Enhanced new particle formation observed in the northern midlatitude tropopause region

Li-Hao Young, David R. Benson, William M. Montanaro, Shan-Hu Lee, Laura L. Pan, David C. Rogers, Jorgen Jensen, Jeffrey L. Stith, Christopher A. Davis, Teresa L. Campos, Kenneth P. Bowman, William A. Cooper, and Leslie R. Lait

Received 5 October 2006; revised 24 December 2006; accepted 16 February 2007; published 25 May 2007.

The free troposphere and lower stratosphere is a source region for new particle formation. In particular, nucleation can be active near the tropopause because of low temperatures. Here we show enhanced new particle formation observed during midlatitude tropopause folds. Number concentrations and size distributions of particles with diameters from 4 to 2000 nm were measured in the midlatitude tropopause region on 1 and 7 December 2005 during the NSF/NCAR GV Progressive Science Missions. High number concentrations of ultrafine particles with diameters from 4 to 9 nm, ranging from ~700 to 3960 cm⁻³, were measured during tropopause folds. Our observations show that stratospheric and tropospheric air exchange during tropopause folding events, with a large gradient of temperature and relative humidity, may have enhanced new particle formation. Our results are consistent with other modeling predictions showing that nucleation rates are increased with mixing of two air masses with different temperatures and relative humidities. In addition, new particle formation events were also associated with vertical motion that may also have brought higher concentrations of water vapor and aerosol precursors (that originate at the ground level) from lower altitudes to higher altitudes where temperatures and surface areas are lower. The average ultrafine particle concentrations for the regions that were not affected by tropopause folds were also high (>100 cm⁻³), indicating that nucleation is active in the tropopause region, in general. Our results suggest that atmospheric dynamics, such as stratosphere and troposphere exchange and vertical motion, affect new particle formation in this region.


1. Introduction

[2] Nucleation (gas-to-particle conversion) is a source of new particles. Nucleation usually starts from the formation of sulfuric acid because sulfuric acid has a relatively low vapor pressure (for example, <0.001 torr at 300 K) compared to other atmospheric gas phase species. Temperature and relative humidity are important thermodynamic parameters as they affect vapor pressures of condensable species, and nucleation rates are highly dependent on these two factors [Seinfeld and Pandis, 1998]. Surface area of preexisting aerosols is a sink of nucleation. In the presence of high surface areas, condensable species condense on, and small particles coagulate with the preexisting aerosol particles. Nucleation initially produces thermodynamically stable clusters (TSCs) (<3 nm, hence not measurable with currently available detection techniques) and these TSCs grow to larger sizes by condensation and coagulation [Kulmala, 2003].

[3] New particle formation events, identified by high number concentrations of nuclei mode particles, have been observed widely [Kulmala et al., 2004; and references herein], but these measurements are mostly limited to boundary layer conditions. In situ, size-resolved measurements in the free troposphere and lower stratosphere are scarce, despite the potential importance of these particles that grow to cloud condensation nuclei (CCN). The upper troposphere and lower stratosphere have several factors favorable for particle formation, such as low temperature and low surface area density of preexisting aerosols. Large-scale particle formation has been observed [Hermann et al., 2003] in the typical upper troposphere and lower stratosphere conditions with sufficient sun exposure and low aerosol surface area [Lee et al., 2003]. Binary homogeneous nucleation (BHN) [Brock et al., 1995] or ion induced...
Table 1. Measured Number Concentrations With Diameters From 4–9 nm \( (N_{4-9}) \) and 4–2000 nm \( (N_{4-2000}) \), Surface Area Density, RHI, and Temperature of the Air Masses Corresponding to Regions of Enhanced New Particle Formation During Tropopause Folding on 1 December 2005 (as Also Shown in Figures 1, 2, 3, and 4 and Table 2) and 7 December 2005 (as Also Shown in Figures 5, 6, 7, and 8 and Table 2)\(^a\)

<table>
<thead>
<tr>
<th>Date and Region No.</th>
<th>Leg Altitude, km</th>
<th>Horizontal Distance, km</th>
<th>( N_{4-9} ), cm(^{-3} )</th>
<th>( N_{4-2000} ), cm(^{-3} )</th>
<th>Surface Area, ( \mu \text{m}^2/\text{cm}^3 )</th>
<th>RHI, %</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 December 2005</td>
<td></td>
<td></td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>161</td>
<td>1030 ± 470</td>
<td>1150 ± 510</td>
<td>1.1 ± 0.9</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>26</td>
<td>1450 ± 440</td>
<td>1530 ± 450</td>
<td>0.2 ± 0.1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>52</td>
<td>3960 ± 1840</td>
<td>3990 ± 1830</td>
<td>0.2 ± 0.1</td>
<td>37</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>52</td>
<td>2430 ± 1960</td>
<td>2440 ± 1960</td>
<td>0.1 ± 0.1</td>
<td>46</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>82</td>
<td>2030 ± 780</td>
<td>2360 ± 780</td>
<td>1.7 ± 0.9</td>
<td>21</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>213</td>
<td>1710 ± 610</td>
<td>2370 ± 640</td>
<td>12.4 ± 11.0</td>
<td>36</td>
<td>70</td>
</tr>
<tr>
<td>New Particle Formation(^b)</td>
<td>N/A</td>
<td>N/A</td>
<td>460 ± 820</td>
<td>620 ± 900</td>
<td>4.0 ± 6.7</td>
<td>16</td>
<td>91</td>
</tr>
<tr>
<td>Non-new Particle Formation(^c)</td>
<td>N/A</td>
<td>N/A</td>
<td>10 ± 20</td>
<td>160 ± 130</td>
<td>4.2 ± 4.1</td>
<td>22</td>
<td>89</td>
</tr>
<tr>
<td>7 December 2005</td>
<td></td>
<td></td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>1(^d)</td>
<td>10</td>
<td>65</td>
<td>790 ± 190</td>
<td>1160 ± 260</td>
<td>0.9 ± 0.3</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>2(^d)</td>
<td>10</td>
<td>94</td>
<td>740 ± 460</td>
<td>1000 ± 450</td>
<td>2.2 ± 0.3</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>3(^d)</td>
<td>8</td>
<td>62</td>
<td>700 ± 210</td>
<td>1030 ± 220</td>
<td>1.3 ± 0.5</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>4(^d)</td>
<td>7</td>
<td>267</td>
<td>1520 ± 810</td>
<td>1840 ± 840</td>
<td>1.6 ± 0.4</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>5(^d)</td>
<td>5</td>
<td>23</td>
<td>830 ± 130</td>
<td>1250 ± 230</td>
<td>4.3 ± 0.3</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>6(^d)</td>
<td>6</td>
<td>146</td>
<td>2060 ± 550</td>
<td>2450 ± 620</td>
<td>1.1 ± 0.6</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>New Particle Formation(^d)</td>
<td>N/A</td>
<td>N/A</td>
<td>490 ± 770</td>
<td>730 ± 1000</td>
<td>5.2 ± 32.8</td>
<td>7</td>
<td>64</td>
</tr>
</tbody>
</table>

\(^a\)The numbers in the first column also correspond to those indicated in these figures and Table 2. Leg altitudes and horizontal distances for the chosen air parcels are also shown here. For aerosol concentrations, one standard deviation (1\( \sigma \)) values are shown. For RHI and temperature, the differences (range) between the maximum and minimum values are shown to for indication of atmospheric mixing.

\(^b\)About 86% of the total particles satisfied the three criteria of new particle formation.

\(^c\)About 14% of the total particles did not satisfy the criteria of new particle formation.

\(^d\)One hundred percent of the total particles satisfied the three criteria of new particle formation.

nucleation (IIN) can be important in this region [Lee et al., 2003; Lovejoy et al., 2004]. Recent global aerosol modeling simulations by Lucas and Akimoto [2006] also suggested that ternary homogeneous nucleation (THN) involving ammonia may play a dominant role in the troposphere and lower stratosphere. THN predictions often show that an enhancement of nucleation requires sufficient NH\(_3\) concentrations, at least several parts per trillion by volume even at low temperatures (for example, 240 K) [Napari et al., 2002]. However, measurements of ammonia (and condensable organic species) at high altitudes are currently not available. It is also possible that at lower temperatures (for example, <240 K), nucleation barriers of homogeneous nucleation can disappear [Yu, 2002] and in these conditions, there may be a mix of different nucleation mechanisms.

[4] New particle formation can be enhanced by the mixing of two air masses with different temperatures and relative humidities over ice (RHI), such as in large eddies and waves, small-scale turbulence, and convection, as shown by numerical calculations of BHN [Easter and Peters, 1994; Kerminen and Wexler, 1996; Lesniewski and Friedlander, 1995; Nilsson and Kulmala, 1998; Nilsson et al., 2000; Khosrawi and Konopka, 2003]. This is because nucleation rates exhibit nonlinear dependence on temperature and RHI. For example, an increase of 2 to 3 K in temperature can reduce particle nucleation rates by an order of magnitude [Easter and Peters, 1994]. Previous particle formation observations in the free troposphere and lower stratosphere were in fact often explained by atmospheric dynamics-induced mixing. Three-year aerosol size distributions measured on a German commercial aircraft at the latitude range from \( \sim 5^\circ \) to \( \sim 50^\circ \)N showed that new particle formation in the tropopause region may be affected by photochemistry and atmospheric dynamics [Hermann et al., 2003]. A number of aircraft measurements of condensation nuclei (CN) showed that atmospheric mixing is a source of new particles in the midlatitude free troposphere up to the lower stratosphere [Schröder and Ström, 1997; Nyeki et al., 1999; de Reus et al., 1998, 1999; Wang et al., 2000]. BHN calculations indicated that new particle formation can be enhanced in the tropopause region because of the troposphere and stratosphere exchange, and these calculations are consistent with the Stratosphere-Troposphere Experiment by Aircraft Measurements (STREAM) observations in Ireland in 1996 and 1998 [de Reus et al., 1998; Khosrawi and Konopka, 2003]. For example, high particle concentrations from 6–18 nm (up to 400 cm\(^{-3} \)) measured near the tropopause during STREAM-98 were attributed to the large fluctuation in temperature (\( \sim 12 \) K) during the mixing processes [Khosrawi and Konopka, 2003]. Note that BHN has been used for these calculations, but the nucleation theories of BHN (and THN) have not been vigorously tested by experiments. Also, air mixing may also affect nucleation rates even in multicomponent systems (THN or IIN), but these effects have not been investigated.

[5] Several observations in the free troposphere also showed that new particle formation can be active when convection occurs [de Reus et al., 1999, 2000, 2001; Clement et al., 2002; Twohy et al., 2002; Lee et al., 2003; Minikin et al., 2003], because vertical motion can bring higher concentrations of SO\(_2\) and SO\(_2\) precursors (for example, DMS) that originate from the ground level to higher altitudes where temperatures are much lower. Aircraft observations of upper tropospheric fine particles in the Northern and
Figure 1. Measured altitude, potential temperature ($\theta$), RHI, temperature ($T$), water mixing ratio, $N_{4-9}$, $N_{4-2000}$, and surface area density for 1 December 2005. The periods of enhanced new particle formation are indicated with the shaded areas and numerical numbers from 1 to 6; these numbers also correspond to those indicated in Figures 2, 3 and 4, and Tables 1 and 2.
Southern Hemisphere midlatitudes by Minikin et al. [2003] showed higher CN concentrations in the Northern Hemisphere (up to \(10^8\) cm\(^{-3}\)) than those in the Southern Hemisphere (up to \(10^4\) cm\(^{-3}\)), indicating the strong influence of anthropogenic activities on aerosol formation in the upper troposphere.

New particle formation studies were carried out during the National Science Foundation (NSF)/National Center for Atmospheric Research (NCAR) Gulfstream V (GV) Progressive Science Missions in December 2005. There were ten research flights during the Progressive Science Missions. The primary objectives of the Progressive Science Mission new particle formation studies were to investigate the effects of sun exposure on nucleation and the latitude and altitude dependence of new particles. There are two companion papers on Progressive Science Mission new particle formation studies. The current study is the part 1 paper that focuses on atmospheric dynamics effects on nucleation. The part 2 paper describes the entire mission results (D. R. Benson et al., New particle formation observed in the free troposphere and lower stratosphere: Effects of photochemistry, surface area and vertical convection on aerosol nucleation, manuscript in preparation, hereinafter referred to as Benson et al. part 2 paper). The Benson et al. part 2 paper shows that (1) substantially high concentrations of ultrafine particles were measured during nighttime, (2) new particle formation in the free troposphere were closely associated with low surface area density and vertical motion, and (3) the measured ultrafine particles (<10 nm) during the Progressive Science Missions were lower in the extratropics than in the midlatitude, a similar trend as in Hermann et al. [2003].

In the present paper, we show in situ observations of new particle formation two tropopause folding events near midlatitude jet streams in the winter over the continental United States. We identify the stratosphere, troposphere, and tropopause using the measured ambient temperature, potential temperature, RHI, water vapor, and ozone concentrations. Our observations suggest that new particle formation is enhanced during tropopause folds and with vertical motion.

2. NSF/NCAR GV Progressive Science Missions and Methods

The NSF/NCAR GV is also known as the High-performance Instrumented Airborne Platform for Environmental Research (HIAPER), a newly built high altitude aircraft to serve the environmental research needs of the university community. The Progressive Science Mission was the first science mission with the GV. The primary objective of the Progressive Science Missions is that “prior to the commencement of regular missions support, NSF and NCAR have decided to carry out a series of progressive science missions in order to provide NCAR and external community personnel with the opportunity to fully familiarize themselves with the capabilities of the new GV and to perform initial basic research with the aircraft” [National Center for Atmospheric Research, 2003]. This mission is also described at http://www.eol.ucar.edu/raf/Projects/ProgSci/.

This study presents measurements from two research flights on 1 and 7 December 2005, which were associated with tropopause folds. These two flights were designed to investigate the chemical characteristics of air masses inside and around stratospheric intrusions during tropopause folds as part of the Stratosphere Troposphere Analyses of Regional Transport (START) experiments (L. L. Pan, Chemical behavior of the tropopause observed during the
Stratosphere-Troposphere Analyses of Regional Transport (START) experiment, a manuscript in preparation to be submitted to *Journal of Geophysical Research*, 2007). These two flights ranged latitudes from 33° to 48°N, longitudes from 92° to 105°W, and altitudes up to 14 km. Large scale tropopause folding also took place along the jet stream in the midlatitude regions over the continental United States on these 2 days (as will be described in section 3).

Aerosol number concentrations with diameters from 4 to 2000 nm were measured with the University of Denver nuclei mode aerosol size spectrometer (NMASS) and focused cavity aerosol spectrometer (FCAS) with a low-pressure, near isokinetic inlet [Jonsson et al., 1995; Brock et al., 2000; Lee et al., 2004]. Briefly, NMASS consists of five condensation nuclei counters (CNCs) operated in parallel with the downstream pressure 60 mbar. NMASS measures cumulative number concentrations of particle sizes larger than 4, 8, 15, 30, and 64 nm, respectively, with the different supersaturation conditions in the five CNCs. The FCAS uses light scattering to measure the size of an aerosol in the diameter range from 90 to 1000 nm, by assuming that the particle is a spherical, sulfuric acid liquid aerosol. The aerosol sampling rate was 10 Hz, but the data presented here were averaged over 30 s to improve particle counting statistics. Continuous number-size distributions from 4 to 2000 nm were obtained by combining NMASS and FCAS measurements and using an inversion algorithm based on the work of Markowski [1987]. The inversion also incorporates corrections for size-dependent anisokinetic sampling, diffusion losses, and instrument counting efficiency. The particle concentrations presented here are based on the actual air

**Figure 3.** (a) $N_{d>9}$ and (b) H$_2$O mixing ratio measured on 1 December 2005. Thermal tropopause height, calculated from temperature lapse rate, is indicated by the orange dotted line. PV = 2 surface is also shown for comparison. Four flight legs A to D are shown with arrows indicating the flight direction. The numbered circles from 1–6 are the regions where enhanced new particle formation took place.
The aerosol is heated during the sampling and transported to the sensing volume in both the NMASS and FCAS. A passive, near-isokinetic inlet is used for NMASS and FCAS [Jonsson et al., 1995]. The passive, near-isokinetic inlet slows the flow from the true air speed of the aircraft to velocities on the order of 10 m s\(^{-1}\). This slowing is accompanied by compressive and dissipative heating that warms the flow by at least 20 K from the ambient temperature. The sample line enters the aircraft cabin and additional heat transfer takes place. The aerosol is heated to 28°C in the NMASS and 33°C in the FCAS prior to the actual measurements. Calculations suggest that most of the water evaporates from the particles prior to measurement. Other volatile species so be evaporating in sampling and transport to the sensing volumes. The chemical compositions of aerosol particles are unknown and we assume that the chemical composition of aerosols is sulfuric acid and water. The correction on the inlet passive heating is straightforward for the larger sulfuric acid particles and utilizes the known thermodynamic relationships for solutions of water and sulfuric acid. For nanometer sized particles, the Kelvin effect must be taken into account. Models considering the evolution of the aerosol make use of back trajectory calculations which permit the variations in RH as a function of time to be taken into account. The length of the sample tube is such that the loss of nanometer size particles is acceptably small.

The effect of shattered cloud droplets and ice crystals in the aircraft inlet may be an issue [Murphy et al., 2004]. Cloud shattering issues have been examined during the previous Cirrus Regional Study of Tropical Anvils and Cirrus

Figure 4. NOAA HYSPLIT backward trajectory results for air masses corresponding to the enhanced new particle formation on 1 December 2005. Vertical variation is also shown for indication of convection. See Table 2 for more trajectory information.
Table 2. Meteorological Parameters Derived From the 3-Day NOAA HYSPLIT Trajectory Calculations for Air Parcels Corresponding to the Enhanced New Particle Formation During Tropopause Folding on 1 December 2005 (as Shown in Figure 1 and Table 1) and 7 December 2005 (as Shown in Figure 5 and Table 1)a

<table>
<thead>
<tr>
<th>Date and Region No</th>
<th>Altitude, km</th>
<th>Temperature, K</th>
<th>RHI, %</th>
<th>Precipitation Cumul., mm</th>
<th>Solar Flux, W m(^{-2})</th>
<th>Sun Fractionb</th>
<th>Mean</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Min</th>
<th>Max</th>
<th>Cumul., mm</th>
<th>Hour, hr</th>
<th>Cumul.</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 December 2005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>9.0</td>
<td>8.0</td>
<td>10.1</td>
<td>226</td>
<td>222</td>
<td>232</td>
<td>23</td>
<td>5</td>
<td>52</td>
<td>2.3</td>
<td>9</td>
<td>231</td>
<td>1995</td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.5</td>
<td>1.4</td>
<td>8.9</td>
<td>272</td>
<td>230</td>
<td>287</td>
<td>83</td>
<td>71</td>
<td>98</td>
<td>7.0</td>
<td>21</td>
<td>799</td>
<td>0.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.3</td>
<td>0.7</td>
<td>8.4</td>
<td>276</td>
<td>231</td>
<td>289</td>
<td>85</td>
<td>58</td>
<td>100</td>
<td>16.2</td>
<td>13</td>
<td>644</td>
<td>0.63</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.3</td>
<td>0.2</td>
<td>8.0</td>
<td>271</td>
<td>232</td>
<td>286</td>
<td>88</td>
<td>62</td>
<td>100</td>
<td>13.9</td>
<td>20</td>
<td>2491</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.6</td>
<td>2.4</td>
<td>6.4</td>
<td>258</td>
<td>244</td>
<td>276</td>
<td>80</td>
<td>51</td>
<td>98</td>
<td>14.5</td>
<td>13</td>
<td>3556</td>
<td>0.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.2</td>
<td>3.8</td>
<td>6.0</td>
<td>242</td>
<td>233</td>
<td>251</td>
<td>52</td>
<td>16</td>
<td>94</td>
<td>2.5</td>
<td>15</td>
<td>4151</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 December 2005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6.8</td>
<td>5.2</td>
<td>10.4</td>
<td>249</td>
<td>217</td>
<td>262</td>
<td>71</td>
<td>37</td>
<td>99</td>
<td>32.3</td>
<td>44</td>
<td>4498</td>
<td>0.63</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>9.9</td>
<td>9.0</td>
<td>10.5</td>
<td>214</td>
<td>209</td>
<td>223</td>
<td>61</td>
<td>21</td>
<td>94</td>
<td>3.7</td>
<td>15</td>
<td>2212</td>
<td>0.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.3</td>
<td>6.7</td>
<td>8.0</td>
<td>230</td>
<td>224</td>
<td>236</td>
<td>58</td>
<td>4</td>
<td>100</td>
<td>1.9</td>
<td>11</td>
<td>3001</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>7.1</td>
<td>6.0</td>
<td>8.1</td>
<td>229</td>
<td>219</td>
<td>238</td>
<td>47</td>
<td>13</td>
<td>100</td>
<td>1.1</td>
<td>6</td>
<td>3294</td>
<td>0.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5.8</td>
<td>4.4</td>
<td>7.3</td>
<td>240</td>
<td>224</td>
<td>259</td>
<td>21</td>
<td>3</td>
<td>87</td>
<td>5.1</td>
<td>14</td>
<td>4502</td>
<td>0.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.7</td>
<td>5.2</td>
<td>6.3</td>
<td>238</td>
<td>231</td>
<td>249</td>
<td>40</td>
<td>6</td>
<td>92</td>
<td>1.1</td>
<td>9</td>
<td>3001</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The region numbers indicated in the first column also correspond to those indicated in these figures and Table 1. Mean, maximum, and minimum values of altitude, temperature, and RHI are shown, along with the cumulative precipitation, solar flux intensity, and sun fraction.

Sun exposure fraction is the average ratio of the sun exposure hours in a day during the three preceding days.

The archived data of these measurements are available from the NCAR’s ftp site (ftp://ftp.atd.ucar.edu/pub/archive/RAF-projects/ProgSci/). The water mixing ratios and RHI were derived from the measured total static pressure, temperature, and dew point. The thermal tropopause, potential vorticity (PV), and potential temperature contour were calculated based on the Global Forecast System (GFS) of the National Centers for Environmental Predictions (NCEP). The GFS model output includes the vertical component of the vorticity along with the conventional meteorological variables.

Three-day backward trajectory calculations were performed with the NOAA Air Resource Laboratory (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) program [Draxler and Rolph, 2003] with the Final Run of GFS model archive data. Trajectories were also calculated from NASA Goddard Space Flight Center (GFSC) isotropic TRAJ model with the DAO the meteorological fields. Solar flux and precipitation data were obtained from the HYSPLIT trajectory calculations. Sun exposure fractions, defined as the average ratio of the sun exposure hours in a day during the previous proceeding days (3 days in this study) of the air mass, were obtained from HYSPLIT and TRAJ calculations.

3. Results

New particle formation events were identified with the following three criteria together: (1) N\(_{4-6}\) > N\(_{6-9}\), (2) N\(_{4-9}\) > 1 cm\(^{-3}\), and (3) the ratio of N\(_{4-9}\) over total aerosol number concentrations (N\(_{4-2000}\) > 1.15). The first two criteria are the same as used in the previous upper troposphere and lower stratosphere new particle formation studies [Lee et al., 2003, 2004]. Because the polar lower stratospheric N\(_{4-2000}\) is only ~15 cm\(^{-3}\) whereas the tropical upper tropospheric N\(_{4-2000}\) is two orders of magnitude higher [Lee et al., 2003], by adding the third criterion, similar minimum fractions of N\(_{4-9}\) in N\(_{4-2000}\) can be taken into account throughout the entire free troposphere and lower stratosphere for identification of new particle formation. About 86% of the aerosols measured on 1 December 2005 satisfied the above three criteria of new particle formation, with N\(_{4-9}\) of 460 ± 820 cm\(^{-3}\) and N\(_{4-2000}\) of 620 ± 900 cm\(^{-3}\) (Table 1). One hundred percent of the particles measured on 7 December 2005 showed new particle formation feature with the average N\(_{4-9}\) of 490 ± 770 cm\(^{-3}\) and N\(_{4-2000}\) of 730 ± 1000 cm\(^{-3}\) (Table 1).

In addition to new particle formation events, we have also identified the “enhanced” new particle formation events during tropopause folds, when N\(_{4-9}\) was higher than the average N\(_{4-9}\) in new particle formation regions of the same day with a time span of >120 s (corresponding to spatial scales of >25 km). Some regions that had high ultraviolet particle concentrations with a shorter time span (for example, those at 42 N and 13 km) (Figure 3) were not included in this category.

3.1. Case Study I: 1 December 2005

Figure 1 shows the measured altitude, potential temperature, RHI, temperature, water mixing ratio, N\(_{4-9}\), N\(_{4-2000}\), and surface area density as a function of universal
Figure 5. The same as for Figure 1, except that the data shown here are for 7 December 2005. The numbers indicated here correspond to those in Figures 6, 7, and 8, and Tables 1 and 2.
time on 1 December 2005. The GV flew over a relatively flat terrain between Garden City, Kansas, and Duluth, Minnesota. The areas with enhanced new particle formation are shaded in Figure 1. In these enhanced event areas the \( N_{4-9} \) ranged from \( \sim 1030-3960 \, \text{cm}^{-3} \), which is considerably higher than the average \( N_{4-9} \) measured on this day \((190 \pm 380 \, \text{cm}^{-3})\) (Table 1). Note that there were also large variations in RHI, water vapor, and temperature within these enhanced event regions.

Figure 6. The same as for Figure 2, except that the data shown here are for 7 December 2005.

Aerosol size distributions also indicate strong new particle formation for these enhanced event regions (Figure 2). Aerosol size distributions showed three modes, with peaks at <10, \( \sim 20 \), and \( \sim 70-200 \, \text{nm} \). The dominant peaks at <10 nm indicate recent new particle formation. The Aitken mode particles at \( \sim 20 \, \text{nm} \) resulted from the growth of newly formed particles. The peaks at \( \sim 70-200 \, \text{nm} \) particles are representative of the typical accumulation mode particles in the upper troposphere and lower stratosphere. These three modes were also identified by previous upper troposphere and lower stratosphere studies [Lee et al., 2003], although the number concentrations measured in these 2 days were higher than those by Lee et al. [2003].

Figure 3 shows the flight track of 1 December 2005 as a function of latitude and altitude. This day’s measurements were made near the tropopause. Water vapor mixing ratios had steep gradients in the tropopause region. Ozone measurements also confirmed similar tropopause heights (not shown). Tropopause heights, in general, are approximately from 10 to 12 km at midlatitudes (M. J. Mahoney, private communication, 2003), but on this day tropopause height decreased to \( \sim 5 \, \text{km} \) at 42°N latitude. Water and ozone mixing ratios in these regions were also much higher than at higher altitudes for the same latitudes, a clear indication of tropopause folding. Because of the intrusion of stratospheric air into the troposphere during folding events, large gradients of water vapor mixing ratio and temperature occurred within these enhanced event areas near the tropopause. For example, RHI differences were up to 70%, and temperature differences up to 5 K (Table 1). Aerosol nucleation calculations have shown that nucleation rates can be substantially higher when two different air masses mix [Easter and Peters, 1994; Nilsson and Kulmala, 1998; Nilsson et al., 2000; Khosrawi and Konopka, 2003]. If comparing with these modeling calculations, it is very likely that these large RHI and temperature differences have contributed to the measured high number concentrations of ultrafine particles.

In addition to tropopause folds, strong vertical convection also took place in the enhanced event regions (Figure 4). Convection brings high concentrations of \( \text{SO}_2 \) (and other aerosol precursors) and water vapor from lower altitudes to higher altitudes where temperatures and surface area densities are lower, favoring new particle formation. For example, the highest \( N_{4-9} \) in region 3 was associated with the strongest convection where the air parcel was uplifted rapidly from \( \sim 1 \) to \( \sim 8 \, \text{km} \) within the past 24 hours. Hence vertical motion may also be also responsible for the measured high concentrations of new particles (Table 1). Also, the air parcel had strong cumulative solar flux and sun exposure fraction (thus higher OH concentrations) (Table 2). These observations also underscore the importance of photochemistry on new particle formation.

Surface area densities in these enhanced event regions were much lower (<1.7 \( \mu \text{m}^2 \, \text{cm}^{-3} \)) except for region 6, compared to the average surface area density measured on this day, \( \sim 4 \, \mu \text{m}^2 \, \text{cm}^{-3} \) (Table 1). It was consistent that a low surface area is associated with new particle formation during the Progressive Science Missions (Benson et al. part 2 paper). For example, there was no enhancement of new particle formation when the surface area density was extremely high (up to \( \sim 27 \, \mu \text{m}^2 \, \text{cm}^{-3} \)) even RHI was high (for example, at
However, there were also some exceptions. As illustrated in region 6 (at $\sim 4$ km) (Figure 3), enhanced new particle formation took place with the high surface area density of $\sim 12.4 \mu m^2 cm^{-3}$. Although there were no measurements of sulfuric acid and other aerosol precursors during this mission, we speculate that higher concentrations of aerosol precursors at these low altitudes contributed to the observed new particles. It is possible that aerosol formation takes place even with high surface area densities, when sufficient aerosol precursors are present. We attempted to find correlations of surface area densities with precipitation fluxes, but there was no clear link between the surface area and the HYSPLIT precipitation flux (Table 2). Rather, surface area was a function of altitude: higher surface area densities at lower altitudes. This is because of the primary aerosol sources at the ground level and higher RHI at lower altitudes.

### 3.2. Case Study II: 7 December 2005

Another tropopause folding experiments were made on 7 December 2005 ($s 5–8$). The flight was above the Rockies mountainous region between Cheyenne, Wyoming, and Phoenix, Arizona on this day. Nearly 100% of the samples showed the new particle formation feature; the average concentrations of the $N_{4–9}$ and $N_{4–2000}$ on this day were even higher than those on 1 December 2005 (Table 1). The entire flight was very close to the tropopause region (Figure 7). These results imply that nucleation is active in the tropopause region.

The regions with enhanced new particle formation, however, had lower $N_{4–9}$ ($\sim 700–2060 \text{ cm}^{-3}$) and $N_{4–2000}$ ($\sim 1000–2450 \text{ cm}^{-3}$) than on 1 December 2005 ($\sim 1030–3960 \text{ cm}^{-3}$ $N_{4–9}$) (Table 1). This is because of the weaker tropopause folding than on 1 December 2005, as determined by how much PV = 4 surface and the thermal tropopause were separated (not shown). The biggest difference between these two days was the “broken” feature of the tropopause cross section, as shown as the double dip in PV = 2 contour (Figure 2). Trajectory calculations also indicate that air masses originated from the remote, northern Canadian continent (Figure 8) where $SO_2$ concentrations are lower than those from the polluted US continent (case study I).
which may be also responsible for the lower ultrafine particles. The cumulative solar flux and sun exposure fraction were comparable for both days (Table 2), so OH concentrations were probably similar.

4. Discussions and Conclusions

[24] High number concentrations of ultrafine particles measured in the tropopause region are within the same range as that of the work of Hermann et al. [2003] but slightly higher than those by Lee et al. [2003]. Although the tropopause and the polar stratosphere are the active areas where nucleation occurs because of low temperatures [Carslaw and Kärcher, 2006], they are not the only areas in the free troposphere and lower stratosphere where new particle formation occurs. New particle formation takes place in the entire upper troposphere and lower stratosphere from the tropics to the polar region [Hermann et al., 2003; Lee et al., 2003]; our GV studies also showed a widespread new particle formation in the free troposphere and lower stratosphere (>78%) (Benson et al. aper). High ultrafine particles were also observed even in cirrus clouds [Lee et al., 2004], and near orographic clouds during nighttime [Wiedensohler et al., 1997; Meters et al., 2005]. The present study shows specific case studies in the midlatitude tropopause region, associated with tropopause folding and vertical motion. These atmospheric dynamics-induced, “enhanced new particle formation” events are consistent with the numerical predictions showing that nucleation rates are a nonlinear function of RHI and aerosol precursor concentrations [Easter and Peters, 1994; Seinfeld and Pandis, 1998; Nilsson and Kulmala, 1998; Nilsson et al., 2000; Khosrawi and Konopka, 2003].

[25] The case study I results are surprisingly similar to the case study I shown by Lee et al. [2003], which demonstrated, using a convection event in the midlatitude upper troposphere, that low surface area and low temperatures are critical factors for nucleation. Twohy et al. [2002] have shown that most new particle formation events observed in the midlatitude upper troposphere are often associated with vertical convection, although they reported higher particle number
concentrations (up to 45,000 cm\(^{-3}\)) than other studies. Vertical mixing brings higher aerosol precursors up to higher altitudes where temperatures and surface areas are lower. When air masses experience rain or cloud scavenging during convection, surface area can be even lowered. All these factors together create an ideal condition for particle nucleation: higher precursor concentrations and RHI and lower surface area and temperatures.

[26] There is also the possibility that commercial aircraft emission plumes produce high number concentrations of particles [Hagen et al., 1996; Kärcher et al., 1998; Yu et al., 1998] and we have examined those events during the Progressive Science Missions. Results from the GV Terrain-Induced Rotor Experiment (T-REX) (2006) showed that plume emissions often produce spikes of particle number concentrations at the diameter >40 nm with a short time span (for example, a few seconds) and these particles also showed a strong correlation with CO and water vapor (not shown here). We have seen only four events of these quick (<10 s) spikes of particle concentrations with the diameter ~50 nm during these 2 days measurements used in the present study and but those samples did not satisfy new particle formation criteria. For the enhanced new particle formation events shown here, there were high concentrations of ultrafine particles with diameters <10 nm with a longer time span (>120 s). From these reasons, we believe that the effects of aircraft plumes on ultrafine particles reported here are likely negligible.

[27] It is noticeable that the fractions of new particle formation events were very high in the tropopause region (86–100%) (Table 1). These high fractions may be explained with the stratosphere and troposphere exchange and vertical motion. However, it is also important to identify when new particle formation does not occur. About 22% of the total particles measured in the free troposphere and lower stratosphere in the Northern Hemisphere extratropics and midlatitudes during the Progressive Science Missions did not show the new particle formation feature; these nonevent regions had either relatively higher surface areas (>10 \(\mu m^2\) cm\(^{-3}\)) at lower altitudes or were not associated with vertical convection (Benson et al. part 2 paper). For example, as also shown in Table 1, the surface area densities measured in the regions corresponding to new particle formation were lower than those in the nonevent regions, suggesting that lower surface area is a favorable condition for new particle formation. Because there are limited aerosol precursors in the free troposphere and lower stratosphere, nucleation is very sensitive to surface area densities. Similarly, because of the relatively low surface areas in this region (for example, 4–6 \(\mu m^2\) cm\(^{-3}\) on average) (Table 1), the effects of convection are also important. These results are consistent with the work of Lee et al. [2003] which showed that ultrafine particles in the upper troposphere and lower stratosphere are a function of both surface area and sun exposure hours (sun exposure hours are approximately representative of sulfuric acid production rates when SO\(_2\) concentrations are nearly constant), rather than a function of surface area alone.

[28] We have shown here high frequency and magnitude of new particle formation observed in the midlatitude tropopause region. About 86–100% of the aerosol size distributions measured his region showed the new particle formation feature, with the average \(N_{4-9}\) of \(\sim460–490\) cm\(^{-3}\) and the average \(N_{4-2000}\) of \(\sim620–730\) cm\(^{-3}\) (Table 1). In the regions with enhanced new particle formation the \(N_{4-9}\) ranged from \(\sim700–3960\) cm\(^{-3}\) and the \(N_{4-2000}\) ranged from \(\sim1000–3990\) cm\(^{-3}\) (Table 1). The water vapor and ozone measurements and backward trajectory calculations support the argument that these high ultrafine particles are associated with tropopause folds and convection. The current global aerosol modeling predictions do not include the effects of atmospheric dynamics on particle formation and our results suggest that these effects should be taken into account in order to correctly predict aerosol number concentrations in the free troposphere and lower stratosphere.

[29] There are several factors that influence new particle formation, such as aerosol precursor concentrations, aerosol surface area density, atmospheric mixing, convection, and cloud processing. It is difficult to understand the effects of each factor on nucleation, based on the measured aerosol size distributions alone. More comprehensive, long-term field studies, including aerosol precursors and chemical composition of ultrafine particles, will be required. Laboratory studies of aerosol nucleation kinetics and thermodynamics, especially under atmospherically relevant conditions, are also needed to reduce the uncertainties in the current aerosol nucleation theories.

[30] Acknowledgments. This study was supported by a NSF fund awarded to Kent State University (ATM-0507799) and the Kent State Startup fund to SHL, and also in part supported by a NSF grant to Texas A&M (ATM-0605739). NCAR is sponsored by NSF, but any opinions expressed in this publication do not necessarily reflect the views of NSF.

We thank J. C. Wilson for providing NAMSS and FCAS, R. Gao for ozone measurements; and scientists, engineers, and pilots involved in the NSF/NCAR GV (HIAPER) Progressive Science Missions. We also thank anonymous reviewers for helpful comments.

References


D. R. Benson, S.-H. Lee, W. M. Montanaro, and L.-H. Young, Department of Chemistry, Kent State University, 302 Williams Hall Kent, OH 44240, USA. (slee19@kent.edu)

K. P. Bowman, Department of Atmospheric Sciences, Texas A&M University, College Station, TX, USA.

T. L. Campos, W. A. Cooper, J. Jensen, D. C. Rogers, and J. L. Stith, Research Aviation Facility, National Center for Atmospheric Research, Boulder, CO, USA.

C. A. Davis and L. L. Pan, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO, USA.

L. R. Lait, Goddard Space Flight Center, National Aeronautics and Space Administration, Greenbelt, MD, USA.