1 A new balance formula to estimate new particle formation rate: reevaluating the effect of coagulation scavenging

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6 Abstract. A new balance formula to estimate new particle formation rate is proposed. It is derived from aerosol general 7 dynamic equation in the discrete form and then converted into an approximately continuous form for analysing data from new 8 particle formation (NPF) field campaigns. The new formula corrects the underestimation of the coagulation scavenging effect 9 occurred in previously used formulae. It also clarifies the criterions in determining upper size bound in measured aerosol size 10 distributions for estimating new particle formation rate. A NPF field campaign was carried out from March 7th to Apr. 7th, 11 2016, in urban Beijing, and a diethylene glycol scanning mobility particle spectrometer equipped with a miniature cylindrical differential mobility analyser was used to measure aerosol size distributions down to ~1 nm. 11 typical NPF events were 12 13 observed during this period. Measured aerosol size distributions from 1 nm to 10 µm were used to test the new formula and 14 those widely used ones. Previously used formulae that perform well in relatively clean atmosphere where nucleation intensity 15 is not strong were found to underestimate the comparatively high new particle formation rate in urban Beijing because of their 16 underestimation or neglect of the coagulation scavenging effect. Coagulation sink term is the governing component of the 17 estimated formation rate in the observed NPF events in Beijing, and coagulation among newly formed particles contributes a 18 large fraction to the coagulation sink term. Previously reported formation rates in Beijing and in other locations with intense 19 NPF events might be underestimated because the coagulation scavenging effect was not fully considered, e.g., formation rates 20 of 1.5 nm particles in Beijing are underestimated by 58.9% on average in this campaign if neglecting coagulation among 21 particles in nucleation mode.

22 1 Introduction

New particle formation (NPF) is a frequently occurring phenomenon in atmospheric environment. In a typical NPF event, gaseous precursors burst out into particles due to nucleation and lead to a rapid increase in atmospheric aerosol population. Nucleated particles can grow quickly to increase the number concentration of cloud condensation nuclei (Kerminen et al., 2012; Kuang et al., 2009; Leng et al., 2014) and thus has indirect impacts on radiative forcing and global climate (Lohmann & Feichter, 2005). Continuous growth of nucleated particles also provides increasing aerosol surface area for heterogeneous physicochemical processes. NPF studies can trace back to the early 20th century (Aitken, 1911) and NPF events have been observed in various atmospheric environment, e.g., from city to countryside, from desert (Misaki, 1964) to rain forest (Zhou, 30 2002), from continent to the ocean (Covert et al., 1992), from the equator (Clarke et al., 1998) to polar area (Covert et al.,

31 1996; Park et al., 2004), and from troposphere to stratosphere (Lee et al., 2003).

32 Formation rate at which the growth flux past a certain diameter is a key parameter to quantitatively describe NPF events. Different formulae have been used to estimate new particle formation rate from measured aerosol size distributions and they 33 34 mainly originate from two approaches. One is from the definition of nucleation rate (Heisler & Friedlander, 1977; Weber et 35 al., 1996) and the other is a population balance method (Kulmala et al., 2001; Kulmala et al., 2012). Consistency of these two 36 approaches was tested using a numerically simulated NPF event and a relative error of less than 20% was reported (Vuollekoski et al., 2012). The simulated NPF event has a maximum formation rate of less than 1 cm⁻³ s⁻¹. However, the reported formation 37 rates in the atmosphere vary in a large scale, e.g., approximately from 10^{-2} to 10^4 cm⁻³ s⁻¹ (Kulmala et al., 2004). Suffering 38 39 from the assumptions made in these two approaches, their validity in describing NPF events with high formation rate needs to be further explored. A high fraction of newly formed particles is scavenged by coagulation before they grow into larger 40 particles. Both approaches potentially underestimate the contribution of coagulation scavenging when calculating formation 41 42 rate from measurement data. They may perform well in clean atmospheric environment where nucleation intensity is not strong 43 and aerosol concentration is relatively low, i.e., the coagulation scavenging effect is less important.

44 The effect of coagulation scavenging is more prominent when estimating formation rate of sub-3 nm particles because of their 45 high diffusivities and high concentrations during NPF events. Due to instrument limitations, aerosol size distributions of sub-46 3 nm particles were not available in many previous NPF field campaigns. Recent developments in diethylene glycol (DEG) condensation particle counters (CPC, Iida et al., 2009; Vanhanen et al., 2011) made it feasible to develop new scanning 47 48 mobility particle spectrometers (SMPS) for extending aerosol size distribution measurement from ~3 nm down to ~1 nm (Jiang, 49 et al., 2011a; Franchin et al., 2016). These new spectrometers were deployed in atmospheric observations (Jiang, et al., 2011b) 50 and in chamber measurements (Franchin et al., 2016) to study NPF. A miniature cylindrical differential mobility analyser 51 (mini- cyDMA, Cai et al., 2017) was developed to improve the performance of the DEG-SMPS.

52 In many locations of China, high emissions lead to both high concentrations of gaseous precursors and high atmospheric 53 aerosol concentration. NPF was frequently observed even in megacities such as Beijing and Shanghai (Wu et al., 2007; 54 Kulmala et al., 2016; Wang et al., 2017). In most previous studies, the above population balance method was used to estimate 55 new particle formation rates in China. The reported formation rates of 3 nm particles and larger ones were typically in the range of 1-10 cm⁻³ s⁻¹ (Wang et al., 2013; Leng, et al., 2014; An et al., 2015; Qi et al., 2015). One study in Shanghai reported 56 a rate of 112.4 to 271.0 cm⁻³ s⁻¹ for the formation of 1.5 nm particles inferred from a DEG-CPC (Xiao et al., 2015). For these 57 58 intense NPF events, the above balance approach may underestimate the coagulation scavenging effect and thus lead to 59 underestimation in the reported formation rate. In addition, applying new SMPSs to measure aerosol size distributions down 60 to ~ 1 nm will help to better quantify the formation rate and its governing factors in typical locations of China.

61 When estimating new particle formation rates, various particle size ranges were used in previous formulae. The definition 62 approach tries to limit the size range towards the minimum detected diameter (Kuang et al., 2008; Weber, et al., 1996), while 63 studies with the population balance method have used various size ranges. Some studies used the aerosol size distributions 64 from the minimum detected diameter up to 25 nm (Kulmala et al., 2001; Dal Maso et al., 2005; Wu et al., 2007; Wang et al., 65 2013). Kulmala et al. (2004) recommended the upper size bound as the maximum size that the critical cluster can reach during 66 a short time interval of growth. There are also studies using narrower size range such as from 3 nm to 6 nm (Sihto et al., 2006; Paasonen et al., 2009; Wang et al., 2011; Vuollekoski et al., 2012) and from 1.34 nm to 3 nm (Xiao et al., 2015). In principle, 67 68 the estimated formation rates may vary when different particle size ranges are used. Assumptions made while deriving these 69 formulae should be fully considered when proposing criterions to choose particle size range.

In this study, a new population balance formula for estimating new particle formation rate was derived from aerosol general dynamic equation to properly account for the effect of coagulation scavenging, especially for analysing intense NPF events. A NPF field campaign was carried out in Beijing. Aerosol size distributions down to ~ 1 nm were measured using the DEG-SMPS equipped with the mini- cyDMA. Data from this campaign and from literature are used to test the new formula and other widely used formulae. Different formulae are compared and their applicability in analysing intense NPF events are addressed. Criterions to choose particle size range for formation rate estimation are proposed and evaluated. Governing components of the new formation rate in Beijing are discussed and compared to those from other locations in the world.

77 2 Theory

78 **2.1 The new balance formula to estimate formation rate**



where J_k is the formation rate of particles at size d_k ; N is particle number concentration and $N_{[d_k,d_u)}$ is defined as total number concentration of particles ranged from d_k to d_u (particles with diameters of d_u are not accounted for); d_i refers to the lower bound of each measured size bin; $\beta_{(i,g)}$ is the coagulation coefficient when particles with the diameter of of d_i collides with particles with the diameter of d_g ; n is particle size distribution function which equals dN/dd_p ; and GR_u is particle growth rate at d_u , i.e., dd_u/dt . d_u is the upper bound of the size range for calculation. d_{min} is the size of minimum cluster in theory and the lowest size limit of measuring instrument in practice. The last three terms in the right hand side (RHS) of Eq. (1) are coagulation sink term (*CoagSnk*), coagulation source term (*CoagSrc*) and condensational growth term, respectively.

89 The two assumptions of Eq. (1) are that (a) transport, dilution, primary emission and other losses except for coagulation loss 90 in the size range from d_k to d_u are comparatively negligible; (b) when deriving the fourth term in the RHS of Eq. (1), net 91 coagulation (net result of both formation and scavenging due to coagulation) of any particle larger than d_u with other particles 92 is negligible. These two assumptions above are also the criterions to determine d_u . The mathematical expression of population 93 balance in Eq. (1) in the discrete form is illustrated by Fig. 1. Time rate of change of particles at d_k is equal to source minus 94 sink. Source are the condensational flux into d_k (J_k) and formation due to coagulation among smaller particles/clusters 95 $(CoagSrc_k)$. Sink are the condensational flux out of $d_k(J_{k+1})$ and scavenging due to coagulation with other particles/clusters 96 (CoagSnk_k). Nucleation rate, I, is defined as J_k when d_k is the size of the critical cluster (nuclei). Equation (1) is obtained by 97 adding these single population balance equations up from d_k to d_u , converting it from the discrete form into the continuous 98 form, and approximating J_u with the product of measured n_u and GR_u . Note that Eq. (1) is still an approximate formula of 99 particle formation rate because *CoagSnk* and *CoagSrc* are calculated by size bins and the coagulation effect of particles smaller than d_{min} is not accounted for. For rigorous mathematical derivation and detailed illustration, please refer to Appendix A. 100

101 **2.2 Previous approaches to estimate formation rate**

102 The population balance method proposed in previous study is shown in Eq. (2) (Kulmala et al., 2001; Kulmala et al., 2012), $\frac{N_{12}}{N_{12}}$

$$J_{k} = \frac{-(a_{k}, d_{u})}{dt} + CoagS_{m} \cdot N_{[d_{k}, d_{u})} + \frac{(a_{k}, d_{u})}{(d_{u} - d_{k})} \cdot GR_{[d_{k}, d_{u})}$$
(2)

104 where coagulation sink, $CoagS_m$, is defined as Eq. (3).

$$CoagS_m = \int_0^{+\infty} \beta_{(i,m)} n_i \mathrm{d}d_i \tag{3}$$

The subscript m corresponds to the representing diameter, d_m , for particles ranged from d_k to d_u . d_m is often estimated as the geometric mean diameter of d_k and d_u . Equation (1) and (2) look similar because they are both derived from the general dynamic equation, while their detailed differences are illustrated in Appendix B.

109 The definition approach to calculate new particle formation rate is shown in Eq. (4) (Heisler & Friedlander, 1977; Weber et 110 al., 1996; Iida et al., 2006; Kuang et al., 2008; Kuang et al., 2012).

$$111 J_k = n_k \cdot GR_k (4)$$

Equation (4) focuses on the flux into d_k and is theoretically correct in continuous space of particle diameter. However, when applying Eq. (4) in practice, size distribution of particles smaller than d_k is required, which is difficult to obtain (See Appendix B). Usually diameter bins larger than d_k are used to estimate particle formation rate when using the practical expression of Eq. (4) (e.g., Eq. (9) defined in section 4.3). As illustrated in Fig. 1, such approximation essentially neglects the first three terms in the RHS of Eq. (1), and may lead to underestimation of particle formation rate because of neglecting the coagulation scavenging effect especially when analysing intense NPF events.

2.3 Previous formulae for comparison

119	Equation (5) is a widely used balance formula to estimate formation rate in previous studies (Kulmala et al., 2001; Dal Maso
120	et al., 2005; Wu et al., 2007; Shen et al., 2011; Wang et al., 2013), $dN_{[1525]}$ $N_{[1525]}$
121	$J_{1.5} = \frac{(1.5,25)}{dt} + N_{[1.5,25)} \sum_{d_i=1.5\text{nm}} \beta_{(i,8)} N_i + \frac{(1.5,25)}{(25-1.5) \text{ nm}} \cdot GR_{[1.5,25)} $ (5)
122	where N_i is the number concentration of size bin i. Corresponding to those in Eq. (2), d_u is 25 nm and d_m is 8 nm in Eq. (5). By
123	comparing Eq. (5) with Eq. (1), it can be concluded that Eq. (5) estimates $CoagSnk$ using a representative $CoagS_m$ and neglect
124	CoagSrc. Growth rates in all formulae in section 2.2 were estimated using mode-fitting method suggested in Kulmala et al
125	<mark>(2012).</mark>
126	When calculating $CoagS_m$, particles smaller than d_m (Kulmala et al., 2012) or even d_u are neglected in some previous studies
127	Corresponding formulae are shown in Eq. (6) and Eq. (7), respectively. The only difference among Eq. (5), Eq (6), and Eq. (7
128	is the lower bound when calculating $CoagS_m$ in the second term in the RHS of these equations.
129	$J_{1.5} = \frac{dt}{dt} + N_{[1.5,25)} \sum_{d_i = 8nm} \beta_{(i,8)} N_i + \frac{r_{[1.5,25)}}{(25 - 1.5) nm} \cdot GR_{[1.5,25)} $ (6)
130	$J_{1.5} = \frac{\mathrm{d}N_{[1.5,25)}}{\mathrm{d}t} + N_{[1.5,25)} \sum_{d_i=25\mathrm{nm}}^{+\infty} \beta_{(i,8)} N_i + \frac{N_{[1.5,25)}}{(25-1.5)\mathrm{nm}} \cdot GR_{[1.5,25)} $ (7)
131	The upper bound, d_u , is selected as 6 nm is some recent studies (Sihto et al., 2006; Riipinen et al., 2007; Paasonen et al., 2009
132	Wang et al., 2011; Vuollekoski et al., 2012; Wang et al., 2015) as shown in Eq. (8).
133	$J_{1.5} = \frac{dV_{[1.5,6]}}{dt} + N_{[1.5,6]} \sum_{d_i=1.5\text{nm}}^{1.5} \beta_{(i,3)} N_i + \frac{V_{[1.5,6]}}{(6-1.5) \text{ nm}} \cdot GR_{[1.5,6]} $ (8)
134	It should be clarified that d_k in Eq. (5)-(8) was usually 3 nm in previous studies due to the absence of sub-3 nm particle size
135	distributions, and d_m in Eq. (8) was 4 nm rather than 3 nm in previous studies because 4 nm is almost the geometrical mean
136	diameter of 3 nm and 6 nm. Particles smaller than 6 nm were neglected when estimating the coagulation sink term in some
137	studies, although its uncertainties will not be discussed here. The expression of condensational growth term, i.e., the third term
138	in the RHS of Eq. (8) varies with studies, however, it does not influence the generality of the following discussion.
139	In previous studies, several size bins larger that d_k , typically 3 nm, were adopted when using the practical formula of the
140	definition approach (Weber et al., 1996; Kuang et al., 2008), while here the size range from 1.5 nm to 2.5 nm is applied to
141	estimate $J_{1.5}$ as shown in Eq. (9).
142	$J_{1.5} = \frac{P_{[1.5,2.5]}}{(2.5 - 1.5) \mathrm{nm}} \cdot GR_{[1.5,2.5]} $ (9)

143 **3 Experiment**

A NPF field campaign was carried out in Beijing. The observation period was from March 7th to April 7th, 2016. The monitoring site locates on the top floor of a four-storey building in the centre of the campus of Tsinghua University. Tsinghua situates in the northwestern urban area of Beijing and the fourth-ring road is ~2 km away to the south of the monitoring site. The site has been a PM_{2.5} monitoring station since 1999 (He et al., 2001; Cao et al., 2014) and there is no tall building nearby. Potential pollution sources around are the three cafeterias on campus that may produce cooking aerosol during meal time, locate ~170 m away on the northeast, ~170 m away on the north, and ~350 m away on the northwest, respectively.

A DEG-SMPS equipped with a mini- cyDMA specially designed for classification of sub-3 nm particles was deployed to measure particles in the size range of 1-5 nm (Cai et al., 2017). A particle size distribution system, including a SMPS with a TSI nano DMA, a SMPS with a TSI long DMA and an aerodynamic particle sizer, was used to measure particles in the size range of 3 nm to 10 μ m in parallel (Liu et al., 2016). Other instruments whose data are not used in this analysis are not listed here.

A C++ program was used to invert particle size distribution from raw counts while incorporating diffusion losses inside the sampling tube, diffusion losses and charging efficiencies of the bipolar neutralizers, penetration efficiencies and transfer functions of DMAs, and detection efficiencies of CPCs (Hagen and Alofs, 1983; Jiang et al., 2011a). Particle density was assumed to be 1.6 g/cm³ according to local observation results (Hu et al., 2012). Accommodation coefficient (i.e., coagulation efficiency) was assumed to be unity and temperature was assumed to be a constant value of 285 K, the average temperature during the observation period.

161 4 Results and discussion

162 **4.1 Upper size bound for formation rate calculation**

163 New particle formation rates using different upper size bound, d_u of 3 nm, 6 nm, 10 nm and 25 nm were calculated. Since the 164 maximum size that new particles formed by nucleation have reached varies with time, the upper size bound should not be a 165 constant value to minimize the interference of background particles. A varying upper size bound, d_b , was visually determined 166 as the largest size bin in the size range from 3 nm to 25 nm whose frequency density (particle size distribution), $dN/d\log d_p$, 167 was larger than 28,000 #/cm³. Here 28,000 was determined visually according to measured intensity plot of particle size 168 distributions as an approximate boundary for newly formed particles and background particles. The value should be campaign 169 specific or even event specific. Fig. 2(a) indicates that d_b is almost the boundary for particles formed due to nucleation. 170 Estimated $J_{1.5}$ using 20,000 #/cm³ as the boundary differed little from that using 28,000 #/cm³, indicating the estimated $J_{1.5}$ is 171 insensitive to the value for boundary. It is reasonable to regard d_b as a relatively credible value when compared to others. Note 172 that when using d_b as the upper size bound, dN/dt term of newly formed particles in Eq. (1) is approximated by that of sub-25

173 nm particles to avoid potential influence of varying size range on particle number concentration.

174 As shown in Fig 2(b), estimated $J_{1.5}$ using d_b and a constant value of 25 nm as the upper bounds are almost the same (the mean 175 relative error is 2.2%). Maximum difference between these two choices is ~10% which appears before 8:00 when d_b is less 176 than 5 nm and the number concentration of sub-25 nm particles is ~2 times of sub-6 nm particles and ~3 times of sub-3 nm 177 particles. It indicates the influence of non-freshly nucleated particles on estimating $J_{L,5}$ is not important because their 178 comparatively low diffusivities even though their concentration is comparatively high at the beginning of NPF events. 179 Estimated $J_{1.5}$ using d_u of 6 nm and 10 nm are in good consistency with that using d_b before 10:00 (the mean relative errors are 180 4.8% and 2.6%, respectively). However, when particles formed by nucleation grow beyond, calculated $J_{1,5}$ is underestimated 181 when using 6 nm and 10 nm as the upper bound. For example, the mean relative errors of estimated $J_{1.5}$ using d_u of 6 nm and 182 10 nm between 10:30 and 15:00 are 18.6% and 12.8%, respectively. When calculating $J_{1.5}$ using 3 nm as d_u , an average 47% 183 underestimation was found for this event.

The reason of underestimation when using smaller d_u can be illustrated by Fig. 2(c). J_u is estimated by $n_u \cdot GR_u$ in Eq. (1). This estimation may be not accurate when d_u is small because the assumption that net coagulation of any particle larger than d_u with other particles is negligible may be violated. As illustrated in the derivation of Eq. (1) in Appendix A, a nearly zero J_u is preferred when using Eq. (1). However, as shown in Fig 2(c), estimated J_3 is still a large fraction compared to $J_{1.5}$, while J_6 and J_{10} are 27.8% and 17.6% of $J_{1.5}$ on average between 10:30 and 15:00, respectively. Although J_u is approximated by $n_u \cdot GR_u$ rather than simply neglected, this approximation may still lead to uncertainties.

Since $J_{1,5}$ estimated by the varying d_b and a constant value of 25 nm are almost the same with an acceptable relative error even under the interference of non-freshly nucleated particles, 25 nm was adopted as the upper bound for calculating *J* in this study. Since d_u is "proper large" as defined by the two criterions, it is also reasonable to neglect J_u for simplicity. It should be clarified that 25 nm is not necessarily valid for all other studies, because the upper bound should be determined by the two criterions and can be campaign specific. However, it can be concluded that a very small upper bound such as 3 nm is not recommended because particles formed by nucleation surely grow larger than 3 nm in a typical NPF event while intense primary emission of particles around 3 nm is rarely observed in the atmosphere (unless near the emission sources).

197 **4.2 Comparison with previous formulae**

198 Estimated $J_{1.5}$ values using Eq. (1) and Eq. (5)-(9) on March 13th are shown in Fig. 3. d_k , d_u , and d_{min} are 1.5 nm, 25 nm, and

199 1.3 nm, respectively, when using Eq. (1). It can be concluded that except for Eq. (8), other formulae significantly underestimate

- 200 $J_{1.5}$ compared to Eq. (1). By comparing contribution of each terms in the RHS of Eq. (1) and Eq. (5)-(9), it was found that the
- 201 underestimation of formation rates is mainly caused by the underestimation of *CoagSnk*. Equation (9) simply neglects *CoagSnk*

202 as well as other terms (dN/dt and CoagSrc) compared to Eq. (1), so its result is the lowest among six formulae. Equation (5) 203 estimates CoagSnk using an average $CoagS_m$, which lead to underestimation because CoagS at 8 nm happens to be smaller 204 than those at most other diameters in the size range from 1.5 nm to 25 nm, as illustrated in Appendix B. Equation (6) and (7) 205 neglects particles smaller than 8 nm and 25 nm when calculating CoagS_m, respectively. Such simplification may be reasonable 206 for relative clean atmosphere where nucleation intensity is not strong, however, these approximations are not suitable for 207 analysing typical NPF events in Beijing where coagulation among nucleation mode particles is a major proportion of CoagSnk. 208 J_{L5} estimated using Eq. (8) agrees well with that estimated using Eq. (1), however, it does not mean that 6 nm serve as a better 209 upper size bound than 25 nm. The agreement between results estimated using Eq. (1) and (8) is because that the estimation of 210 CoagSnk tends to be more accurate when using an average $CoagS_m$ in a narrower size range and the underestimation in this 211 case is coincidently cancelled out by the overestimation of formation rate caused by neglecting *CoagSrc*.

212 The importance of coagulation scavenging among newly formed particles due to nucleation is illustrated in Fig. 4. Scavenging 213 due to coagulation with particles smaller than d_p is neglected, as mathematically defined in the formula in Fig. 4(a). CoagSnk 214 increases rapidly with the decrease in d_p rather than maintain an approximately constant value during NPF periods, indicating 215 coagulation among nucleated particles contribute a considerable fraction to CoagSnk in Beijing. The necessity of sub-3 nm 216 particle size distribution is also demonstrated, which means estimated J_3 may also be underestimated due to the absence of 217 sub-3 nm data, as illustrated in Appendix B. Approximation of CoagSnk estimated using a representative $CoagS_m$ is also shown 218 in Fig. 4(b), indicating the underestimation of new particle formation rate when applying Eq. (5) to analyse NPF events in 219 Beijing. However, calculated CoagSnk on a non-NPF event day as well as at non-NPF periods on NPF day is almost unaffected 220 by the coagulation scavenging effect of particles in nucleation mode (smaller than 25 nm), because number concentration of 221 nucleation mode particles at non-NPF time is comparatively low.

222 **4.3** Characteristics of estimated formation rate in Beijing

223 For NPF events observed in the Beijing campaign, CoagSnk is a governing component of the estimated $J_{1.5}$. Estimated 224 formation rate on March 13th and the four terms in the RHS of Eq. (1), i.e., dN/dt, CoagSnk, CoagSrc, and the condensational 225 growth term, are shown in Fig. 5. CoagSnk is almost the same with the estimated $J_{1.5}$ in Beijing, while the difference between 226 them is mainly due to dN/dt whose absolute value is comparatively higher at the beginning and the end of the NPF event. The condensational growth term, $n_u \cdot GR_u$, is negligible compared to other terms, which is reasonable since J_u is supposed to be 227 228 unimportant when determining d_u in Eq. (1). The governing role of *CoagSnk* in estimated formation rate in Beijing emphasizes 229 the importance of fully considering the coagulation scavenging effect among particles formed by nucleation. Equation (5)-(9) 230 may fit well in relatively clean atmospheric environment where new particle formation rate is comparatively low, such as in 231 Hyytiälä, and agreement of Eq. (8) and Eq. (9) has been reported in a numerically simulated NPF event in which J_3 is less than 232 1 cm⁻³s⁻¹ (Vuollekoski et al., 2012). However, problems appear when applying them in urban Beijing because of 233 underestimating the governing fraction of estimated $J_{1.5}$, i.e., *CoagSnk*.

234 Coagulation sink, CoagS, is not the major reason for the governing role of CoagSnk in Beijing. It is generally considered that 235 the atmosphere in typical urban area in China, such as Beijing, is comparatively polluted. However, observed NPF events 236 mainly occurs on clean days when the air mass comes from north or northwest of Beijing. Mean PM_{2.5} mass concentration 237 reported by the nearest national monitoring station, Wanliu station, was 10.4 µg/cm³ during all NPF events in this campaign. 238 Aerosol surface area concentration is characterized by Fuchs surface area, A_{Fuchs} (McMurry, 1983), and condensation sink, CS 239 (Kulmala et al., 2001), which are often used to examine the coagulation scavenging effect. The positive correlation between 240 A_{Fuchs} and CS is illustrated in McMurry et al. (2005), while CS can be regarded as the CoagS of sulphuric acid molecules. Fig. 241 6(a) shows the comparison of A_{Fuchs} and CS in Beijing to those in other locations around the world. A_{Fuchs} and CS during NPF 242 events in this study are higher than those in Hyytiälä, similar to those observed in Boulder, and lower than those in Atlanta, 243 Mexico City, and New Delhi. This indicates coagulation sink in urban Beijing on NPF days is in common range rather than 244 higher than most other places around the world.

Nucleation intensity in urban Beijing, characterized by number concentration of particles larger than 3 nm, is found to be higher than those in Hyytiälä and Atlanta (as shown in Fig. 6(b)). Number concentration of sub-3 nm particles is not accounted for to maintain comparability. Although A_{fuchs} and CoagS represent the relative importance of the coagulation scavenging effect (McMurry, 1983; Kulmala et al., 2001), it is the CoagSnk that reflects the number of particles lost due to coagulation scavenging in the size range of d_k to d_u . Equation (1) shows that CoagSnk is approximately proportional to the square of particle number concentration. This explains the governing status of CoagSnk in estimated formation rates in urban Beijing in intense NPF events.

252 Fig. 7 further illustrate the underestimation in new particle formation rates in China due to previously used formulae, especially 253 for Eq. (7) which neglects coagulation among sub-25 nm particles and Eq. (9) which simply neglects net coagulation effect. 254 Mean $J_{1.5}$ estimated in this study using Eq. (5), Eq. (7), and Eq. (9) are 87.1%, 41.1% and 15.7% of that estimated using Eq. 255 (1). Mean J_3 estimated using Eq. (5), Eq. (7), and Eq. (9) are 87.3%, 49.9% and 30.7% of that estimated using Eq. (1). J_3 256 reported in previous studies in urban Beijing (Wu et al., 2007; Yue et al., 2009; Wang et al., 2013; Wang et al., 2015), Shanghai 257 (Xiao et al., 2015) and Shangdianzi, the regional background station of North China Plain (Shen et al., 2011; Wang et al., 258 2013), are also shown in Fig. 7. Higher formation rates are anticipated if the coagulation scavenging effect are fully considered 259 when analysing these NPF events. Note that sub-3 nm particles is also accounted when calculating J_3 in this study, while not 260 in previous ones except for the campaign in Shanghai.

261 4 Conclusions

262 A new balance formula to estimate new particle formation rate derived from aerosol general dynamic equation was proposed. 263 The new formula estimates the effect of coagulation scavenging better compared to previously used ones. Two criterions in 264 determining the upper bound for calculation were proposed. A NPF campaign in urban Beijing was carried out in spring of 265 2016. Aerosol size distributions down to ~ 1 nm was measured and used to test the new formula and those widely used ones in 266 previous studies. It was found that formation rates in urban Beijing are underestimated to different extents in previously used 267 formulae, and the underestimation of the coagulation scavenging effect (corresponding to coagulation sink term) is the major 268 reason. Coagulation among particles in nucleation mode was found to be important when estimating the coagulation 269 scavenging effect in urban Beijing and neglecting it can lead to an average 58.9% underestimation in the estimated formation 270 rate of 1.5 nm particles. Coagulation sink term is the governing component of the estimated formation rate in urban Beijing. 271 Although higher than those in relative clean atmosphere such as in Hyytiälä, coagulation sink (expressed in the form of Fuchs 272 surface area and condensation sink) in urban Beijing on NPF days is lower than those reported in Atlanta and Mexico City. 273 However, number concentration of particles formed due to nucleation in urban Beijing is comparatively high, which lead to 274 high coagulation loss. Formulae used in previous studies may perform well when describing relative weak NPF events in clean 275 atmosphere, while they underestimate the coagulation scavenging effect when analysing intense NPF events. Formation rates 276 reported in previous studies for urban Beijing and other locations with intense NPF events might be underestimated because 277 of their underestimation or neglect of the coagulation scavenging effect.

278 Appendix A

279 Derivation of nucleation rate from aerosol general dynamic equation

Nucleation rate is the rate at which particles grow past the size of the critical cluster (nuclei). However, a more specific and microscopic definition of nucleation rate is needed for any further calculation, and it should be easily and unambiguously transferred into a mathematical expression. Here we adopt the definition based on droplet current (Eq. 10.1, Friedlander, 2000): $J_g = \beta_{(1,g-1)} N_1 N_{g-1} - \alpha_g s_g N_g$. (A1)

Formation rate, J_g , is the excess rate of the passage from g-1 (cluster or particle with g-1 molecules) to g by condensation over the passage from g to g-1 by evaporation. If g is the size of the critical cluster, J_g is defined as nucleation rate, I. N_g is the number concentration of cluster g; $\beta_{(i,j)}$ is the coagulation coefficient of i and j, and it can be theoretically estimated by diameter of i and j (Eq. 13.56, Seinfeld & Pandis 2006); α_g is the monomer evaporation flux from g; and s_g is the effective surface area of g for evaporation. Only formation due to condensational growth is considered in the definition of Eq. (A1), while formation due to coagulation of smaller clusters is not taken into account. This is based on the assumption that critical clusters are mainly

- 290 formed due to condensational growth of sulfuric acid and other chemical species. The formation of critical cluster by 291 coagulation does not influence the generality of the following derivation and can be readily incorporated, and it will be clarified
- 292 at the end of Appendix A.
- The other basic equation for the derivation is the general dynamic equation in the discrete form (Eq. 11.3, Friedlander 2000), $\frac{dN_g}{dt} = \frac{1}{2} \sum_{\substack{i+j=g\\i+j=g}} \beta_{(i,j)} N_i N_j \sum_{i=2} \beta_{(i,g)} N_i N_g + \beta_{(1,g-1)} N_1 N_{g-1} \beta_{(1,g)} N_1 N_g \alpha_g s_g N_g + \alpha_{g+1} s_{g+1} N_{g+1}$ (12) 293 294 (A2)

295 As shown in Eq. (A2), time rate of change of cluster or particle number concentration, dN_g/dt in the left-hand side (LHS), is 296 determined by formation due to coagulation of smaller clusters and (or) particles, coagulation scavenging with pre-existing 297 clusters and particles, condensational growth from g-1 and to g+1, and evaporation to g-1 and from g+1, corresponding to the 298 six terms in the right-hand side (RHS) of Eq. (A2), respectively. The evaporation terms (corresponding to the fifth and sixth 299 terms in the RHS) may be zero or nearly zero when g is large, however, their exact values have no influence on derivation. An 300 important assumption to be noted is that meteorological transport, dilution, primary emission of g and other losses (e.g., wall 301 loss) are not included in Eq. (A2).

302 Notice that the last four terms in the RHS of Eq. (A2) are equal to $J_g - J_{g+1}$ by substituting Eq. (A1) in. Replacing subscript g

303 with the critical cluster size, k, we have:

$$I := J_k = \frac{dN_k}{dt} + \sum_{i=2}^{\infty} \beta_{(i,k)} N_i N_k - \frac{1}{2} \sum_{\substack{i+j=k\\i,j\geq 2}} \beta_{(i,j)} N_i N_j + J_{k+1}$$
304 (A3)

- 305 The expression of Eq. (A3) is similar to Eq. (A6) in Kuang et al. (2012), which was also obtained using the balance method. J_{k+1} is usually a relatively large term in Eq. (A3), and it can be accounted for by iteration. Equation (A5) is obtained by $I - J_{k+1} = \frac{dN_k}{E!} + \sum_{i=1}^{+\infty} \beta_{(i,k)} N_i N_k - \frac{1}{2} \sum_{i=1}^{\infty} \beta_{(i,j)} N_i N_j$ summing E! I (A3) up from subscript k to u-1 as shown in Eq. (A4), where u is the particle size at the upper bound of the 306
- 307 $\cdot \cdot dN$

$$I = \frac{d\sum_{g=k}^{u-1} N_g}{dt} + \sum_{g=k}^{u-1} \sum_{i=2}^{+\infty} \beta_{(i,g)} N_i N_g - \frac{1}{2} \sum_{g=k}^{u-1} \sum_{\substack{i+j=g\\i,j\geq 2}} \beta_{(i,j)} N_i N_j + J_u$$
10
(A5)

3

311 In the RHS of Eq. (A5) are the time rate of change of the particle concentration, the coagulation sink term, the coagulation 312 source term and the condensational growth term, respectively. Note that when particle u is large enough, J_{u} is nearly zero, i.e., $\lim_{u\to\infty} J_u = 0$, because of their negligible condensational growth and low number concentration compared to those of freshly

nucleated small particles. Equation (A6) is obtained by replacing the upper bound, u, with infinite and further simplified by
combining the second and third term in the RHS of Eq. (A5).

316
$$I = \frac{\frac{d \sum_{g=k}^{N_g}}{\partial t} + \frac{1}{2} \sum_{g=k}^{+\infty} \sum_{i=k}^{+\infty} \beta_{(i,g)} N_i N_g}{\sum_{g=k}^{N_g} N_i N_g}$$
(A6)

Theoretically, Eq. (A6) can be used to estimate *I* since each term in the RHS can be calculated. However, the validity of Eq. (A6) faces higher risk of violation when applied in real atmosphere due to non-negligible primary emission sources, since Eq. (A6) is a balance equation for the whole aerosol population rather than a limited size range of the nucleation mode. It's both more cautious and efficient to use Eq. (A5) with a proper particle size u and a reasonable estimation of J_u .

When using measured particle size distribution to estimate *I*, Eq. (A5) has to be converted from the discrete form into the continuous form, i.e., Eq. (A7). Since measured size bins are finite, Eq. (A7) is expressed in the summation form rather than the integration form. Practically, Eq. (A7) is only an estimation of Eq. (A5) because coagulation is calculated by size bins, differentiation form. Practically, Eq. (A7) is only an estimation of Eq. (A5) because coagulation is calculated by size bins, while particles size size size size as the second size bins are finite, Eq. (A6) because coagulation is calculated by size bins, define particles size size size as the second size bins are finite, Eq. (A6) because coagulation is calculated by size bins, define particles size size as the second size as the second size bins because coagulation is calculated by size bins, define particles size size as the second size as the second size bins because coagulation is calculated by size bins, define as the second size bins are finite, Eq. (A7) because coagulation is calculated by size bins, define as the second size bins as the second size bins because coagulation is calculated by size bins, define as the second size bins are finite, Eq. (A7) because coagulation is calculated by size bins, define as the second size bins are finite, Eq. (A7) because coagulation is calculated by size bins, define as the second size bins are finite, Eq. (A7) because coagulation is calculated by size bins, define as the second size bins are finite, Eq. (A7) because coagulation is calculated by size bins, define as the second size bins are finite, Eq. (A7) because coagulation is calculated by size bins, define as the second size bins are finite, Eq. (A7) because coagulation is calculated by size bins, define as the second size bins are finite, Eq. (A7) because coagulation is calculated by size bins, define as the second size bins are finite, Eq. (A7) because coagulation is calculated by size bins, define as the second size bins are finite, Eq. (A

(A7)

325

 d_{min} is theoretically the minimum cluster size. The defined relationships, $d_i^3 + d_{j+1}^3 = d_g^3$ and $d_i^3 + d_{j+1}^3 = d_g^3$, are to assure 326 that all particles smaller than d_{y} are accounted for only once. Note that the size bin from d_{u-1} to d_{u} is denoted by subscript u-1, 327 so the upper bound of the size range for calculation is d_u . $N_{[d_k,d_u)}$ is defined as the number concentration in the size range 328 from d_k to d_u (particles with diameters of d_u are not accounted for), corresponding to $\sum_{g=k}^{u-1} N_g$ in the discrete from. d_u is a "proper 329 large" size at which diameter J_{μ} is negligible compared to the sum of the others three terms in the RHS of Eq. (A7). "Proper 330 331 large" is defined by the following two criterions: the one is d_u shouldn't be too large so that the calculated nucleation rate is 332 non-negligibly affected by transport or primary emissions; the other is d_u shouldn't be too small so that the calculated 333 nucleation rate is underestimated because J_u is still too large to be neglected or to be estimated by growth rate (as illustrated in the following paragraph). These two criterions seem to be contradictory, however, as illustrated in Fig. 2b, calculated 334 335 nucleation rate is usually not sensitive to the upper bound because J_u decreases rapidly with the increase of d_u since the freshly 336 nucleated particles are usually in a relatively narrow size range, especially during strong NPF events.

The fourth term in the RHS of Eq. (A7), J_u , is usually so small that it can be simply neglected when d_u is proper large. However, an approximate term is recommended for better estimation. Here we introduce a sufficient but possibly unnecessary condition that net coagulation effect between any particle larger than d_u and other particles can be neglected. Define $\frac{N_{[d_u, d_u + \Delta d)}|_r}{r}$ as

- number concentration of particles in a narrow size range from d_u to $d_u + \Delta d$ at time t. After a very short time dt, these particles
- 341 grow into the size range from d_u +dd to d_u + Δd +dd, which is based on the assumption that diameter growth is equal for different
- 342 particles in such narrow size and time range, while number concentration remains the same since there is no particle loss.
- Particles in the size range from $d_u + \Delta d$ to $+\infty$ at time t grow up to the size range from $d_u + \Delta d + dd$ to $+\infty$, correspondingly. And
- 344 since the size range is narrow enough, it's reasonable to assume that concentration of particles is equally distributed in the size

345 range from
$$d_u$$
 to $d_u + \Delta d + dd$, i.e.,

$$\frac{N_{[d_i,d_j)}}{N_{[d_m,d_n]}} = \frac{d_j - d_i}{d_n - d_m}, \text{ for any } d_i, d_j, d_m, d_n \in [d_u, d_u + \Delta d + dd)$$
(A8)

Particle size distribution function, *n*, and growth rate, *GR*, are defined as Eq. (A9) and A(10), respectively. Equation (A11) is

obtained by combining Eq. (A6), Eq. (A8), Eq. (A9), and Eq. (A10).

$$n_{u} = \frac{\mathrm{d}N}{\mathrm{d}d}\Big|_{d_{u}} = \lim_{\Delta d \to 0} \frac{N_{[d_{u}, d_{u} + \Delta d]}}{\Delta d}$$
(A9)

$$GR_{u} = \frac{dd}{dt} \Big|_{du} = \frac{dd}{dt} \Big|_{du} \Big|_{du} = \frac{dd}{dt} \Big|_{du} \Big|_{du} \Big|_{du} \Big|_{du}$$
(A10)

$$351 = \frac{N_{[d_u, d_u + \mathrm{d}d]}\Big|_{t+\mathrm{d}t} + N_{[d_u + \mathrm{d}d, +\infty)}\Big|_{t+\mathrm{d}t} - N_{[d_u, +\infty)}\Big|_{t}}{\mathrm{d}t}$$

$$352 = \frac{N_{[d_u,d_u+dd)}\Big|_{t+dt}}{dt}$$
$$= \lim_{\Delta d \to 0} \frac{dt}{N_{[d_u,d_u+dd)}\Big|_{t+dt}}}{N_{[d_u+dd,d_u+\Delta d+dd)}\Big|_{t+dt}} \cdot M_{[d_u+dd,d_u+\Delta d+dd)}\Big|_{t+dt}}$$
$$= \lim_{\Delta d \to 0} \frac{dd}{\Delta d \cdot dt} \cdot N_{[d_u,d_u+\Delta d)}\Big|_{t}$$

$$= n_u \cdot GR_u \tag{A11}$$

355 Finally combining
$$d_{d}$$
 $d_{g}=d_{k}$ $d_{d}=d_{min}$ $d_{g}=d_{k}$ $d_{d}=d_{min}$ d_{d} $d_{g}=d_{k}$ $d_{d}=d_{min}$ d_{d} $d_{g}=d_{g}$ d_{g

The first term in the RHS of Eq. (A12) is the change in the number concentration of particles ranged from d_k to d_u . The second and third terms are particle loss to coagulation scavenging and particle formation by coagulation, named as coagulation sink term (*CoagSnk*) and coagulation source term (*CoagSrc*), respectively (Kuang et al, 2012). The fourth term is the condensational growth term, which is an approximation of the formation rate, J_u . This balance formula derived from aerosol general dynamic equation can also be expressed as Eq. (A13).

$$I = \frac{dN_{[d_k,d_u]}}{dt} + CoagSnk - CoagSrc + n_u \cdot GR_u$$
(A13)

363 When applying Eq. (A12) in practice, d_k is usually the assumed size of the critical nuclei (or the lowest size limit of instrument, 364 corresponding to formation rate, J_k , rather than nucleation rate, I). The dN/dt term can be obtained either by differentiating 365 between adjacent time bins or fitting in a continuous time period. CoagSnk and CoagSrc can be directly calculated from particle size distribution, where d_{min} is the minimum detected particle diameter. If formation by coagulation of smaller clusters is also 366 367 included in the definition of nucleation rate, calculation of CoagSrc (the third term in the RHS of equation A(12)) should begin 368 with d_{k+l} instead of d_k , which usually affects little since the difference is only a size bin and the whole *CoagSrc* is usually a 369 minor term of J in atmosphere environment. Growth rate can be estimated by different methods (Weber et al., 1996; Weber et 370 al., 1997; Kulmala et al., 2012; Lehtipalo et al., 2014), or the growth term can be simply neglect if d_u is proper large.

It should be clarified that the formation rate calculated using Eq. (A12) may be underestimated because coagulation scavenging by particles and clusters smaller than d_{min} is neglected due to the limitation of measuring instruments. As illustrated in Fig. 6(a), *CoagSnk* calculated using d_p larger than 3 nm is ~ 89.1% of that using d_p larger than 1.5 nm. It could be inferred that the calculated J_3 was slightly underestimated in some previous studies lacking size distribution for sub-3 nm particles. While in this study, measured particles down to 1.3 nm are accounted for when calculating $J_{1.5}$ and J_3 . Neglecting coagulation between clusters may also have a non-negligible effect on the calculated results (McMurry 1983), which calls for measurement of major molecular clusters participating in nucleation if more accurate formation rate is to be obtained.

378 Appendix B

379 Relationships with previous approaches

Since the new balance approach proposed in this study is based on aerosol general dynamic equation with a reasonable assumption that net coagulation of any particle larger than the "proper large" upper bound, d_u , and other particles can be neglected, its inner relationships with former approaches can be elucidated by making additional assumptions and approximations.

Formation rate is defined as the flux that particles grow pass through the given size, and can be expressed as Eq. (B1), where k is the number of molecules contained by the particle (Heisler & Friedlander, 1977; Weber et al., 1996; Kuang et al., 2008; Kuang et al., 2012). Note that Eq. (B1) is valid only when it is in the continuous space of particle diameter, while a more accurate expression in the discrete form is shown as Eq. (B2). $J_k = n_k \cdot GR_k$ (B1)

$$J_k = n_{k-1} \cdot GR_{k-1} \tag{B2}$$

- 390 Eq. (B2) is believed to be theoretically correct since the only condensational flux into d_k is the growth of smaller clusters or
- 391 particles with diameter of d_{k-1} . Although in similar expression with Eq. (A11), Eq. (B2) focuses on the flux into rather than out
- 392 of the size bin for calculation, and there's no need to account for coagulation scavenging, as illustrated in Fig. 1.
- 393 A theoretical expression of GR proposed in previous study is shown as Eq. (B3), where α is herein the coagulation efficiency 394 (fraction of collisions that successfully result in coagulation), V_1 is the volume increment when adding a single gaseous 395 precursor, and v is the mean thermal velocity of the gaseous precursor (Weber et al., 1996). Here we update the equation by 396 considering different chemical species and describing coagulation by β , as shown in Eq. (B4). The subscript c denotes different 397 chemical species of monomers participating in the condensational growth of cluster k-1, and N_{1c} is their corresponding number
- 398 concentration. Coagulation efficiency is included in each $\beta_{(1c,k)}$ (Eq. 13.56, Seinfeld & Pandis 2006). $GR_k = \frac{\alpha V_1 N_1 v}{2}$

400

$$GR_{k-1} = \frac{\sum_{c} \beta_{(1c,k-1)} N_{1c} N_{k-1}}{n_{k-1}}$$
(B3)
(B4)

401 Eq. (B2) is theoretically correct, however, it faces difficulties when applying in practice, since n_{k-1} is obtained by approximation 402 over some size range around d_k rather than the true frequency density at cluster k-1, dN_{k-1}/dd_{k-1} . Moreover, because size 403 distribution smaller than d_k is difficult to obtain, the size range for estimation is usually larger than d_k . For example, the formula 404 to estimate J_3 using nano-SMPS data in Kuang et al. (2008) is shown as Eq. (B5). Although Eq. (B5) seems to be an estimation 405 of Eq. (B2), they are essentially two different equations. This is because the measured particle number concentration in the 406 size range for calculation, i.e., N_{3-6} in Eq. (B5), has been affected by coagulation. By comparing with Eq. (A13), it can be 407 concluded that dN/dt, CoagSnk and CoagSrc are simply neglected in Eq. (B5), while Eq.(B2) does not suffer from this problem 408 by its definition.

409
$$J_{3} \approx \frac{N_{3-6}}{3 \text{ nm}} \cdot GR_{1-3}$$
(B5)

410 There are also problems in estimating GR_{k-1} . Equation (B4) is only a theoretical formula, since it is nearly impossible to 411 determine all the chemical species contributing to nucleation and their corresponding coagulation coefficients in the 412 complicated atmospheric environment. GR calculated by sulfuric acid itself using Eq. (B3) may lead to underestimation (Kuang 413 et al., 2010), while uncertainties also exist in the approaches which fit particles size distribution to obtain GR (Kulmala et al., 414 2012; Lehtipalo et al., 2014) because the effect of coagulation on measured size distribution is also neglected. So conclusively, 415 Eq. (B2) is considered to be theoretically correct, however, it's not recommend to be applied for analyzing NPF events with 416 high coagulation scavenging.

417 The other approach is a balance method based on a macroscopic point of view shown as Eq. (B6) (Kulmala et al., 2001; 418 Kulmala et al., 2004), and here we adopt the equation in the most recent paper (Kulmala et al, 2012). Usually d_m is the geometric 419 mean diameter of d_k and d_u . However, coagulation between any particle smaller than d_m or even d_u with another particle (with 420 any size) is sometimes neglected when it comes to calculation, such as the formula suggested in Kulmala et al (2012) shown

421 as Eq. (B7).

$$J_{k} = \frac{dN_{[d_{k},d_{u})}}{dt} + CoagS_{m} \cdot N_{[d_{k},d_{u})} + \frac{N_{[d_{k},d_{u})}}{(d_{u} - d_{k})} \cdot GR_{[d_{k},d_{u})}$$
(B6)

423

$$CoagS'_{m} = \sum_{d_{i}=d_{m}}^{+\infty} \beta_{(i,m)} N_{i}$$
(B6)
(B7)

424 Eq. (B6) appears similar to Eq. (A13) since they both originate from the population balance method, however, there are some 425 differences between them.

(B7)

426 Firstly, the upper bound of particle size in Eq. (B6), d_u , is lack of strict definition and discussion. As discussed in Appendix A, 427 d_u should be decided by the two criterions that effects of transport and primary emission are negligible and the condensational 428 growth term, J_{u} , is relative small compared to J_k . The upper bound of 25 nm is usually reasonable since high concentration of 429 particle formed by nucleation predominates the coagulation sink term during strong new particle formation time, while the 430 upper bound of 6 nm may lead to underestimation when freshly formed particles grow beyond, as discussed in the main text.

431 Secondly, scavenging by coagulation with particles smaller than d_m is not included if using Eq. (B7) to calculate CoagS. As shown in Fig. B1, *CoagS* is always larger than CoagS', and their difference increases as d_m increases. $CoagS'_{8nm}$ is ~31% of 432 $CoagS_{8nm}$, indicating a large amount of underestimation when using Eq. (B7). Note that Eq. (3) and the approximation formula 433 434 (estimated with condensation sink) proposed by Lehtinen et al. (2007) does not suffer from this problem.

435 Thirdly, the second term in the RHS of Eq. (B6) is not always a reasonable approximation of *CoagSnk* in Eq. (A12) and Eq. 436 (A13). Theoretically, the relationship between CoagSnk and CoagS is shown as Eq. (B8), while $CoagS_m$ is chosen as the 437 representative value when estimating J using Eq. (B6).

$$CoagSnk = \sum_{d_g=d_k}^{r_u} CoagS_g \cdot N_g$$
(B8)

439 However, neither is CoagS a relatively constant value versus particle diameter nor is $CoagS_m$ the mean value of CoagS in calculated size range from d_k to d_u . As illustrated in Fig. B1, coagulation coefficient with 8 nm particles decreases rapidly with 440 the increase in d_i when particle is smaller than 8 nm. The minimum value of $\beta_{(d_i,8nm)}$ appears at d_i around 8 nm because 441 particles with similar thermal velocities are more difficult to collide with each other. The calculated CoagS' during a strong 442 NPF event on Mar. 27th, 2016 appears monotonously decreasing with the increase of d_m , while the calculated CoagS has a 443 minimum value at 6.7 nm because CoagS is mainly attributed to nucleation mode particles during NPF events. In this example, 444 $CoagS_{8nm}$ and $CoagS_{8nm}$ are ~22.6% and ~7.2% of $CoagS_{1.5nm}$, respectively, indicating non-negligible underestimation of 445 446 coagulation sink term as well as nucleation rate when using a constant $CoagS_m$ instead of a varying value (as a function of 447 particle diameter).

448 Fourthly, particle formation by coagulation is neglected in Eq. (B6). The absence of *CoagSrc* will lead to an overestimation of

449 nucleation rate. However, it sometimes coincidently cancels out with the underestimation caused by using $CoagS_m$ to 450 approximate CoagSrc, as discussed in the main text.

- 451 Fifthly, the growth term in Eq. (B6) is estimated over the whole size range from d_k to d_u , while in Eq. (A12) it is mathematically
- 452 restricted at the upper bound, d_u . n_u is usually smaller than mean value in the size range from d_k to d_u during a NPF event, and
- 453 recent work have revealed that the observed *GR* is size dependent (Kuang et al., 2012; Kulmala et al., 2013; Xiao et al., 2015).
- 454 For example, as shown in Fig. B2, *GR* varies with time in the NPF event on Apr. 3rd, 2016, and was linearly fitted in different
- diameter ranges. The mean GR of particles ranged from 2 nm to 25 nm is ~7.47 nm/h, while GR_{25} is ~10.86 nm/h. At 11:30
- 456 on Apr. 3^{rd} , n_{25} (dN/dlog d_p at 25 nm) is 164 #/cm³, while the mean *n* of particles ranged from 2 nm to 25 nm is 4755 #/cm³.
- 457 The calculated condensational growth term in Eq. (B6) is ~20 times of that in Eq. (A12).
- In relatively clean environment with weak NPF events, Eq. (B6) may work well since the calculated J_k is mainly predominated by dN/dt. However, when number concentration of aerosol formed by nucleation and (or) background aerosol is high, i.e.,
- 460 when CoagSnk is the major component of J_k , Eq. (B6) underestimates the formation rate (and nucleation rate) due to
- 461 underestimation of the coagulation scavenging effect.
- 462

463 Acknowledgement

- 464 Financial supports from the National Science Foundation of China (21422703, 41227805 & 21521064) and the National Key
- 465 R&D Program of China (2014BAC22B00 & 2016YFC0200102) are appreciated.

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627 Figure 1: Schematic of the general dynamic equation.



630Figure 2: Comparison of formation rates estimated using different upper bounds, d_u . (a) A typical new particle formation event.631Dashed gray lines represent different d_u in Eq. (1). Solid black lines corresponds to d_b , i.e., the varying upper bound determined by632 $dN/dlogd_p$. (b) Estimated formation rates with different upper bound, d_u , using Eq. (1). (c) Estimated formation rates with different

 d_k using Eq. (1). d_u equals 25 nm and d_{min} equals 1.3 nm in the four scatter plots.



636 Figure 3: Comparison of formation rates estimated by different formulae.





Figure 4: (a) CoagSnk as a function of d_p , where d_p is the accounted minimum diameter when calculating $CoagS_g$ for particles at all different d_g , and scavenging due to coagulation with particles smaller than d_p is neglected, as the defined by the formula in panel (a). The dashed line corresponding to CoagSnk on a non-NPF day is also monotonously decreasing with the increase of d_{min} by a negligible slope. (b) Time evolution of CoagSnk versus time on a NPF day (Mar. 13th) and a non-NPF day (Mar. 12th). d_p is defined the same with that in panel (a). N is the number concentration of particles in the size range from 1.5 nm to 25 nm, while $CoagS_{8nm}$ is calculated using Eq. (3).



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Figure 5: Contribution of each term to the estimated formation rate. dN/dt is obtained by fitting and shown in absolute value with solid and dashed lines corresponding to positive and negative parts, respectively. Note the upper bound, d_u , equals d_b as defined

649 section 4.1 for better accuracy, however, it doesn't affect the generality of the result.



651

652 Figure 6: (a) Comparison of Fuchs surface area and condensation sink in Beijing (when NPF events occurred) with those in other 653 locations. NPF days were classified by condensation sink in urban Beijing in 2004 (Wu et al., 2007). Condensation sink on NPF days 654 in New Delhi was reported by Kulmala et al. (2005). ANARChE (Mcmurry et al., 2005) and MILAGRO (Iida et al., 2008) were conducted in Atlanta and Tecamac, respectively, while EUCCARI (Manninen et al., 2009), QUEST II (Sihto et al., 2006), QUEST 655 656 IV (Riipinen et al., 2007) was conducted in SMEAR II (Dal Maso et al., 2005), Hyytiälä. AFuchs data in MILAGRO, ANARChE, 657 Boulder, EUCCARI, QUEST II, and QUEST IV were published in Kuang et al. (2010). The ends of coloured rectangular correspond 658 quartiles, while error bar represents the 10th and 90th percent value. (b) Comparison of peak number concentration of particles 659 larger than 3 nm during NPF events in this study with those in Atlanta and other published data. Note that the published values 660 (light orange points) in previous studies are not necessarily the mean values of the whole campaign periods.



Figure 7: Estimated $J_{1.5}$ and J_3 using different equations. Previously reported J_3 in China were included for comparison. The ends of coloured rectangular correspond to the minimum value and the maximum value, respectively. *: The upper size bound to estimate formation rate, d_u , is 6 nm (rather than 25 nm) in Wang et al., 2015 and Xiao et al., 2015.



Figure B1: Coagulation coefficient and calculated coagulation sink during a typical NPF event. *CoagS* and *CoagS'* are defined in Eq. (B7) and Eq. (B8), respectively, and d_m in this figure is treated as a variable rather than a constant value. The upper and lower star denote $CoagS'_{8nm}$ and $CoagS_{8nm}$ which are used in the second term in the RHS of Eq. (5) and Eq. (6) to approximate CoagSnk, respectively.



Figure B2: Size and time dependent growth rate on a NPF day observed in Beijing. Representative diameters are obtained by
lognormal fitting of nucleation mode particles in each time bin, and *GR* is linearly fitted in each section.