in China (Kulmala et al., 2006 and references therein). Both the

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primarily emitted and secondarily formed particles can grow up to size of 50–100 nm, acting as cloud condensation nuclei (CCN) in the atmosphere (Gunthe et al., 2009). It is estimated that NPF globally contributes up to 50% of the atmospheric CCN (Spracklen et al., 2008; Trostl et al., 2016).

So far, the generally recognized NPF goes through the processes of nucleation of gaseous vapors which form molecular clusters, and the growth of clusters to the detectable sizes or even larger particles (Kulmala et al., 2005). Condensable vapors, such as sulfuric acid and organic condensable vapors generated from the oxidation of sulfur dioxide (SO_2) and volatile organic compounds (VOCs), respectively (Sihto et al., 2006; Trostl et al., 2016), play critical roles in both nucleation and particle growth. During NPF, the newly formed particles are also lost through coagulation and further growth into larger size particles (Kulmala et al., 2001; Dal Maso et al., 2002). Therefore, intensive NPF events were always observed in pristine environments where the condensation sinks were weak (*e.g.*, 0.02–0.025 s^{-1}) with low concentration of pre-existing particles in the atmosphere (Weber et al., 1997; Allan et al., 2006; Modini et al., 2009). However, recent observations in China clearly identified NPF processes in the heavily polluted environments with the condensation sink up to ~0.1 s^{-1} (Xiao et al., 2015). This likely implied different mechanisms in terms of nucleation and particle growth. Cluster activation theory and kinetic nucleation have been proposed to illustrate the nucleation mechanisms of sulfuric acid (Kulmala et al., 2006; Yu, 2006). However, these theories are occasionally not adequate to explain the observed particle formation rate. For example, either of them cannot interpret the intensive NPF processes observed during a dust event in China (Nie et al., 2014). Although the alternative particle formation mechanisms, like uptake of photochemical oxidants and heterogeneous reactions on dust surface, were suspected, the exact nucleation mechanisms are still unknown or left to be verified (Nie et al., 2014). Recently, the base-stabilization mechanism has been known to account for a great fraction of particle formation rates in the atmosphere. Specifically, either ammonia of 100 pptv or dimethylamine of 3 pptv could enhance the particle formation rates by up to 1000 folds, due to the significant reduction of acid vapor evaporations (Kirkby et al., 2011; Almeida et al., 2013). For particle growth, both sulfuric acid and organic condensable vapors are believed to be critical contributors, while the relative importance of them needs to be identified in different cases (Boy et al., 2005; Trostl et al., 2016). On the other hand, particle growth is generally size dependent ruled by Kelvin effect (smaller particles have higher Kelvin barrier, requiring higher saturation ratio of condensable vapors to drive particle growth). Therefore, the roles of sulfuric acid and organic condensable vapors in particle growth may be also size dependent. For example, Trostl et al. (2016) indicated that the saturation concentration of organic vapors that contributed to growth of nucleated particles should be less than $10^{-4.5}$ μg/m^3. In addition, Lehtipalo et al. (2016) indicated that particle growth was accelerated by the bases that were capable of stabilizing sulfuric acid clusters (*e.g.* ammonia and dimethylamine). As such, further studies are necessary to advance our understanding on the formation and growth of atmospheric nanoparticles.

Hong Kong is a subtropical megacity on the coast of South China Sea (SCS), adjoining the fast-developing Pearl River Delta (PRD) region in South China. The geographical location makes it a unique place to study NPF, because it is influenced by both clean air from SCS and dirty air laden with SO_2 and VOCs from PRD (Guo et al., 2009; Jiang et al., 2010). In addition, the vehicle density in Hong Kong is among the highest over the world, implying that local emissions of nanoparticles and their precursors are also considerable. Although our previous studies (Guo et al., 2012; Wang et al., 2014) observed the NPF and particle burst events at a mountainous and an urban site in Hong Kong, the roles of SO_2 and VOCs in particle formation and growth are not well recognized. This study focused on the formation and growth of nanoparticles at two contrastive sites in Hong Kong. The relationships of sulfuric acid vapor and the formation rates of first-generation oxidation products of VOCs (proxies of organic condensable vapors, as discussed below) with NPF were explored.

2. Methodology

2.1. Site description

Field measurements of nanoparticles, VOCs and trace gases were carried out from September 17 to November 22, 2013 at Tung Chung (TC) in southwestern Hong Kong. To the northwest of the site (22.29° N, 113.94° E) is the Pearl River Estuary where PRD originated air pollutants often accumulate (Wang et al., 2003; Zheng et al., 2010). The site is located in the downwind area of urban Hong Kong and city clusters in the PRD region in cold season (October–March) under prevailing northeasterly winds. In warm season (April–September) southerly winds originating from SCS dominate at the site, diluting air pollution. The potential local sources of air pollutants around this site include the Hong Kong international airport (HKIA, ~3 km to the northwest), a nearby airport highway and the residential activities. Previous study indicated that the impact from the airport on VOCs levels at TC was insignificant (Guo et al., 2007; https://www.hongkongairport.com/eng/sustainability/environmental-management/DraftAOAQSReport.pdf), recently further confirmed by the Environmental Impact Assessment Report for Expansion of Hong Kong International Airport into a Three-Runway system (http://www.epd.gov.hk/eia/register/report/eiareport/eia_2232014/html/Ch%205%20-%20Air%20Quality.pdf). Industrial and vehicular emissions in Hong Kong and PRD were the main sources of VOCs. In addition, TC is a newly developed residential town with few industries and less dense transportation. Hence, it was defined as a suburban site in previous studies (Guo et al., 2009). Field measurements were also conducted at a Hok Tsui (HT) in August, November and December 2011. This site (22.22° N, 114.25° E) is at the tip of southeastern Hong Kong, facing SCS and having very sparse anthropogenic sources. Therefore, it has served as a background site in Hong Kong for decades (Lee et al., 2002; Wang et al., 2009). Fig. 1 shows the geographical location of both sites.

2.2. Field measurements

Atmospheric particle number concentrations in the size range of 5.5–350.4 nm were monitored by a Scanning Mobility Particle Sizer (SMPS) coupled with a butanol-based Condensation Particle Counter (Grimm, model 5.400, Germany) at both sites. Particles were counted in 44 size bins every 4 min, according to their mobility in a differential mobility analyzer mounted in the SMPS. The air was drawn into the instrument through a 1.5 m conductive tube (ID: 0.8 cm), and the particle diffusion losses in the tubing were taken into account in the data analysis. To guarantee the data quality, the instrument was operated following the protocols introduced in Wang et al. (2014). It should be noted that about half of the data were missing for the measurements at both TC and HT, due to instrumental maintenance.

Concentrations of SO_2, carbon monoxide (CO), ozone (O_3), nitric oxide (NO) and nitrogen dioxide (NO_2) at TC were downloaded from the website of Hong Kong Environmental Protection Department (HKEPD, http://epic.epd.gov.hk/EPICDI/air/station/). The data were checked by a quality system in accordance with the Hong