CCN Spectra, Hygroscopicity, and Droplet Activation Kinetics of Secondary Organic Aerosol Resulting from the 2010 Deepwater Horizon Oil Spill

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Abstract

Secondary organic aerosol (SOA) resulting from the oxidation of organic species emitted by the Deepwater Horizon oil spill were sampled during two survey flights conducted by a Na-

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tional Oceanic and Atmospheric Administration (NOAA) WP-3D aircraft in June 2010. A new
technique for fast measurements of cloud condensation nuclei (CCN) supersaturation spectra
called Scanning Flow CCN Analysis (SFCA) was deployed for the first time on an airborne
platform. Retrieved CCN spectra show that most particles act as CCN above (0.3±0.05)% su-
persaturation, which increased to (0.4±0.1)% supersaturation for the most organic-rich aerosol
sampled. The aerosol hygroscopicity parameter, κ, was inferred from both measurements of
CCN activity and from humidified-particle light extinction, and varied from 0.05-0.10 within
the emissions plumes. However, κ values were lower than expected from chemical composi-
tion measurements, indicating a degree of external mixing or size-dependent chemistry, which
was reconciled assuming bimodal, size-dependent composition. The CCN droplet effective
water uptake coefficient, γ_{cond}, was inferred from the data using a comprehensive instrument
model, and no significant delay in droplet activation kinetics from the presence of organics was
observed, despite a large fraction of hydrocarbon-like SOA present in the aerosol.

**Introduction**

The explosion and loss of the Deepwater Horizon (DWH) oil platform on 20 April 2010 resulted
in the release of millions of barrels of oil into the waters of the Gulf of Mexico during April-July,
2010 (1). While a large portion of the oil-gas mixture remained dissolved or dispersed in the water
column, a substantial portion reached the water surface and evaporated into the atmosphere over a
period of hours to days (2, 3). Volatile organic carbon (VOC) and intermediate volatility organic
carbon (IVOC) species are oxidized in the atmosphere, which lowers their volatility causing them
to nucleate new particles or condense onto existing aerosol particles. Termed secondary organic
aerosol (SOA), these particles are an important but uncertain contributor to adverse air quality and
climate change (4, 5).

In this paper, we present a detailed characterization of the hygroscopic and droplet-forming
properties of SOA formed in the vicinity of the DWH site during two survey flights conducted
by the National Oceanic and Atmospheric Administration (NOAA) WP-3D aircraft on 8 and 10
June 2010. These survey flights provide a unique case study of hydrocarbon-derived SOA that has experienced relatively little atmospheric oxidative processing and whose concentrations exceed those of the more oxidatively-aged organic aerosol background. Both fresh and aged SOA coexist in urban environments, although the latter species are usually much more abundant (6), and, hence, may obscure the influence of the former on measured cloud condensation nuclei (CCN) activation and droplet growth.

**Methodology**

The observational data were obtained on two survey flights conducted near the site of the DWH oil platform (28°44′12″N, 88°23′13″W) on 8 and 10 June 2010. Data were filtered to include only those sampled within the lower portion of the marine boundary layer at between 50 and 150 meters altitude above sea level. Intermittent periods with elevated CO mixing ratios (>150 ppbv), indicative of combustion sources, were rarely observed but were also excluded from the dataset in order to focus solely on the SOA signature. This filtering process also excludes the interception of the plume from a surface oil burn southwest of the DWH site on 8 June (7). Flight tracks near the DWH site are shown in Figure 1, while the entire, unfiltered flight tracks are provided in the supporting information.

**CCN and Aerosol Measurements**

CCN concentration measurements were obtained using a Droplet Measurement Technologies (DMT) stream-wise thermal-gradient cloud condensation nuclei counter (CCNC) (9, 10), which exposes an aerosol to a specified water vapor supersaturation and counts and sizes the droplets that form. Since the supersaturation in the instrument is sensitive to pressure fluctuations, the pressure inside the growth chamber was kept constant at 500 hPa using a flow orifice and active control system. On 8 June, the CCNC was operated at a constant flow rate (0.5 L min⁻¹) and a single supersaturation of 0.33% for the duration of the flight, while on 10 June, the CCNC supersaturation was
dynamically scanned over a range of supersaturations (0.2-0.7%) every 15 seconds using Scanning Flow CCN Analysis (SFCA) (11). Supersaturations were calibrated in terms of the CCNC internal temperature gradient and flow rate using size-classified ammonium sulfate aerosol and Köhler theory (12–14). The supersaturation absolute uncertainty is estimated to be ±0.04%.

Subsaturated hygroscopicity measurements were obtained from a cavity ringdown (CRD) spectrometer measuring aerosol extinction at 532 nm wavelength under both dry (10%RH) and humidified (70-95%RH) conditions (15). Gas phase absorption at 532 nm wavelength was measured using a designated filtered CRD channel and subtracted from the aerosol measurements but was observed to be low during both flights.

Fine mode dry particle size distribution measurements (0.004 to 1 µm diameter) were obtained every second from an ultra-high sensitivity aerosol size spectrometer (UHSAS) and a nucleation mode aerosol size spectrometer (NMASS). The NMASS consists of five condensation particle
counters (0.004, 0.008, 0.015, 0.030, and 0.055 µm cutoff diameters) that are coupled to the UHSAS distribution using a nonlinear inversion algorithm to obtain the complete size distribution (16, 17).

Non-refractory, sub-micron aerosol chemical composition was measured using a compact time-of-flight aerosol mass spectrometer (C-ToF-AMS) with a pressure-controlled inlet (18, 19). The instrument was operated in “mass spectrum” mode to obtain bulk (i.e., size-averaged) mass spectra with a 0.1 Hz resolution and in “time-of-flight” mode to obtain size-resolved mass spectra, which were then averaged over 5 minute periods to improve signal-to-noise. The mass spectra were integrated to calculate the total mass loadings for sulfate, nitrate, ammonium, and organic aerosol components. The C-ToF-AMS collection efficiency (CE) parameterization of Middlebrook et al.(20) was used in the data inversion, resulting in an average CE for the flights of ∼0.46 and 0.48. Mass loadings of elemental carbon were obtained from a single particle soot photometer (SP2) and were found to be much smaller than the non-refractory mass measured by the C-ToF-AMS (7, 21). Comparison of the total aerosol mass measured by the C-ToF-AMS and SP2 with that derived from the measured size distribution, shows reasonable agreement (slope = 1.11-1.18, $R^2$=0.91-0.93), verifying the applicability of the chosen C-ToF-AMS CE.

**Coupled CCNC Instrument Model**

An important feature of the DMT CCNC is the ability to measure the size distribution of activated droplets leaving the instrument flow chamber; this makes it possible to retrieve information about CCN activation kinetics. To first order, this can be done by qualitatively comparing the measured droplet size distribution to that obtained for calibration aerosol (e.g., (NH$_4$)$_2$SO$_4$ or NaCl) at the same instrument operating conditions (flow rate, pressure, and applied temperature gradient). If the measured mean droplet size exceeds that for calibration aerosol, slow activation kinetics can be ruled out, while a lower measured mean droplet size may suggest slow kinetics. Termed Threshold Droplet Growth Analysis, this procedure has been applied in a number of past studies with success (22). However, in addition to the basic instrument operating parameters, droplet sizes are also
dependent on the aerosol size distribution, and to a lesser extent, the aerosol number concentration in the growth chamber (22). We use a detailed numerical model to deconvolve these dependencies, allowing the quantification of composition impacts on droplet activation kinetics in terms of an empirical water uptake coefficient, $\gamma_{\text{cond}}$, that accounts for gas- and particle-phase mass transfer resistances, solute dissolution kinetics, and for the sticking probability of a water vapor molecule colliding with a growing water droplet.

The coupled CCNC instrument and droplet growth model (10, 22), together with recent improvements by Raatikainen et al. (23) is used here to numerically solve the coupled momentum, mass, and energy balance equations for an aerosol population traversing the CCNC flow field. Model predictions of both the droplet number concentration and size distribution leaving the CCNC growth chamber are compared to the measurements in order to determine the value of $\gamma_{\text{cond}}$ that gives the best agreement between predicted and measured droplet sizes.

Analysis

The ability of a particle to act as a CCN depends on its size, chemical composition, and on the ambient water vapor supersaturation (12). This compositional dependence is commonly parameterized in terms of a hygroscopicity parameter, $\kappa$, in Köhler theory (24)

$$\kappa = \frac{4}{s^2D_{p,c}^3} \left( \frac{4\sigma M_w}{3RT \rho_w} \right)^3$$

where $s$ is the water vapor supersaturation, $D_{p,c}$ is the particle critical dry diameter (above which all particles act as CCN), $\sigma$ is the surface tension of the solution droplet, $R$ is the gas constant, $T$ is the absolute temperature, and $M_w$ and $\rho_w$ are the molar mass and density of water, respectively. In this study, the surface tension of pure water (71.4 mJ m$^{-2}$) is assumed. Following Moore et al. (25) and as described in the supporting material, $\kappa$ is calculated by integrating the aerosol size distribution above some $D_{p,c}$ so that the integrated concentration matches the measured CCN concentration at a specified supersaturation. This value of $D_{p,c}$ is then used in Eq. (1) to find $\kappa$. Given the range of
supersaturation and observed $D_{p,c}$, a more complex form of Eq. (1) is not necessary.

While the hygroscopicity parameter is unable to unambiguously account for complex aerosol mixing state or surface tension impacts, using the above approach offers a simple way to parameterize composition for global models and is applicable to other measures of water uptake, such as in subsaturated conditions. While $\kappa$ is expected to be similar for both water vapor saturation ratios less than and greater than unity, solution non-ideality or surface tension effects in the former may yield a derived subsaturated $\kappa$ that is somewhat lower than for supersaturated cloud droplets, which are more dilute (24, 26, 27).

The subsaturated humidity dependence of the CRD aerosol extinction was used to derive the aerosol humidification factor, $\gamma_{\text{ext}}$, as

$$\frac{\sigma_{RH}}{\sigma_{RH_{\text{ref}}}} = \left[ \frac{1 - RH}{1 - RH_{\text{ref}}} \right]^{\gamma_{\text{ext}}}$$

where $\sigma_{RH}$ is the measured aerosol extinction at relative humidity, RH. In this work, the reference RH is 10%, while the elevated RH is 85%. The humidification factor represents the dependence of aerosol extinction on RH, which results from changes in the particle size and refractive index upon humidification. Thus, $\gamma_{\text{ext}}$ and $\kappa$ are related quantities and one can employ Mie theory with a number of assumptions to independently derive $\kappa$ from $\gamma_{\text{ext}}$. These calculations were performed using the CRD data together with the measured dry particle size distribution and a prescribed refractive index (RI) of 1.45 - $0i$. Further details regarding the calculation approach and sensitivity to the RI assumption and $\sigma$ uncertainty are presented in the supporting information.

**Results and Discussion**

**CCN Activity and Hygroscopicity**

Figure 1 shows the collocated spatial distribution of the CCN-derived $\kappa$ and the organic aerosol volume fraction for the low-level flight legs near the DWH site. Greater variability in $\kappa$ for ad-
jacent points far from the DWH site on 10 June exceeds that seen on 8 June, which may reflect size-dependent aerosol composition because the changing instrument supersaturation during SFCA operation on 10 June also changes the size range over which CCN measurements are most sensitive (i.e., diameters near $D_{p,c}$). Winds on 8 June were light with variable direction, while a more sustained southeasterly flow was present on 10 June. This gives rise to a distinct plume of low-hygroscopicity, organic aerosol to the northwest of the DWH site on the 10th. de Gouw et al. (3) examined the gas- and aerosol-phase composition on this day for a plume transect near the DWH site (P1) and a transect farther downwind (P2). They found a narrow plume of VOCs surrounded by a much broader plume of hydrocarbon-like SOA, with the organic aerosol concentration and size distribution both increasing from P1 to P2 (3). Transport calculations based on wind speed and direction suggest that the enhancement in SOA results from less-volatile IVOC precursors (likely C_{14} to C_{16} compounds), which evaporate over a period of hours to days after surfacing and are chemically transformed to SOA within a few hours in the atmosphere (3). The importance of a sustained wind direction in dispersing the oil emissions is apparent from the lack of an appreciable organic fraction south of the DWH site on the 10th, but a wider impacted area on the 8th. Satellite imagery of the spill extent (gray shaded region in Figure 1) on both days does not necessary coincide with enhancements in gas- or aerosol-phase species, suggesting that the “highly-aged” portion of the oil slick consists of low volatility compounds, which do not contribute appreciably to SOA.

The changes in the total particle size distribution ($dN_{CN}/d\log D_p$) and CCN supersaturation distribution ($dN_{CCN}/ds$) across different organic aerosol fractions are shown in Figure 2. The solid trace denotes the geometric means and the circles denote the mean values for P1 and P2. A small accumulation mode of a few thousand particles per cm$^3$ is present at all organic fractions with a significant Aitken mode appearing at organic fractions above 60%. The mean size of the Aitken mode increases by roughly three-fold over the observed range of organic fractions, consistent with condensational growth from semi-volatile organic vapors. A large Aitken mode is also present in Figure 2 between 30%-40% organics, which reflects the sampling of freshly nucleated particles in the absence of organic condensation on existing large particles just upwind of the DWH.
site (28). For organic volume fractions less than 75-80%, the peak of the CCN distribution is around \((0.30 \pm 0.05)\%\) supersaturation, which broadens considerably and shifts to approximately \((0.4 \pm 0.1)\%\) supersaturation at the highest organic fractions.

The increase in critical supersaturation coincides with an increase in the mean particle diameter, which implies a significant decrease in the particle hygroscopicity since increasing particle size tends to strongly decrease the critical supersaturation. This is shown by the inverse correlation between \(\kappa, \gamma_{\text{ext}}\), and organic volume fraction in Figure 3a,b. The overall \(\kappa\) for an aerosol containing \(n\) components is calculated as

\[
\kappa = \sum_{i} \varepsilon_i \kappa_i
\]  

(3)

where \(\varepsilon_i\) and \(\kappa_i\) are the volume fraction and hygroscopicity of the \(i\)-th aerosol component, respectively. Two-component mixing lines were calculated from Eq. (3) assuming a constant inorganic hygroscopicity, \(\kappa_{\text{inorg}}\), of 0.6 and a constant organic hygroscopicity, \(\kappa_{\text{org}}\), of either 0 or 0.1 (dashed traces in Figure 3a). It can be seen from Figure 3a that the observed aerosol hygroscopicity lies below even the \(\kappa_{\text{org}}=0\) mixing line, which likely reflects size-dependent composition or a partially externally-mixed aerosol population not captured by these simple, but commonly-employed mixing rules. Extrapolating the piecewise linear fit of the median \(\kappa\) data in Figure 3a to \(\varepsilon_{\text{org}}=1\) yields an effective \(\kappa_{\text{org}}=0.05\). In modeling the condensational growth rate of SOA near the DWH site, Brock et al. (28) assumed an intermediate-volatility organic species with a molar mass of 0.292 kg mol\(^{-1}\) and density of 1000 kg m\(^{-3}\). From Köhler theory, the hygroscopicity of a pure, soluble organic aerosol can be found as \(\kappa_{\text{org}} = (M_w/\rho_w)(\rho_{\text{org}}/M_{\text{org}})\nu_{\text{org}}\), where \(\rho_{\text{org}}, M_{\text{org}},\) and \(\nu_{\text{org}}\) are the density, molar mass, and van’t Hoff factor of the organic solute, respectively (36). Using the values of \(\rho_{\text{org}}\) and \(M_{\text{org}}\) from Brock et al. (28) with an assumed unit van’t Hoff factor yields a value of 0.06, which is consistent with the CCN-derived estimate.

A number of ambient and SOA chamber studies have shown that the pure organic hygroscopicity increases with increasing organic oxygenation (29–32). The C-ToF-AMS mass fraction of the \(m/z\) 44 peak to total organic mass, \(f_{44}\), is correlated with the organic O:C ratio (33, 34), and the rela-
Figure 2: Average particle size distributions (top) and CCN supersaturation distributions (bottom) plotted versus the C-ToF-AMS organic volume fraction for the 10 June flight. Solid traces denote the geometric mean diameter and supersaturation in the top and bottom figures, respectively, calculated for a single mode. Circles show the mean values for the intercepted plume at P1 and P2 (±1 standard deviation).
tionship between $\kappa_{\text{org}}$ and $f_{44}$ or O:C has been reported for some previous measurements \((30–32)\). From Figure 3c, it can be observed that aerosol composed almost entirely of SOA are less-oxidized than aerosol composed only partially of SOA. This trend reflects the varying contribution of the low-O:C, fresh SOA and the higher-O:C, aged background organic aerosol to the total aerosol composition, where the former dominate at high $\varepsilon_{\text{org}}$ near the DWH site and the latter dominate at lower $\varepsilon_{\text{org}}$ outside of these SOA plumes. Using three parameterizations for $\kappa_{\text{org}}$ and a constant $\kappa_{\text{inorg}}=0.6$ yields the shaded regions shown in Figure 3a, which considerably overpredict the aerosol hygroscopicity parameter by a similar amount as the $\kappa_{\text{org}}=0.1$ mixing line.

As shown in Figure 2, a distinct accumulation size mode is present throughout the survey flights with a more prominent Aitken size mode associated with the organic-rich aerosol near the DWH site. Consequently, size-resolved C-ToF-AMS chemical composition was used to look for compositional differences between the two modes, which may explain the overprediction shown in Figure 3a. As discussed in the supporting information, a lower size-resolved, organic volume fraction $\varepsilon_{\text{SR,org}}$ was observed for the accumulation mode (\(\sim 0.4-0.8\)) versus the Aitken mode (\(\sim 0.85-1\)). While the larger-sized particles affect the bulk (i.e., size-averaged) C-ToF-AMS composition more so than the smaller particles, the Aitken-mode-dominated number size distribution is a more important determinant of CCN activity. Using the average composition for each mode, $\kappa$ was calculated for both the accumulation mode and the Aitken mode aerosol assuming $\kappa_{\text{org}}=0.05$ and $\kappa_{\text{inorg}}=0.6$. The overall $\kappa$ is then obtained from a CCN number-weighted average of the two modes and is shown as the blue shaded region in Figure 3, where it can be seen that predictions of $\kappa$ based on a two-mode, size-dependent composition are in much better agreement with observations than those obtained from bulk (i.e., size-averaged) composition, both using the same simple mixing rule assumptions.

A comparison between the supersaturated, CCN-derived $\kappa_{\text{CCN}}$ and the subsaturated, CRD-derived $\kappa_{\text{CRD}}$ is shown for the entire June 8th flight in Figure 4d. For most of the flight, the mean value of $\kappa_{\text{CRD}}$ is approximately 50% less than $\kappa_{\text{CCN}}$ (Figure S3), although the data are highly correlated assuming a constant 50% bias ($R^2 = 0.75$) and the propagated uncertainty of $\kappa_{\text{CCN}}$ is
Figure 3: Distribution of (a) CCN-derived hygroscopicity, (b) extinction humidification factor, and (c) $f_{44}$ ratio and O:C ratio (from the Aiken et al. (33) correlation) plotted versus C-ToF-AMS organic volume fraction. Boxes denote the median and interquartile range for all observations from both flights between 50 and 150 meters altitude, while the numbers beside each box denote the number of 0.1 Hz points used in the calculation. Solid traces are fits to the median data. Circles show the mean values for the intercepted plume at P1 and P2 on June 10th ($\pm$ 1 standard deviation). Shaded areas and dashed traces in (a) are $\kappa$ predictions from different compositional assumptions. The organic volume fraction bin centered at 0.25 in (c) has been excluded due to low signal-to-noise.
relatively large. A similar discrepancy (~30-50%) has been previously observed for comparison of CCN-derived hygroscopicities and those inferred from subsaturated measurements with an humidified tandem differential mobility analyzer (HTDMA) (26, 27, 35). This suggests that while the humidification of organic-rich aerosol appears to have a small effect on their size and light scattering (κ_{CRD} ~ 0.01-0.05), these particles have a greater contribution to CCN activation (κ_{CCN} ~ 0.05-0.10).

The derived organic hygroscopicity of ~ 0.05 is on the low end of past studies looking at the CCN-derived κ of SOA produced from the oxidation of IVOCs, but is consistent with some past subsaturated hygroscopic growth results. For example, Jimenez et al. (29) report κ_{org} ~ 0.06 from hygroscopic growth measurements of aerosol in Mexico City and from the smog chamber oxidation of α-pinene for aerosol with O:C ~ 0.4. Meanwhile, CCN measurements have found κ_{org} of 0.04 for β-caryophyllene SOA produced via ozonolysis (36), of 0.01-0.10 for SOA derived from the OH oxidation of n-heptadecane (O:C ~ 0.1-0.2) (32), and of 0.07-0.10 for SOA derived from the OH oxidation of longifolene (O:C ~ 0.2-0.3). This work is contrasted with many other studies of ambient SOA in the literature that find higher κ on the order of 0.1-0.3 (37–41), likely due to the more-aged nature of the sampled aerosol, which increases both κ and O:C. Thus, this work provides important observations of the CCN-derived hygroscopicity of relatively unoxidized SOA derived from IVOCs that likely require less oxidation in the atmosphere to form reaction products which partition into the aerosol phase (42, 43). Near local emissions sources such as in urban environments, the presence of these less hygroscopic SOA species may partially explain some large CCN overpredictions based on measured aerosol composition (44).

**Droplet Activation Kinetics**

Figure 4a,b presents the droplet size distribution of activated CCN in the CCNC (normalized by the total number of droplets), the number-averaged mean droplet size, and the modeled mean droplet size for aerosol with an effective water uptake coefficient, γ_{cond}, of 0.2. It can be seen that the temporal variability is strongly correlated for the measured and modeled mean droplet sizes
when accounting for supersaturation depletion effects from moderate CCN concentrations in the CCNC growth chamber (\(\sim 1000-3000 \text{ cm}^{-3} \text{ STP}\)) (22). Neglecting the depletion effects leads to a larger mean droplet size and much less variability in the predictions, which is not in agreement with observations. This is because, even though supersaturation depletion has a limited effect on the measured CCN concentration, it can have an observable effect on the measured droplet size distribution. The simulated traces were corrected by a constant 2.3 \(\mu\text{m}\) bias, which gives the best agreement between the \(\gamma_{\text{cond}}=0.2\) simulated and observed droplet sizes (see supporting information). Simulations of the activation and growth of ammonium sulfate calibration aerosol reveal a 2.1 \(\mu\text{m}\) model overprediction bias, which is in good agreement with the correction bias applied here. Regression analysis of the modeled versus measured mean droplet sizes indicates that a constant value of \(\gamma_{\text{cond}}\) between 0.1 and 0.2 best reproduces the observed droplet size variability for the entire dataset.

While it is known that droplet formation is less sensitive to changes in \(\gamma_{\text{cond}}\) in the range of 0.1-1 versus lower values (45), the exact value of \(\gamma_{\text{cond}}\), even for pure water droplets, remains uncertain with reported values in the range of 0.04 to 1 (46–49). The most realistic value is probably between 0.06 and 0.3 (47, 48, 50). As the inferred coefficients in this study are similar to the reference values for pure water, this suggests that the fresh SOA generated near the DWH site do not promote kinetic delays upon condensation on ambient CCN. Given the relatively low hygroscopicity and hydrocarbon-like nature of the organic species (O:C ratios \(\sim 0.4-0.5\) around the plume), this is a somewhat unexpected result. Previous work has shown that hydrophobic organic compounds may retard water uptake through slow dissolution, which reduces the amount of solute in the droplet and shifts the water vapor-liquid equilibrium more towards the gas-phase than if all of the solute had immediately dissolved (51). Alternatively, organics may form compressed films on the droplet surface, which increases the condensational mass transfer resistance (52). A number of past studies have found distinctly slower activation kinetics for smog-chamber SOA resulting from the photo-oxidation of \(\beta\)-caryophyllene (53), aerosol above the Pacific marine boundary layer (54), biogenic aerosol in rural Canada (55), and both urban and rural aerosol at ground-based locations around the
Figure 4: Timeseries of measured (a, b) and modeled (b) droplet sizes of activated CCN in the CCNC during the June 8th flight. Shown for comparison are the measured CCN concentrations and dry extinction at 532 nm (c) and the aerosol organic volume fraction and hygroscopicities derived from the supersaturated CCN and subsaturated cavity ring down measurements (d). The shaded regions in (d) denote the propagated uncertainty of each κ (±1 standard deviation), whose calculation is described in the supporting material.
United States (56). Lance et al. (57) examined airborne measurements of CCN in Houston, TX, during the 2006 GoMACCS campaign and found no evidence for slow activation kinetics (57), contrary to Ruehl et al. (54) and Asa-Awuku et al. (58), who did observe delayed CCN activation from concurrent ground-based and airborne platforms. Since some of these studies were carried out with size-selected aerosol (i.e., a small fraction of the overall CCN concentration was sampled at a time), supersaturation depletion effects may not have caused the apparent kinetic delays. A potential difference may be the phase state of the aerosol (e.g., glassy/amorphous versus partially-deliquesced) and its impact on water uptake kinetics. Given that most kinetic delays were reported for dry aerosol may lend some support to this hypothesis. A previously-deliquesced aerosol state is consistent with the current results as even a small amount of residual water could inhibit glassy transition and promote rapid activation kinetics. If true, this suggests that condensation of even the most hydrophobic SOA onto existing inorganic CCN may not impact activation kinetics. This finding is relevant for the growth of newly-formed particles in the atmosphere, which have been hypothesized to form as H$_2$SO$_4$ seeds and grow to CCN-relevant sizes primarily through the condensation of SOA from IVOCs and VOCs (59–61).

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Supporting Information Available

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Supporting information for: CCN Spectra, Hygroscopicity, and Droplet Activation Kinetics of Secondary Organic Aerosol Resulting from the 2010 Deepwater Horizon Oil Spill

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Flight Overview Maps
Figure 1: Complete aircraft trajectories for the survey flights on 8 June (top) and 10 June (bottom). Both flights originate and end in Tampa, Florida. Markers are colored by the CCN-derived hygroscopicity. The gray shaded area represents the extent of surface oil ($I$). The ordinate and abscissa denote degrees latitude and longitude, respectively.
**CCN-Derived Hygroscopicity**

The CCN-derived hygroscopicity parameter, $\kappa_{CCN}$, is obtained from the supersaturation-dependent CCN concentration and aerosol size distribution following Moore et al. (2):

1. The normalized cumulative size distribution was calculated for each particle size bin as

$$n_{cum}(D_p) = \frac{1}{N_{CN}} \int_{4\text{nm}}^{D_p} dN_{CN} d\log D_p$$

   where $D_p$ is the particle diameter, $N_{CN}$ is the fine particle concentration larger than 4 nm, $dN_{CN}$ is the fine particle concentration in the bin, and $d\log D_p$ is the bin width in logarithm space.

2. The CCN-active aerosol fraction, $R_a = N_{CCN}/N_{CN}$ was calculated, where $N_{CCN}$ is the measured CCN concentration at a given supersaturation. For an internally-mixed aerosol whose composition does not vary with size, all particles larger than some critical supersaturation, $D_{p,c}$, act as CCN. Thus, $D_{p,c}$ can be found directly by interpolating the normalized cumulative size distribution as $R_a = 1 - n_{cum}(D_{p,c})$.

3. The interpolated value of $D_{p,c}$ is used in Köhler theory (Eq. 1 in the main text) to find $\kappa_{CCN}$. Since $\kappa$ is strongly dependent on the critical diameter through its cubic dependence in Köhler theory, determining $D_{p,c}$ is likely to be the largest source of uncertainty in deriving $\kappa_{CCN}$. Consequently, we also calculate the sensitivity of the derived $\kappa_{CCN}$ to uncertainties associated with $N_{CCN}$ and $N_{CN}$. The relative CN concentration uncertainty, $\varepsilon_{CN}$ is reported as 11%, while $\varepsilon_{CCN}$ depends on the concentration-dependent Poisson statistical uncertainty as well as that due to the CCNC flow rate uncertainty ($\varepsilon_{Q_{CCN}} \sim 7\%$). Thus, the overall uncertainty of $R_a$ is

$$\varepsilon_{R_a} = \sqrt{\varepsilon_{CN}^2 + \left(\frac{\varepsilon_{CCN}}{N_{CCN}Q_{CCN}}\right)^2 + \varepsilon_{Q_{CCN}}^2}$$
where $\tau_{CCN}$ is the OPC integration time (1 second), $Q_{CCN}$ is the CCNC sample flow rate ($45.45 \text{ cm}^3 \text{ min}^{-1}$). In addition to accounting for the uncertainty of the activated ratio, $R_a$, an additional 10% uncertainty was applied to $D_{crit}$ after interpolation in Step 2 above to account for the UHSAS sizing uncertainty (3). The derived uncertainty in $\kappa_{CCN}$ was found to vary significantly between 50-200% during the flight on 8 June (see Figure 3 and Figure 4 in the main text).

**CRD-Derived Hygroscopicity**

The data from the cavity ringdown (CRD) spectrometer were used to infer the hygroscopicity parameter, $\kappa$, as follows:

1. The extinction-derived humidification factor, $\gamma_{ext}$, was used to calculate the change in extinction between a dry particle at 10%RH and a humidified particle at 85%RH, $f(85\%RH)$, as

$$f(85\%RH) = \frac{\sigma_{85\%RH}}{\sigma_{10\%RH}} = \left[\frac{1 - 0.85}{1 - 0.10}\right]^{\gamma_{ext}} \quad (3)$$

where $\sigma_{RH}$ is the aerosol extinction at relative humidity, RH.

2. Mie theory equations (4) were iteratively solved to find the hygroscopic growth factor, $g(85\%RH) = \frac{D_p(85\%RH)}{D_p(10\%RH)}$, that reproduces the measured humidified light extinction at 85%RH, where $D_p(RH)$ is the RH-dependent particle diameter. The Mie theory calculations were performed at the CRD laser wavelength of 532 nm and used the fine particle size distribution ($D_p < 2 \mu m$) with a prescribed complex refractive index (RI) of 1.45 - $0i$ that is characteristic of alkane and aromatic species (5). At each iteration step, the humidified particle refractive index is calculated by volume-weighting the dry particle refractive index with that of water (1.33 - $0i$).

3. The hygroscopicity parameter, $\kappa$, is then calculated for each aerosol size distribution bin as in Petters and Kreidenweis (6)
κ = (g^3 - 1) \left( \exp \left( \frac{A}{DpR} \right) - 1 \right) \tag{4}

where \( A = \frac{(4M_w \sigma_w)}{(RT \rho_w)} \), \( R \) is the ideal gas constant, \( T \) is the absolute temperature of the measurement, and \( \sigma_w, M_w \) and \( \rho_w \) are the surface tension, molar mass, and density of water, respectively. The overall \( \kappa \) is calculated as a volume-weighted average of the \( \kappa \) for all size distribution bins.

Table 1: Pure component densities and refractive indices used to compute \( \kappa_{C RD} \).

<table>
<thead>
<tr>
<th>Component</th>
<th>Density (kg m(^{-3}))</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium Sulfate</td>
<td>1769(^a)</td>
<td>1.53 – 0.00(^{ia,b})</td>
</tr>
<tr>
<td>Ammonium Nitrate</td>
<td>1725(^a)</td>
<td>1.61 – 0.00(^ia)</td>
</tr>
<tr>
<td>Organic Carbon</td>
<td>1400(^c)</td>
<td>1.45 – 0.00(^id)</td>
</tr>
<tr>
<td>Elemental Carbon</td>
<td>1800(^e)</td>
<td>1.95 – 0.79(^ie)</td>
</tr>
<tr>
<td>Water</td>
<td>996(^a)</td>
<td>1.33 – 0.00(^ia)</td>
</tr>
</tbody>
</table>

\(^a\)Green and Perry, (7)  
\(^b\)Toon et al., (8)  
\(^c\)Alfarra et al., (9)  
\(^d\)Riazi and Al-Sahhaf, (5)  
\(^e\)Bond and Bergstrom, (10)

Implicit in the above method is the assumption that the aerosol are internally-mixed and can be described well by a single, complex refractive index. To test the sensitivity of the derived \( \kappa_{C RD} \) to the RI assumption, the measured aerosol composition from a compact time of flight aerosol mass spectrometer (C-ToF-AMS) and a single particle soot photometer (SP2) was used to compute an RI based on a volume-weighted average of the pure component refractive indices (Table 1). As shown in Figure 2a, the derived \( \kappa_{C RD} \) is insensitive to the assumed RI over the range of observed values (Figure 2b,c) with the uncertainty in \( \kappa_{C RD} \) from this assumption estimated to be less than 0.02, absolute. While elemental carbon has the potential to significantly impact aerosol extinction because of its large RI, the low mass loadings observed during the the 8 June flight do not appear to have a large influence (Figure 2b,c). The observed insensitivity of \( \kappa_{C RD} \) to the refractive index assumption may not be true for some heterogeneous environments with large local sources of
elemental carbon, however, the finding is consistent with at least one previous study (11). Uncertainties arising from the measurement of \( f(RH) \) were found to vary between 5-8%, on average, which were propagated in the calculation procedure above to find the \( \kappa_{CRD} \) uncertainty over the range of observed values (shown in Figure 3 and Figure 4 in the main text). This uncertainty analysis neglects uncertainties associated with the aerosol size distribution measurement, such as non-idealities arising from particle non-sphericity, inhomogeneity, or core-coating structure. Thus, the derived \( \kappa_{CRD} \) uncertainty should be considered a lower limit.

Figure 3 shows a direct comparison between \( \kappa_{CCN} \) and \( \kappa_{CRD} \) for the June 8 flight, with the corresponding timeseries shown in Figure 4 of the main article. Overall, the CRD-derived hygroscopicity is approximately two-fold lower than the CCN-derived hygroscopicity, with \( \kappa_{CCN} \) ranging from 0.05-0.6, while \( \kappa_{CRD} \) varies from 0.01-0.2. A linear fit between the two quantities gives a slope of 0.47 and a coefficient of determination, \( R^2 = 0.75 \). An interesting feature of Figure 3 is that a clear minimum value of \( \kappa_{CCN} \) is apparent between 0.05-0.10, despite wider variation in \( \kappa_{CRD} \). Similarly, \( \kappa_{CRD} \) reaches a maximum value of 0.15-0.20, despite much wider variation in \( \kappa_{CCN} \). These asymptotic limits coincide with high and low organic volume fractions, and seem to imply that organic species reduce subsaturated hygroscopic growth more so than CCN activation.

**Size-Dependent CCN Composition**

Figure 4 shows the size-resolved organic aerosol volume fraction (\( \varepsilon_{SR,org} \)) plotted versus the bulk (i.e., size-averaged) organic volume fraction (\( \varepsilon_{org} \)). The Aitken mode aerosol contains mostly organics (\( \varepsilon_{SR,org} \sim 0.85-1 \)), but its influence is eclipsed by the more-massive accumulation mode aerosol resulting in lower values of bulk \( \varepsilon_{org} \). A 100-nm cutsize was used to differentiate the two modes, and the average composition in each mode was used to determine the modal \( \kappa = \varepsilon_{SR,org} \kappa_{org} + \varepsilon_{SR,inorg} \kappa_{inorg} \), assuming \( \kappa_{org} = 0.05 \) and \( \kappa_{inorg} = 0.6 \). As shown the lower part of Figure 4, the accumulation mode \( \kappa \) is roughly two-fold greater than the Aitken mode \( \kappa \). The modal \( \kappa \) were linearly regressed against the bulk \( \varepsilon_{org} \), and were combined in an aerosol number-weighted
average to find the overall aerosol hygroscopicity, shown as filled circles in Figure 4. Using a
number-weighted average versus a volume-weighted average is analogous to assuming the two
modes are externally mixed rather than internally mixed.
Figure 2: (a) Comparison plot of the CRD-derived hygroscopicity for the 8 June flight calculated assuming constant and composition-dependent refractive indices. Data from the high altitude transit legs are excluded. (b,c) Frequency of occurrence of the real and imaginary parts of the composition-dependent refractive index during the 8 June flight.
Figure 3: Comparison plot of the CRD-derived and CCN-derived hygroscopicity parameters observed during the 8 June flight.
Figure 4: Average size-resolved organic volume fraction ($\varepsilon_{SR,org}$) from the C-ToF-AMS (top) and calculated modal hygroscopicity parameters ($\kappa$) (bottom) plotted versus the bulk (i.e., size-averaged) C-ToF-AMS organic volume fraction $\varepsilon_{org}$ for both flights. The 2-Mode $\kappa$ is an aerosol number-concentration-weighted average of the linear fits to the Aitken and accumulation mode $\kappa$. 
Coupled CCNC and Droplet Growth Model

A detailed description of the coupled CCNC instrument and droplet growth model is given by Raatikainen et al. (12), so only a brief description is included here. A simplified form of the coupled model was employed here, which assumes parabolic velocity fields while solving the water vapor and energy conservation equations. Neglecting explicit calculation of the velocity fields has a negligible effect on the simulation results, but substantially decreases the necessary computational time (12). The model has been successfully applied in the past to simulate the instrument behavior for both steady-state and transient operation (13–15). Recent work by Lathem and Nenes (16) has shown that moderately high CCN concentrations in the growth chamber can slightly decrease the centerline supersaturation profile. This effect appears to be unimportant for measurements of CCN concentrations below $10^4$ cm$^{-3}$ (16), which is the typical mode of operation. However, supersaturation depletion can have a detectable effect on the OPC-measured droplet size distribution when the CCN concentrations exceed several hundred per cm$^3$. The model can be used to simulate the CCN droplet size distributions, both with and without such supersaturation depletion effects as a function of the effective water uptake coefficient, $\gamma_{\text{cond}}$. The optimal value of $\gamma_{\text{cond}}$ is then found by iteratively matching the simulated and measured droplet size distributions.

As described in detail by Raatikainen et al. (12), a number of uncertainties exist that challenge the simulations. For example, aerosol mixing state and size-dependent composition give rise to a polydisperse hygroscopicity distribution, which is poorly-constrained. Additionally, there are various instrument non-idealities (e.g., column thermal resistance, possible OPC sizing biases, incomplete wetting of the column wall and overall mass transfer coefficient changes, non-linearity of the wall temperature profile). To quantify the impact of these effects, CCN droplet distributions for ammonium sulfate calibration aerosol were compared to those predicted by the model, and it was found that the model simulations overpredict the measured mean droplet size by approximately 2.1 $\mu$m, which agrees well with the correction bias of 2.3 $\mu$m uncovered for $\gamma_{\text{cond}}$=0.2 (Table 2) and applied to the June 8th simulation timeseries in Figure 4 of the main article.

Figure 5 shows 1:1 comparison plots for the uncorrected simulated mean droplet size ($D_{p,\text{sim}}$)
versus the OPC measured mean droplet size ($\bar{D}_p$), and the linear regression coefficients are listed in Table 2. It can be seen that forcing the regression slope to unity has a negligible effect on the coefficient of determination for all simulations except those where supersaturation depletion effects are neglected. Simulations assuming $\gamma_{cond}=0.05-1$ show the best correlation with observations ($R^2 \sim 0.51$), and the overprediction bias for the $\gamma_{cond}=0.1-0.2$ simulations is most similar to the $2.1 \mu m$ bias identified from calibrations. The correlation worsens significantly for $\gamma_{cond} < 0.05$ or when depletion effects are neglected. Thus, the regression analysis indicates that CCN near the Deepwater Horizon oil spill do not exhibit slow activation kinetics and derived values of $\gamma_{cond}$ are consistent with those for ammonium sulfate calibration aerosol and previously reported values for pure water droplets (17, 18).

Table 2: Linear regression coefficients between modeled and observed mean droplet sizes for model simulations with varying water uptake coefficients and with supersaturation depletion effects considered or turned off. Both 1-parameter ($\bar{D}_{p,sim} = \bar{D}_p + \text{Bias}$) and 2-parameter ($\bar{D}_{p,sim} = \text{Slope} \times \bar{D}_p + \text{Bias}$) are listed.

<table>
<thead>
<tr>
<th>Model Simulation</th>
<th>$\gamma_{cond}$</th>
<th>Depletion Effects?</th>
<th>1-Parameter Fit</th>
<th>2-Parameter Fit</th>
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<td></td>
<td>$\gamma_{cond}$</td>
<td></td>
<td>$R^2$</td>
<td>Slope</td>
</tr>
<tr>
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</tr>
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<tr>
<td>0.04</td>
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<tr>
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<tr>
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<td>0.66</td>
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<tr>
<td>0.01</td>
<td>No</td>
<td>-0.19</td>
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<tr>
<td>0.008</td>
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<td>No</td>
<td>-1.10</td>
<td>0.04</td>
<td>0.52</td>
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</table>
Figure 5: Comparison plots of the simulated CCN droplet sizes obtained from the instrument model versus the measured mean droplet sizes during the 8 June flight. Solid traces are a 1-parameter linear fit (constant bias), and dashed traces are a 2-parameter linear fit (slope and bias). Regression coefficients are listed in Table 2.
References


