The Effects of Gasoline Sulfur Level on Emissions from Tier 2 Vehicles in the In-Use Fleet

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Background & Objective

- **Vehicle emissions have long been known to exhibit "NOx creep" due to sulfur in the fuel**
- **Recent gasoline sulfur programs**
  - Looked at effect shortly after a "cleanout cycle"
  - Didn't attempt to assess impact on emissions from in-use fleet
- **This study assesses sensitivity of in-use Tier 2 vehicles to fuel sulfur level**
  - What is the level of reversible catalyst activity loss in the in-use fleet?
  - Do emission benefits of lower sulfur (<10 ppm) continue with mileage accumulation?
  - What level of overall emission reduction is expected from the in-use fleet?

Design Overview - Vehicles

- **Recruited 81 vehicles from owners in SE Michigan**
  - MY 2007-2009 passenger cars and light trucks with 20,000 to 40,000 odometer miles
  - Targeted five vehicles each from make/model/engine "classes" selected for EPAct program to be representative of national sales in 2007-8 timeframe

Vehicle Make	Vehicle Model
FORD	500, Explorer, F150, Focus
HONDA	Civic, Odyssey
NISSAN	Altima
DODGE	Caliber, Caravan
TOYOTA	Corolla, Sienna, Tacoma
CHEVROLET	Cobalt, Impala, Silverado
JEEP	Liberty
SATURN	Outlook

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Design Overview - Fuels

- **Two non-ethanol test fuels**
  - Purchased bulk delivery of typical “Tier 2 cert fuel” with 5 ppm sulfur
  - Segregated and adjusted a portion up to 28 ppm

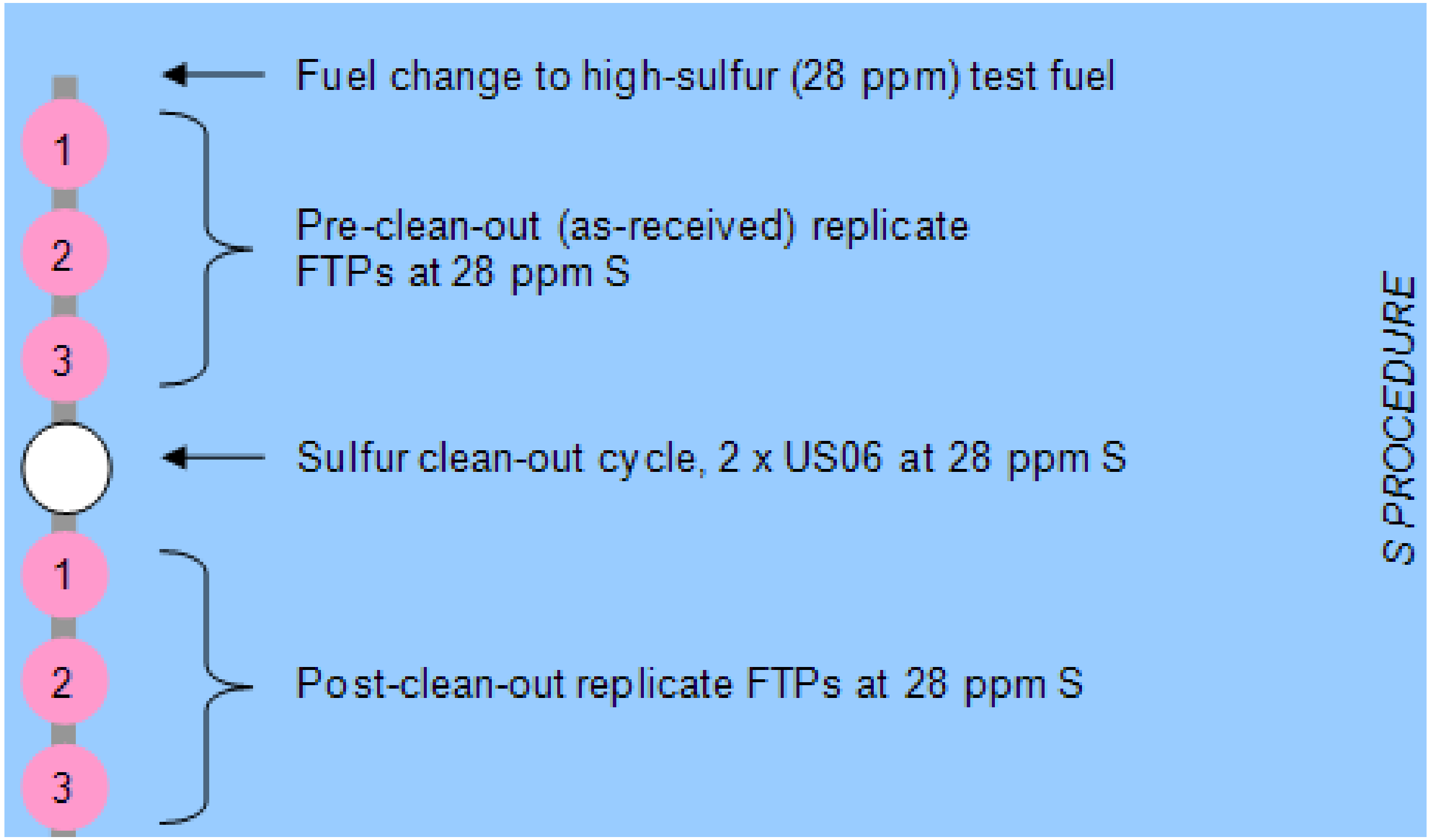
Fuel Property	ASTM Method	Low S Test Fuel
Sulfur	D2622	5 ppm
Total Aromatics	D5769	31.2 Vol%
Olefins	D1319	0.5 Vol %
T50	D86	221°F
T90	D86	317°F
RVP	D5191	9.0 psi

Design Overview - Procedures

- **3-bag FTP cycle at 75°F**
- **Measured gaseous pollutants and PM mass by bag**
- **High-speed/load "clean-out" consisting of two back-to-back US06 cycles**
- **Focus on three research questions:**
  - What is "clean-out effect" with 28 ppm test fuel?
    - Is sulfur loading on the catalyst reversible? How do emissions from recruited vehicles differ before/after a clean-out cycle?
  - What is "clean-out effect" with 5 ppm test fuel?
    - Are emissions immediately following the clean-out cycle different at different sulfur levels?
  - What is the effect of sulfur level with mileage accumulation?

Procedures: Clean-out Effect at 28 ppm

Assess effect of reversible sulfur loading in the catalyst immediately after vehicle arrives (all 81 vehicles)

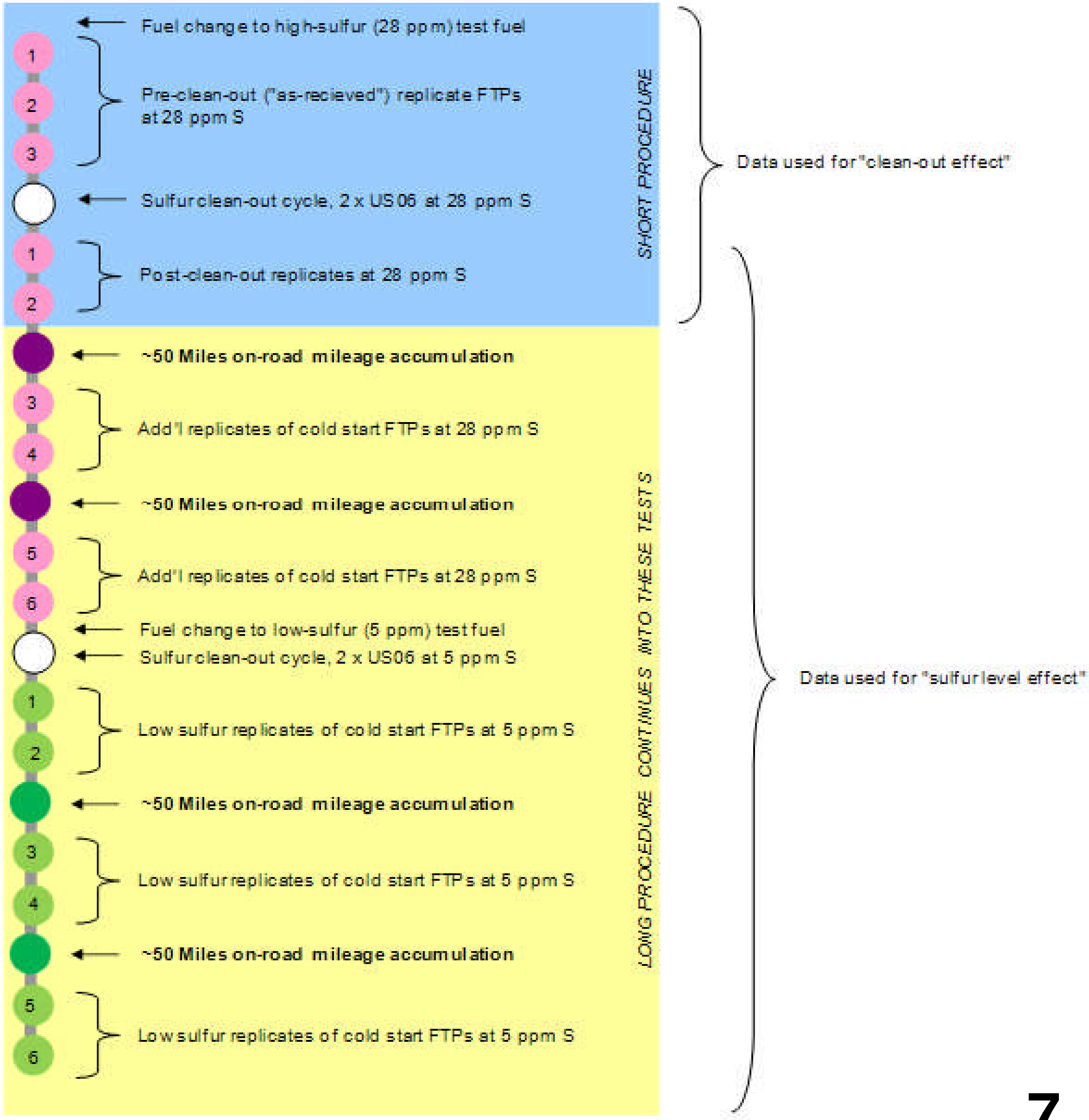


Procedures: Sulfur Level Effect

Assess change in emissions as a function of sulfur level over mileage accumulation

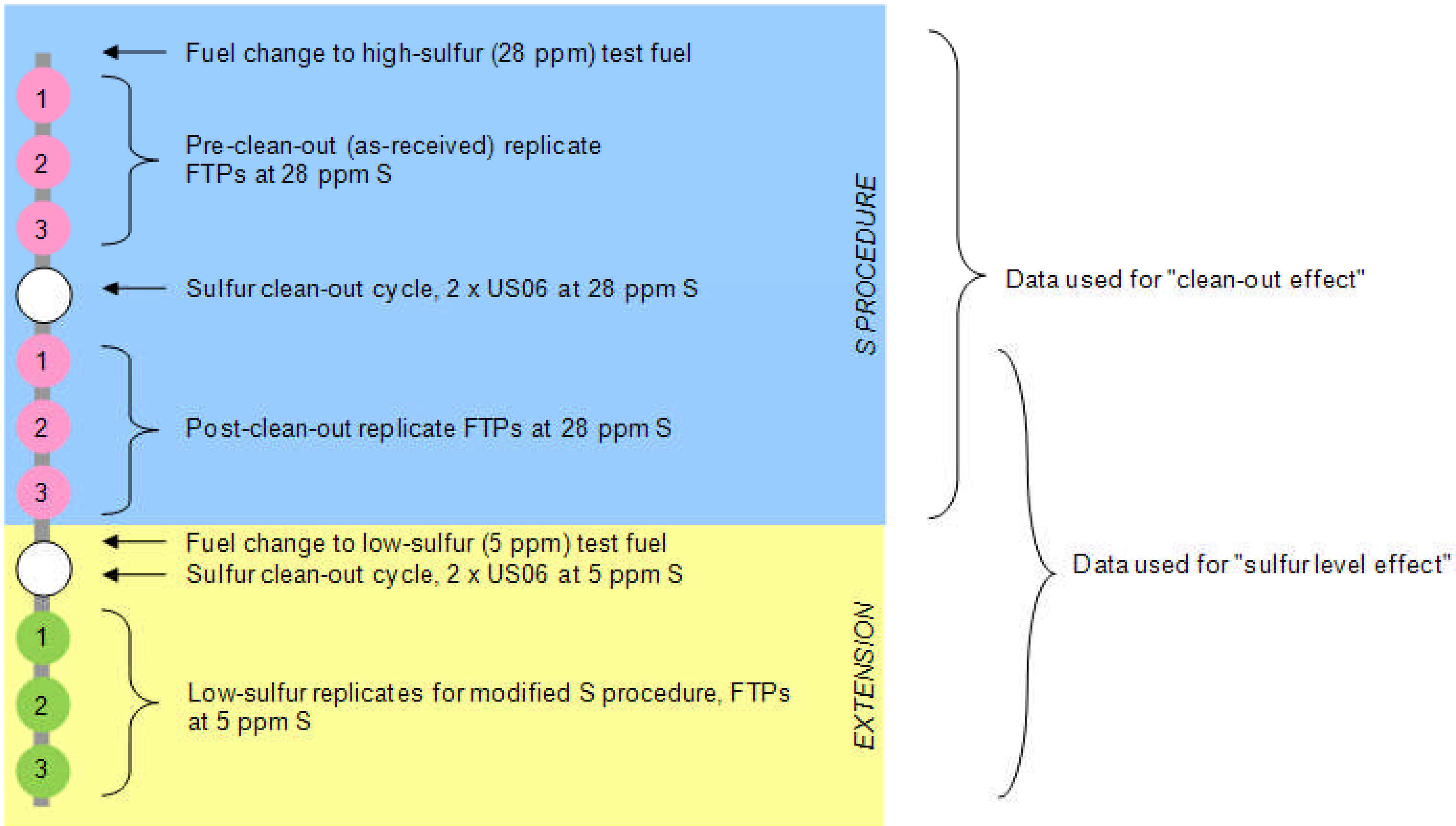
Subset of one sample of each make/model performed additional series of repeated emission tests covering up to 180 miles on each sulfur level

Alternated FTP tests with on-road mileage accumulation on routes with speeds and loads similar to FTP



Procedures: Clean-out Effect at 5 ppm

After mid-term review of available data, the short procedure was extended to include additional tests on low-sulfur fuel to provide information about an immediate sulfur level effect (23 vehicles including data from this and previous slide)



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Data Analysis and Results

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Analyzed Pollutants

- **Measured**
  - Total hydrocarbons (THC) reported by Flame Ionization Detector (FID)
  - Oxides of nitrogen (NO_x)
  - Carbon monoxide (CO)
  - Methane (CH4)
  - Particulate matter (PM) mass
- **Calculated**
  - Non-methane hydrocarbons (NMHC): THC minus CH4
  - Oxides of nitrogen plus Non-methane organic gases (NO_x+ NMOG)

Analyzed Bags

- **FTP cycle**
  - Bag 1: initial "cold start"
  - Bag 2: "hot running"
  - Bag 3: "hot start"
  - Bag 1 – Bag 3: isolated "cold start"
  - FTP composite
- **Consistent statistical methodologies applied in the analysis of all pollutants and bags**
- **Sulfur level analysis of oxides of nitrogen (NO_x) from Bag 2 presented in greater detail**
  - *for illustrative purposes*
  - *Sulfur level analysis most relevant in MOVES context*

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Statistical Methodology

- **Transformation of emission measurements by natural logarithm**
  - Data showed log-normal distribution (positive skewness)
  - Log-transformation necessary
    - to stabilize the variance
    - to obtain linearity between the dependent variable and the fixed and random effects
    - to normalize the distribution of the residual

- **Once the final model was fit, the difference of least squares means between the fixed effects of interest were <u>reverse-transformed</u> to estimate the percent reduction in emissions**

Modeling Approach

- **Analyzed using linear mixed model below:**

$$Y_i = X_i\beta + Z_i u_i + \varepsilon_i$$

where β and u_i are fixed and random effects parameters, respectively, and ε_i is the random residuals. β is the same for all vehicles, and u_i is allowed to vary over vehicles

- Considered superior to the ordinary least squares used by the univariate and multivariate procedure
- More robust and flexible in modeling the covariance structure for “repeated measures data”
- Capable of including vehicles with missing data and handling irregularly spaced measurements
- Better accounts for within-vehicle mileage dependent interactions

Modeling Approach (cont'd)

- **Used top-down model fitting strategy**
  - Fit preliminary models to detect outliers
    - Less than 1 percent of the measurements removed as outliers
  - Start with a saturated model with all candidate fixed effects
  - Select a model with most optimal covariance structure
    - Compound symmetry
      - Modeled for the effect of cleanout and sulfur effect on cleanout
      - Assumes measurements from same vehicle have homogeneous variance and the correlation among measurement is constant
    - First-order Autoregressive
      - Modeled for the in-use sulfur effect
      - Assumes that the variances are homogeneous and the correlations decline exponentially with time
  - Reduce the fixed effects portion of the model to fit the final model

Imputation of measurements with low concentration

- **Occurs when a dilute emission measurement lower than the measured background; below the limit of quantification (LOQ)**
- **Unlikely that tailpipe emissions are truly zero during a test**
- **The zero measurement can be:**
  - Left as zeroes
    - Not allowed because the measurements needed to be log-transformed
  - Deleted
    - Result in reduced sample size, less statistical power, and larger standard errors
  - Replaced with an imputed value
    - Using each vehicle's own data to perform imputation is a commonly used method in longitudinal study
    - Since the observations below LOQ appear to be randomly distributed across sulfur levels and vehicles, they were imputed

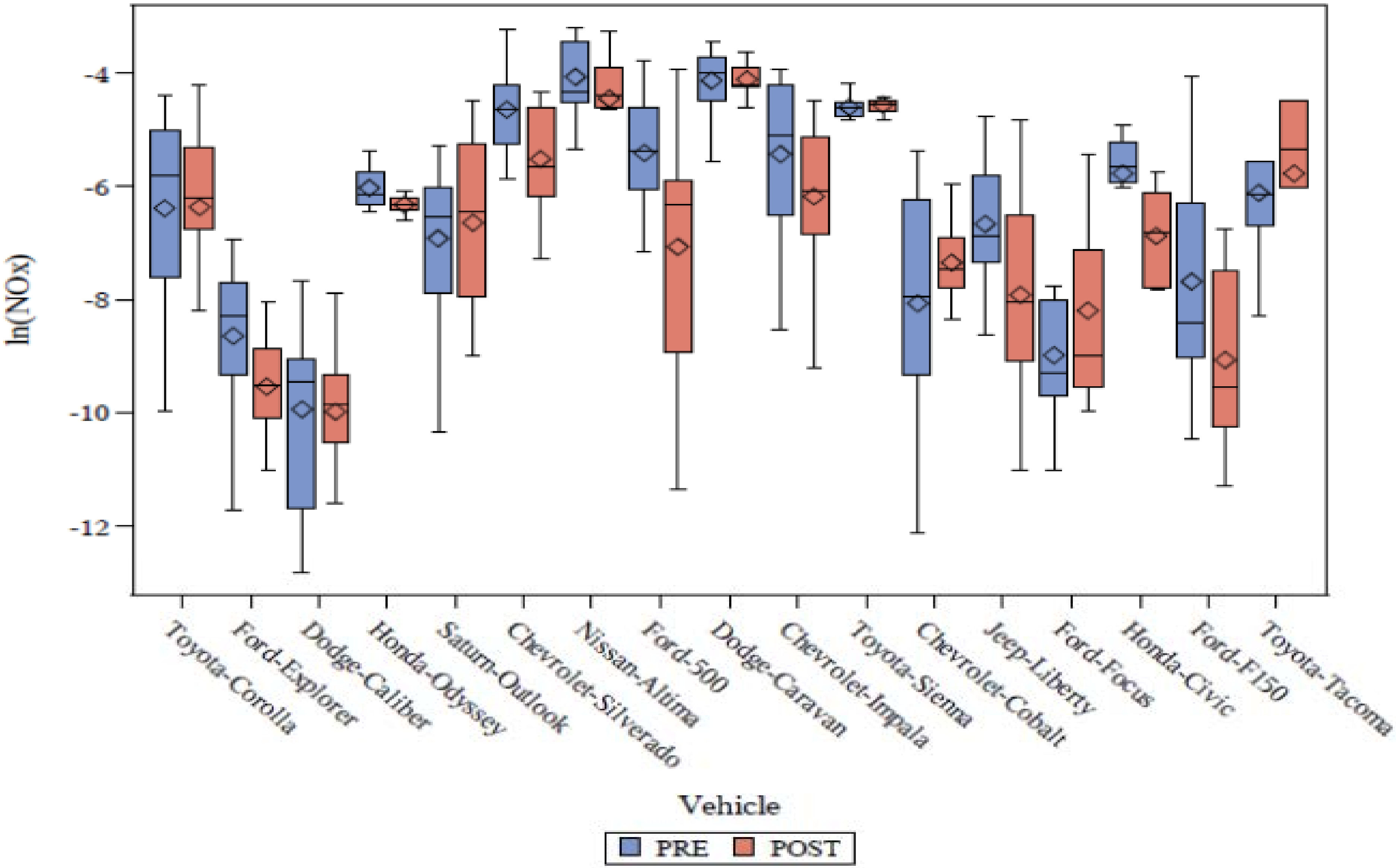
Imputation of measurements with low concentration (cont'd)

- **How?**
  - Performed single-imputation using half the minimum of a valid measurement from a given mileage bin for the vehicle with zero values
- **Rationale**
  - Recognize that emission measurements below the LOQ must be smaller than any quantified value
- **Pros**
  - Minimizes the likelihood of artificially reducing the natural variance of the data
- **Cons**
  - Exists a potential to inflate the reliability estimates as the number of imputed values increase
  - However, since the number of measurements with imputed values are ~10 percent at most, one can expect good estimates of reliability of measures
- **Sensitivity analyses performed with and without the imputed values to assess the potential for introducing bias**
- **Number of measurements with zero values provided in the Appendix**

Effect of Clean-Out

- **Objective:**
  - To assess the in-use reversible sulfur loading in the catalyst at the fuel sulfur level of 28 ppm
  - By comparing "as-received" emission measurements (pre-cleanout) to the measurements after the back-to-back US06 cycles (post-cleanout) at 28 ppm
- **Data from original and modified 'Short' procedures**
- **17 vehicle families; 81 unique vehicles**
- **Number of measurements: n = 479**
  - pre-cleanout: n = 242
  - post-cleanout: n = 237
- **Mixed model**
  - Dependent variable (Y_i): natural logarithm of emissions
  - Fixed effects (X_i): cleanout status, vehicle type, and the interaction terms
  - Random effects (Z_i): vehicle family

Box-plot of vehicle families by pre- and post-cleanout at 28 ppm



The diamond and the line represent the mean and the median, respectively; box represents the interquartile range between 25th and 75th percentile; the error bars show the full data range

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Percent Reduction in Emissions: pre- vs. post-cleanout at 28 ppm

	NO_x (p value)	THC (p value)	CO (p value)	NMHC (p value)	CH4 (p value)	PM (p value)
Bag 1	–	–	4.7% (0.0737)	–	–	15.4% (< 0.0001)
Bag 2	31.9% (0.0009)	16.5% (0.0024)	–	17.8% (0.0181)	15.3% (0.0015)	–
Bag 3	38.3% (<0.0001)	21.4% (<0.0001)	19.5% (0.0011)	27.8% (<0.0001)	12.0% (<0.0001)	24.5% (<0.0001)
FTP Composite	11.4% (<0.0001)	4.1% (0.0187)	7.6% (0.0008)	3.0% (0.0751)	6.9% (0.0003)	13.7% (<0.0001)
Bag 1 – Bag 3	–	–	4.2% (0.0714)	–	–	–

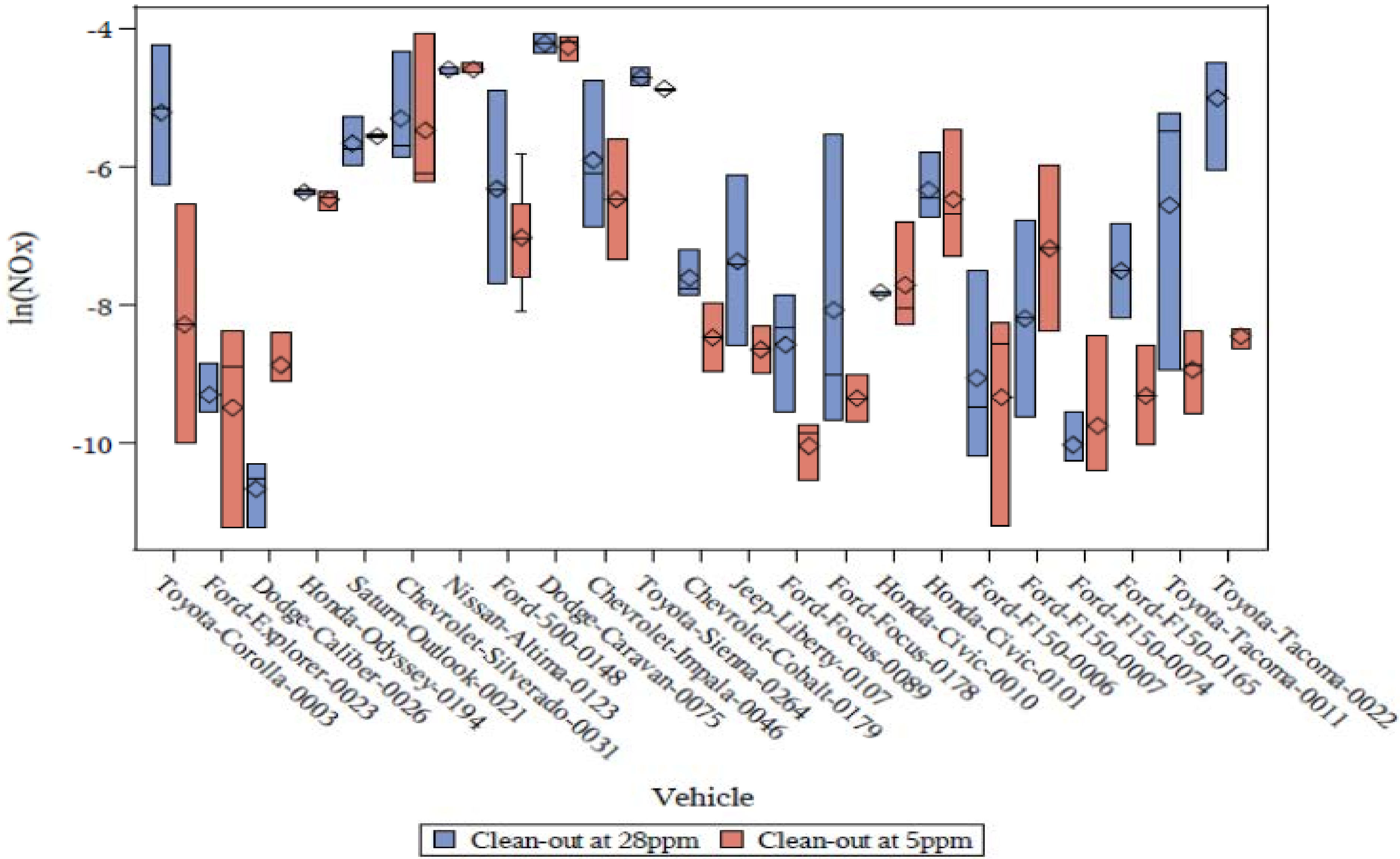
The clean-out effect is not significant at α = 0.10 when no reduction estimate is provided.

- Catalyst efficiency loss due to sulfur loading is occurring in the Tier 2 in-use fleet
- Not modeled explicitly in MOVES2013

Sulfur Effect on "Clean-Out"

- **Objective:**
  - To study the differences in the effectiveness of the clean-out procedure between 28 ppm and 5 ppm fuel sulfur levels
  - By comparing the first three repeat FTP tests from each sulfur level following the back-to-back US06 cycles
- **Data from a subset of original and modified 'Long' procedures and modified 'Short' procedure**
  - Mileage accumulation less than 50 miles
- **17 vehicle families; 23 unique vehicles**
- **Number of measurements: n = 132**
  - Cleanout at 28 ppm: n = 68
  - Cleanout at 5 ppm: n = 64
- **Mixed model**
  - Dependent variable (Y_i): natural logarithm of emissions
  - Fixed effects (X_i): sulfur level, vehicle type, and the interaction terms
  - Random effects (Z_i): each vehicle

Box-plot of vehicle emissions by clean-out sulfur level at 28 ppm and 5 ppm



The diamond and the line represent the mean and the median, respectively; box represents the interquartile range between 25th and 75th percentile; the error bars show the full data range

Percent reduction in emissions: Clean-out at 28 ppm vs. 5 ppm

	NO_x (p value)	THC (p value)	CO (p value)	NMHC (p-value)	CH4 (p-value)	PM
Bag 1	5.9% (0.0896)	5.4% (0.0118)	7.3% (0.0023)	4.6% (0.0465)	11.1% (<0.0001)	–
Bag 2	47.3% (0.0010)	40.2% (<0.0001)	–	34.4% (0.0041)	53.6% (<0.0001)	–
Bag 3	51.2% (<0.0001)	35.0% (<0.0001)	10.1% (0.0988)	45.0% (<0.0001)	25.4% (<0.0001)	–
FTP Composite	17.7% (0.0001)	11.2% (<0.0001)	8.3% (0.0003)	8.8% (0.0003)	21.4% (<0.0001)	–
Bag 1 – Bag 3	–	–	5.8% (0.0412)	–	–	–

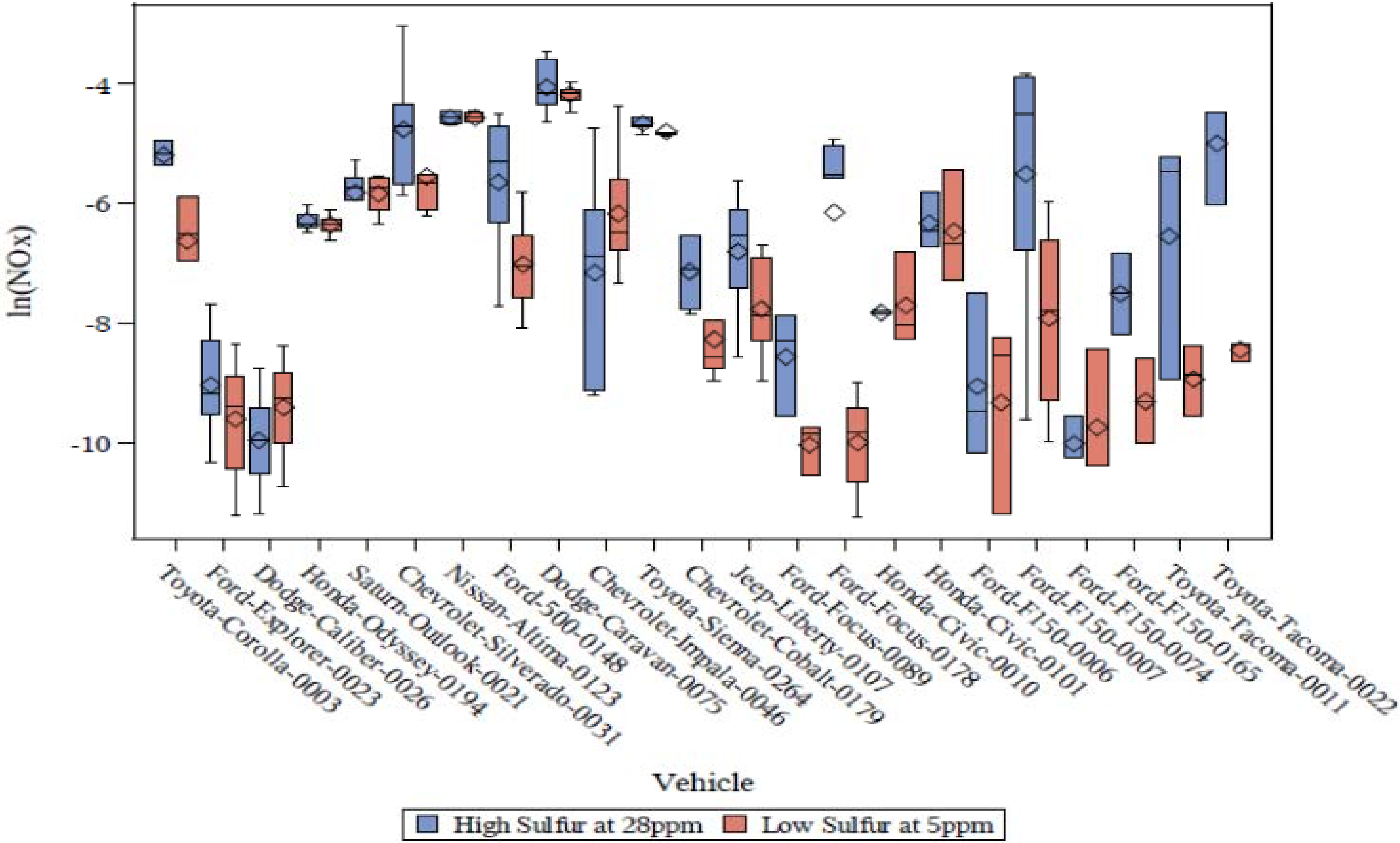
The effect is not significant at $\alpha = 0.10$ when no reduction estimate is provided.

- The effectiveness of high speed/load procedures in restoring catalyst efficiency are limited by fuel sulfur level
- Not modeled explicitly in MOVES2013

Overall Emission Reduction for 28 ppm vs. 5 ppm

- **Objective:**
  - To examine the in-use effect of sulfur level on emissions over time as vehicles operate on two different fuel sulfur levels at 28 ppm and 5 ppm
  - By performing repeated emission tests following a clean-out at 28 and 5 ppm fuel sulfur with accumulation of mileage
- **Data from original and modified 'Long' procedures and modified 'Short' procedure**
- **17 vehicle families; 23 unique vehicles**
- **Number of measurements: n = 228**
  - 28 ppm sulfur: n = 114
  - 5 ppm sulfur: n = 114
- **Mixed model**
  - Dependent variable (Y_i): natural logarithm of emissions
  - Fixed effects (X_i): sulfur level, accumulated mileage, vehicle type, and the interaction terms
  - Random effects (Z_i): each vehicle

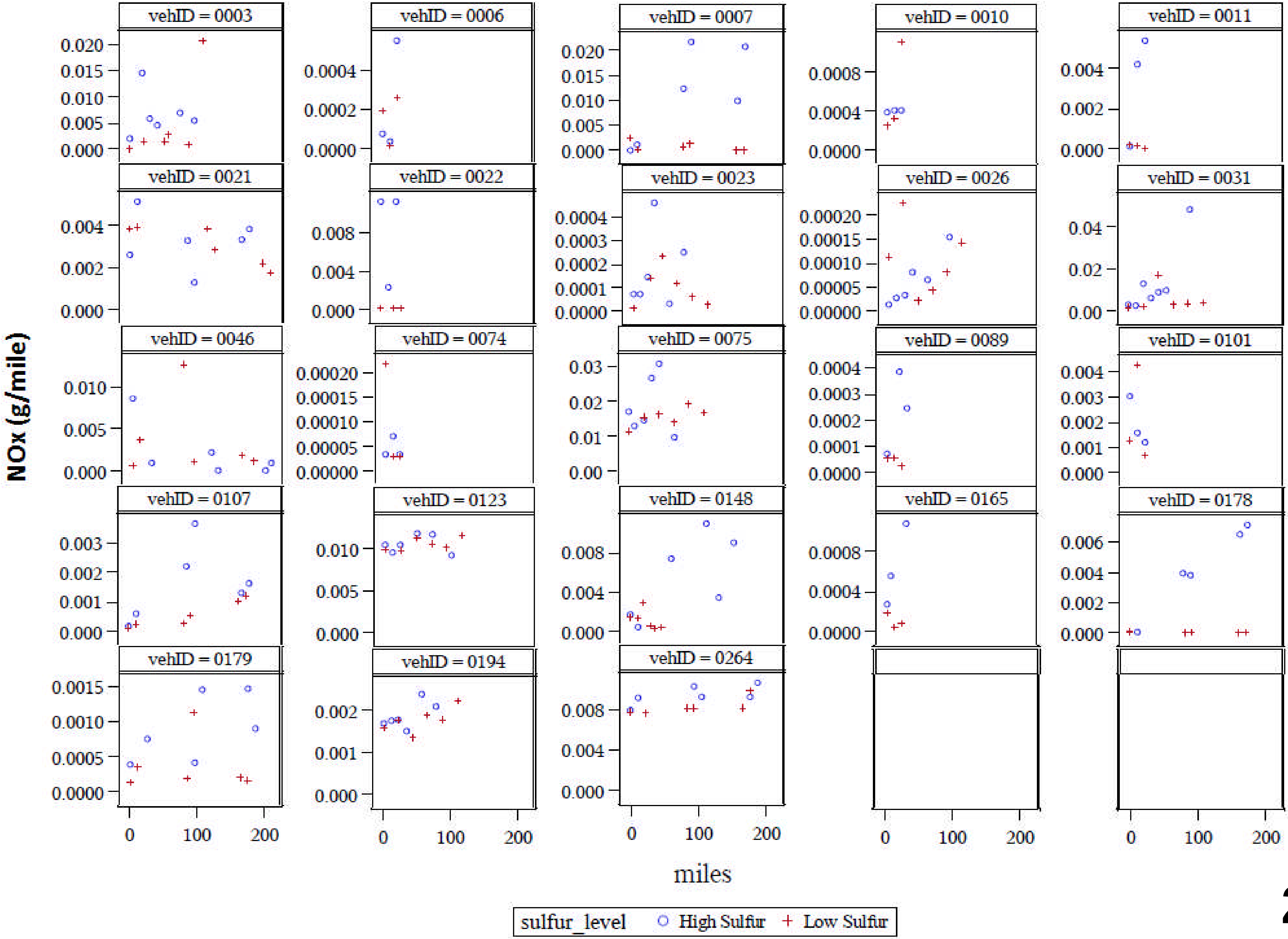
Box-plot of vehicle emissions by sulfur level at 28 ppm and 5 ppm



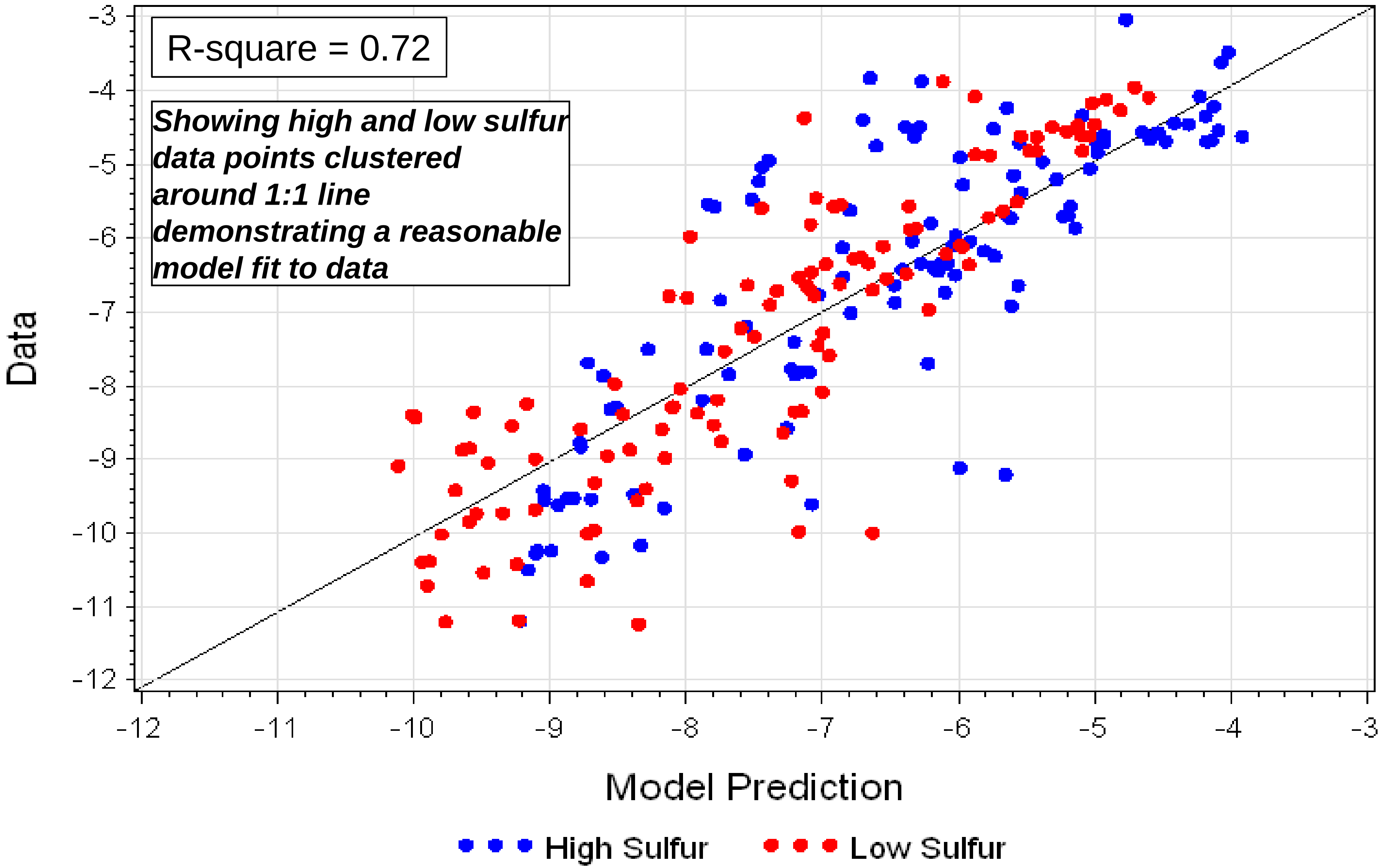
The diamond and the line represent the mean and the median, respectively; box represents the interquartile range between 25th and 75th percentile; the error bars show the full data range

NOx Bag 2: Data plot

Comparison of high sulfur (28 ppm) in blue to low sulfur (5 ppm) in red for all vehicles



Effect of Sulfur Level on NOx Bag 2: Data vs. Model Prediction



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Percent reduction in emissions: fuel sulfur level of 28 ppm vs. 5 ppm

	NO_x (p value)	THC (p value)	CO (p value)	NMHC (p value)	CH4 (p value)	NO_x+NMOG (p value)	PM‡
Bag 1	10.7% (0.0033)	8.5%† (0.0382)	7.5%† (0.0552)	7.5% (< 0.0001)	13.9%† (< 0.0001)	N/A	–
Bag 2	59.2% (< 0.0001)	48.8% (< 0.0001)	– ‡	44.8%† (0.0260)	49.9% (< 0.0001)	N/A	–
Bag 3	62.1% (< 0.0001)	40.2% (< 0.0001)	20.1% (< 0.0001)	49.9% (< 0.0001)	29.2% (< 0.0001)	N/A	–
FTP Composite	23.0%† (0.0180)	13.0%† (0.0027)	11.9%† (0.0378)	10.6%† (0.0032)	25.8%† (< 0.0001)	17.3% (0.0140)	–
Bag 1 – Bag 3	– ‡	5.2% (0.0063)	4.3% (0.0689)	5.1% (0.0107)	4.6% (0.0514)	N/A	–

† Model with significant sulfur and mileage interaction term. ‡ Sulfur level not significant at α = 0.10. For THC bag 1 and CH4 bag 1, because the effect of clean-out was not statistically significant, the reduction estimates are based on the estimates of least squares means.

- Reducing fuel sulfur levels from 28 to 5 ppm expected to bring significant reductions in NO_x, NMHC, and other pollutants of interest in the in-use fleet
- Basis for the new sulfur model in MOVES2013

Sensitivity Analyses

Effect of low concentration measurements

- **Two measurement concentration screening levels**
  - 100 ppb: based on the lower end of the instrument manufacturer's stated calibration range
  - 50 ppb: chosen at half the stated calibration range
- **Vehicles with measurements falling below the screening level above were removed and models were refit**
- **Results (NO_x Bag 2)**

Model Description	Num. of Vehicles	Num. of Observations	Model Estimate of Bag 2 NO_x Reduction
Final NO_x bag 2 model	23	228	59.2%
50 ppb vehicle screen	17	174	60.5%
100 ppb vehicle screen	11	120	70.2%

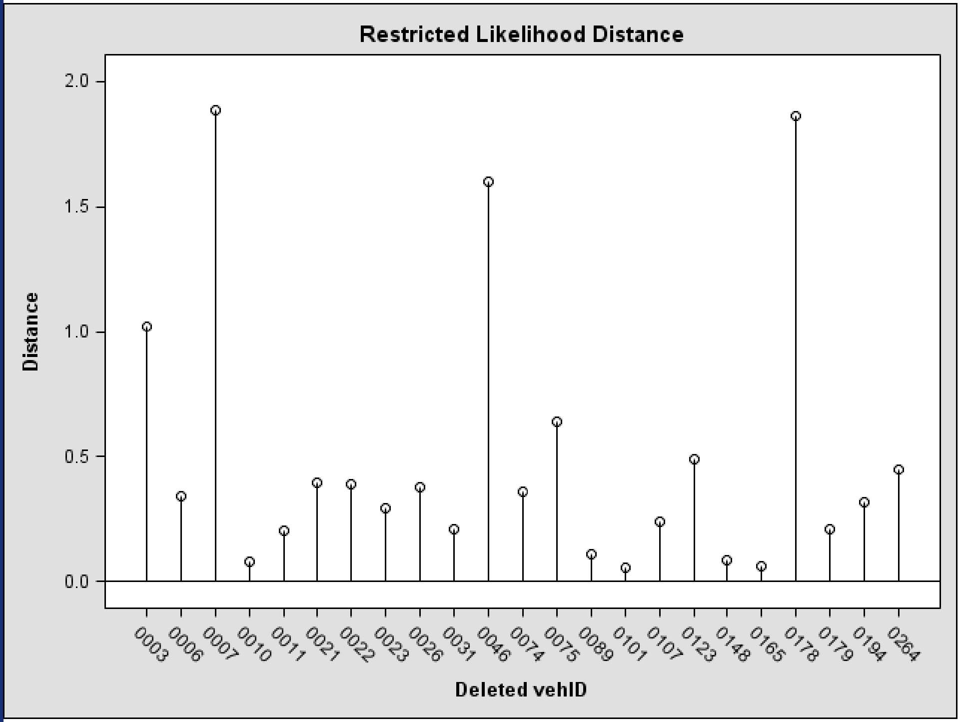
Effect of imputation

- **Compare the models**
  - With and without imputed values for Bag 2 NO_x
  - Mixed model re-fit using a new dataset with all imputed values removed, consisting only of actual measurements

- **Impact of imputed values on final model (NO_x Bag 2)**

	Estimate	Std. Err.	DF	*tValue*	*Probt*	*% Reduction*
Model with imputed values	-0.8953	0.2040	68	-4.39	<.0001	59.2%
Model without imputed values	-0.8618	0.2001	64.1	-4.31	<.0001	57.8%

Effect of Influential Vehicles



- **Influential vehicles**
  - removed as an additional test of robustness
  - Identified by examining the restricted likelihood distance (RLD)
- **Removed vehicles**
  - IDs 0007, 0046, and 0178
  - NOTE: no specific grounds for excluding these vehicles from the mixed model analysis
- **Result**
  - the percent reduction in emissions from 28 ppm to 5 ppm changed to 50.9% compared to the reduction of 59.2% from the final model

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Summary of Findings

- **Current study assessed the emission reductions expected from in-use Tier 2 light duty vehicles with reduction in gasoline sulfur content from 28 ppm to 5 ppm**

- **The overall findings of significant emission benefits of ≤10 ppm sulfur in Tier 2 vehicles are in agreement with other recent studies by EPA and automobile and catalyst manufacturers [1,2,3]**

- **The sensitivity analyses performed for Bag 2 NO_x demonstrated that the magnitude and statistical significance of the model predictions remained statistically significant**
  - Within a range of 51-70% reduction (vs. baseline at 59%)
  - Suggesting robustness of the results

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Implementation in MOVES

- **Percent reduction in in-use emissions from 28 ppm to 5 ppm fuel sulfur applied (from slide 27)**
  - Bag 2: running exhaust; Bag 1 – Bag 3: starts exhaust
  - For model years 2001 and later gasoline vehicles
  - Applies multiplicatively to other fuel effects in MOVES (i.e., EPAct fuel model)
  - Applies ONLY for sulfur levels below 30 ppm
    - For sulfur levels above 30 ppm, and for pre-2001 MY vehicles, the original sulfur effect from the complex model remains in place
- **Existing "floor" to the sulfur correction modified**
  - In MOVES2010, sulfur algorithm utilized log-log relationship for sulfur level below 30 ppm
    - Fuel adjustment 'floor' of 0.85 was added to avoid undue extrapolation of data at lower sulfur levels (i.e., reduction due to sulfur ≤ 15%)
  - In MOVES2013, the sulfur "floor" was changed to 0.40
    - considering the reduction in emissions from current sulfur program
    - i.e., reduction due to sulfur ≤ 60%

Implementation in MOVES (cont'd)

- **The new sulfur correction equation:**

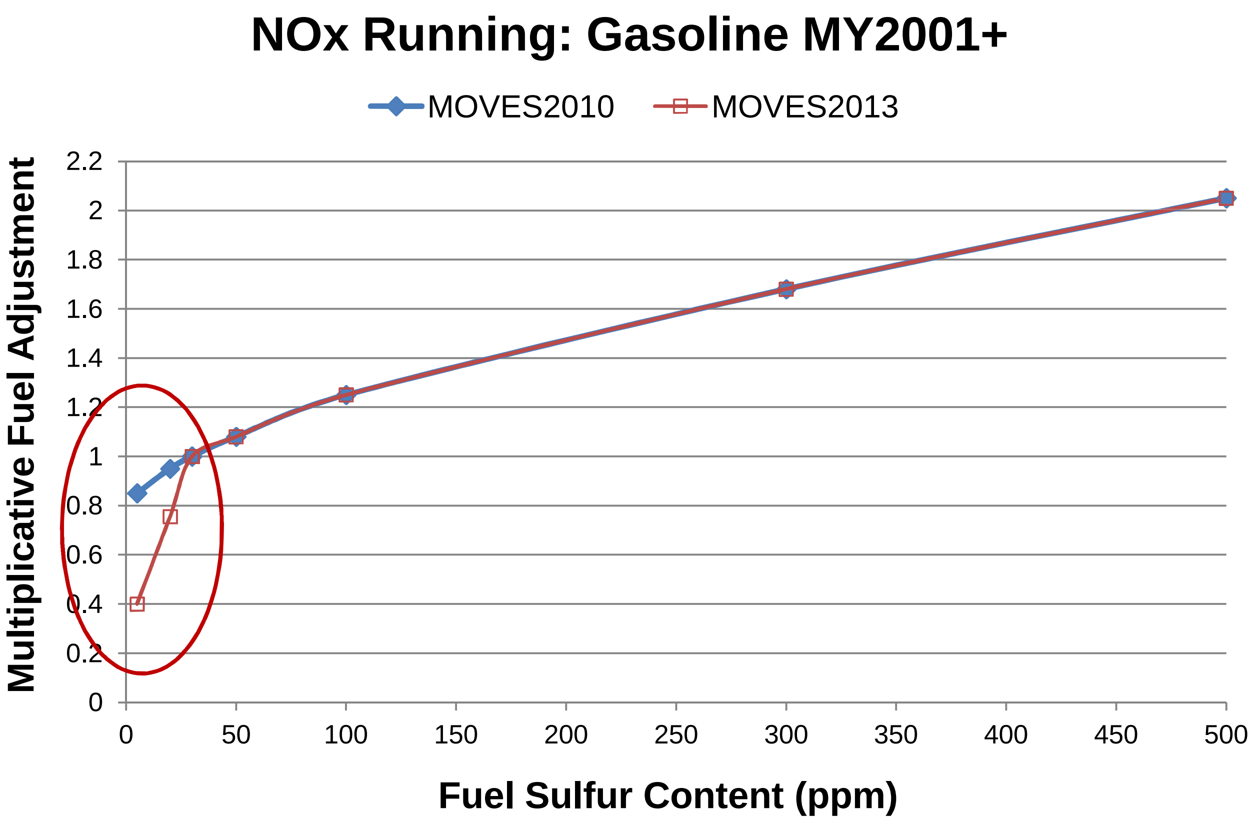
$$sulfur\ effect = \left[1.0 - Coeff_{sulfur} * (30 - sulfurLevel)\right]$$

- **Following values for the sulfur coefficients by pollutant, process, and vehicle type were used to populate the "GeneralFuelRatioExpression" table**

Vehicle Type	THC		CO		NO_X		PM	
	Starts	*Running*	*Starts*	*Running*	*Starts*	*Running*	*Starts*	*Running*
Motorcycle	0	0	0	0	0	0	0	0
Passenger Car, Passenger Truck & Light Commercial Truck	0.002237	0.020336	0.001866	0	0	0.024459	0	0
All other Vehicle Types†	0	0.015488	0	0.009436	0	0.027266	0	0

† Estimated based on Tier 2 Bin 8 light-duty trucks

Sulfur Fuel Effect – MOVES2010 vs. MOVES2013



Further Reading

The study report and dataset are available via the OTAQ website:

http://www.epa.gov/otaq/fuelsmodel.htm

Footnotes
1. Chapter 6 of the Regulatory Impact Analysis for the Control of Hazardous Air Pollutants from Mobile Sources Final Rule, EPA 420-R-07-002.
2. Ball D., Clark D., Moser D. (2011). *Effects of Fuel Sulfur on FTP NOx Emissions from a PZEV 4 Cylinder Application.* SAE 2011 World Congress Paper 2011-01-0300. SAE International: Warrendale, PA.
3. Shapiro, E. (2009). *National Clean Gasoline, An Investigation of Costs and Benefits.* Published by the Alliance of Automobile Manufacturers, Washington, DC.

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John White
Cay Yanca
& probably others…

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Questions?

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Appendix

Number of measurements with zero values

	Clean-out at 28 ppm data (N = 479)					
	NO_x	THC	CO	NMHC	CH4	PM
Bag 1	0	1 (0.2%)	0	1 (0.2%)	1 (0.2%)	1 (0.2%)
Bag 2	32 (6.7%)	6 (1.3%)	33 (6.9%)	32 (6.7%)	4 (0.8%)	2 (0.4%)
Bag 3	0	1 (0.2%)	21 (4.4%)	35 (7.3%)	1 (0.2%)	1 (0.2%)
FTP Composite	0	1 (0.2%)	0	1 (0.2%)	1 (0.2%)	2 (0.4%)
Bag 1 – Bag 3	0	1 (0.2%)	0	1 (0.2%)	1 (0.2%)	1 (0.2%)
	Clean-out at 5 ppm data (N = 132)					
	NO_x	THC	CO	NMHC	CH4	PM
Bag 1	0	0	0	0	0	0
Bag 2	14 (10.6%)	2 (1.5%)	3 (2.3%)	5 (3.8%)	3 (2.3%)	0
Bag 3	2	0	1 (0.8%)	8 (6.1%)	0	0
FTP Composite	0	0	0	0	0	0
Bag 1 – Bag 3	0	0	0	0	0	0
	Sulfur level data (N = 228)†					
	NO_x	THC	CO	NMHC	CH4	PM
Bag 1	0	0	0	0	0	0
Bag 2	18 (7.9%)	2 (0.9%)	8 (3.5%)	9 (3.9%)	3 (1.3%)	2 (0.9%)
Bag 3	3 (1.3%)	0	3 (1.3%)	6 (2.8%)	0	0
FTP Composite	0	0	0	0	0	0
Bag 1 – Bag 3	7 (3.1%)	0	1 (0.4%)	0	0	15 (6.6%)

† The sulfur level data for NMHC Bag 3 had 215 measurements.