Distinct particle properties between ultrafine and accumulation modes under clean and polluted urban environments

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Key Points:

- Fast changing phenomena in aerosol hygroscopicity between clean and pollution periods were observed frequently
- Distinct properties and different formation processes of ultrafine and accumulation modes particles were found in urban environments

Plain Language Summary

The mass concentration of ultrafine mode particles in the atmosphere is extremely low and their properties are hardly investigated by the mass-dependent instruments. Hygroscopicity tandem mobility analyzer (H-TDMA) renders possibility to study sources and chemical processes of ultrafine mode particles because its measurement is based on the measurement of aerosol number concentration and aerosol hygroscopicity can indirectly reflect aerosol chemical compositions. Properties of ultrafine and accumulation mode particles were found very different under clean and polluted urban environments and their different formation processes were studied in this paper.

1、Introduction

In the atmosphere, the mass concentration of aerosol particles in Nucleation and Aitken modes with dimeter less than 100 nm (Dp < 100 nm) contributes very little to PM_1 and $PM_{2.5}$ although their number concentrations are always high. Hygroscopicity tandem differential mobility analyzer (HTDMA) renders possibility to estimate aerosol chemical compositions indirectly based on particle hygroscopic property. The hygroscopic growth factor (GF) is defined as $D_p(RH)/D_p(dry)$, which is the ratio of wet diameter at a certain relative humidity (RH) and dry diameter. GFs for different chemical species differ drastically. HTDMA can measure the GF probability distribution function (GF-PDF) for any specified diameter particles. Detailed information on the aerosol hygroscopicity conveyed in the measurements of HTDMA can be used to study aerosol sources. This is because GF-PDF pattern depends on aerosol chemical composition and mixing state, which are highly related with aerosol formation and aging processes. The measurement of HTDMA is based on aerosol number concentration, which is high in D_p < 100 nm. Therefore, HTDMA can make up the deficiency of mass-dependent instruments in studying the properties of ultrafine mode particles. Hygroscopicity parameter probability distribution function (κ-PDF) can be derived from GF-PDF according to κ-Köhler theory.

2 、One case showing fast changing phenomena in aerosol hygroscopicity between clean and pollution periods

Fast changing phenomena in aerosol hygroscopicity between clean and pollution periods were observed frequently in our campaign. One case is shown in Figure 1. The 40 and 150 nm GF-PDF patterns shifted during the quick transition from pollution to clean periods at about 01:00 LT on November 27. Compared with pollution period, the less-hygroscopic (LH) mode of 40 nm particles became weaker and more-hygroscopic (MH) mode became stronger during clean period. However, the GF-PDF pattern of 150 nm particles shifted contrarily with that of 40 nm particles, which showed enhanced NH mode and weaken MH mode during clean period. From pollution to clean periods, NF_{LH} of 40 nm particles decreased from 0.50 to 0.31, while that of 150 nm particles increased from 0.36 to 0.43. This suggests that there are less particles in hydrophobic Nucleation and Aitken modes, but more in hydrophobic accumulation mode during clean than pollution periods. Simultaneously, the PM_1 chemical mass fractions shows more hydrophobic compounds (POA and BC) during clean than pollution periods (25% to 44%). This can be used to interpret the variation of NF_{LH} in accumulation mode particles, but not in Nucleation and Aitken modes particle.

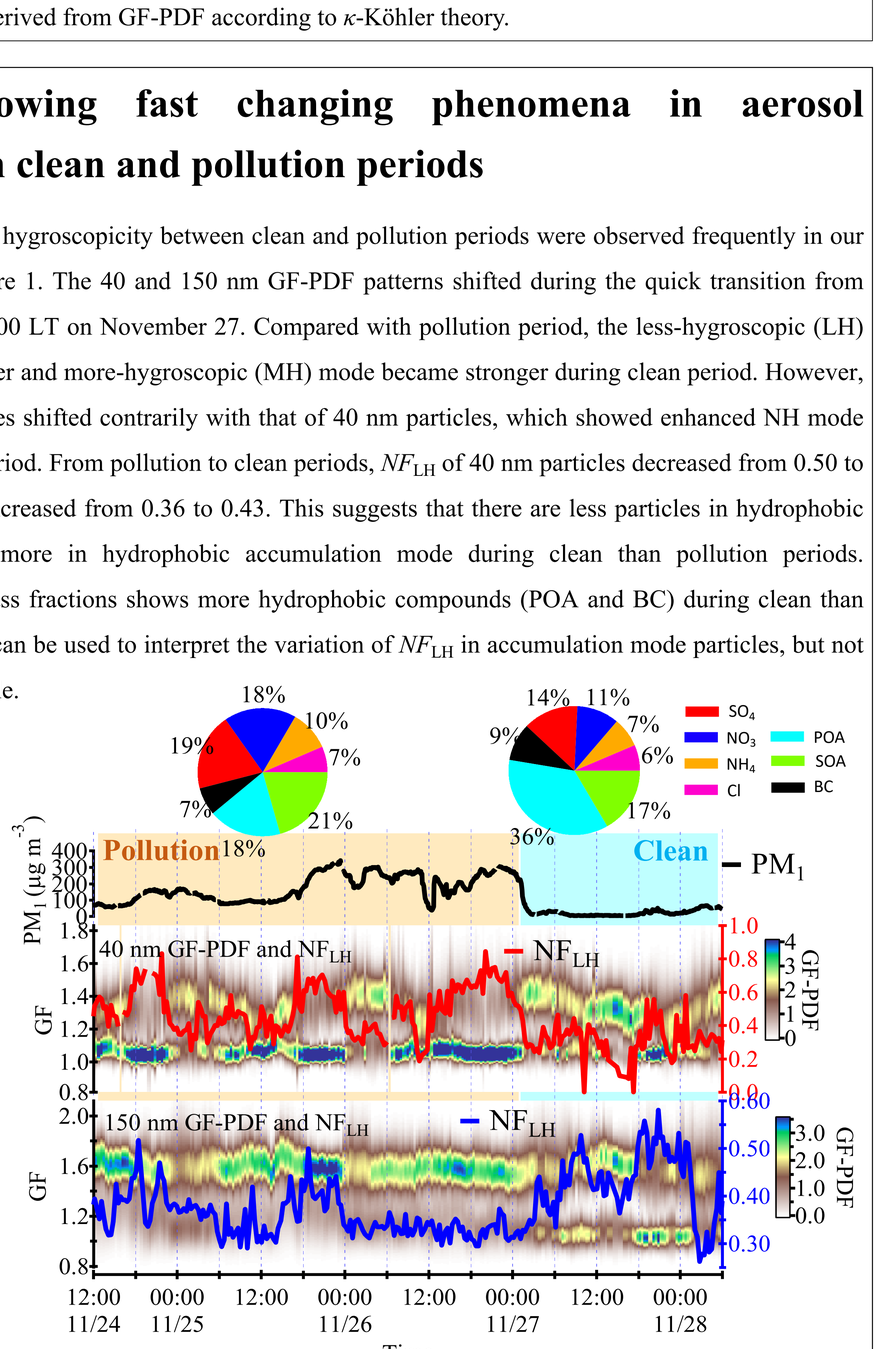

Figure 1. One case showing time series of PM_1, GF-PDF and number fraction of LH mode (NF_{LH}) of 40 and 150 nm particles between clean and pollution periods. The Pie charts are mass fractions of different chemical species in PM_1 during the corresponding clean or pollution periods.

In this study, 40 and 150 nm particles are chosen as ultrafine (Nucleation and Aitken modes) and large (accumulation mode) particles to discuss their different sources and chemical processes.

3、Discussion

Figure 2 depicts the GF_m of 40 nm particles is higher during clean periods than that during pollution periods, while GF_m of 80-200 nm particles shows adverse changing trends. This suggests very different chemical compositions between 40 nm and 80-200 nm particles. Figure 2 also shows larger NF_{LH} for 40 nm particles, but smaller NF_{LH} for 80-200 nm particles during pollution than clean periods. The opposite trends of GF and NF_{LH} between 40 nm and 80-200 nm particles implies different sources and chemical processes of them. This difference is hard to be analyzed by these mass-based instruments.

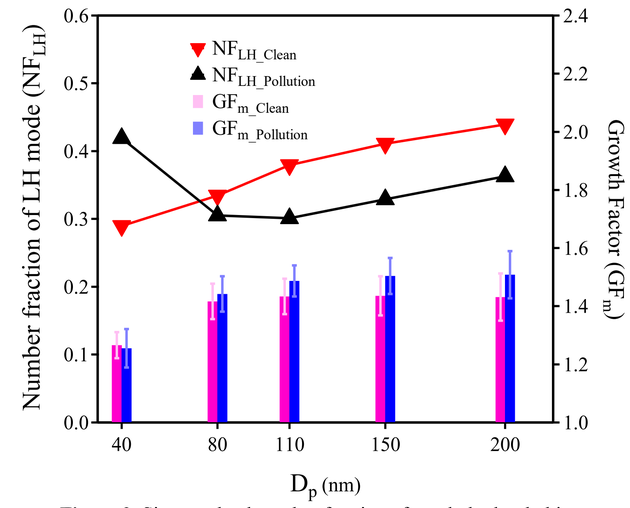

Figure 2. Size-resolved number fraction of nearly hydrophobic mode particles (NF_{NH}) and mean growth factor (GF).

The κ-PDF pattern of 40 nm particles shows very different diurnal variations between clean and pollution periods (Fig. 3a-b). During clean periods MH mode of 40 nm particles was enhanced and LH mode was weakened in κ-PDF of 40 nm particles. Figure 3e shows NF_{LH} of 40 nm particles decreased from ~0.4 at 12:30 LT to ~0.2 at 14:30 LT at about 12:00 LT with the evolution of new particle formation (NPF). All these suggest during clean periods the increase of 40 nm particles in daytime is mainly from NPFs and more hygroscopic compounds are formed. The κ-PDF diurnal variation of 40 nm particles during pollution periods is very different with that during clean periods (Fig. 3b). The MH mode weakens and LH mode strengthens in daytime. NF_{LH} shows three obvious peaks (Fig. 3f), which correspond to three cooking and rush hours.

The κ-PDF for 150 nm particles during the clean and pollution periods had similar diurnal variation patterns, with some differences (Fig. 3c and 3d). First, κ_{m_MH} is lower during clean than pollution periods, especially in nighttime. Second, NF_{LH} is higher during clean than pollution periods. The diurnal variation pattern of NF_{LH} during clean periods also exhibit three peaks corresponding to three rush hours (Fig. 3e), while that during pollution periods shows slight variation in all day. All these suggests 150 nm particles are influenced by local primary emission during clean periods. The low and almost invariable NF_{LH} (Fig. 3f) during pollution periods suggests most of 150 nm particles are internally mixed. This is likely related with heterogeneous reactions on the particle surface.

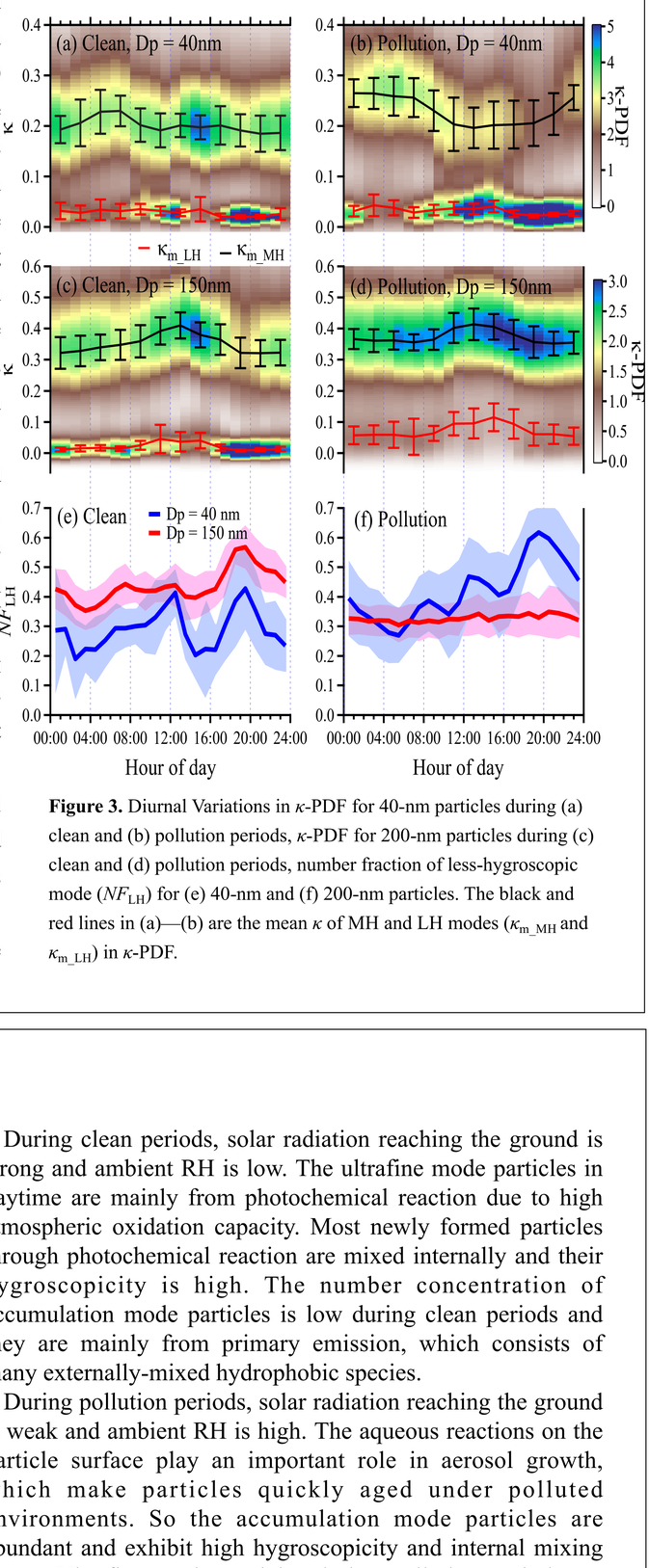

Figure 3. Diurnal Variations in κ-PDF for 40-nm particles during (a) clean and (b) pollution periods, κ-PDF for 200-nm particles during (c) clean and (d) pollution periods, number fraction of less-hygroscopic mode (NF_{LH}) for (e) 40-nm and (f) 200-nm particles. The black and red lines in (a)—(b) are the mean κ of MH and LH modes (κ_{m_MH} and κ_{m_LH}) in κ-PDF.

4、A hypothesis of mechanism

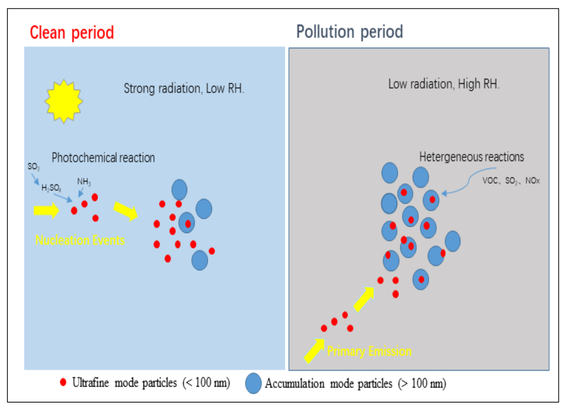

Figure 4. Schematic representation of the main chemical processes for ultrafine (< 100 nm) and accumulation (> 100 nm) modes particles during clean and pollution periods.

During clean periods, solar radiation reaching the ground is strong and ambient RH is low. The ultrafine mode particles in daytime are mainly from photochemical reaction due to high atmospheric oxidation capacity. Most newly formed particles through photochemical reaction are mixed internally and their hygroscopicity is high. The number concentration of accumulation mode particles is low during clean periods and they are mainly from primary emission, which consists of many externally-mixed hydrophobic species.

During pollution periods, solar radiation reaching the ground is weak and ambient RH is high. The aqueous reactions on the particle surface play an important role in aerosol growth, which make particles quickly aged under polluted environments. So the accumulation mode particles are abundant and exhibit high hygroscopicity and internal mixing status. Ultrafine mode particles during pollution periods are mainly from primary emission due to the weak photochemical reaction. These ultrafine mode particles are coagulated by large particles and also can grow quickly through aqueous chemical reactions, which is obvious in nighttime when ambient RH can exceed 60 %.

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