Air pollution and traffic: Searching for the missing emissions

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2 National Centre for Atmospheric Science, University of York.
Established in 2013, the UK’s first dedicated atmospheric chemistry laboratory
800 m², £2M, state of the art labs
Local and global air pollution, stratospheric ozone depletion, climate change
45 researchers from seven academic groups
Science and evidence support to Defra

http://wacl.org.uk/
The rise of diesel

- Over the last 10 years there has been a huge increase in the fraction of diesel used worldwide.
- Manufacturers estimate that by 2040 diesel will be the number 1 transport fuel globally (ExxonMobil, BP, OPEC).

Exxon Mobil, Outlook for Energy: A view to 2040, 2016
The rise (and fall?) of diesel

Volkswagen AG
Audi AG
Volkswagen Group of America, Inc.

David Gennacoopoulos
Executive Vice President Public Affairs and General Counsel
Volkswagen Group of America, Inc.
2200 Ferdinand Porsche Drive
Hemdon, VA 20171

Stuart Johnson
General Manager
Engineering and Environmental Office
Volkswagen Group of America, Inc.
3801 Hamlin Road
Auburn Hills, MI 48326

Re: Notice of Violation

Dear Mr. Gennacoopoulos and Mr. Johnson:

The United States Environmental Protection Agency (EPA) has investigating Volkswagen AG, Audi AG, and Volkswagen Group of America for compliance with the California Air Resources Board (CARB) regulations. As detailed in this Notice of Violation (NOV), the EPA has manufactured and installed defeat devices in certain model year 2009 and 2013 model year 2.0 liter engines. These defeat devices by inoperative elements of the vehicles’ emission control system that exist to comply with CAA emission standards. Therefore, VW violated section 203(a)/(b) of the CAA, 42 U.S.C.

Comparison of Airborne NOx Flux to NAEL Emission Estimates

NOx Flux/ mg m^-2 hr^-1

- 0.00 - 1.00
- 1.01 - 2.00
- 2.01 - 3.00
- 3.01 - 4.00
- 4.01 - 5.00
- 5.01 - 6.00
- 6.01 - 8.00
- 8.01 - 10.00
- 10.01 - 12.00
- 12.01 - 15.00
- 15.01 - 18.00
- 18.01 - 20.00
- 20.01 - 22.00
- 22.01 - 25.00
- 25.01 - 30.00
- 30.01 - 35.00
- 35.01 - 40.00
- 40.01 - 50.00
- 50.01 - 60.00
- 60.01 - Above

Remote sensing data

Volkswagen AG
Audi AG
Volkswagen Group of America, Inc.

Carslaw and Rhys-Tyler, 2013, Atmospheric Environment, Vol. 81 339-347

Vaughan et al., Faraday Discuss., 2015, DOI: 10.1039/C5FD00170F
Diesel Emissions

Diesel engine → DOC

NO >> NO₂
CO >> CO₂
HC >> CO₂ + H₂O

DOC → DPF

Soot oxidation by NO₂
C + O₂ >> CO₂

DPF → Emission

NOₓ, CO, CO₂, PM + oxidised VOCs + unburnt fuel

If the NOₓ is too high, what about the hydrocarbons (and should we care)?
Volatile Organic Compounds and Air Quality

Volatile organic compounds (VOC) + Oxidants (OH-, O₃, NO₃)

Anthropogenic and biogenic gaseous emissions

Less volatile organics

Condensation/coagulation

Secondary Organic Aerosols

Gas phase oxidation

Volatile organic compounds (VOC) + Oxidants (OH-, O₃, NO₃) → Ozone

Gas phase oxidation (NOx)
Current national emission estimates drive both policy and observation.
- This *relative* distribution should be typical of most developed countries.
- As a result of tighter regulations, levels of smaller hydrocarbons are declining.

The $C_n$ emissions have been estimated by applying the speciated inventory of emission sources of Passant (2002) to the most recent estimates of non-methane hydrocarbon source apportionment for each country.
Are diesel emissions important for urban SOA?

- SOA formation potential depends on reactivity and volatility of emissions
- Conflicting results make this difficult to answer

Results indicate less volatile components of diesel emissions “intermediate” volatility organic compounds (IVOC) play key role

But are they emitted in high amounts and what is effect of conditions, after-treatment, age of car………?

Novel studies are needed to identify and quantify “missing” emissions that appear to contribute substantially to SOA production

London versus Los Angeles

- A lot of the previous studies of the impact of diesel on atmospheric SOA have been carried out in the USA.
- There are huge differences between London and LA.

<table>
<thead>
<tr>
<th></th>
<th>Area (km²)</th>
<th>Number of inhabitants</th>
<th>Population density (inhabitants per km²)</th>
<th>Cars per household</th>
<th>% public green space</th>
<th>% diesel use</th>
<th>Average T (°C) in winter and summer</th>
<th>Average hours of sunlight in winter and summer (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>London</td>
<td>1572¹</td>
<td>7,825,200¹</td>
<td>4978¹</td>
<td>0.8⁵</td>
<td>38.4¹</td>
<td>57⁷</td>
<td>3 and 18.9⁹</td>
<td>2.2 and 5.9¹¹</td>
</tr>
<tr>
<td>North Kensington</td>
<td>12.13²</td>
<td>158,700³.⁴</td>
<td>13,087³.⁴</td>
<td>0.6⁶</td>
<td></td>
<td>56³.⁷</td>
<td>13.8 and 21.4¹⁰</td>
<td>6.6 and 11.1¹²</td>
</tr>
<tr>
<td>LA</td>
<td>10510¹</td>
<td>9,818,605¹</td>
<td>934¹</td>
<td>1.9²</td>
<td>6.7¹</td>
<td>13³</td>
<td>13.8 and 21.4¹⁰</td>
<td>6.6 and 11.1¹²</td>
</tr>
<tr>
<td>Bakersfield</td>
<td>244.77²</td>
<td>357,603⁴</td>
<td>1461⁴</td>
<td></td>
<td></td>
<td>33³</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References
⁻¹World Cities Cultural Report, 2013
⁻²Calculated from number of inhabitants and population density
⁻³Values for Kensington and Chelsea
⁻⁴Census, July 2012
⁻⁵US Census Bureau
⁻⁶UK Office of National Statistics
⁻⁷Department of Energy and Climate Change statistics
⁻⁸Gentner et al (2012)
⁻⁹metoffice.gov.uk, mean daily temperature
⁻¹⁰los-angeles.climatemps.com/temperatures.php
⁻¹¹metoffice.gov.uk, mean daily hours of sunshine
⁻¹²los-angeles.climatemps.com/sunlight.php

- Care needs to be taken when comparing to previous studies.
Research Approach

A better understanding of VOC emissions and aerosol chemistry will help to understand SOA sources.

New technologies

High resolution chromatography and mass spectrometry

Field measurements

Atmospheric simulations

Clearflo – London 2012
ACACCIA – Arctic, 2013
OP3/ACES – Borneo, 2008

York Aerosol Chamber
EUPHORE, Valencia
Manchester Aerosol Chamber
Why is measuring VOCs difficult?

- Low concentrations – parts per trillion
- Complex matrix
- Huge range of polarities
- Isomeric complexity

For \( \text{C}_{10} \) – more than a million organic compounds possible

\( \text{C}_{14} \) \( \text{C}_{15} \)

Unidentified complex mix seen

GC does not have sufficient resolving power for full speciation

Liang et al., JEM, 2005

Goldstein and Gallbaly, ES&T, 2007
Comprehensive two-dimensional gas chromatography (GC × GC)

- 2 GC columns used with different separation mechanisms
- Connected via a modulator
  - cryogenic, thermal, valve

Allows much better speciation of complex mixtures

Viewed as a contour plot

Taken from Blomberg et al., J. Chrom. A, 972, 2002, 137-173
Atmospheric Applications

- GCXGC first extended to the atmosphere in 2000
- Can separate over 600 volatile organic species in urban air.
- The raised baseline seen late in 1D-GC was found to be a constantly co-eluting mix of hundreds of low volatility compounds at low concentrations.

Up to 70x signal enhancement due to very narrow peaks (10-200 ms)

Improved background

Structured chromatograms – “roof-tiles”

Monoaromatic bands benzne + A=C<sub>2</sub>, B=C<sub>3</sub>, C=C<sub>4</sub>, D=C<sub>5</sub>, E=C<sub>6</sub>, F=C<sub>7</sub>, G=C<sub>8</sub>, H=naphthalene.

Chemical banding assignments, 1; aliphatic, 2; olefins, 3; oxygenates, 4; mono aromatics, 5; polyaromatics.

*Lewis et al., 2000, Nature, 405, 778-781*  
*Hamilton et al., 2003, Atmos. Env., 37, 589-602*
Clean Air for London (Clearflo) Project
Measurement Sites

- Rural:
  - Chilbolton
  - Harwell

- Urban background:
  - North Kensington

- Elevated:
  - BT Tower (180m)
  - KCL Roof (35 m)

- Kerbside:
  - Marylebone Road
VOC Measurements

- Hourly measurements of 78 VOCs
- Winter and Summer 2012
- In total, 2667 samples
  - DC-GC measured volatile VOCs
    - C$_1$-C$_7$ hydrocarbons and selection of OVOCs
  - GC $\times$ GC-FID, less volatile fraction
    - C$_6$-C$_{13}$ hydrocarbons and a large groups of OVOCs

Dunmore et al., ACP, 15, 9983-9996, 2015
GC × GC measurements of VOCs

GC × GC-FID plot from winter 2012-02-07 at 08:32
Using GC × GC to group compounds

Number of isomers in each group

<table>
<thead>
<tr>
<th>Groups</th>
<th>Isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6 Aliphatics</td>
<td>9</td>
</tr>
<tr>
<td>C7 Aliphatics</td>
<td>10</td>
</tr>
<tr>
<td>C8 Aliphatics</td>
<td>25</td>
</tr>
<tr>
<td>C9 Aliphatics</td>
<td>28</td>
</tr>
<tr>
<td>C10 Aliphatics</td>
<td>40</td>
</tr>
<tr>
<td>C11 Aliphatics</td>
<td>41</td>
</tr>
<tr>
<td>C12 Aliphatics</td>
<td>37</td>
</tr>
<tr>
<td>C13 Aliphatics</td>
<td>30</td>
</tr>
<tr>
<td>C4 substituted monoaromatics</td>
<td>16</td>
</tr>
<tr>
<td>Monoterpenes</td>
<td>25</td>
</tr>
</tbody>
</table>
Average diurnal profiles of VOCs

Carslaw and Ropkins, Environmental Modelling and Software, 2012, Openair software for R
Assigning VOCs to emission sources

- We split the VOCs by $C_n$ and functionality to investigate relative emission strength

But what is the source of the VOCs?

Source apportionment
- Assume 60% diesel use in London
- Assume NAEI correctly apportions the split between natural gas and gasoline
- Use the liquid fuel composition to apportion a % of $>C_6$ to diesel and gasoline
- Estimate primary OH reactivity

$$\text{OH reactivity (s}^{-1}) = ([\text{VOC}] \text{ (ppbv) } \times 10^{-9} \times [M]) \times k_{OH}(298 \text{ K})$$
Inventory Comparison

- Assuming that
  1. our winter observations are made ‘at source’
  2. UK inventory correctly estimates the emission for toluene*

- Significant inventory under-reporting for the higher carbon number species

*Langford et al., ACP, 2010.
Estimating the unmeasured diesel emissions

- The combined approach used in Clearflo covers around:
  - 95% of gasoline emissions range
  - 20-35% of diesel emissions range

- Therefore we can estimate the unmeasured diesel gaseous emissions

- Seasonal average unmeasured gas phase VOC mass concentrations in London from diesel
  - 60.6-130.5 μg m⁻³ in winter
  - 21.3-45.9 μg m⁻³ in summer

Gentner D R et al. PNAS 2012;109:18318-18323
Impact on SOA formation

- We can investigate the potential SOA source of the different sources
- Use the aerosol yield to estimate the “potential” SOA mass
  - *i.e.* how much SOA could form from 1 m$^3$ of London air (assuming no losses)

Y values taken from Ait-Helal et al., ACPD, 2014, Odum et al., ES&T, 1996
Adding the diesel IVOC to current inventories

- In order to model the impacts of diesel related IVOCs on ozone and SOA, they need to be added to the inventory
- Used the EMEP4UK model and added diesel IVOC to the Road Transport emission category

<table>
<thead>
<tr>
<th>Table 2: Comparison of diesel and gasoline NMVOCs in the UK National Atmospheric Emissions Inventory (NAEI) with the urban background ambient concentrations measured during the ClearFlow winter Intensive Observation Period in London.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAEI 2012</td>
</tr>
<tr>
<td>Diesel-(I)VOCs</td>
</tr>
<tr>
<td>Gasoline-VOCs</td>
</tr>
<tr>
<td>Diesel/Gasoline</td>
</tr>
</tbody>
</table>

$^a$ Dunmore et al. (2015).

- Extra diesel IVOC added as pentadecane to every country in model domain using same factor as UK
  - Average $C_n$ of diesel is 14.9 (Gentner et al., 2012)
  - Rate constant with OH and SOA yields are known
  - Linear alkane is good representation of average rate of reaction of all isomers

Ots et al., ACP., 16, 6453-6473, 2016
Addition of diesel IVOC improves model measurement agreement.

Diesel IVOC account for on average 30% of the annual SOA in UK in model.
Testing diesel emissions in the lab

- The NERC funded COM-PART* project aims to improve our understanding of diesel exhaust emissions and what happens after they are released
- Universities Manchester, York and Birmingham
- Real world driving conditions

Diesel engine → Atmospheric simulation chamber → Measure emissions and secondary pollution

*Combustion Particles in the Atmosphere, Properties, Transformation, Fate and Impact
Testing diesel emissions in the lab

- VW light duty 4-cylinder 1.9L SDi diesel engine
- Mounted on a test rig and coupled to an eddy current dynamometer.
- After-treatment: DOC fitted but not a DPF. This setup is representative of the EURO-4 standard.

Example GCXGC chromatogram of diesel exhaust during COM-PART

Note: emissions will depend on engine conditions, maintenance, age etc...
Impact of engine conditions on IVOC emissions

- How do the diesel hydrocarbon emissions vary under different driving conditions?

**CS** = Cold start  
**exhaust temp** = 85 °C  
**SJ** = short journey from cold  
**exhaust temp** = 169 °C  
**WI** = warm idle after load  
**exhaust temp** = 298 °C

**Contribution of VOCs classes**
Overview of all experiments

Factor of up to 100 difference in total speciated VOCs depending on conditions

Chemical composition of emissions changes with temperature and load

The DOC tested was efficient at removing low molecular weight VOCs (90-100 %)
BUT this dropped rapidly as C\textsubscript{n} increased (C\textsubscript{12} = 0-13 %)
Air pollution in China

- Recent £5.5M NERC-MRC funded an Air Pollution and Human Health in Chinese Megacity program
- Joint with National Natural Science Foundation of China
- 5 projects were funded
  - Sources & emissions of air pollutants in Beijing (AIRPOLL-Beijing) led by Prof Roy Harrison.
  - An integrated study of air pollution processes in Beijing (AIRPRO) led by Prof Ally Lewis
  - Effects of air pollution on cardiopulmonary disease in urban & peri-urban residents in Beijing (AIRLESS) led by Prof Frank Kelly
Beijing site location

- Tower site at the Institute of Atmospheric Physics, between the 3rd and 4th ring roads

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<table>
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<tbody>
<tr>
<td>1</td>
<td>Flux</td>
</tr>
<tr>
<td>2</td>
<td>Manchester</td>
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<tr>
<td>3</td>
<td>Leeds</td>
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<tr>
<td>4</td>
<td>York</td>
</tr>
<tr>
<td>5</td>
<td>IAP</td>
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<tr>
<td>6/7</td>
<td>PKU</td>
</tr>
</tbody>
</table>
Improved IVOC speciation in Beijing — first look!
Conclusions

- In recent years there has been a shift to increasingly diesel-powered fleets in many developed cities
  - Changing the balance of hydrocarbons in urban air
- Unnoticed due to the lack of meaningful measurement infrastructure
- There are already very significant policy challenges for many developed cities relating to the control of NO\textsubscript{2} from modern diesel vehicles
- This study indicates that there may also be a similar, but currently un-recognized, policy challenge to controlling reactive carbon emissions and their contributions to secondary pollutants
- Need further studies of ambient levels of IVOC and their emissions from diesel vehicles.
Acknowledgements

- NERC for funding
- Riinu Ots and Prof. Mat Heal
- Dr David Carslaw
- Dr Richard Derwent
- ClearfLo contributors
- COMPART participants
- Prof Stephen Belcher
- Thanks to you all for listening
• Diesel v petrol composition

• Diesel emission controls

- Diesel engine
- DOC
  - NO >>> NO₂
  - CO >>> CO₂
  - HC >>> CO₂ + H₂O
- DPF
  - Soot oxidation by NO₂
  - C + O₂ >> CO₂
- Emission
Sampler, water trap and GC × GC-FID were built into a single rack.
Impact of diesel emissions on OH reactivity

We calculated primary OH reactivity for unspeciated compounds using rate constants of compounds with similar functionality:
- α-pinene for monoterpenes
- 1,3-diethylbenzene for C₄ monoaromatics
- n-alkane for the aliphatic groups
- n-dodecane for all unmeasured diesel VOCs
Comparison of weekdays versus weekend

- In LA, where diesel are generally heavy-duty trucks, previous studies observed differences between gasoline and diesel VOCs at weekend versus weekday
- Bahreini et al., saw a lower toluene/benzene ratio (i.e. increased photochemistry) at the weekend as a result

A similar analysis of Clearflo shows clear differences between weekdays (red) and weekends (blue)

BUT Petrol and Diesel tracers follow similar trends

Toluene/benzene ratio is higher at weekend

- Due to higher diesel use in London, the LA trends are not observed

Bahreini et al., GRL, 2012, DOI:10.1029/2011GL050718
Air pollution and human health

- Urban population
  - 3% in 1800’s to 47% by the end of the 21st century

- As such urban air pollution has become a significant factor in global health
  - Costs UK society up to £20 billion per year
  - Exposure to particulate matter alone estimated to reduce life expectancy ~ 7-8 months
Estimated VOC OH reactivity in London

**Diesel**
- Winter = 5.5 s\(^{-1}\)
- Summer = 1.9 s\(^{-1}\)

**Gasoline**
- Winter = 1.7 s\(^{-1}\)
- Summer = 0.8 s\(^{-1}\)

- Diesel emissions are 61% of calculated OH reactivity in winter and 36% in summer.
Impact on ozone formation

- We have calculated a ozone production potential using the maximum incremental reactivity (MIR) scale.

- In winter, almost 50% of ozone formation potential is from diesel hydrocarbons.

- In summer, around 25% but doesn’t account for chemistry.

*Figure 7.* Contribution of emission sources to ozone formation potential, where diesel is representative of total diesel emissions and the error bars show the uncertainty of the unobserved diesel fraction calculation.
Conclusions

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  - Changing the balance of hydrocarbons in urban air
- Unnoticed due to the lack of meaningful measurement infrastructure
- There are already very significant policy challenges for many developed cities relating to the control of NO\textsubscript{2} from modern diesel vehicles
- This study indicates that there may also be a similar, but currently un-recognized, policy challenge to controlling reactive carbon emissions and their contributions to secondary pollutants
Testing diesel emissions: COM-PART project

- The Combustion Particles in the Atmosphere project (NERC) is a joint project between Manchester, York and Birmingham (Harrison)
- Aims to study the properties, transformations and impact of diesel emissions across a range of engine loads and atmospheric conditions

Manchester Aerosol Chamber

Gases (NO, CO, CO$_2$, VOC)

Primary particles

SOA
COM-PART Early Results

- Clearflo method modified for higher time resolution
- 25 minute run time but poor chromatography

Diesel exhaust – cold start

Petrol evaporative emissions
Acknowledgements

- NERC for funding
- Dr David Carslaw
- Dr Richard Derwent
- ClearfLo contributors
- Prof Stephen Belcher
- Leco and Markes International for instrument assistance
- Bachok campaign participants and University of Malay

Thanks to you all for listening