Environmental Science & Technology

Article

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Predicting the Effects of Nanoscale Cerium Additives in Diesel Fuel on Regional-Scale Air Quality

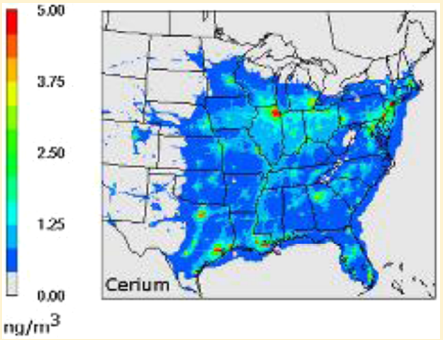
Garnet B. Erdakos,*[,§,†] Prakash V. Bhave,[†,⊥] George A. Pouliot,[†] Heather Simon,[‡] and Rohit Mathur[†]

[†]Atmospheric Modeling and Analysis Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, United States

[‡]Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, United States

Supporting Information

ABSTRACT: Diesel vehicles are a major source of air pollutant emissions. Fuel additives containing nanoparticulate cerium (nCe) are currently being used in some diesel vehicles to improve fuel efficiency. These fuel additives also reduce fine particulate matter ($PM_{2.5}$) emissions and alter the emissions of carbon monoxide (CO), nitrogen oxides (NO_x), and hydrocarbon (HC) species, including several hazardous air pollutants (HAPs). To predict their net effect on regional air quality, we review the emissions literature and develop a multipollutant inventory for a hypothetical scenario in which nCe additives are used in all on-road and nonroad diesel vehicles. We apply the Community Multiscale Air Quality (CMAQ) model to a domain covering the eastern U.S. for a summer and a winter period. Model calculations suggest modest decreases of average $PM_{2.5}$ concentrations and relatively larger decreases in particulate elemental carbon. The nCe additives also have an effect on 8 h maximum ozone in summer. Variable effects on HAPs are predicted. The total U.S. emissions of fine-particulate cerium are estimated to increase 25-fold and result in elevated levels of airborne cerium (up to 22 ng/m^3), which might adversely impact human health and the environment.



INTRODUCTION

Every year, diesel vehicles in the United States consume approximately 50 billion gallons of fuel and emit 300 000 tons of fine particulate matter ($PM_{2.5}$) to the atmosphere.[1,2] The elemental and organic carbon (EC and OC) that comprise a large fraction of diesel particulate matter (DPM) have environmental and health implications. EC, or black carbon, is the dominant light-absorbing constituent of the atmosphere,[3] playing a key role in climate change. Organic material in diesel soot, such as polycyclic aromatic hydrocarbons (PAHs), is potentially mutagenic and carcinogenic.[4−6] Redox-active metals in DPM are also of significant health concern.[7] Efforts to reduce DPM emissions include the use of oxidation catalysts, diesel particulate filters (DPFs), low-sulfur diesel fuels, and fuel additives. Some additives also improve fuel economy.

One class of diesel fuel additives gaining usage in recent years consists of engineered nanomaterials composed of cerium compounds (nCe). Three nCe-based additives are marketed worldwide, although individual product sales and use data are not publicly available. Eolys, manufactured by Rhodia Electronics & Catalysis, is used in combination with a DPF in over 4 million vehicles outside the U.S. The nCe-based Envirox additive is manufactured by Energenics Ltd. and distributed in Europe, Asia Pacific, Canada, and India. Platinum Plus, manufactured by Clean Diesel Technologies, Inc., contains at least 7 times as much nCe as platinum by mass, and had been registered for use in on-road vehicles in the U.S. until October 2011. Envirox and Platinum Plus can be used in off-road diesel vehicles in the U.S., but neither is currently registered with the EPA for use in on-road vehicles.

Whereas the reduction of DPM emissions is a clear benefit of nCe-based additives, the simultaneous increase in cerium emissions might offset that benefit. The human-health effects of inhaling cerium-laden soot are a subject of active investigation,[8−10] while the risk to aquatic ecosystems and soil organisms is less of a concern.[11] Beyond these first-order effects of adding cerium to the environment, numerous studies have demonstrated that nCe additives alter the magnitude of other pollutants emitted from diesel engines. Widespread use of these additives may thus have a significant impact on air quality. For example, changes in nitrogen oxides (NO_x) and volatile organic compound (VOC) emissions resulting from nCe additive usage could affect ambient levels of ozone, PM, and hazardous air pollutants (HAPs).

The objective of this study is to predict the potential impacts of widespread nCe-additive usage on regional-scale air quality. The Community Multiscale Air Quality (CMAQ) model with multipollutant capability[12] is employed to predict atmospheric concentrations of criteria air pollutants (CAPs) and HAPs for a

Received: August 18, 2014
Revised: September 30, 2014
Accepted: October 1, 2014
Published: October 1, 2014

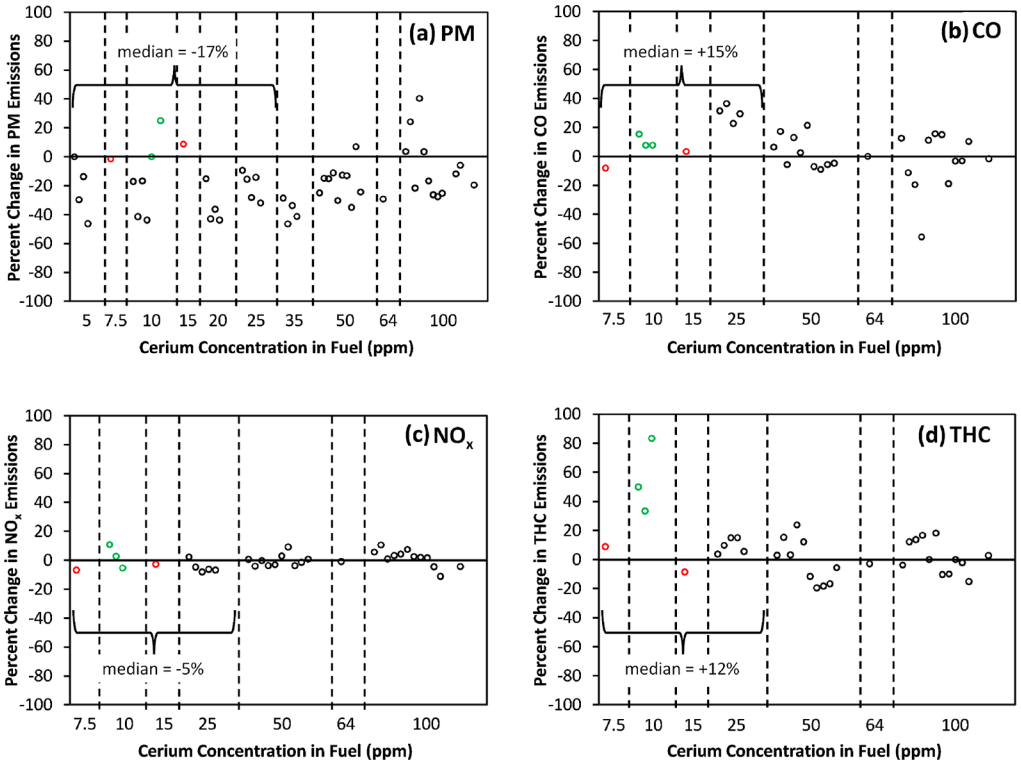


Figure 1. Relative changes in emissions of (a) PM, (b) CO, (c) NO_x, and (d) THC measured in the ten studies listed in Table S2-1. Individual changes from each pair of data (emissions without additive and with additive) are plotted as open circles. Red symbols correspond to Platinum Plus, green to Envirox, and black to Eolys. Median percent changes across all test pairs that used ≤25 ppm of Ce are used for the present modeling investigation (see Table S2-2, Supporting Information for raw data, mean values, and standard errors).

hypothetical scenario in which all on-road and nonroad diesel vehicles in the eastern U.S. use nCe additives. Simulations of a 1 month long period during winter and summer with addition of nCe to all diesel fuels are compared with base case simulations that use standard emission inputs. The indicators of air quality we investigate in this work include ground-level concentrations of $PM_{2.5}$, O_3, and several HAPs. Also, atmospheric cerium concentrations across the eastern U.S. under such a scenario are predicted for the first time. Prediction of local-scale air quality impacts very near major roadways, including effects on particle size distribution, is the subject of a separate study.[13]

MATERIALS AND METHODS

Available Emissions Data. Our search of the literature uncovered 30 journal articles, trade publications, and fuel-additive-registration documents reporting measurements of emissions from diesel engines operating with and without nCe additives (see Table S1-1 of the Supporting Information). Taken together, these studies cover all the marketed nCe additives (i.e., Eolys, Envirox, and Platinum Plus), a wide range of dosing levels (i.e., 5 to 100 ppm of Ce); light-duty, medium-duty, and heavy-duty diesel engines; various base fuels; several different engine test cycles; tests performed with and without DPFs.

Most of the studies applied the Eolys additive, likely due to its widespread use with DPFs in passenger vehicles in Europe. Although some manufacturers are using DPFs to meet the 2007 PM standards, the U.S. diesel fleet is presently composed primarily of heavy-duty vehicles not yet equipped with DPFs. Furthermore, engine size and aftertreatment technology have a major impact on the effectiveness of nCe additives.[14,15] Therefore, we focus our attention on ten reports that provide emissions data from heavy-duty engines without DPFs (see Table S2-1, Supporting Information). In those studies, emissions from engines were first measured using a standard fuel. Next, the engines were run on the fuel dosed with nCe additive and emission measurements were repeated.

We compile the data from these studies and compute relative changes in PM, carbon monoxide (CO), NO_x, and total hydrocarbon (THC) emissions for each pair of measurements (with and without nCe additive). The relative changes are plotted in Figure 1. Much of the variability seen in Figure 1 can be attributed to the range of test parameters noted above, because it is well-known that different engines, base fuels, and test protocols can result in substantially different emissions.[16] For completeness and comparison, we also compile the data for engines using a DPF, and present the relative changes in those emissions in Figure S4-1 (Supporting Information).

An accurate assessment of the air quality impact of nCe additives depends not only on the THC emissions level but also on the ozone-forming potential (i.e., reactivity) of individual HCs whose emissions are affected by the additives. In three studies, gas-phase emissions were analyzed for more than 200 individual VOCs.[17−19] The nCe additives caused substantial changes in emissions of some VOCs. A total of 92 HC compounds that were measured in these studies are represented in the CMAQ modeling system. Emissions data for all of these compounds are provided in Table S2-3 (Supporting Information). In regional-scale photochemical models such as CMAQ, individual hydrocarbons are grouped into a smaller number of model compounds for treatment within an atmospheric chemistry mechanism. For the present CMAQ

Table 1. Domainwide Emissions for 2005 (Average of Winter and Summer Days) and Median Percent Change (%Δ) in Diesel Emissions Due to nCe Additives

species	all sources (ton/day)	on-road diesel (ton/day)	nonroad diesel (ton/day)	%Δ	confidence level[a]
PM	10483	178	286	−17	very high
CO	238986	1912	1550	+15	high
NO_x	35095	4066	2091	−5	medium
NO	30580	3515	1808	−5	medium
NO_2	4515	551	283	−5	medium
VOC	142084	309	297	+12	high
PM species					
EC	1074	132	221	−11	high
OC	2809	32.5	50.3	−53	high
SO_4	505	0.624	0.831	+11	low
NO_3	43.0	0.205	0.315	+11	low
other	6052	12.1	14.1	+11	low
cerium	0.2[b]	0	0	b	high
VOC species[c]					
TERP	22687	4.17	3.35	+14	very low
XYL	4557	19.6	16.7	−22	medium
TOL	5265	28.9	22.4	+22	medium
IOLE	5922	2.05	1.66	−94	medium
ALD2	75.6	11.7	17.3	−7.5	low
ALDX	224	46.2	31.2	+9.3	high
OLE	6993	16.7	16.1	−1.6	high
ETHA	1714	0	0.688	−50	very low
ETH	4312	14.1	25.7	+20	low
FORM	2479	25.2	30.4	−9.7	medium
PAR	38060	157	136	+26	high
UNR	3732	27.4	25.5	+11	high
NVOL	23.4	2.02	1.19	+14	very low
naphthalene	28.7	0.246	0.136	+600	very low
m-xylene	819	1.30	2.57	−38	low
o-xylene	292	0.453	0.899	−50	low
toluene	1895	1.16	4.90	−48	low
benzene	2456	4.15	6.66	−11	low
acrolein	49.1	1.34	0.995	−55	low
1,3-butadiene	702	2.37	0.610	−40	very low
acetaldehyde	2576	10.7	17.4	−1.4	low
formaldehyde	744	29.1	38.7	−2.8	low

[a]A qualitative confidence level is assigned to each percent change value based on the computed errors listed in Table S2-2 (Supporting Information) and the number of measurements for each corresponding species. [b]Total emissions of cerium are computed as the product of those reported by Reff et al.[2] and the estimated fraction (84%) from eastern U.S. sources based on state-by-state CO_2 emission data from the U.S. Energy Information Administration; the median mass fraction of cerium in DPM computed from the available diesel emission test data is 0.005. [c]VOC species are listed in order of decreasing molecular weight; lumped model compounds and the compounds treated individually in CMAQ are listed above and below the dashed line, respectively.

modeling exercise, we use the Carbon Bond 2005 (CB05) mechanism.[20] The right-most column of Table S2-3 (Supporting Information) indicates the CB05 mechanism species to which each measured compound is mapped.

In the case of PM, a comprehensive assessment of nCe additives should consider their effects on the size distribution and chemical composition as well as the total PM mass. Several studies, including some listed in Table S2-1 (Supporting Information), have shown that nCe additives shift the emissions distribution toward smaller particle sizes in the nuclei mode.[15,21−25] However, only one study listed in Table S2-1 (Supporting Information) reported the effect of an nCe additive on bulk chemical composition.[23] Measurements of cerium in DPM emissions were made in four of the studies listed in Table S2-1 (Supporting Information),[17−19,26] from which we compute a median emissions ratio (Ce/DPM = 0.005) when an nCe additive is used.

Development of Model-Ready Emissions Inventory. Base case emissions were generated with the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system[27] using the 2005 National Emissions Inventory (NEI), with which the Comprehensive Air Quality Model with Extensions (CAMx) and the CMAQ model have been evaluated.[28,29] These emissions are summarized for relevant species in Table 1 as averages of the winter and summer days considered in our modeling study. From this summary, we discern that onroad and nonroad diesel engines emit 33% of the total EC emissions across the eastern U.S., 18% of NO_x, 9% of formaldehyde, and over 30% of the large aldehydes (ALD2 and ALDX). For all other species listed in Table 1, except for the NVOL model compound (representing other nonvolatile species), diesel

vehicles contribute less than 5% of the domainwide emission total from all sources.

Diesel emissions are consistently higher in summer than in winter (base case summer emissions of diesel PM, VOC, and NO_x are 63%, 47%, and 26% higher, respectively), primarily because of construction and agricultural activities during summer. Due to warmer temperatures, total PM emissions from all sources are ~30% lower in summer, while total VOC emissions are 4 times greater. Biogenic emissions account for a large part of increased VOC emissions in summer. Total emissions of NO_x vary little between the two seasons, since increased emissions due to construction and agricultural activities in summer are offset by increased emissions due to residential heating in winter.

To predict the air quality impacts of nCe additives at typical dosing levels (~10 ppm), we restrict our attention to data for nCe levels ≤25 ppm in fuel. This subset of data is provided in Table S2-2 (Supporting Information) and bracketed in Figure 1. (An analogous subset of data for measurements on engines using a DPF is summarized in Table S4-1 and Figure S4-1, Supporting Information.) These data consistently demonstrate a reduction in PM mass emissions with additive usage (Figure 1a). Significant increases in both CO and THC emissions are also observed (Figure 1b,d). In contrast, the additives have minimal effect on NO_x emissions (Figure 1c). The directions of these changes are consistent with the expected effects of nCe additives, which promote the oxidation of diesel soot particles to HC, CO_2, and CO, and slightly reduce the activation energy of the oxidation reaction.[26] The median changes in PM, CO, NO_x, and THC emissions utilized in our modeling exercise are −17%, +15%, −5%, and +12%, respectively (see %Δ column in Table 1). To quantify the spread of the data we compute the standard error associated with each of the median change values (see Table S2-2, Supporting Information). For the four bulk pollutants discussed here, median emission changes differ from zero by at least one standard error.

Although base case CO and NO_x emission inputs can be modified directly using the median percent change values shown in Table 1, modification of HC and PM emissions is not straightforward. The HCs modeled in CMAQ include individual VOCs such as benzene and formaldehyde, as well as lumped model compounds such as PAR (i.e., paraffins) and OLE (i.e., olefins). Model-ready emission inputs for those lumped compounds are calculated with the Speciation Tool version 2.0,[30] which maps individual HCs to model compounds in a given chemical mechanism. We use a spreadsheet version of that tool to compute mass fractions of lumped model compounds from the emission data in Table S2-3 (Supporting Information). Percent changes for each lumped compound and each pair of emission tests are then computed, from which the median percent change is derived for each compound (see Table S2-4, Supporting Information). Finally, the percent change for each lumped compound is normalized to ensure that the THC emissions increase by an amount (+12%) that is consistent with the data from the larger body of literature, as summarized in Table S2-2 (Supporting Information).

The final percent change values for 13 lumped VOCs affected by nCe additives are listed in Table 1. Although the nCe additives dramatically affect diesel emissions of certain lumped species (e.g., IOLE, ETHA, PAR), diesel vehicles contribute less than 1% of their total emissions. For the lumped VOCs that diesel vehicles contribute substantially (i.e., ALD2 and ALDX), nCe additives have a modest impact on emissions (%Δ = −7.5% and +9.3%, respectively). Therefore, we do not anticipate significant changes in ambient ozone to result from changes in the reactivity of the VOC mixture.

Nine speciated HC compounds in the emission studies are modeled explicitly in CMAQ. These compounds are classified as HAPs and their percent change values are listed in Table 1. Large increases in emissions of individual HAP species may be a concern in near-road environments. For example, naphthalene emissions are found to increase substantially (an order of magnitude) in one study using the Envirox additive (see Table S2-3, Supporting Information). Furthermore, at an air quality monitoring station in close proximity to a bus route in the U.K., the annual-average ambient concentrations of 24 out of 30 measured PAH compounds increased after introduction of the Envirox additive to the bus fleet.[31]

The PM emissions input to v4.7 of the CMAQ system must be speciated into OC, EC, SO_4, and NO_3 ions, and other mass (PM_{Other}). OC and EC emissions with and without the use of nCe additive were measured by Skillas et al.,[23] and their median percent changes were computed from those data. The percent change of each model PM compound was then normalized to ensure a 17% decrease in total PM, as described above for HCs. (Analogous percent changes in speciated emissions from heavy-duty engines with DPFs are presented in Table S4-2, Supporting Information.)

Model-ready emission inputs for the nCe-impacted scenario are generated by applying the relative emissions changes listed in Table 1 (%Δ) to all on-road and nonroad diesel vehicle emissions included in the base case inventory. We estimate air quality impacts of these changes by comparing the air pollutant concentrations predicted by the CMAQ model in the base case and modified emissions scenarios. Considering the standard errors listed in Table S2-2 (Supporting Information) and the number of available data points for each of the individual species listed in Table 1, we assign a qualitative confidence level for each computed emissions change. These confidence levels (see Table 1) apply not only to the percent changes in emissions due to nCe additive usage, but also to the estimated air quality impacts discussed below.

Modeling Approach. The CMAQ model is one of the most extensively evaluated models for simulating regional-scale air quality.[32] CMAQ v4.7 with multipollutant capability[12,33] is used in this study to calculate CAP and HAP concentrations for two 25 day periods in 2005 (January 6−30 and July 6−30). Two simulations are performed for each period: (1) a base case simulation using the standard emission inputs, and (2) an nCe-impacted case using the modified emission inputs described above. A common set of meteorology inputs generated using the Meteorology-Chemistry Interface Processor (MCIP) with MM5 data[34] is used in both simulations.

For this work, the model domain covers the eastern U.S. with a grid of 279 × 240 12 km cells and 24 vertical layers. The impact of nCe additives may be underestimated near the boundaries, since boundary concentrations were obtained from a coarse-grid continental U.S. domain simulation that did not consider the effect of nCe additives on emissions. Allowing for an 11 day spin-up period, in which initial pollutant concentrations are stabilized, we present ground-level results from the last 2 weeks in each simulation.

RESULTS

Effect on Emissions. Maps of current cerium emissions and those estimated for our hypothetical scenario are shown in

Figure S2-1a (Supporting Information). Assuming widespread usage of nCe additives, we project the total U.S. emissions of fine-particulate cerium to increase by a factor of 25, from present-day levels of 69 tons/yr to 1750 tons/yr in the future. Base case and modified emissions of HAP species for which diesel vehicles contribute ≥5% of the total emissions are also shown in Figure S2-1 (Supporting Information). As shown in these maps, emissions are projected to increase most in urban areas and highway corridors.

Impact on Ambient Ce Concentrations. Concentrations of fine-particulate cerium averaged over our 14 day winter period (1/17−1/30/2005) are mapped in Figure 2. We predict

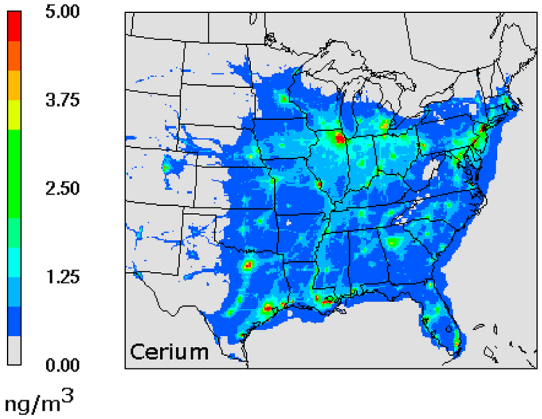


Figure 2. Predicted surface-level concentrations of cerium due to use of nCe diesel fuel additives. Concentrations are calculated as the product of the mean DPM concentrations (1/17−1/30/2005) and median fraction of cerium in DPM computed from diesel engine emissions data in four studies[17−19,26] listed in Table S2-1 (Supporting Information).

a domainwide-average cerium concentration of 0.5 ng/m^3 and a maximum value of 22 ng/m^3. As expected, the highest concentrations are predicted in major cities and along interstate highways where diesel traffic is greatest. The upper limit of the scale shown in Figure 2 (5 ng/m^3) is roughly 1 order of magnitude larger than the level of cerium measured at a monitoring site impacted by the use of Envirox in the Stagecoach bus fleet in Newcastle, U.K.[35] Only buses using the additive likely impacted the cerium concentrations at that site, compared to on-road and nonroad fleet-wide usage, which we model in this work. On the other hand, predictions of Ce concentrations are within the range of values (5−25 ng/m^3) simulated for a street canyon using the U.S. EPA HIWAY2 model.[35] Closer agreement with the street canyon simulation is likely a result of their assumption that *all* vehicles use nCe fuel additives. Predicted cerium concentrations are generally much larger than existing ambient levels measured in previous studies.[36]

Impact on Ambient $PM_{2.5}$ Concentrations. For the base case emissions, 14 day average $PM_{2.5}$ concentrations predicted in the winter and summer months were 6.3 and 4.5 μg/m^3, respectively, across the entire domain (see Table S3-1, Supporting Information). Domainwide-average changes in $PM_{2.5}$ concentration were less than 0.05 μg/m^3 during both seasons. Absolute changes on one summer day (7/20/2005) are shown in Figure 3a and the corresponding change in EC is mapped in Figure 3b. A similar set of maps for one winter day, as well as relative changes for both species and seasons, are

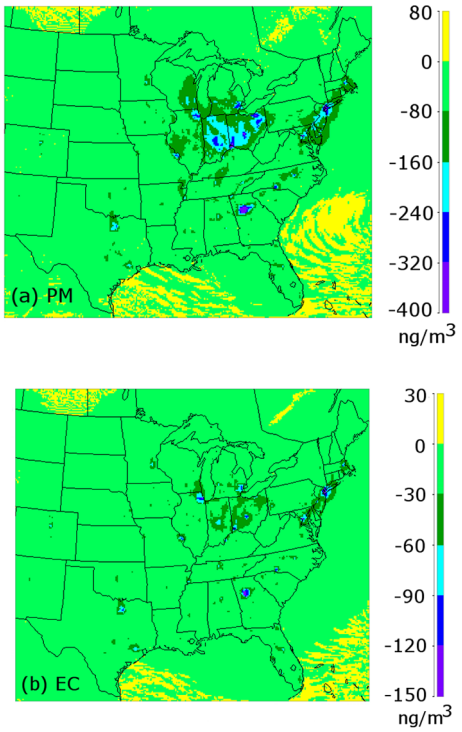


Figure 3. Predicted changes in summer (7/20/2005) (a) $PM_{2.5}$ (PM) and (b) EC 24 h average concentrations due to nCe diesel fuel additives. Note the different scales across the panels.

included in Figure S3-1 (Supporting Information). The greatest predicted changes as seen in Figure 3 are decreased $PM_{2.5}$ and EC concentrations in urban areas. For example, in one grid cell near Atlanta, a −2.5% change in $PM_{2.5}$ is predicted. The corresponding relative change in EC (−9.3%) is nearly four times greater because diesel sources make such a large contribution to total EC emissions. In comparison with these changes, the maps for the selected winter day in Figure S3-1 (Supporting Information) show a greater extent of decreased $PM_{2.5}$ and EC concentrations in the Southeast.

Impact on Ambient O_3 Mixing Ratios. The decrease in NO_x and increase in VOC emissions from diesel vehicles using nCe additives, as illustrated in Figure 1, have potential to affect ozone mixing ratios. The nominal predicted relative changes are shown for one summer day (7/28/2005) in Figure 4. Mixing ratios decrease over much of the domain, likely due to the slight decrease in NO_x emissions when nCe additives are used. In

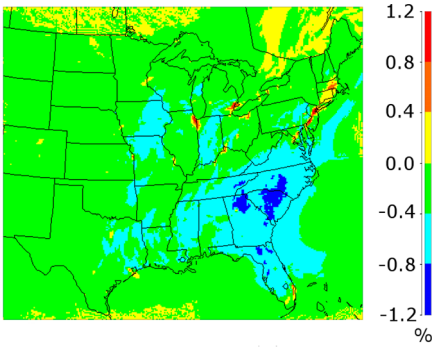


Figure 4. Relative changes in predicted 8 h maximum ozone concentrations due to use of nCe diesel fuel additives on 7/28/2005.

dx.doi.org/10.1021/es504050g | *Environ. Sci. Technol.* 2014, 48, 12775−12782

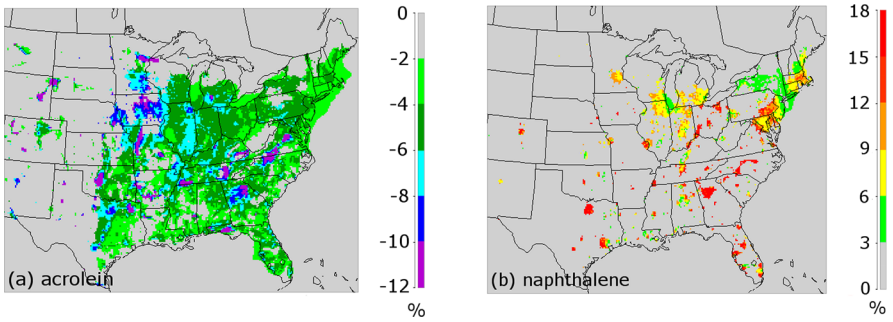


Figure 5. Relative changes in predicted 14 day summer (7/17−7/30/2005) average concentrations of two HAPs: (a) acrolein and (b) naphthalene, due to use of nCe diesel fuel additives. Note the different scales across panels. These species are considered based on a combination of their roles as key atmospheric pollutants, the size of diesel source contributions to their emissions, and the extent to which nCe additives modify their emissions. Extremely low base case concentrations occur in many areas of the model domain, particularly the central states, and result in extraordinarily large relative changes. Therefore, only relative changes computed for base concentrations >0.001 ppbV are shown in these panels.

urban areas across the Northeast and Midwest, however, we predict O_3 increases resulting from the NO_x emission reduction and slight VOC increase. We predict the greatest decreases in O_3 over the Southeast, likely due to NO_x-limitation and the abundance of biogenic VOCs in that part of the domain. These patterns of change in O_3 are consistent with modeling studies that consider the impacts of NO_x emissions changes on ozone.[37] It is important to emphasize that our confidence in the predicted O_3 changes here is constrained by the Medium confidence level assigned to the NO_x emission changes (see Table 1), due to considerable variability in those underlying data.

Impact on Ambient HAP Concentrations. As noted above, diesel vehicles contribute a significant fraction to the emissions of only a few of the VOC species included in our model simulations. Nevertheless, widespread use of nCe additives would substantially alter diesel engine emissions of several HAPs: acrolein, naphthalene, acetaldehyde, and formaldehyde (see Table 1). Average relative changes in model-predicted ambient concentrations of acrolein and naphthalene for the 14 day summer period are illustrated in Figure 5. (Analogous plots for the winter period, as well as acetaldehyde and formaldehyde in both winter and summer, are shown in Figure S3-2, Supporting Information.) Averaged over the 14 day summer period and all urban areas in the domain, predicted changes in concentrations of acrolein and naphthalene are −5% and +8%, respectively. In some locations, we predict acrolein to decrease by 85% and naphthalene to increase by 39%. The plots in Figure S3-2 (Supporting Information) show that, compared to the summer period, predicted increases in naphthalene concentration are ubiquitous across much of the modeling domain, whereas predicted decreases in acrolein are generally smaller in magnitude and occur over less area of the modeling domain. The relative changes in ambient levels of acetaldehyde and formaldehyde during summer are comparatively small (see Table S3-1, Supporting Information) because their production is driven more by photochemical reactions than primary emissions.[38]

■ DISCUSSION

Our combined analyses of the emissions data from nCe additive tests, the total diesel emissions of each pollutant relative to other sources in the inventory, and the atmospheric chemistry and transport of those pollutants, enable identification of the most critical data needs. First, additional measurements showing that nCe additives reduce total DPM emissions are not a priority because evidence of this is abundant and reasonably consistent across studies (see Figure 1a). However, additional measurements describing how the nCe additives affect PM composition, especially the organic speciation and metals, are greatly needed. Most notably, there is a dearth of information on the cerium concentrations within the DPM when nCe additives are used.

Second, there is little need for additional measurements of CO and total HC emissions from diesel vehicles using nCe fuel additives. Although we found some lack of agreement across emission studies (see Figure 1b,d), the value of conducting additional tests and refining our central estimates is diminished by the fact that diesel vehicles contribute very little to the total emissions of CO and HC. On the other hand, additional measurements of speciated HC emissions are critically needed, especially naphthalene and acrolein, for which relatively few existing measurements are available and considerable air quality impacts are predicted to result from the emissions changes caused by nCe additives. Aside from two pairs of data points for naphthalene, measurements of PAH emissions are lacking.

Third, numerous studies have demonstrated that nCe additives shift the distribution of DPM to small particle sizes. However, few studies have addressed the more critical question for risk assessments: What particle size is the cerium emitted in? For this, measurements of the size-resolved chemical composition are needed (e.g., using impactors). Armed with such information, it would be possible to estimate the region of the respiratory tract where most of the cerium will deposit and to conduct subsequent health studies.

Finally, our investigation shows that the majority of available data are from studies that tested the Eolys nCe additive, which is not currently registered with the EPA; and it supports the need for additional emissions testing focused on the Envirox and Platinum Plus additives, which can be used in off-road diesel vehicles in the U.S. These data limitations apply to heavy-duty diesel engines equipped with DPFs, as well as to those without DPFs. Moreover, as shown in Tables S4-1 and S4-2 (Supporting Information), there are less emissions data available for diesel engines with DPFs than without DPFs. This greater data limitation is important to consider for future emissions measurements, as new vehicles with DPFs continue to be introduced into the U.S. diesel fleet. It would be useful to design future emissions characterization studies with engine types, standard fuels, and testing protocols that are consistent across studies, thereby reducing uncertainty due to the inherent variability of diesel emissions data.

We predict that widespread use of nCe diesel fuel additives across the U.S. would have a measurable effect on regional air quality. Both $PM_{2.5}$ and EC will decrease over most of the eastern U.S. On average, across the 14 day winter and summer periods we model here, the percent change in EC exceeds that of $PM_{2.5}$ by a factor of 5 in urban areas. Reduction in EC concentrations has potential policy implications, as EC is a short-lived climate forcer. Our results show that ambient concentrations of $PM_{2.5}$ and O_3 are impacted to a limited extent. We predict O_3 levels to increase in urban areas of the Midwest and Northeast, in contrast to a region-wide O_3 decrease in the Southeast. Although the slight decrease in $PM_{2.5}$ concentrations is desirable, the simultaneous increase in O_3 could offset that benefit in some nonattainment areas. We also predict increased naphthalene and decreased ambient levels of acrolein. Naphthalene is classified by the EPA as a possible human carcinogen, and changes in ambient levels of naphthalene could have implications on the formation of secondary organic aerosol (SOA),[39] thereby enhancing $PM_{2.5}$ concentrations. However, the version of CMAQ used in this study does not include an SOA formation pathway for naphthalene.

Although $PM_{2.5}$ and EC concentrations decrease, the use of nCe diesel fuel additives results in emission of cerium, likely as single and aggregated nanoparticles. While the predicted concentrations of cerium are orders of magnitude lower than the reference concentration (RfC) (200 ng/m^3) for microscale cerium, no RfC has been established for nCe. The increase in ultrafine DPM emissions, along with the observed increase in some HAP emissions, indicates a potential degradation of near-road air quality. This is the subject of a companion study by Gantt et al.,[13] which considers changes in particle mass concentration and number distribution due to nCe additives. Other relevant efforts could be undertaken to further investigate the effects of nCe diesel fuel additives on air quality, including construction of additional emissions scenarios based on available data that consider new control strategies (e.g., use of DPFs and ultralow sulfur fuels) to predict the impact of nCe additives on regional and near-road air quality in future years.

■ ASSOCIATED CONTENT

Supporting Information

References for the full set of emissions studies compiled for this work; impacts on emissions from engines not equipped with DPFs; model-predicted impacts on air quality; impacts on emissions from engines equipped with DPFs. This material is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*G. B. Erdakos. Phone: 707-665-9900. Fax: 707-665-9800. E-mail: gerdakos@sonomatech.com.

Present Addresses

[§]Sonoma Technology, Inc., 1455 N. McDowell Boulevard, Suite D, Petaluma, California 94954, USA.

[⊥]International Centre for Integrated Mountain Development (ICIMOD), Kathmandu, Nepal.

Notes

Although this paper has been reviewed and approved for publication, it does not necessarily reflect the policy or views of the U.S. Environmental Protection Agency.

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank, from the EPA, Michele Conlon, Susan Forbes, Bill Linak, Madeleine Strum, David Wong, Deborah Luecken, Bill Hutzell, Kevin Dreher, and Rich Cook. The authors also thank Maria Costantini from the Health Effects Institute and Jan Czerwinski from AFHB, University for Applied Sciences, Biel-Bienne for providing many of the reports on diesel engine emission studies considered in this work.

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