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A case study of single hygroscopicity parameter and its link to the functional groups and phase transition for urban aerosols in Taipei City

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HIGHLIGHTS

- The single hygroscopicity parameters increase with particle size.
- The functional groups of aerosols exhibited strong size dependence.
- The hygroscopicity of organic species is low for Taipei aerosols.

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ABSTRACT

The hygroscopicity, functional groups and phase transitions of urban aerosol particles in Taipei City were studied using a cloud condensation nuclei counter (CCNc) with a scanning mobility particle sizer (SMPS) and an attenuated total reflectance with infrared (ATR-IR) detection technique. With the assumption of larger particles being activated first, the derived single hygroscopicity parameter (κ) exhibited an increasing trend with particle size, i.e., from 0.022 ± 0.01 at 87 ± 10 nm to 0.13 ± 0.03 at 240 ± 20 nm. The collected size-selected particles were characterized using ATR-IR for the functional groups of alkyl, carbonyl, ammonium, sulfate and nitrate, which showed various size dependence patterns, linked to different formation mechanisms. The hygroscopic response based on the ratio (x_{W_solute}) for sample film of absorption by the enhanced water-stretching peak to that by the selected solute showed a better consistency with pure ammonium sulfate for sub-micron size particles. Based on the derived ammonium sulfate volume fraction from IR analysis, the κ received from CCNc measurements was concluded mainly contributed by ammonium sulfate for sub-micrometer particles. The increasing trend of sodium nitrate absorbance at aerosol diameter $\geq$1 μm was due to a reaction of nitric acid with sea salt particles. The micrometer sized particles were apparent not only in a significantly higher x_{W_solute} than pure sodium nitrate but also had a deliquescence RH of 69 ± 1%, similar to that of sodium nitrate-sodium chloride mixtures. Overall, the organic species in this study exhibited a low hygroscopicity with less than 0.036 of contribution for the overall κ, and the major hygroscopic material of urban aerosols consisted primarily of ammonium sulfate in the sub-micrometer particles and sodium nitrate with sea salt in the coarse particles.

1. Introduction

Human activities significantly affect atmospheric systems by increasing greenhouse gases, changing land-surface usage and emitting aerosol-related species (IPCC, 2013; Seinfeld and Pandis, 2006). Greenhouse gases cause a warming effect on the Earth while the direct effect of aerosol particles can have either warming or cooling impact depending on their chemical components and vertical distribution. The indirect effect of aerosol particles by acting as cloud condensation nuclei (CCN) affects the size and lifetime of cloud droplets, which further affects the cloud albedo and hydrological cycle (Andreae et al., 2004; Facchini et al., 1999; Lohmann and Feichter, 2005; Murphy, 2005; Tunved et al., 2006; Twomey, 1974, 1977). The overall effect of aerosol particles tends to depress the warming effect caused by greenhouse gases (IPCC,

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2013). However, there are still significant uncertainties for the impact of aerosols on the Earth system due to their complicate composition. The efficacy of aerosol particles in becoming CCN is strongly dependent on their dry particle size and physical and chemical properties (Dusek et al., 2006; Martin, 2000; Pruppacher and Klett, 1997). Aerosol particles composed with a higher fraction of hygroscopic species, such as ammonium sulfate, ammonium nitrate or oxalic acid, take up significant amount of water to form larger haze particles when the environmental relative humidity (RH) is sufficiently high. Considering an uplifted air parcel, the highly hygroscopic particles with larger size tend to be activated first to form cloud droplets that continue to take up water during their growth and depress the activation of other less hygroscopic or smaller particles (Pruppacher and Klett, 1997; Seinfeld and Pandis, 2006). The manner in which the aerosol particles grow under ambient conditions can be estimated either using the Köhler equation (Pruppacher and Klett, 1997) if the entire composition is well known or using the κ-Köhler equation (Petters and Kreidenweis, 2007) if the single hygroscopicity parameter (κ) of the particles can be determined. Due to the direct aerosol emissions such as vehicle emissions and wood burning or the photo-oxidation proceed aerosols, the physical and chemical properties of ambient aerosols showed a strong spatial and temporal variation (Cubison et al., 2008; Duplissy et al., 2011; Furutani et al., 2008; Hallquist et al., 2009; Kuwata et al., 2007; Martin et al., 2013). The spatial variation of aerosol properties, particularly for organic material, increases the complexity of evaluating the impact of aerosol particles and requires further investigation to obtain the spatial hygroscopicity variation and the influence of aging.

Taipei City is the largest metropolitan area in Taiwan, with an area of ~272 km^2 and a population of ~2.6 million. The local emissions in Taipei City are primarily from anthropogenic sources, such as vehicle and cooking emissions, with negligible direct contributions from industry. Sulfate was found to be one of the most common hygroscopic chemical species in aerosol particles in Taipei and accounted for ~20% of the annual average PM2.5, followed by organic carbon (OC) at ~16% and undetermined species at ~50% (Chang et al., 2010; Chou et al., 2005). The monthly and diurnal variations of sulfate fraction in aerosols from 2002 to 2008 were not significant, whereas the PM2.5, EC and OC exhibited a similar diurnal cycle with an increasing trend starting at ~9:00 a.m. (Chang et al., 2010). The mass fraction of ammonium sulfate as a function of the aerosol particle size displayed a bell shape with maxima near 1 μm, based on both Asian outflow and local emission aerosols in Taipei collected in January 2003 by Chou et al. (2005). With its varying physicochemical properties, the aerosol composition affected the atmosphere heating at various levels and the CCN activity via the solute effect, and the surface tension influence on the Kelvin term further modified the convection pattern and precipitation efficiency (Andreae et al., 2004; Facchini et al., 1999; Lohmann and Feichter, 2005; Murphy, 2005; Tunved et al., 2006; Twomey, 1974, 1977). In this study, we report a detailed characterization of the hygroscopicity of ambient urban aerosols in Taipei City during the period June 7–11, 2012. The required apparent minimum aerosol diameters for activation into cloud droplets were derived as a function of time and then converted into the single hygroscopicity parameter. Because the major hygroscopic organic species usually have specific functional groups, such as hydroxyl or carbonyl, the technique of attenuated total reflectance with infrared (ATR-IR) detection was applied to characterize the functional groups of the size-selected particles and to monitor the absorption variation with RH. Further investigation of the relationship between the IR analysis and hygroscopicity is discussed.

2. Experimental methods

The measurements were conducted in Taipei City, Taiwan, during the period June 7–11, 2012, local time (LT = GMT + 08:00) on the campus of National Taiwan University (NTU, 25.014896° N, 121.53896° E), which is located in a metropolitan area. There are two major expressways and one major local bus station near NTU. The sampling site was located on the second floor of building A of the Department of Atmospheric Sciences. The experimental setup consisted of two parts: the measurement of CCN activity using a cloud condensation nuclei counter (CCNc) and the filter analysis for the functional groups and phase transitions using an ATR-IR. The air quality was based on data reported by a Taiwan Environmental Protection Administration (Taiwan EPA) station in Kuting, which is located ~1 km northwest of NTU. There was no precipitation during the study period. The temperature was 25–35 °C with 60–90% of RH. The wind speed is approximately in the range of 1–3 m/s coming from southwest. The CO and NOx were 550 ± 260 and 25 ± 12 ppb, respectively, with profiles in a regular trend of two peaks associated with traffic loading in the morning and late afternoon. SO_2 has a mixing ratio of 2.4 ± 1.2 ppb, which suggested no significant industrial emission contribution nearby over this period.

2.1. Cloud activation measurement

2.1.1. CCN instrumentation

The hygroscopicity of ambient aerosols was measured using a cloud condensation nuclei system including a thermal-gradient CCN counter (CCNc, Droplet Measurement Technologies, Colorado) (Roberts and Nenes, 2005), a condensation particle counter (CPC, TSI 3776) and a scanning mobility particle sizer (SMPS, TSI 3936) as shown in Fig. 1, with detail described in our previous study (Hung et al., 2014). Briefly, the size number concentration of ambient aerosols was characterized for the size range of 14–680 nm and at a sampling interval of 5 min. The total sampling flow was 1.1 L min^{-1} and passed through a 1-m-long diffusion dryer filled with silica gel to reduce the RH to less than 35% before entering the CCNc, CPC and SMPS in parallel. The supersaturation (SS) of CCNc was calibrated using ammonium sulfate particles with the osmotic coefficient as a function of ammonium sulfate concentration (Ally et al., 2001) as described in previous study (Hung et al., 2014). The temperature gradient (ΔT) of CCNc was varied by 3–16 K and corresponded to 0.09–0.90% of SS as summarized in the Supplemental Table S1. Six SS conditions were set with a duration time of 10 min for each SS. The last 5 min of data for each given SS was applied for the analysis to ensure the well establishment of new SS condition.

2.1.2. Apparent required minimum diameter (D_{SS}) for activation

Based on the assumption that the particles of a given size are

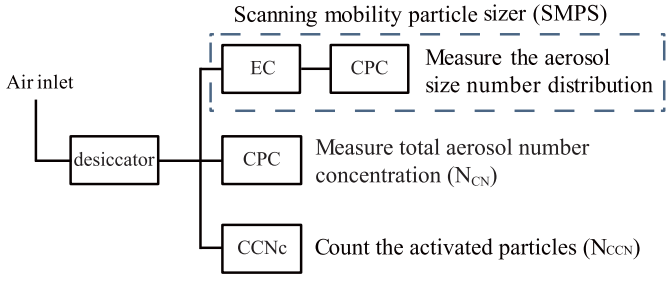

Fig. 1. The experimental setups of the CCNc, CPC and SMPS systems.