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# Worldwide data sets constrain the water vapor uptake coefficient in cloud formation

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**Cloud droplet formation depends on the condensation of water vapor on ambient aerosols, the rate of which is strongly affected by the kinetics of water uptake as expressed by the condensation (or mass accommodation) coefficient,  $\alpha_c$ . Estimates of  $\alpha_c$  for droplet growth from activation of ambient particles vary considerably and represent a critical source of uncertainty in estimates of global cloud droplet distributions and the aerosol indirect forcing of climate. We present an analysis of 10 globally relevant data sets of cloud condensation nuclei to constrain the value of  $\alpha_c$  for ambient aerosol. We find that rapid activation kinetics ( $\alpha_c > 0.1$ ) is uniformly prevalent. This finding resolves a long-standing issue in cloud physics, as the uncertainty in water vapor accommodation on droplets is considerably less than previously thought.**

global climate | hydrological cycle | precipitation

Atmospheric aerosols affect the radiative balance of the Earth, directly through absorption and scattering of solar radiation and indirectly by influencing the microphysical properties, abundance, and lifetime of clouds. The magnitude of the indirect aerosol radiative forcing represents the most uncertain component of the estimated anthropogenic effect on climate (1). Cloud properties are intimately tied to the activation of individual aerosol particles and subsequent growth of the newly formed droplets by accretion of water vapor. This process depends on the rate of transfer of water vapor to droplets; the fraction,  $\alpha_c$ , of water molecules impinging on the surface of droplets that are incorporated in the droplet, the so-called uptake coefficient (2), is a critical parameter in global climate models.

The value of  $\alpha_c$  has been a subject of research for decades; it is commonly determined as an adjustable parameter to match growth rate measurements of droplets containing a well-defined concentration of solute (2, 3). The prevailing view is that  $\alpha_c$  for a pure water surface is close to unity. Actual cloud droplets, however, may contain solutes or surface films that affect growth kinetics even at low concentrations (4, 5), because slow solute dissolution (6) or glassy or highly viscous aerosol phases (7) may suppress droplet growth rates. The effective  $\alpha_c$  (that accounts for all water uptake processes) for droplets activated on ambient particles may be considerably lower than unity, with estimates of  $\alpha_c$  for ambient droplets ranging from  $10^{-5}$  to 1.0 (8–14). The smallest values in this range are unlikely to be representative of the global aerosol population, but several of these studies report values of  $\alpha_c$  between  $10^{-1}$  and  $10^{-2}$ , indicating significantly slower water uptake rates than that for pure water droplets.

Droplet formation in climate model simulations can be very sensitive to variations in  $\alpha_c$ , owing to the dependence of cloud

droplet number concentration ( $N_d$ ) on the maximum supersaturation that develops in clouds. The latter is controlled by a balance between supersaturation generation (from radiative or expansion cooling) and depletion from condensation of water vapor on existing droplets. A smaller value of  $\alpha_c$  results in slower water vapor condensation, allowing supersaturation to develop more fully and increasing  $N_d$  before reaching its maximum. This phenomenon is demonstrated by the sensitivity of global annual average vertical distributions of  $N_d$  to  $\alpha_c$ , computed with a state-of-the-art climate model for preindustrial (Fig. 1A) and current-day emissions (Fig. 1B). As expected,  $N_d$  correlates directly with aerosol concentration. Decreasing  $\alpha_c$  from 1.0 to 0.1 results in a 10–15% increase in  $N_d$  for current day emissions, whereas reducing  $\alpha_c$  to  $10^{-2}$  and  $10^{-3}$  leads to considerable increases in  $N_d$  by factors of 1.5–1.8 and 2.0–2.5, respectively (Fig. 1C). This  $N_d$  variability far surpasses the predicted 20–40% change in  $N_d$  between preindustrial and current-day emissions (for constant  $\alpha_c$ ; Fig. 1D). The implication is that for aerosol–cloud–climate interaction studies, the extent to which  $\alpha_c$  varies over space and time (especially if  $\alpha_c < 0.1$ ) is critical in understanding its contribution to  $N_d$  variability; hence, global cloud properties and climate. Little is known, however, concerning the spatial and temporal distribution of  $\alpha_c$ . This uncertainty translates to a considerable, but unconstrained, source of uncertainty in estimating aerosol indirect forcing.

Measurements of the droplet size distribution resulting from exposure of aerosol particles to a given water vapor supersaturation, the so-called Cloud Condensation Nuclei (CCN) data, can provide the fundamental information on which values of  $\alpha_c$  can be inferred. For this, threshold droplet growth analysis (TDGA) (15–18) is based on comparing the growth of activated CCN against a standard particle that rapidly grows [e.g.,  $(\text{NH}_4)_2\text{SO}_4$  CCN with  $\alpha_c > 0.1$  (19)] for identical measurement conditions. If droplet sizes from ambient particles are similar to the standard, they are considered to have similar  $\alpha_c$ ; a smaller droplet size may suggest slower growth kinetics (and lower  $\alpha_c$ ). TDGA is designed to detect

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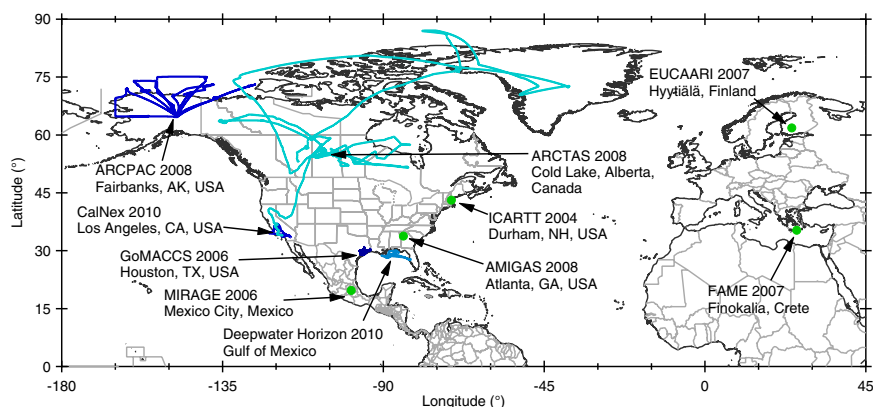
The authors declare no conflict of interest.

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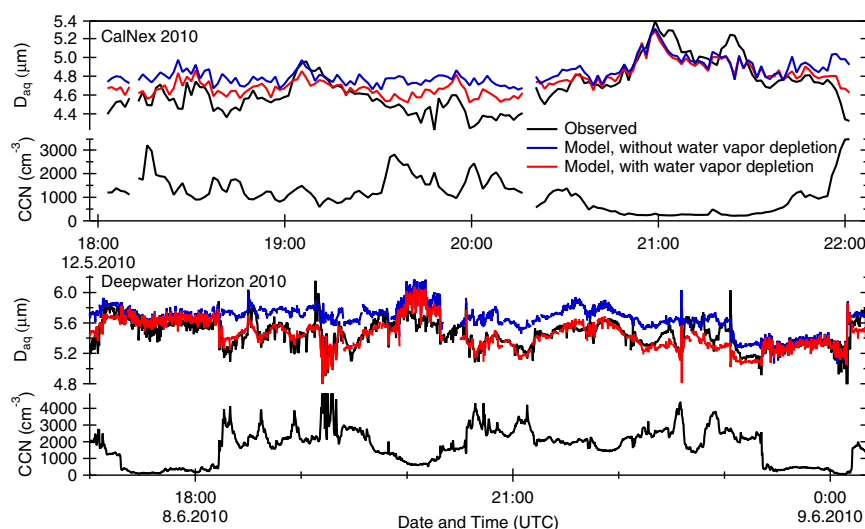
**Fig. 2.** Campaign sites (green markers) and flight tracks (light and dark blue lines) of the globally representative data sets considered in this study. Analysis of the data sets is presented in *SI Text* and in previous publications (14–16).

prediction biases. Because activated droplet size is a function of aerosol size distribution, hygroscopicity, instrument operating conditions (accurately known), and  $\alpha_c$  (not known), one can simulate the activation and growth of CCN in the Droplet Measurement Technologies CCN counter using a prescribed (constant)  $\alpha_c$ . If the difference between observed and predicted droplet size is essentially constant for all of the data, then a constant  $\alpha_c$  is assumed valid. Indeed, this is found to be the case for our globally relevant data sets. Prescribing  $\alpha_c = 0.2$  [which is representative of fast activation kinetics (19)] captures the temporal variability of measured droplet size (Fig. 3) to within a constant bias and a  $0.3\text{-}\mu\text{m}$  variance (Fig. 4), which characterizes normal instrument variability and the essentially unresolvable range of  $\alpha_c$  between 0.1 and 1.0 (19, 21). With this result and the fact that TDGA suggests that the majority of particles activate as rapidly as  $(\text{NH}_4)_2\text{SO}_4$ , one concludes that  $\alpha_c > 0.1$  is globally representative. Regions of the globe not directly sampled (e.g., eastern Asia, Amazon) generally follow one of the air types of Table 1; CCN activation kinetics of globally important secondary organic aerosol generated in environmental chambers further supports the model of rapid activation (*SI Text*).

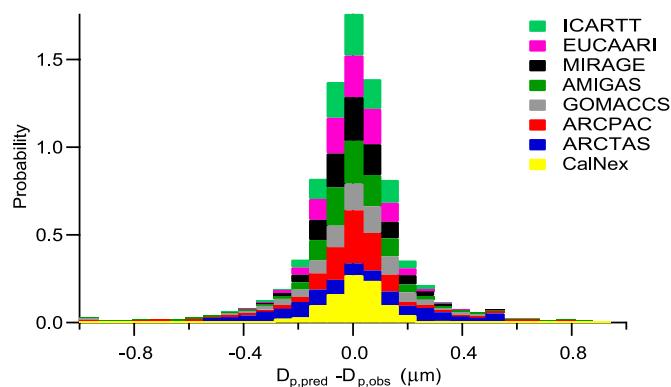
Important implications arise from our results. First,  $\alpha_c$  is effectively constant for all the data considered, even for particles composed largely of organics with very low oxygen content. Anthropogenic (compositional) impacts on  $\alpha_c$  are therefore limited to the 0.1–1.0 range, considerably reducing the uncertainty for cloud droplet number prediction in climate models. This study resolves a decades-long uncertainty in cloud physics on the value of  $\alpha_c$ , because it appears that  $\alpha_c$  for ambient aerosol can be represented in models with a constant value in the 0.1–1.0 range.

### Materials and Methods

**Ambient CCN Data Sets Considered.** CCN data are collected with a Droplet Measurement Technologies continuous flow streamwise thermal gradient chamber (22, 23). This instrument consists of a continuous flow tube in which the sample flow is focused on the column centerline by using a larger sheath flow. Chamber walls are kept wet, and a positive wall temperature gradient is maintained by three sets of thermo-electric coolers. Because water vapor diffuses faster than heat in air, supersaturation increases with distance from the wall, reaching a maximum at the column centerline. Due to the entry length effects, particles are first exposed to a quickly increasing relative humidity until a relatively stable maximum supersaturation is reached. Activated droplets exiting the chamber are counted and sized (20 size bins from 0.5 to



**Fig. 3.** Characteristic observed and predicted time series of number-average droplet diameter for  $\alpha_c = 0.2$ . Constant 1- and  $2.3\text{-}\mu\text{m}$  offsets were added to the observed droplet sizes from the CalNex and Deepwater Horizon campaigns, respectively. The Deepwater Horizon data are from ref. 14. Neglecting to simulate the supersaturation depression from condensation of water vapor on CCN leads to a larger and considerably less variable predicted mean droplet size than observed. Depletion effects are more prominent for DWH because the presence of coarse mode sea salt leads to larger-size droplets that cause greater total condensation and water vapor depletion for a given particle concentration. In both data sets, applying TDGA would misidentify the presence of slow growth kinetics.



**Fig. 4.** Probability density distributions of the difference between average predicted ( $\alpha_c = 0.2$ ) and observed droplet diameters in the CCN instrument for all the data analyzed in this study. The observed droplet sizes are corrected for a constant bias expressing droplet sizing shifts in the CCN instrument and model prediction uncertainties, as described in *SI Text*. For all the data shown, predicted droplet size exhibits variability that is within instrument uncertainty, meaning that the effective uptake coefficient is effectively constant for all the data. Combining the results of TDGA on the same data leads to the conclusion that rapid droplet growth kinetics (with  $\alpha_c$  between 0.1 and 1.0) is globally prevalent.

10.0  $\mu\text{m}$ ) by an optical particle counter. Instrument supersaturation, typically as a function of wall temperature gradient, is determined by conducting calibration experiments with ammonium sulfate or sodium chloride aerosol. The data sets for which CCN measurements are analyzed are described in detail in *SI Text*.

**CCN Instrument Model Description.** The coupled instrument and droplet growth model (19), freely available at <http://nenes.eas.gatech.edu/Experiments/CFSTGC.html>, calculates flow velocity, pressure, and supersaturation profiles from the measured sample pressure, column temperatures, sample and sheath flow rates, and calibrated maximum supersaturation. Flow velocities and supersaturation profiles are then used in a Lagrangian droplet growth model to calculate the growth and activation of CCN as they flow through the instrument chamber. The growth model input parameters are  $\alpha_c$ , dry particle size distributions, and hygroscopicity. Number concentrations are needed to account for water vapor depletion effects because CCN chamber supersaturation is decreased due to water vapor condensation on growing droplets, leading to coupling between the instrument and droplet growth models (20).

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**Global Simulations.** The impact of the mass accommodation coefficient  $\alpha_c$  on cloud properties and indirect aerosol radiative forcing was estimated using the community atmosphere model (CAM5.1), which is a state-of-the-art atmospheric general circulation model with fully coupled aerosol–cloud interactions (24). We used the model configured with the finite volume dynamic core, with a horizontal resolution of  $1.9^\circ \times 2.5^\circ$  and 30 levels in the vertical. The three-mode version of the modal aerosol module (MAM3) was used, which considers aerosol sulfate, ammonium, nitrate, primary organic matter, secondary organic aerosol, black carbon, sea salt, and dust; particles are distributed into Aitken, accumulation, and coarse lognormal modes with prescribed geometric SD. The mode diameter varies as aerosol number and total mass change. The MAM3 is coupled to a double moment cloud microphysics scheme. Particles can be removed by wet removal mechanisms or regenerated to interstitial aerosol after cloud droplets evaporate. Activation of aerosol to cloud droplets is calculated with the (25) parameterization, which includes the effect of  $\alpha_c$  on the activation process. Simulations with  $\alpha_c = 1, 10^{-1}, 10^{-2}$ , and  $10^{-3}$  were performed for current-day and preindustrial emissions of aerosol precursors, with climatological sea surface temperatures and ice cover. Emissions data sets used in the simulations are those of ref. 26 for both the present day (year 2000) and preindustrial simulations (year 1850). The vertical distribution of emissions follows the protocol of ref. 27. The reported fields of in-cloud droplet number concentrations correspond to the annual average from the last 5 y of simulation, after allowing 1 y of simulation for spin-up. The annual average spatial distribution of cloud number concentrations for preindustrial and current-day emissions are provided in *SI Text*.

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