Diesel Emissions: Risk, Measurement and Controls

Tom Slavin CIH, CSP, CSHM

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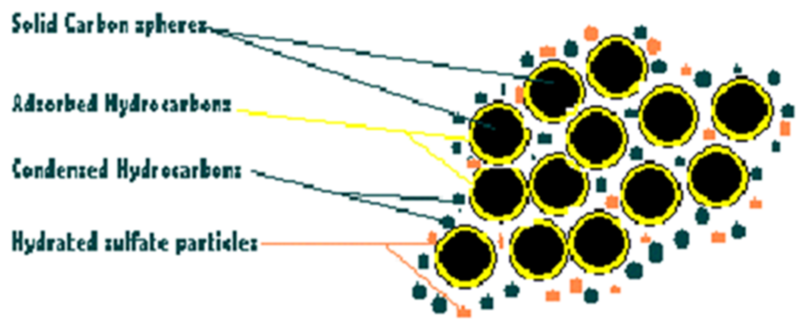
Diesel Exposure and Risk

- What exactly is diesel engine exhaust
- How to measure diesel engine exhaust
- Impact of control technologies on diesel exhaust
- Health risk and 2012 IARC conclusion: carcinogenic to humans (category 1)
- What does all this mean for an industrial hygienist?

What is Diesel Exhaust?



- Diesel exhaust is a mixture
  - carbonaceous particulate
  - complex organic compounds
  - organic and inorganic gases
- Diesel exhaust is a variable mixture

Composition of Diesel Exhaust

- Gas phase
  - Oxygen
  - Carbon dioxide
  - Nitrogen
  - Carbon monoxide
  - Water vapor
  - Nitrogen Oxides (especially NO)
  - Sulfur Compounds (especially Sulfur Oxides)
  - Volatile Organic Compounds
  - Low MW Hydrocarbons

Composition of Diesel Exhaust

- Particulate phase
  - Mostly elemental carbon (soot)
  - About 20% to 40% adsorbed organic compounds
  - Also sulfate, nitrate, metals, other trace elements
  - The most toxicologically relevant adsorbed compounds (less than 1% of PM by mass):
    - PAHs
    - Nitro-PAHs
    - Oxidized PAH derivatives
  - 92% of mass is in particles smaller than 1 micron

Substances in Diesel Exhaust Listed by CARB as Toxic Air Contaminants

acetaldehyde
acrolein
aniline
antimony compounds
arsenic
benzene
beryllium compounds
biphenyl
bis[2-ethylhexyl]phthalate
1,3-butadiene
cadmium
chlorine
chlorobenzene
chromium compounds

cobalt compounds
cresol isomers
cyanide compounds
dibutylphthalate
dioxins and dibenzofurans
ethyl benzene
formaldehyde
hexane
lead (inorganic)
manganese compounds
mercury compounds
methanol
methyl ethyl ketone
naphthalene

nickel
4-nitrobiphenyl
phenol
phosphorus
POM, including PAHs
  and their derivatives
propionaldehyde
selenium compounds
styrene
toluene
xylene isomers, mixtures
  o-xylenes
  m-xylenes
  p-xylenes

How is Diesel Exhaust Measured?

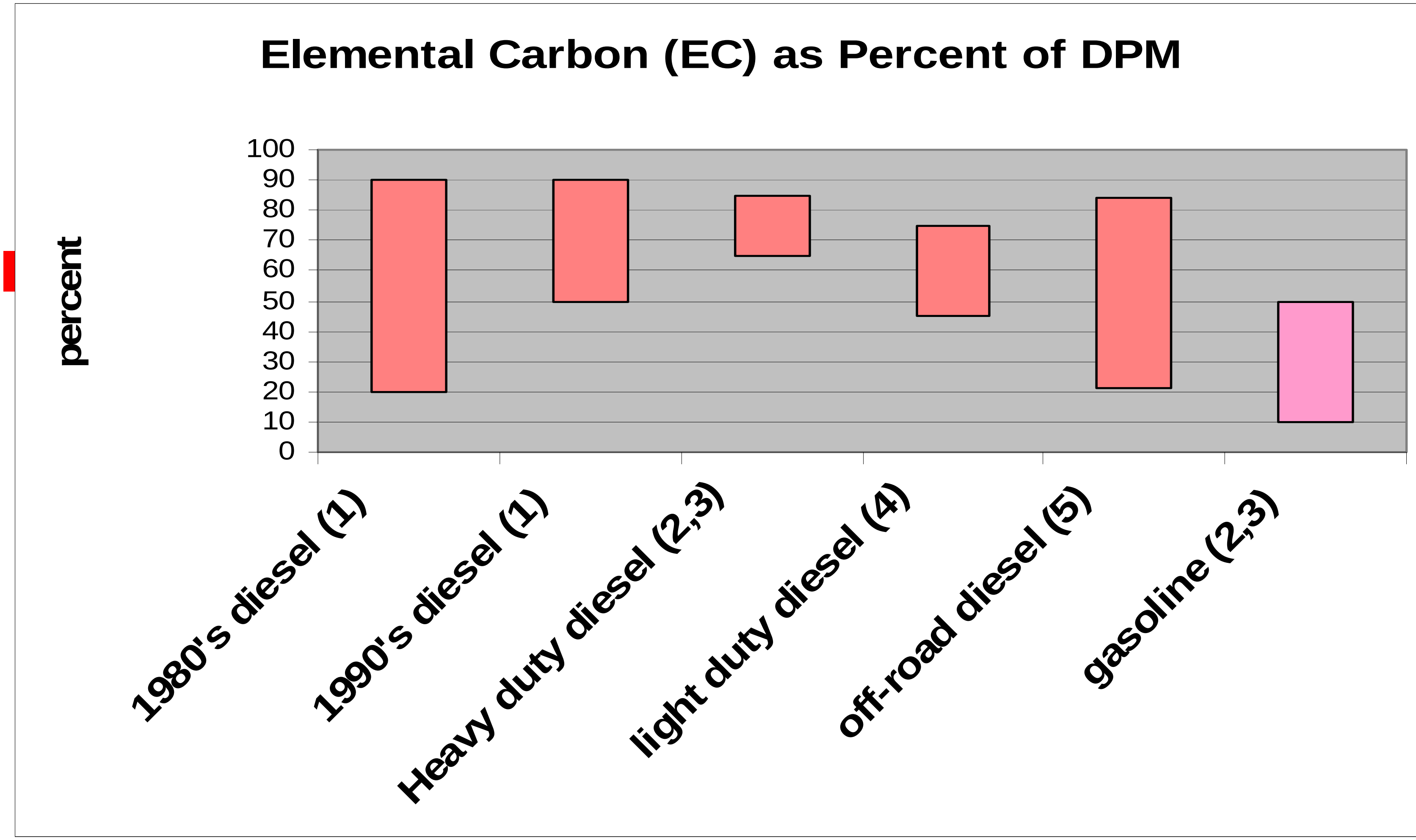
- Individual Components
  - NOx, CO2, CO, PAHs, Aldehydes, PM
  - 41 regulated pollutants
- Surrogates for diesel particulate matter (DPM)

DPM Measurement Strategies

- Strategies using chemical constituents
  - NO_2, CO, Aldehydes, PAHs
  - Elemental Carbon (EC), Total Carbon (TC),
- Strategies using physical properties
  - Size based gravimetrics
    - Respirable particulate matter (RPM), $PM_{2.5}$, $PM_{0.8}$
  - Optical density – black carbon (BC)
  - Particle number (fine, ultrafine, nanoparticle)
- Adjustment strategies
  - Respirable combustible dust (RCD)
  - Adjusted respirable particulate matter (ARPM)
  - Adjusted extractable material (AEM)
  - Adjustments for background material (e.g., coal) ($DEP_{Johnston}$)

DPM Exposure Measurement Strategy Bottom Line

- No unique chemical signature (DNA) for diesel
- Most chemical surrogates (CO, NOx, etc.) are highly variable and inconsistent indicators of DPM
- Gravimetric methods ($PM_{2.5}$, RPM, etc.) include much more than diesel
- Elemental Carbon may be the most accurate indicator
  - Always present in DPM (40-85%)
  - Few interferences or confounders



Key Points:
- Ratio of EC to DPM is variable
- Higher ratios occur at higher loads.
- EC is present in other combustion sources.

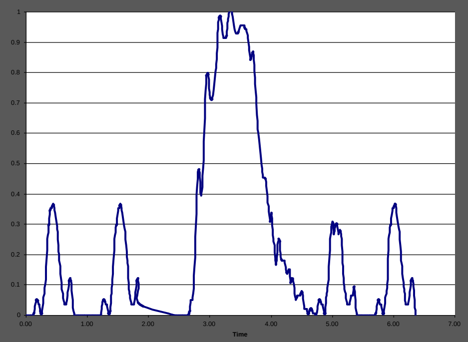
References:
1. EPA (2000)
2. Fujita (1998)
3. Watson (1998)
4. Norbeck (1998)
5. Liu (2005)

Challenges: Changes in Diesel Exhaust and DPM

- Chemical profile of diesel emissions has changed over time due to:
  - Engine design changes
    - Exhaust gas recirculation
    - Injection pressures
    - Combustion shaping
  - Diesel fuel changes (lower sulfur)
  - Emission control devices
- Emissions vary with engine size and duty cycle

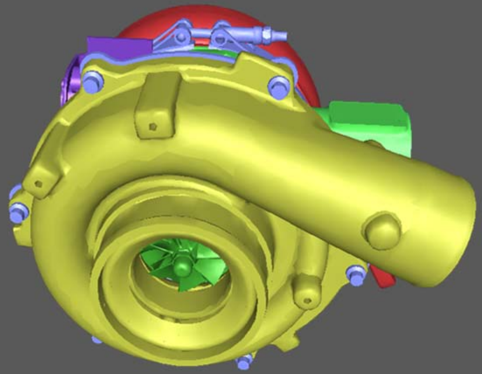
Five Technologies to 2010

Fuel System



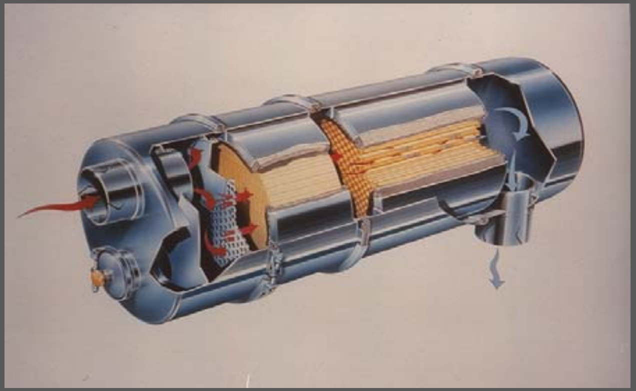
Electronics and Electrical Systems

Boost Technologies



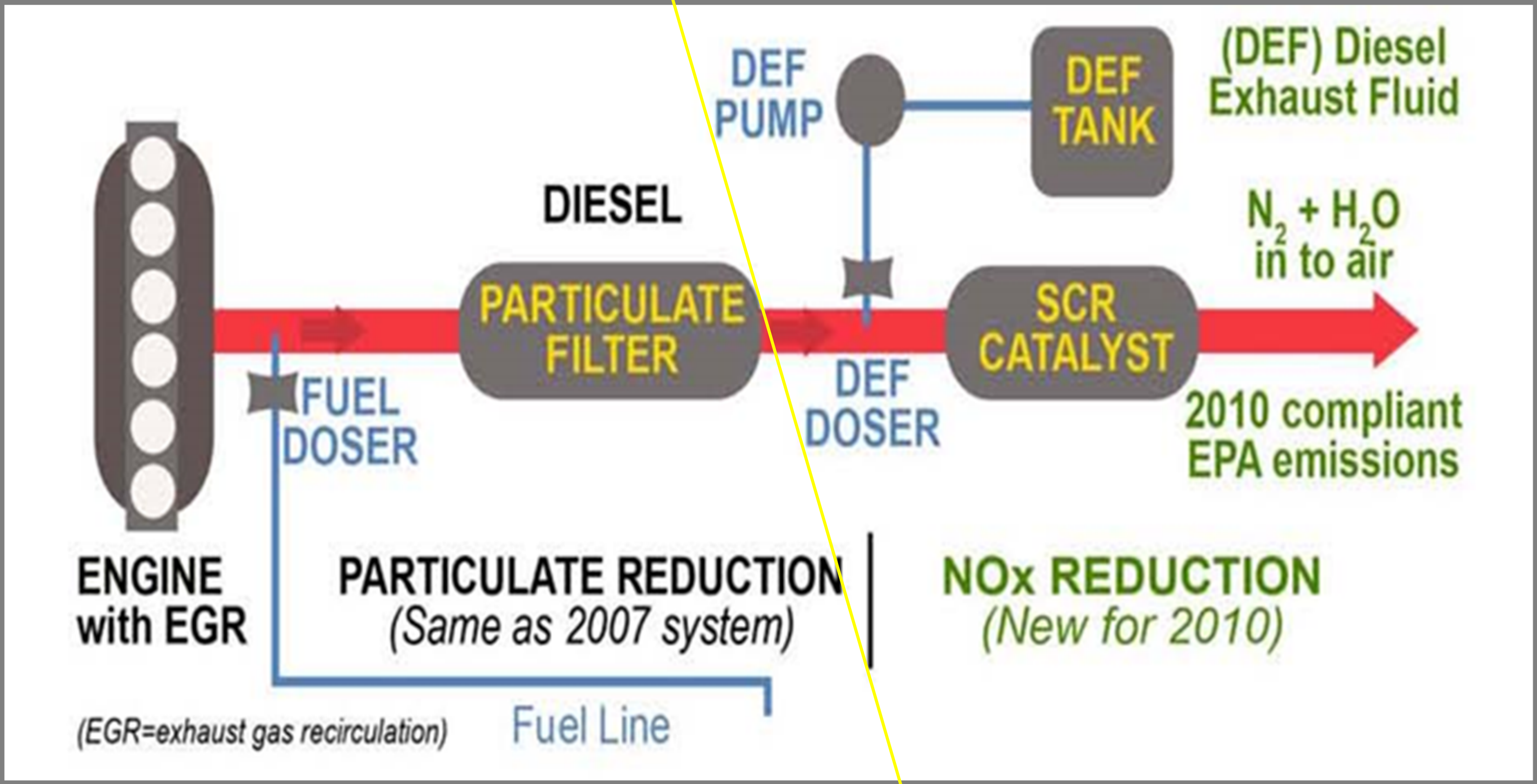
Combustion

Diesel Particulate Filter



Exhaust Gas Recirculation (EGR)

Added in 2010- Selective Catalytic Reduction (SCR)



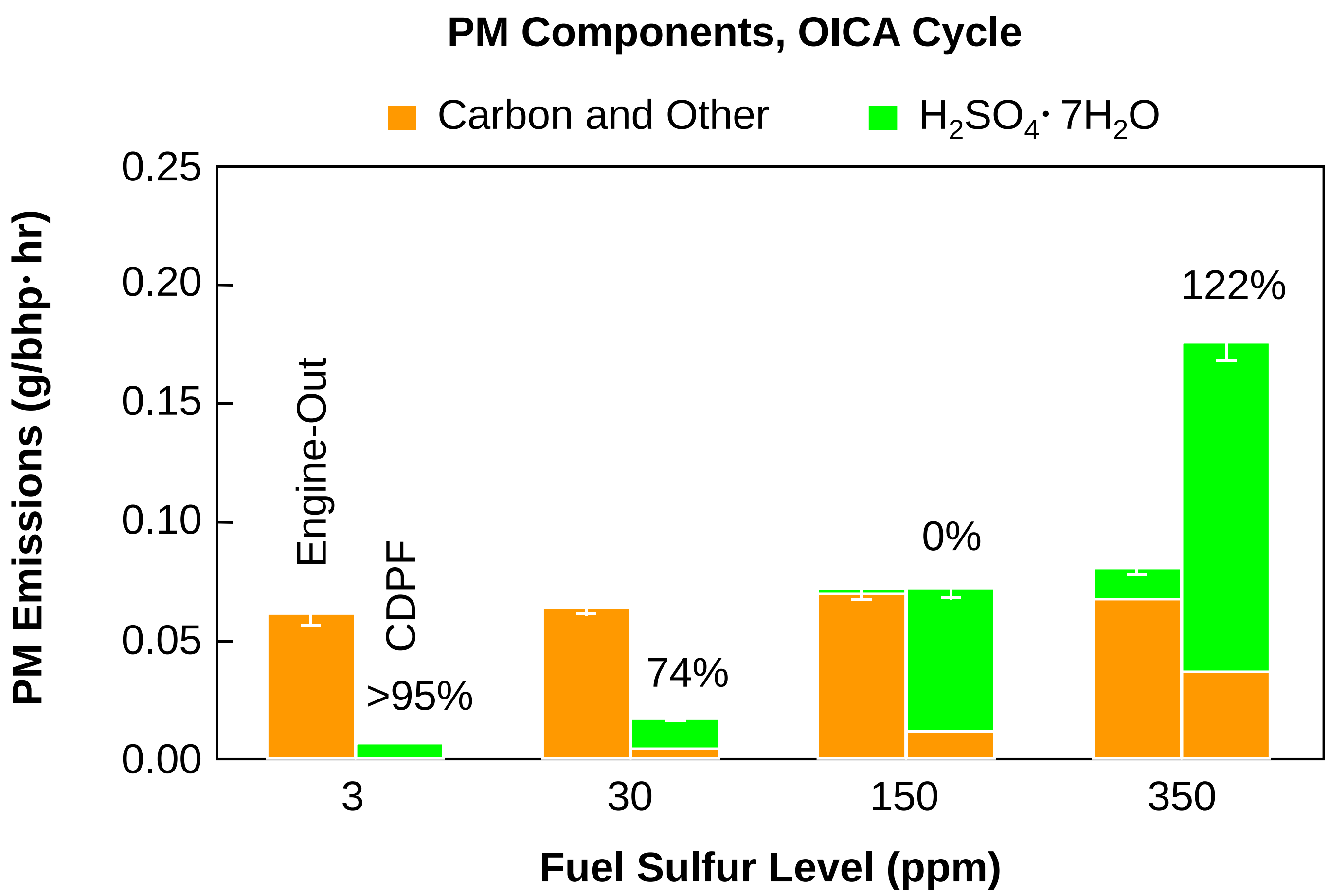
Sulfur Reduction–
Enables Diesel Exhaust Control

History of EPA Regulation of Diesel Fuel Properties

- ⌘Pre-1993 – 2500-ppm sulfur
- ⌘1993 - < 500-ppm sulfur
- ⌘2006 - <15-ppm sulfur

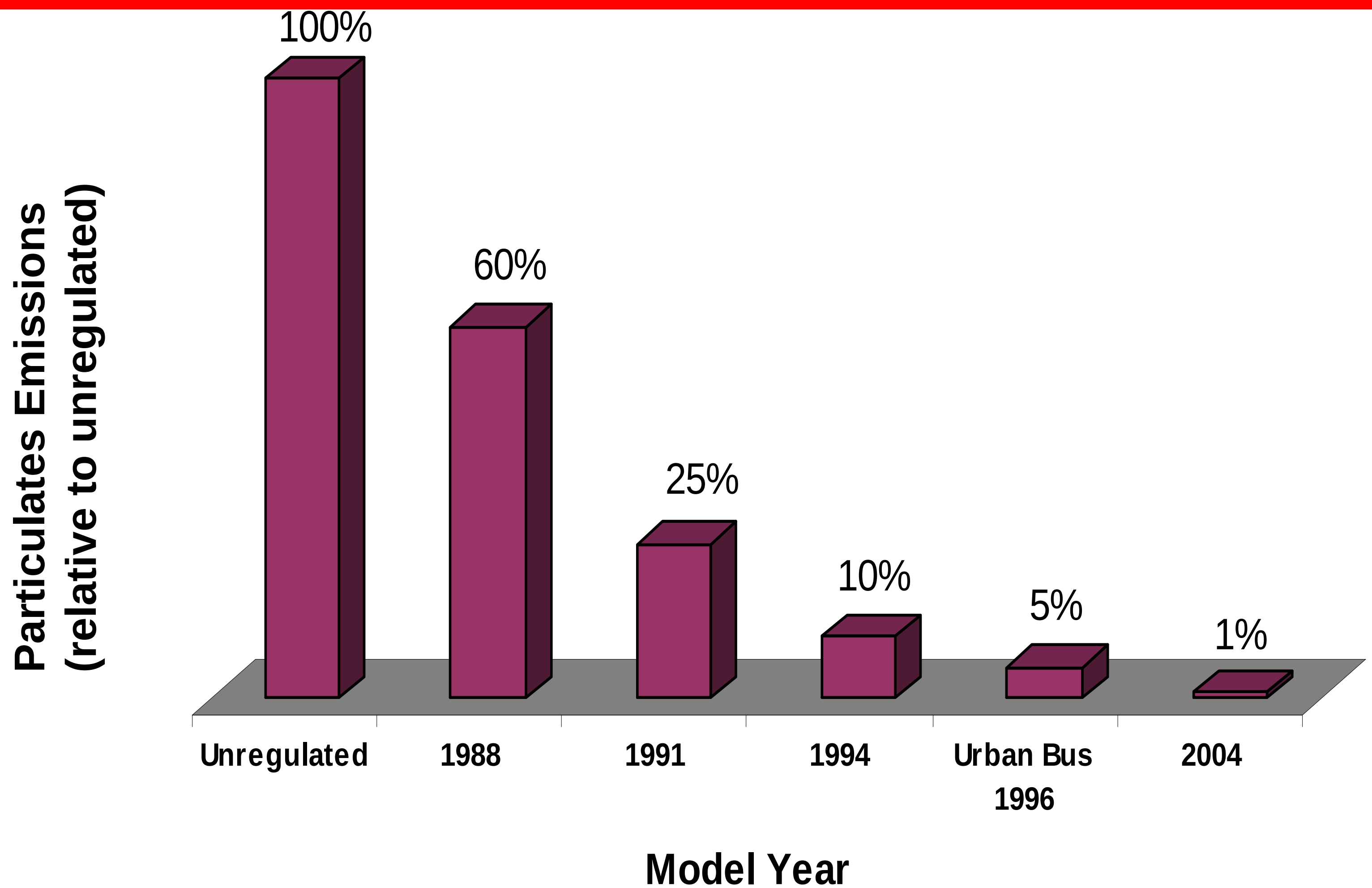
Countries with poor control of diesel fuel quality cannot use lower emission technology

DPF Decreases Carbon PM But Increases Sulfate PM as a Function of Fuel Sulfur Content

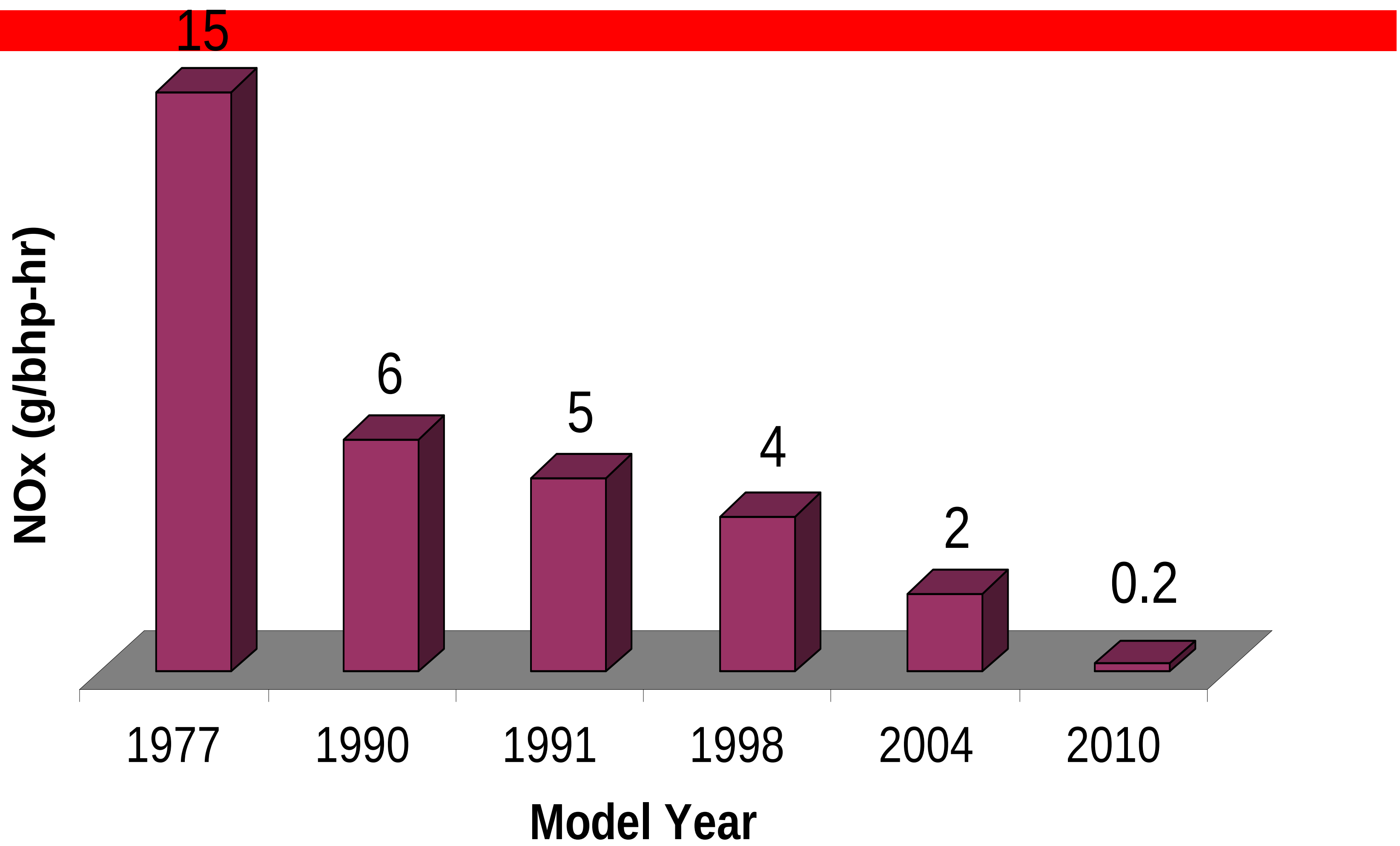


Diesel emissions control sulfur effects project (DECSE)

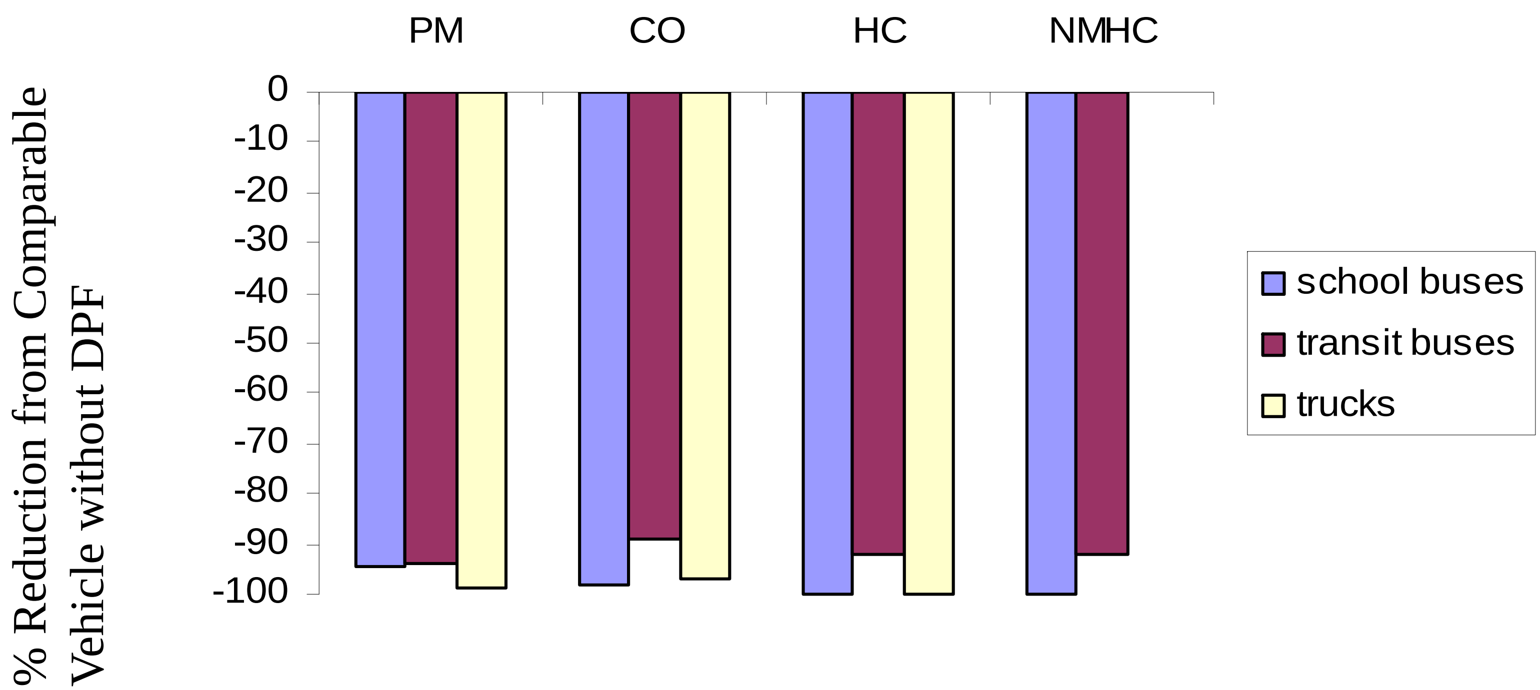
Reducing US Diesel PM Emissions



Reducing US NOx Emissions

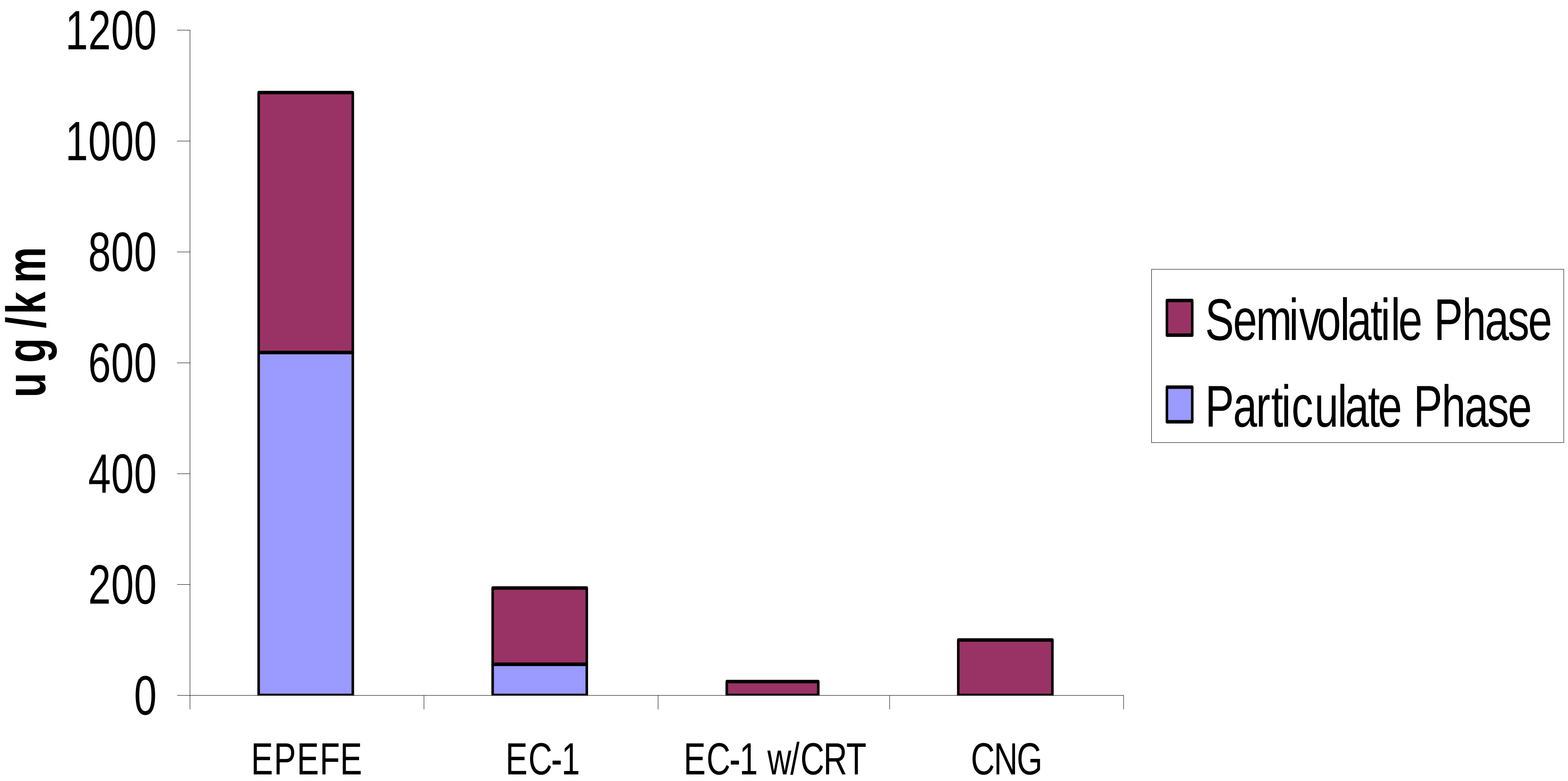


New Diesel Technology Reduces Regulated Emissions



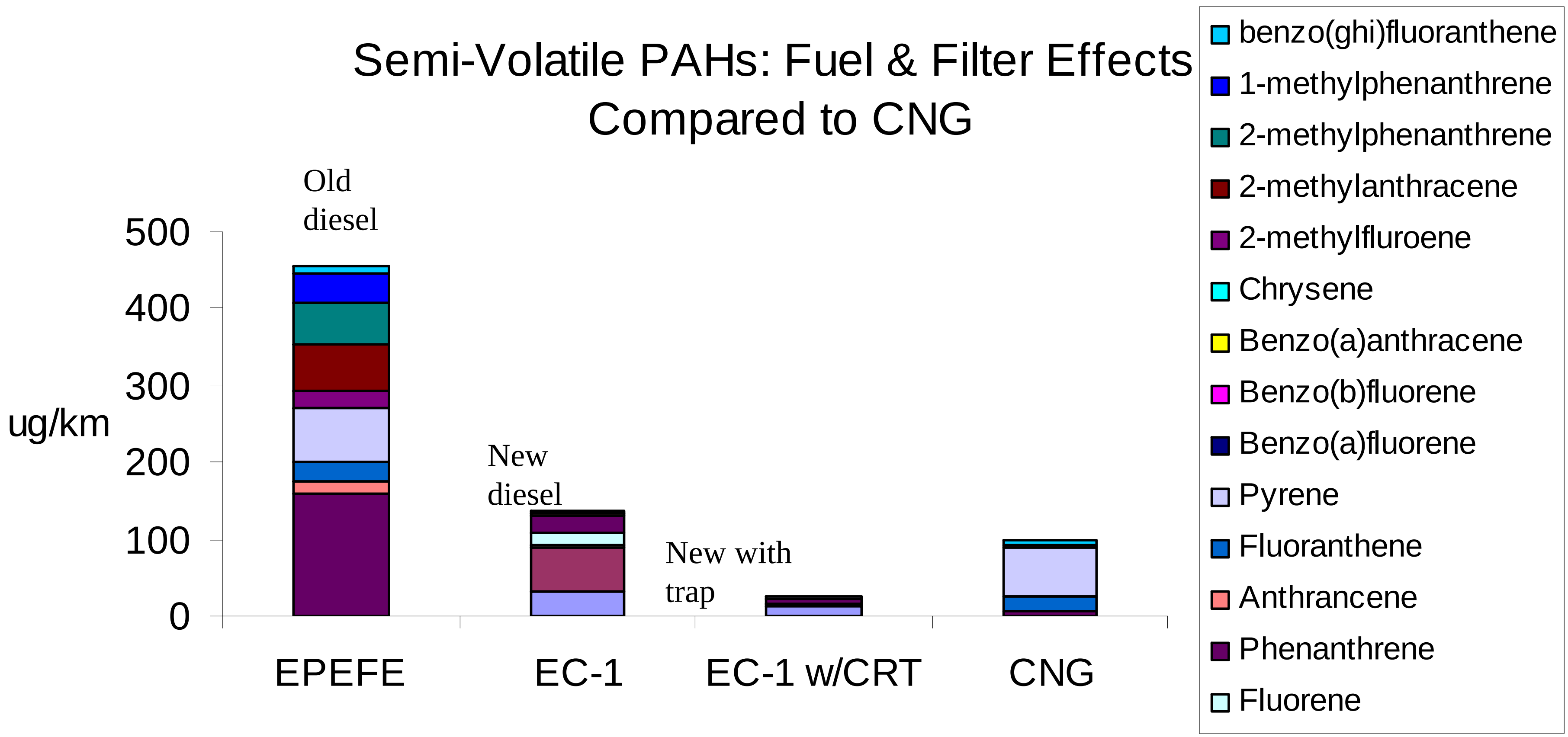
(Ullman 2003, Lev-On 2003, Lapin 2007)

Swedish Study: Total PAHs



Composition of Diesel Exhaust:

PAH profile of new diesel looks more different than old diesel.



(Ullman 2003, Lev-On 2003, Lapin 2007)

Changes in Diesel Exhaust

- Fewer particulates (less EC)
- Different combustion products at different stages of exhaust system
- Less adsorption of semivolatiles
- Emission control byproducts (ammonia slip)
- Catalytic conversion (SO_2 to SO_3)
- New diesel is different from old diesel
- What about particle number?

Particulate Matter

Term	Particle Size
PM_{10}	<10 microns (mass)
$PM_{2.5}$	< 2.5 microns (mass)
PM_{1}	<1 micron (mass)
Fine	0.1 to 1 micron
Ultrafine	0.01 to 0.1 micron (10-100 nm)
nanoparticles	0.01 to 0.1 micron (10-100 nm)

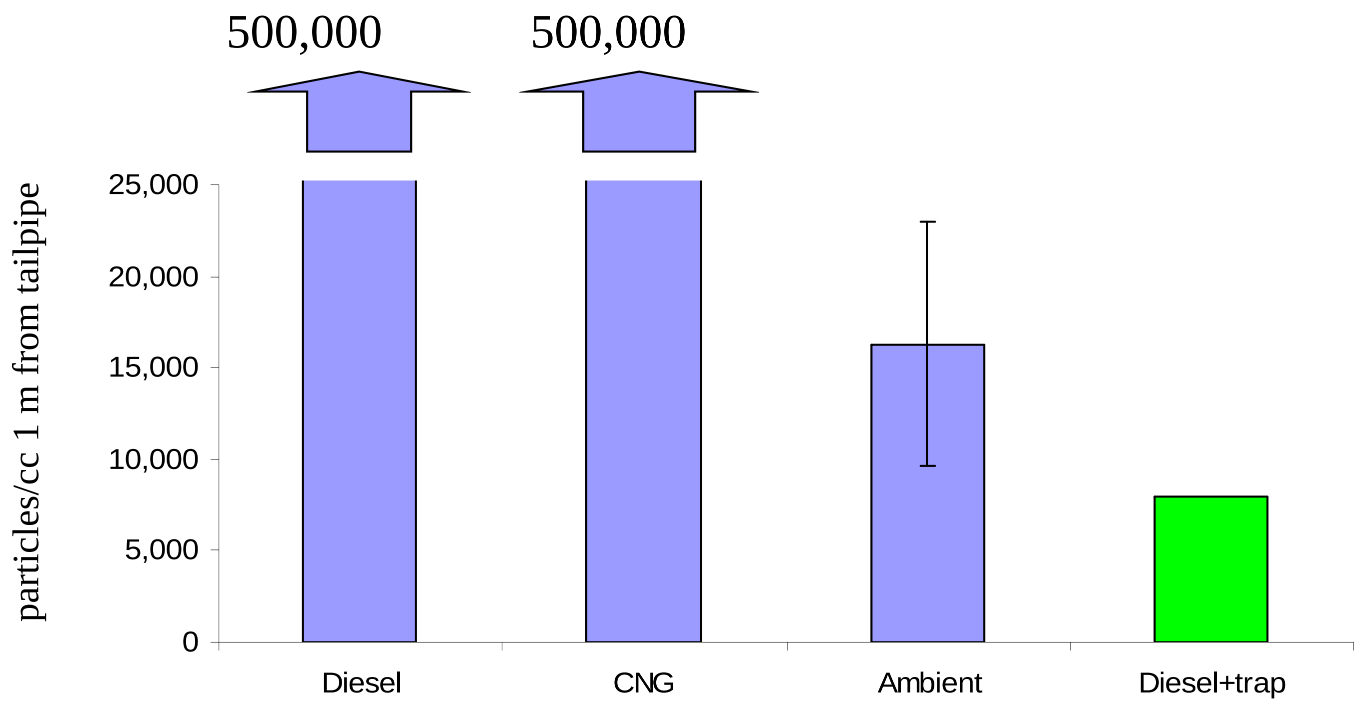
Clean Air Task Force Study Shows that Buses with Particle Traps Filter Chicago Air

Conventional bus (on left) reads 500,000 ultrafine particles/cc, the upper limit of detection for the PTrak. The bus with a particle trap (on right) reads 9,570 particles/cc—a level that was one third lower than the ambient particle level (~15,000 particles/cc) in Chicago on that day.

From: CATF School Bus Particulate Matter Study, January 2005

New Diesel Technology Reduces Ultrafine Particulate Emissions

- Ultrafine particulate emissions lower than ambient levels



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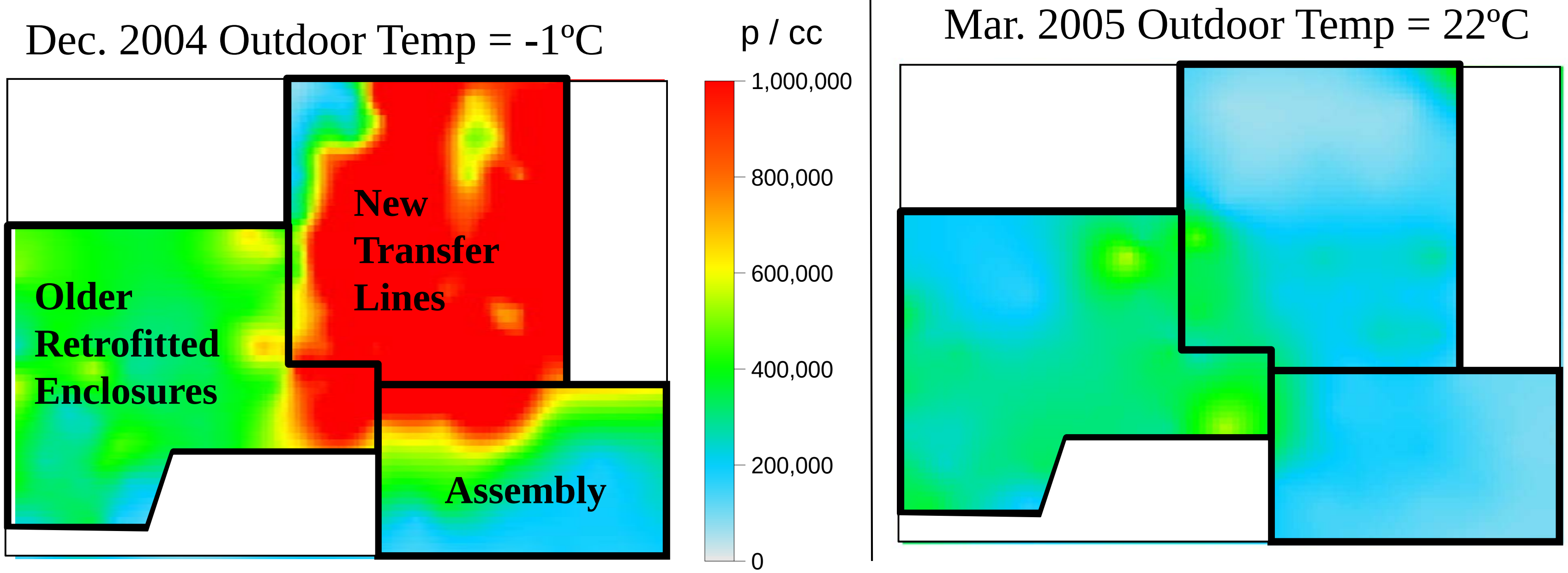
(Clean Air Task Force 2005)

Visible Particles do not Correspond to Ultrafine Particles



Ultrafine particles in an engine assembly plant

- Primary mass source is machining
- Primary particle source is gas fired makeup air

Key Points: Natural gas is "clean" with respect to visible particles, not respirable particles

Some IH sampling issues

- Different emissions from old and new mixed fleets (EC for old; ??? for new)
- Importance of fuel quality control
- Biofuels
- Untreated Exhaust from Leaks (HCHO)
- Crankcase emissions
- Emission control byproducts (ammonia)

Sampling strategy should address problems

DIESEL HEALTH ISSUES

Early Data - Diesel Particulate (DP) Health Effects

- Cellular studies by Paul Kotin in 1954 established solvent extracted chemicals were mutagenic
- Animal studies in rats at maximal doses in mid 1980s showed lung tumors
- Studies of working groups particularly Garshick 1988,1989 and Steenland 1989 showed increased lung cancer risk and dose response with diesel

Later Data: Cell and Animal Studies

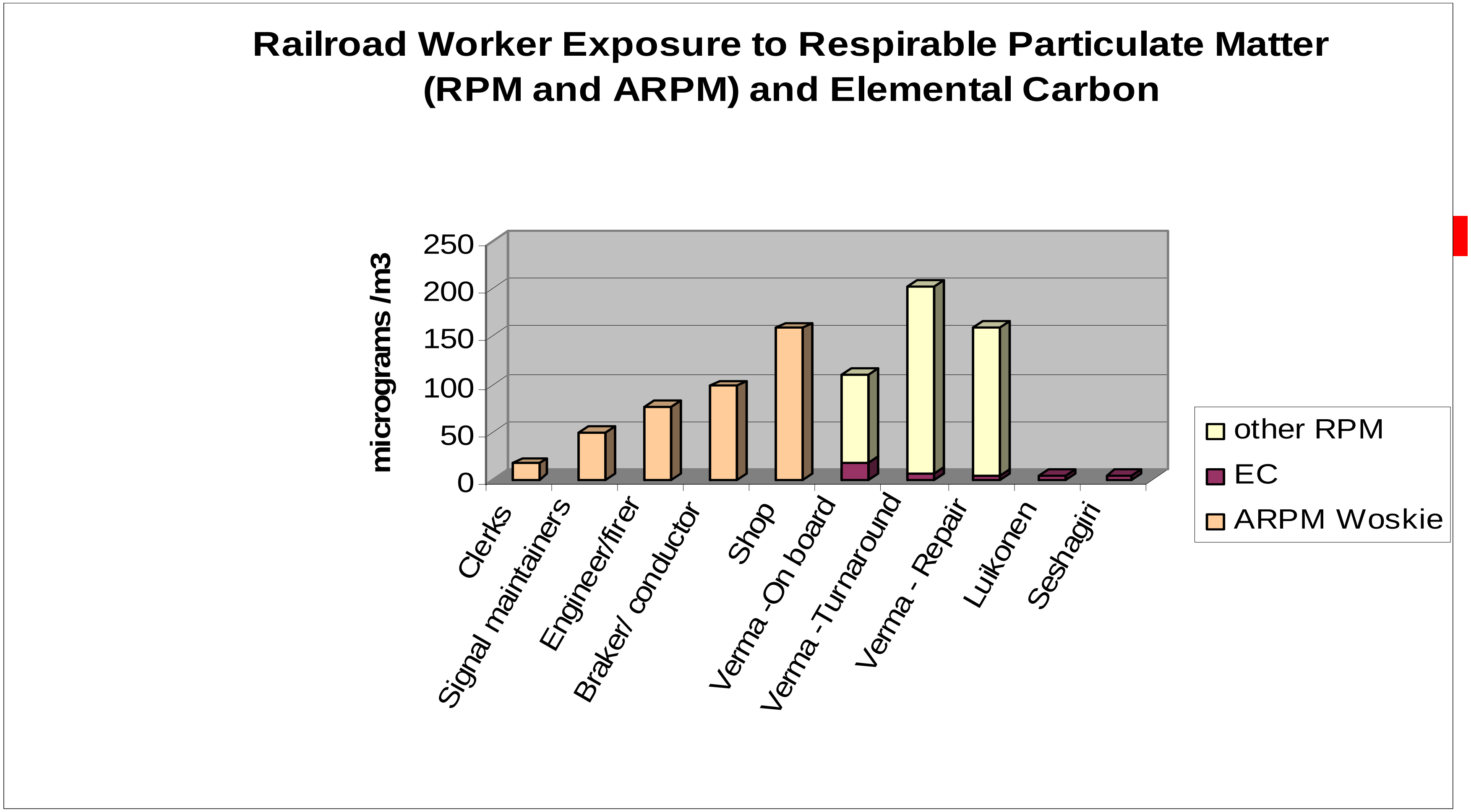
- Cell culture studies with whole diesel particles produce weak mutations (~1 cigarette/2.5 years)
- Studies in mice, hamsters are negative
- Maximum Tolerated Dose (MTD) studies in rats do not show diesel particles to be different from “inert” dusts

Later Data - Epidemiology Studies of Diesel Exhaust

- Only two completed studies measured exposures of diesel
  - Garshick study of railroad workers
  - Steenland (truckers)
  - Both used years worked before and after dieselization

Railroad Worker Exposure to Diesel reconstructed

- Hammond (1988) and Woskie (1988)
  1. Respirable particulate matter (RPM)
  2. Adjusted Respirable Particulate Matter (ARPM)
  3. Adjusted Extractable Matter (AEM)
- Verma (1999, 2003)
  - Elemental Carbon (EC); Respirable Combustible Dust (RCD); RPM
- Seshagiri (2003)
  - EC
- Liukonen (2002)
  - EC; Total Carbon (TC)

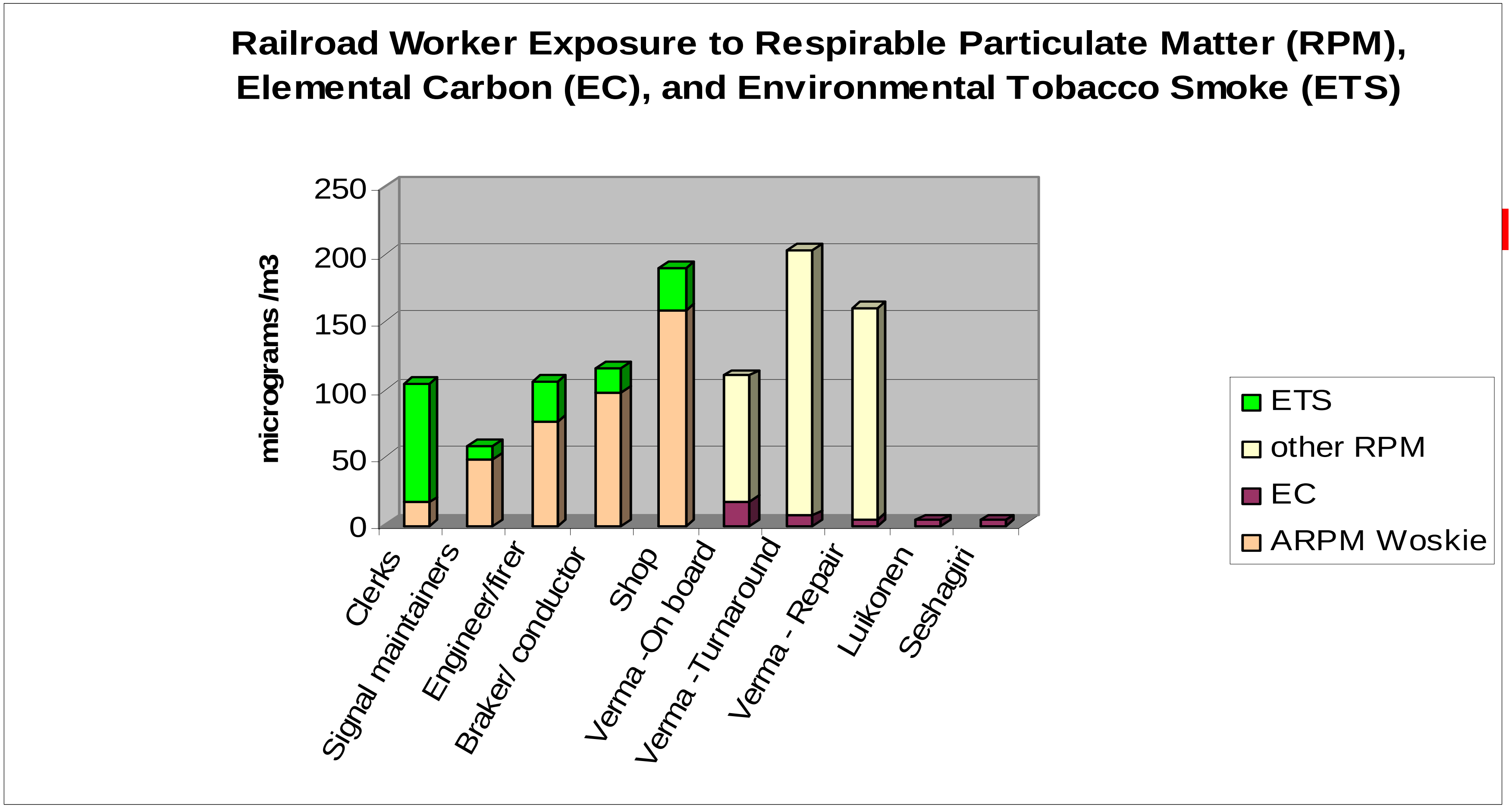


Key Points:

•RPM and ARPM are in the same ballpark across studies; EC results are also consistent

•EC exposures indicate that DPM may be small part of overall RPM exposure

•Characterization of exposure based only on ARPM may be misleading



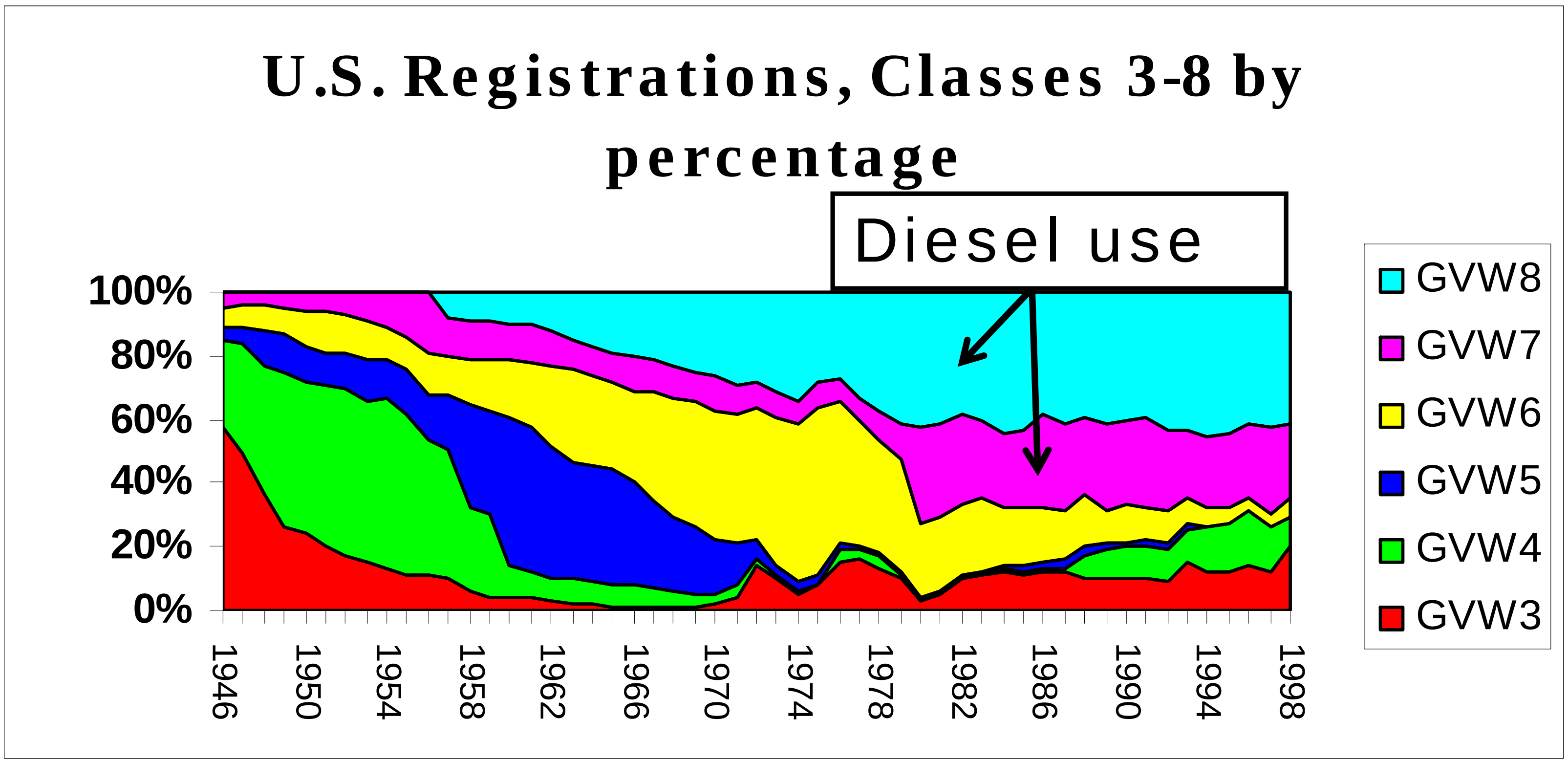
Key Points:

•ARPM data reveals high levels of ETS compared to likely DPM

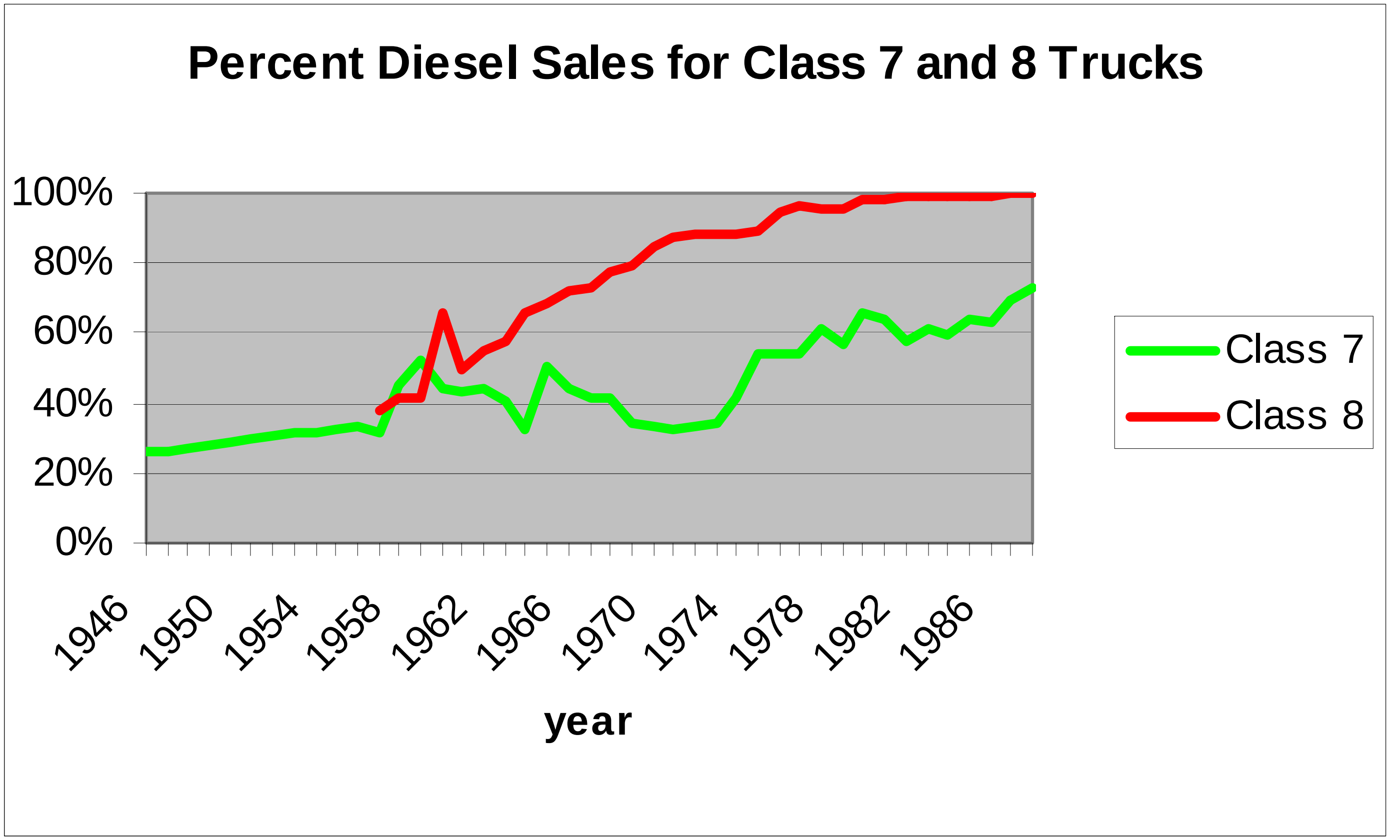
Steenland Trucker Study

- Assumptions
  - 1960 is used as date of truck dieselization.
  - Exposure measurements of diesel taken in 1991 used to estimate exposures to truckers who worked from 1959 to 1983.
- Problems
  - Diesel fleet conversion occurred much later than assumed based on sales and even later based on truck service life of over 10 years.
  - On the road exposures include exhaust from other vehicles, gasoline and diesel
  - Non-diesel exposures for truckers are much greater than diesel exposures
- Diesel exposures for lung haul truckers (class 7/8) are at background levels even after dieselization (Smith et al)

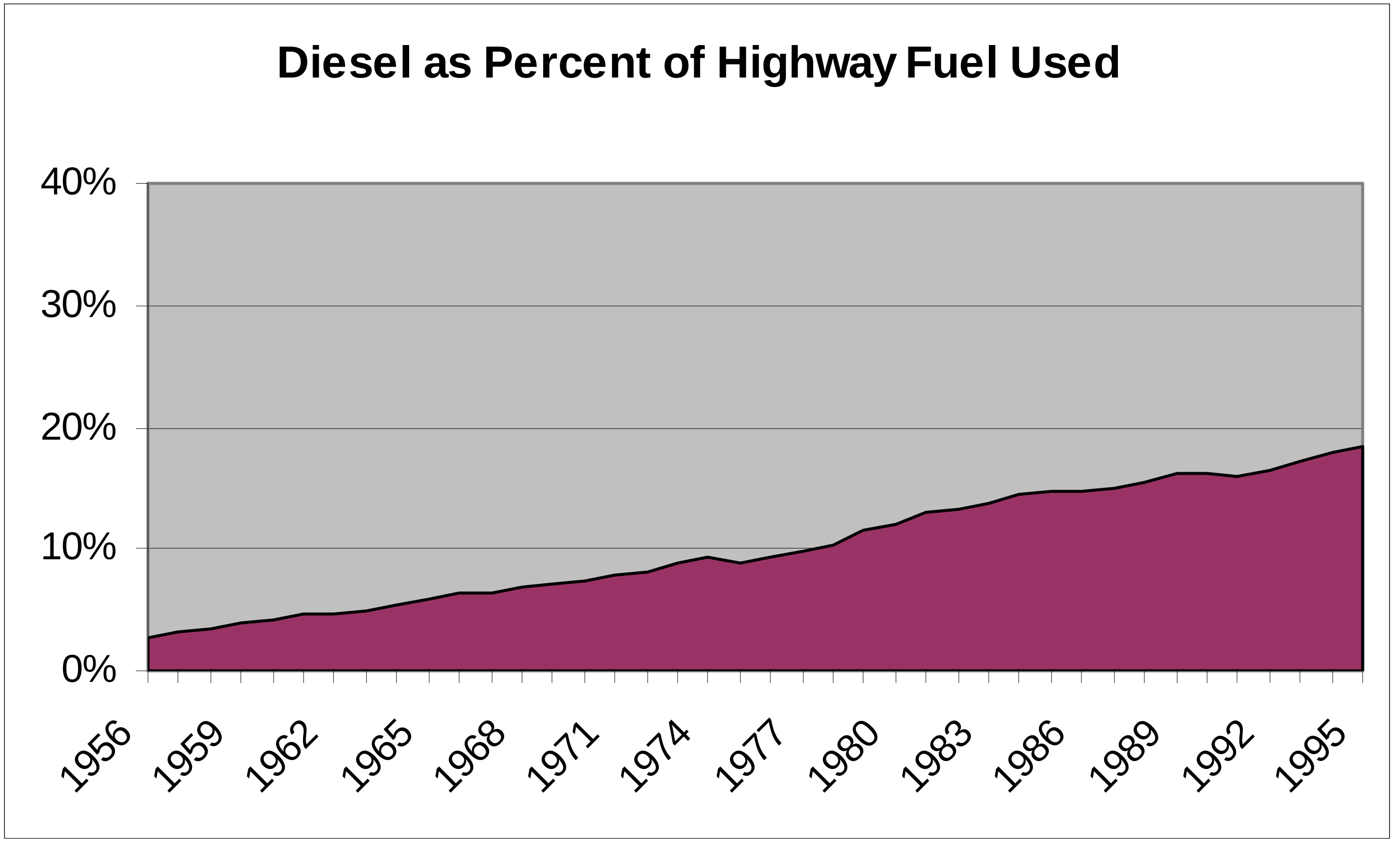
Before 1970 Most Trucks Sold Were in Lighter Gross Vehicle Weight Classes

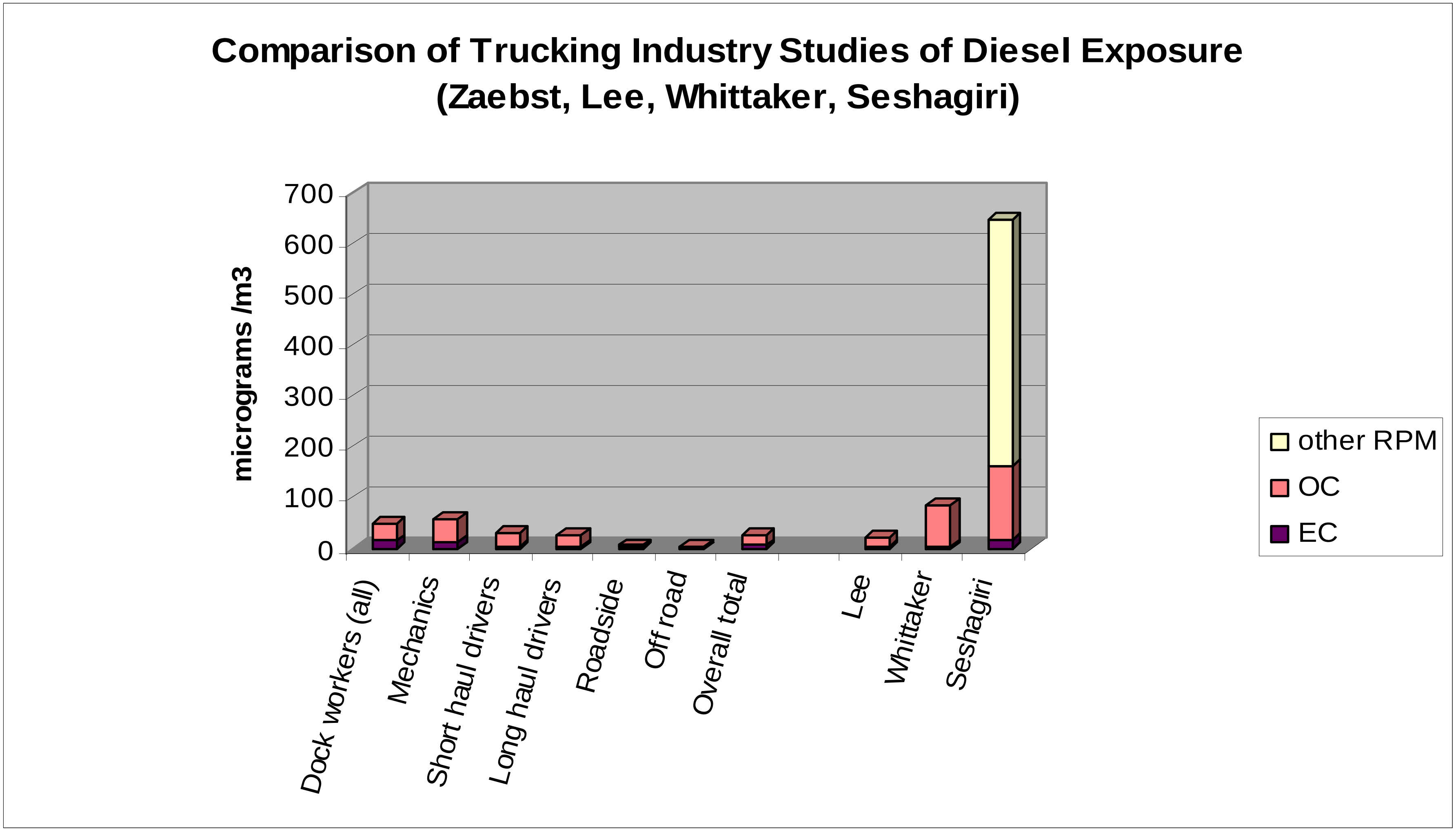


Diesel Percentage of Heavy Duty Truck Sales Increased Gradually and Fleets Converted to Diesel Later than 1960



On the Road Exposures Include Significant Non-Diesel Sources



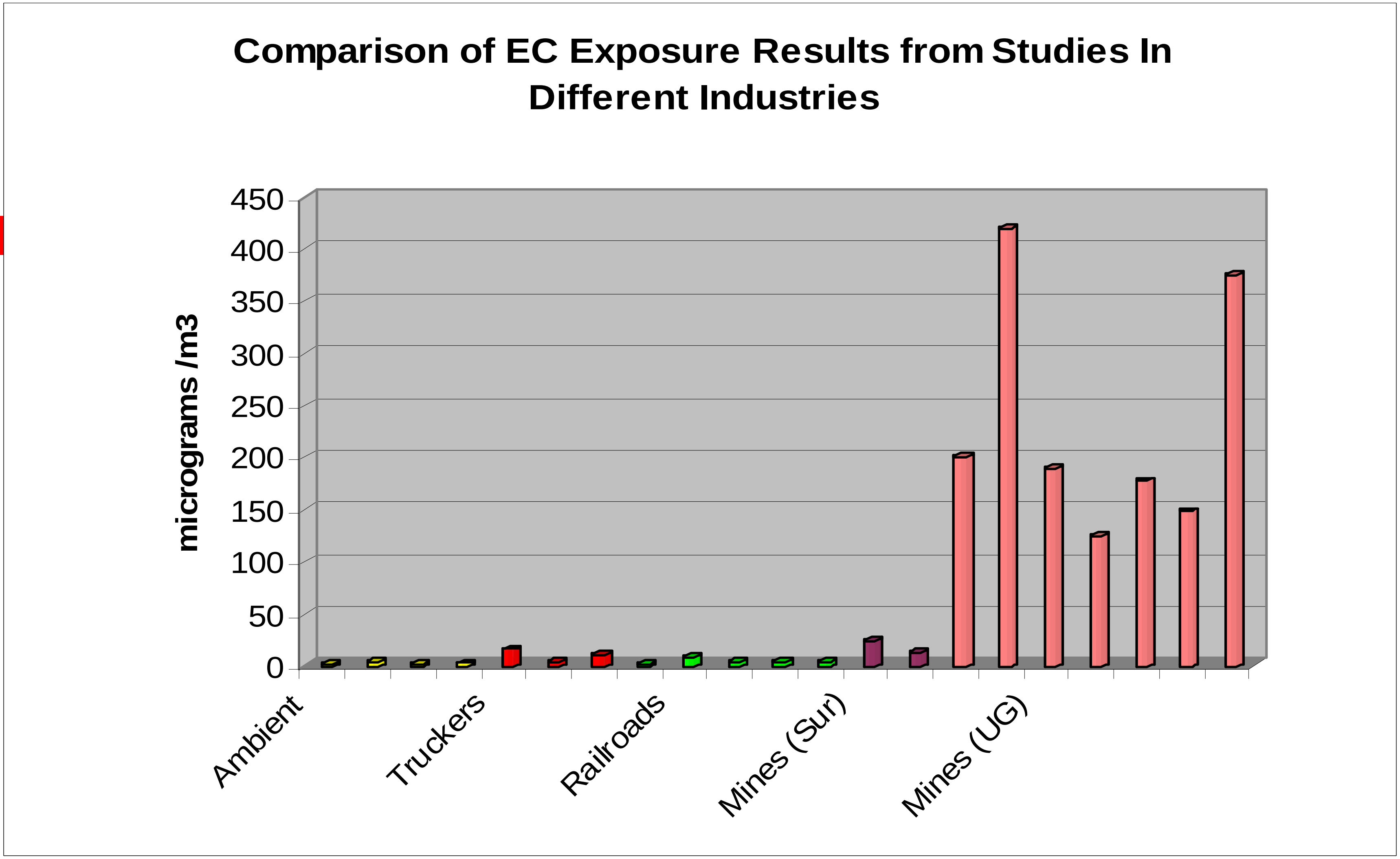


Key Points:

•DPM may be small part of respirable particulate exposure

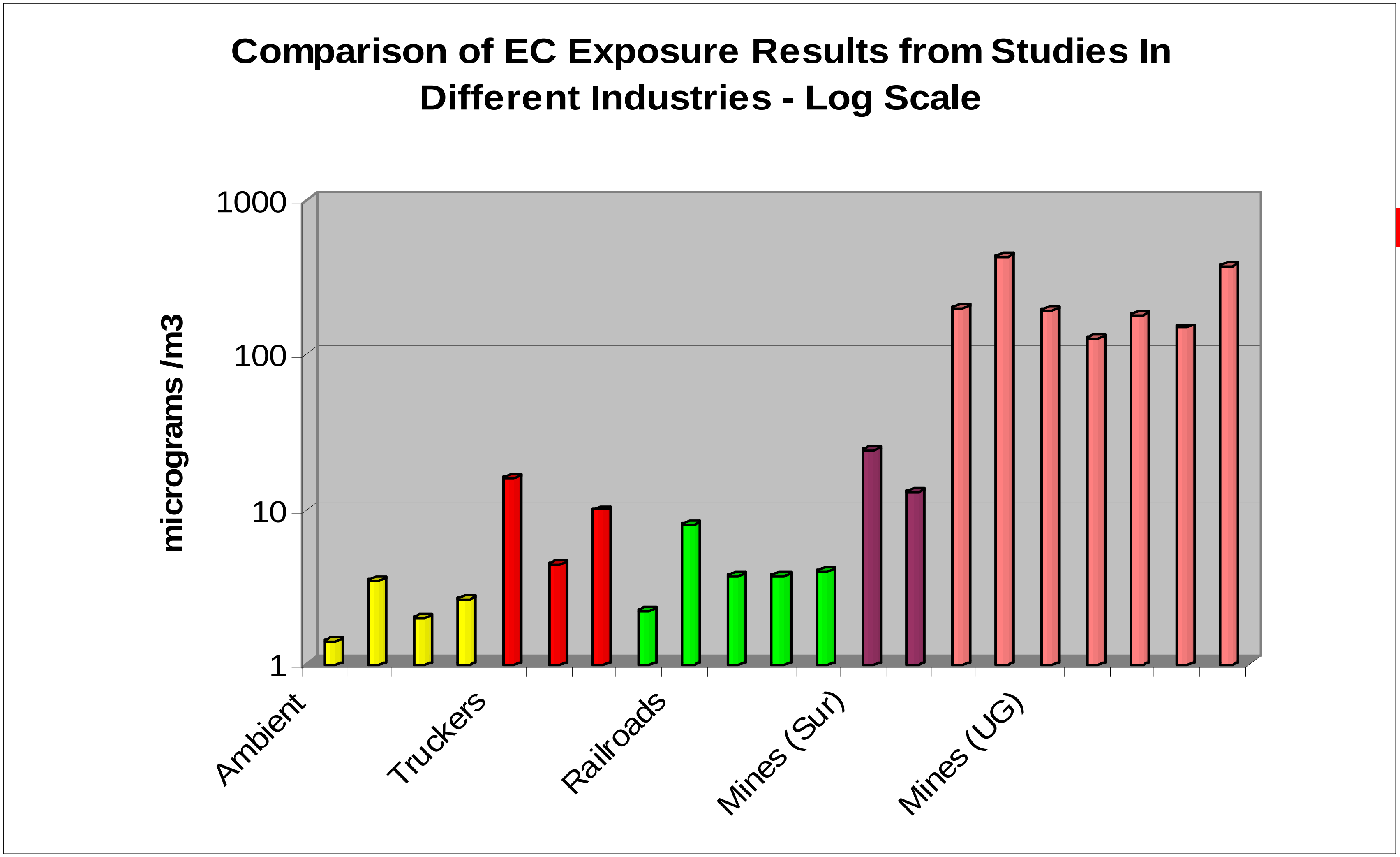
Mining exposures provide another useful population to study relation between lung cancer and diesel exposure

- ⌘Diesel fueled equipment documented in mining for more than 60 years (sufficient latency).
- ⌘Exposures in mines using diesel are relatively high (higher than other occupations by an order of magnitude).
- ⌘Many useful studies have been conducted on miners (often for effects of coal, silica, radiation, or other agents but also relevant to diesel).



Key points:

- EC provides a way to compare exposure study results across industries
- DPM exposure in underground mining is much greater than in other industries.



Key Point:

•Underground mining exposures are an order of magnitude greater than other industries.

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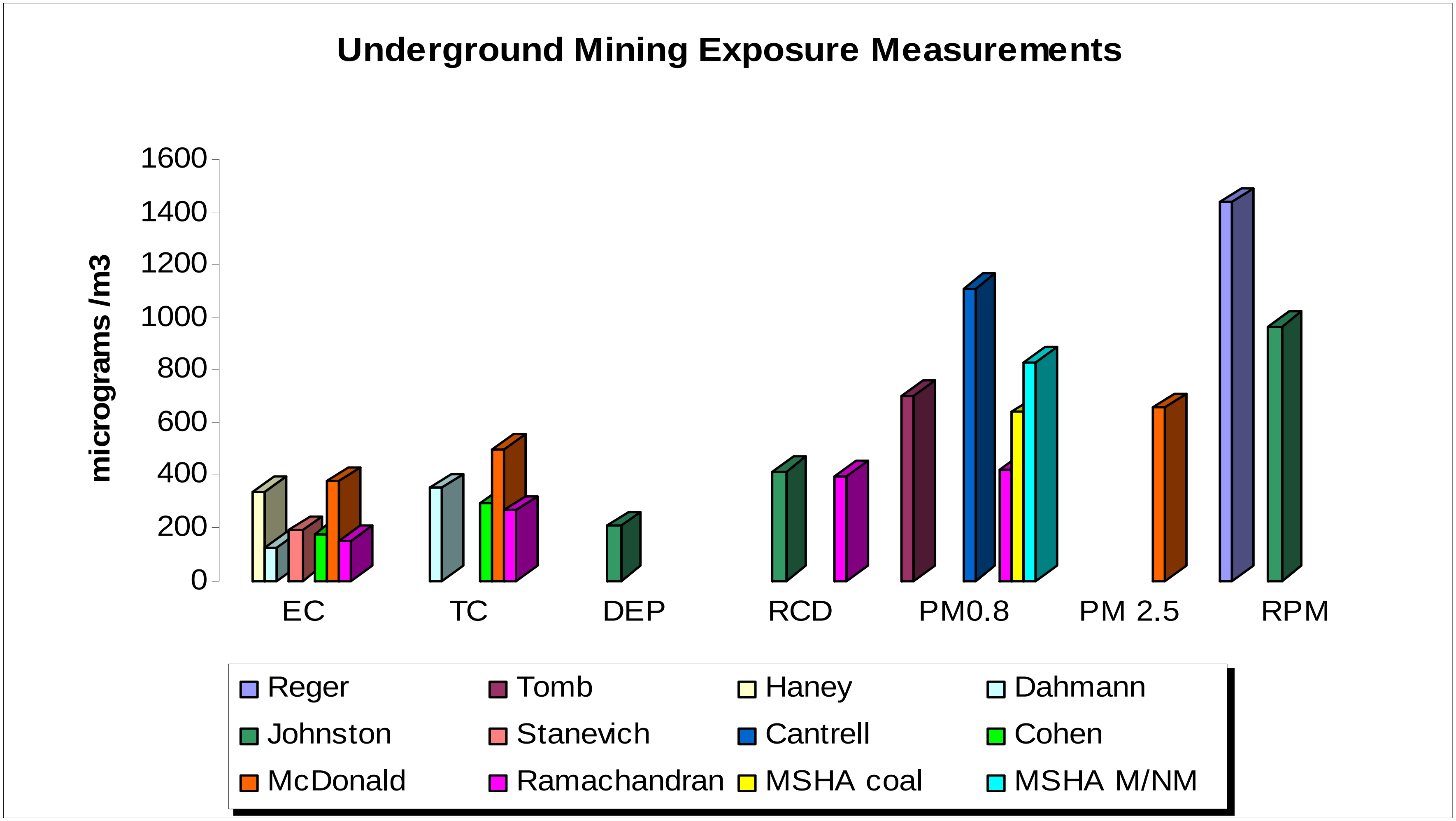
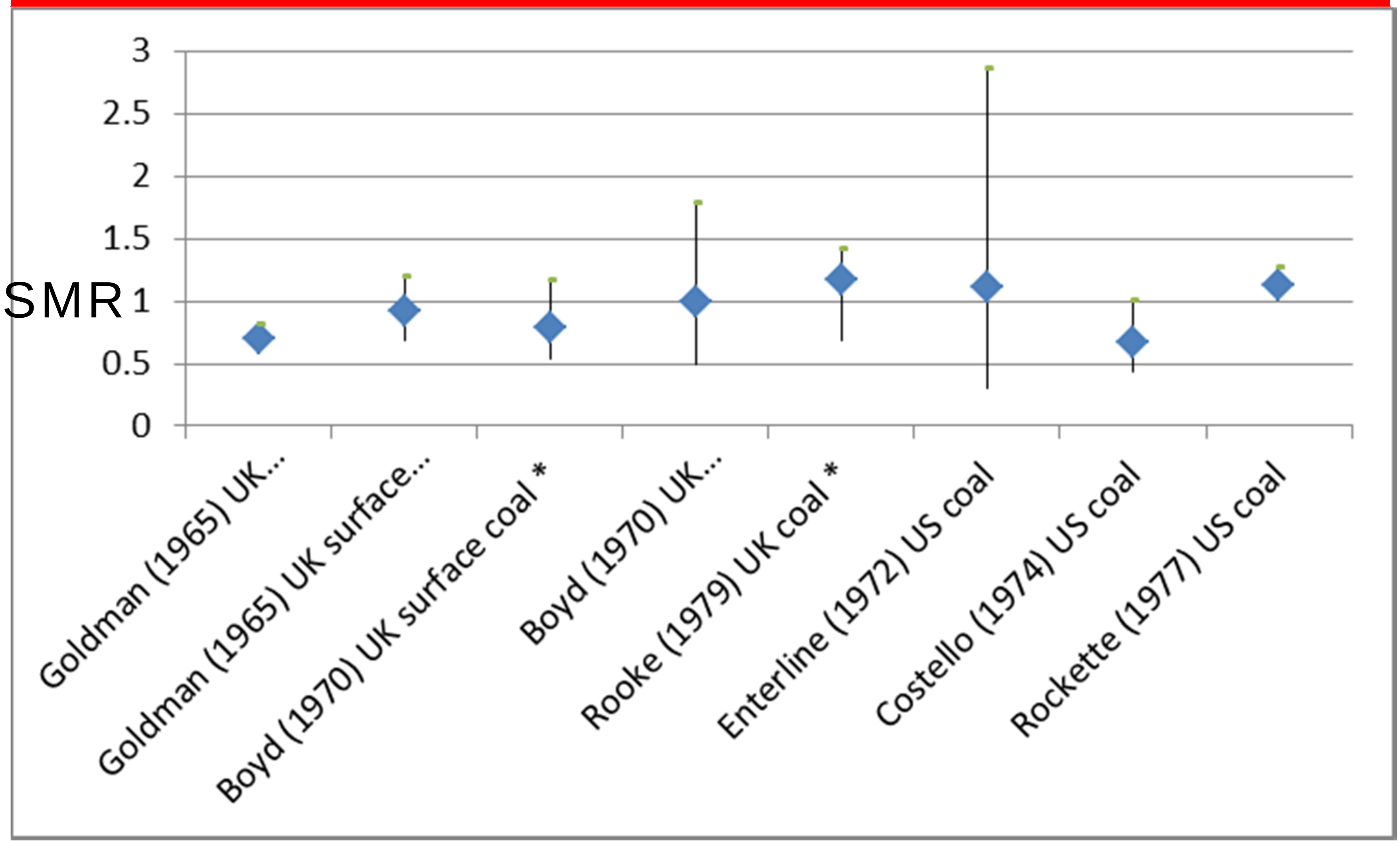


Key Points:

- From left to right methods become more inclusive
- EC results indicate that DPM is significant part of particulate exposure

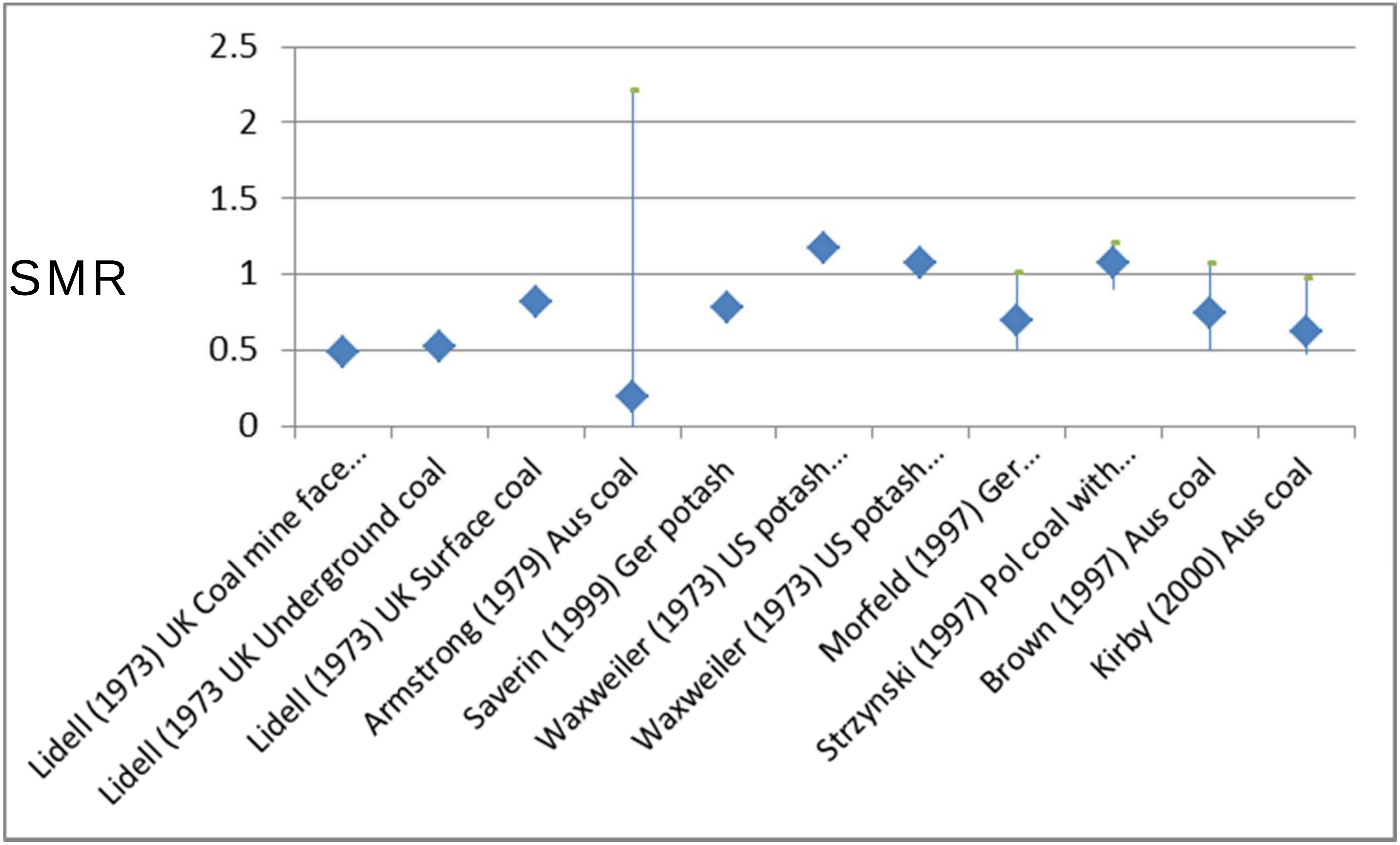
Miners not Exposed to Diesel

Lung Cancer SMR (*PMR) with 95% CI



Miners Exposed to Diesel

Lung cancer SMR and 95% CI where available



IARC Classification

- Lyon, France, June 12, 2012 -- After a week-long meeting of international experts, the International Agency for Research on Cancer (IARC), which is part of the World Health Organization (WHO), today classified diesel engine exhaust as carcinogenic to humans (Group 1), based on sufficient evidence that exposure is associated with an increased risk for lung cancer.

Basis for IARC conclusion: Seven fold increase in lung cancer

The Diesel Exhaust in Miners Study: A Nested Case–Control Study of Lung Cancer and Diesel Exhaust (2011). Debra T. Silverman, Claudine M. Samanic, Jay H. Lubin, Aaron E. Blair, Patricia A. Stewart, Roel Vermeulen, Joseph B. Coble, Nathaniel Rothman, Patricia L. Schleiff, William D. Travis, Regina G. Ziegler, Sholom Wacholder and Michael D. Attfield

The Diesel Exhaust in Miners Study: A Cohort Mortality Study With Emphasis on Lung Cancer (2011). Michael D. Attfield, Patricia L. Schleiff, Jay H. Lubin, Aaron Blair, Patricia A. Stewart, Roel Vermeulen, Joseph B. Coble and Debra T. Silverman

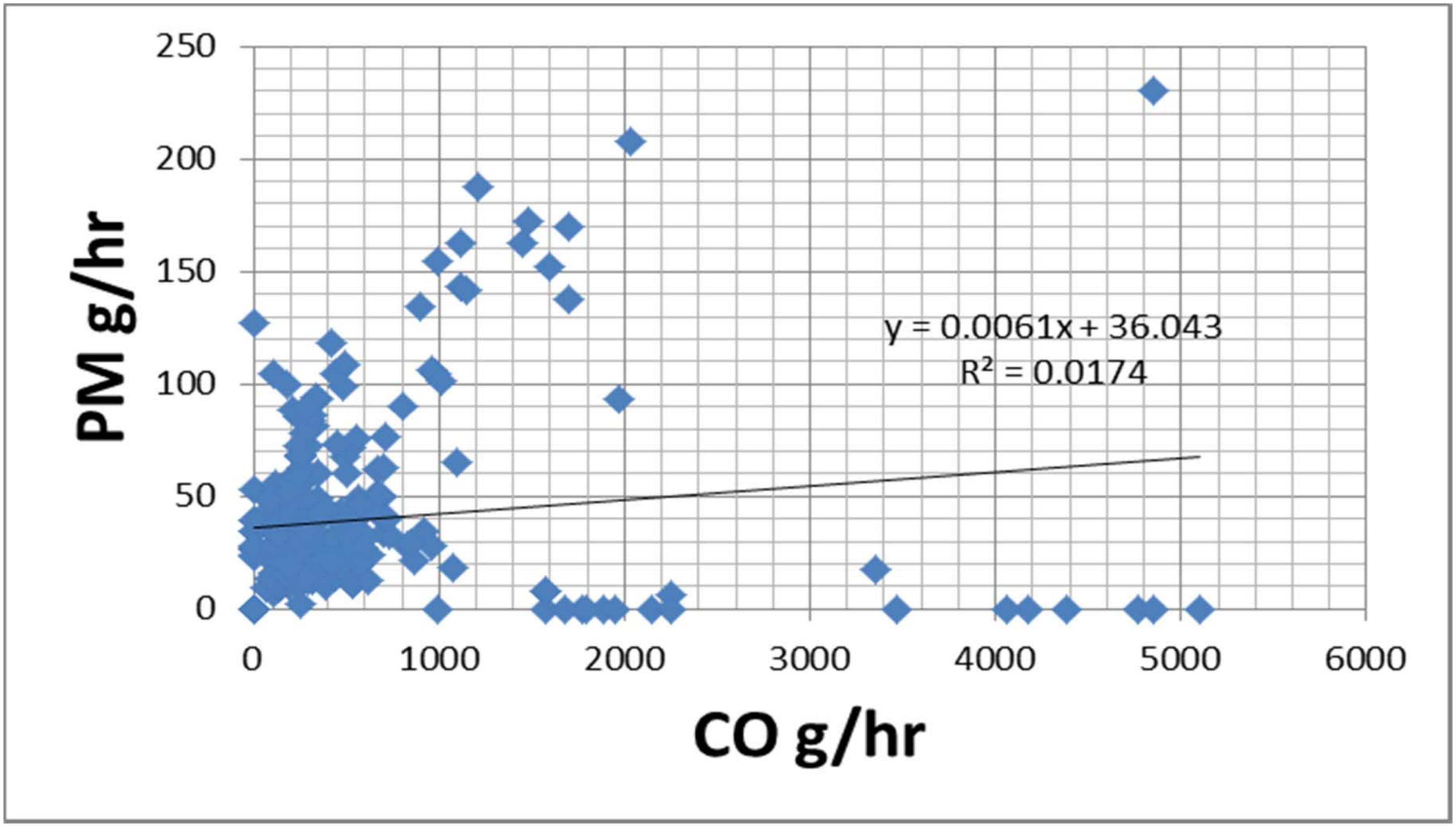
IARC Conclusion

- ⌘New miner study results show 7 fold increase in cancer risk
- ⌘Researchers took 15 years to analyze data
- ⌘Results not consistent with other miner data
- ⌘Data not shared for review despite court orders until after publication

Miner Exposure Data

- Historical measurements and surrogate exposure data, along with study industrial hygiene measurements, were used to derive retrospective quantitative estimates of respirable elemental carbon (REC) exposure for each worker.
- CO used as surrogate for REC

How well is CO related to PM?



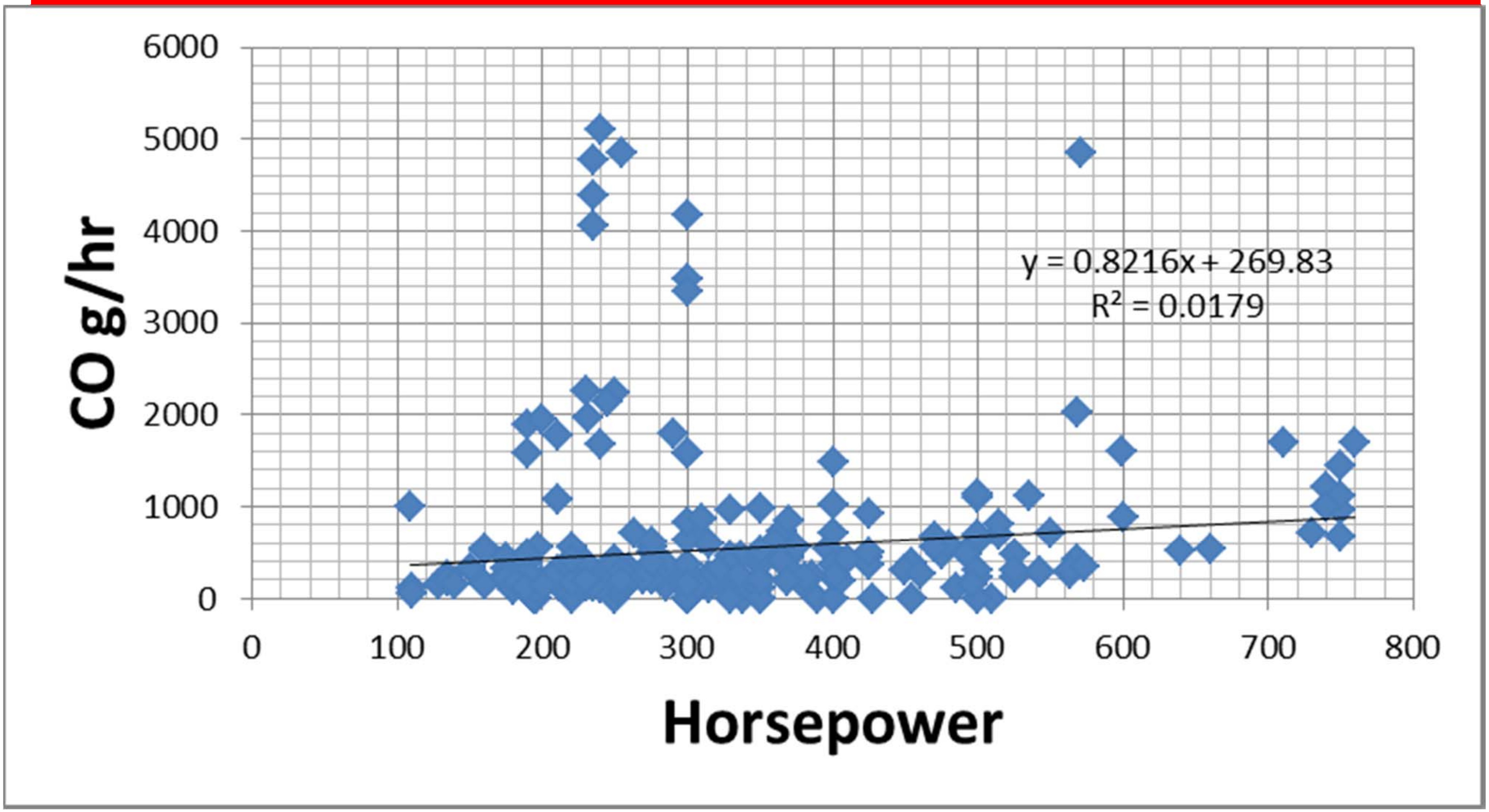
1996 EPA diesel engine certification data

http://www.epa.gov/otaq/certdata.htm#early-lgeng

Use of CO as surrogate

- ⌘Use of CO as surrogate considered "novel" and therefore worthy of publication
- ⌘Many CO measurements below detection level
- ⌘Where no CO measurements available, mining equipment horsepower was used to estimate CO

How well is horsepower related to CO



1996 EPA diesel engine certification data

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http://www.epa.gov/otaq/certdata.htm#early-lgeng

Summary-
Diesel Exposure and Risk

- No Diesel DNA; exposure measurement methods require judgment and assumptions.
- Large differences across DPM measurement methods.
  - Most gravimetric measurement techniques include other exposures.
  - EC may be the most accurate indicator of traditional DPM.
  - New diesel is different from old diesel
- Base measurement strategy on nature of problem
- Diesel exposure health effects
  - New diesel vs. old diesel
  - IARC conclusion is based on a single data set with highly unusual exposure calculation

Abbreviations/Acronyms

- AEM – adjusted extractable matter
- ARPM – Adjusted respirable particulate matter
- BC – Black Carbon
- CARB – California Air Resources Board
- CASAC – Clean Air Science Advisory Committee
- CI – confidence interval
- CO – carbon monoxide
- CO_2 – carbon dioxide
- CNG – compressed natural gas
- CRT – continuously regenerating trap
- DEF – diesel exhaust fluid
- DEP – diesel exhaust particulate
- DP - diesel particulate
- DPF – diesel particulate filter
- DPM – diesel particulate matter
- EC – elemental carbon
- EC-1 – environmental class 1 (10ppm S)
- EGR – exhaust gas recirculation
- EPA – Environmental Protection Agency
- EPEFE – European Programs on Emissions Fuels and Engine technologies
- ETS – environmental tobacco smoke
- GVW – gross vehicle weight
- HC – hydrocarbon
- HCHO – formaldehyde
- HEI – Health Effects Institute
- HP – horsepower
- IARC – International Agency for Research on Cancer
- MTD – maximum tolerated dose
- NMHC – non-methane hydrocarbons
- NO_2 – nitrogen dioxide
- NOx – nitrogen oxides
- OICA – International organization of automobile manufacturers
- p/cc – particles per cubic centimeter
- PAH – polycyclic aromatic hydrocarbons
- PM – particulate matter
- PMR – proportionate mortality ratio
- POM- polycyclic organic matter
- RCD – respirable combustible dust
- REC – respirable elemental carbon
- RPM – respirable particulate matter
- SCR – selective catalytic reduction
- SMR – standardized mortality ratio
- TC – total carbon