NEAR-SOURCE EXPOSURE AND REGIONAL AIR QUALITY MODELING OF INCREASED NO2/NO SPLIT IN NOX EMISSIONS FROM CATALYST-BASED DIESEL PARTICLE FILTERS FOR HEAVY-DUTY DIESEL VEHICLES IN CALIFORNIA

Bart E. Croes[1], Scott Fruin[1], Alberto Ayala[1], Tony Servin[1], Donald Dabdub[2] and Eladio M. Knipping[3]
[1]California Air Resources Board (CARB), Sacramento, California, U.S.A.
[2]University of California, Irvine, California, U.S.A.
[3]EPRI, Palo Alto, California, U.S.A.

INTRODUCTION

Diesel engines have several advantages (e.g., durability, fuel efficiency, fuel availability) in comparison to vehicles using gasoline and alternative fuels, but they adversely affect all aspects of the natural environment – land, water, and air (*Lloyd and Cackette*, 2001). California has designated diesel particulate matter (DPM) as a known carcinogen (*CARB*, 1998) and a major contributor to California's PM-related health and visibility problems (Table 1). Therefore, California Air Resources Board set ambitious goals of a 75% reduction in diesel PM from 2000 to 2010, and 85% by 2020 (*CARB*, 2000).

Table 1. Impact of diesel PM exposure on California (Lloyd and Cackette, 2001)

♦ Premature death (2000 per year)
♦ Lung cancer (250 per year)
♦ Decreased lung function in children
♦ Chronic bronchitis
♦ Increased respiratory and cardiovascular hospitalisations
♦ Aggravated asthma
♦ Increased respiratory symptoms
♦ Lost workdays
♦ Reduction in visibility (10 to 75% of total)
♦ Global warming (2nd to carbon dioxide)

CARB's diesel risk reduction goals will be achieved through new heavy-duty diesel vehicle (HDDV) emission standards, retrofits of existing vehicles, alternative fuels (e.g., natural gas, biodiesel), anti-idling measures, and enhanced enforcement programs. Light-duty diesel vehicles are not yet an issue for California, as diesel-fueled passenger cars and light trucks currently available in Europe are unable to meet CARB's more stringent NO_X emission standard of 0.05 gm/mile (0.03 gm/km) even if they meet the 0.01 gm/mile (0.006 gm/km) PM standard. CARB has adopted a HDDV PM emission standard of 0.01 gm/bhp-hr (0.004 g/megajoule, 90% reduction from current levels) for the 2007 model year, ultra-low-sulfur diesel fuel (15 ppmw) starting June 2006, and retrofit requirements for several engine categories with other sources currently going through the regulatory process (www.arb.ca.gov/diesel/diesel.htm). In order to take advantage of the experience gained in Europe, CARB established the International Diesel Retrofit Advisory Committee (IDRAC) from 2000 to 2004, with representatives from France, Germany, Sweden, and Switzerland.

Catalyst-based diesel particle filters (CB-DPFs, filters preceded by an oxidation catalyst and enabled by ultra-low-sulfur diesel fuel) are integral to the diesel retrofit program. They rely on

the oxidation of NO to NO_2 to lower the ignition temperature for soot and facilitate filter regeneration. Not all NO_2 is consumed, however, and HDDVs equipped with CB-DPFs show an increase in the NO_2/NO split while the total emission of NO_X remains approximately constant (*Ayala, et al.*, 2002). In the atmosphere, NO_X emissions emitted primarily as NO are oxidized to NO_2 by sunlight-induced reactions of VOCs and then lead to formation of ozone, nitric acid, and ammonium nitrate ("secondary" PM, a major component of $PM_{2.5}$ in California). Thus, CARB was concerned that large-scale deployment of CB-DPFs could accelerate formation of these photochemical pollutants, offsetting some of the benefits of reduced DPM. IDRAC members raised the concern of possibly high NO_2 exposures in microenvironments near HDDVs. To investigate these impacts on California's already serious air quality problems, we conducted regional air quality modeling of enhanced secondary pollutant formation (O_3, HNO_3, $PM_{2.5}$) and two types of analysis (microscale dispersion modeling, measurement-based) of near-source NO_2 impacts

EMISSIONS DATA

We conducted chassis dynamometer emissions testing of transit buses at CARB's heavy-duty test facility in Los Angeles (*Ayala et al.*, 2002; www.arb.ca.gov/research/cng-diesel/cng-diesel.htm) and combined with a literature review of other studies conducted around the world to create the emission profile in Table 2 (*Dabdub et al.*, 2005). Without the filter, the NO_2 fraction out of the tailpipe is typically 5% of the total NO_X. Based on measurements following trucks and plume modeling studies, another 5% conversion due to thermal oxidation occurs in the vehicle exhaust plume. For the regional air quality modeling, we also assumed that 2% of the NO_X emissions are in the form of HONO (a key hydroxyl radical source), regardless of the vehicle configuration. Testing over various driving cycles show that NO_X emissions from the CB-DPF are roughly half NO_2 (*Ayala et al.*, 2002), with a theoretical upper limit of 70% (*Warren et al.*, 1998). We were unable to consider filter durability/deterioration.

Table 2. Emission profile for modeling of HDDVs equipped with CB-DPFs.

Pollutant	Reduction
Carbon monoxide (CO)	90%
Total nitrogen oxides (NO_X)*	none
Diesel particulate matter (DPM)	85%
Total volatile organic compounds (VOCs)	90%
Total carbonyls	90%
Formaldehyde	93%
Acetaldehyde	82%
Benzene	77%
Total polycyclic aromatic hydrocarbons (PAHs)	80%
Nitro-PAHs	95%

**Assumed baseline of 10% NO_2 (includes in-plume conversion), 2% HONO, and 88% NO. For the CB-DPFs, NO_2 ranged from 15% to 50%, with the remainder HONO (constant at 2%) and NO.*

REGIONAL AIR QUALITY MODELING

We determined regional photochemical pollutant impacts for 2010 using state-of-the-science air quality models (CIT, CMAQ) with atmospheric chemistry (SAPRC-99, extended LCC) and physics (SCAPE2) applied to the Los Angeles and San Joaquin Valley Air Basins (*Dabdub, et al.*, 2005). We modeled three episodes in Los Angeles (summer, fall, winter) and two in the San Joaquin Valley (summer, winter), assuming penetration of CB-DPFs to 90% of all diesel engines in California. While we expect CB-DPFs to have higher penetration for later

model years, this is a conservative representation of the diesel fleet of the future as HDDVs older than 1988 are expected to be retrofitted with oxidation catalyst technology only.

Table 3 displays results only for Los Angeles, but San Joaquin Valley results are similar. We use the change in peak or maximum values and the change in cumulative 24-hour-average population exposure, where exposure is defined as,

$\sum_{24\ hours} (\sum_{all\ cells} (Concentration - Threshold)\ (Cell\ population)\ /$
$\sum(Population\ in\ cells\ above\ threshold))$ (1)

Table 3. Air quality impacts of 90% penetration of CB-DPFs in the Los Angeles Air Basin.

	Baseline	With CB-DPFs				
Diesel NO_2/NO_X	10%	15%	20%	**25%**	30%	50%
	ppb	% change from baseline				
SUMMER						
Peak 1-hour O_3	136.7	-1	0	**0**	0	1
24-hour O_3 exposure > 90 ppb	166	-3	-2	**0**	2	5
Peak 24-hour HNO_3	15	0	1	**1**	1	2
24-hour HNO_3 exposure	5.4	0	0	**2**	2	4
Peak 24-hour $PM_{2.5}$	112	-3	NA	**NA**	-2	-1
24-hour $PM_{2.5}$ exposure > 65 $\mu g/m^3$	20	-9	NA	**NA**	-8	-6
FALL						
Peak 24-hour $PM_{2.5}$	99.8	-6	NA	**NA**	-5	-3
24-hour $PM_{2.5}$ exposure > 65 $\mu g/m^3$	13.6	-13	NA	**NA**	-13	-13
WINTER						
Peak 1-hour NO_2	156	1	6	**12**	18	41
Peak 24-hour HNO_3	6	0	0	**2**	2	5
Peak 24-hour HNO_3 exposure	2.2	-5	-5	**0**	0	5

At an NO_2 to NO_X ratio of 25% (in bold), the 90% VOC reduction approximately balances the NO_2 increase in terms of O_3 and $PM_{2.5}$ formation. These results are independent of CB-DPF penetration. At higher NO_2 to NO_X ratios, additional O_3 is formed and the DPM reduction benefits of the filters are eroded. Based on these results, and subtracting the 5% conversion in the exhaust plume, CARB adopted an NO_2 to NO_X ratio of 20% as a tailpipe emission limit in 2002. In 2003, a three-year waiver was given to the CB-DPF manufacturers in recognition of their difficulties in meeting the goal and the 85% DPM reduction offered by the particle filters. NO_2 levels increase even with the tailpipe limit, so we did a more detailed analysis to determine if the filters will lead to violations of the California 1-hour ambient air quality standard for NO_2, which is currently attained Statewide.

EVALUATION OF NEAR-SOURCE NO_2 IMPACTS

We conducted two types of analyses for near-sources impacts – microscale dispersion models and a measurement-based approach. Both analyses used health-protective assumptions.

1.1. Microscale Dispersion Modeling

Two scenarios were modeled: 1) alongside a freeway with high truck volume using the CAL3QHCR line dispersion model; and 2) 20 idling school buses (four groups of five) through a loading queue over a 20-minute period using the ISCST3 Gaussian plume model. We selected a 1.5-km segment of the 710 Freeway in Long Beach for the first analysis

because it is the busiest truck corridor in California (year 2000 average of 189,936 vehicles per day for the weekday and 117,262 vehicles per day for the weekend). For both analyses, we assumed a NO_2 to NO_X ratio of 40%, 90% penetration of the filters to the diesel fleet, and that oxidation of NO to NO_2 is limited by ambient O_3 levels as observed at nearby stations. We used hourly observations of truck volumes and air quality to compute peak 1-hour NO_2 concentrations of 180 ppb (30 ppb above baseline) for Scenario 1 and 170 ppb (50 ppb above baseline) for Scenario 2. Even under these extreme conditions, NO_2 concentrations were well below the California 1-hour standard of 250 ppb.

1.2. Measurement-based Approach

We investigated three scenarios using measurements collected from instrumented vehicles:
Driving on the 710 Freeway, based on CARB's on-road NO and NO_2 measurements (*Westerdahl et al.*, 2005).
Riding in a trap-equipped diesel school bus, with re-entrainment of a fraction of the bus's own exhaust into the cabin ("self pollution") based on measurements from the CARB Children's School Bus Exposure Study (*Behrentz et al.*, 2004).
Closely following a trap-equipped diesel school bus in stop-and-go traffic based on the dilution rates calculated for low-speed and low-exhaust pipes (*Chan et al.*, 2001), high-speed dilution rates (*Kittelson et al.*, 1988; *Brown et al.*, 2000), and idling measurements (*Allansson et al.*, 1999). This scenario had a high uncertainty.

Because it is the unique concurrence of events that creates the worst-case scenario, we assumed these three scenarios occur with typical (~50th percentile) concentrations (labeled "high" due to the high exposure scenario conditions). However, for evaluation of these exposure scenarios individually, we also calculated "extreme" (~90th percentile) concentrations. The post-filter NO_2 fractions are assumed in the high case to be 50% of the total NO_X and 70% for the extreme case. For comparison to the non-compliant "high" and "extreme" cases, we included the current 20% NO_2 fraction limit using the same scenario conditions as the "high" scenario, except for a higher market penetration.

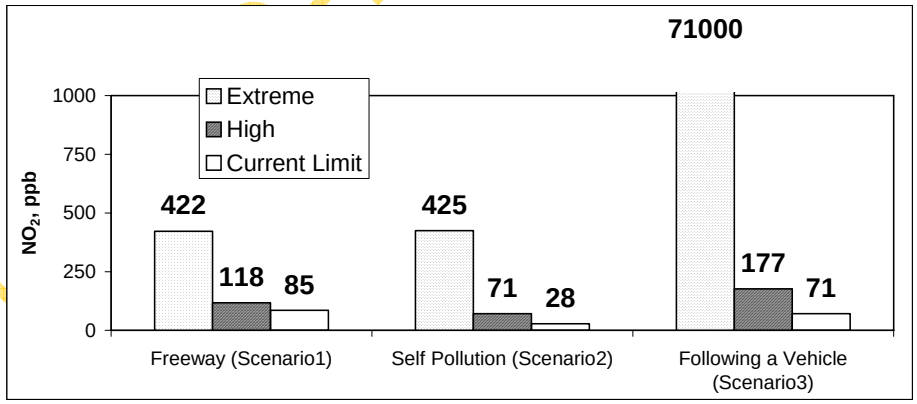

Figure 1. NO_2 concentrations in near-source scenarios.

We assumed 15 minutes to be a more reasonable duration of exposure under the simultaneous concurrence of the three scenarios, and converted the 1-hour California standard of 250 ppb to a 15-minute standard of 370 ppb based on a modification of Haber's Law (*ten Berge et al.*, 1986). Even under these very unlikely conditions (filter-equipped school bus with significant self-pollution closely following another filter-equipped school bus on the 710 Freeway), total NO_2 levels (184 ppb) for HDDVs meeting the current level are below 370 ppb (see Figure 1), even when we add in the worst-case result of 180 ppb from the microscale dispersion

modeling analysis. In addition, the higher the potential NO_2 exposures, the greater the corresponding reductions in diesel PM due to the use of filters.

CONCLUSIONS AND IMPLICATIONS

Catalyst-based diesel PM filters provide 80-95% reductions in PM, VOCs, and air toxics, but an increased NO_2/NO split. This increased NO_2 accelerates ozone, nitric acid, and secondary $PM_{2.5}$ formation. Photochemical modeling shows 15% NO_2 (over the 5% engine-out baseline) is offset by the 90% VOC reduction offered by the filters. Microscale dispersion modeling and a measurement-based analysis show that no near-source exceedances of California's NO_2 standard are expected with the 20% tailpipe limit.

While CB-DPFs appear to be the dominant technology for meeting more stringent future PM emission standards for HDDVs, there are other PM emission reduction solutions currently available that do not rely on NO_2. Thus, this study is of validity only for CB-DPF retrofits. Furthermore, new diesel engines in the future will most likely rely on not only PM, but also on NO_X aftertreament for meeting more stringent emission standards (50% reduction for 2007 model year and 90% in 2010). Thus, the potential problems associated with NO_2 increases are particular, at present time, to the CB-DPF-equipped diesel fleet for which NO_X aftertreatment are not envisioned under the current retrofit plan. CARB is currently exploring regulatory options for the NO_2 limit to account for both NO_X aftertreatment and pre-filter baseline NO_2 levels different than 5%, and to provide increased manufacturer certification flexibility in order to preserve the significant DPM benefits from CB-DPF deployment.

DISCLAIMER

The statements and opinions expressed in this paper are solely the authors' and do not represent the official position of CARB. The mention of trade names, products, and organizations does not constitute endorsement or recommendation for use.

REFERENCES

Allansson, R., P. Tancell, A.P. Walker and J.P. Warren, 1999: NO_2 emissions from a CRT filter-equipped truck in simulated public environments.

Ayala, A., N.Y. Kado, R.A. Okamoto, B.A. Holmén, P.A. Kuzmicky, R. Kobayashi and K.E. Stiglitz, 2002: Diesel and CNG heavy-duty transit bus emissions over multiple driving schedules: Regulated pollutants and project overview. *SAE Transactions Journal of Fuels and Lubricants*, 735-747.

Behrentz, E., D.R. Fitz, D. Pankratz, L.D. Sabin, S.D. Colome, S. Fruin and A.M. Winer, 2004: Measuring self-pollution in school buses using a tracer gas technique. *Atmos. Env.*, 38, 3735-3746.

Brown J.E., M.J. Clayton, D.B. Harris and F.G. King, Jr., 2000: Comparison of the particle size distribution of heavy-duty diesel exhaust using a dilution tailpipe sampler and an in-plume sampler during on-road operation. J. Air & Waste Manage. Assoc., 50, 1407-1416.

Chan, T.L., G. Dong, C.S. Cheung, C.W. Leung, C.P. Wong and W.T. Hung, 2001: Monte Carlo simulation of nitrogen oxides dispersion from a vehicular exhaust plume and its sensitivity studies. Atmos. Env., 35, 6117-6127.

California Air Resources Board, 1998: Proposed identification of diesel exhaust as a Toxic Air Contaminant. Sacramento, California.

California Air Resources Board, 2000: Diesel Risk Reduction Plan. Sacramento, California.

Dabdub, D., E.M. Knipping, A. Ayala, B.E. Croes, A, Servin, J. DaMassa and D. Drechsler, 2005: Impact of NO_2/NO split in NO_X emissions from diesel sources equipped with catalyst-based particle traps. *J. Air & Waste Manage. Assoc.*, in review.

Kittelson, D.B., P.A. Kadue, H.C. Scherrer and R.E. Lourein, 1988: Characterization of diesel particles in the atmosphere. Coordinating Research Council AP-2, Project Group Final Report, Atlanta, Georgia.

Lloyd A.C. and T.A. Cackette, 2001: Diesel engines: Environmental impact and control; J. Air & Waste Manage. Assoc, 51, 809-847.

ten Berge W.F., A. Zwart and L.M. Appelman, 1986: Concentration-time mortality response relationship of irritant and systemically acting vapours and gases. Journal of Hazardous Materials, 13, 301-309.

Warren, J.P., R. Allansson, P.N. Hawer and A.J.J. Wilkins, 1998: Effects on after-treatment on particulate matter when using the Continuously Regenerating Trap (CRT). *IMechE* S491/006/98, UK.

Westerdahl, D., S. Fruin, T. Sax, P.M. Fine and C Sioutas, 2005: Mobile platform measurements of ultrafine particles and associated pollutant concentrations on freeways and residential streets in Los Angeles. *Atmos. Env.*, 39, 3597-3610.