Supplementary Material for "Decreasing particle number concentrations in a warming atmosphere and implications" by Yu, F., et al.

Long-term measurements of particle number concentrations and effects of CN counters

In recognition of its importance in controlling aerosol indirect radiative forcing, number concentrations of atmospheric particles have been measured extensively in various regions around the globe in the last decade. However, long-term CN measurements lasting more than 15 years, which are critical for assessing how climate change and emissions may have influenced the CN values, and associated feedback processes, are quite limited. Beginning in the middle 1970s, NOAA/ESRL's Global Monitoring Division (GMD) has carried out long-term CN measurements at four remote baseline stations (Bodhaine, 1983). The GMD has another site at Bondville, Illinois (BND) which has recorded CN values since 1994. In addition, German Antarctic station Neumayer (NEU) has measured CN since 1993 (Weller and Lampert, 2008). To our knowledge, these are the only stations around the globe having more than 15 years of CN data that are available in the public domain. It should be noted that the Australian "Atmospheric Baseline" program began CN measurements at Cape Grim (40.7 S, 144.7E) in the late 1970s (Gras, 1990), but the long-term Cape Grim CN data are not yet available.

Figure S1 shows monthly mean CN concentrations observed at the six stations, with color shades indicating the types of CN counters used (gray: GE counter; yellow: TSI-3760; pink: TSI-3010; light blue: TSI-3022A). NOAA started measurements in the mid-1970's with water-based CN counters made by General Electric (GE). The GE counters were replaced with butanol-based counters (TSI-3760) in (1990, 1988, 1992, 1989) for (BRW, MLO, SMO, SPO), and the 3760's at (BRW, SMO) were replaced with TSI-3010 counters in (2007, 2004). Different CN counters have different counting efficiency curves. The 50% particle detection efficiency diameters (d_{50}) are ~ 8 nm for GE counters (Liu and Kim, 1977), ~ 15 nm for the TSI-3760 running at a flow rate of 1.4 lpm (Wiedensohler et al., 1997), ~ 12 nm for the TSI-3010 running at a temperature difference of 17 ^{o}C (Wiedensohler et al., 1997), and ~ 7 nm for the TSI-3022A (Weller and Lampert, 2008).

Because of the differences in the detection efficiencies, CN values measured by different counters are expected to differ, with the magnitude of the differences depending on particle size distribution as well as factors such as sampling and counter operational conditions. Efforts were made to operate both GE and TSI counters during overlap periods to determine if a correction factor is needed to maintain continuity for the long-term CN data across instrument changes (Bodhaine, 1990). Based on the comparisons of two months of overlapping data obtained at MLO for February-March, 1989, Bodhaine (1990) showed that GE and TSI-3760 counters gave comparable results (within a few percent) in typical background air masses sampled at MLO. We were not able to find any other reports or data that can provide further comparisons of CN values during instrument overlap periods at the NOAA baseline stations. In order to make use of the unique 30+ year period of CN data for a long-term trend study, it is important to assess further the effects of CN counter replacements on the recorded CN values.

The major difference among various CN counters used during different time periods, as indicated in Fig. S1, is the counting efficiency for particles < ~15 nm. While it is known that CN values measured by counters with different lower cutoff sizes may differ significantly during strong nucleation periods, when the particle number concentrations are dominated by nucleation mode particles < ~ 20 nm, such differences are expected to be much smaller in well-aged air masses because of the relatively short lifetime of small nucleation mode particles. The fractions of particles smaller than ~15 nm (in terms of number concentration) are likely to be small at four NOAA baseline stations because clean well-aged background air masses were sampled at these stations. Figure S2a shows mean particle size distributions measured at MLO in downslope air masses during 7/15-7/27/1992 (from Weber and McMurry, 1996), and SPO during 11/25-12/15/2000 and 12/16-12/29/1998 (from Park et al., 2004). For comparison, the annual mean particle size distributions observed at a clean background site at Pallas, Finland during 2002-2004 are also given (data from CREATE Aerosol Database at NILU, data PI: Hatakka Juha of the Finnish Meteorological Institute). Pallas site lies on the northern edge of the boreal forest zone with very sparsely populated surrounding areas.

While the measurements of size distributions at MLO and SPO only lasted a few weeks, and the size of the smallest bins was > 15 nm, it can be seen from Fig. S2a that the shapes of the size distributions at MLO and SPO are similar to those at Pallas, all indicating a sharp decrease in particles smaller than ~15-20 nm. To estimate quantitatively the differences in the CN values measured by different counters, we use the annual mean particle size distributions observed at Pallas, which, similar to the four NOAA baseline stations, provides a clean background site. Figure S2b presents the cumulative fraction of particles larger than a given diameter (in terms of number concentration), calculated from the annual mean size distributions observed at Pallas as shown in Fig. S2a. It is clear from Fig. S2b that, in a typical background air mass, the number fraction of particles smaller than 15 nm is < ~5%. As a result, the differences in CN values derived using CN counters with a d_{50} (50% counting efficiency size) of ~ 8 nm (GE counter), ~ 12 nm (TSI-3010), and ~15 nm (TSI-3760) are likely to be less than 5%. This is supported by almost identical (within a few percent) CN values measured by a GE counter and TSI-3760 at MLO during February/March, 1989 when both CN counters were operating (Bodhaine, 1990). In addition, except for SPO site around 1989, no obvious systematic shift can be seen in the monthly mean CN values at BRW, MLO and SMO when the counters were replaced (Fig. S1). The reason for a systematic increase in CN values at SPO after 1989 (by ~ 50%) is unclear, but is unlikely due to the change in d_{50} (from ~ 8 nm for the GE counter to ~15 nm for the TSI-3760), since the TSI-3760 with a larger d_{50} should have counted *fewer* particles.

The analysis presented above indicates that CN counter changeovers at BRW, MLO, and SMO are likely to have produced a relatively small variance of ~5%, and thus would not affect the derived long-term decreasing trend in CN of more than 10%/decade. At SPO, the CN data based on both GE and TSI-3760 counters cannot be combined to derive a long-term trend because of the obvious systematic shift associated with the CN counter replacement. Nevertheless, if we separate the CN time series into two periods covered by a single type of counter (GE: 1974-1989 and TSI-3760: 1989-2010), the decreasing trends during both periods is clearly seen. In the main text, we only show the 20+ years of TSI-3760 data for SPO.

In summary, both the 30+ years of CN data from four NOAA baseline stations (where two or three CN counters were used sequentially over the period) and the 15+ years of CN data at BND and NEU (where a single CN counter was used) show unambiguously the decreasing trends in particle number concentrations in the background atmosphere.

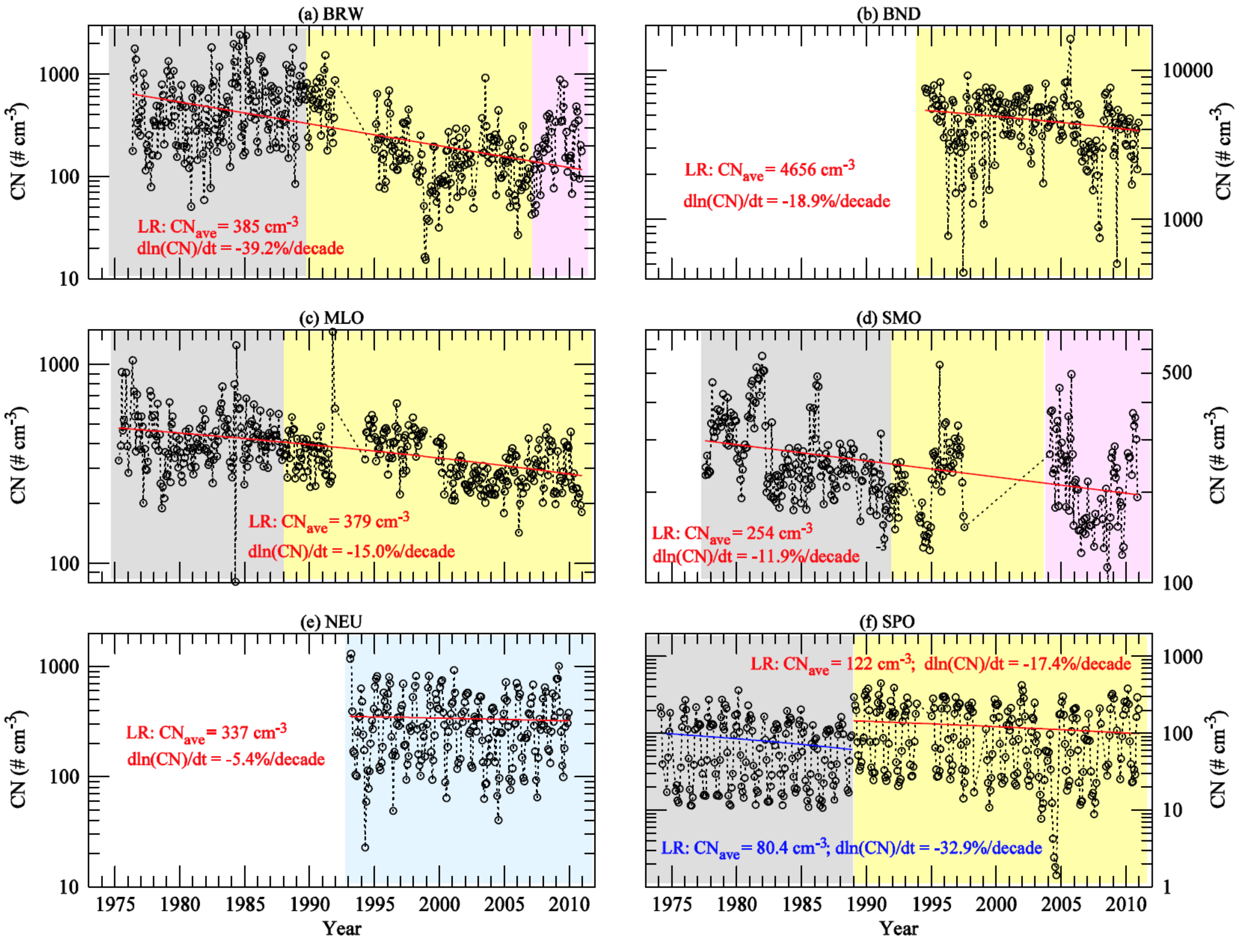

Figure S1. Monthly mean number concentration of condensation nuclei (CN) measured at four NOAA baseline stations at Barrow, Alaska (BRW), Mauna Loa Observatory, Hawaii (MLO), American Samoa (SMO), and South Pole Observatory (SPO), one NOAA regional station at Bondville, Illinois (BND), and one German Antarctic station at Neumayer (NEU). Different CN counters were used during different periods and at different stations, as indicated by the color shades (gray: GE counter; yellow: TSI-3760; pink: TSI-3010; light blue: TSI-3022A). In the figure, linear regressions (LR) of CN data are also shown, with mean values and slopes provided in the legend.

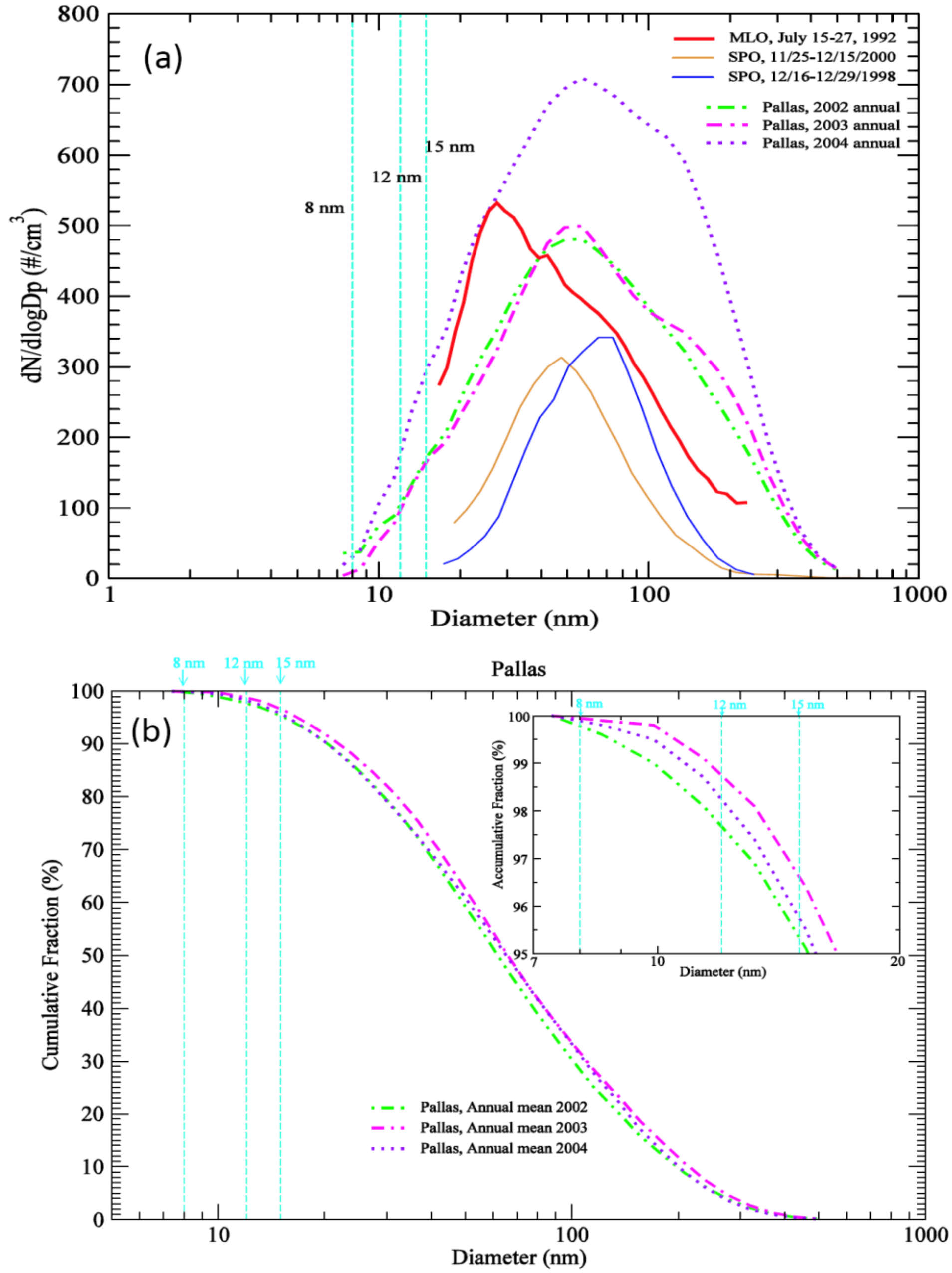

Figure S2. (a) Mean particle size distributions measured at MLO during 7/15-7/27/1992 (from Weber and McMurry (1996)), SPO during 11/25-12/15/2000 and 12/16-12/29/1998 (from Park et al. (2004)), and a remote site in Pallas, Finland (67.97 ^{o}N, 24.12 ^{o}E) during 2002-2004 (from CREATE data base). (b) Cumulative fraction of particles larger than a given diameter (in terms of number concentrations), calculated using annul mean size distributions observed at Pallas as shown in panel (a).

Supplementary References

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