1 **A comprehensive study about the in-cloud processing of nitrate through**

2 **coupled measurements of individual cloud residuals and cloud water**

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25 **Key points**

26 • We show the direct observational evidence for the enhanced nitrate formation in the
27   cloud water and residual particles.

28 • The variation of in-cloud nitrate could be well predicted by the [NOx][O_3], droplets'
29   surface area, and temperature.

30 • Hydrolysis of N_2O_5 served as a potentially important route for the in-cloud formation of
31   nitrate even during the daytime.

32

33 **Abstract**

34   Nitrate aerosol has become an increasingly important component of fine particles. While

35 the formation and evolution of nitrate in airborne particles are extensively investigated, little

36 is known about the formation of nitrate in clouds. Here we present a detailed investigation

37 on the in-cloud formation of nitrate based on the size-resolved mixing state of nitrate in the

38 individual cloud residual and cloud-free particles by single particle mass spectrometry, and

39 the mass concentrations of nitrate in the cloud water and $PM_{2.5}$ at a mountain site (1690 m

40 a.s.l.) in southern China. The results show a significant enhancement of nitrate mass fraction

41 in cloud water and relative intensity of nitrate in the mass spectra of the cloud residual

42 particles, underlining a critical role of in-cloud processing in the formation of nitrate. Based

43 on the size distribution of relative intensity of nitrate in individual particles, we exclude the

44 gas phase scavenging of HNO_3 and the facilitated activation of nitrate-containing particles

45 as the major contribution for the enhanced nitrate. Regression analysis and theoretical

46 calculations further reveal that nitrate is highly related (R^2 = ~0.6) to the variation of

47 $[NO_x][O_3]$, temperature and droplet surface area in clouds. Accounting for droplet surface

48 area greatly enhances the predictability of the observed nitrate compared with using

49 $[NO_x][O_3]$ and temperature. Our results indicate a critical role of in-cloud formation of

50 nitrate via N_2O_5 hydrolysis, even during the daytime, attributed to the diminished light in

51 clouds. The detailed observation would benefit future investigations of the evolution and

52 oxidative impacts of nitrate.

53

1. Introduction

Aerosol nitrate is an increasingly important component of $PM_{2.5}$, in particular, contributing to haze formation in China (*Guo et al.*, 2014; *Wen et al.*, 2018; *Lu et al.*, 2019; *Tian et al.*, 2019; *Xu et al.*, 2019; *Fu et al.*, 2020; *Liu et al.*, 2020b; *Zheng et al.*, 2020). As a key inorganic component in cloud water, nitrate can also modify microphysical properties of cloud, influence aqueous-phase processes in droplets and affect ecosystem after wet deposition (*Schneider et al.*, 2017). Notably, aerosol nitrate is an important product in the cycling of odd nitrogen (*Chang et al.*, 2011; *Huang et al.*, 2018; *Zheng et al.*, 2020; *Zhang et al.*, 2021), playing significant roles in tropospheric ozone and OH production (*Scharko et al.*, 2014; *Kaur and Anastasio*, 2017; *Ye et al.*, 2017a; *Ye et al.*, 2017b), and contributing to net aerosol composition and radiative forcing (*Bauer et al.*, 2007; *Xu and Penner*, 2012; *Hauglustaine et al.*, 2014).

Aerosol nitrate originates from the oxidation of NOx, which refers to gas phase oxidation of NO_2 by the hydroxyl radical (OH) and then condensation (daytime chemistry) and the hydrolysis of N_2O_5 (nighttime chemistry) to nitrate in aqueous particles, initiated by the oxidation of NO_2 by ozone (O_3) to produce the NO_3 radical (*Seinfeld and Pandis*, 2006). In contrary to aerosol sulfate formation, which is dominated by aqueous phase reactions, both gas phase oxidation and the hydrolysis of N_2O_5 represent the major processes forming nitrate aerosols (*Chen et al.*, 2020; *Xiao et al.*, 2020). The formation mechanism and the associated controlling factors of aerosol nitrate at the ground level have been extensively investigated. Apart from precursors and oxidants, the formation and evolution of nitrate

75   depend on the availability of ammonia (NH_3) as well as environment conditions (e.g.,

76   temperature (T), relative humidity (RH)), and the presence of other ionic species in

77   particulate phase (*Chen et al.*, 2018; *Shi et al.*, 2019; *Chen et al.*, 2020; *Fan et al.*, 2021; *Lin*

78   *et al.*, 2021).

79   Comparatively, detailed observational investigations and the possible mechanisms

80   governing nitrate behavior upon in-cloud processes are scarce, although it is well-known

81   that clouds play an important role in the transport and transformation of tropospheric

82   pollutants (*Ervens*, 2015; *McNeill*, 2017; *Li et al.*, 2020b). *Drewnick et al.* (2007) and

83   *Prabhakar et al.* (2014) reported that the relatively enhanced nitrate in clouds was associated

84   with the composition of the activating cloud condensation nuclei (CCN), rather than

85   preferential scavenging of nitric acid (HNO_3) in clouds. Differently, there are also studies

86   highlighting the predominant role of nitric acid partitioning in nitrate formation in clouds, in

87   contrary to nucleation scavenging of sulfate (*Leaitch et al.*, 1988; *Hayden et al.*, 2008;

88   *Schneider et al.*, 2017). *Hayden et al.* (2008) also noted that potential contributions from

89   gas-phase N_2O_5 cannot be ruled out. However, the relative role of in-situ formation of nitrate

90   in clouds remains poorly quantified, and the controlling factors remain unclear. Therefore,

91   more detailed investigations are required to integrate the role of cloud in processing of nitrate

92   in the troposphere.

93   The aim of this study is to illustrate the in-cloud formation mechanisms of nitrate and

94   evaluate the relative contribution of each pathway to nitrate in cloud water for daytime and

95   nighttime. To this aim, the mixing state of individual cloud residual, interstitial and cloud-

96   free particles were measured in high-time resolution with a single particle aerosol mass

97   spectrometer (SPAMS). The combination of a counter flow virtual impactor (CVI) and

98   aerosol mass spectrometry (including SPAMS) allows for the high-time resolved

99   observations of size and chemical compositions of submicron cloud RES particles (*Hao et*

100   *al.*, 2013; *Boone et al.*, 2015; *Lin et al.*, 2017; *Zhang et al.*, 2017). In addition, cloud water

101   and PM$_{2.5}$ samples were collected, and the chemical compositions were measured to provide

102   additional quantitative evidence.

103

104   **2. Experimental section**

105   **2.1 Aerosol and cloud measurements**

106   Aerosol and cloud measurements were performed at the Mt. Tianjing site (24°41′56″N,

107   112°53′56″E, 1690 m a.s.l.) in southern China, as described in detail by *Lin et al.* (2017),

108   during 9 May – 4 June 2018 and 13 November – 9 December 2020. Cloud events can be

109   distinguished by a sudden drop of visibility (to < ~1 km) and a sharp increase of relative

110   humidity (RH) to > 95%, as record by sensors equipped with a ground-based counterflow

111   virtual impactor (GCVI) (Model 1205, Brechtel Mfg. Inc., USA) (*Lin et al.*, 2017). Overall,

112   nineteen cloud events (lasting more than six hours) were identified for 2018 spring and ten

113   for 2020 winter, as also marked in Fig. S1. The visibility was generally lower than 0.1 km

114   during the cloud events, versus as high as 80 km during cloud-free periods. Besides a

115   relatively long cloud event throughout 9 – 12 May, the cloud events were typically observed

116   during nighttime for 2018 spring, associated with a prominently diurnal variation of RH and

117   visibility. The RH during the daytime ranged between 70-80%, and raised to > 95% during

118   nighttime. The duration of cloud events was in a range of 6-24 hours for 2020 winter. Air

119   masses from the southern continental and marine areas dominated over the 2018 spring,

120   versus southwestern continental areas over the 2020 winter (Fig. S2), obtained by HYSPLIT

121   4.9 (http://ready.arl.noaa.gov/HYSPLIT.php) (*Draxler and Rolph*, 2012).

122   An incorporation of counterflow virtual impactor (CVI) or GCVI allows the separation

123   of interstitial gases and aerosols from cloud droplets that are evaporated to obtain the cloud

124   RES particles (*Pratt et al.*, 2009; *Bi et al.*, 2016; *Roth et al.*, 2016). Briefly, the GCVI was

125   applied to collect the cloud droplets with predefined size (7.5-8.5□ μm in the present study)

126   with the cloud RES particles as output after dried in the evaporation chamber (with an air

127   flow temperature at 40 °C) (*Shingler et al.*, 2012). The influence of cloud-free air can be

128   negligible as the number concentration of GCVI output particles was measured to be ~1 cm⁻

129   ³, but at a magnitude of $\sim 10^3$ cm^{-3} in the cloud-free air. In the present study, the number

130   concentration of the cloud RES particles sampled during the cloud events was at a level of

131   ~100 cm^{-3} on average. In addition, a PM$_{2.5}$ inlet was used to deliver cloud INT particles

132   during cloud events or cloud-free particles.

133

134   **2.2 SPAMS measurements and data processing**

135   A SPAMS (Hexin Analytical Instrument Co., Ltd., Guangzhou, China), an Aethalometer

136   (AE-33, Magee Scientific Inc.), and a scanning mobility particle sizer (SMPS; MSP

137   Cooperation) were deployed to characterize the physical and chemical properties of the

138   sampled particles. The instruments were connected downstream the GCVI or $PM_{2.5}$ inlets.

139   Cloud RES and cloud INT particles were alternately sampled with an interval of ~1 h during

140   some randomly selected cloud events. When there is no cloud, these instruments were

141   connected to the $PM_{2.5}$ inlet in order to measure the cloud-free particles. In the present study,

142   aerosol surface area (SA) for cloud-free particles were directly calculated from the size

143   distribution data obtained from SMPS, whereas it can only be estimated based on the same

144   data for the cloud residues assuming a mean droplet size at 7 μm. We recognize the possible

145   uncertainty, but the estimated SA should correlate with real values and thus does not affect

146   our conclusions.

147   The vacuum aerodynamic diameter (d_{va}) and mass spectral information for individual

148   particles could be obtained by the SPAMS (*Li et al.*, 2011). A brief description on the

149   performance of the SPAMS can also be found in the Supplement. Over the sampling period

150   for 2018 spring and 2020 winter, a respective ~20, 000, 000 particles with mass spectral

151   information were analyzed, using the FATEs toolkit based on Matlab (The MathWorks, Inc.)

152   (*Sultana et al.*, 2017). The particles were classified by an adaptive resonance theory-based

153   neural network algorithm (*Song et al.*, 1999), with the inputs of ion peak intensities. Seven

154   types with distinct mass spectral characteristics (Fig. S3), accounting for > 95% of all the

155   detected particles, were obtained for further analysis. Defined as fractional peak area of each

156   m/z relative to the sum of peak areas in a mass spectrum, relative peak area (RPA) is

157   generally applied to represent the relative amount of a species within a particle (*Jeong et al.*,

158   2011; *Healy et al.*, 2013). The presence of nitrate can be identified with ion peaks (defined

159   as five times the noise signal) at m/z -62 $[NO_3]^-$ or m/z -46 $[NO_2]^-$. Approximate 70-80% of

160   all the detected particles in the size range of 100-2000 nm contained nitrate ion signals for

161   our measurements.

162

163   **2.3 Cloud water/PM$_{2.5}$ collection and chemical analysis**

164   A Caltech Active Strand Cloud Water Collector (CASCC2) was applied to collect cloud

165   water (with droplet size > 3.5 μm). The average cloud liquid water content (LWC) for each

166   sampling period can be derived from the equation: $LWC = \Delta m / (\Delta t \times \eta \times Q)$, based on each

167   sample mass (Δm), duration time (Δt), flow rate ($Q = 5.8\ m^3\ min^{-1}$), and collection efficiency

168   ($\eta = 86\%$).

169   A total of 58 / 53 cloud water samples were collected over the nineteen / ten cloud events

170   for 2018 spring and 2020 winter, respectively, with the duration time ranging between 2 and

171   10 hours. The pH for collected samples were immediately measured using a pH meter

172   (Mettler Toledo, Switzerland) after filtered through a 0.22 μm filter, followed by kept at -

173   20 ℃ until the analysis.

174   PM$_{2.5}$ samples were collected on quartz filters using a PM$_{2.5}$ sampler (PM-PUF-300,

175   Mingye Instruments, China) at a flow rate of $300\ L\ min^{-1}$. The filter were pre-conditioned in

176   450 ℃ for 6 hours to eliminate the potential influence of organics. In total, 20 / 36 PM$_{2.5}$

177   samples were collected for the 2018 spring and 2020 winter, respectively. The samples were

178   kept at -20 ℃ immediately until further analysis. These samples are representative for the

179   cloud-free particles or cloud INT particles during cloud events.

180   Cloud water and PM$_{2.5}$ samples were analyzed with ion chromatograph (Metrohm 883

181   IC plus, Switzerland) for water soluble inorganic ions (Na$^+$, NH$_4^+$, K$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$, NO$_3^-$,

182   and SO$_4^{2-}$) and total organic carbon analyzer (Vario, Elementar, Gemany for 2018 samples

183   and TOC-V, Shimadzu, Japan for 2020 samples) for water soluble organic carbon (WSOC).

184   The overall uncertainty for the concentration of each species is calculated to be < 15% based

185   on parallel analyses. The nitrate mass fractions in cloud water and PM$_{2.5}$ were calculated by

186   dividing the nitrate concentration by the sum of the measured water-soluble inorganic ions

187   and water-soluble organic matter (estimated by 1.6*WSOC).

188

189   **2.4 Box modeling of nitrate formation in cloud**

190   A multiphase chemical box model (RACM-CAPRAM) was used to explain the nitrate

191   formation mechanisms. The model is and constrained by observations. It couples the

192   regional atmospheric chemistry mechanism version 2 (RACM2; including 363 chemical

193   reactions) and the chemical aqueous-phase radical mechanism version 2.4 (CAPRAM2.4;

194   including 438 chemical reactions) to account for gas- and aqueous-phase atmospheric

195   chemistry (*Ervens et al.*, 2003; *Wen et al.*, 2018). This model has been utilized previously to

196   simulate the nighttime nitrate formation in Beijing and Shanghai (*Pathak et al.*, 2009).

197   The average concentration of NO$_2$ (~25 ppb) and O$_3$ (~100 ppb) for gas-phase precursors

198   and LWC (0.1 g m^{-3}) for cloud droplets, obtained from the in-situ measurements, were taken

199   as representative parameters for the atmosphere condition at Mt. Tianjing, and used as initial

200   conditions for model simulation. The detailed initial conditions for the model are listed in

201   the SI Table S1. Several comparisons through varying the LWC and photolysis rate were

202   considered in order to investigate the role of LWC and photolysis on the formation of nitrate

203   in the cloud. Three major pathways for nitrate formation are considered in this model: (1)

204   The oxidation of NO_2 by the OH radical produces HNO_3 and partitioning of gaseous HNO_3

205   into the aqueous phase; (2) The hydrolysis reactions of N_2O_5; and (3) The aqueous-phase

206   reactions of NO_3 radicals.

207

208   **3. Results and discussion**

209   **3.1. Enhanced in-cloud production of nitrate**

210   Figure 1 shows the statistical results of the nitrate mass fractions in cloud water and

211   $PM_{2.5}$ and the hourly average RPA of nitrate in the cloud-free, cloud residual, and cloud

212   interstitial particles. It can be seen that the mass fraction of nitrate in cloud water (~20% on

213   average) is obviously higher than those in $PM_{2.5}$ (< 15% on average) during cloud-free

214   periods and cloud events for both 2018 spring and 2020 winter. Consistently, RPA of nitrate

215   was substantially enhanced in the cloud INT particles and particularly cloud residues,

216   relative to the cloud-free particles. The influence of air mass on the enhanced nitrate can be

217   ruled out for 2018 spring as they similarly originated from southern areas over the whole

218   campaign period (Fig. S2). While the air masses originated from several regions during 2020

219   winter, they did not show the difference between cloud-free periods and cloud events (Fig.

220   S2). Therefore, such enhancement points to the in-situ formation, preferential update of nitric

221   acid and/or scavenging of nitrate-rich particles during cloud processing.

222   There are several pathways that might contribute to the enhanced nitrate in cloud

223   droplets, including (1) the scavenging of gas-phase HNO_3, (2) the preferential activation of

224   nitrate-rich particles, and (3) in-cloud aqueous production of nitrate via reaction of NO_3

225   radicals or hydrolysis of N_2O_5 (*Sellegri et al.*, 2003; *Fahey et al.*, 2005; *Hayden et al.*, 2008).

226   The mechanism via the dissolution of NO_2 and its aqueous phase oxidation is relatively slow

227   and unlikely to be a significant source of cloud water nitrate (*Seinfeld and Pandis*, 2006).

228   We first exclude the scavenging of gas-phase HNO_3 as a major pathway through the

229   analysis of size distribution of nitrate RPA and RPA ratio (nitrate/sulfate), although all gas

230   phase HNO_3 could be scavenged and present in the aqueous phase in a typical cloud with

231   LWC > 0.1 g m^{-3} (*Seinfeld and Pandis*, 2006). As can be seen in Fig. 2, the RPA of nitrate

232   and RPA ratios of nitrate/sulfate distributes relatively stable over the measured size range,

233   which suggests that the gas phase scavenging of HNO_3 is not the dominant pathway in the

234   present conditions. This is because gas-phase mass transfer would lead to enhanced nitrate

235   in the smaller droplets with higher total surface area (*Drewnick et al.*, 2007). In contrast,

236   sulfate is mainly due to nucleation scavenging which, depending on the size distribution of

237   preexisting aerosols, could result in being shifted toward larger sizes. As also discussed in

238   the following section, the formation of HNO_3 would be certainly suppressed by the presence

239   of cloud.

240   We also indicate that the contribution of preferential activation of nitrate-rich particles

241   should also be limited since such a process would lead to depletion of nitrate in the cloud

242   interstitial particles relative to the cloud-free particles. But this is not the case, as the RPA of

243   nitrate and RPA ratios of nitrate/sulfate in the cloud interstitial particles are considerably

244   higher than those in the cloud-free particles (Fig. 2). Both the enhanced nitrate in the cloud

245   residual and interstitial particles suggest the in-cloud formation of nitrate, although the

246   variation of RPA cannot provide a quantitative view. The enhancement of nitrate in the cloud

247   interstitial particles may also indicate that in-cloud condition facilitates the formation of

248   nitrate even in the inactivated particles. Similar results have also been observed in our

249   previous study for oxalate. Consistently, the formation of nitrate in the cloud interstitial

250   particles also grows their size towards the larger mode, i.e., cloud RES particles, compared

251   with the cloud-free particles (Fig. S4).

252

253   **3.2. In-cloud nitrate formation**

254   A theoretical estimation of nitrate production for 2020 winter is performed based on the

255   well-established kinetic characteristic of reactions between NO_2 and O_3 and uptake of N_2O_5

256   onto aerosol/droplet surfaces that formed HNO_3 (SI text S1), corresponding to the nighttime

257   chemistry. It is reasonable since the heterogeneous hydrolysis of N_2O_5 within aerosol

258   particles, fog, or cloud droplets has been shown to be much faster than homogeneous

259   hydrolysis under typical tropospheric conditions (*Chang et al.*, 2011; *Wang et al.*, 2017).

260   Through integrating the rate equations, as listed in SI text S1, the solution for aqueous phase

261   production of HNO_3 can be obtained (*Seinfeld and Pandis*, 2006):

262    $$[HNO_3] = \frac{[NO_x]}{2} \left\{ 1 + \frac{1}{\tau_{NO_x} - \tau_{N_2O_5}} \left[\tau_{N_2O_5} \exp\left(-\frac{t}{\tau_{N_2O_5}}\right) - \tau_{NO_x} \exp\left(-\frac{t}{\tau_{NO_x}}\right) \right] \right\}$$

263   Thus, the conversion of NOx to HNO_3 through the hydrolysis of N_2O_5 depends on the

264   two lifetimes τ_{NO_x} and $\tau_{N_2O_5}$, as defined by the reaction kinetics (SI text S1). The key

265   reaction that formed aqueous phase nitrate is related to the effective reaction of N_2O_5 on the

266   surface of wet aerosol or droplets (*Holmes et al.*, 2019), and therefore, depends on the

267   concentration of NO_2 and O_3 ($[NO_2][O_3]$), the available aerosol/droplet SA, and temperature.

268   Besides the reaction kinetics, temperature could also have influence on the hydrolysis of

269   N_2O_5 (*Chang et al.*, 2011; *Chen et al.*, 2018).

270   As shown in Fig. 3, the theoretically calculated in-cloud nitrate production assuming a

271   typical uptake coefficient of N_2O_5 $\gamma = 0.06$ (*Seinfeld and Pandis*, 2006) could well match the

272   measured nitrate concentrations well ($R^2 = 0.38$ and 0.60 with $p < 0.01$ for daytime and

273   nighttime, respectively), varying in a wide range of ~1 mg L^{-1} to ~60 mg L^{-1} for 2020 winter.

274   The correlation coefficients are obviously higher than those predicted using only $[NOx][O_3]$

275   ($R^2 = 0$ and 0.54 for daytime and nighttime, respectively). This is consistent with previous

276   results that the nighttime production of N_2O_5 and HNO_3 would be proportional to the

277   concentration of NO_2 and O_3 ($[NO_2][O_3]$) when assuming N_2O_5 and the NO_3 radical are both

278   in steady state considering their short lifetimes (*Wang et al.*, 2017; *Li et al.*, 2018). The result

279   also highlights the significance of SA in the in-cloud N_2O_5 hydrolysis in the build-up of

280   nitrate through in-cloud processing, even during the daytime. A further comparison of

281    $[NOx][O_3]$ and SA for the cloud events and cloud free periods, as shown in Fig. S5, also

282   supports the above discussion that the higher fraction of nitrate cannot be well explained by

283   the variations of $[NOx][O_3]$, but rather by the enhanced SA due to the presence of droplets

284   (Fig. S5b), which is > 5 times on average that for aerosol particles during cloud-free periods.

285 In the present study, the average LWC of cloud droplets is at a level of $\sim 10^5$ μg m^{-3}, 3-4

286 magnitude higher than those for urban haze conditions. As previously reported, high aerosol

287 LWC (campaign average at ~ 50 μg m^{-3}) induced fast heterogeneous uptake coefficient of

288 N_2O_5 is prevalent in urban haze (*Chang et al.*, 2011; *Wang et al.*, 2017), and results in

289 enhanced nitrate in highly humid condition (*Neuman et al.*, 2003; *Pathak et al.*, 2009; *Wang*

290 *et al.*, 2009).

291   The theoretical estimate indicates that the hydrolysis of N_2O_5 may substantially

292 contribute to the in-cloud production of nitrate even during the daytime, consistent with the

293 observation results as discussed in Section 3.1. It is also noted that theoretically predicted

294 nitrate production from the hydrolysis of N_2O_5 represents $\sim 5\text{-}10\%$ of the measured nitrate

295 (Fig. 3) based on our assumption. It explains $\sim 1\text{-}3\%$ increase in the nitrate mass fraction in

296 clouds, whereas the in-cloud processing contributed to $> 5\%$ increase (Fig. 1). One reason is

297 that the assumed $\gamma = 0.06$ might not be representative for N_2O_5 uptake in cloud droplets. It

298 is likely not a major reason since the previously reported γ for liquid water was generally of

299 the same magnitude, although some higher γ (0.2-0.4) was also observed for deliquescent

300 sodium sulfate particles (*Sander et al.*, 2015). Another reason is that the SA estimated by the

301 size distribution data of cloud residues obtained by the GCVI-SMPS only represents part ($<$

302 50%) of the cloud droplets, as GCVI was set to sample droplets larger than 8.0 μm in the

303 present study.

304   Furthermore, a simplified regression and a random forest analysis are also performed

305 for the high-time resolved RPAs of nitrate obtained by the SPAMS, with [NOx][O$_3$], SA,

306   and temperature as inputs, separated for the cloud RES and cloud-free particles, as detailed

307   in SI text S2. Note that the concentration of NOx is used here to replace the concentration of

308   NO_2, since most of NO data were not available for the 2018 spring. The effect should be

309   limited since NO could be negligible when the air masses are dominantly attributed to long

310   range transport, which could also be supported by the data (NO, ~0.1 μg m^{-3}, < 2% of NO_2

311   concentration) in 2020 winter. As expected, the nitrate RPA in the cloud RES particles is

312   highly correlated to the predicted ones (R^2 = 0.75 and 0.71 with p < 0.01 for daytime and

313   nighttime, respectively), even during the daytime (**Fig. 4**). An inclusion of temperature and

314   SA in the model substantially improves the correlation coefficient R^2, which is originally

315   0.16 and 0.31 between the nitrate RPA and [NOx][O_3] for daytime and nighttime,

316   respectively. Similarly, the correlation coefficients (R^2 = 0.45 and 0.66 for daytime and

317   nighttime, respectively) are lower for 2018 spring than 2020 winter, without the availability

318   of SA data. The results are generally consistent with those obtained from random forest

319   analysis, as shown in Fig. S6. Without the input of SA, [NOx][O_3] and temperature only

320   explains 52-61% of the observed nitrate RPA for cloud residual particles in 2018 spring,

321   compared with 72-80% in 2020 winter. Compared with the cloud residual particles, the

322   predictions for the nitrate RPA in the cloud-free particles are of lower coefficients. Such

323   difference between the cloud residual and cloud-free particles also reflects the critical role

324   of SA in the hydrolysis of N_2O_5 in cloud droplets.

325

326   **3.3. Relative importance of N_2O_5 hydrolysis pathway to nitrate in clouds**

327   The relative contribution of nitrate formation in cloud droplets and cloud-free particles

328   is also assessed using the CAPRAM model, as shown in Fig. 5. The relative contribution

329   difference between the cloud droplets and cloud-free particles is primarily attributed to the

330   different LWC setting, which is tightly linked to the cloud droplets' SA. Furthermore, the

331   comparison between cloud scenarios with different LWC setting (0.05 g m^{-3} versus 0.15 g

332   m^{-3}) also shows an enhanced contribution of N_2O_5 hydrolysis to nitrate with increasing LWC.

333   The result supports the above discussion that SA substantially facilitates the hydrolysis of

334   N_2O_5.

335   Nitrate is known to form predominantly by the hydrolysis of N_2O_5 ($> 80\%$) for both the

336   cloud droplets and cloud-free particles for the nighttime. However, both Fig. 3 and Fig. 4

337   indicate the potential importance of the heterogeneous N_2O_5 hydrolysis to nitrate formation

338   during the daytime. This is likely attributed to the substantial attenuation of the incident solar

339   radiation by clouds, in which the visibility was as low as < 0.1 km over this study. Previous

340   studies have also indicated the effect of clouds in the vertical redistribution of the

341   photochemical activity (*Liu et al.*, 2006; *Hall et al.*, 2018). Most comparatively, *Brown et al.*

342   (2016) observed a discrepancy between the modelled and observed N_2O_5 during a daytime

343   fog episode in Hong Kong, and attributed to the uptake of N_2O_5 to fog droplets. Their

344   calculation infers that daytime production of soluble nitrate via N_2O_5 can be substantially

345   faster than photochemical conversion through $OH+NO_2$ in the polluted fog episodes (*Brown*

346   *et al.*, 2016).

347   The model results in Fig. 5 with the consideration of photolysis rate are, to some extent,

348   consistent with our observations. The overall contribution of N_2O_5 hydrolysis pathways

349   increases by ~20% (from ~50-60% to ~70-80%) when the photolysis rate is reduced to 30%

350   of the default setting. For daytime only, the contribution of this pathway also increase from

351   nearly 0 to ~20% during noon hours and ~40% for morning hours. A similar model study

352   also indicates that N_2O_5 hydrolysis contributed to 30% of daytime nitrate formation at Mt.

353   Tai.(*Zhu et al.*, 2020) Attributed to the substantial attenuation of incident solar radiation by

354   clouds and high loading of $PM_{2.5}$, the daytime N_2O_5 hydrolysis has also been observed to be

355   an important formation pathway for nitrate in the haze episodes in Xi'an (China), increased

356   from 8.2% to 20.5% of the total nitrate over 14:00–16:00 by further model simulation,(*Wu*

357   *et al.*, 2021) and contributed ~10% of nitrate in the north China plain during daytime in

358   winter (*Liu et al.*, 2020a). Note that our model calculation represents a rough estimation of

359   relative contribution to the formation of nitrate, since biogenic volatile organic compounds

360   (which are not available or considered in our model calculation) could also have a potentially

361   important impact on nitrate formation through affecting the oxidant concentrations

362   (*Aksoyoglu et al.*, 2017; *Zhang et al.*, 2019), yet remains to be quantified.

363

364   **4. Conclusions and atmospheric implications**

365   The presented results provide direct evidence that in-cloud aqueous processing, in

366   particular, the hydrolysis of N_2O_5 contributing to the enhanced nitrate in cloud residues. We

367   highlight that hydrolysis of N_2O_5 serves as the critical route for the in-cloud formation of

368   nitrate, even during the daytime. The dependence of in-cloud nitrate formation on cloud

369   droplets' SA extends the observation that higher RH facilities the formation of nitrate in wet

370   aerosols (*Neuman et al.*, 2003; *Pathak et al.*, 2009; *Wang et al.*, 2009). Our results would

371   also help constrain the model simulation (*Holmes et al.*, 2019), as global model studies

372   disagree on the relative importance of processes contributing to nitrate production in cloud.

373   There are also studies neglecting N_2O_5 and NO_3 uptake in clouds (*Alexander et al.*, 2009; *Xu*

374   *and Penner*, 2012; *Hauglustaine et al.*, 2014). Given that N_2O_5 hydrolysis acts as a major

375   sink of NOx in the atmosphere (*Yan et al.*, 2019), further model updates may improve our

376   understanding on the global dominant nitrate-production pathways and the feedback that

377   reduces the effectiveness of air pollution mitigation (*Alexander et al.*, 2020; *Chan et al.*,

378   2021). In addition, significant hydrolysis of N_2O_5 in cloud may also pose substantial effect

379   on the tropospheric ozone budget (*Riemer et al.*, 2003; *Voulgarakis et al.*, 2009; *Strode et al.*,

380   2017), which needs further investigation.

381   Our results also indicate that in-cloud formed nitrate remains in particulate phase after

382   cloud evaporation (Fig. S7), changing the mixing state of individual particles. Enhanced

383   aerosol nitrate is expected to have higher hygroscopicity after cloud evaporation (*Hodas et*

384   *al.*, 2014; *Sun et al.*, 2018), and therefore, an increase of the particles' ability to act as cloud

385   condensation nuclei after their cloud passage (*Roth et al.*, 2016). This is different from that

386   observed in California coast that the nitrate-to-sulfate mass ratio decreases rapidly with

387   cloud height, due to the volatilization during drop evaporation pushes NO_3 to the gas phase

388   (*Prabhakar et al.*, 2014). In addition, vertical turbulent mixing of the residual aerosols from

389   evaporating cloud droplets may contribute to the nitrate aerosol loading during the daytime

390   at the ground level (*Tao et al.*, 2018).

391   As sulfate is reduced in the future through emission controls (*Chu et al.*, 2020; *Li et al.*,

392   2020a), higher nitrate fraction is expected through cloud cycling (*Li et al.*, 2020a), which

393   might also contribute to cloud acidification (*Guo et al.*, 2012). The observational evidence

394   of a rising trend of nitrate in cloud has been previously reported for the California's San

395   Joaquin Valley (*Herckes et al.*, 2007; *Herckes et al.*, 2015). It is also noted that the limited

396   dependence of nitrate formation on the [NOx][O_3] in the cloud suggest a possibility that

397   controlling NOx and O_3 might be offset in the cloudy regions. Given the significance of both

398   emission and deposition on the variations of nitrate (*Zhai et al.*, 2021) and the contribution

399   of the transported NOx and O_3 to the notable effect and complex process of cross-regional

400   nitrate formation (*Qu et al.*, 2021), knowledge of the in-cloud formation of nitrate would

401   also benefit $PM_{2.5}$ pollution control target over a larger scale.

402 **Data availability**

403 Data used in this paper will be uploaded to Zenodo after the paper is accepted.

404 **Competing interests**

405 The authors declare that they have no conflict of interest.

406 **Author contribution**

407 **Xinhui Bi and Guohua Zhang:** conceptualization, methodology, formal analysis, resource,

408 writing-original draft, writing-review & editing; **Xiaodong Hu and Wei Sun:** methodology,

409 investigation, formal analysis, writing-original draft; **Yuxiang Yang, Ziyong Guo, Yuzhen Fu:**

410 investigation; **Haichao Wang, Shengzhen Zhou, Zongbo Shi:** investigation; supervision;

411 **Duohong Chen, Lei Li, Mingjin Tang and Xinming Wang:** resource.

412

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677

679 **Figure 1.** Box-and-whisker plots of (a) the mass fraction of nitrate in $PM_{2.5}$ and cloud

680 water and (b) the RPA of nitrate separated for the cloud-free, cloud residual particles

681 (RES), and cloud interstitial particles (INT), in 2018 spring and 2020 winter,

682 respectively. In a box and whisker plot, the lower, median and upper line of the box

683 denotes the 25, 50, and 75 percentiles, respectively; the lower and upper edges of the

684 whisker denote the 10 and 90 percentiles, respectively.

685 **Figure 2.** Size dependent RPA of nitrate and RPA ratio of nitrate/sulfate, separated

686 for all the detected cloud-free, cloud residual particles (RES), and cloud interstitial

687 particles (INT), in (a) 2018 spring and (b) 2020 winter, respectively.

688 **Figure 3.** Theoretical calculation of the trend of in-cloud produced nitrate from the

689 hydrolysis of N_2O_5 versus the temporal variations of NO_3^- concentration in cloud

690 water in 2020 winter.

691 **Figure 4.** Correlation analysis between the observed RPAs of nitrate and the

692 predicted RPAs of nitrate, with inputs of NO_2, O_3 and LWC, for the (a) cloud-free and

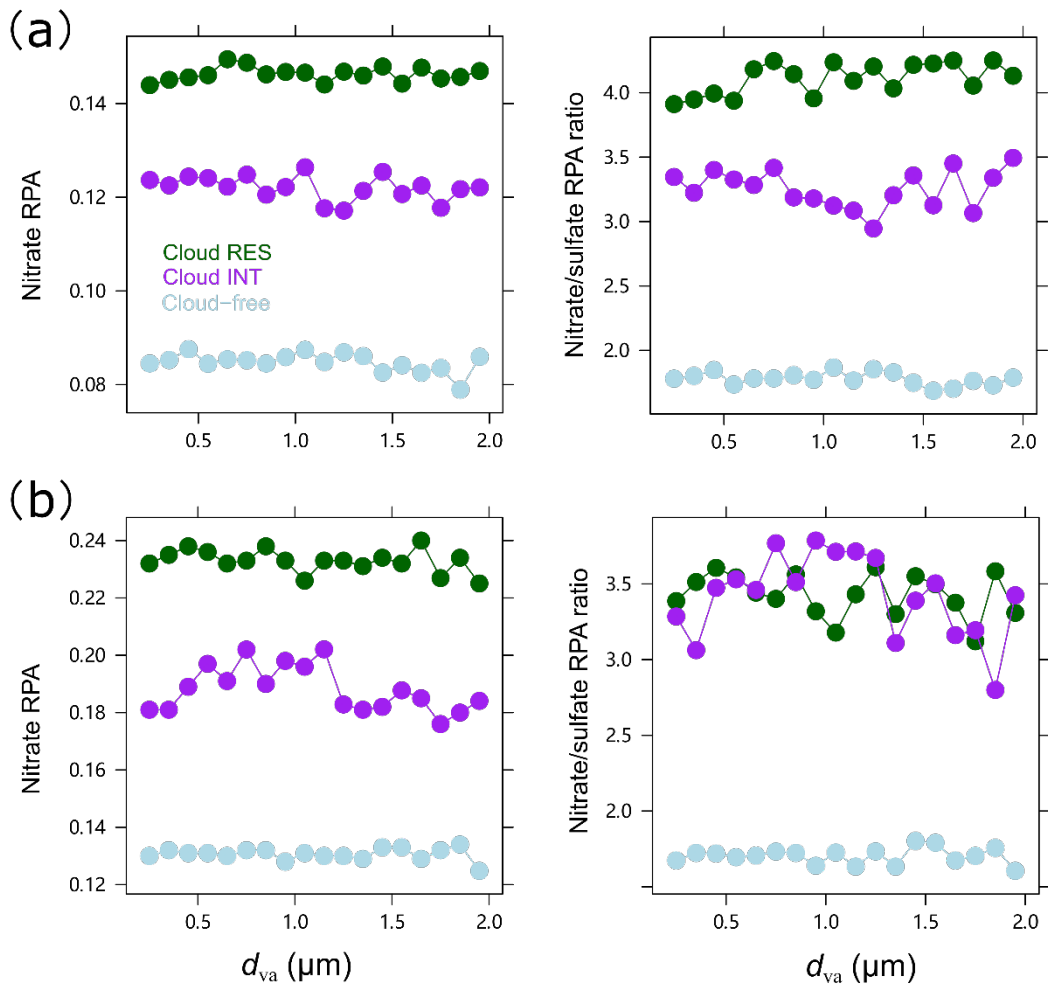693 (b) cloud residual particles (RES), respectively.

694 **Figure 5.** Relative contribution of each pathway to the nitrate production in wet

695 aerosols (WA, 0.5 μm) and cloud droplets (CD, 8μm), respectively, simulated by the

696 RACM-CAPRAM. The atmospheric conditions considered for comparison are LWC

697　(10^{-5}-10^{-4} g cm^{-3} for wet aerosols and 0.05-0.15 g cm^{-3}) and photolysis rates (30%,

698　50%, 100%).

(a)

(b)

699

700   **Fig. 1.**

701

702 **Fig. 2.**

Daytime R² = 0.38
Nighttime R² = 0.60

703

704   **Fig. 3.**

(a) Cloud-free

(b) Cloud RES

705

706   **Fig. 4.**

Fig. 5.