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Publication Date

2010-08-01

University of California Transportation Center
UCTC-FR-2010-15

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July 2010

Effects of Retrofitting Emission Control Systems on In-Use Heavy Diesel Vehicles

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Received March 1, 2010. Revised manuscript received May 9, 2010. Accepted May 21, 2010.

Diesel engines are now the largest source of nitrogen oxides (NO_x) and fine particulate black carbon (soot) emissions in California. The California Air Resources Board recently adopted a rule requiring that by 2014 all in-use heavy trucks and buses meet current (2007) exhaust particulate matter (PM) emission standards. Also by 2023 all in-use heavy-duty vehicles will have to meet current NO_x emission standards, with significant progress in achieving the requirements for NO_x control expected by 2014. This will require retrofit or replacement of older in-use engines. Diesel particle filters (DPF) reduce PM emissions but may increase the NO_2/NO_x emission ratio to $\sim 35\%$, compared to $\sim 5\%$ typical of diesel engines without particle filters. Additionally, DPF with high oxidative capacity reduce CO and hydrocarbon emissions. We evaluate the effects of retrofitting trucks with DPF on air quality in southern California, using an Eulerian photochemical air quality model. Compared to a 2014 reference scenario without the retrofit program, black carbon concentrations decreased by $12 \pm 2\%$ and $14 \pm 2\%$ during summer and fall, respectively, with corresponding increases in ambient ozone concentrations of $3 \pm 2\%$ and $7 \pm 3\%$. NO_2 concentrations decreased by 2–4% overall despite the increase in primary NO_2 emissions because total NO_x emissions were reduced as part of the program to retrofit NO_x control systems on in-use engines. However, in some cases NO_2 concentrations may increase at locations with high diesel truck traffic.

1. Introduction

Heavy-duty diesel engines are an important source of air pollution on urban, regional, and national scales (1–3). Although they account for only 2% of the on-road vehicle fleet and 4% of the vehicle-km traveled, heavy-duty trucks are responsible for over half of nitrogen oxide (NO_x) and exhaust particulate matter (PM) emissions from on-road mobile sources (4). The importance of diesel engine emissions has been growing since 1990 due to success in controlling light-duty gasoline engine emissions, the failure of early efforts to control diesel NO_x emissions, and a 3-fold higher growth rate of diesel fuel sales compared to gasoline (5, 6).

In contrast to earlier diesel emission control strategies that relied on combustion modifications and improved engine designs (for example, exhaust gas recirculation), current control strategies now typically include exhaust after-treatment (7). Diesel particle filters (DPFs) trap particles in

the exhaust stream and remove them through an oxidative process. DPFs may be configured with either active or passive methods for removal of accumulated particles. A typical active process is triggered by an increase in exhaust backpressure and involves injection of fuel onto a heated catalyst resulting in oxidation of carbon particles trapped on the filter. Passive regeneration cycles typically include a catalyst upstream of the particle filter; the catalyst promotes oxidation of nitric oxide (NO) present in the exhaust to nitrogen dioxide (NO_2). NO_2 in turn is used to help remove carbon particles from the filter to prevent it from plugging. With a passive filter NO_2 emissions are dependent on the NO_x flux and exhaust temperature (7). Other approaches and many variations on the above examples exist; emissions vary based on the oxidative capacity of the filter and other factors (8).

Urea-based selective catalytic reduction (SCR) is an effective approach to controlling NO_x emissions from heavy-duty engines. The use of SCR requires urea distribution infrastructure. Urea is preferable to ammonia as the reducing agent because it can be stored in liquid form and is safer and easier to handle. Other approaches include lean NO_x traps (LNT) that periodically regenerate by reducing NO_x with fuel, and lean NO_x catalysts that adsorb NO_x under lean conditions and can also use fuel to reduce the NO_x to N_2 . Conversion efficiencies of lean NO_x traps and catalysts have not matched SCR, however, development is ongoing (7).

DPF and SCR systems have not yet been widely deployed on diesel engines in the United States. Nationally, new heavy-duty diesel engines were required to meet more stringent exhaust PM and NO_x emission limits starting with the 2007 and 2010 engine model years, respectively. However, because of the long service life and slow rate of turnover for heavy-duty engines, the California Air Resources Board (CARB) has adopted an in-use emissions control rule that requires heavy-duty vehicle owners to retrofit or replace older engines (9). This program is intended to accelerate reductions in diesel exhaust emissions that would otherwise occur more gradually due to fleet turnover. As a result, all on-road heavy-duty diesel trucks operating in California are expected to meet current new-engine exhaust PM emission standards by 2014. The adoption of best available control technology for NO_x will proceed at a slower pace, to be completed by 2023. By 2014, half of the in-use heavy trucks in large fleets (4 or more vehicles) will be required to meet current new-engine emission standards for NO_x (9). Different rules and schedules for implementing NO_x controls apply to independent operators and small truck fleets (9). Side effects of the new emission controls may include reduced engine efficiency and changes in emissions of pollutants such as nitrogen dioxide (NO_2), nitrous acid (HONO), and ammonia (NH_3) (10, 11).

To date the main concern about DPF systems appears to be increased primary NO_2 emissions. For example, Carslaw (12) and Carslaw et al. (13) showed that at many sites throughout London, NO_2 concentrations did not decrease along with NO_x between 1997 and 2003, and the increase in the measured NO_2/NO_x ratio could be linked to the use of DPFs and an increase in the fraction of light-duty diesel vehicles. Jenkin et al. (14) reported a 7% increase in mean O_3 mixing ratios when modeling the effects of increases in NO_2/NO_x emission ratios in southern England. A positive side effect of DPF systems is that measured emissions of carbon monoxide, total hydrocarbons, and polycyclic aromatic hydrocarbons are reduced significantly when an oxidation catalyst is used with a DPF (8, 15).

The diesel engine replacement/retrofit program in California will lower exhaust PM emissions, but may also increase

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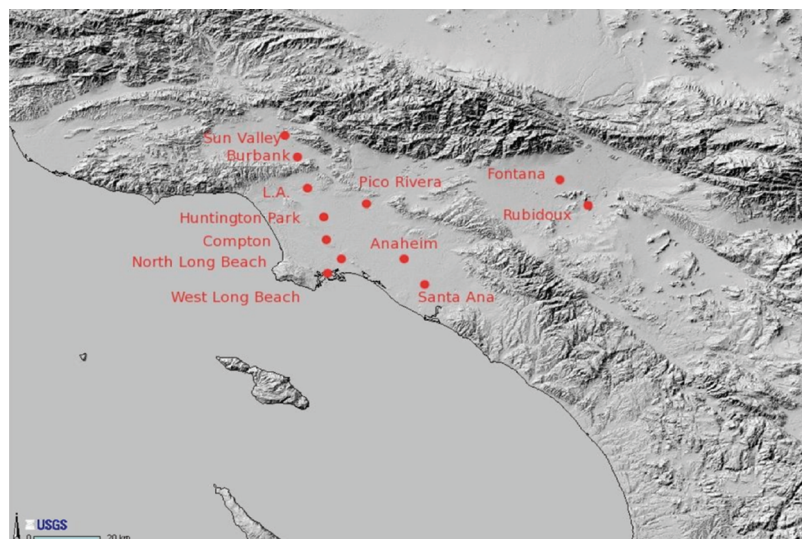


FIGURE 1. Map of southern California air quality study domain, including surface observation sites used for model evaluation.

the NO_2/NO_x emission ratio from <10 up to ~35% over a relatively short time period (i.e., by 2014). Since the schedule for reducing diesel NO_x emissions is more gradual compared to that for exhaust PM, increases in concentrations of NO_2 and related pollutants may be observed. Therefore, the objective of this study is to assess the impacts of diesel engine emission controls on ambient air quality, by comparing future emission scenarios with and without the accelerated diesel engine replacement/retrofit program. To make these comparisons, an Eulerian photochemical air quality model was applied to southern California for both summer (high ozone) and fall (high PM and NO_2) conditions. Air quality end points assessed here include O_3 and NO_2 in the gas phase, as well as fine particulate mass and its constituents.

2. Methods

Air Quality Model. The Community Multiscale Air Quality or CMAQ model (16) version 4.6, with the SAPRC99 gas-phase chemical mechanism (17) and the AE4 aerosol module (18) was used to evaluate air quality for baseline (2005) and two alternative future (2014) emission scenarios. The choice of future year in this study was determined by the schedule for completing installation of particle filters on (or replacing) older on-road heavy-duty diesel engines in California. Gridded hourly meteorological fields were developed using the Mesoscale Meteorological model (MM5) version 3.6.1 (19). Both meteorological fields and pollutant inflow boundary conditions for the air quality model are further described by Millstein and Harley (20).

The southern California modeling domain used in this study has 65×40 grid cells with 5 km horizontal resolution. Figure 1 shows the modeling domain and locations of special study sites where $\text{PM}_{2.5}$ mass and chemical composition were measured (21). Fifteen vertical model layers were used in a telescoping scheme, with the lowest layer being 36 m thick, and the topmost layer ending at a height of ~15 km above sea level. Two simulation periods, summer (July 6–August 29) and fall (October 30–December 7), were considered in this study. During these time periods in 2005, wildfires did not have a major impact on air quality within the modeling domain.

Baseline Emissions. Anthropogenic emissions estimates for 2005 were originally developed by the South Coast Air Quality Management District and the California Air Resources Board (22). Baseline emissions from diesel-powered construction equipment were multiplied by 0.20 and 0.32 for NO_x and exhaust PM, respectively, to match updated estimates of these emissions developed based on off-road

engine fuel use by Millstein and Harley (23). The spatial distribution of emissions was also adjusted as construction activities had moved on to new locations further inland relative to those specified in the baseline inventory. The revisions to construction emissions led to increased relative importance of on-road diesel engine emissions that are the focus of the present study.

The chemical composition of NO_x emissions from on-road vehicles was revised downward from a 10% NO_2 fraction assumed to apply uniformly to all sources in the baseline inventory, to 5 and 1% NO_2 for heavy-duty diesel and light-duty gasoline vehicles, respectively, as measured in a summer 2006 highway tunnel experiment under loaded-mode driving conditions (24). These values may not accurately represent heavy-duty diesel NO_2 emission fractions under other driving conditions, especially at idle or for slow-speed/stop-and-go urban driving. Again based on highway tunnel measurements of loaded-mode driving (25), diesel $\text{PM}_{2.5}$ emissions were speciated as follows: 64% EC, 32% OC, and 4% other material. Additionally, weekend emission estimates for selected source categories were adjusted to match activity patterns reported by Chinkin et al. (26) for southern California.

Baseline anthropogenic emissions for fall 2005 and summer/fall 2014 simulation periods were estimated by adjusting summer 2005 emission estimates using scaling factors for each pollutant and source category. Scaling factors were derived from tabulated seasonal planning inventories for 2005 and 2014 (22). Biogenic emissions were estimated using the BEIGIS model (27); separate estimates were available for each day of 2005 (28). Biogenic emissions were left unchanged in the 2014 simulations.

Forecasts of future anthropogenic emissions in southern California reflect the effects of population growth and all emission control rules adopted prior to 2006. Baseline emission forecasts for 2014 do not include the effects of the new rule requiring in-use diesel engine retrofits. The effects of other recently adopted rules requiring emission reductions at ports (29) and reductions of greenhouse gas emissions (30) are also not included here. The 2014 emission inventory accounts for growth in the number of trucks on the road, as well as fleet turnover which acts by replacing older trucks with new ones that meet current new-engine emission standards for PM and NO_x . Thus significant (~50%) reductions in diesel truck emissions are forecast to occur between 2005 and 2014 even without the in-use engine retrofit/replacement rule, as shown in Figure 2.

Emissions for 2014 Retrofit Scenario. Additional reductions in PM and NO_x emissions due to accelerated retrofits

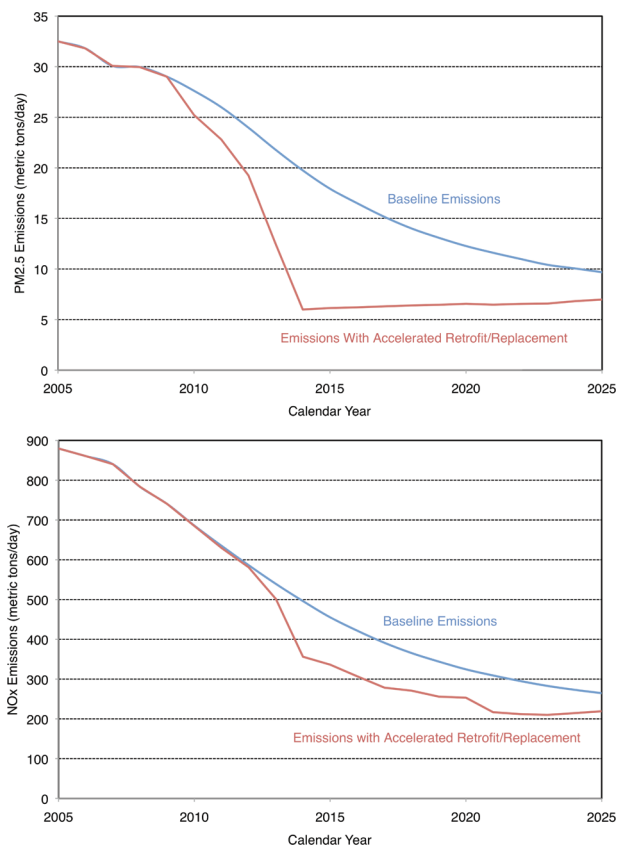


FIGURE 2. On-road heavy-duty diesel engine exhaust particulate matter and nitrogen oxide emission trends (California state totals), with and without new rules to accelerate retrofit/replacement of older engines. Source: California Air Resources Board (31).

and engine replacements, beyond what can be expected from fleet turnover, have been estimated by CARB staff (31) and are shown in Figure 2. Emissions of NO_x from on-road diesel vehicles are reduced by 28% relative to the baseline 2014 emission scenario. Similarly, exhaust PM emissions are reduced by 70% (speciation of PM emissions was left unchanged, however it is likely that use of diesel particle filters will influence the composition of PM as well as total mass emitted). Emission scaling factors were derived from the ratio of 2014 emissions for the two cases shown in Figure 2. Additional small adjustments to account for emissions from lighter vehicles (below 6350 kg or 14000 lb gross vehicle weight) that will not be subject to retrofits were also included in the calculations. Minor contributions to total CO and VOC emissions in the 2014 baseline inventory from on-road diesel engines were reduced by the same relative amounts as PM in the retrofit scenario, which is approximately the expected outcome if DPFs equipped with an oxidation catalyst are installed (15). CARB requires that retrofit control technologies for PM must be at least 85% efficient (9).

The NO_2/NO_x emission ratio for on-road heavy-duty diesel engines was increased from 5% in the baseline inventory, based on tunnel measurements of in-use trucks (24), to 35% in the 2014 retrofit scenario, based on dynamometer tests of diesel trucks with and without installed DPF (15). The retrofit scenario reflects universal use of DPF systems to control exhaust PM emissions. Some increase in NO_2/NO_x emission ratio may occur by 2014 even without the accelerated retrofit program, though this effect on fleet-average NO_2 emissions will be small because any new DPF-equipped trucks must also meet low- NO_x emission standards that apply to new engines. Retrofit of DPF systems on older engines with higher NO_x emission rates has much greater potential to increase fleet-average NO_2 emissions.

TABLE 1. Normalized (%) Differences (Mean \pm Standard Deviation; $N = 10$ Sites for PM Species and $N = 7$ Sites for Gaseous Pollutants) in Concentrations of Fine Particulate Mass, Elemental Carbon, and Nitrate, As Well As O_3 and NO_2 in the Gas Phase

	EC ^a	NO ₃ ^{-a}	O ₃ ^b	NO ₂ ^a	PM _{2.5} ^a
2005 predicted vs observed values					
summer	+14 \pm 33	-20 \pm 23	+15 \pm 12	+23 \pm 33	+20 \pm 16
fall	-2 \pm 25	+11 \pm 25	+13 \pm 30	-4 \pm 21	+19 \pm 32
2014 baseline vs 2005 baseline model					
summer	-22 \pm 3	-15 \pm 11	+10 \pm 7	-32 \pm 8	-9 \pm 3
fall	-26 \pm 2	-2 \pm 5	+39 \pm 14	-26 \pm 8	-6 \pm 2
2014 retrofit vs 2014 baseline model					
summer	-12 \pm 2	+2 \pm 2	+3 \pm 1	-4 \pm 3	-0.8 \pm 0.4
fall	-15 \pm 2	+5 \pm 1	+7 \pm 2	-2 \pm 3	-0.6 \pm 0.3

^a Comparisons of 24-h average concentrations were made using weekday values only for each location shown in Figure 1. A normalized (%) difference was calculated for each site and season then averaged over the network of surface observation sites, $[(C_1 - C_2)/C_2]$, where $C_1 = 2005$ predicted, 2014 baseline, and 2014 retrofit values, and $C_2 = 2005$ observed, 2005 predicted, and 2014 baseline values, respectively. ^b Ozone comparisons were done using 8-h peak concentrations (10 a.m. to 6 p.m.) rather than 24-h average values.

3. Results and Discussion

Tables S1 and S2 (in the Supporting Information) show major sources of EC and NO_x emissions in southern California. The total emissions, summed over all sources, of EC and NO_x , are 14 and 5% lower, respectively, for the on-road diesel engine retrofit scenario compared to the 2014 baseline. Reductions in on-road diesel truck emissions alone are much larger, 70 and 28% for PM and NO_x , respectively, as shown in Figure 2. While on-road diesel exhaust is the largest single source of EC and NO_x emissions, many other sources also contribute significantly to total emissions, and these other sources limit the air quality impact of reductions in on-road diesel emissions. Separate efforts and new rules (not included in this study) seek to control emissions from some of these sources, for example marine engines and off-road construction equipment. The contribution of on-road diesel engines to EC emissions summed over all sources is reduced from 23 to 9% between the 2014 baseline and retrofit scenarios, as shown in Tables S1 and S2. Note in Table S3 that anticipated changes in emissions between 2005 and 2014 reflect increased emphasis on controlling diesel engine emissions, and therefore include greater relative reductions in NO_x compared to CO and VOC. In contrast, during the 1990s, emissions of CO and VOC decreased more rapidly than NO_x (4, 32).

Model Evaluation for 2005. Air quality model predictions for 2005 were compared to observations made at 12 special study sites from the Multiple Air Toxics Exposure Study (MATES-III; (21)), where speciated 24-h average fine particle concentrations were measured every third day. The network of observation sites used for model evaluation is shown in Figure 1. As shown in Table 1, there were no large systematic biases in model predictions of the pollutants examined here for 2005 (fine particulate mass, EC, and nitrate; O_3 and NO_2 in the gas phase). Though more extensive gaseous pollutant measurements are available (i.e., daily data at a larger number of sites), for consistency, the evaluation of NO_2 and O_3 predictions was limited to the same sites for which speciated $\text{PM}_{2.5}$ measurements were available. Given uncertainties in absolute predicted concentrations both compared to observations in 2005 and for the future 2014 scenarios, we focus

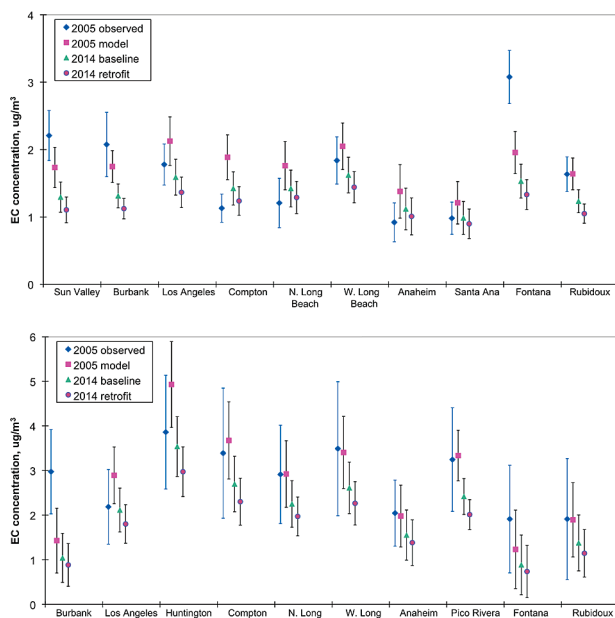


FIGURE 3. Observed and modeled elemental carbon (EC) concentrations for summer (top) and fall (bottom) seasons. All values shown are 24-h averages for weekdays only; standard deviations indicate extent of day-to-day variability at each site.

on changes in model predictions relative to a 2014 baseline without diesel retrofits.

More detailed comparisons of model predictions with observations on a site-by-site basis are shown in Figure 3 for EC, and in Figures S1–S4 for other pollutants. As expected, EC and NO₂ concentrations were higher during fall, whereas O₃ concentrations were higher during summer. EC concentrations were overpredicted during the summer at Compton and North Long Beach; both of these sites are located close to the ports of Los Angeles and Long Beach. Fall season predictions at these locations matched the observations more closely. EC concentrations at Fontana were under-predicted, especially during the summer. These under-predictions were pervasive, not isolated to a few days or extreme events. A search of satellite imagery of the surrounding area suggested local sources, such as railroad and trucking facilities, may be the cause of the elevated EC concentrations. NO_x emissions from these facilities also affected observed concentrations of O₃ and NO₂: in both summer and fall there was evidence of ozone titration (and therefore decreased O₃ and increased NO₂) at Fontana (see Figures S3–S4). Comparison of 2005 modeled values to observations at Burbank during the fall (but not summer when a different flow regime prevails) also showed underestimation of EC and ozone titration effects similar to those seen at Fontana. The Burbank site is located about 500 m away from an interstate highway (I-5) that is a major truck route in and out of the Los Angeles basin. The 5-km horizontal resolution of the emission inventory and the air quality model are not sufficient to resolve plume-scale dispersion near major freight-handling facilities and highways. We expect the effects of diesel controls at locations near large emission sources, such as Fontana and Burbank, to be larger than the average effects reported here. Effects on ambient air quality may be observed prior to 2014 at some sites, as controls on diesel vehicles serving ports and rail yards are required as of 2010.

Effects of Emission Controls in 2014. Both 2014 baseline and retrofit scenarios yield lower particulate EC and nitrate, and higher O₃ concentrations relative to 2005, in response to changes in PM and NO_x emissions. Relative to the 2014 baseline, reductions of 12 ± 2% and 14 ± 2% in average EC concentrations are predicted for the diesel retrofit scenario,

in summer and fall respectively. Changes in other pollutants were small relative to changes in EC. As shown in Table 1, the reductions in EC due to the on-road diesel retrofit program are not as large as EC reductions expected due to decreases in emissions from all sources between 2005 and the 2014 baseline scenario.

The largest absolute reductions in EC from the in-use diesel retrofit program occur around central Los Angeles and near the port where truck traffic is high. These locations not only have high average EC levels but also relatively high population density. The use of regional scale metrics, such as tons of emissions reduced per day, does not reflect the collocation of EC reductions and population density. The negative effects of diesel retrofits on ambient O₃ concentrations are also largest near central Los Angeles, an upwind VOC-limited region where NO_x reductions can lead to O₃ increases. While absolute increases to ozone are similar in both seasons (1–3 ppb across the greater Los Angeles area), larger relative increases in O₃ are forecast to occur during fall when baseline O₃ concentrations are lower. The predicted spatial distributions of 24-h average EC and NO₂ concentrations and daytime 8-h average O₃ concentrations, as well as changes to those concentrations due to diesel retrofits, can be seen in Figure 4 and Figures S5–S6.

Changes to NO₂ concentrations reported in Table 1 require careful interpretation, as there are competing underlying effects. By 2014 about half of all in-use diesel trucks are expected to have NO_x after-treatment, thus reducing total emissions. This reduction in NO_x emissions leads to lower secondary NO₂ formation, and at the regional scale this could offset increased primary NO₂ emissions from the retrofit of older trucks with DPF. During summer when NO₂ lifetime is shortest, NO₂ concentrations are predicted to decrease by 4 ± 3%. During the fall, when photochemical activity levels are lower, average NO₂ concentrations decrease by only 2 ± 3% and small increases are seen near central Los Angeles and the port (see Figure S5). Increased exposure to primary NO₂ emissions from DPF-equipped engines remains a concern at the plume scale near major roadways and freight-handling facilities. At the air basin scale, retrofitting of NO_x control equipment on in-use diesel engines will play an important role in mitigating the effect of increased primary NO₂ emissions associated with DPF retrofits on older engines.

While increases in O₃ concentrations also are predicted in densely populated areas, the O₃ increases are smaller in a relative sense for both seasons, when compared to expected decreases in EC. However, whether the predicted increases in ozone levels and decreases in EC levels lead on balance to public health benefits is unclear. Jerrett et al. (33) found the risk of death from respiratory causes increased with exposure to higher levels of ozone and the risk of death from cardiovascular causes increased with exposure to higher ambient PM_{2.5} levels. Environmental justice issues also arise when considering the question of diesel engine emission control: Marshall (34) found that in southern California, low-income and nonwhite populations were disproportionately exposed to diesel PM_{2.5} pollution but not ozone.

While this research evaluates the effects of the retrofit regulations on local air quality, the reduction of black carbon emissions has been suggested as a potential method to reduce anthropogenic warming effects (35). Unger et al. (36) found reductions of U.S. on-road black carbon emissions may decrease radiative forcing in the short term. Control of in-use diesel emissions offers the possibility of addressing both local air quality and regional and global climate change problems.

Discussion of Uncertainties. The most important emission inventory uncertainties relevant to the present study are the changes in on-road diesel emissions that will occur by 2014 with and without the retrofit program. Emissions

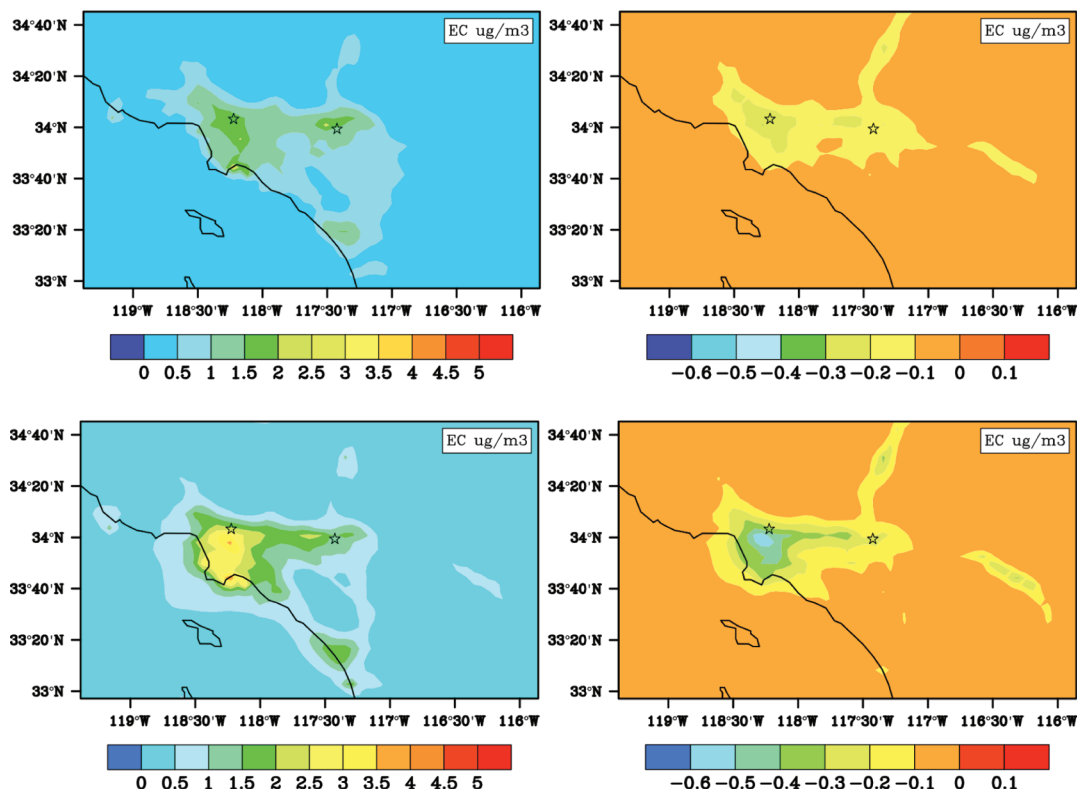


FIGURE 4. Left panel: Average modeled summer (top) and fall (bottom) concentrations of EC. All weekday hours were averaged. Right panel: Difference between 2014 retrofit scenario and the 2014 baseline scenario. The stars are (from west to east) downtown Los Angeles and Rubidoux.

from other source categories (e.g., on-road gasoline engines, off-road mobile sources, dust emissions in the fine mode, biomass burning) also affect the relative importance of on-road diesel engine emissions and their control. This study does not include the effects of other new air pollution control efforts that are being pursued in parallel with control of on-road diesel vehicle emissions. For example, control of marine engine and wood-burning emissions (37) will lead to additional PM reductions that are not considered here. Also this study modeled air quality over 3 months (2 summer and 1 fall), emphasizing diesel retrofit impacts on peak ozone (summer) and peak PM_{2.5} (fall) levels, but not addressing annual average PM_{2.5} which is also of concern.

This study evaluated the use of passive, highly oxidative DPF to control PM emissions from on-road diesel vehicles. This is a standard approach to emissions control for long-haul truck applications, but other control technology options exist and may be preferred in some situations. Many of these alternate approaches lead to less NO₂ emission increase than the DPF scenario considered here.

A key decision to be faced by vehicle owners will be whether to retrofit or replace their equipment. Accelerated replacement of older vehicles, rather than retrofit, could lead to different air quality outcomes, and provides tangible returns on investment to vehicle owners in the form of longer service life and greater reliability associated with new vehicles. New engines must meet current NO_x emission standards and would not be subject later to further retrofit/replacement requirements. NO_x emission reductions would therefore be accelerated, and possible increases in NO₂/NO_x emission ratios would be of less consequence since total NO_x would be lower. Another important issue is the longer-term durability of new and retrofit emission control systems on in-use diesel engine emissions beyond 2014 when most of the installed emission control systems will still be relatively new. Retrofit control systems may be chosen based on lowest

cost rather than suitability for the intended vehicle/application, and may therefore malfunction.

As shown in Figure 2, in the baseline scenario both NO_x and PM_{2.5} emissions from heavy-duty diesel vehicles are forecast to decrease with a characteristic time (half-life) of 7–8 years, reflecting the combined effects of growth in travel and fleet turnover in the on-road heavy-duty vehicle sector. This corresponds to a 9–10% per year reduction in emissions of both pollutants, which is a higher rate than has been achieved in past years. For example, Ban-Weiss et al. (25) found that heavy-duty diesel NO_x and PM emission factors measured on-road decreased between 1997 and 2006 by 3 and 5% per year, respectively, and these numbers do not account for growth in diesel fuel use over the same period which offset some of the reductions. Also diesel vehicle fleet turnover is expected to have slowed due to weakness in the U.S. economy since 2008. If baseline diesel emission reduction forecasts by 2014 are too optimistic, then the effects of DPF retrofits could be larger in 2014 than what is reported in Table 1.

The response of secondary fine particulate nitrate to changes in NO_x emissions merits further discussion and study. Offsetting effects on the rates of relevant reactions such as OH + NO₂ (forming nitric acid) and O₃ + NO₂ (forming nitrate radical) can lead to nonlinear air quality responses to changes in NO_x emissions. For example, hydroxyl radical (OH) concentrations may increase in response to lower NO₂, since NO₂ concentration is an important factor in determining OH. As a result, nitric acid formation rates at urban receptors may be buffered against changes in NO₂. On the other hand, weekend reductions in NO_x emissions lead to lower observed particulate nitrate levels in California (38), in contrast with model predictions reported here. Reductions in PM_{2.5} mass may be larger than reported in Table 1 for the 2014 retrofit scenario if ambient nitrate levels decrease in response to lower NO_x emissions.

Additional effects on air quality that were not modeled may result from changes to formation of HONO from reaction of NO₂ with semivolatile organic species present in diesel exhaust (39). Reductions in diesel primary organic aerosol (POA) emissions were included in this study, however potential effects on secondary organic aerosol of partitioning and oxidation of POA (40) were not quantified here.

Acknowledgments

We gratefully acknowledge the University of California Transportation Center for providing financial support for this study. We thank Bong Kim, Satoru Mitsutomi, and Jean Ospital of the South Coast Air Quality Management District, as well as Bruce Jackson and Klaus Scott of the California Air Resources Board.

Supporting Information Available

Table S1–S2 (Domain-wide NO_x and EC emissions by sector, summer and fall), Table S3 (emission estimates for CO, NO_x, NMOC, NH₃, PM_{2.5}, EC by year and scenario), Figure S1–S4 (observed and modeled nitrate, PM_{2.5}, O₃, and NO₂ concentrations), Figure S5–S6 (seasonal map of modeled ozone and NO₂ concentrations for the 2014 baseline and predicted changes to the baseline). This information is available free of charge via the Internet at <http://pubs.acs.org/>.

Literature Cited

- Lloyd, A. C.; Cackette, T. A. Diesel engines: environmental impact and control. *J. Air Waste Manage. Assoc.* **2001**, *51*, 809–847.
- Sawyer, R. F.; Harley, R. A.; Cadle, S. H.; Norbeck, J. M.; Slott, R.; Bravo, H. A. Mobile sources critical review. *Atmos. Environ.* **2000**, *34*, 2161–2181.
- Yanowitz, J.; McCormick, R. L.; Graboski, M. S. In-use emissions from heavy-duty diesel vehicles. *Environ. Sci. Technol.* **2000**, *34*, 729–740.
- Kirchstetter, T. W.; Harley, R. A.; Kreisberg, N. M.; Stolzenburg, M. R.; Hering, S. V. On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles. *Atmos. Environ.* **1999**, *33*, 2955–2968.
- Fuel Oil and Kerosene Sales 2005*; DOE/EIA-0535(05); Energy Information Administration, U.S. Department of Energy: Washington DC, 2006.
- Harley, R. A.; Marr, L. C.; Lehner, J. K.; Giddings, S. N. Changes in motor vehicle emissions on diurnal to decadal time scales and effects on atmospheric composition. *Environ. Sci. Technol.* **2005**, *39*, 5356–5362.
- Johnson, T. V. *Diesel Emission Control in Review*; SAE Technical Paper Series no. 2006-01-0030, 2006.
- Heeb, N. V.; Schmid, P.; Kohler, M.; Gujer, E.; Zennegg, M.; Wenger, D.; Wichser, A.; Ulrich, A.; Gfeller, U.; Honegger, P.; Zeyer, K.; Emmenegger, L.; Petermann, J.-L.; Czerwinski, J.; Mosimann, T.; Kasper, M.; Mayer, A. Impact of low- and high-oxidation diesel particulate filters on genotoxic exhaust constituents. *Environ. Sci. Technol.* **2010**, *44*, 1078–1084.
- Initial Statement of Reasons for Proposed Rulemaking, Adoption of the Proposed Regulation for In-Use On-Road Diesel Vehicles*; California Air Resources Board: Sacramento, CA, 2008; <http://www.arb.ca.gov/regact/2008/truckbus08/tbisor.pdf>.
- Jeong, S.; Lee, S.; Kim, W. Numerical study on the optimum injection of urea-water solution for SCR deNO_x system of a heavy-duty diesel engine to improve deNO_x performance and reduce NH₃ slip. *Environ. Eng. Sci.* **2008**, *25*, 1017–1036.
- Johnson, D. R.; Bedick, C. R.; Clark, N. N.; McKain, D. L. Design and testing of an independently controlled urea SCR retrofit system for the reduction of NO_x emissions from marine diesels. *Environ. Sci. Technol.* **2009**, *43*, 3959–3963.
- Carslaw, D. C. Evidence of an increasing NO₂/NO_x emissions ratio from road traffic emissions. *Atmos. Environ.* **2005**, *39*, 4793–4802.
- Carslaw, D. C.; Ropkins, K.; Bell, M. C. Change-point detection of gaseous and particulate traffic-related pollutants at a roadside location. *Environ. Sci. Technol.* **2006**, *40*, 6912–6918.
- Jenkin, M. E.; Utembe, S. R.; Derwent, R. G. Modelling the impact of elevated primary NO₂ and HONO emissions on regional scale oxidant formation in the UK. *Atmos. Environ.* **2008**, *42*, 323–336.
- Herner, J. D.; Hu, S. H.; Robertson, W. H.; Huai, T.; Collins, J. F.; Dwyer, H.; Ayala, A. Effect of advanced aftertreatment for PM and NO_x control on heavy-duty diesel truck emissions. *Environ. Sci. Technol.* **2009**, *43*, 5928–5933.
- Byun, D.; Schere, K. L. Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system. *Appl. Mech. Rev.* **2006**, *59*, 51–77.
- Carter, W. P. L. *Implementation of the SAPRC-99 Chemical Mechanism into the Models-3 Framework*; Report to the United States Environmental Protection Agency; College of Engineering, University of California: Riverside, CA, 2000; <http://www.engr.ucr.edu/~carter/SAPRC/>.
- Binkowski, F. S.; Roselle, S. J. Models-3 Community Multiscale Air Quality (CMAQ) model aerosol component. 1. Model description. *J. Geophys. Res.* **2003**, *108* (D6), 10.1029/2001JD001409.
- Air Quality Management Plan for the South Coast Air Basin, Appendix V, Modeling and Attainment Demonstration*; South Coast Air Quality Management District: Diamond Bar, CA, June 2007; <http://www.aqmd.gov/aqmp/07aqmp/07AQMP.html>.
- Millstein, D. E.; Harley, R. A. Impact of climate change on photochemical air pollution in southern California. *Atmos. Chem. Phys.* **2009**, *9*, 3745–3754.
- Multiple Air Toxics Exposure Study III in the South Coast Air Basin Final Report*; South Coast Air Quality Management District: Diamond Bar, CA, September 2008; <http://www.aqmd.gov/prdas/matesIII/MATESIIIFinalReportSept2008.html>.
- Air Quality Management Plan for the South Coast Air Basin, Appendix III, Base and Future Year Emissions Inventories*; South Coast Air Quality Management District: Diamond Bar, CA, June 2007; <http://www.aqmd.gov/aqmp/07aqmp/07AQMP.html>.
- Millstein, D. E.; Harley, R. A. Revised estimates of construction activity and emissions: effects on ozone and elemental carbon concentrations in southern California. *Atmos. Environ.* **2009**, *43*, 6328–6335.
- Ban-Weiss, G. A.; McLaughlin, J. P.; Harley, R. A.; Kean, A. J.; Grosjean, E.; Grosjean, D. Carbonyl and nitrogen dioxide emissions from gasoline- and diesel-powered motor vehicles. *Environ. Sci. Technol.* **2008**, *42*, 3944–3950.
- Ban-Weiss, G. A.; McLaughlin, J. P.; Harley, R. A.; Lunden, M. M.; Kirchstetter, T. W.; Kean, A. J.; Strawa, A. W.; Stevenson, E. D.; Kendall, G. R. Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles. *Atmos. Environ.* **2008**, *42*, 220–232.
- Chinkin, L. R.; Coe, D. L.; Funk, T. H.; Hafner, H. R.; Roberts, P. T.; Ryan, P. A.; Lawson, D. R. Weekday versus weekend activity patterns for ozone precursor emissions in California's South Coast Air Basin. *J. Air Waste Manage. Assoc.* **2003**, *53*, 829–843.
- Scott, K. I.; Benjamin, M. T. Development of a biogenic volatile organic compounds emission inventory for the SCOS97-NARSTO domain. *Atmos. Environ.* **2003**, *37*, S39–S49.
- Scott, K. Planning and Technical Support Division, California Air Resources Board, Sacramento, CA, personal communication, July 2009.
- Proposed Emission Reduction Plan for Ports and Goods Movement in California*; California Air Resource Board: Sacramento, CA, April 2006; http://www.arb.ca.gov/planning/gmperp/march21plan/march22_plan.pdf.
- Climate Change Scoping Plan*; California Air Resources Board: Sacramento, CA, 2008; <http://www.arb.ca.gov/cc/scopingplan/document/scopingplandocument.htm>.
- Sax, T. Mobile Source Emission Inventory Branch, California Air Resources Board, Sacramento, CA, personal communication, May 2010.
- Parrish, D. D.; Trainer, M.; Hereid, D.; Williams, E. J.; Olszyna, K. J.; Harley, R. A.; Meagher, J. F.; Fehsenfeld, F. C. Decadal change in carbon monoxide to nitrogen oxide ratio in US vehicular emissions. *J. Geophys. Res.* **2002**, *107* (D12), 10.1029/2001JD000720.
- Jerrett, M.; Burnett, R. T.; Pope, C. A.; Ito, K.; Thurston, G.; Krewski, D.; Shi, Y. L.; Calle, E.; Thun, M. Long-Term Ozone Exposure and Mortality. *N. Engl. J. Med.* **2009**, *360*, 1085–1095.
- Marshall, J. D. Environmental inequality: Air pollution exposures in California's South Coast Air Basin. *Atmos. Environ.* **2008**, *42*, 5499–5503.
- Hansen, J.; Sato, M.; Ruedy, R.; Lacis, A.; Oinas, V. Global warming in the twenty-first century: An alternative scenario. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 9875–9880.
- Unger, N.; Shindell, D. T.; Wang, J. S. Climate forcing by the on-road transportation and power generation sectors. *Atmos. Environ.* **2009**, *43*, 3077–3085.

- (37) *Air Quality Management Plan for the South Coast Air Basin*; South Coast Air Quality Management District: Diamond Bar, CA, June 2007; <http://www.aqmd.gov/aqmp/07aqmp/07AQMP.html>.
- (38) Millstein, D. E.; Harley, R. A.; Hering, S. V. Weekly cycles in fine particulate nitrate. *Atmos. Environ.* **2008**, *42*, 632–641.
- (39) Gutzwiller, L.; Arens, F.; Baltensperger, U.; Gaggeler, H. W.; Ammann, M. Significance of semivolatile diesel exhaust organics for secondary HONO formation. *Environ. Sci. Technol.* **2002**, *36*, 677–682.
- (40) Robinson, A. L.; Donahue, N. M.; Shrivastava, M. K.; Weitkamp, E. A.; Sage, A. M.; Grieshop, A. P.; Lane, T. E.; Pierce, J. R.; Pandis, S. N. Rethinking organic aerosols: Semivolatile emissions and photochemical aging. *Science* **2007**, *315*, 1259–1262.

ES1006669