Validation of Source Attribution of Fine Particle Emissions from Mobile Sources





M. P. Fraser, B. Buzcu, Z. Yue, G. McGaughey, N. Desai, D. Allen, R. Seila, W. Lonneman and R. Harley

RICE

Overview

- Introduction and Motivation
- Procedures
 - Collection and analysis of PM
 Chemical Mass Balance Modeling
- Results
- Conclusions



Introduction

- Mobile sources of fine PM
 - Mobile sources represent 16% of non-fugitive dust emissions in U.S. EPA PM2.5 Emission Inventory
 - Diesel-engines represent 60% and gasoline-engines represent 40% of total emissions from mobile sources
- In urban areas, responsible for elevated levels of fine PM

- Local PM "hot-spots", occupational exposure



Uncertainty about the relative contribution of gasoline versus diesel engines to ambient fine PM levels **EPA Emission inventory: 60% diesel Receptor Modeling Applications** Schauer et al (1996): 78% diesel Zheng et al. (2002): 72% diesel Watson et al. (2002): 74% gasoline*

* Includes contribution of cold start and poorly maintained vehicles



Importance of Gasoline-Diesel Split

- Evaluate the efficacy of possible control strategies
- Determine the health effects of ambient PM levels

- Diesel PM is suspected human carcinogen



Test Accuracy of Receptor Models to Separate Gas and Diesel



- Collected PM in
 Washburn Tunnel
 - Single bore, forced ventilation tunnel
- Capture different mixture of gasoline and diesel vehicles
- Apply receptor models to pollutant concentrations in tunnel



Measurements in Washburn Tunnel

- Collected samples of gas-phase and particle-phase species in tunnel and in ventilation air
- Determined pollutant emission index:

$$E_{(P)} = \frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO]}$$



Traffic Monitoring

Using monitored traffic volumes, divided samples into high fraction diesel and low fraction diesel vehicle traffic

Diesel vehicle traffic relatively constant, but gasoline vehicles (light-duty) increased during evening rush hour



Date	Time (CDT)	Gasoline- Powered Vehicles (per hour)	Diesel- Powered Vehicles (per hour)	Fraction of Diesel Vehicles
8/29/0 0	1200 – 1400	873	48	5.4
8/30/0 0	1200 – 1400	1113	72	6.4
8/30/0 0	1600 – 1800	2334	55	2.4
8/31/0 0	1200 – 1400	1145	51	4.4
8/31/0 0	1600 – 1800	2658	53	2.0
9/1/00	1200 – 1400	1359	59	4.5

× RICE

Date	Time (CDT)	Fraction of Diesel Vehicles	Percentage Carbon from Diesel Vehicles	Emission Index PM2.5 (g/kg C)
8/29/ 00	1200 – 1400	5.4	20.7	0.50
8/30/ 00	1200 – 1400	6.4	23.0	0.48
8/30/ 00	1600 – 1800	2.4	10.1	0.30
8/31/ 00	1200 – 1400	4.4	16.1	0.55
8/31/ 00	1600 – 1800	2.0	7.7	0.24
9/1/0 0	1200 – 1400	4.5	16.5	0.35

TRICE









Molecular Marker Technique

•Identify and quantify organic compounds that are unique to different emission sources

•Use ambient quantification of same compounds to trace emissions from source to receptor



Chemical Mass Balancing

$$\mathbf{C}_{(ij)} = \mathbf{S} \mathbf{a}_{(jk)} \mathbf{s}_{(ik)} + \mathbf{e}_{(ij)}$$

where: i = compounds (1, 2, ...) j = samples (1, 2, ...) k = sources (1, 2, ...)

- **C** = concentration of species in ambient samples
- **a** = emission source strengths
- s = source profiles
- e = difference between ambient concentration and reconstructed source contribution



Molecular Markers Used in CMB Used to separate 3 sources: diesel, gasoline road dust

11 Organic Compounds

- normal alkanes
- petroleum biomarkers
- polycyclic aromatic hydrocarbons
- alkanoic acids

3 Bulk Composition Species

- Al, Si
- Elemental Carbon



Sample Analysis

Organic Extraction using recovery standards

Analysis by gas-chromatography and mass spectrometry

Quantification using authentic standards

Extraction efficiency and blowdown loss monitored with recovery standards



CMB Results

	1200-1400 CDT	1400-1600 CDT	
Gasoline-Powered Vehicles	1252 per hour	2496 per hour	
Diesel-Powered Vehicles	55 per hour 54 per hour		
Measured PM2.5	99.1 \pm 4.2 ng m⁻³	$102.8 \pm 4.5 \text{ mg m}^{-3}$	
CMB Gasoline Exhaust	17.6 ± 4.7 mg m ⁻³	28.8 ± 6.6 mg m ⁻³	
CMB Diesel Exhaust	64.3 ± 8.4 ng m ⁻³	67.3 ± 9.1 mg m ⁻³	
CMB Road Dust	4.8 ± 0.7 mg m ⁻³	5.7 ± 0.9 mg m ⁻³	
Percentage of Measured Mass Apportioned by CMB	87.5%	99.0%	

RICE

CMB Results







Conclusions

Source apportionment modeling can accurately separate gasoline and diesel exhausts

In this case, diesel emissions contribute ~65% of fine PM from mobile sources*

Can be used to determine relative contributions for determing control strategies or health impacts

* Does not include cold start operations

