Air pollution and traffic: Searching for the missing emissions

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Wolfson Atmospheric Chemistry Laboratories

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- Established in 2013, the UK's first dedicated atmospheric chemistry laboratory
- 800 m^2, £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

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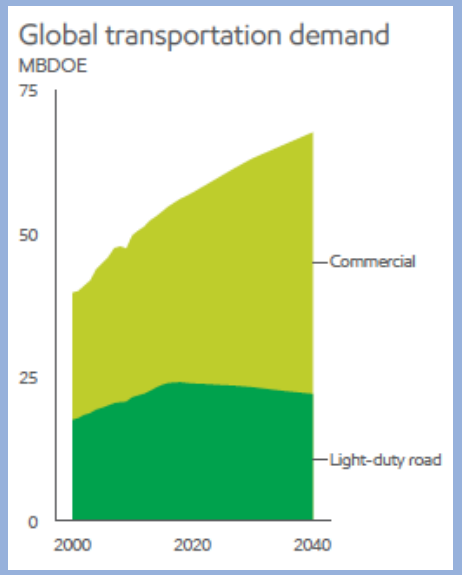
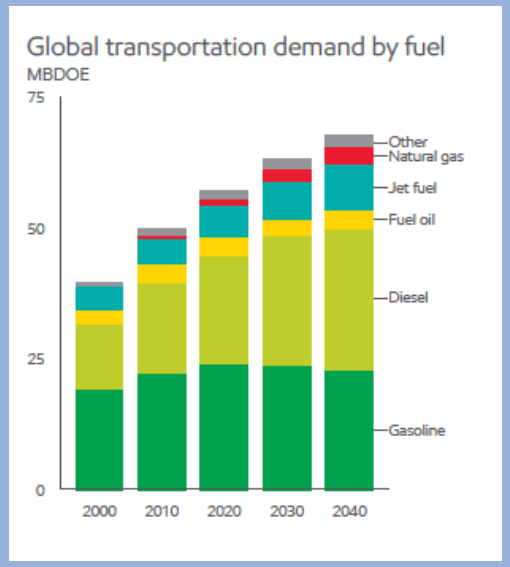
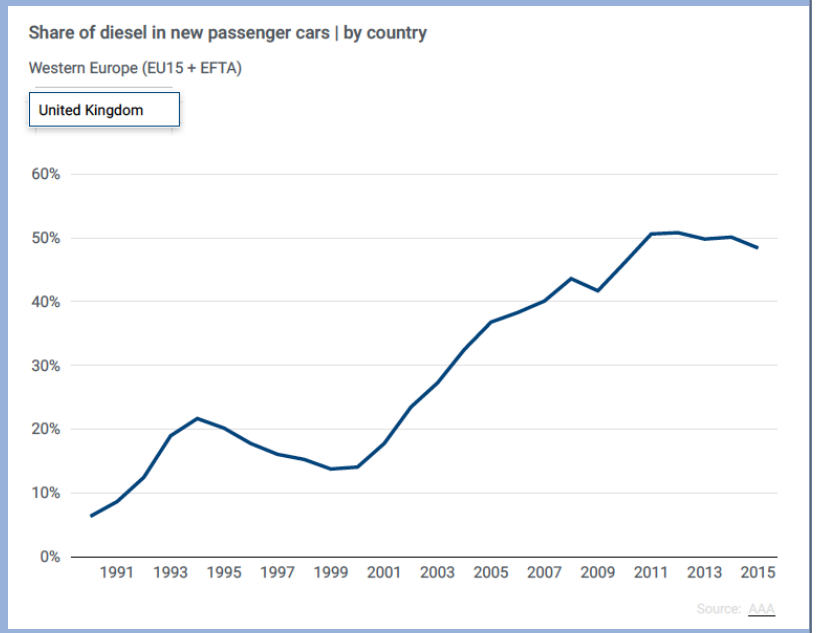
http://wacl.org.uk/

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)



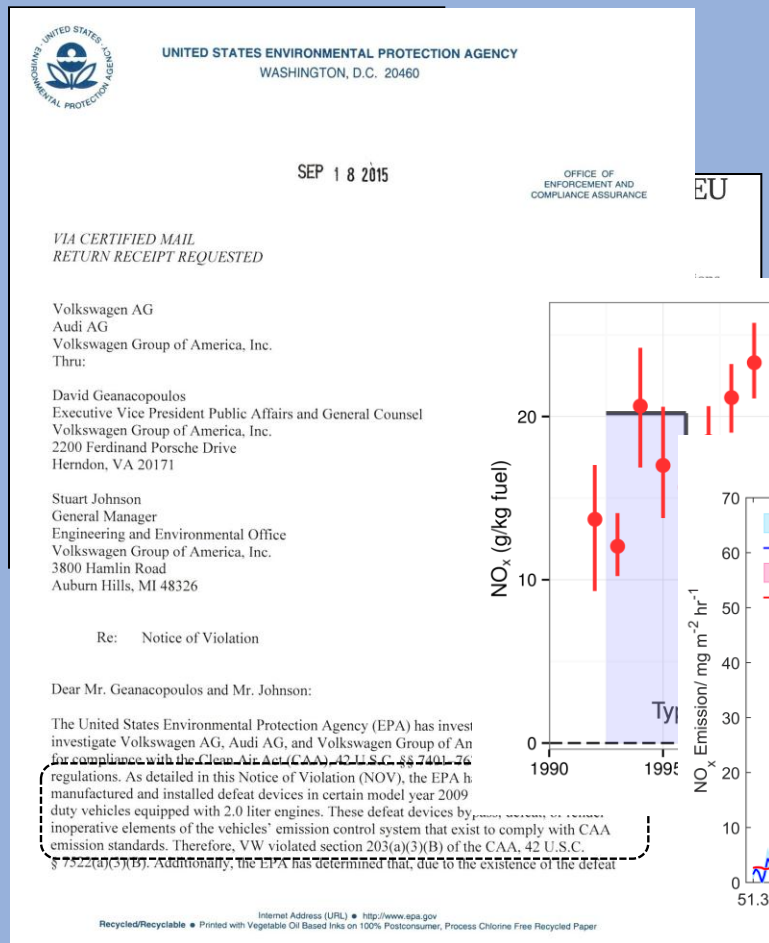




Exxon Mobil, Outlook for Energy: A view to 2040, 2016

http://www.acea.be/statistics/tag/category/diesel-penetration

The rise (and fall?) of diesel



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

SEP 18 2015

OFFICE OF ENFORCEMENT AND COMPLIANCE ASSURANCE

VIA CERTIFIED MAIL
RETURN RECEIPT REQUESTED

Volkswagen AG
Audi AG
Volkswagen Group of America, Inc.
Thru:

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

Stuart Johnson
General Manager
Engineering and Environmental Office
Volkswagen Group of America, Inc.
3800 Hamlin Road
Auburn Hills, MI 48326

Re: Notice of Violation

Dear Mr. Geanacopoulos and Mr. Johnson:

The United States Environmental Protection Agency (EPA) has invest
investigate Volkswagen AG, Audi AG, and Volkswagen Group of An
for compliance with the Clean Air Act (CAA), 42 U.S.C. §§ 7401-76
regulations. As detailed in this Notice of Violation (NOV), the EPA h
manufactured and installed defeat devices in certain model year 2009
duty vehicles equipped with 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)(3)(B) of the CAA, 42 U.S.C.
§ 7522(a)(3)(B). Additionally, the EPA has determined that, due to the existence of the defeat

Internet Address (URL) • http://www.epa.gov
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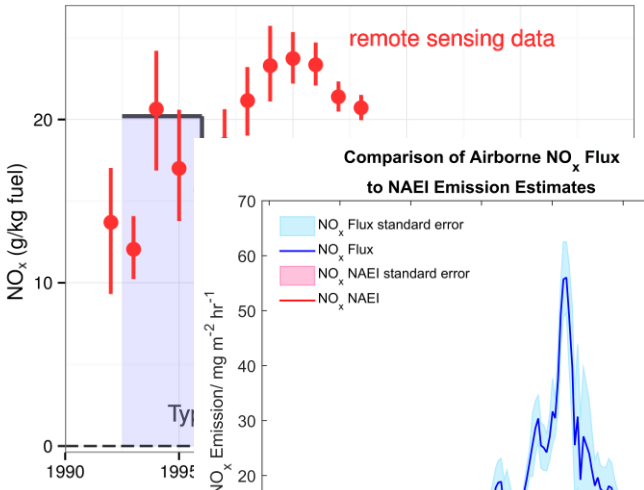
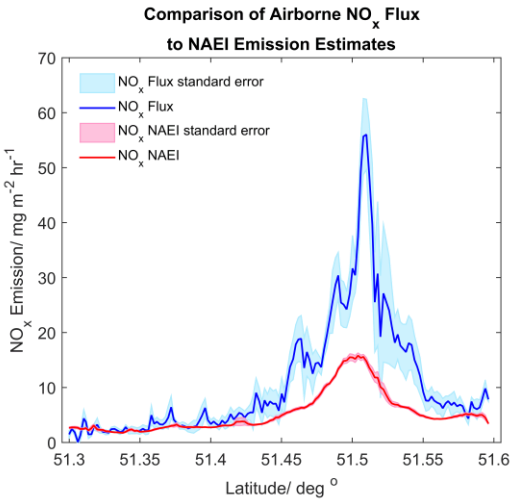
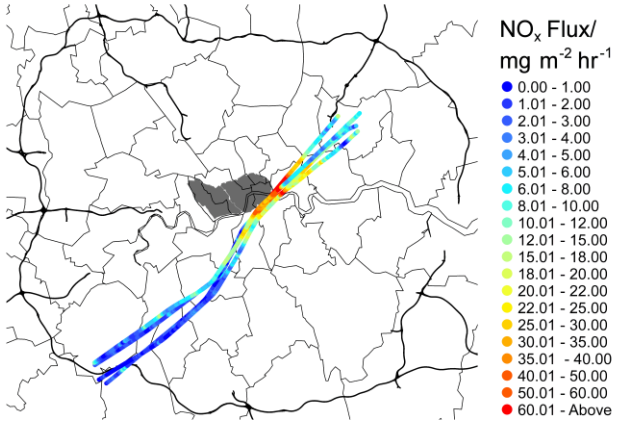






Carslaw and Rhys-Tyler, 2013, Atmospheric Environment, Vol. 81 339-347

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

Diesel Emissions

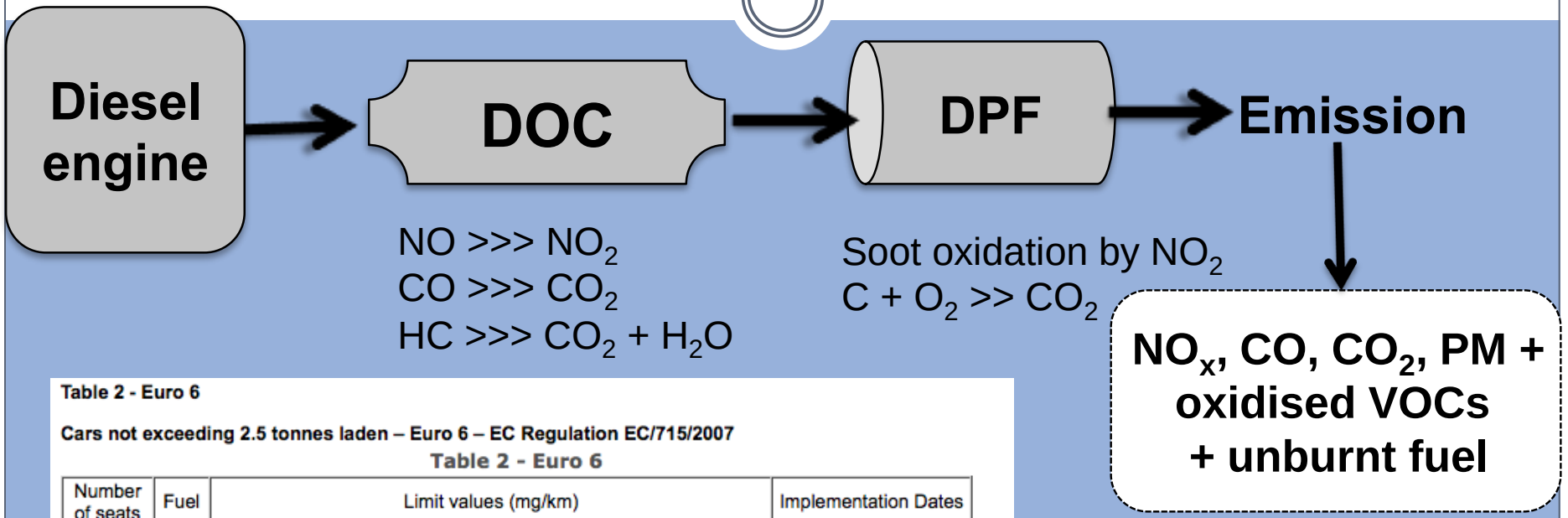


Table 2 - Euro 6

Cars not exceeding 2.5 tonnes laden – Euro 6 – EC Regulation EC/715/2007

Table 2 - Euro 6

Number of seats	Fuel	Limit values (mg/km)							Implementation Dates	
		CO	THC	NMHC	NOx	THC+NOX	PM	Particles (number/km)	Type Approval of new models	All Models
up to 9	P	1000	100	68	60	-	5.0/4.5	-	1/09/14	1/09/15
up to 9	D	500	-	-	80	170	5.0/4.5	$6{,}0 \times 10^{11}$	1/09/14	1/09/15

Key: P- petrol, D – diesel, CO – carbon monoxide, HC – hydrocarbons, NOx – oxides of nitrogen, PM – particulate matter.

If the NOx is too high, what about the hydrocarbons (and should we care)?

Volatile Organic Compounds and Air Quality

Secondary Organic Aerosols

Condensation/ coagulation

Less volatile organics

Gas phase oxidation

Volatile organic compounds (VOC) + Oxidants ($OH^{\cdot}$, O_3, $NO_3^{\cdot}$)

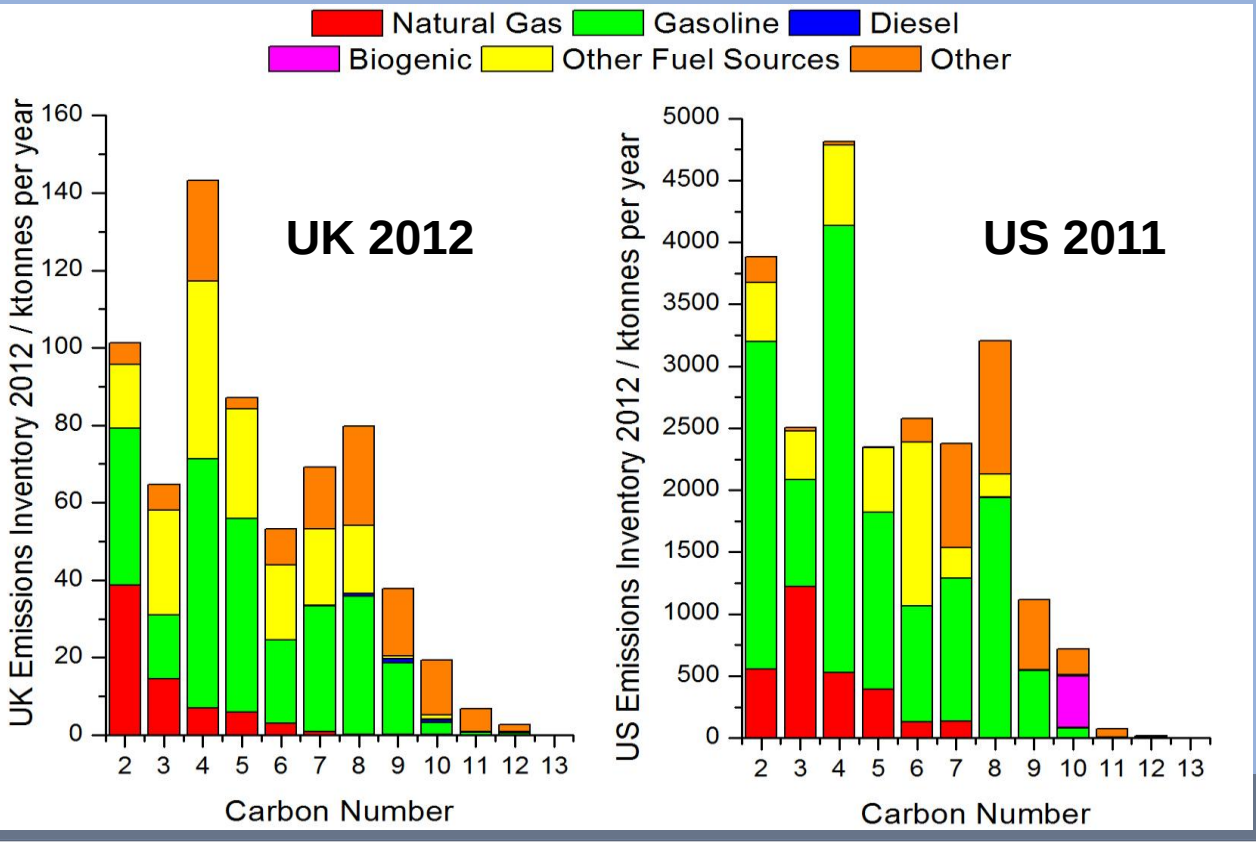
Gas phase oxidation (NOx)

Ozone

Anthropogenic and biogenic gaseous emissions

Emission Inventories

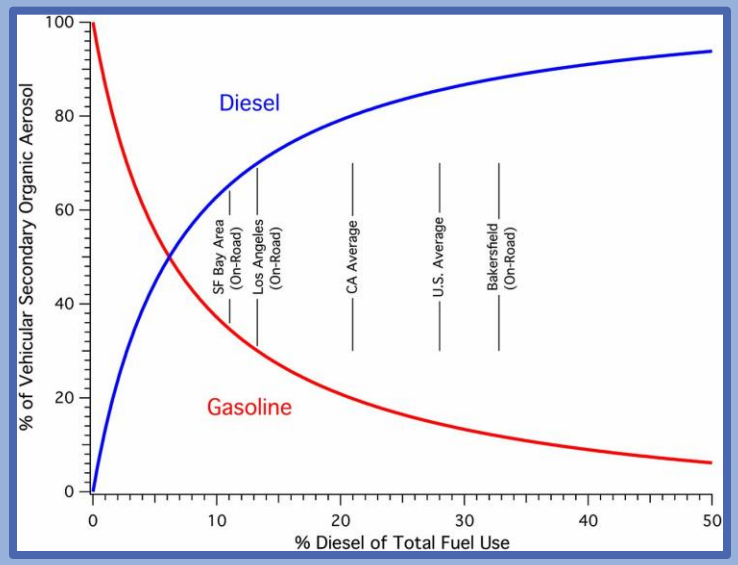
- Current national emission estimates drive both policy and observation
  - This *relative* distribution should be typical of most developed countries
- As a result of tighter regulations, levels of smaller hydrocarbons are declining



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

Gentner et al. PNAS 2012;109:18318-18323

Gentner et al. ES&T, .2017, 51, 1074−1093.

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

	Area (km^2)	Number of inhabitants	Population density (inhabitants per km^2)	Cars per household	% public green space	% diesel use	Average T (°C) in winter and summer	Average hours of sunlight in winter and summer (hours)
London	1572[1]	7,825,200[1]	4978[1]	0.8[6]	38.4[1]	57[7]	3 and 18.9[9]	2.2 and 5.9[11]
North Kensington	12.13[2]	158,700[3,4]	13,087[3,4]	0.6[6]		56[3,7]		
LA	10510[1]	9,818,605[1]	934[1]	1.9[5]	6.7[1]	13[8]	13.8 and 21.4[10]	6.6 and 11.1[12]
Bakersfield	244.77[2]	357,603[5]	1461[4]			33[8]		

References

[1]World Cities Cultural Report, 2013

[2]Calculated from number of inhabitants and population density

[3]Values for Kensington and Chelsea

[4]Census, July 2012

[5]US Census Bureau

[6]UK Office of National Statistics

[7]Department of Energy and Climate Change statistics

[8]Gentner et al (2012)[3]

[9]metoffice.gov.uk, mean daily temperature

[10]los-angeles.climatemps.com/temperatures.php

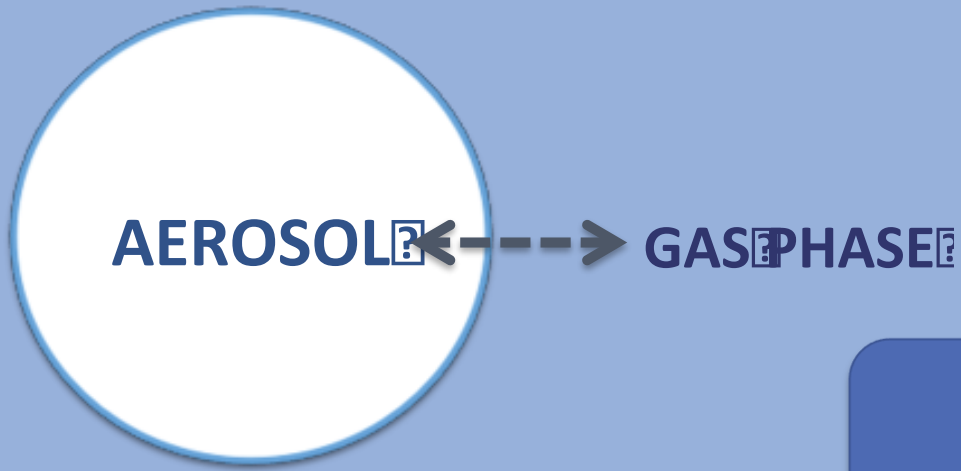
[11]metoffice.gov.uk, mean daily hours of sunshine

[12]los-angeles.climatemps.com/sunlight.php

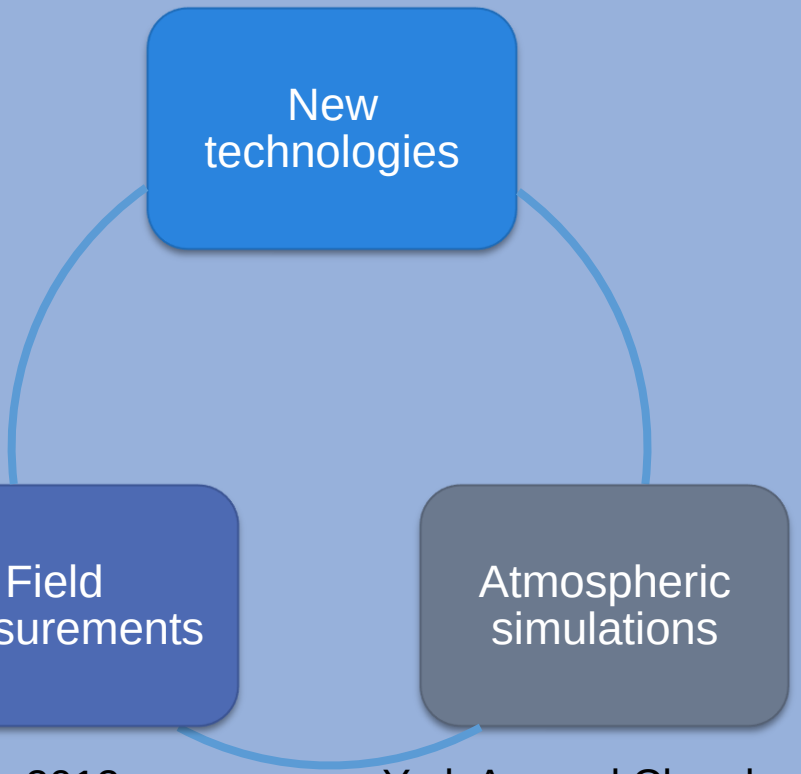
- Care needs to be taken when comparing to previous studies.

Research Approach

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



High resolution chromatography and mass spectrometry



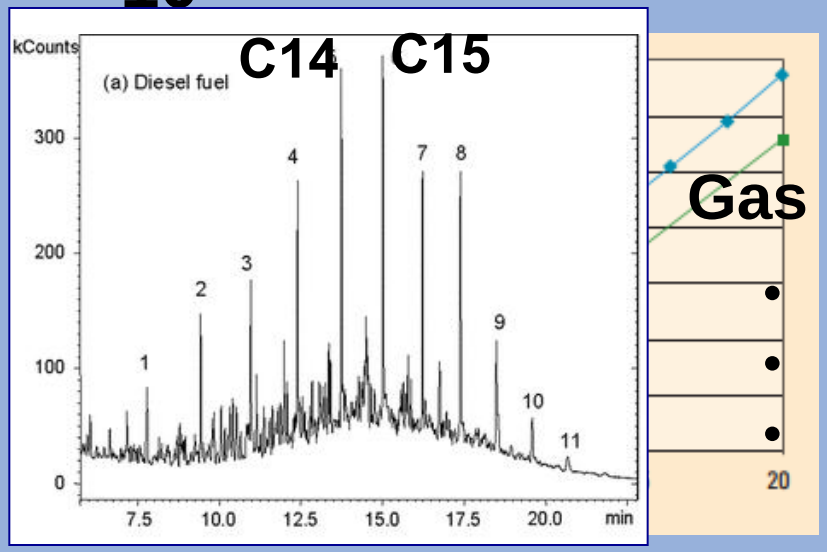
Clearflo – London 2012
ACACCIA – Arctic, 2013
OP3/ACES – Borneo, 2008

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

C_{10} +? H O N S Cl Br F P I



Gas chromatogram of diesel fuel

n-alkanes can be identified

Unidentified complex mix seen

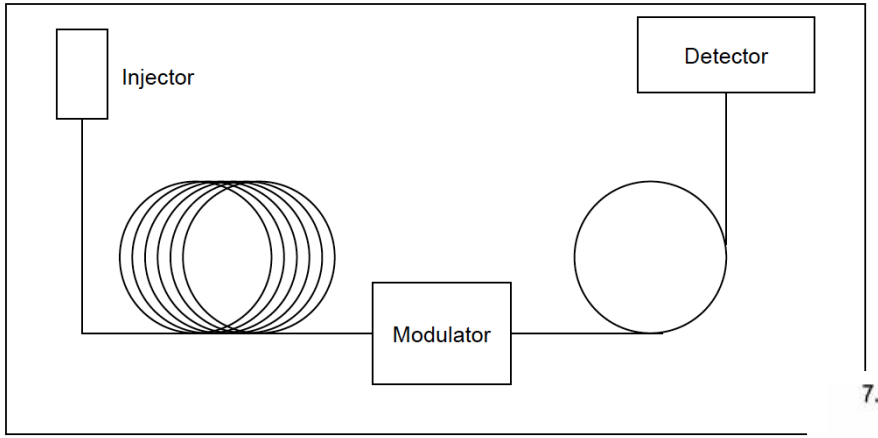
GC does not have sufficient resolving power for full speciation

- For C_{10} – more than a million organic compounds possible
- Many of which are likely in the atmosphere

Liang et al., JEM, 2005

Goldstein and Gallbaly, ES&T,2007

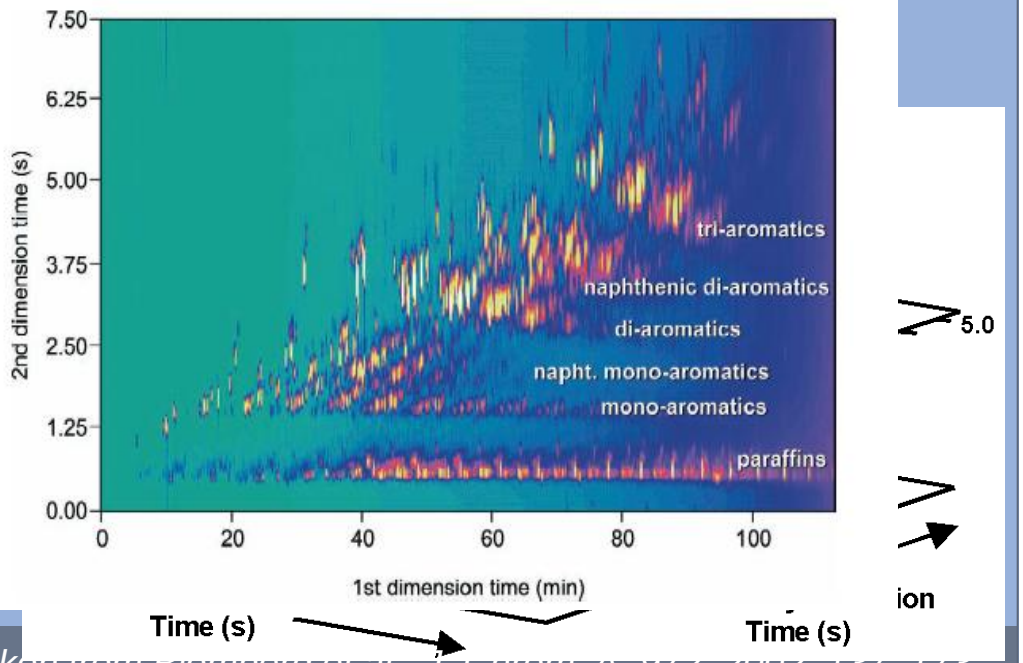
Comprehensive two-dimensional gas chromatography (GC × GC)



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

Allows much better speciation of complex mixtures

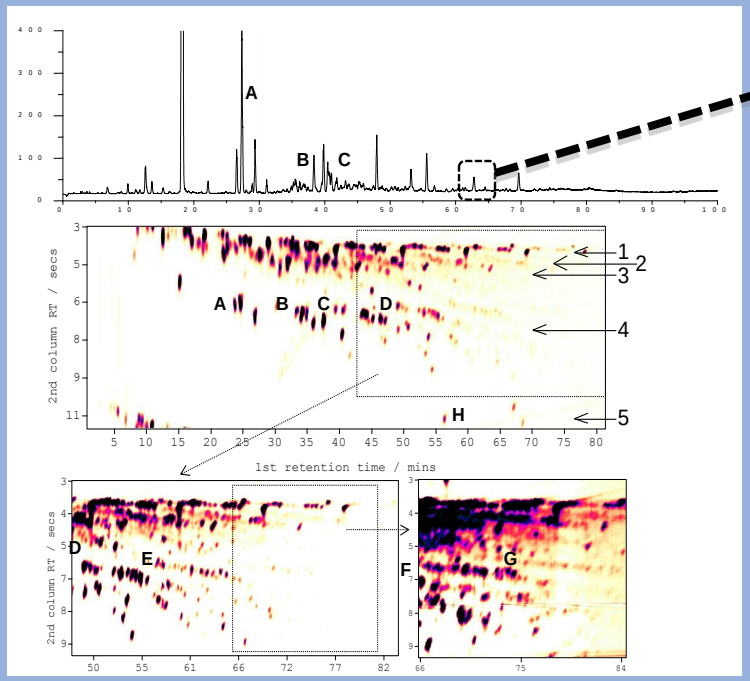
Viewed as a contour plot

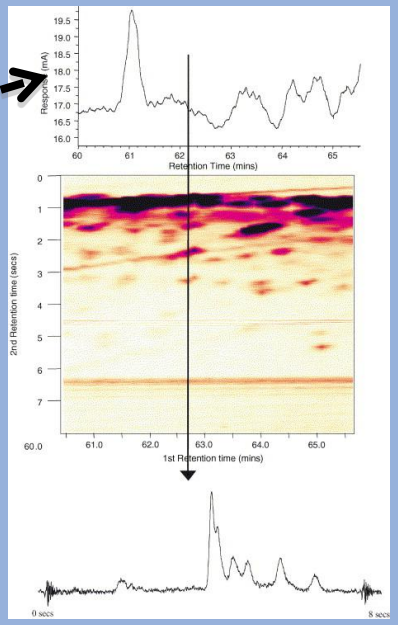


Taken from Blomberg et al., J. Chrom. A, 972, 2002, 137–173

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_2, B=C_3, C=C_4, D=C_5, E=C_6, F=C_7, G=C_8. 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

University of Reading

University of Leicester

Centre for Ecology & Hydrology
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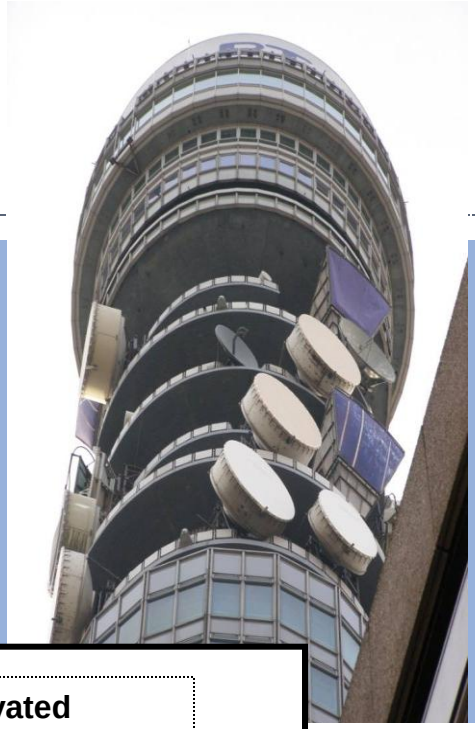
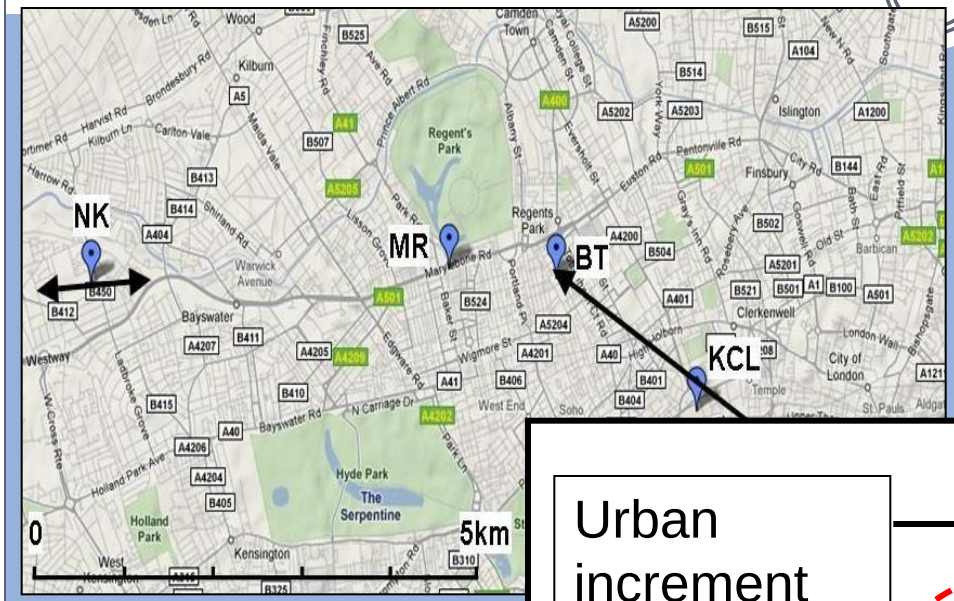
Measurement Sites





Urban increment

Elevated

BT Tower (180m)

KCL Roof (35 m)

Rural

Chilbolton

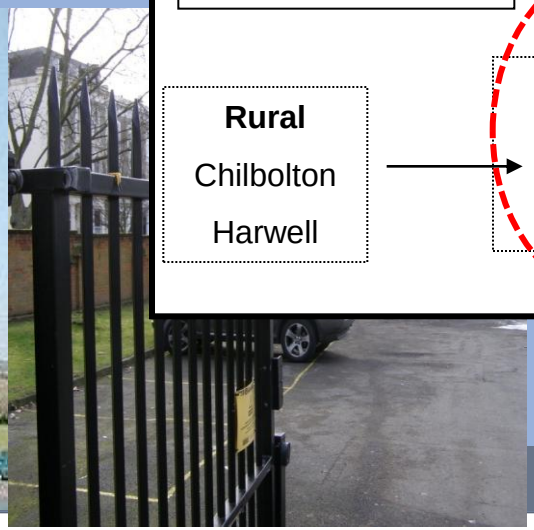
Harwell

Urban background

North Kensington

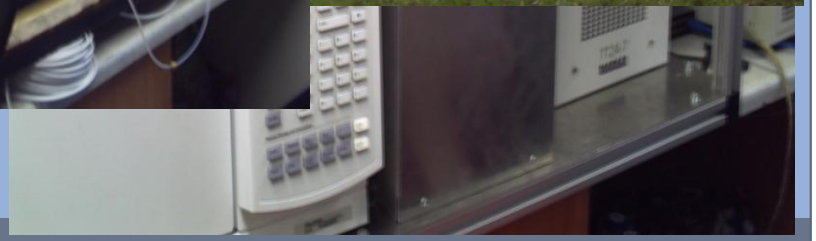
Kerbside

Marylebone Road



VOC Measurements

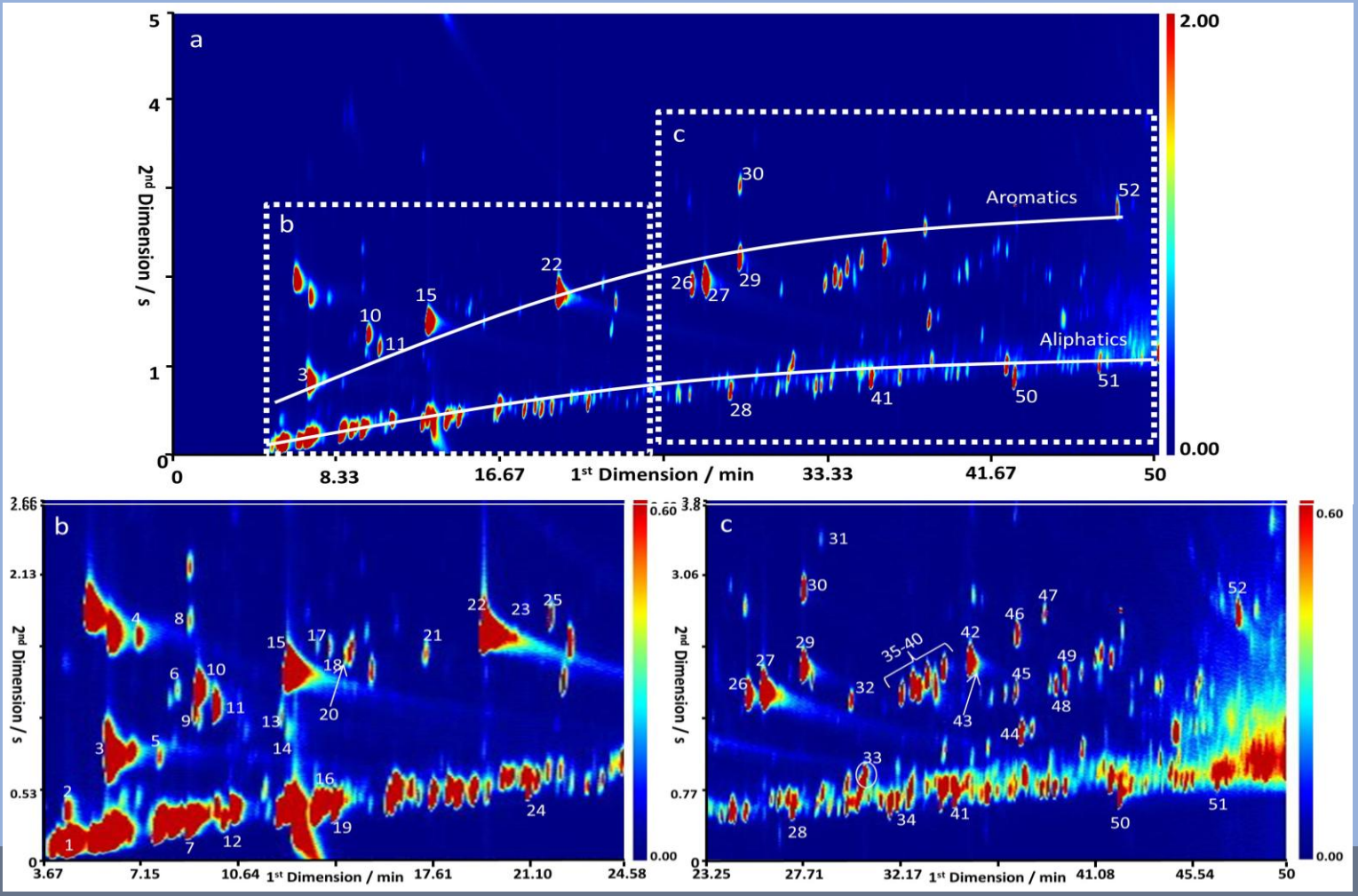
- Hourly measurements of 78 VOCs
- Winter and Summer 2012
- In total, 2667 samples
  - DC-GC measured volatile VOCs
    - C_1-C_7 hydrocarbons and selection of OVOCs
  - GC × GC-FID, less volatile fraction
    - C_6-C_{13} hydrocarbons and a large groups of OVOCs



Dunmore et al., ACP, 15, 9983-9996, 2015

GC × GC measurements of VOCs

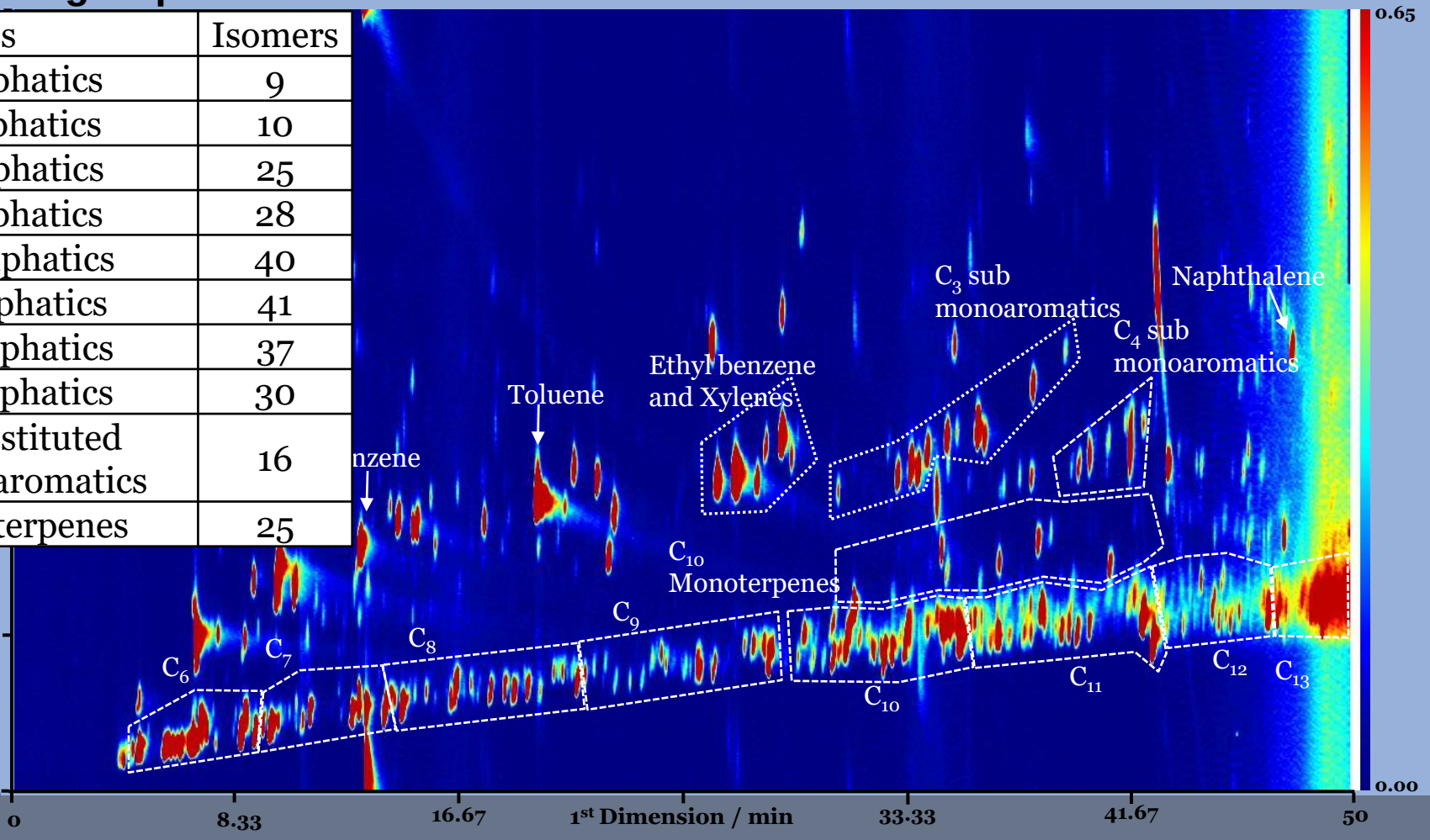
GC × GC-FID plot from winter 2012-02-07 at 08:32



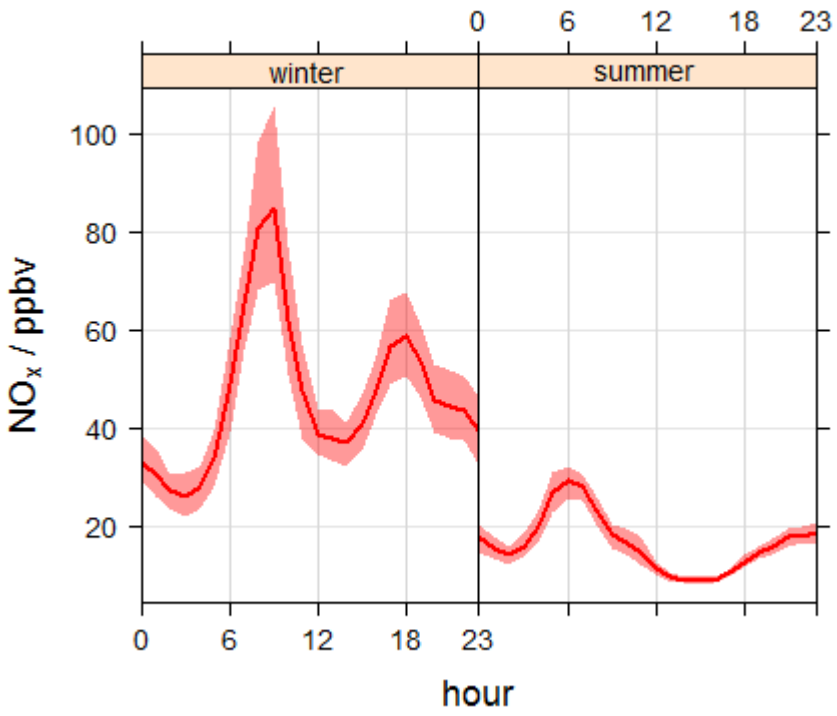
Using GC × GC to group compounds

Number of isomers in each group

Groups	Isomers
C_6 Aliphatics	9
C_7 Aliphatics	10
C_8 Aliphatics	25
C_9 Aliphatics	28
C_{10} Aliphatics	40
C_{11} Aliphatics	41
C_{12} Aliphatics	37
C_{13} Aliphatics	30
C_4 substituted monoaromatics	16
Monoterpenes	25

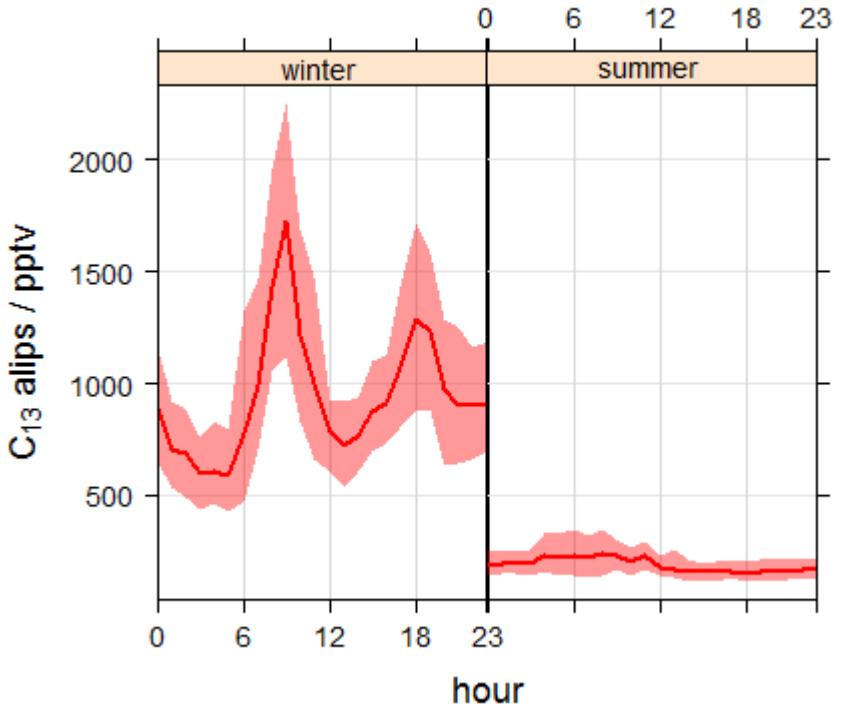


Average diurnal profiles of VOCs



NO_x, 24 hour daily cycle

Isoprene, 24 hour daily cycle



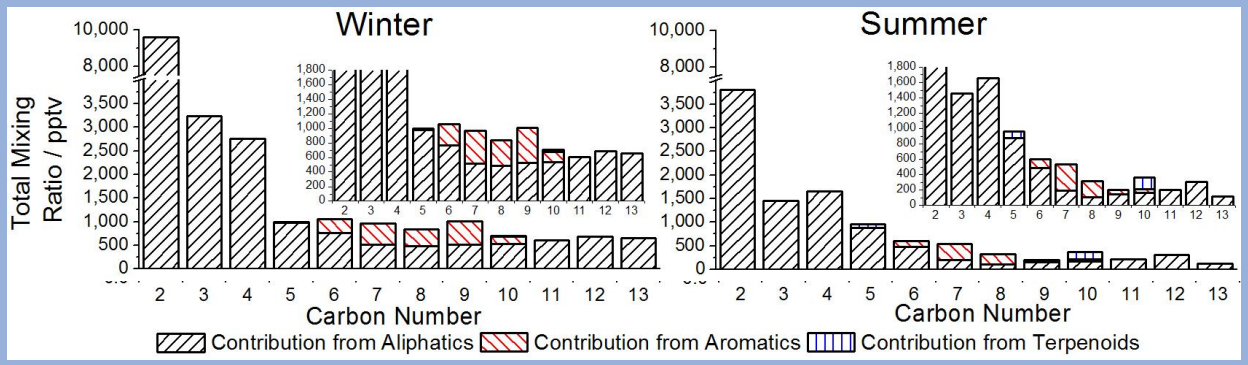
C_{13} grouped alkanes, 24 hour daily cycle

Toluene, 24 hour daily cycle

Carslaw and Ropkins, Environmental Modelling and Software, 2012, Openair software for R

Assigning VOCs to emission sources

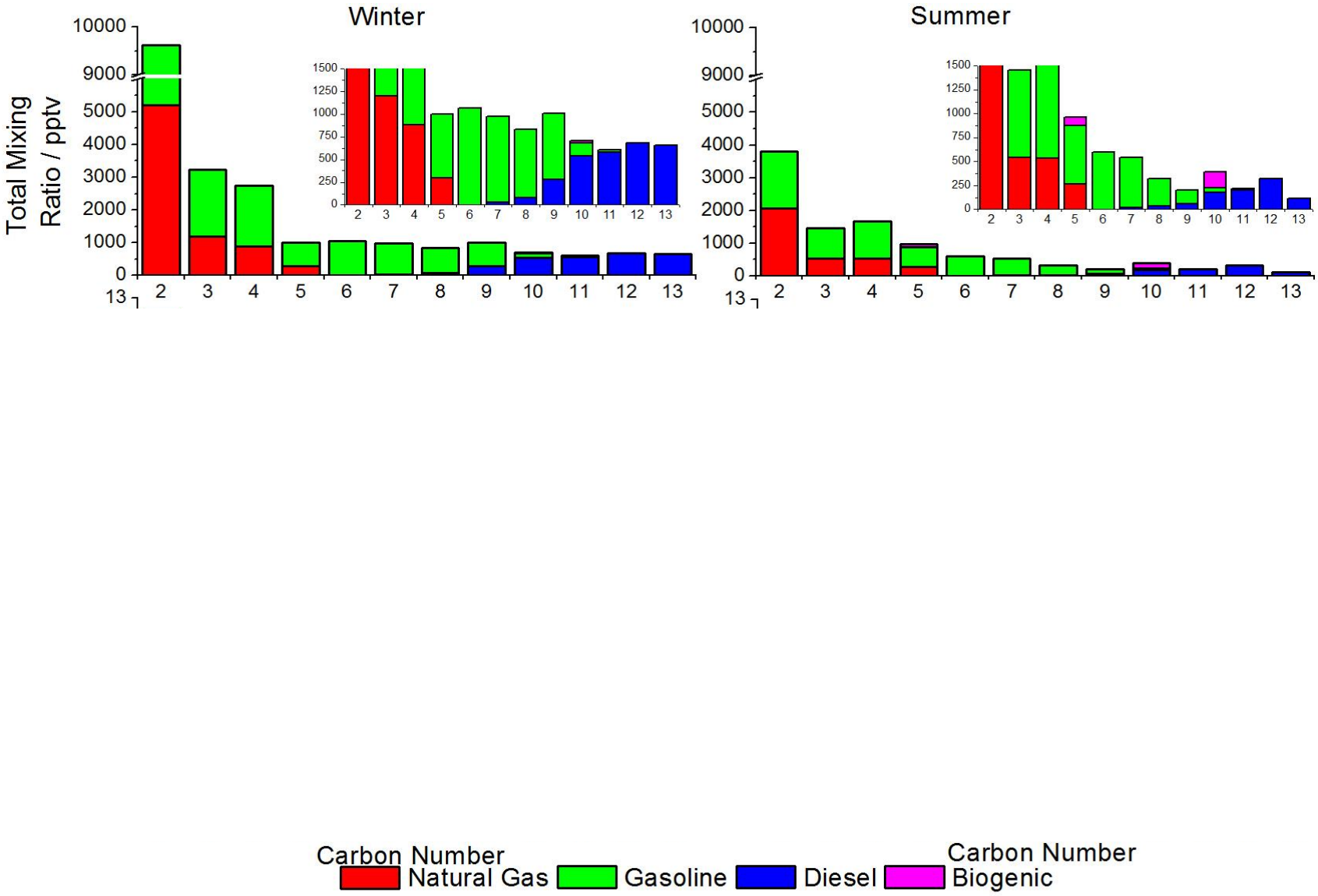
- We split the VOCs by C_n and functionality to investigate relative emission strength



Seasonal average mixing ratios

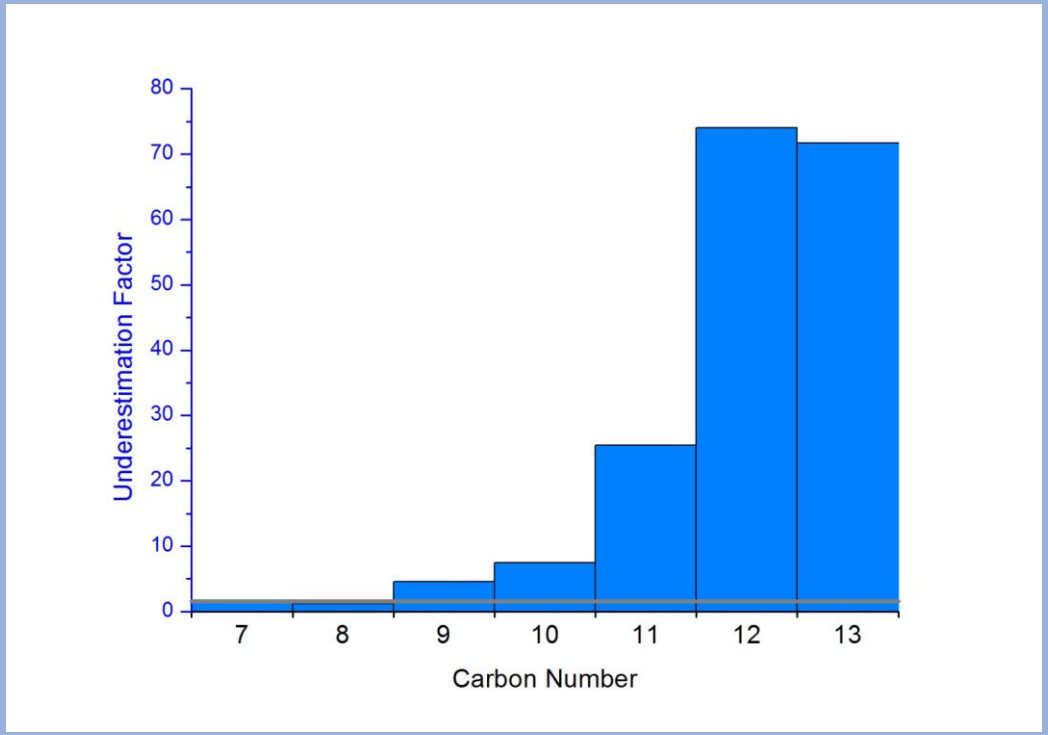
- But what is the source of the VOCs?
- Source apportionment
  - Assume 60 % diesel use in London
  - Assume NAEI correctly apportions the split between natural gas and gasoline
  - Use the liquid fuel composition to apportion a % of >C_6 to diesel and gasoline
  - Estimate primary OH reactivity

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


Winter
Summer
Total Mixing Ratio / pptv
10000
9000
5000
4000
3000
2000
1000
0
1500
1250
1000
750
500
250
0
2 3 4 5 6 7 8 9 10 11 12 13
Carbon Number
Natural Gas
Gasoline
Diesel
Biogenic
Carbon Number

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

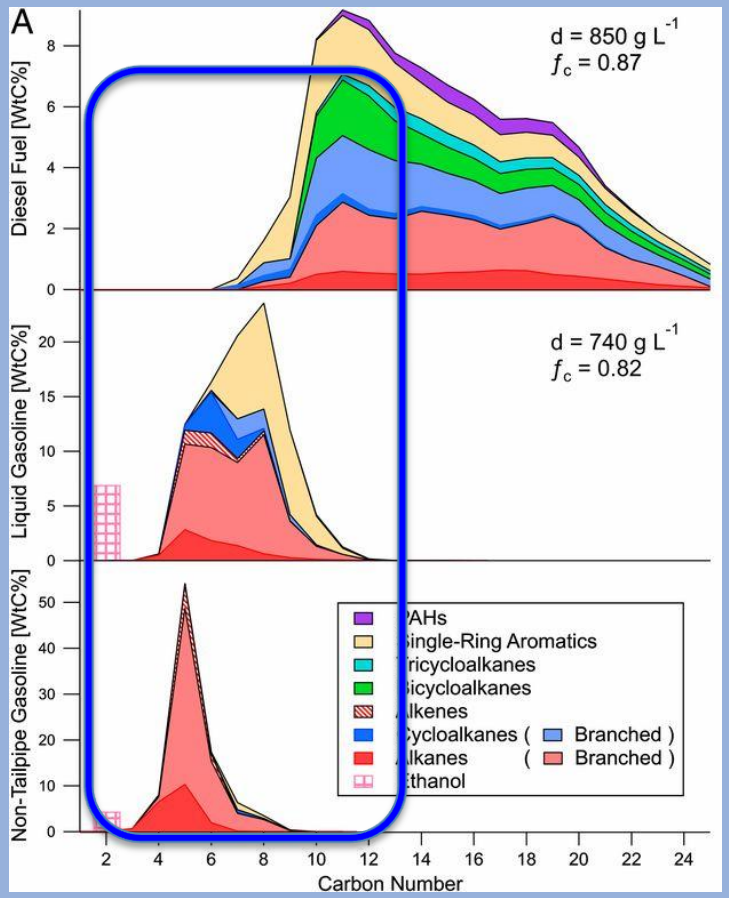


*Langford et al., ACP, 2010.

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

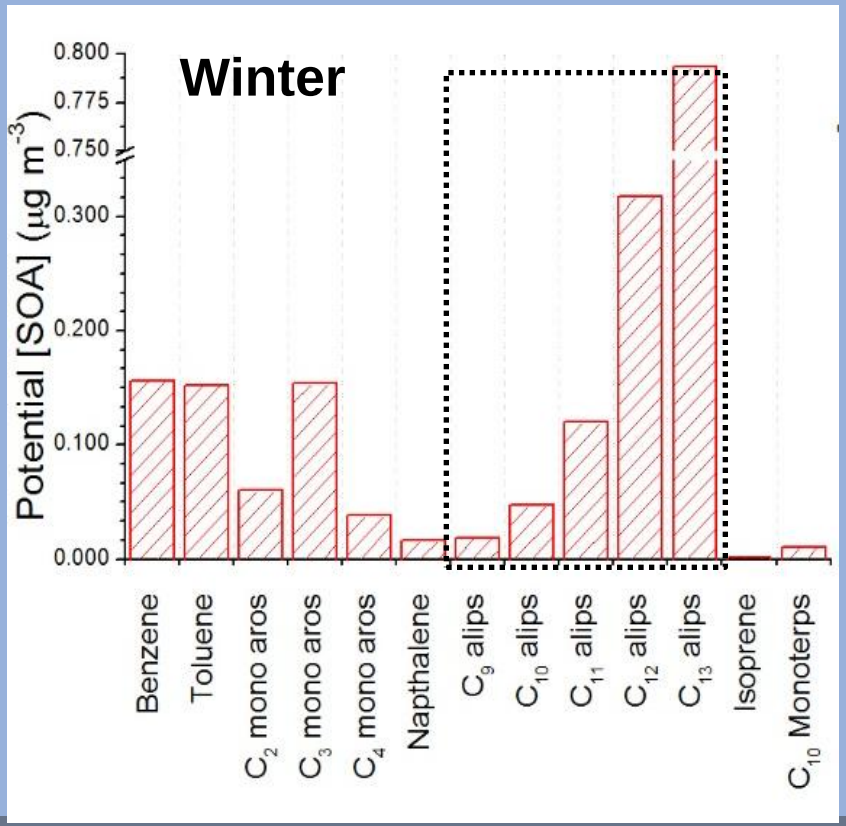
Distribution of mass in diesel and gasoline fuel and nontailpipe gasoline emissions.

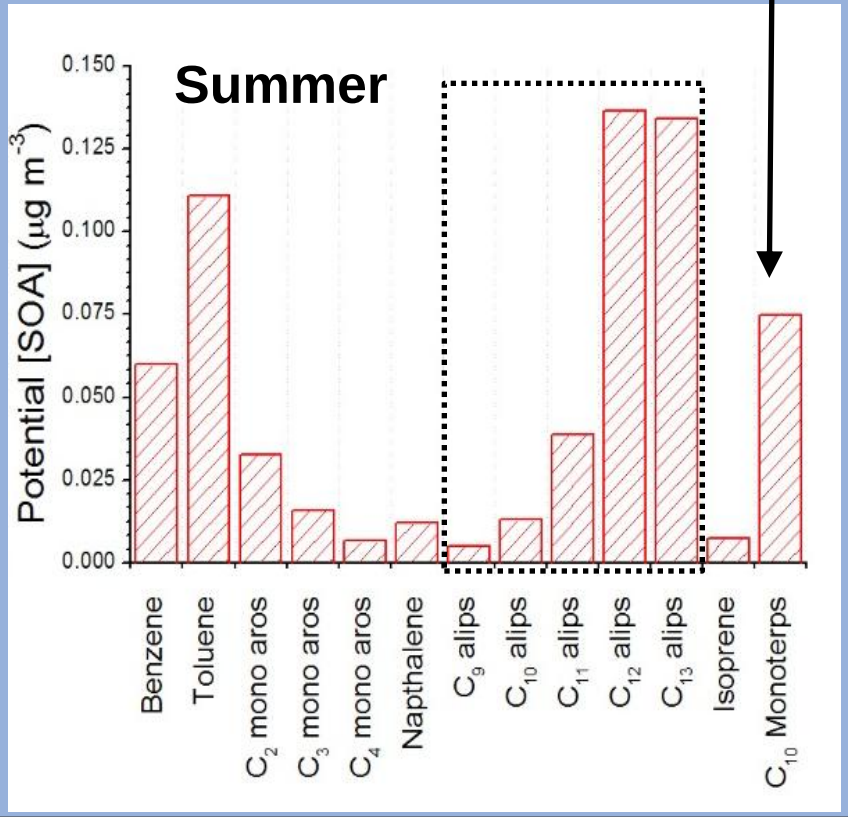


Gentner D R et al. PNAS 2012;109:18318-18323

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

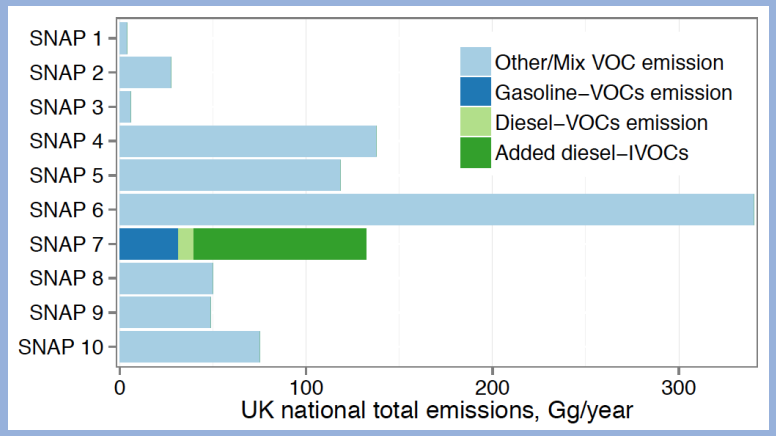
Adding the diesel IVOC to current inventories

- 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 2. Comparison of diesel and gasoline NMVOCs in the UK National Atmospheric Emissions Inventory (NAEI) with the urban background ambient concentrations measured during the ClearfLo winter Intensive Observation Period in London.

	NAEI 2012	Measurements [a]
Diesel-(I)VOCs	8 $Gg\,yr^{-1}$	107 $\mu g\,m^{-3}$
Gasoline-VOCs	31 $Gg\,yr^{-1}$	33 $\mu g\,m^{-3}$
Diesel/Gasoline	0.26	3.2

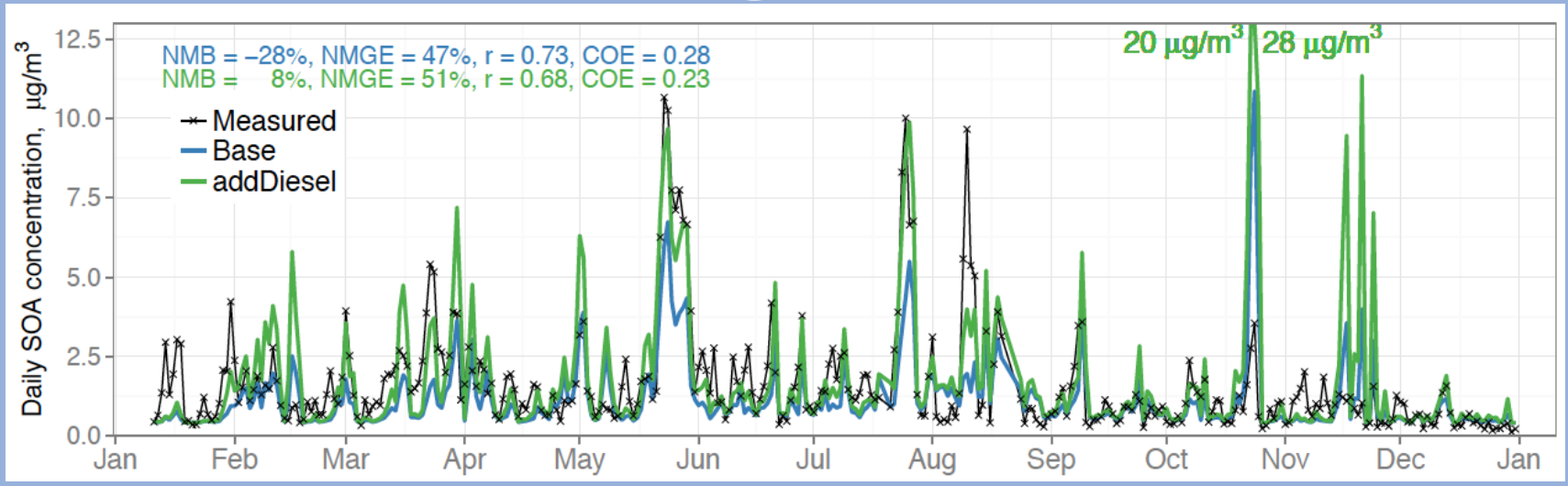
[a] Dunmore et al. (2015).



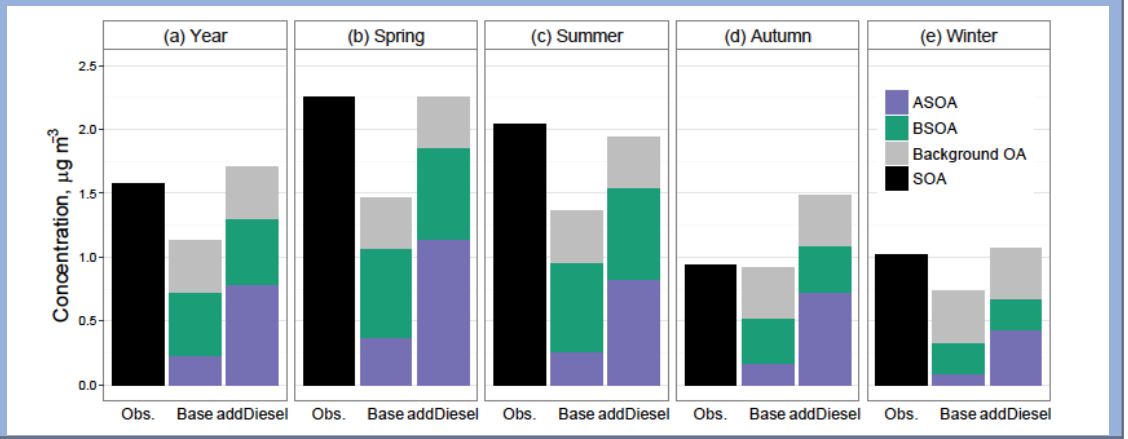
- Extra diesel IVOC added as pentadecane to every country in model domain using same factor as UK
  - Average C_n of diesel is 14.9 (Gentner et al., 2012)
  - Rate constant with OH and SOA yields are known
  - Linear alkane is good representation of average rate of reaction of all isomers

Ots et al., ACP., 16, 6453-6473, 2016

Annual SOA formation from diesel IVOC



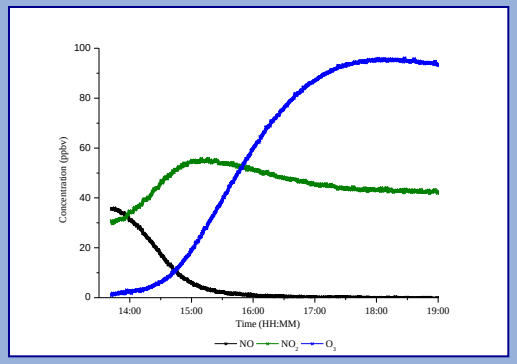
- Addition of diesel IVOC improves model – measurement agreement
- Diesel IVOC account for on average 30 % of the annual SOA in UK in model



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

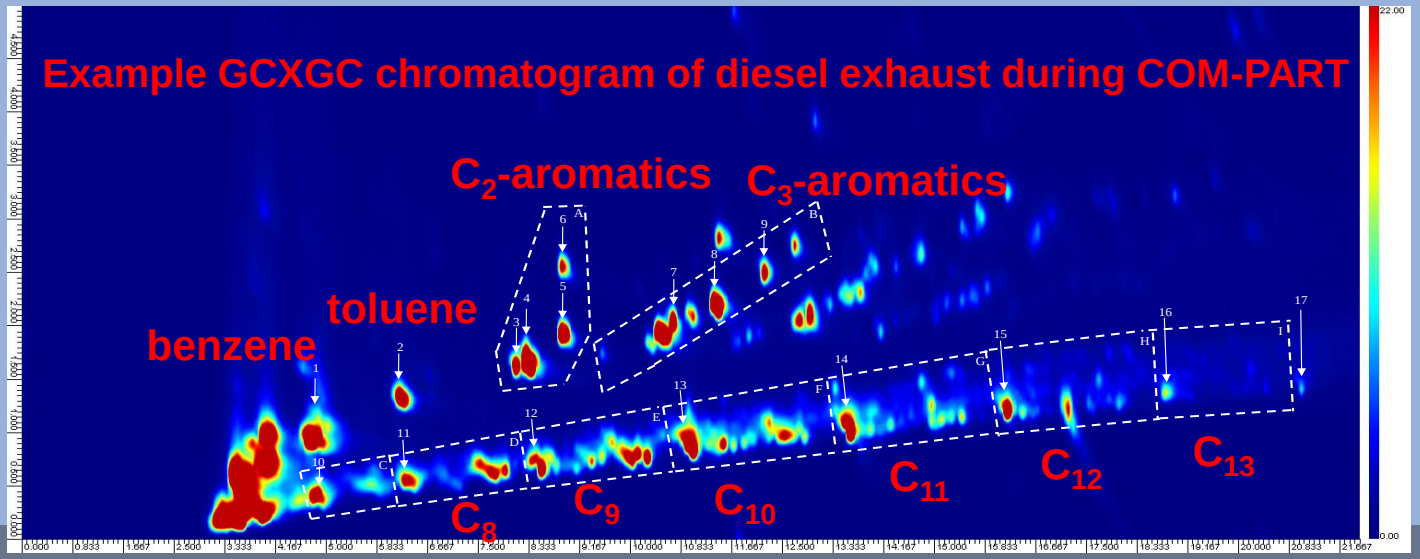
Diesel engine → **Atmospheric simulation chamber** → **Measure emissions and secondary pollution**



**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.

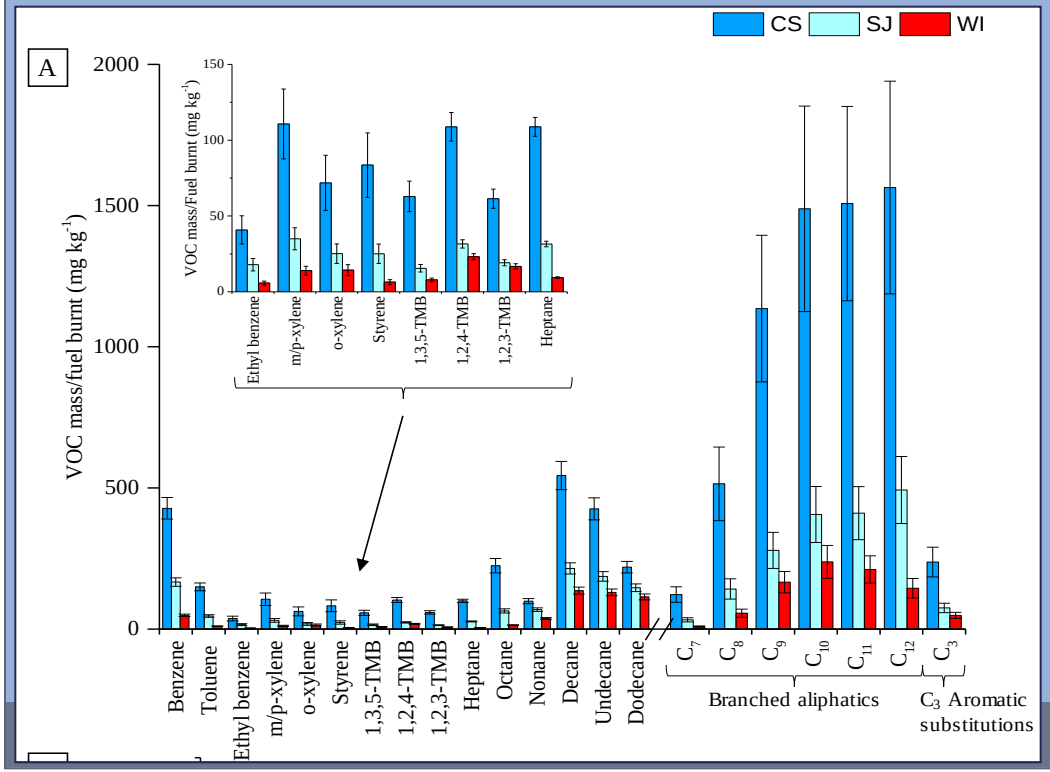


Note: emissions will depend on engine conditions, maintenance, age etc…

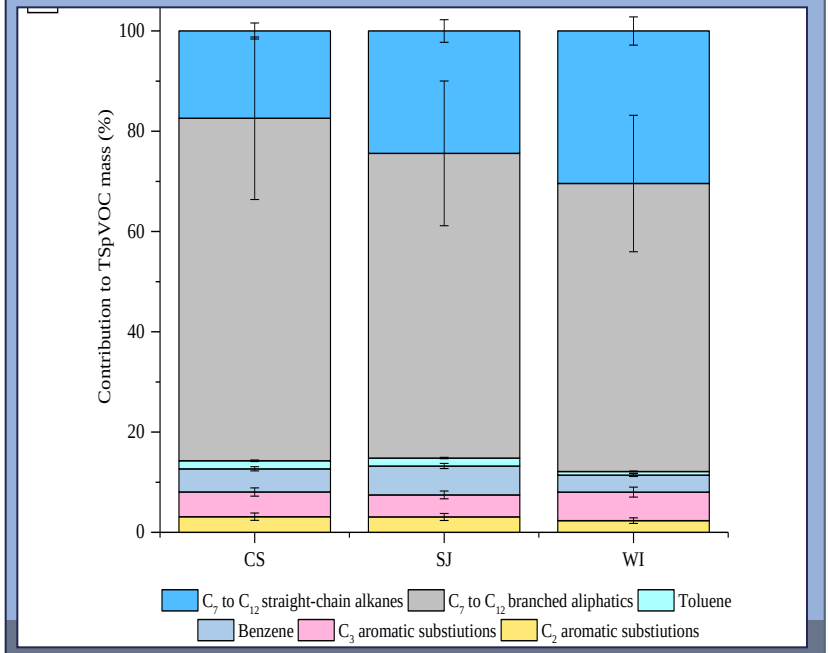
Impact of engine conditions on IVOC emissions

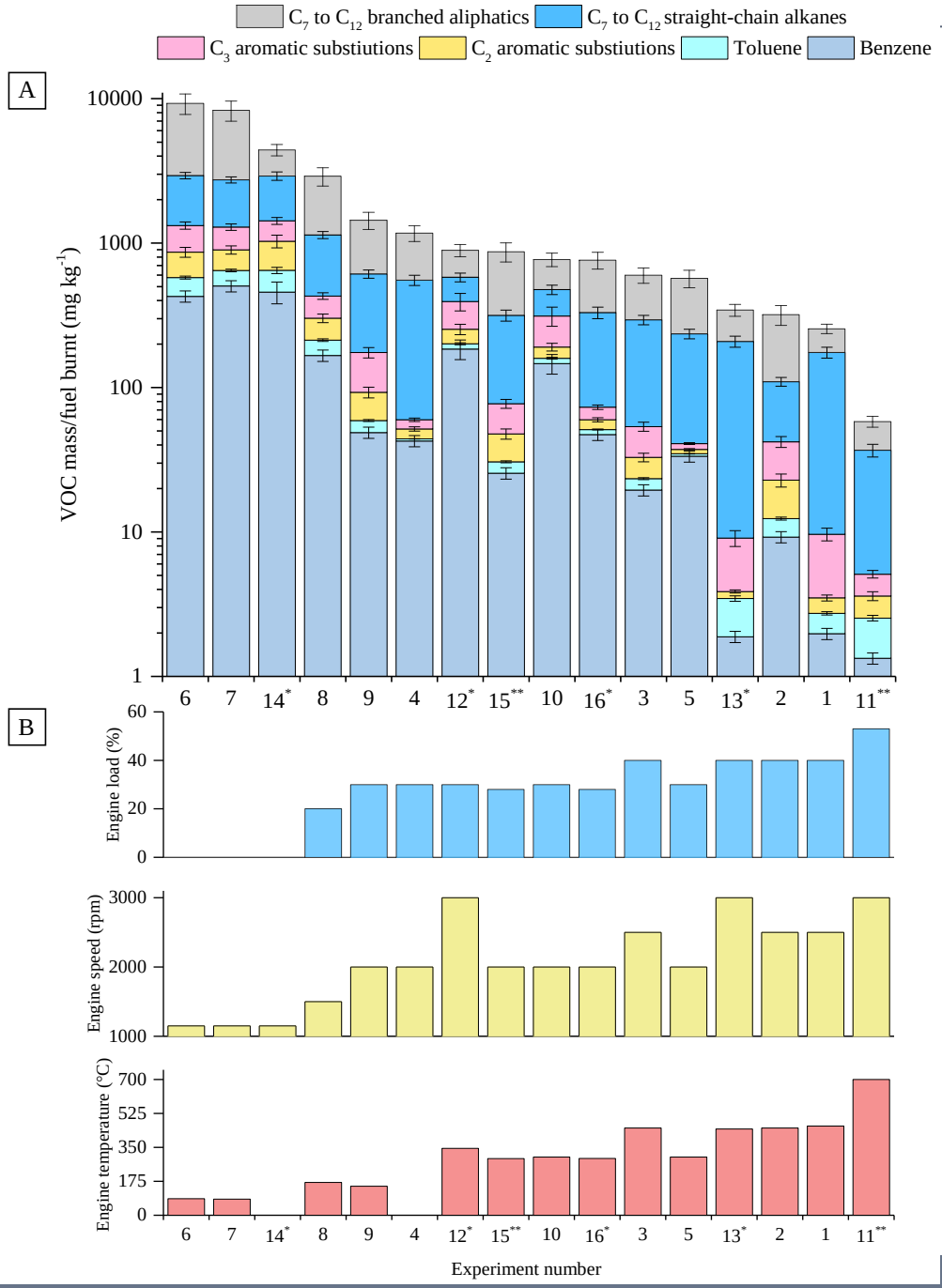
- How do the diesel hydrocarbon emissions vary under different driving conditions?

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

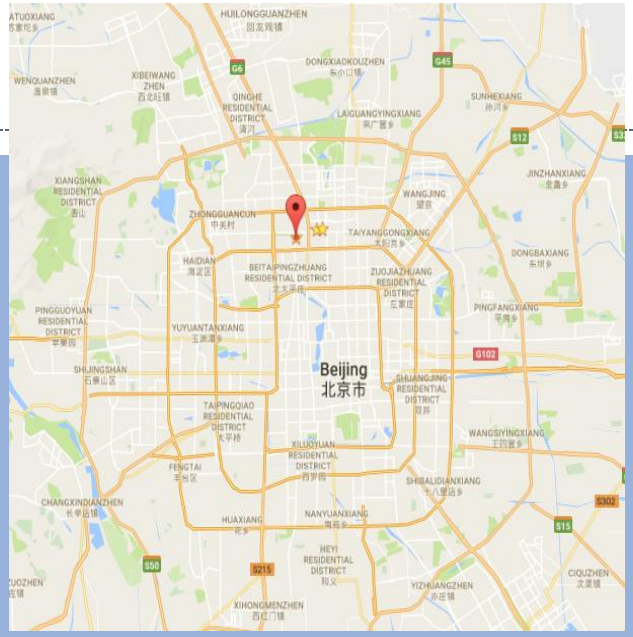
Chemical composition of emissions changes with temperature and load

The DOC tested was efficient at removing low molecular weight VOCs (90-100 %)
BUT this dropped rapidly as C_n increased (C_{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

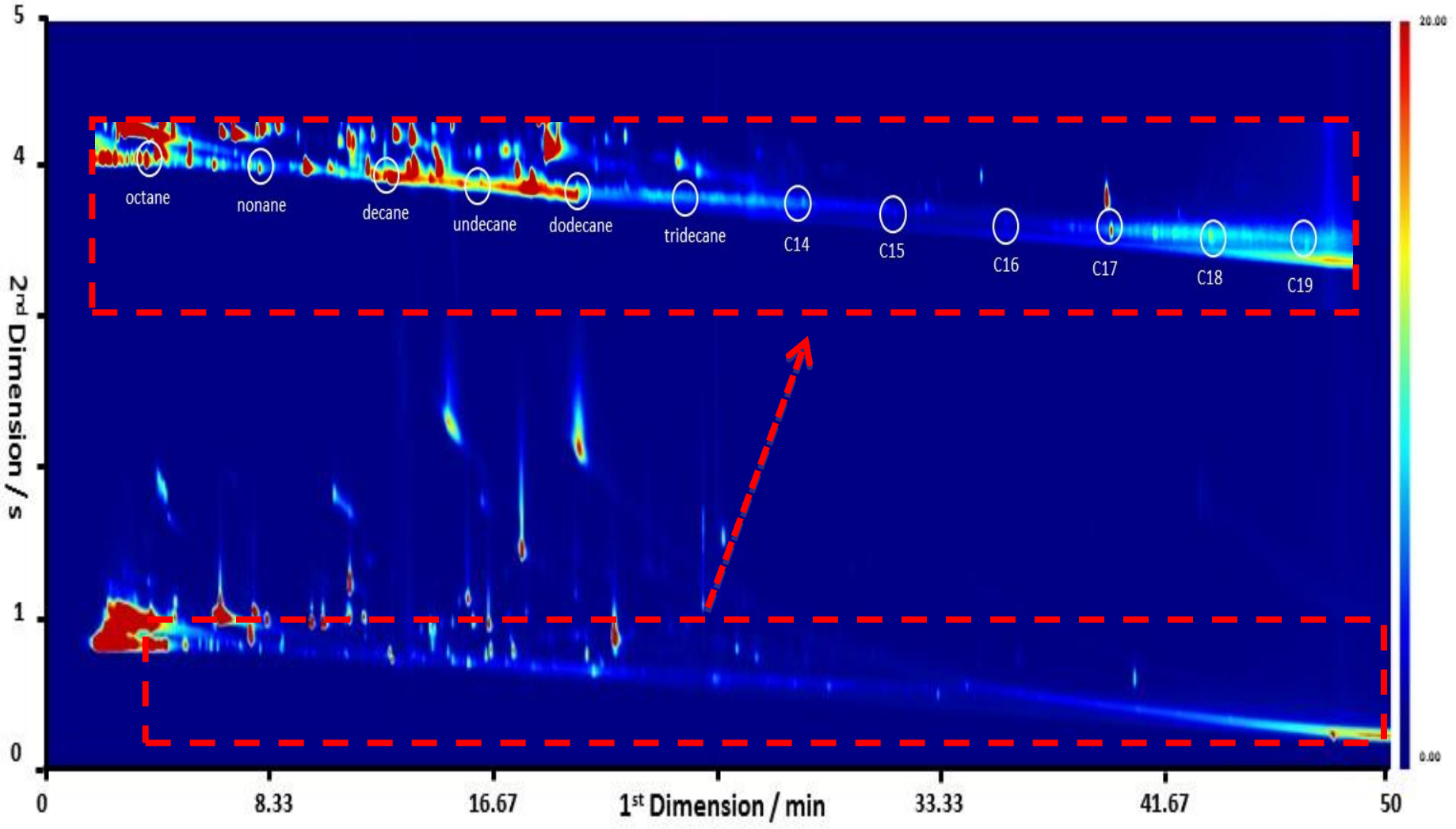
Beijing site location



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

1	Flux
2	Manchester
3	Leeds
4	York
5	IAP
6/7	PKU

Improved IVOC speciation in Beijing –first look!



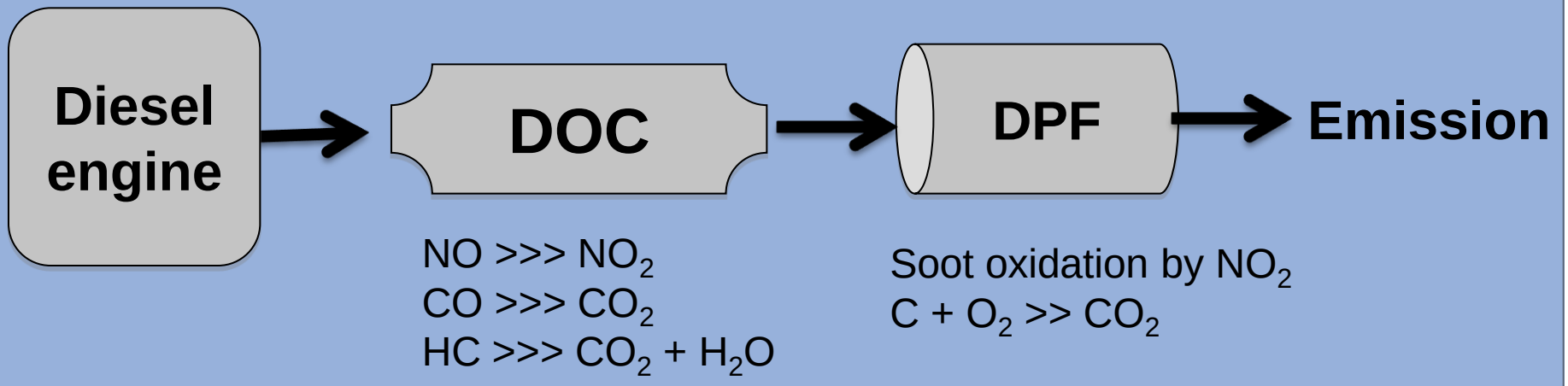
Conclusions

- 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_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.

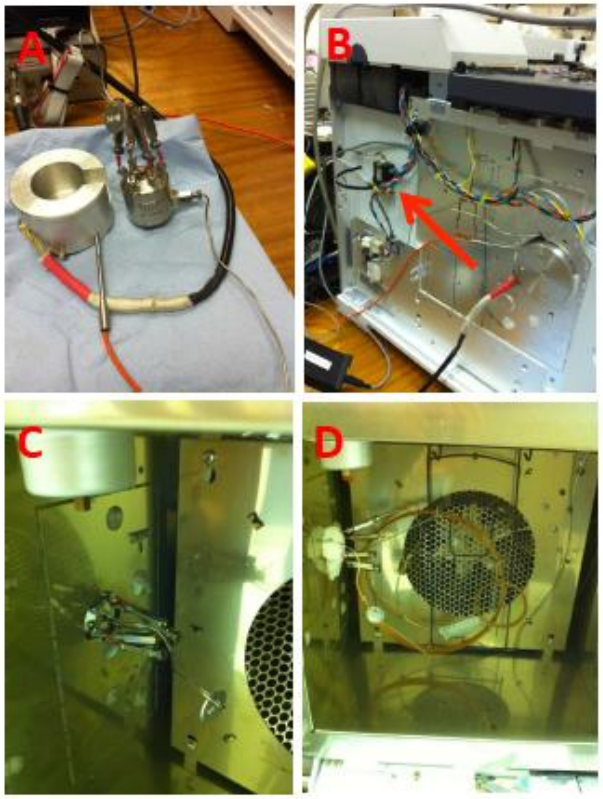
Acknowledgements

- 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

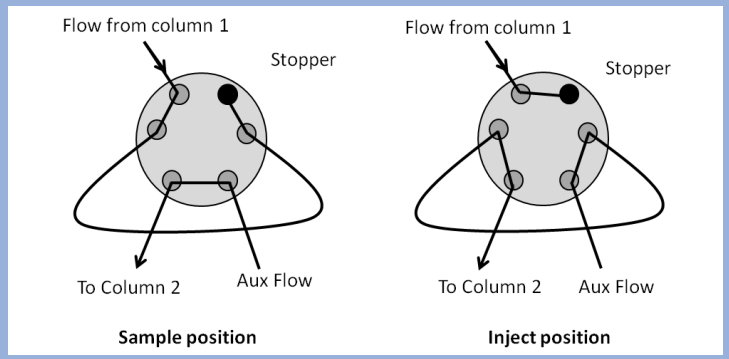


Field Portable GC × GC-FID



- Sampler, water trap and GC × GC-FID were built into a single rack

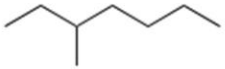
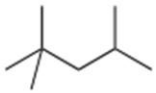
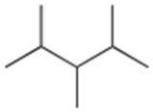
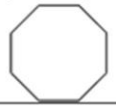
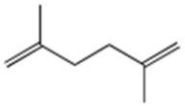
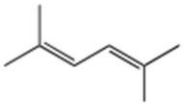
Total Transfer Valve Modulated GC × GC



Lidster et al., J. Sep. Sci., 2011, 7, 812-821

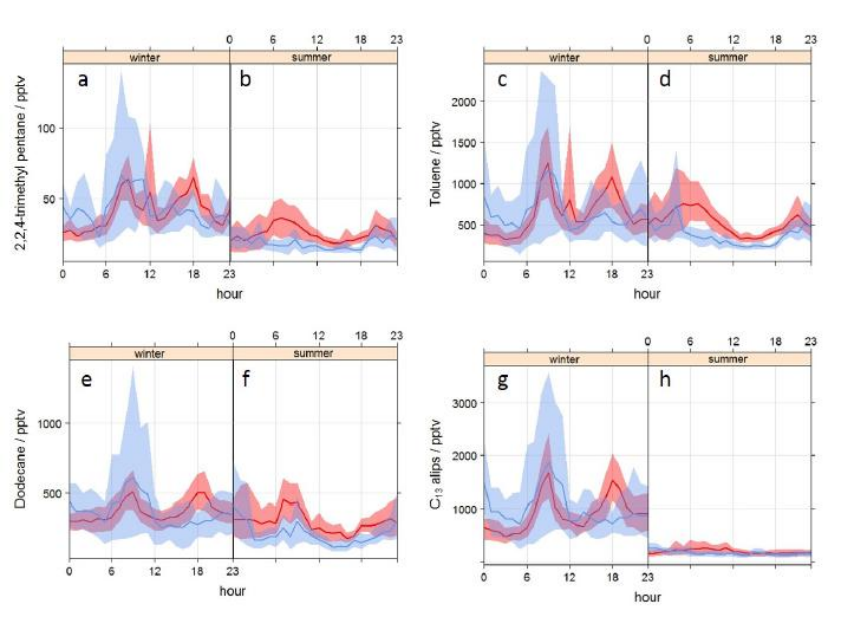
Impact of diesel emissions on OH reactivity

- We calculated primary OH reactivity for unspeciated compounds using rate constants of compounds with similar functionality
  - α-pinene for monoterpenes
  - 1,3-diethylbenzene for C_4-monoaromatics
  - *n*-alkane for the aliphatic groups
  - *n*-dodecane for all unmeasured diesel VOCs

Species	Structure	$10^{12} \times k_{OH}$[a] (cm^3 $molecules^{-1}$ s^{-1}) Measured[b]	Calculated[c]
Alkanes (linear, branched, cyclic)			
n-octane		8.11	8.28
2-methylheptane		-	8.28
3-methylheptane		-	8.56
2,2,4-trimethylpentane		3.34	4.64
2,3,4-trimethylpentane		6.46±0.21[d]	8.54
2,2,3,3-tetramethylbutane		0.97	1.00
cyclooctane		13.3[e]	11.3
Alkenes/dienes			
1-octene		41.4±0.80[f]	33.0
trans-4-octene		69.0[g]	68.9
2,5-dimethyl-1,5-hexadiene		120±2.00[g,h]	105
2,5-dimethyl-2,4-hexadiene		220±10.0[g,h]	261

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

Pollution link to irregular heartbeat and lung clotting

By Helen Briggs
BBC News, Health, Science, Environment

Air pollution kills millions each year, says study

By Mark Kinver
Environment reporter, BBC News

Outdoor air pollution is estimated to contribute to more than two-and-a-half million deaths each year, a study has suggested.

It calculated that, each year, 470,000 people died as a result of ozone and 2.1 million deaths were linked to fine particulate matter.

Air pollution increased respiratory and heart disease risks, with the young, elderly and infirm most vulnerable.

The findings appear in **the Environmental Research Letters journal**.

"Epidemiological studies have shown that ozone and PM2.5 (particulates with a diameter of less than 2.5 microns - about 30 times thinner than the width of a human hair) have significant influences on human health, including premature mortality," an international team of scientists wrote.

Air pollution is considered to be one of the major environmental risks facing the world's population

BRUCE MACKIE/SPL

erse effect on heart health

f developing an irregular search suggests.

Related Stories

nk to health,

Department of Geography
University of Cologne
Germany

Mega egacities Taskforce)

Pollution link to premature mortality, BBC News

Estimated VOC OH reactivity in London

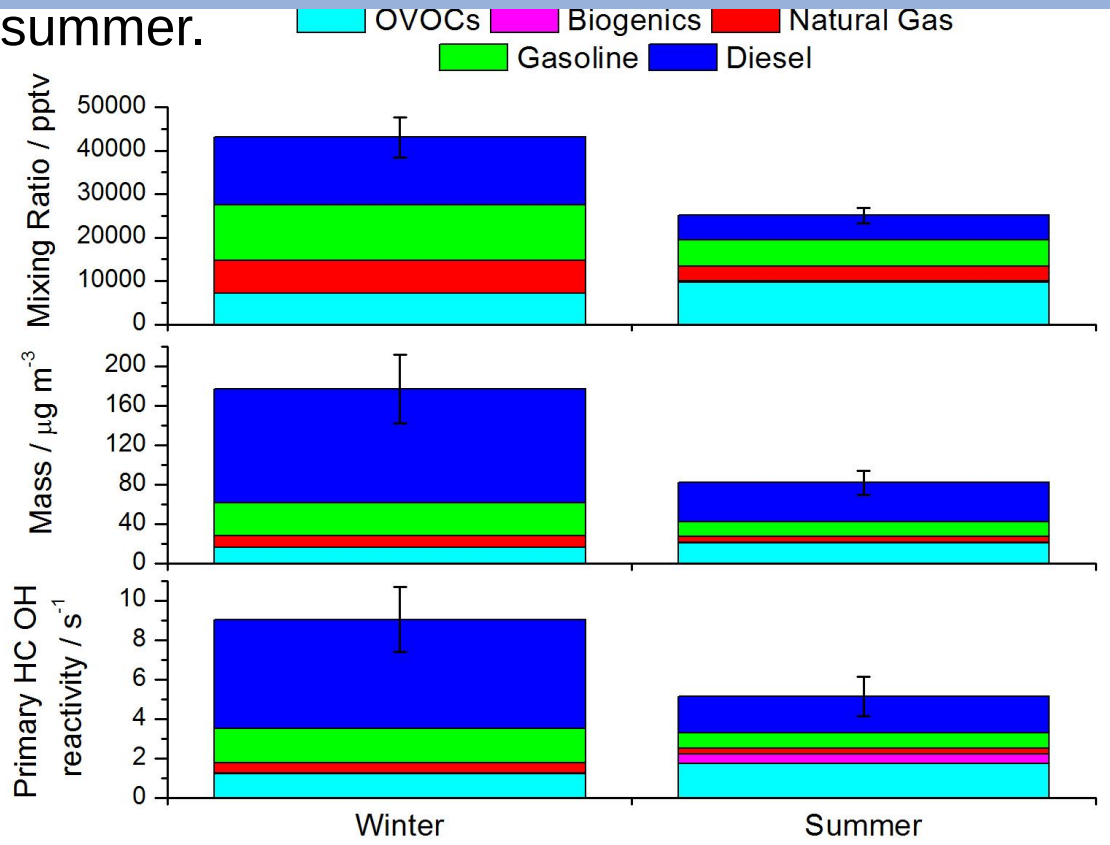
Diesel

- 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

Contributions of emission source to total mixing ratio, mass and OH reactivity for winter and 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

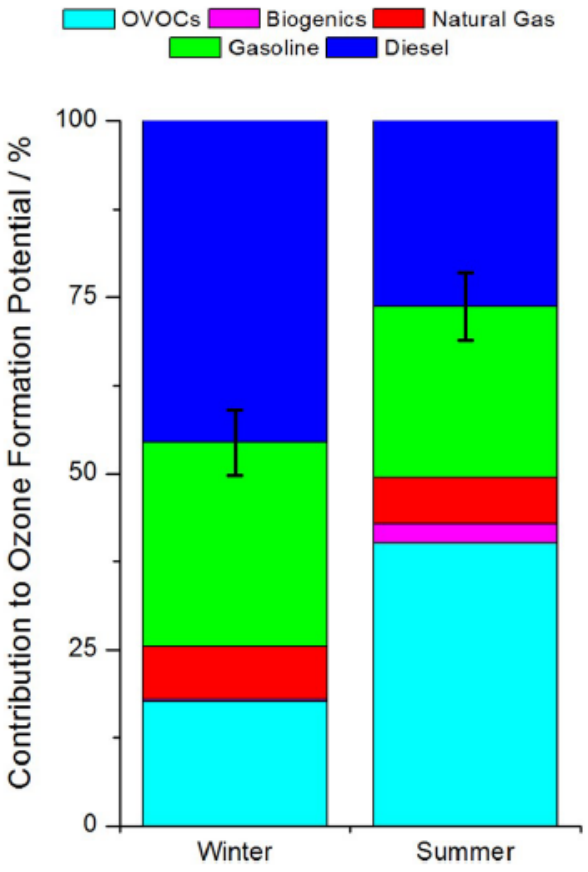


Figure 7. Contribution of emission sources to ozone formation potential, where diesel is representative of total diesel emissions and the error bars show the uncertainty of the unobserved diesel fraction calculation.

Conclusions

- 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_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)

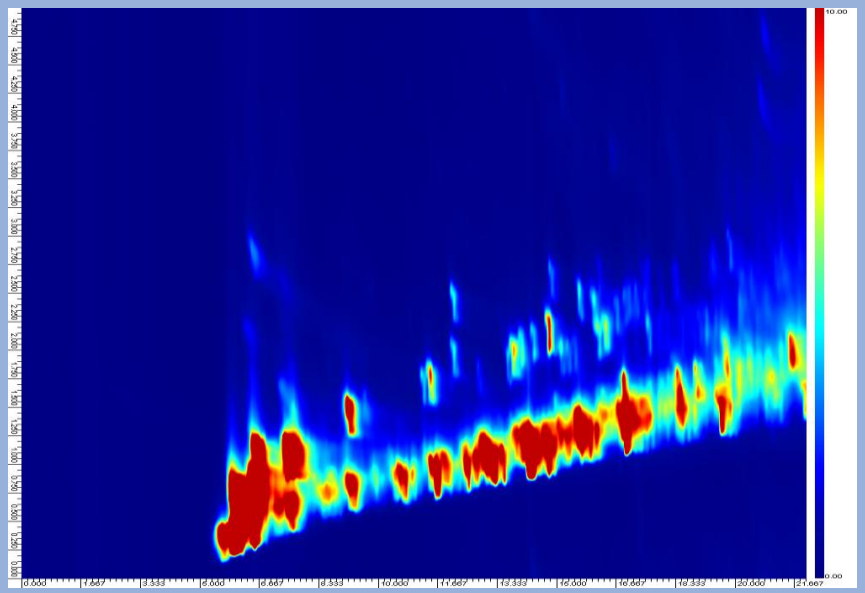
Primary particles

SOA

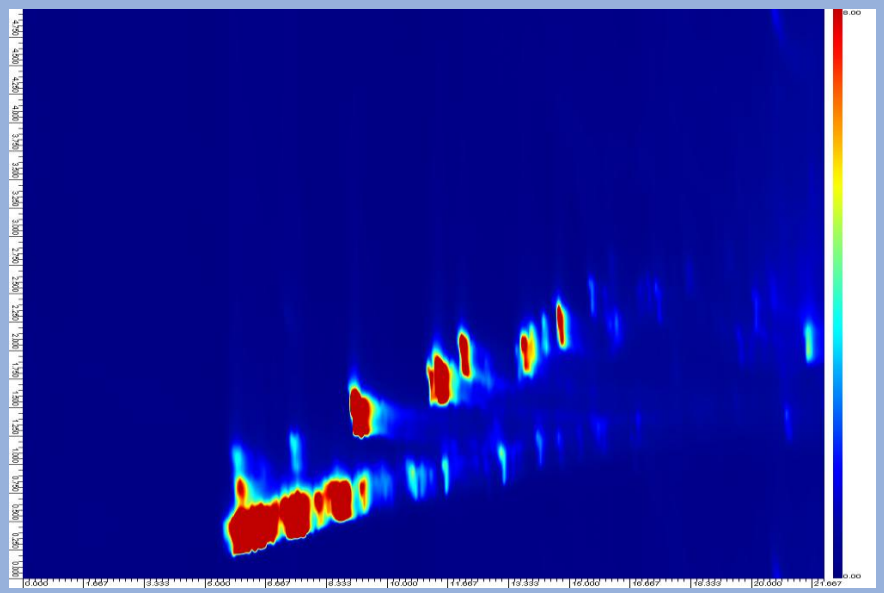
COM-PART Early Results

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

Diesel exhaust – cold start



Petrol evaporative emissions



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- Bachok campaign participants and University of Malay

NERC SCIENCE OF THE ENVIRONMENT

National Centre for Atmospheric Science
NATURAL ENVIRONMENT RESEARCH COUNCIL

THE WOLFSON FOUNDATION

Thanks to you all for listening