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# Interactions of Flame-Generated Incipient Nanoparticles with Water

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We experimentally examined the Cloud Condensation Nuclei (CCN) forming potential of Organic Carbon (OC) nanoparticles formed in non-sooting premixed flames. Flame-generated particles were grown by coagulation, and the fraction of particles that grow in a humid environment was measured as a function of dry particle size. A differential mobility analyzer is used select particles of a particular size, and their total concentration as well as the concentration of only those particles that grow in a humid environment (S=0.8) was measured simultaneously. Flame-generated particles in the size range 30-60 nm did not grow to droplets larger than 300nm. For NaCl particles produced by electrospray, also tested in the same conditions, half grew by condensation for dry particles with a diameter of 28 nm, in good agreement with earlier works, validating our experimental approach. While the results are preliminary, they suggest that freshly emitted OC nanoparticles are unlikely to act as CCN. Future work should examine larger flame-generated particles exposed to humid environments with higher S and how atmospheric transformations by oxidization and UV radiation affect the CCN-forming potential of combustion-generated OC nanoparticles.

## 1. Introduction

Water is an important component of atmospheric aerosols contributing to nucleation events, particle growth, and cloud and fog formation. Wet deposition by rain, snow, cloud interception and fog deposition is a major scavenging pathway for removing gas and aerosol phase pollutants from the atmosphere. The solubility of Particulate Matter (PM) in water affects how the particles may interact, translocate, be stored in and/or excreted from biological and ecological systems. The interaction of particulate and gaseous pollution and with water vapor and droplets is also important for affecting clould albedo and climate by the "indirect" effect (Seinfeld and Pandis, 1998). One of the largest uncertainties in models predicting climate change is understanding how anthropogenic aerosols affect cloud characteristics (Dusek, et al. 2006). The ability of

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Organic Carbon Particulate Matter (OC PM) to act as cloud condensation nuclei (CCN) is particularly not well-understood.

Studies comparing clouds upwind and downwind of industrial sources, cities, or fires, or clouds formed in the exhaust plumes of ships and airplanes compared to clouds in the same general location but outside the exhaust plume generally find that clouds formed in the presence of combustion emissions have significantly higher number concentration and smaller droplet diameters than clouds in more pristine airsheds (Kaufman, et al. 2005, Schröder, et al. 1998, Russell, et al. 2000, Hobbs, et al. 2000). Also, large amounts of organic material have been reported in atmospheric cloud droplets so that the ability of OC PM to act as CCN is now considered as important as sulphates (Novakov and Penner, 1993, Fuzzi, et al. 2002). Carbonaceous and organic particulate matter constitute the majority of combustion-generated particulate matter (PM) and of atmospheric ultrafine PM smaller than 100 nm (Hughes, et al. 1998), but their growth potential in humid environments is not yet well understood.

In this paper, we investigate the growth potential of incipient flame-generated organic nanoparticles in humid environments. The investigated flames produce aerosols that are relevant models for the carbonaceous fraction of PM in combustion emissions since they are similar to aerosols in the emissions of internal combustion engines used in vehicles or industrial exhaust plumes. Non-sooting ethylene-air flames are used to generate the test aerosol. Earlier works showed that flame generated OC PM can be isolated from gas phase OC and more graphitic soot particles in water samples collected by scrubbing combustion exhausts, but it is not clear whether these particles are present in solution or merely suspended in the hydrosols (D'Alessio, et al. 2009). Most of the particles produced in non-sooting flames are smaller than 10 nm, which is well below reported activation diameters ($d_{activation}$ or diameter at which 50% of the particles are activated as CCN or grow into droplets) even for soluble particles like NaCl, $d_{activation}$ = 26 nm for Supersaturation, S=0.8 (Corrigan and Novakov, 1999, Cruz and Pandis, 1997), but particles can grow by coagulation in the exhaust manifold or dilution plume. Therefore, we allowed the particles to grow by coagulation at low temperature to sizes larger than activation diameters reported for NaCl and tested the CCN-forming potential of the coagulated aerosol. Because of their known solubility and relevance in atmospheric aerosols, NaCl particles are used as the soluble-particle standard in studies examining the CCN-forming potential of aerosols composed of particular compounds (Corrigan and Novakov, 1999, Cruz and Pandis, 1997). In the present work, we also measured activation curves for NaCl particles in order to validate our experimental set up and for comparison with the flame-generated particles. These measurements are a first cut at determining if freshly admitted flame-generated OC PM may act as CCN.

## 2. Experimental Set-up

We used two particle generation systems to produce test aerosols and measure their CCN-activation curves. NaCl nanoparticles were produced by electrospray. A McKenna burner was used to produce flame-generated OC nanoparticles in laminar flat premixed atmospheric pressure ethylene-air flames. The electrospray source used was designed

similar to the one described by Chen, et al. (1995). The NaCl particles were produced by pushing a 150 mM solution of NaCl in bidistilled laboratory water through a 30 micron silica capillary with a sharpened, uncoated tip. The capillary tip faced a metal plate with a 1 mm hole used to eliminate satellite drops and their dried residues. A voltage difference of 3-5 kV was applied directly to the spray solution and the flat plate. Carbon dioxide was used as the drying gas to avoid Corona discharge. The so-called silver bullet and cone-jet stable operating modes were observed through a microscope and by measuring their output currents (Chen, et al. 1995), and the measurements were done using cone-jet mode with an applied voltage ranging from about 4.2-4.5 kV.

Flame products were drawn from a C/O=0.67 ethylene air flame with cold gas velocity=10 cm/s. This flame is considered non-sooting since the particles do not absorb radiation with wavelengths in the visible or produce measurable laser induced incandescence; the optical properties of the particles suggest that they are OC polymer-like structures made up of aliphatic functionalities and aromatic moieties with less than 3 rings (D'Alessio, et al. 2009). Since this flame produces particles that are mostly smaller than 10 nm, we allowed them to coagulate at low temperature by drawing the particles through a 6 cm long 2 mm ID tube oriented horizontally with its inlet centered 15 mm above the burner surface. In this section of sampling line, the aerosol was undiluted. Successive dilution occurred in an ejector pump used to draw the particles through the initial tube and in a secondary dilution probe with variable dilution ratio (on the order of several hundred) required to reduce the particle concentration to the detection range for the CPC detector.

Particles of a specific size were selected with a Differential Mobility Analyzer (TapCon 3/150 DMA). The monodisperse size-selected aerosol flow was split to simultaneously measure the total particle concentration with a Condensation Particle Counter (TSI CPC 3760A) and only the fraction of particles that grow by condensation of water-vapor using an ad-hoc CPC operating with water as the working fluid. The TSI CPC measured the total particle concentration, with 100% efficiency for particles larger than 10 nm, which act as Condensation Nuclei for N-butanol (called CN). The water-based CPC measured only those particles that grow by condensing water on their surface to a droplet with diameter larger than 300 nm, named Cloud Condensation Nuclei (CCN). Using the nomenclature and methods reported in the literature (Cruz and Pandis, 1997, Corrigan and Novakov, 1999), the results are presented in CCN-activation curves or plots of the fraction of particles that grow (CCN/CN) as a function of size-selected dry particle diameter.

The water-based CPC is a turbulent-mixing type CPC, which exposes incoming aerosols to a vapor concentration by mixing the incoming cold aerosol flow with a hot flow issued from a saturator in a small tee. The humidified aerosol flow then travels through a growth section and droplets that are larger than 300 nm are counted at the end of the growth section by an optical particle counter (Biotest APC plus). Previous works describe in detail the design of the turbulent-mixing CPC and demonstrate its ability to grow/detect particles as small as 1 nm operating with organic working fluids (Sgro and Fernández de la Mora, 2004, Kim, et al. 2003). In this work, we use water as the

working fluid, and did not operate in optimal supersaturation conditions to grow all particles. Instead, we set the variable operating conditions of the CPC that determine the supersaturation in the mixing section (saturator flow, saturator temperature, and incoming aerosol temperature) to values that enabled the measurement of CCN-activation curves of NaCl particles generated by electrospray with the same size of combustion-generated particles. It is not easy to measure or infer S in the mixing section of the CPC since the temperature distribution within the mixing tee of the CPC is complex and not measured. Our approach was to measure CCN-activation curves for NaCl at fixed operating conditions in the CPC to infer the supersaturation by comparison with reported activation curves for NaCl particles for various S in the literature, even though they used different particle generation methods and a thermal diffusion-type CCN counter (model M-1 of DH Associates) (Cruz and Pandis, 1997, Corrigan and Novakov, 1999).

## 3. Results

Figure 1 shows the size distributions of the NaCl and flame-generated OC nanoparticles used in this work. The concentration of electrospray-generated NaCl aerosol was orders of magnitude lower than that of the flame-generated aerosol. The concentration of all NaCl particles was lower than the detection limit of the FCE and below $10^3$ particles/cm$^3$, the concentration that begins to produce relevant coincidence errors in the optical detector of the CPC. The concentration of coagulated and diluted flame-generated particles was much higher. For flame-generated particles smaller than 40 nm, the concentration determined by the CPC detector was significantly less than that determined by the FCE, due to coincidence errors. The actual size distribution of the flame-generated OC nanoparticles is that measured by the FCE for d<40 nm and that measured by the CPC for d>40 nm, as indicated by the line in Fig. 1.

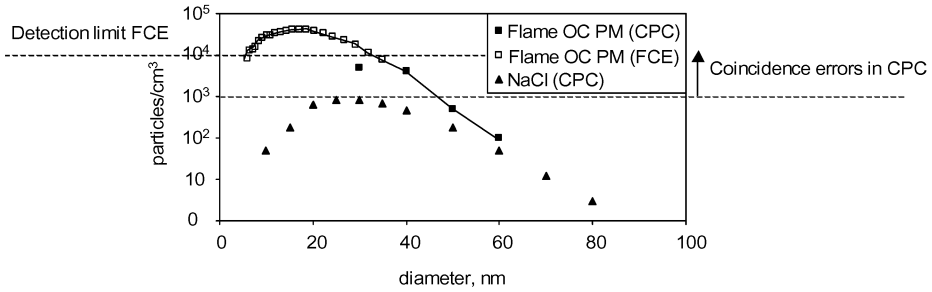


*Figure 1: Size distributions flame-generated OC PM and electrospray dried NaCl particles used in tests to measure their activation curves.*

Figure 2 shows the fraction of particles activated by condensation selecting 25 nm particles with the DMA and changing the electrospray operating conditions to produce different amounts of particles. The fraction of particles grown (CCN/CN=0.1 for 25 nm NaCl particles in Fig. 2) is independent of particle concentration.

Figure 3 plots the CCN-activation curves for the NaCl and flame-generated OC test particles. The conditions in the water-based CPC was constant for both test particles,

but, unlike the NaCl particles, the flame-generated OC particles tested (with diameters in the size range 30-60 nm) did not show any growth.

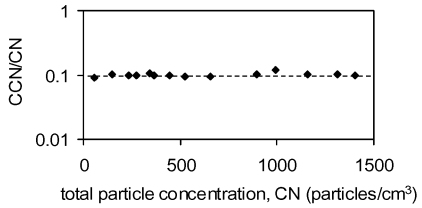


*Figure 2: Fraction of 25 nm NaCl activated by condensation as a function of particle concentration.*

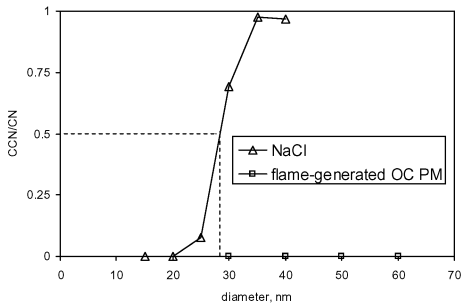


*Figure 3: Activation curves measured for electrospray dried NaCl particles and flame-generated OC particles.*

The activation diameter for the NaCl particles, for which 50% of the dry particles tested were grown into droplets larger than 300 nm, was $d_{activation}$=28 nm. Comparing our results with reported activation diameters for NaCl in the literature from measurements with a thermal diffusion chamber type CCN (Cruz and Pandis, 1997, Corrigan and Novakov, 1999) allows us to infer an S of about 0.8 in the water-based CPC.

Increasing the flow rate and/or the temperature of the saturator in the water-based CPC (which increases S), we observed no significant particle growth prior to homogeneous nucleation of droplets, which were observed without particles flowing to the CPC (obtained experimentally by setting the DMA volts to zero). The observation that flame-generated OC particles did not grow in these experiments for S=0.8 implies that freshly emitted flame generated OC nanoparticles are not likely to act as cloud condensation nuclei. This result agrees with observations of Weingartner, et al. (1997) who measured growth factors with tandem DMA measurements of diesel exhaust particles; they reported rather low growth factors for S=0.8-1 ($d_{wet}/d_{dry}$ =1.05), and negative growth factors indicating particle restructuring for particles emitted in idling conditions. The results presented here are preliminary. Future works should investigate higher S, flame-generated particles larger than 60 nm and the effects of atmospheric particle transformations by oxidation and exposure to UV radiation. The observation that cloud and fog droplets contain large amounts of organics (Novakov and Penner, 1993, Fuzzi, et al. 2002) warrants further research in this area.

## References

Chen, D.-R., Pui, D. Y. H., Kaufman, S. L., 1995, Electrospraying of conducting liquids for monodisperse aerosol generation in the 4 nm to 1.8 μm diameter range, J. Aerosol Sci. 26, 963-977.

Corrigan, C. E. and Novakov, T., 1999, Cloud condensation nucleus activity of organic compounds: a laboratory study, Atmos. Environ. 33,2661-2668.

Cruz, C. N. and Pandis, S. N., 1997, A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei, Atmos. Environ. 31, 2201-2214.

D'Alessio, D'Anna, A., Minutolo, P., Sgro, L. A. Nanoparticles of Organic Carbon (NOC) formed in flames and their effects in urban atmospheres, 2009, in Combustion Generated Fine Carbonaceous Particles, Bockhorn, H. D'Anna, A. Sarofim, A. F. Wang, H., eds. Karlsruhe University Press, Karlsruhe.

Dusek, U., Frank, G. P., Hildebrandt, L., Curtius, J., Schneider, J., Walter, S., Chand, D., Drewnick, F., Hings, S., Jung, D., Borrmann, S., Andreae, M. O., 2006, Size matters more than chemistry for cloud-nucleating ability of aerosol particles, Science, 312, 1375-1378.

Fuzzi, S. Facchini, M. C., Decesari, S., Matta, E., Micrcea, M., 2002, Soluble organic compounds in fog and cloud droplets: what have we learned in the past few years?, Atmos. Res. 64: 89-98.

Hobbs, P.V., Garrett, T.J., Ferek, R.J., Strader, S.R., Hegg, D.A., Frick, G.M., Hoppel, W.A., Gasparovic, R.F., Russell, L.M., Johnson, D.W., O'Dowd, C., Durkee, P.A., Nielsen, K.E., Innis, G., Emissions from Ships with respect to Their Effects on Clouds, J. Atmos. Sci. 57 (2000) p. 2570-2590.

Hughes, L. S., Cass, G. R., Gone, J., Ames, M. Olmez, I., 1998, Physical and Chemical Characterization of Atmospheric Ultrafine Particles in the Los Angeles Area, Environ. Sci. Technol. 32, 1153-1161.

Kaufman, Y. J., Koren, I., Remer, L. A., Rosenfeld, D., Rudich, Y., The effect of smoke, dust, and pollution aerosol on shallow cloud development over the Atlantic ocean, 2005, Proc. Natl. Acad. Sci., 32, 11207–11212.

Kim, C. S., Okuyama, K., Fernández de la Mora, J., 2003, Performance evaluation of an improved particle size magnifier (PSM) for single nanoparticle detection, Aerosol Sci. Technol. 37, 791–803.

Novakov, T. and Penner, J. M. 1993, Large contribution of organic aerosols to cloud-condensation-nuclei concentrations. Nature, 365, 823–826.

Russell, L. M., Noone, K. J., Ferek, R. J., Pockalny, R. A., Flagan, R. C., Seinfeld, J. H., Combustion organic aerosol as cloud condensation nuclei in ship tracks, J. Atmos. Sci. 57 (2000) 2591-2606.

Schröder, F. P., Kärcher, B., Petzold, A., Baumann, R., Busen, R., Hoell, C., Schumann, U., 1998, Ultrafine aerosol particles in aircraft plumes: in situ observations, Geophys. Res. Letters, 25, 2789-2792.

Seinfeld, J. H. and Pandis, S. N., 1998, Atmospheric Chemistry and Physics, from air pollution to climate change, John Wiley, NY.

Sgro, L. A. and Fernández de la Mora, J., 2004, A simple turbulent mixing CNC for charged particle detection down to 1.2 nm, Aerosol Sci. Technol. 38, 1-11.