Near-road modeling and measurement of cerium-containing particles generated by nanoparticle diesel fuel additive use

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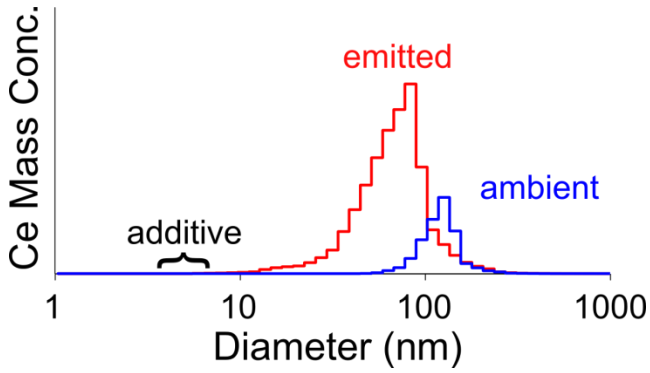
ABSTRACT

Cerium oxide nanoparticles (nCe) are used as a fuel-borne catalyst in diesel engines to reduce particulate emissions, yet the environmental and human health impacts of the exhaust particles are not well understood. To bridge the gap between emission measurements and ambient impacts, size-resolved measurements of particle composition and mass concentration have been performed in Newcastle-upon-Tyne, United Kingdom, where buses have used an nCe additive since 2005. These observations show that the non-crustal cerium fraction thought to be associated with the use of nCe has a mass concentration ~0.3 ng m^{-3} with a size distribution peaking at 100-320 nm in aerodynamic diameter. Simulations with a near-roadway multi-component sectional aerosol dynamic model predict that the use of nCe additives increases the number concentration of nuclei mode particles (<50 nm in diameter) while decreasing the total mass concentration. The near-road model predicts a downwind mass size distribution of cerium-containing particles peaking at 150 nm in aerodynamic diameter, a value similar to that measured for non-crustal cerium in Newcastle. This work shows that both the emission and atmospheric transformation of cerium-containing particles needs to be taken into account by regional modelers, exposure scientists, and policymakers when determining potential environmental and human health impacts.



TOC/Abstract Art

INTRODUCTION

Recent attention has been paid to the environmental release of engineered nanomaterials, both because of their increasing use in consumer products and their poorly understood ecosystem/health impacts.[1,2] In the atmosphere, engineered nanomaterials are in the form of nanoparticles (defined as having at least one dimension <100 nm) with different physical and chemical characteristics than the bulk material from which they are made.[3] One such characteristic important to the function of nanoparticles is reactivity, which can be maximized by large surface area and/or surface defects.[4] Cerium oxide (ceria) nanoparticles (nCe) are one type of engineered nanomaterial whose function employs this increased reactivity as an additive in diesel fuel to decrease particulate emissions and improve fuel economy.[5] nCe has been used as a catalyst in diesel fuel additives in on-road vehicles in the U.K. (since 2003), New Zealand (since 2005), and Canada (since 2010). Cerium-based diesel fuel additives are commercially available under the brand names Eolys™ (Rhodia Electronics & Catalysis), Envirox™ (Energenics Europe Limited), and Platinum Plus® (Clean Diesel Technologies Incorporated). Envirox is currently used in 8300 Stagecoach buses in the U.K. and Canada, reportedly cutting the fleet's fuel consumption and CO_2 emissions by 5% (Stagecoach news release, 2013). This reported CO_2 emission reduction is consistent with that of laboratory-based studies which range from no change in emissions to a 6% reduction.[6,7]

The World Health Organization (WHO) has recently labeled outdoor air pollution a leading environmental cause of mortality (leading to 3 million premature deaths annually), particularly from particles with a diameter <2.5 μm ($PM_{2.5}$) which are linked to lung cancer and pulmonary disease.[8-10] In addition, the WHO's International Agency for Research on Cancer has classified diesel engine exhaust as carcinogenic to humans.[11] A specific toxicological role has been

identified for nuclei mode (<50 nm in diameter) particles due to their ability to cross cellular membranes.[12] Cassee et al.[2] summarized several epidemiological studies that reported adverse health effects associated with exposure to high levels of cerium,[13-15] but noted that chronic inhalation and toxicology studies for nCe were not available. Cassee et al.[16] observed few detrimental effects in mice exposed to exhaust from diesel fuel doped with an nCe additive relative to standard diesel fuel, and suggested that the associated decrease in particle number may limit the human health impact. Lin et al.[17] reported oxidative stress in human cancer cells exposed to 20 nm ceria particles at concentrations from 3.5 to 23.3 μg mL^{-1}. Kumari et al.[18] observed size- and dose-dependent toxicity of ceria in human neuroblastoma cells, with 25 nm particles at concentrations >100 μg mL^{-1} damaging the cells and 3 μm particles having no impact. Widespread use of nCe additives in diesel fuel across the United States has been predicted to result in airborne concentrations of cerium as high as 22 ng m^{-3} while reducing elemental carbon, increasing naphthalene, and causing modest reductions in particulate matter less than 2.5 micrometers in diameter ($PM_{2.5}$), ozone, and acrolein on a regional scale (G. Erdakos, pers. comm.). The air quality impact of nCe additives very near major roadways has not been assessed extensively.

While the emitted particle number concentration and subsequent impact of nCe is affected by many factors (engine temperature/load, particle filters, nCe dosage, etc), several studies[19,20] have shown that the recommended dose (25 and 5-10 ppm for Eolys and Envirox, respectively) of nCe in diesel fuel increases the peak nuclei mode number concentration by a factor of 5 while decreasing the peak accumulation mode number concentration by 50%. Increased nuclei mode number may be the result of new particle formation, reduced coagulation, and/or primary emission of the nCe from the additive.[1,20] The decrease in the peak number concentration near 100 nm in diameter from the addition of nCe results in an overall decrease in the mass of particulate matter

(PM) emitted during combustion, especially in the organic carbon (OC) and black carbon (BC) mass emissions.[19,21] Chemical analyses of nuclei and accumulation mode particles from the exhaust of nCe-dosed diesel fuel revealed that cerium accounted for most (up to 100%) of the nuclei mode particle mass compared to <15% for accumulation mode particles which are dominated by BC.[19] Electron microscopy of particles emitted from nCe-dosed diesel fuel indicated the presence of fine ceria particles 5 to 7 nm in diameter "decorating" carbonaceous aggregates with a mobility diameter of 50 nm.[20]

Two studies[1,5] documented the change in atmospheric cerium concentrations following the introduction of the Envirox additive to the London Stagecoach bus fleet at the end of 2003 and all buses operated in Newcastle by Stagecoach in 2005. Park et al.[5] found no increase in cerium concentrations at two U.K. sites (London and Greenwich) after the Envirox introduction and attributed the absence of an increase to the low number of buses using nCe relative to the volume of nearby traffic.[1] In Newcastle, however, a statistically significant increase in the ambient cerium concentration (from 0.145 to 0.612 ng m^{-3}) was observed in particulate matter less than 10 micrometers in diameter (PM_{10}) measurements after the Envirox introduction. Envirox and other nCe additives are reported to improve the performance of diesel particle filters that substantially reduce cerium emissions, but these filters are not used in the Stagecoach bus fleet.

Although accurate characterization of nanoparticles in the atmosphere can be difficult due to their variability in particle behavior and long sampling times,[22,23] experimental studies have given detailed insight into the chemical and physical properties of the particulate emissions from diesel fuel with and without the nCe additive. Emission-based studies need to be extended to understand the atmospheric evolution of exhaust particles from the tailpipe to the ambient atmosphere in real-world conditions such as an urban environment where human exposure can occur. After exiting

the tailpipe, microphysical processes including condensational growth and coagulation can shift the emitted ceria to larger particle sizes. It is necessary to determine the particle size range in which ambient cerium is most concentrated at different distances from the road for human health assessments, since particle size determines the region of the respiratory tract where the cerium is most likely to deposit and potentially cause damage.[3] This is also important for assessing ecosystem damage because the deposition rate of particles is governed by their size.[24] Therefore, the primary objective of this study is to determine the distribution of cerium across the overall particle size range in a near-road environment where nCe additives are used. By combining observations of size-resolved cerium concentrations in Newcastle with a multi-component model of aerosol microphysics, this study will equip future researchers to estimate the human/environmental health effects of utilizing nCe additives in diesel fuel.

OBSERVATIONAL AND MODEL DESCRIPTION

Ambient Measurements. The Newcastle-upon-Tyne, UK, measurement campaign took place in August 2012 (after preliminary measurements in February and March 2012) at the Automatic Urban and Rural Network (AURN) site near the Civic Center on St. Mary's Place (54.98°N,-1.61°W). Located near the city center, the AURN site is within 0.5 km of the Haymarket and Eldon Square bus stations operated in part by Stagecoach Group and ~100 meters from the St. Mary's Place bus stop frequented by Stagecoach buses. Photographic evidence and published schedules indicate that several bus routes operated by Stagecoach travel within one block of the AURN monitoring site, leading to hundreds of passages per day near the site. The AURN site is the same site where a four-fold increase in ambient cerium levels was documented in 2005 following introduction of Envirox to the Stagecoach bus fleet.[5]

During the August 2012 campaign, a series of size-resolved and bulk PM_{10} measurements (summarized in Table 1) were collected at the Newcastle site. PM_{10} observations were made using two Partisol 2025 samplers (Thermo Fisher Scientific, Waltham, MA), with one sampling during the high traffic periods (daytime, 08:00 to 20:00 local time) and the other during low traffic periods (nighttime, 20:00 to 08:00). Size-resolved particles were sampled using a nanoMOUDI 125R impactor (MSP Corporation, Shoreview, MN). The nanoMOUDI sampled particles for 7 days with 12 stages for aerodynamic diameters ranging from <0.01 to <18 μm. For the Partisol and nanoMOUDI samples, filters were analyzed for total particle mass via gravimetry and metal speciation via High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS). BC concentrations were measured during the campaign using a micro aethalometer (Magee Scientific Model AE22) every 5 minutes and averaged hourly. Concurrent hourly measurements of PM_{10} and $PM_{2.5}$ were also collected by tapered element oscillating microbalance (TEOM) 1400 (Thermo Fisher Scientific, Waltham, MA) samplers at the same site as part of the AURN.

Sectional Aerosol Model Configuration. The modeling component of this study employs the near-road multicomponent aerosol dynamics model as described by Zhang and Wexler[25] and Zhang et al.[26], but expanded to explicitly treat the evolution of the cerium-containing particle size distribution and mixing state. The 'road-to-ambient' sub-module of the model is used to simulate atmospheric processes that occur on exhaust particles within 3-10 minutes after emission.[25] The near-road model incorporates dilution, coagulation, deposition, and condensation/evaporation, with dilution and condensation/evaporation shown to be the dominant mechanisms in determining the downwind size distributions.[25] Model inputs of the size- and chemically-resolved mass and number concentration of fresh diesel exhaust generated with and without the nCe additive are developed from previously-reported laboratory measurements of the particle size distribution[19-

[21,27] and chemical composition.[19,21,28] See the supplemental material for details on the development of the model emission inputs.

As model input, we use an exhaust particle size distribution located 30 meters away from the tailpipe (approximating the distance from tailpipe to roadside) after having been rapidly diluted (keeping the same size distribution) immediately after emission. Roadside exhaust concentrations of 10 μg m^{-3} for the simulation without nCe and 8.3 μg m^{-3} for the simulation with nCe were used based on the ~17% observed average decrease in total PM due to usage of the additive (G. Erdakos per. comm.). The 10 μg m^{-3} concentration for the simulation without nCe is not intended to reflect a specific observed concentration but rather to be representative of a major highway such as the one used to develop the model.[26] Upon initialization, the model tracks the atmospheric evolution of the exhaust plume (number, mass, mixing state, etc.) up to a distance of 300 meters from the roadway for particles ranging from 1 to 10000 nm in Stokes diameter. Other user-specified inputs include the emitted particle mixing state, background particle size distribution, and meteorological conditions. For both the simulations with and without the use of an nCe additive described in this study, externally-mixed diesel exhaust particles are emitted along with organic gases lumped by volatility (mass concentration of 44 μg m^{-3} with 67% considered semi-volatile and 33% having low volatility)[26] into an urban atmosphere (background particle number concentration of 1.4×10^5 cm^{-3})[28] with meteorological conditions similar to those of Zhang et al.[26] (surface wind speed of 1 m s^{-1}, temperature of 25°C, relative humidity of 0%). The Zhang et al.[26] meteorological inputs represent summertime conditions in an urban environment and allow for 5 minutes of atmospheric processing to occur on the exhaust particles before they reach 300 meters. In a future study, the impact of meteorology, background particle concentration, and emission magnitude/mixing state

175 on the predicted composition and concentration of exhaust particles with and without nCe additive
176 usage is examined by changing these model inputs.

177 RESULTS

178 **Newcastle Observations.** The time series of August 2012 hourly concentrations for PM_{10},
179 $PM_{2.5}$, BC, and cerium reveals that cerium concentrations are a small fraction of the overall mass
180 concentrations and range from 0.1 to 1 ng m^{-3} (Figure S1). These cerium concentrations are
181 consistent with that of Park et al.[5]who reported 0.612 ng m^{-3} after the introduction of Envirox.
182 There is a diurnal variability of cerium levels in PM_{10} averaging 0.56 ng m^{-3} during the daytime
183 and 0.33 ng m^{-3} at night. The Earth's crust is known to be a significant source of cerium via wind-
184 blown dust and may have contributed to the observed levels of cerium in Newcastle PM_{10}. Crustal
185 cerium is estimated from total cerium by using the average continental crust ratio of cerium to
186 lanthanum and assuming that lanthanum has no significant non-crustal sources (see Figure S2).
187 Assuming a cerium/lanthanum ratio of 6.65:3.9 for continental crust,[30] the diurnal variation of the
188 non-crustal cerium fraction is more pronounced than that of total cerium with the daytime
189 concentration (0.28 ng m^{-3}) a factor of 2.5 larger than the nighttime concentration (0.11 ng m^{-3}).
190 Unlike total PM_{10} and $PM_{2.5}$ whose daytime and nighttime concentrations are similar, Figure 1
191 shows that the daytime increase in cerium relative to nighttime concentrations is consistent with
192 that of BC whose major source in Europe is transportation (especially diesel engines).[31] Wind rose
193 plots of the BC and $PM_{2.5}$ concentrations (Figure S3) as a function of wind direction qualitatively
194 show that they have distinct source regions, with the highest BC concentrations occurring from
195 the west (downwind of the Newcastle bus station) and the highest $PM_{2.5}$ concentrations occurring
196 from the northeast (downwind of the Port of Tyne). The average cerium/PM_{10} concentration ratio
197 as measured by the Partisol samplers was 24 ng Ce/mg PM_{10}, within the range of values (10-50 ng

198 Ce/mg PM_{10}) reported after the introduction of Envirox to Stagecoach buses and well above the
199 values (5-15 ng Ce/mg PM_{10}) typical of the period before the Envirox introduction.[2]

200 Cerium particle mass concentrations from the 12-stages of the nanoMOUDI, given in Figure 2,
201 reveal a bimodal distribution accounting for 0.005% of the PM_{10} and 0.01% of the PM_1 in
202 Newcastle. The submicron cerium mass distribution peaks in the 180-560 nm aerodynamic
203 diameter size range, while a second supermicron peak is centered at 4 µm in diameter. Using the
204 6.65:3.9 cerium/lanthanum ratio for continental crust,[30] the estimated non-crustal cerium makes
205 up 60% of the total cerium mass with a single peak in the 100-320 nm aerodynamic diameter size
206 range and low supermicron concentrations. This estimated non-crustal fraction as a function of
207 particle size is similar for several other Lanthanide elements with crustal sources (Figure S2).
208 Although a factor of 3 lower in magnitude, a similar non-crustal cerium particle mass size
209 distribution (peaking in 100-180 nm aerodynamic diameter size range and low supermicron
210 concentrations) was observed from preliminary nanoMOUDI measurements at the Newcastle site
211 in March 2012 (Figure S4).

212 **Model Predictions.** Figure 3 shows the predicted exhaust particle size distribution (given as a
213 function of the Stokes diameter) based on previous emission studies for the simulations with and
214 without the use of nCe at near-road conditions. For the emitted size distribution (at 30 meters from
215 the roadway), the number concentration of nuclei mode particles is much larger (up to a factor of
216 30 higher) when the nCe additive is used. Due to more efficient soot combustion from the use of
217 the nCe additive, the emitted number concentration of particles between 50-100 nm in diameter is
218 nearly a factor of 2 lower than exhaust without nCe. Between 100 and 1000 nm in diameter,
219 differences in the emitted size distributions with and without nCe are not robust. Although evident
220 as slightly higher concentrations in the number size distribution (Figure 3), the mass size

distributions in Figure 4 show a distinct peak in supermicron size range with nCe that is not present in the emissions without nCe. This peak was attributed to aggregation enhanced by platinum particles contained in the specific nCe-containing additive (Platinum Plus®) used in the study.[21] As the size distribution of supermicron particles was only observed in one study,[21] it is not known whether other nCe additives exhibit a supermicron peak in the emitted particle mass size distribution. The emitted surface area size distribution in simulations with and without the use of nCe are predicted to be similar because of similarities in the number size distribution in the 100 to 1000 nm diameter size range (Figure S5) which dominate the typical urban aerosol surface distribution.[29]

Changes in total particle mass and number concentrations. The total number of exhaust particles in the simulation without usage of the nCe additive decreases by nearly 80% from the emitted (30 meters from the roadway, 48080 cm^{-3}) to ambient (300 meters from the roadway, 10820 cm^{-3}) conditions. A similar decrease in particle number concentration with distance is also predicted for exhaust with the nCe additive. Figure 3 shows that most of the decrease in number concentration occurs for nuclei mode particles, where condensation and dilution combine to rapidly decrease the number and grow particles out of the nuclei size range. This decrease in the nuclei mode is especially significant with the nCe additive because of the initially higher number concentration. Particles with a diameter of ~150 nm have an ambient number concentration higher than the emitted concentration (Figure 3), indicating that condensation and to a lesser degree coagulation leads to particle growth into this size range. Ambient supermicron number concentrations are lower than the emitted concentrations in both pairs of simulations due to dilution and deposition. Some small differences in the downwind particle number size distributions remain, with the simulation using an nCe additive having higher number

concentrations for the nuclei mode and lower concentrations for accumulation mode. Overall, we predict that the use of nCe additives will not substantially influence the ambient particle size distribution more than 300 meters from a major roadway.

The reduction in nuclei mode and supermicron particles due to condensation, deposition, and coagulation causes a narrowing of the ambient particle mass size distribution that peaks at 100 nm in diameter (Figure 4). Total mass concentrations decrease with distance from the road in both pairs of simulations, but the additional mass from condensation largely compensates for the mass lost from deposition and dilution. The simulation with nCe shows a larger decrease in the ambient particle mass (-1.2 μg m^{-3}) than without (-0.8 μg m^{-3}) because it has a larger fraction in the supermicron size range which has low condensation and high deposition rates. Again, this result may be an artifact of the supermicron peak observed in a single emission characterization study based on Platinum Plus®.[21]

Changes in nCe additive-derived ceria particle mass concentration. Like other exhaust particles, the modeled atmospheric evolution of cerium-containing particles from nCe is dominated by dilution and condensation. Because cerium-containing particles are emitted mainly in the nuclei mode, dilution and condensation simultaneously decrease their total number and increase their size in the ambient atmosphere. Dilution of cerium-containing particles in the atmosphere results in an 80% decrease in the mass concentration from 30 to 300 meters. By 300 meters from the roadway, ceria makes up only 2% of the total particle mass (down from 8% at 30 meters) with a size distribution that peaks at ~100 nm in Stokes diameter (Figure 5). Concurrent with the decrease in mass concentration, the peak Stokes diameter in the mass size distribution of cerium-containing particles is predicted to grow by 35 nm (50 nm in aerodynamic diameter) in the transition from emitted to ambient conditions. This growth is predicted to occur from the

condensation of organic gases onto the non-volatile cerium-containing particles, consistent with smog chamber experiments showing that secondary organic aerosols readily coat ceria nanoparticles.[32] Beyond 300 meters, we expect continued condensation to result in a size distribution of cerium-containing particles approaching that of other accumulation mode particles.

The ambient mass size distribution of cerium-containing aerosols predicted by the model compares favorably with the estimated non-crustal cerium mass size distribution at the Newcastle site. Figure 2 shows that the peak concentration predicted by the model at 300 meters (≈ 150 nm aerodynamic diameter) is within the size range of peak concentration of non-crustal cerium from the nanoMOUDI (100-320 nm aerodynamic diameter) deployed in Newcastle. Both the observed and modeled mass size distributions of non-crustal cerium-containing particles are mainly within the submicron size range. The combination of freshly-emitted and aged cerium-containing particles with different size distributions sampled at the Newcastle site could contribute to the lower kurtosis of the observed distribution relative to the predicted distribution, as well as the wider bin widths of the nanoMOUDI. Although the model is primarily used to understand the changes in the size and concentration of exhaust particles from roadside to ambient conditions rather than absolute concentrations, it's worth noting that the ambient ceria mass concentration predicted by the model (0.15 μg m^{-3}; 0.12 μg Ce m^{-3}) is much larger than the average cerium concentration observed at Newcastle (~0.5 ng m^{-3}) because it does not reflect the specific terrain, meteorology, bus frequency, and roadside concentration of the measurement site. If a smaller roadway exhaust concentration increment had been assumed in our model (e.g., 1.0 instead of 10 μg m^{-3}), the magnitude of model predictions would have been in closer agreement with the Newcastle observations.

DISCUSSION

In order to help regional modelers, exposure scientists, and policymakers better understand the potential environmental and human health impacts of nCe additive use in diesel fuel, we have combined ambient observations and modeling to determine the magnitude, size, and atmospheric evolution of cerium-containing particles. The atmospheric mass concentration of cerium measured at the Newcastle site (~0.5 ng m^{-3}) is several orders of magnitude below the inhalation reference concentration of 0.9 µg m^{-3}, suggesting that the human health risks associated with nCe in the ambient atmosphere are likely to be low.[33] However, large uncertainties still exist concerning the acceptable level of cerium in the atmosphere (which is likely a function of particle size) because environmental and human health toxicity studies do not always use cerium particles with a size distribution representative of laboratory and ambient measurements.[2,33] For regional-scale air quality considerations, the use of an nCe additive may be beneficial due to the improved fuel economy and reduced emissions of exhaust particles. This is consistent with our roadside modeling simulations predicting a 17 and 23% decrease in the roadside and ambient exhaust particle mass concentration, respectively, with the use of an nCe additive. However, increased roadside concentrations of nuclei mode particles containing cerium may be of concern because the solubility of engineered nanoparticles has been shown to be inversely related to size.[34] The 100-320 nm (aerodynamic diameter) peak in the ambient non-crustal cerium mass distribution observed at Newcastle and predicted by the model is within the size range of moderate alveolar deposition and associated cardiovascular effects.[3] To definitively determine an acceptable ambient level of atmospheric cerium concentrations, exposure studies need to determine impacts as a function of size (particularly for particle diameters <500 nm where cerium concentration peaks) and composition (including the cerium/ceria fractionation, ceria/soot mixing state, solubility, etc.) in addition to the mass concentration.

FIGURES

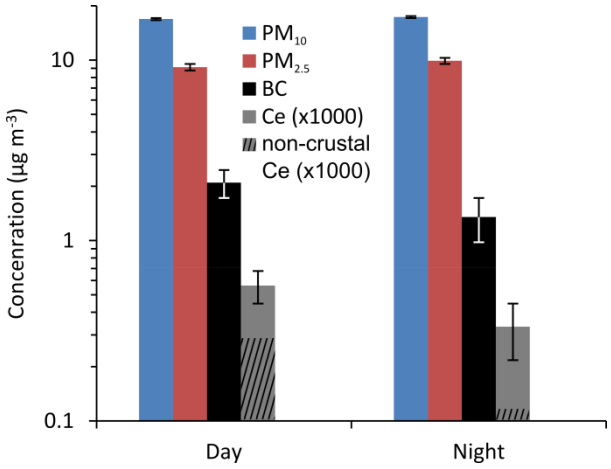
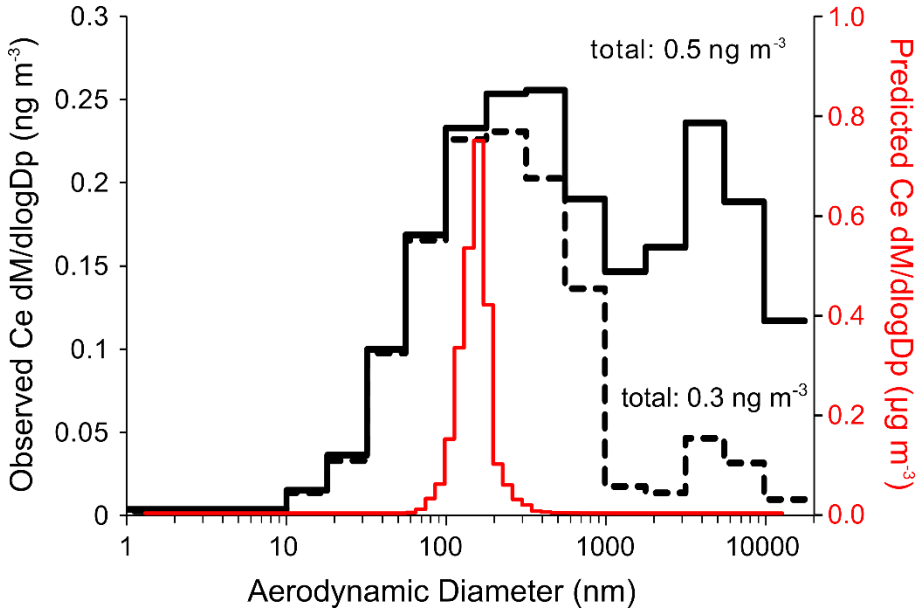


Figure 1. Average mass concentrations of AURN-measured PM_{10} and $PM_{2.5}$, black carbon, and PM_{10}-cerium at the Newcastle site during the daytime (08:00-20:00) and nighttime (20:00-08:00) hours when all constituents were measured concurrently (22-25 August 2012). The error bars represent the standard error and the crosshatching represents the non-crustal cerium concentration estimated by the lanthanum mass concentration and the assumption of a 6.65:3.9 cerium/lanthanum ratio for continental crust.[30]



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322 Figure 2. Size-resolved mass concentration of cerium-containing particles measured by the
323 nanoMOUDI sampler from 17-24 August 2012 in Newcastle, UK (black lines) and predicted by a
324 sectional aerosol model at 300 meters from the roadway during the use of an nCe additive (red
325 line). The dashed black line represents the non-crustal concentration of cerium as estimated by
326 the mass concentration of lanthanum and the assumption of a 6.65:3.9 cerium/lanthanum ratio for
327 continental crust.[30]

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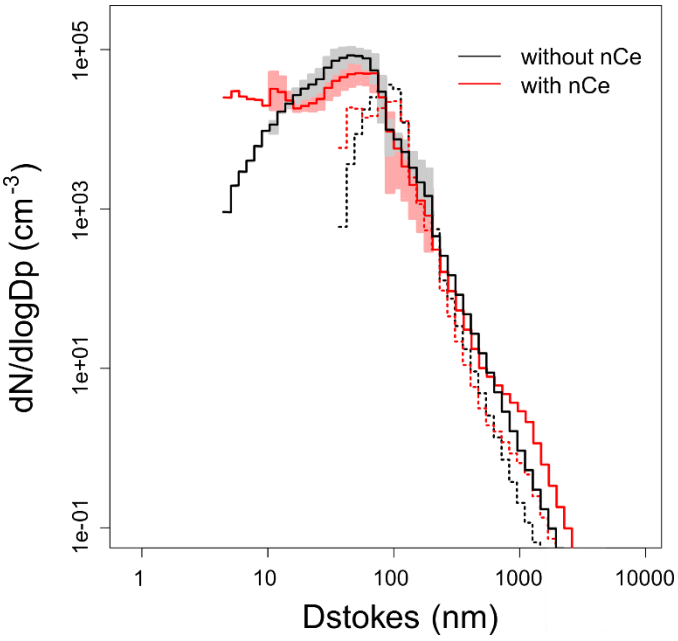
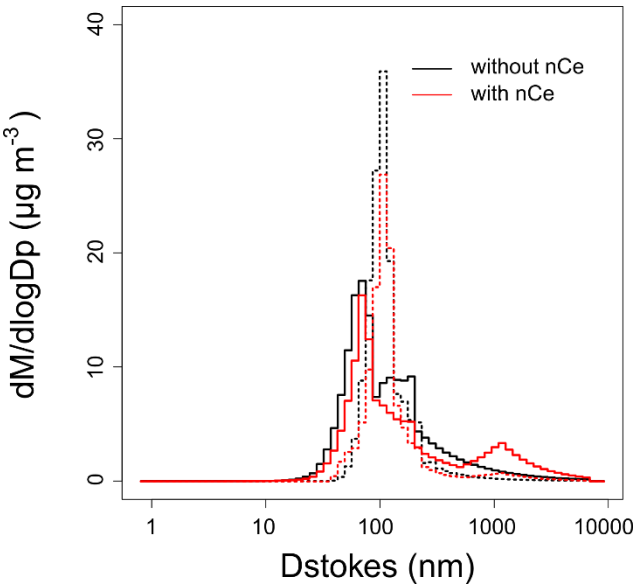


Figure 3. Predicted exhaust particle number size distribution with and without the use of an nCe additive at 30 meters (solid lines) and 300 meters (dotted lines) from the roadway. The shaded area represents the maximum and minimum of the 30 meter distribution from the individual emission studies.[19-21,27]



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336 Figure 4. Predicted exhaust particle mass size distribution with and without the use of an nCe

337 additive at 30 meters (solid lines) and 300 meters (dotted lines) from the roadway.

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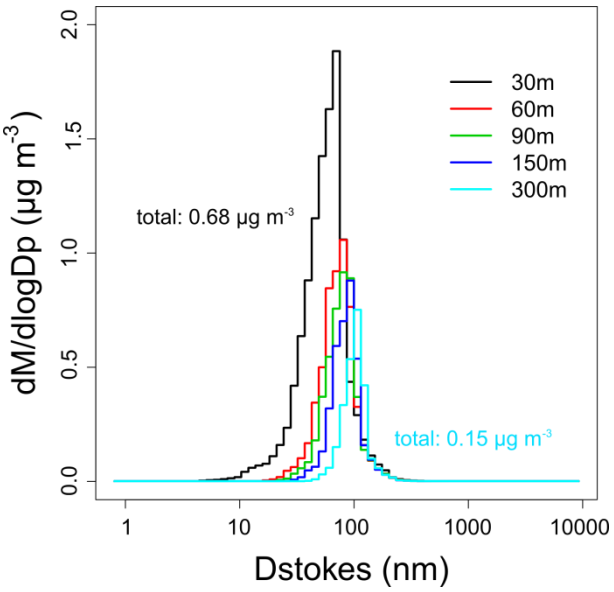

339

340 Figure 5. Predicted mass size distribution of cerium-containing particles from the use of an nCe

341 additive by distance from the roadway.

342 TABLES.

343 Table 1. List of samplers used for data collection in Newcastle, UK during the August 2012
344 campaign.

Sampler	Dates	Integration Time	Notes
Aethalometer	16-31 August	5 minutes	Measures BC, averaged hourly
TEOM 1400 FDMS	1-31 August	1 hour	Measures PM_{10} and $PM_{2.5}$, operated by the Automatic Urban and Rural Network (AURN)
Partisol	8-14, 23-25 August	12 hours	2 samplers with one measuring daytime (08:00-20:00) and the other nighttime (20:00-08:00) PM_{10}. Chemical composition determined by High-Resolution Inductively Coupled Plasma Mass Spectrometry HR-(ICPMS) bulk analysis
nanoMOUDI	17-24 August	7 days	Chemical composition determined by High-Resolution Inductively Coupled Plasma Mass Spectrometry HR-(ICPMS) bulk analysis

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Supporting Information Available

This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information for:

Near-road modeling and measurement of cerium-containing particles generated by nanoparticle diesel fuel additive use

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This supporting information contains 13 pages: 2 tables, 9 figures.

Additional Model Documentation

All particle size distributions in the model are a function of the Stokes diameter, which was calculated from the mobility diameters measured during emission characterization tests using the relationship between mobility diameter and effective density for diesel exhaust aerosols under engine loads of 50 and 75% (see Figure S6) from Park et al.[1] A single particle size distribution for use as an emission input in the sectional aerosol model is created by combining (see Figure S7) and normalizing (see Figure S8) the size distributions of Czerwinski et al.,[2] Skillas et al.,[3] and Jung et al.[4] (CSJ) by the minimum number concentration in the ultrafine mode between 12 and 24 nm Stokes diameter, calculating the mean number value of CSJ for each size bin, and extending the distribution to the supermicron size range by normalizing the Okuda et al.[5] size distribution with the size bins that overlap the CSJ normalized distribution. The size-resolved chemical composition of diesel exhaust without the cerium oxide nanoparticle (nCe) additive is based on Kleeman et al.,[6] while a cerium/non-cerium fraction of exhaust with nCe is given by Okuda et al.[5] for particles with a Stokes diameter > 62 nm and Skillas et al.[3] for Stokes diameters ≤ 62 nm. For the Kleeman et al.[6] composition data given in Table S1, the mobility diameters are converted to Stokes diameters and a nonlinear least-squares polynomial regression is calculated for the three chemical components of the exhaust (elemental carbon (EC), organic carbon (OC), and "Other") as a function of aerosol size and applied to all model size bins. After conversion from mobility to Stokes diameter, a nonlinear least-squares lognormal regression of the Skillas et al.[3]/Okuda et al.[5] cerium mass fraction for exhaust with nCe (Table S2) is calculated and applied to all model size bins. The Kleeman et al.[6] composition regression is then applied to the non-cerium fraction of the exhaust. The resulting chemical composition of the exhaust aerosol mass size distribution with and without nCe is shown in Figure S9.

Additional Tables

Table S1. The chemical composition of diesel fuel exhaust particles as a function of the mobility diameter derived from Figure 4 of Kleeman et al.[6]

Mobility Diameter (nm)		Composition (%)		
		EC	OC	Other
< 123		60.8	30.5	8.7
123	287	65.5	28.2	6.2
287	517	61.3	27.4	11.2
517	905	72.6	18.8	8.6
905	1616	NA	NA	NA
> 1616		6.3	61.7	32.0

Table S2. The mass fraction of cerium oxide in diesel fuel exhaust particles with an nCe additive as a function of the mobility diameter.

Mobility Diameter (nm)		CeO_2 Fraction (%)	Reference
< 54		100	Skillas et al.[3]
54	123	11.2	Skillas et al.[3]
123	404	1.2	Okuda et al.[5]
404	808	0.9	Okuda et al.[5]
808	1616	0.7	Okuda et al.[5]
1616	4040	0.2	Okuda et al.[5]
> 4040		0.1	Okuda et al.[5]

Additional Figures

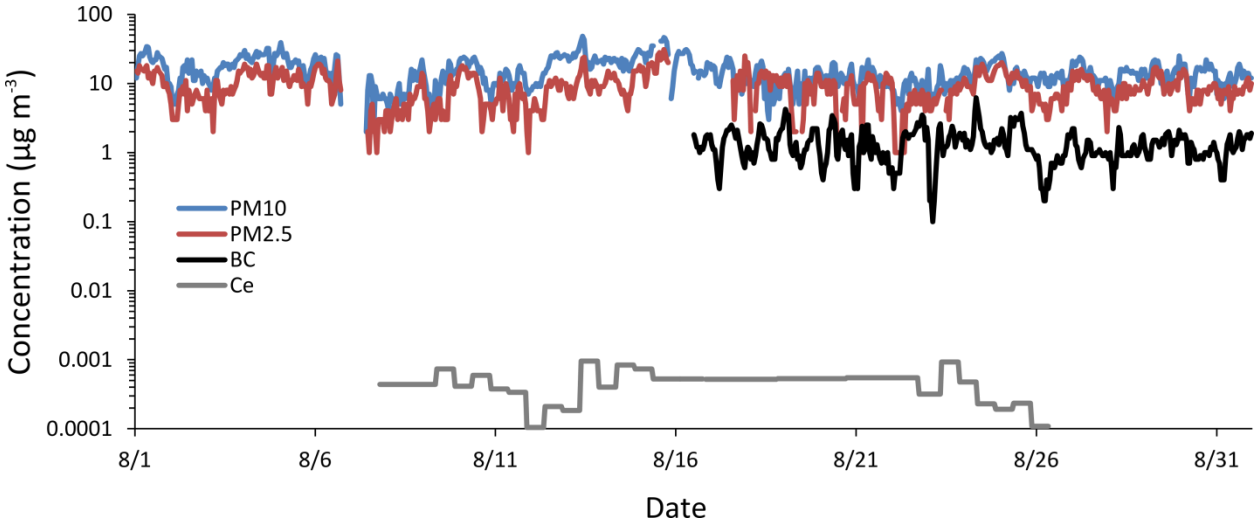


Figure S1. Mass concentrations of AURN-measured PM_{10} and $PM_{2.5}$, BC, and cerium in PM_{10} at the Newcastle site for August 2012.

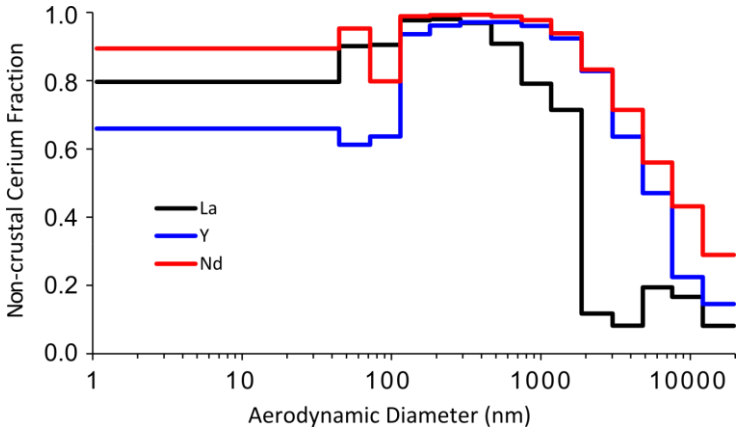


Figure S2. Size-resolved non-crustal mass fraction of cerium-containing particles in Newcastle estimated from the continental crust Lanthanide elemental ratios.[7]

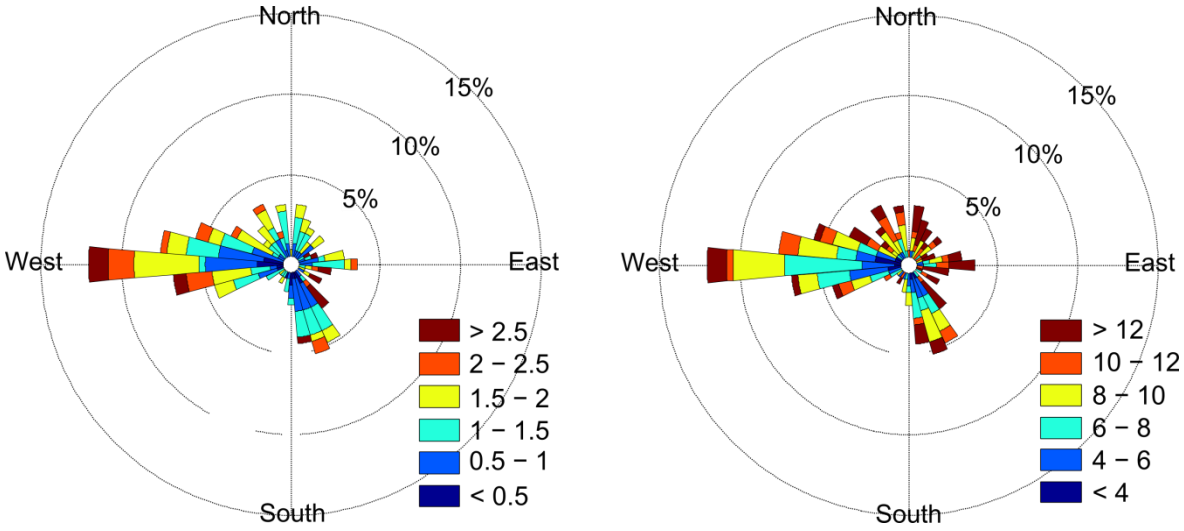


Figure S3. Pollution rose of AURN-measured BC (left) and $PM_{2.5}$ (right) concentrations (in units of µg m^{-3}) as a function of wind direction for August 21-31 2012 when concurrent BC, $PM_{2.5}$, and wind direction measurements are available.

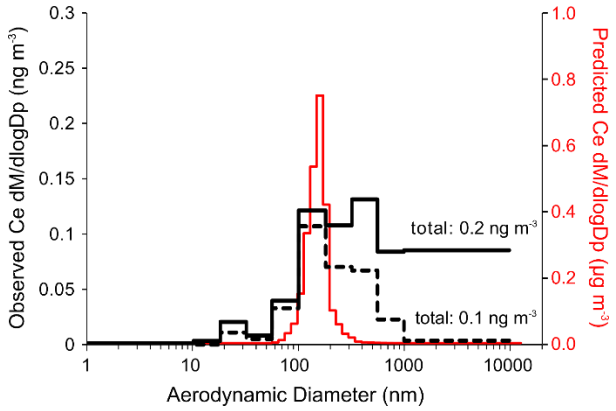


Figure S4. Size-resolved mass concentration of cerium-containing particles measured by the nanoMOUDI sampler from 15-22 March 2012 in Newcastle, UK. The dashed line represents the non-crustal concentration of cerium as estimated by the mass concentration of lanthanum and the assumption of a 6.65:3.9 cerium/lanthanum ratio for continental crust.[7]

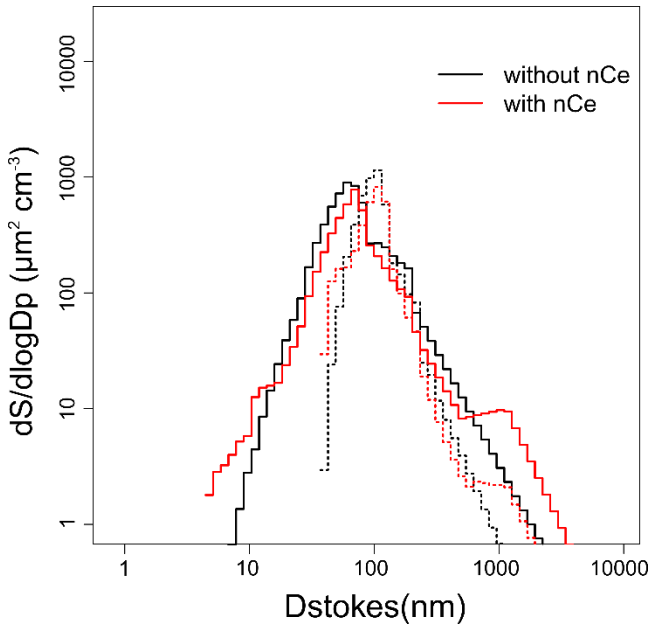


Figure S5. Predicted exhaust particle surface area size distribution with and without the use of an nCe additive at 30 meters (solid lines) and 300 meters (dotted lines) from the roadway.

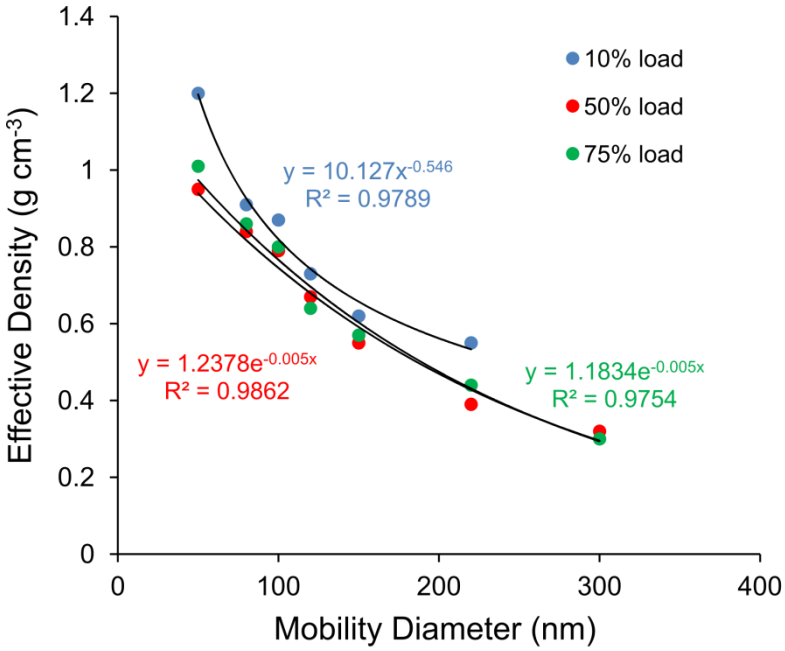
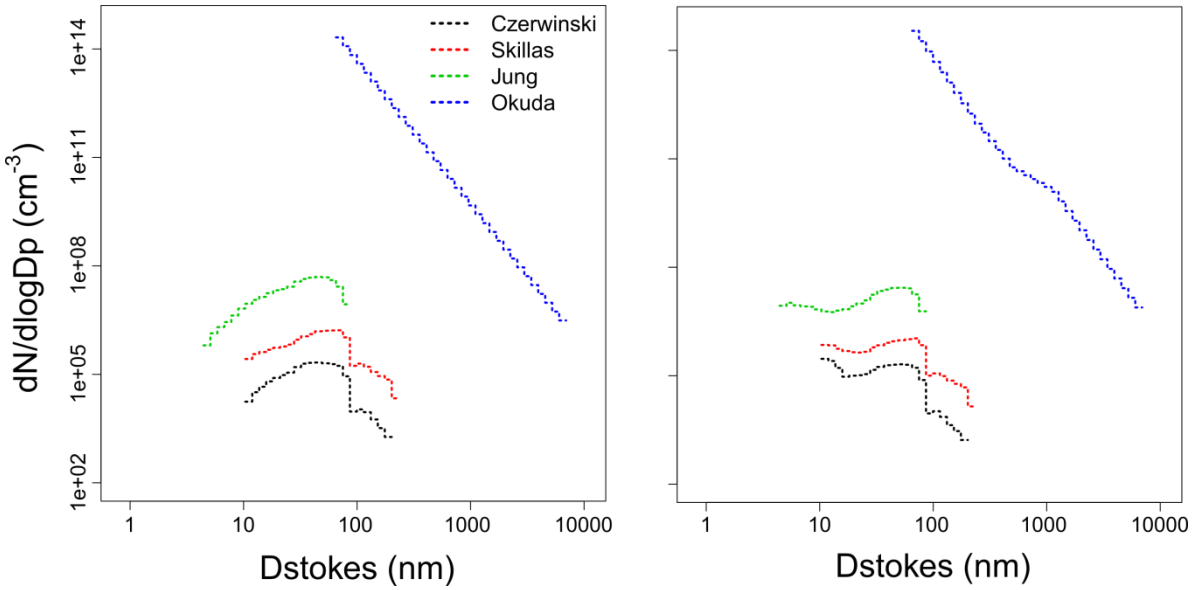


Figure S6. Plot of effective density against mobility diameter at 10%, 50%, and 75% engine load and the corresponding power fit for the 10% load and exponential fit for the 50% and 75% load relationships from Park et al.[1]



79

80 Figure S7. Emitted particle number size distribution (in Stokes diameter) from previous exhaust
81 studies without (left) and with (right) an nCe additive.

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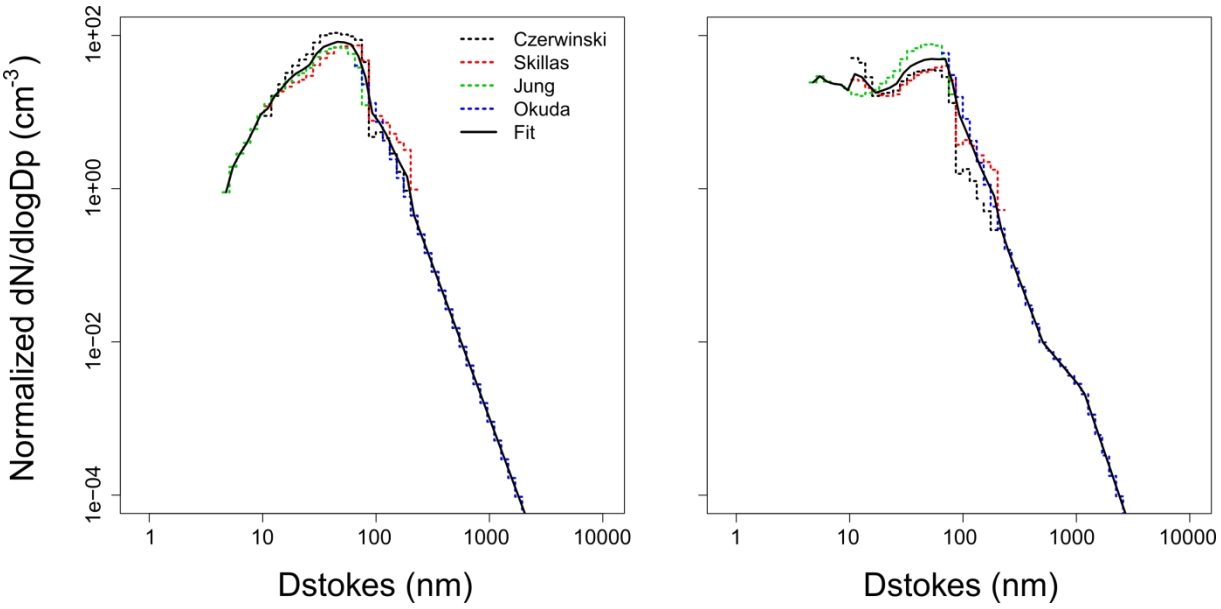

Figure S8. Normalized emitted particle number size distribution from previous exhaust studies without (left) and with (right) an nCe additive and the fitted line representing the mean of the previous studies.

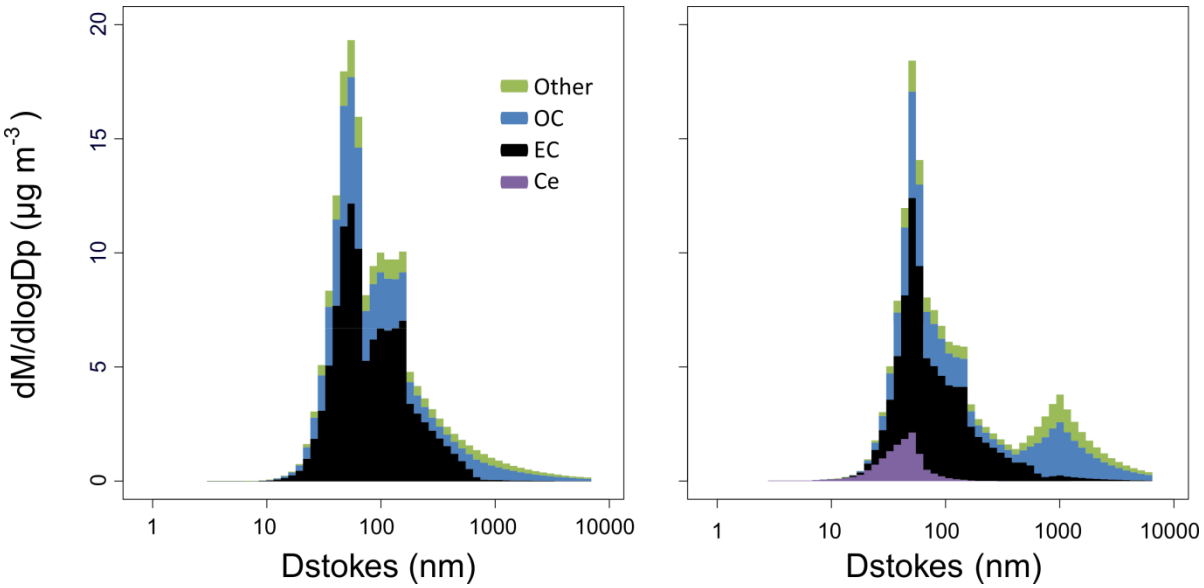

Figure S9. Predicted chemical composition of the emitted particle mass size distribution without (left) and with (right) the nCe additive.

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