ROYAL SOCIETY OF CHEMISTRY | ENVIRONMENTAL CHEMISTRY GROUP

July 2017

ECG *Bulletin*

Diesel emissions and air quality. This edition features a meeting report and articles from our 2017 DGL symposium and lecture on the chemistry, health effects, and policy of diesel emissions. On pp. 12-14, Distinguished Guest Lecturer Professor Frank Kelly writes about his group's research on the health effects of diesel emissions.

Environmental Briefs. We publish our first Early Careers Environmental Briefs, written by students in the environmental sciences. Harrison Frost writes about sources and legislative control of particulate emissions (pp. 20-21), and Georgina Smith reports on policies controlling hydrofluorocarbon emissions (pp. 22-23). We welcome further suggestions for this series.

Also in this issue. ECG member Brian Graham tells us about his work at the National House Building Council (p. 3); Julia Fahrenkamp-Uppenbrink reviews "The long shadows — a global environmental history of the second world war" (p. 4); and Roger Reeve and Graham Mills report from the third in a series of biennial one-day meetings on the analysis of complex environmental matrices (pp. 5-8).

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Cover image:
Rush hour traffic on a city road.
Credit: Repina Valeriya/ Shutterstock

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The ECG Interview: Brian Graham

ECG committee member Brian Graham is an analytical chemist working in the contaminated land industry. His job is to ensure that soil contamination is remediated before building commences.

What inspired you to become a chemist? I always had an interest in how things work or why things happen. Becoming a scientist therefore was a natural choice for me. Chemistry provides lots of opportunities because it can be used to help people and solve problems. From paints to pharmaceuticals, chemistry is challenging and interesting, and it was that variety of options that attracted me.

Why did you specialise in environmental chemistry? I enjoy working outdoors and have an interest in conservation. I also found analytical chemistry interesting and did an MSc in Environmental Analysis, thus combining two areas that I enjoyed. Without proper environmental protection, people will not be safe. I hope in my own small way I am helping the planet and people.

Could you describe your current job? As Senior Geo-environmental Engineer at the National House Building Council (NHBC), my role is to ensure that land on which our customers want to build is suitable for these building projects. When contamination is found prior to building, I assess the reports of the builder's consultant to ensure that the site investigation has been carried out to the correct standard. If remediation work is needed, I check to ensure that the work was carried out correctly and that the land is suitable for occupation.

What is your advice for anyone considering a career in this area? Environmental protection is and will continue to be important as pressures grow on limited food and water resources, and as waste in all its forms becomes a bigger issue. In the contaminated land industry, we have gone from landfilling almost all wastes in the 1990s to using a whole variety of treatment approaches, such as bioremediation, solidification and groundwater treatments; many more treatments are likely to be developed. Most of them require use of scientific techniques, often based on chemistry. These changes will create opportunities (and careers) for chemists and make chemistry a promising career choice, especially if our important work becomes better rewarded in future. I would advise trying out as many different areas of chemistry as possible and before committing to one specific area — you never know what you might like until you try.

What are some of the challenges of communicating science? One of the big challenges is persuading people that what we do is useful and protects them, their families and the environment, and that environmental regulations are not just some other burden on their lives. There are success stories such as removing lead from paint and providing a non-toxic version that works just as well, and making objects out of materials that can be recycled, when previously they would have been sent to landfill. Many more challenges remain for chemists to improve the environment.

What is the most rewarding aspect of your career so far? I have found it most rewarding when I have been able to help people with a difficult issue and enabled them to overcome that challenge. I have also enjoyed working on many different types of project over the years, from individual houses to some of the biggest infrastructure projects in the UK.

If you weren't a scientist what would you do? If I was not a scientist I would probably work in IT or outdoors in conservation.

Book review

The long shadows of war

Julia Fahrenkamp-Uppenbrink (ecgbulletin@hotmail.co.uk)

The human horror of the Second World War has been the subject of a multitude of books, films, and personal narratives. The book *The Long Shadows*, edited by Simo Laakkonen, Richard Tucker, and Timo Vuorisalo, shows that the war's environmental impacts were also pervasive, not only in countries involved in the war but also in others that supplied resources for the war effort. Some of these long shadows of the war still persist today.

Perhaps the first image that comes to mind when thinking of the environmental effects of the Second World War is the devastation caused by aerial bombing, particularly at Hiroshima and Nagasaki. In a series of insightful and well written essays, *The Long Shadows* highlights some less obvious environmental effects, from forest clearing and ethnic conflict in Burma to the industrial supply chains that linked forest destruction in British Guiana to chemical pollution and hydropower construction in Canada. The common thread is the pervasive nature of modern industrial war, which leaves no part of society or the environment untouched.

For example, Paul Josephson explains that as the Soviet army retreated from the German advance in 1941, they took most resources with them and destroyed what they had to leave behind. Over the next four years, an area of about five million square kilometres of the former Soviet Union became a constant battlefield, with most major cities levelled, woods burned, infrastructure destroyed, and the debris of modern industrial war, from unexploded ordnance to spilled chemicals, polluting the countryside. Industrial production and settlement shifted permanently to previously sparsely regions in the north and west of the country. After the war, concern for the environment was brushed aside. Particularly in the production of plutonium, the Soviets paid "little attention to the grotesque environmental costs," with impacts that were still felt when the Soviet Union broke up in 1991.

In the forests of Northern India and Burma, the war also left environmental scars with persistent impacts. As Richard Tucker reports, from 1937, road building across regions of the Himalayas previously largely inaccessible to modern transport, opened up vast tracts of forest to exploitation. In India, displaced people cleared hill forests for survival. Throughout the region, the postwar period was marked by increased ethnic conflict; in Burma, conflict between newly armed local tribes and nationalists led to a decades-long civil war. The resulting disruption of resource management systems caused substantial and ongoing environmental degradation.

But the tentacles of modern industrial war reached even further. As Matthew Evenden describes, ever increasing amounts of aluminium were needed as the Second World War progressed, principally for aircraft production. Large tracts of forest were cleared in British Guiana to mine bauxite; according to Evenden, the resulting landscapes were "best described as lunar." The mineral was then transported by fossil-fuelled ship to Canada, where a vast system of hydropower dams was built to generate the power needed to smelt bauxite and produce aluminium metal. Effects on fisheries were seen as unavoidable collateral damage; chemical pollutants from aluminium production continue to linger in the fjord beds. After the war, new uses for aluminium in domestic products were quickly found, showing the links between wartime and peacetime production.

Perhaps the most unexpected angle is that taken by Outi Ampuja, who discusses what he terms the acoustic ecology of war, based in part on interviews with Finnish veterans. Ampuja finds that when asked about wartime sounds, veterans quickly talk about their feelings, particularly their fears, rather than recounting events. Many soldiers and civilians have lasting memories of wartime sounds. One veteran talks of how a breaking branch can mentally take him back to the front; thunderstorms can cause panic, and wartime sounds infiltrate the veterans' dreams. I was reminded of my mother's panic when she heard the sound of low-flying aircraft, even decades after her wartime childhood. As Ampuja writes, the wartime experiences of sound can live on in the minds of the following generations. In this as in many other ways, we are still living with the environmental effects of the Second World War.

The Long Shadows, edited by Simo Laakkonen, Richard Tucker, and Timo Vuorisalo, OSU Press, 2017. ISBN 9780870718793

Meeting report

What's new in the analysis of complex environmental matrices 2017

Roger Reeve (University of Sunderland, roger.reeve@sunderland.ac.uk) and Graham Mills (University of Portsmouth, UK , graham.mills@port.ac.uk)

Over 70 delegates and speakers attended this one-day meeting on 3rd March 2017 at the Royal Society of Chemistry, Burlington House, London. The meeting was organised by the RSC's Environmental Chemistry Group (Dr Roger Reeve), Separation Science Group (Professor Graham Mills) and Water Science Forum. Speakers discussed the monitoring and screening of a wide range of regulatory and emerging pollutants (such as pharmaceuticals and personal care products) and the detection of potentially hazardous compounds in dusts and consumer products. There were also exhibitions by instrument manufacturers and suppliers of laboratory consumables.

Seven presentations were given by UK academic institutions, government agencies, and industry, with keynote lectures by Dr Jaroslav Slobodnik (Environmental Institute, Slovak Republic) on the harmonisation of techniques used to analyse emerging environmental pollutants in European river basins and Professor Jacob de Boer (Vrije Universiteit, Amsterdam, Netherlands) on the use of direct probe mass spectroscopy to analyse exposure of humans to brominated and non-brominated flame retardants from household dust.

Professor Graham Mills (University of Portsmouth, UK) opened the meeting, welcomed the delegates and chaired the morning session. The first presentation, **'Screening of complex forensic and environmental samples using high resolution analysis and *in silico* data mining tools'**, was given by Dr Leon Barron (King's College London, UK). Analysis of contaminants in river water and wastewater can be divided into targeted analysis of known compounds and untargeted analysis. Untargeted analysis indicates, in the first instance, all resolvable components. Between these approaches, suspect screening is employed. *In silico* methods can help identify chemicals during suspect screening. Application of this technique identified pharmaceuticals, personal care products, illicit drugs, and explosives. Possible inputs of pharmaceuticals into the environment are shown in Figure 1. The methodology for analysing the medical drugs (100 mL water sample, solid-phase extraction, with liquid chromatography-high resolution mass spectrometry) produced 166 components for screening, of which 40 were selected for quantitative analysis. Artificial neural network analysis of the components can predict chromatographic retention times and was used for the preliminary identification of new compounds in the samples. LogD (the logarithm of

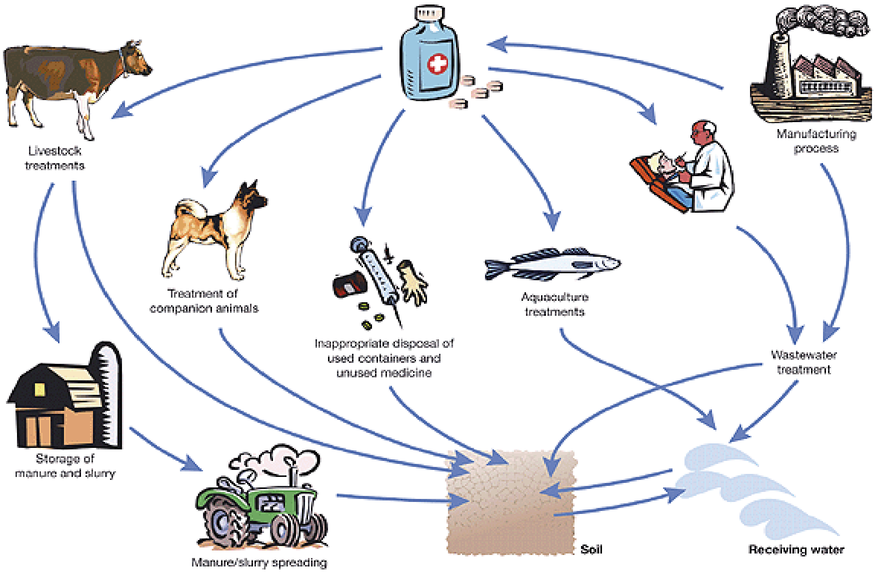

Figure 1. Possible inputs of pharmaceuticals into environmental waters.

the distribution coefficient D), logP (the logarithm of the partition coefficient P), number of C/O groups and benzene rings contributed most to the fitting. This analysis complemented identification by data mining of the high resolution mass spectroscopy data. Although these methods are an aid to identification, they are not intended to replace the traditional use of standards, but instead intended to be used to optimise the analytical effort needed to quantify a large number of components.

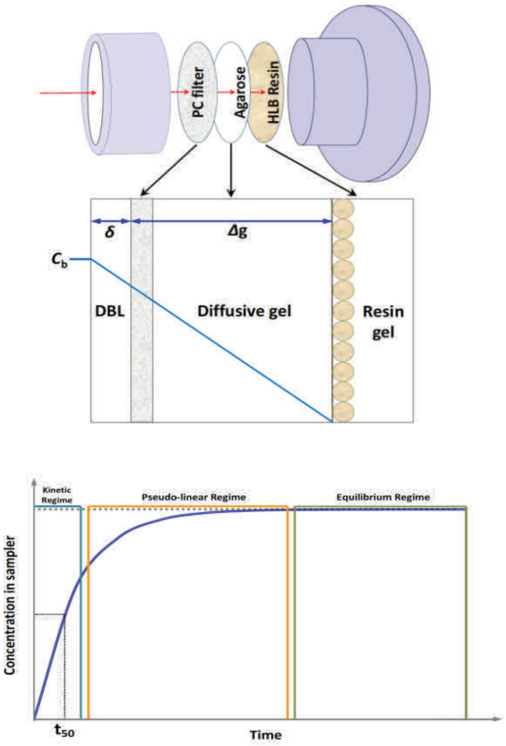

Figure 2. *Diffusive gradients in thin films (DGT) Passive Sampler.*

Dr Andrew Sweetman (Lancaster University, UK) discussed **'Use of passive samplers as a potential compliance tool within the EU Water Framework Directive'**. Passive samplers can be used over many days, giving time weighted average results as an alternative to averaging several sequential grab water samples. The specific type of sampler investigated was DGT (diffusive gradients in thin films), originally developed to determine metal lability, but now being developed for antibiotics, personal care products, pharmaceuticals, pesticides and flame retardants. A diffusion layer is sandwiched between two resin gels (HLB resin is used most commonly), as shown in Figure 2. The sampler is deployed in the environment and left to sequester pollutants over 1-2 weeks, after which time the accumulated components are extracted from the resin and the masses determined. Using knowledge of the diffusion rates masses can be related back to the dissolved concentration in the environment. The dissolved concentration reflects the biologically available fraction, but does not directly provide 'total concentrations' required by the EU Water Framework Directive. An estimate of this value can be made using partition theory. In field tests, the method has been compared with auto-sampling and grab water sampling. Successful field trials of this technique have been conducted in the Liuxi river, China (Figure 3) and at a wastewater treatment plant. Further work is needed to define sampling rates and operating range and to assess the potential of DGT samplers for predicting 'total concentrations' for a wide range of chemicals.

Professor Colin Creaser (Loughborough University, UK), in his presentation **'Combining ion mobility spectroscopy with mass spectroscopy for the analysis of complex samples: the potential for environmental analysis'**, introduced this technique, which at present has relatively few applications, but shows great promise for environmental analysis. Two formats were discussed. In drift-tube ion-mobility spectroscopy (DTIMS) separation is achieved by the differential mobilities of ions in the presence of an electric gradient and a buffer gas. Field asymmetric ion mobility spectroscopy (FAIMES) has an oscillating field which selects individual ions, similar to quadrupole mass filters in conventional mass spectrometers, but it is able to be used at atmospheric pressure. As a stand alone instrument, the technique is transportable and has field based applications. It is easy to use, has rapid response and high sensitivity, but a narrow dynamic range (1-2 orders of magnitude) and low resolution, limiting applications to simple mixtures such as BTEX (benzene, toluene and xylenes). To overcome the limited resolution within the laboratory, the technique can be coupled to conventional quadrupole or time of flight mass spectrometers. Applications included electrospray ionisation-DTIMS-quadrupole mass spectrometry for the targeted analysis of sulfonylurea herbicides in river water and haloacetic acids in water. For non-targeted analysis, collisional cross-sections, which are derived from the drift time, can be correlated with library or other standards for identification of analytes. This aspect was illustrated by identification of cyclophosphamides in wastewater. Use of the techniques gives improved performance over standard methods for targeted high throughput quantitative analysis and increased peak capacity for non-targeted applications.

Professor Stuart Harrad (University of Birmingham, UK) discussed the problem of **'Brominated flame retardants in waste consumer articles'**. There is widespread use of these compounds in consumer products such as carpet underlays and furniture, in building insulation foam and also in electronic waste. Their concentrations in human milk appear to be increasing over time whilst other high molecular mass neutral pollutants such as polychlorinated biphenyls (PCBs) are decreasing. New legislation now requires electronic waste to be separated from other waste streams and the material recovery is tightly controlled. In less developed countries, electronic waste disposal may be more rudimentary and the compounds may enter the wider environment and hence the food chain. Exposure to brominated flame retardants via eating food produced around the rudimentary recycling plants in Taizhou City, Eastern China has been shown to be significantly higher than in remote locations. Laboratory work investigated a change in leaching rates with variation of disposal conditions such as contact time, temperature and the waste matrix. Leaching from furniture and waste fabrics appeared facile, leading to the conclusion that more sustainable waste management for these products as well as for electronic waste is needed. The immensity of the problem was confirmed by a detailed analysis of brominated flame retardant concentrations in a wide range of consumer products. The use of hand held x-ray fluorescence (XRF) spectrometers was suggested for disposed product analysis (monitoring bromine) rather than conventional gas chromatography-mass spectroscopy or liquid chromatography-mass spectroscopy; preliminary testing suggested a low incidence of false-positive results.

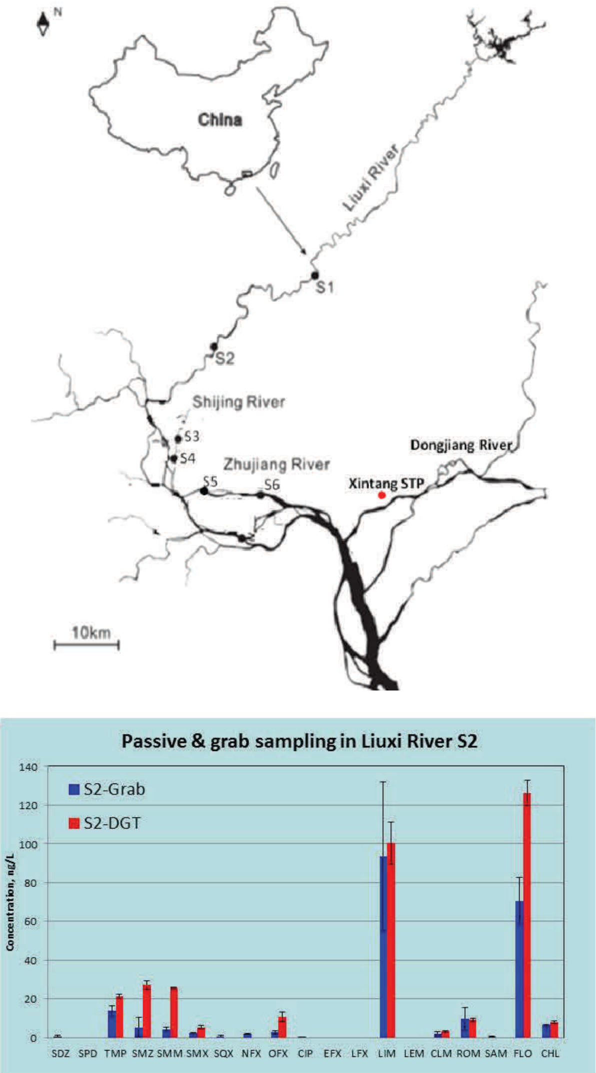

Figure 4. Field testing of DGT passive samplers captures a wide range of antibiotics

The morning finished with the first keynote lecture by Dr Jaroslav Slobodnik (Environmental Institute, Kos, Slovak Republic) on **'Non-target screening of environmental pollutants in the context of risk assessment of European river basins: the NORMAN network perspective'**. The NORMAN network within the EU (http://www.normandata.eu) has been set up to enhance the exchange of information on emerging environmental substances, their validation and harmonisation of analytical techniques. There is currently no satisfactory explanation of the ecological status of most European river basins; current priority substances do not explain all the effects. This lack of an explanation may be due to emerging pollutants (pharmaceuticals, personal care products, biocides, transformation products). Attention is usually focussed on well-known contaminants and less on metabolites and transformation products. Individual pollutants are also assessed assuming they occur in isolation and not in mixtures. Of the many compounds present, only a few determine the risk, hence the need for prioritisation. The NORMAN network and ECOTOX database provides a methodology and resources for prioritisation. Suspect and non-target screening approaches should be integrated into the screening process. Prioritisation should be determined on a broader basis than in current schemes and may be achievable by establishing open-access databases and multivariate analysis of environmentally detected chemical patterns and toxicity profiles.

Lunchtime provided an opportunity for delegates to network and inspect the sponsors' exhibitions. After lunch, Professor Mills introduced the second keynote speaker, Professor de Boer, after which the afternoon was chaired by Dr Roger Reeve (University of Sunderland, UK).

Professor de Boer (Vrije Universiteit, Amsterdam, Netherlands) discussed **'Human exposure to environmental contaminants: direct probe time-of flight mass spectroscopy reveals a multitude of chemicals**

indoors ’. The talk centred around flame retardants, starting with brominated compounds and then non-brominated alternatives, including chloroparaffins and phosphorus-based compounds. There are neurotoxicity concerns for the latter group. Samples of indoor dust contain complex mixtures of flame retardants as well as other chemicals. Direct probe mass spectroscopy, which introduces the solid sample directly into the ionisation chamber of the mass spectrometer, has been used as a fast screening technique (typically 5 min per sample) for compliance with legislation. As many retardants are highly non-polar, atmospheric pressure chemical ionisation APCI and APPI (atmospheric pressure chemical ionisation and photoionisation) are suitable ionisation techniques. The method avoids losses found in techniques using extraction/separation.

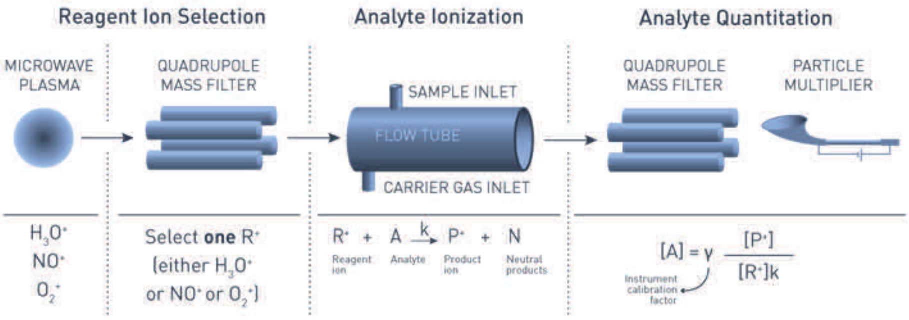

Figure 4. Selected Ion Flow Tube Mass Spectrometry

Monitoring taste and odour substances in drinking water is a regulatory requirement linked to acceptable ‘wholesomeness’ of potable water. Mr Gavin Mills (Severn Trent Water PLC, UK) described **‘Advances in the identification of tastes and odours in drinking water’** including the current state of the art methodology. Sample preparation for injection into the gas chromatograph is automated using Instrument Top Sample Preparation (ITSP) cartridges. These provide solid phase extraction clean up of the sample as part of the automation system. Gas chromatography triple quadrupole mass spectrometry is useful for routine work whereas gas chromatography quadrupole time of flight, with greater sensitivity and selectivity, allows simultaneous determination of targeted and non-targeted compounds. A supplementary ‘detector’, an odour port allows individually eluting compounds to be matched to the odours. Examples were given of identification and determination of low-level ‘tasty’ compounds found in water samples, one of which was not even present on international databases.

Ms Erika Castringanò and Mr Luigi Lopardo from Professor Barabara Kasprzyk-Hordern’s group at the University of Bath, UK gave a presentation that asked the question **‘Can urban water profiling inform our understanding of the state of environmental and public health?’** The main example, provided for context, concerned the misuse of pharmaceutical drugs, which appear in wastewater. The drugs (as with most pharmaceuticals) are chiral and single enantiomers are used for legitimate medicinal application. Drugs bought on the street are less pure and can contain a mixture of the enantiomers. Analysis of the water samples by extraction-LC-MS using chiral LC columns allows the concentrations of the enantiomers to be determined leading to an estimation of the relative proportions of the legal and illicit use of the drugs. Investigations of water profiling have been extended to endocrine disruptors and determination of metabolic biomarkers. *In vitro* studies combined with urban water analysis can be used to determine public exposure.

Dr Mark Perkins (Anatune Ltd., UK) in his presentation **‘VOC measurements in ambient air using Selected Ion Flow Tube Mass Spectrometry – automation and calibration considerations’** described developments in the technique to produce an autonomous air monitoring system. The work was in collaboration with Dr Marvin Shaw at the University of York, UK. The selected-ion flow-tube mass spectrometer (SIFT-MS) technique (Figure 4) involves the chemical ionisation of the analyte by selected positive precursor ions. These ions are produced from humidified air by a microwave plasma which means no external gas supplies are needed allowing autonomous field use. Although the technique allows concentrations to be determined directly without standards using library reaction rate data, high accuracy calibration uses traceable gas standards. Prior to deployment, optimisation included sensitivity and limit of detection. Current field trials in Beijing, China are evaluating the robustness and reproducibility of the SIFT-MS in routine field deployment, and determining the accuracy and precision of the SIFT-MS for measuring real time trace level VOC mixing ratios.

The above synopses were prepared by Roger Reeve and Graham Mills based on the presentations and slides supplied by the speakers. The industry meeting sponsors were Agilent Technologies, Anatune Ltd., Hichrom Ltd., Imspex Diagnostics Ltd., Kinesis, Markes International and Thames Restek Ltd. Financial support is also acknowledged from the Environment Sustainably and Energy Division of the RSC, which facilitated the attendance of the two international speakers.

Meeting report

Inside the engine — from chemistry to human health

Laura Newsome (Univ. of Manchester, laura.newsome@manchester.ac.uk)

The 2017 ECG Distinguished Guest Lecture and symposium was held on 1st March 2017, exploring the chemistry of diesel engine emissions, emissions policy, and how this is affecting human health. The ECG Distinguished Guest Lecture was given by Professor Frank Kelly, King's College London.

In the introductory talk, **Dr Claire Holman (University College London/Brook Cottage Consultants)** explored the links between diesel vehicles and poor air quality. Today, media interest in this topic is higher than it has been at any time since the late 1980s/ early 1990s. The key air pollutants in most of our cities are nitrogen dioxide (NO_2) and fine particulate matter (PM) in urban areas, both of which are predominantly emitted by diesel engines. Indeed, most of the air quality management areas in the UK are due to high concentrations of NO_2. The biggest contributor to NO_x (oxides of nitrogen, including NO_2) is road traffic (80%).

Many car manufacturers installed 'defeat devices', which switch off pollution control technology after a certain period of time or below a threshold temperature to avoid engine damage.

Vehicle manufacturers tend to prefer to improve vehicle emissions by improving the engine rather than adding an additional component to treat the exhaust. However, there is a trade-off between generating CO_2, NO_x and particulates; often if the engine is improved to treat one type of emission then issues can arise with another type. For example, reducing CO_2 and hydrocarbon emissions can lead to an increase NO_x emissions. CO_2 is the primary cause of climate change, which is a global issue requiring global agreement whereas air pollution is a more regional or national issue, where local and national action can have direct benefits for local inhabitants. This disconnect results in an interesting tension between efforts to tackle climate change and air pollution.

Vehicle emissions are measured in a laboratory using a chassis dynamometer to confirm compliance with the EU Type Approval test. Emission test results show that emissions from diesel cars have improved substantially in the last decade, but are still considerably higher than those for petrol cars. Yet, currently around 30% of cars (and 50% of new cars) are diesel, largely because of incentives for buying them as they were perceived to be better for the climate (lower CO_2 emissions per kilometre travelled). Critically, the reduction in emissions observed in the laboratory tests have not been reflected in data from real driving conditions, which are typically up to six times greater.

All new cars have some sort of abatement technology fitted, but to aid performance these are not always activated under all driving conditions. In fact, many car manufacturers installed 'defeat devices', which switch off pollution control technology after a certain period of time or below a threshold temperature to avoid engine damage. For example, the vehicles produced by one manufacturer switches off their pollution control after 22 minutes (and it has been noted that the typical laboratory emission test lasts 20 minutes), and others may be predominantly switched off in temperatures typical of northern European climates.

Although Volkswagen received much of the bad press, Dr Holman concluded that their most recent models actually had one of the lowest on-road emissions, compared to other manufacturers, although their on-road real world emissions were still nearly double the test cycle limit for NO_x. As a result of these issues, from 2019 all new vehicles will be subject to a 'real driving' emissions test with the permitted limit initially being 2.1 times that for the laboratory tests in 2019, and this will decrease to 1.5 times by 2020/21.

Dr Jacqueline Hamilton (University of York) began her talk by noting that diesel use is increasing worldwide, not just in Europe, and by 2040 diesel will be the predominant fuel globally. After exiting the engine in modern vehicles, diesel emissions in modern vehicles including NO_x, CO, CO_2, PM, volatile organic carbon compounds (VOCs) and unburnt fuel pass through an oxidising catalyst, then a diesel particulate filter, before being emitted as exhaust. VOCs are important as they can be oxidised to form ozone, are implicated in the oxidation of NO to NO_2 and can form secondary organic aerosols (SOAs) through condensation onto pre-existing aerosols. Both ozone and SOAs are known to be toxic.

The concentrations of pollutants measured in the atmosphere by flying a plane over London were much larger than calculations based upon the National Emissions Inventory would suggest. There has been controversy over the role that diesel plays in generating SOA. Although levels of smaller hydrocarbons in the air are falling, the speaker argued that the (largely neglected) intermediate size (> C_{10}) volatile organic compounds from diesel exhaust may be key to understanding the concentrations of SOAs in the atmosphere. This is becoming more important as diesel cars are now known to be the largest contributor to urban SOA formation when they make up more than 10% of cars on the road.

London has some of the highest NO_2 concentrations in the world. Credit: Brian Minkoff/Shutterstock

Measuring VOC emissions is difficult and has therefore often been overlooked. They are present at parts per billion to parts per trillion concentrations in a complex matrix (air), and have a vast range of polarities and isomeric complexity. A new technique called two dimensional mass spectrometry (GC-GC-MS) can separate out over 600 VOCs from an urban air sample. This is a powerful tool to identify the sources of hydrocarbons in the atmosphere and, potentially, their contribution to SOA formation. Two dimensional gas chromatography has been used to measure VOCs in London air and in diesel exhaust in laboratory test conditions, and the most recent deployment is in a project looking at air quality in Beijing.

While the National Emissions Inventory shows good agreement with atmospheric measurements for molecules with few carbon atoms, those greater than C_{10} in size can be underestimated by a factor of 70. However, this discrepancy can be accounted for once the emission of intermediate VOCs from diesel engines is included in the models. Dr Hamilton concluded that diesel emissions contribute up to 30% of SOA in the UK. The shift to diesel in the UK has changed the balance of hydrocarbons in the atmosphere, but this shift has been unnoticed due to a lack of measurement infrastructure. However, new research is now highlighting the importance of pollutants other than CO_2 and NO_2 from diesel emissions.

Simon Birkett (Clean Air London) explained that modern air quality legislation was first introduced by the Clean Air Act of 1956 following the Great London Smog in 1952. However, London currently has some of the highest NO_2 concentrations in the world. Mr Birkett therefore asserted that similar pioneering action needs to be taken.

In the 1980s, concerns rose about lead in petrol, leading to the development of the three way catalytic converter. The Thatcher government played a key role in developing UK environmental policy, which was first published in the 'This Common Inheritance' report in 1990 and discussed unleaded petrol, carbon dioxide and ozone. Even in 1990/1991, there was knowledge and awareness of the health effects of diesel emitted particles (the 1992 issue mentioned that small particles from diesel fuel may contribute to cancer). But it was not until 2012 that the International Agency for Research on Cancer classified diesel fuel as carcinogenic. During the early 1990s, a focus on fuel efficiency and hence lower CO_2 emissions meant that diesel was nevertheless prioritised. Since then, all successive governments have promoted diesel to act on climate change concerns.

Mr Birkett compared effect of diesel emissions on air quality today to passive smoking in the 1970s; health impacts were acknowledged by the WHO, but efforts to tackle the problem still took decades. Moreover, he called it ironic that increasing diesel use has not lowered carbon dioxide emissions, as originally intended. The speaker called for a "One Atmosphere" strategy that does not focus just on air quality or on carbon dioxide, but rather tackles both at the same time. His ambition would be to rid London of all fossil fuels by 2033 — this would require acting now as, for example, new diesel taxis registered this year will be around for 15 years.

The symposium closed with the ECG Distinguished Guest Lecturer, **Professor Frank Kelly (King's College London),** who spoke on "Traffic Pollution and Health in London, Umea and Beijing". He began his talk by describing the WHO air pollution pyramid; at the bottom all people exposed to air pollution have unnoticed (but consequential) physiological changes. Moving up, a proportion of people will have symptoms such as running eyes and asthma, and at the top of the pyramid there are 29,000 annual deaths in the UK linked to particles in the atmosphere (PM$_{2.5}$).

Umea in Sweden has pristine air and world class research facilities and is thus a perfect place to study the effects of air pollution using an ozone exposure chamber or by performing investigative bronchoscopy on medical student volunteers after controlled exposure to air pollution. A two-hour exposure to ozone caused an inflammatory response, with neutrophils shown to enter the lungs. This effect was also observed after exposure to diesel exhaust at concentrations commonly found in the environment, as well as the expression of genes associated with an immune system response, and activation of bronchial mucosal cells.

> **A six year study called EXHALE of children at schools close to main roads, conducted in East London, … showed that everyday exposure to air pollution had an adverse effect on lung growth in children.**

The immune response to particulates in our lungs damages the tissues and causes long term impacts. Macrophages engulf black carbon particles (from diesel exhaust) in the lungs, and try to destroy them as they would a bacterial invader by producing free radicals. As there is no bacterium to absorb the free radicals, they end up killing the macrophages and causing small levels of cellular damage. Moreover, particles contain metals and organic compounds, so also cause complex chemical reactions at the lung surface.

Damage accumulates over time and can lead to disease such as chronic exposure disease, but the response to air pollution varies widely between subjects. This variation is typical of human exposure studies, and an important aspect of this research is to understand which factors affect this variation and why.

Professor Kelly described experiments that he and his coworkers had conducted using Oxford Street and Hyde Park in London as a natural laboratory to study exposure to 'high' and 'low' pollution levels. The first experiment involved asking asthmatics to take a two hour walk before measuring their lung function using spirometry. Not only was lung function reduced after exposure to Oxford Street pollution (and compared to those who walked in Hyde Park), it was also still reduced 22 hours later. Researchers in Germany found that you have a higher risk of coronary artery calcification (which can lead to heart attacks) the closer you live to a main road, so Professor Kelly used the Oxford Street and Hyde Park natural laboratory to see what effect air pollution had on people with lung disease. Results showed increased airway resistance in ischaemic heart disease patients and increased airway dysfunction and arterial stiffness in patients suffering from chronic obstructive pulmonary disease.

A six year study called EXHALE of children at schools close to main roads, conducted in East London, investigated how exposure to NO$_x$, NO$_2$, PM$_{10}$ and PM$_{2.5}$ might impact on their lung development. The results showed that everyday exposure to air pollution had an adverse effect on lung growth in children. Those exposed to 35 µg/m^3 NO$_2$ had lost 105 ml of lung capacity (5.5%); those with higher exposures of 55 µg/m^3 had lost 165 ml (8.7%). If this deficit is not remedied before the children stop growing, they will have reduced lung capacity throughout their lives. The researchers also found evidence for black carbon from diesel in the children's lungs. Around 65% of their exposure was from their journey to school or in the playground.

In the final part of his lecture, Professor Kelly shifted attention to his recent work in China. The problems seen in London pale into insignificance compared to those in many parts of East Asia today, where heavy traffic and industrial emissions cause severe smog in cities, while indoor air pollution from cooking stoves dominates in rural areas. Ambient air pollution is the fourth biggest killer in China and indoor air pollution is the fifth. Most vehicles in China run on petrol. In ongoing work in Beijing, the researchers have recruited two groups of 120 subjects at two sites, one in the city and one in a nearby rural location. They are using sophisticated personal monitors to gain a detailed picture of individual exposure to a range of pollutants, compare the effects of outdoor and indoor air pollution, and identify the resulting health impacts, with physiological and gene expression studies.

Article

Air Pollution and health: knowledge gained from journeys to Umea, London and Beijing

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In cities across the globe, road transport is an important source of air pollutants that are linked to acute and chronic health effects. In the last 20 years, my research group has investigated these associations in human challenge chamber studies in Umea, Sweden, real world exposure scenarios in London, and recently in the megacity Beijing, China. In this article, I review our findings and those from other groups to show that humankind must advance beyond a fossil fuel-based road transport system.

The main particulate matter (PM) components originating from road traffic are engine emissions, largely comprising elemental carbon and organic carbon, and non-exhaust sources that are often characterised by elevated concentrations of transition metals from brake wear (copper, antimony), tire abrasion (zinc), and road surface wear and dust resuspension (iron). The largest single source is derived from diesel exhaust. Indeed, owing to the increased market penetration of diesel engines in many European countries and the fact that they generate up to 100 times as many particles as comparable gasoline engines with three-way catalytic convertors, diesel exhaust particles contribute significantly to the airshed in many of the world's largest cities.

Owing to the toxic and ubiquitous nature of vehicle derived particles, our early work at the University of

Rush hour traffic on a city road. Credit: Repina Valeriya/Shutterstock

Umea (see the photo) focused on controlled diesel exhaust exposure studies to understand the mechanisms through which diesel exhaust exacerbates respiratory disease, as identified in epidemiological research. To investigate effects on the airways, human volunteers (healthy and/or mild asthmatic) were exposed for one to two hours to whole diesel exhaust (particulates and the associated gas phase emissions) from an idling engine at concentrations ranging from environmentally relevant to those commonly experienced in busy diesel-dominated traffic environments.

The pristine air in Umea, Sweden makes it possible to do controlled exposure experiments to determine the health effects of air pollution. Credit: Andreas Gradin/Shutterstock

By performing blood, bronchoalveolar lavage, and bronchial mucosal biopsy sampling after exposure, these studies have been instrumental in uncovering a systemic and pulmonary inflammatory response, attributed in part to the oxidative properties of exhaust PM (*1–7*). This exposure also upregulates redox-sensitive transcription factors and their associated upstream stress-related mitogen-activated protein kinases in the bronchial epithelium of human airways (*6*). Signalling cascades such as these likely act as the trigger by which diesel PM induce expression of proinflammatory cytokines in airway tissue.

Exposure to combustion-related PM, at concentrations experienced by populations throughout the world, contributes to pulmonary and cardiac disease through multiple mechanistic pathways that are complex and interdependent.

These events, in turn, provide a cellular basis for the rapid influx of neutrophils, lymphocytes, and mast cells from the circulation to the source of the inflammatory focus, namely the airways, as well as the systemic response in the form of neutrophilia and selective lymphopenia in the peripheral blood. These findings supported the well-established and highly regulated fashion in which neutrophils and other inflammatory cells from the blood transit into tissue. This occurs in association with an upregulation of adhesion molecules on the endothelial cells and their respective ligands on the leukocytes, along with release of chemo-attractants from the epithelial and inflammatory cells.

Although diesel exhaust consists of several pollutants, including gases (oxides of nitrogen, carbon, and sulphur) and PM components, it is unlikely that the NO_2 concentrations (0.7 or 1.6 ppm) in the diesel exhaust used in these studies played any major role in the observed inflammatory events. In a study using a similar protocol, exposure to NO_2 alone, at similar or higher concentrations for a longer duration (up to 2 ppm NO_2 for 4 hours) failed to elicit adhesion molecule upregulation or significant changes in inflammatory cells in the bronchial mucosa sampled at the same time point; this observation suggests that the PM content of diesel exhaust is the responsible pollutant (*8*).

Away from orthodox, controlled exposure chamber studies, we next undertook work in London. Using the city as the laboratory, we used real world exposure scenarios to investigate the respiratory effects of short-term exposure to diesel traffic (*9*). In adults with mild to moderate asthma, walking for two hours along a busy city street where traffic is entirely diesel powered (as opposed to in a nearby park) resulted in a significant but asymptomatic reduction in lung function. In line with our studies of humans in exposure chambers and our current understanding of the chain of molecular events, roadside traffic exposures also induced inflammatory changes (*9*).

This evidence from research in Umea and London supports an interactive chain of events linking pollution-induced pulmonary and systemic oxidative stress, inflammatory events, and translocation of particle constituents with an associated risk of vascular dysfunction, atherosclerosis, and ischemic cardiovascular and obstructive pulmonary diseases. It is now clearly recognised that exposure to combustion-related PM, at concentrations experienced by populations throughout the world, contributes to pulmonary and cardiac disease through multiple mechanistic pathways that are complex and interdependent.

In contrast to the UK's long industrial heritage, China has undergone rapid industrialisation over the past few

Smog covered city center of Beijing on 11th October 2014. Credit: TonyV3112/Shuttterstock

decades, adding thousands of kilometres of urban road and hundreds of millions of vehicles. PM emissions from traffic have contributed to increasingly poor air quality in Beijing (see the photo) (*10*), threatening public health (*11*). The severity of air pollution in Beijing was first acknowledged when China was bidding for the Olympic Games in the 1990s. To address the problem, in 1998 the Beijing municipal government introduced the first of 16 stages of air pollution control measures.

Initial measures mainly focused on shutting down small industrial and domestic coal burning stoves and controlling dust from road and construction sites, as well as phasing out old vehicles that did not meet emission standards. During the Beijing Olympics in 2008 (*12*) and the Asia-Pacific Economic Cooperation meeting in Beijing in 2014, aggressive measures were taken to reduce the number of vehicles on the road by allowing cars to be used on only certain days of the week, determined by the last digit of the car license number. This measure resulted in substantial temporary reductions in congestion and pollution concentrations in Beijing and was considered so successful that it was made a routine rule immediately after the Olympics. Today, every car is allowed to drive four days per five weekdays. These efforts to control air pollution in Beijing have shown some success. Concentrations of $PM_{2.5}$ (that is, PM with diameters of 2.5 μm or less) have started to fall in recent years. However, these benefits have been compromised to some extent by the rapid growth in vehicle numbers from 1.5 million in 2000 to 5.6 million in 2015.

In 2016 with funding from the UK's Natural Environment Research Council (NERC) and the Medical Research Council (MRC) under the Newton Programme, we started work on a new project in Beijing, termed AIRLESS (Effects of air pollution on cardiopulmonary disease in urban and peri-urban residents in Beijing). We are examining the impact of air pollution on the health of residents who live in the centre of Beijing, compared with residents who live outside the Beijing urban sprawl in a rural area. The 120 individuals in the rural area are exposed to pollution from coal/biomass type burning, whereas in central Beijing the pollution is more traffic-based. We provide the volunteers with personal air quality monitors and measure their exposure for 24 hours a day for seven days. These data provide us with a unique view of their personal exposure to air pollution. We are also taking biological samples including blood and urine from these individuals, and we are looking for signals to the specific pollutants that they are being exposed to. With this approach, we will learn if the pollution in China results in the same type of biological responses we have seem previously in Umea and London; if not, we will have a better understanding of why different types of air pollution lead to particular biological responses.

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Article

Do diesel vehicles cause poor air quality?

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Poor air quality in the UK is mainly caused by diesel vehicle emissions. Although improvements have been made in the latest generation of diesel vehicles, testing under real driving conditions showed that their emissions of nitrogen oxides are still six times greater than the EU limit value. Diesel engines also emit airborne particulate matter which is thought to contribute to more than 5% of all UK deaths. A new emissions testing regime will begin in 2019, but there is long way to go before health-based air quality objectives will be met.

Air pollution is a major issue in the UK. Exposure to small airborne particles (known as $PM_{2.5}$) contributes to about 6% of all deaths in England, with additional deaths and ill health caused by exposure to nitrogen dioxide.

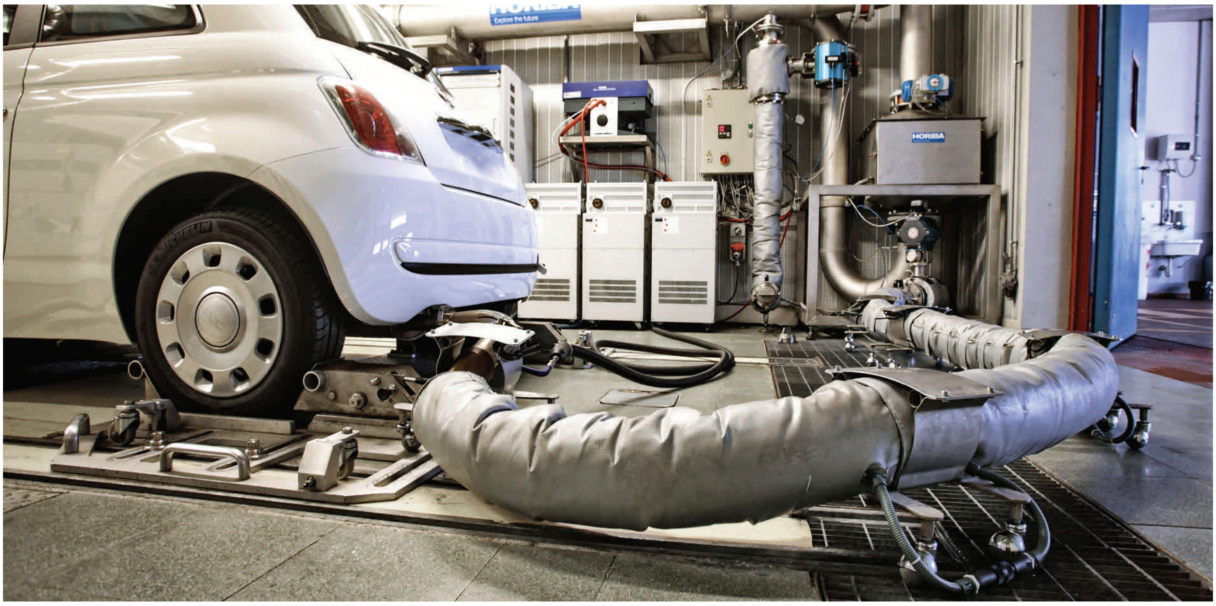
Approximately two thirds of local authorities have declared air quality management areas, mainly for high NO_2 concentrations due to emissions of nitrogen oxides (NO_x) from road traffic. Furthermore, the EU annual mean NO_2 limit value is exceeded in 38 out of the 43 air quality monitoring zones in the UK. In December 2015 the Government published its national air quality plan “Tackling nitrogen dioxide in out towns and cities”. This states that “*on average transport is responsible for 80% of NO_x emissions at the roadside in areas where we need to act to reduce levels*”. Diesel vehicles are the largest source of NO_x. Whilst heavy duty vehicles such as lorries and buses tend to be diesel fuelled, and have been for many years, the number of diesel light duty vehicles (cars and vans) has been increasing. These vehicles have much higher NO_x emissions than their petrol equivalents, but despite this they were promoted by successive governments through more favourable taxation due to their lower carbon dioxide emissions.

NO_x and particulate matter (PM) are commonly produced during combustion processes. NO_x is generally considered to be a combination of nitric oxide (NO) and nitrogen dioxide (NO_2). Most of the NO_x emissions from diesel vehicles are as NO, which is rapidly oxidised in air to NO_2. PM is a heterogeneous mixture of pollutants emitted from many sources, including combustion. PM is also formed in the atmosphere from air pollutants such as NO_x, sulphur oxides and organic compounds.

Generally there is a trade-off in emissions between fuel efficiency (and hence CO_2 emissions), PM and NO_x. For a given fuel efficiency or CO_2 emission an engine can be calibrated to have either low NO_x or low PM emissions, not both. For low CO_2 emissions there are likely to be high NO_x emissions. Consequently, the emission limits for NO_x are more lenient for diesel than for petrol cars. However, there are PM emission limits for diesel vehicles but not for most petrol vehicles, as generally petrol cars have virtually no PM emissions.

New vehicles must pass a series of type approval tests. Car emissions are tested in a laboratory on a rolling road as the car is driven over a standard test cycle. Petrol cars achieve the emission limits in the laboratory by a wide margin; diesel cars less so. However, remote sensing and portable emission measurement systems have shown that emissions from diesel cars are much higher when driven on the road than under laboratory conditions. This is not the case for petrol cars, which achieve similar results in the laboratory and on the road and outperform diesel in both environments. There has been little improvement in NO_x emissions from diesel vehicles (both heavy and light duty) until very recently. For example, the latest generation of diesel vehicles have been shown to have lower on-road NO_x emissions than earlier generations; with Euro 6 cars, for example, having about half the emissions of Euro 5 cars.

This is not a newly identified problem. As far back as 1993 the Quality of Urban Air Review Group (of which I was a member) concluded that “...unless some improvements in the emissions from diesel vehicles can be achieved, there must be considerable concern over any increase in the proportion of diesel vehicles on our



A car emissions testing centre in Turin, Italy, in 2014. New diesel cars will soon have to pass more stringent emissions tests. Credit: MikeDotta/Shutterstock

urban streets as their impact on urban air quality is undoubtedly quite serious" [page 69 in (*1*)]. The diesel share of the new car market has increased from 20% to almost 50% since that report was published. In some other European countries, the share is currently around 70%. Greece used to have the lowest share in the EU until 2011, when a ban on diesel cars in the country's two largest cities, Athens and Thessaloniki, was removed. In just four years diesel car sales increased from 4% to over 60%.

For many years France had one of the highest proportions of diesel cars, reaching a peak of over 75% in 2008. The French car manufacturers, particularly the PSA (Peugeot and Citroen) group, were among the early promoters of diesel cars. In the early 1980s, diesel cars were reliable, durable, and fuel efficient, but unrefined to drive. Two technical advances led to diesel cars becoming as attractive to motorists as petrol cars; turbo-charging and direct injection diesel, and from 2001 their fuel economy benefits led the UK Government to provide tax incentives through a CO_2 based vehicle excise duty.

New post 2015 (Euro 6) petrol cars have much higher carbon monoxide and hydrocarbon emissions than an equivalent generation of diesel car, and slightly higher CO_2 emissions. On the other hand, the NO_x and PM emission from diesel cars are much higher. The political pressure to reduce CO_2 emissions led to some petrol engines becoming more similar to diesel engines, and as a result their NO_x and, particularly, PM emissions are higher. This new type of engines are known as direct injection gasoline or GDI engines and are subject to a PM limit for the first time.

The NO_x emission limit is more lenient than for petrol because of the difficulty in reducing NO_x emissions from diesel cars; diesel cars are permitted to emit 33% more NO_x than petrol cars. This is, however, only one element of the diesel NO_x problem. While on-road NO_x emissions from petrol cars meet the limit value, those from diesel cars are many times higher. The vehicle emissions testing programme (*2*) found that on average, Euro 6 diesel cars emitted more than six times the limit value when driven on the road.

The other problem with diesel cars is that they have much higher primary (direct) NO_2 emissions than petrol cars. Primary NO_2 emissions have a large influence on NO_2 concentrations close to busy roads. Researchers at King's College London have analysed trends in ambient NO_2 concentrations (*3*) at roadside locations in London over the periods 2005-2009 and 2010-2014. Between 2005 and 2009 there was an increase in NO_2 concentrations. However, over the second period there was an average reduction of NO_2 of nearly 10% as well as a large reduction in $PM_{2.5}$ (28%) and black carbon (11%) (*4*). The trends were not fully explained by lower levels of traffic and therefore it is likely that the reduction was due to a decrease in primary NO_2 emissions. Despite the general downward trend in roadside NO_2 concentrations, this was not observed at all roadside monitoring sites.

In relation to high NOx emissions from diesel cars, an analysis (*5*) of the results of the real-world emission testing programmes was undertaken by several European governments in response to the Volkswagen emissions scandal, and showed that there is a huge variation in NO_x emissions when measured as the vehicle is driven on the road, with ironically Volkswagen cars performing the best, but the emissions were still about twice the laboratory-based limit value. The worst performing vehicles, from Renault, Nissan, Fiat and Suzuki, had NO_x emissions more than 14 times the limit value. These high real world emissions are caused by a range of strategies that car manufacturers have adopted for managing the pollution control system. These include both the engine management system recognising the laboratory test cycle, and switching off the emission controls after 22 minutes (the test cycle lasts about 20 minutes). Other manufacturers switch off the system when the ambient temperature is too cold or too hot, or when the engine is under load (i.e. when emissions are high). The average temperature in southern England is in the range of 12 to 15 °C, yet two car manufacturers switch their pollution control systems off when the ambient temperature is less than 17 °C.

Remote sensing and portable emission measurement systems have shown that emissions from diesel cars are significantly higher when driven on the road than under the laboratory conditions. This is not the case for petrol cars.

A new real driving emission (RDE) test is to be introduced for new car types from September 2017, and for all new cars from September 2019. This will limit real driving emissions to 2.1 times greater than the laboratory based limit value. A second stage is to be introduced from January 2020/2021 to reduce the RDE emissions to 1.5 times the laboratory limit. To meet these new requirements, manufacturers may need to combine emission abatement technologies, such as selective catalytic reduction and lean NO_x traps, to ensure they work effectively over the whole operating range of a diesel engine. This may be a challenge for small diesel cars, especially if much larger on-board storage tanks for AdBlue (*6*) are needed, as there is little spare space.

Finally, are the benefits of diesel cars regarding lower CO_2 emissions real? Similar to the NO_x emissions, CO_2 emissions measured in laboratory tests are also much lower than the real driving emissions. Comparison of the official CO_2 emissions with large databases of real fuel consumption data (*7*) suggests that the difference between the laboratory and real world CO_2 emissions has grown since 2001, when the UK first gave an incentive for low CO_2 emitting cars. In 2001, real world CO_2 emissions were 8% higher than laboratory measurements, but this had risen to 40% in 2015. The greatest differences between real world and laboratory emissions were for hybrid vehicles (but the sample size was much smaller), followed by diesel and then petrol cars. The official CO_2 emissions data show similar emissions from petrol and diesel cars; given that real world CO_2 emissions from diesel cars are greater than those measured in the laboratory, there may in reality be little difference between the two car types. However, diesel cars tend to be larger than petrol cars, and comparing average emissions could be considered unfair.

In summary, emissions of air pollutants from petrol cars are well controlled. Controlling NO_x emissions from diesel vehicles has evolved more recently and for many years has not been effective. There is some evidence that the most recent diesel vehicles have lower emissions than earlier generations and this should accelerate with the introduction of RDE tests for cars. There will, however, remain some uncertainty until these vehicles are in use and independently tested. In many towns and cities there remains a long way to go to ensure that health based air quality standards are achieved.

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Article

Air pollution and traffic: searching for the missing emissions

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Since the U.S. Environment Protection Agency issued a Violation Notice of the Clean Air Act to the car manufacturer Volkswagen in 2015, nitrogen dioxide (NO_2) emissions from diesel engines have received considerable public attention (*1*). Diesel cars also emit other pollutants, including volatile organic compounds (VOCs). Recent studies suggest that models underestimate the contribution to VOCs from diesel cars.

Over the last 10 years, diesel fuel usage has increased dramatically worldwide. Exxon Mobil predicts that diesel fuel will be the number one transport fuel globally by 2040 (*2*). In the UK, the fraction of newly registered vehicles using diesel fuel has risen from less than 10% in 1991 to almost 50% in 2015. Recent measurements from London suggest that emission inventories underestimate the emission flux of NO_2 by 30 to 40%, mainly as a result of under-representation of road traffic emissions (*3*).

Although many diesel cars pass emission testing during stringent but predictable laboratory tests, emissions of NO_2 can be many times higher under normal driving conditions (*4*). Diesel vehicles use a range of different emission control technologies to oxidise or remove harmful pollutants such as carbon monoxide, particulate matter, nitrogen oxides (NO_x) and volatile organic compounds (VOCs). The latter two are controlled together as NO_x + VOC, and new vehicles must meet the EURO VI emission standard of 170 mg/km. Mounting evidence suggests that diesel vehicle emissions of NO_x are too high under normal driving conditions, but what about the other pollutants? And should we care?

VOCs play a key role in urban atmospheric chemistry. Their oxidation can lead to the formation of additional toxic pollutants, including ozone and particulate matter. The UK's national atmospheric emission inventory includes diesel VOC emissions, but they are predicted to be small compared to those from gasoline and natural gas burning. Measurements of VOCs in the atmosphere can be difficult, because the concentrations are very low (parts per trillion) and a wide range of volatilities and polarities are present. The diesel fraction is particularly challenging to measure as a result of increasing isomeric complexity as carbon number increases.

Gasoline vapours are usually analysed with gas chromatography, but the higher carbon number in diesel leads to poor resolution and an unresolved complex mixture. Comprehensive two-dimensional gas chromatography (GC×GC) is a high-resolution technique that couples two GC columns of different selectivity. A modulator concentrates discrete bundles of eluent from the first column and injects them onto the second column, where a very fast separation takes place (<10 seconds). This approach gives higher peak capacity and sensitivity and provides structured chromatograms.

The University of York has developed a field portable GC×GC instrument to study the role of diesel VOC emissions. The instrument was deployed during the Clean Air For London (Clearflo) project in North Kensington in 2012 (*5*). This collaborative project involved multiple institutions from across the UK and was funded by the Natural Environment Research Council. Hourly VOC measurements were made using the GC×GC to study VOCs with 6 to 13 carbons, and a dual channel GC system was used to study VOCs with 1 to 7 carbons (*6*). In the example GC×GC chromatogram shown in Figure 1, each spot represents an individual compound. As the carbon number increases along the x-axis, the complexity of the sample also increases; by the end of the analysis, there are too many isomers to allow each individual spot to be isolated. The structured nature of the GC×GC contour space allows us to group similar compounds (such as all aliphatic compounds with 12 carbons) and quantify their contribution to the atmosphere. The results showed that although diesel-related VOCs only represented 20 to 30% of the total hydrocarbon mixing ratio, they comprised more than 50% of the atmospheric hydrocarbon mass and are a dominant local source of secondary organic aerosols. Thus, emissions from diesel vehicles can dominate gas-phase reactive carbon in cities with high proportions of diesel vehicles and, in London, were predicted to contribute up to 50% of the ozone-production potential.

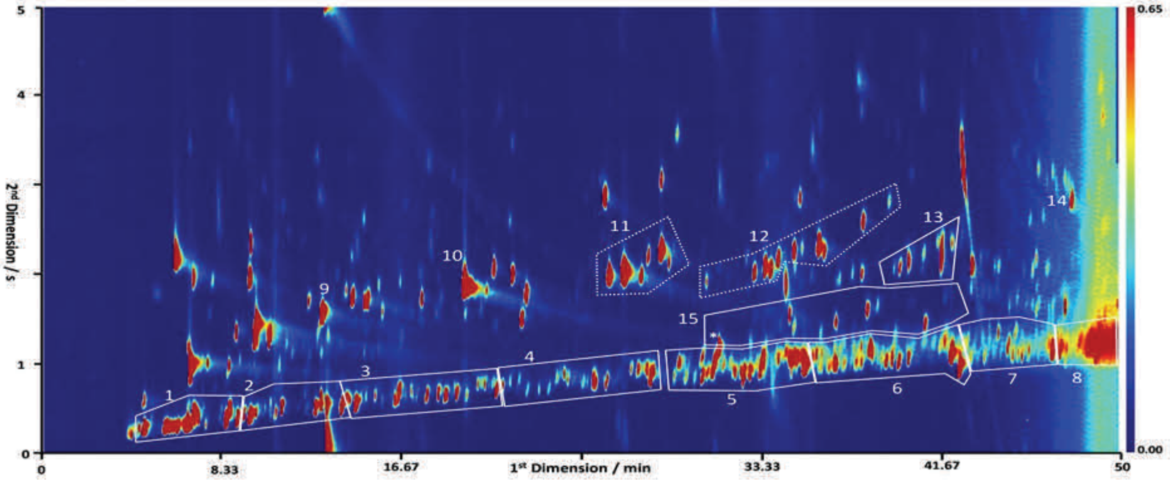

Figure 1. *Example GC×GC-FID chromatogram from London during winter. The x- and y-axes show retentions on the first and second columns, respectively, with the intensity of the compound shown by the coloured contours. The number of carbon atoms in molecules increases along the x-axis. The areas labelled 1 to 8 represent aliphatic groups from* C_6 *to* C_{13}*. The other labels are (9) benzene, (10) toluene, (11)* C_2 *substituted monoaromatics, (12)* C_3 *substituted monoaromatics, (13)* C_4 *substituted monoaromatics, (14) naphthalene, and (15)* C_{10} *monoterpenes.*

Comparing these urban air measurements with the UK emission inventory shows a substantial under reporting of diesel-related hydrocarbons—an underestimation of a factor 4 for C_9 species, rising to a factor of over 70 for C_{12} during winter. Laboratory and ambient measurements give different results for the importance of diesel versus gasoline emissions in the formation of secondary organic aerosols, a type of particulate matter (*7*). To determine the impact of the diesel VOCs observed in London, this additional source needs to be added to emission inventories used in air quality modeling. Ots *et al.* used the EMEP4-UK model to study the impact of diesel VOCs on secondary organic aerosol production in the UK (*8*). They added the diesel emissions as pentadecane and used the same emission profile as in London for every European country. Addition of diesel VOCs improved the model-measurement agreement for SOA, with diesel emissions accounting, on average, for 30% of the annual SOA produced in the model.

Further work is needed to understand the factors that control VOC emissions from diesel vehicles. The COMPART (Combustion Particles in the Atmosphere, Properties, Transformation, Fate and Impact) project aims to improve understanding of diesel exhaust emissions and what happens after they are released. This NERC funded project, involving the Universities Manchester, York and Birmingham, will study the emissions of a diesel engine under different real world driving conditions. The exhaust from a 1.9 L VW diesel engine is injected into an atmospheric simulation chamber (Manchester Aerosol Chamber). The chamber has a series of lights, which can be turned on to simulate different sunlight conditions. Initial results show that the temperature of both the engine and the emissions controls are key factors in determining not only the amount of VOC but also the composition of emissions.

These studies highlight that emissions of VOCs from diesel engines can significantly impact other toxic pollutants in London and other cities across Europe where diesel use is high. As diesel use has risen, the impact on VOC emissions has been largely unnoticed due to the lack of meaningful measurement infrastructure. The control of NO_2 from modern diesel vehicles entails significant policy challenges for many developed cities. There may also be a similar, but currently unrecognized, policy challenge to controlling reactive carbon emissions and their contributions to secondary pollutants.

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Sources and legislative control of $PM_{2.5}$ pollution

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Fine particulate matter ($PM_{2.5}$) is a complex mixture of solid and liquid particles suspended in the air. It is produced directly through industrial processes, and indirectly through reactions in the atmosphere. Due to the impacts of $PM_{2.5}$ on human health and the climate, EU legislation currently focuses on reducing the general background concentration of $PM_{2.5}$. The future for legislative control in the UK after Brexit is uncertain.

$PM_{2.5}$ is a blanket term used to describe fine particulate matter with an aerodynamic diameter of 2.5 µm or smaller. The aerodynamic diameter of airborne particulate matter is defined as the diameter of a sphere with a density of 1000 kg/m^3 and the same settling velocity as the particulate of interest (*1*). This property takes into account the often highly irregular shapes of the particulates, which affect their settling velocities. The aerodynamic diameter determines the depth of penetration into the lungs upon inhalation, and therefore the type and severity of any human health impacts.

$PM_{2.5}$ consists of an amalgamation of suspended solid and liquid particles, which have a range of different sources and hence highly variable morphologies and chemical compositions. $PM_{2.5}$ composition is dominated by sulphates and nitrates, formed from gaseous combustion products. $PM_{2.5}$ also contains polyaromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), elemental carbon, trace metals (such as cadmium, lead, and copper), and water, which is adsorbed onto the particulates (*2*).

$PM_{2.5}$ is a much more persistent pollutant than the larger PM_{10} (fine particulates with aerodynamic diameters of 10 µm or smaller). Due to its finer particle size, smaller aerodynamic diameter, and lower settling velocity, it remains suspended in the atmosphere for much longer and can be deposited thousands of kilometres away from the original emission source (*2*). It has an atmospheric half-life of several days or even weeks and can be deposited on buildings, causing damage by catalysing corrosion reactions (*2*). $PM_{2.5}$ also penetrates more readily into indoor environments, where it is more bioavailable to humans (*3*).

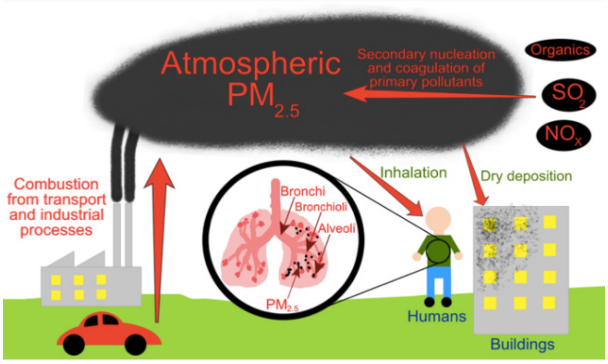

Figure 1 *– A conceptual model for $PM_{2.5}$ shows the main primary and secondary anthropogenic sources in red, the pathways in green, and the receptors in blue.*

Anthropogenic Sources

Direct $PM_{2.5}$ emissions come largely from combustion processes (**Figure 1**). Coal, gasoline, and diesel all release $PM_{2.5}$ during combustion; they are widely used around the world in transportation, energy production, and high temperature industrial processes such as smelting and steel production. Wood burning fires are also an important source. In the UK, non-exhaust vehicle emissions (including brake and tyre wear and road abrasion) are one of the largest growing sources of $PM_{2.5}$. These sources are expected to increase with the number of vehicles on the roads (*1*).

The conversion of primary gaseous pollutants, such as sulphur dioxide, nitrous oxides, and organic compounds, results in the formation of secondary $PM_{2.5}$. These gases react in the atmosphere and undergo nucleation, forming very fine particles, which then coagulate together and increase in size (*2*). Particulates formed in this way are called transformation products and can account for up to 50% of the total $PM_{2.5}$ in some areas (*4*).

Major Impacts

Human Health. Various epidemiological studies have identified $PM_{2.5}$ pollution as an important environmental risk factor for cardiopulmonary diseases and lung cancer (*5*). When inhaled, the fine particle size allows $PM_{2.5}$ to be deposited in the gas exchange region of the lungs. This region contains the alveoli, which have a more vulnerable and sensitive epithelium than the thicker, mucus-protected bronchioles. Exhalation of $PM_{2.5}$ is slower than for larger particles, allowing them to persist in the lungs and increasing the probability of transfer across the alveolar epithelium into the bloodstream and lymphatic system (*2*).

Climate Change. The interactions of $PM_{2.5}$ with radiative forcing and atmospheric processes generally result in temperature reduction. The secondary aerosols in $PM_{2.5}$ exert a negative radiative forcing effect by directly reflecting insolation and by increasing cloud cover. This is because fine particulates act as condensation nuclei for water molecules, resulting in cloud formation. Clouds formed from $PM_{2.5}$ condensation nuclei have more droplets, but each droplet is smaller. This reduces the likelihood of precipitation; the clouds persist in the atmosphere for longer and reflect more insolation (*1*).

$PM_{2.5}$ with a high elemental carbon content exerts a positive radiative forcing effect because the black carbon absorbs reradiated insolation. However, the magnitude of this effect has not been accurately quantified (*1*). What is clear is that the scale of $PM_{2.5}$ pollution and the associated problems, stress the importance of consistent legislation and cooperation between different countries.

Legislative Control

No threshold has been identified below which $PM_{2.5}$ exposure poses no risk to human health (*4*). As a result, EU legislation emphasises general reduction of $PM_{2.5}$ emissions over large areas. The Directive on Ambient Air Quality and Cleaner Air for Europe (2008/50/EC) introduced average exposure indicator target values to reduce exposure to $PM_{2.5}$ at a population level (*1*). These national exposure reduction targets are relative to the 2010 baseline AEI of the member state (**Table 1**). AEI values are calculated by averaging the three year running mean concentrations, measured at urban background locations across the member state.

Initial $PM_{2.5}$ Concentration (µg /m³)	Reduction target (%) to be met by 2020
≤ 8.5	0
> 8.5 – < 13	10
= 13 – < 18	15
= 18 – < 22	20
≥ 22	All appropriate measures to achieve 18 µg /m³

Table 1*. National exposure reduction targets set by the EU (2008/50/EC). From DEFRA, 2012.*

Conclusions

Due to the variable composition of $PM_{2.5}$ pollution and the limited research compared to other pollutants, it is unclear which specific constituents cause the impacts to human health discussed above. It is clear, however, that increased $PM_{2.5}$ exposure increases both the number of hospital admissions and the risk of many diseases. EU legislation rightfully attempts to reduce general public exposure. The UK, although soon no longer a part of the EU, must actively continue to adopt EU directives related to $PM_{2.5}$ into national law. Cooperation between the UK and other European countries is required to control this persistent and transmissible pollutant, as air pollution does not respect international boundaries.

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ECG Early Careers Environmental Briefs (ECGECEB No 2)

Policies controlling hydrofluorocarbon emissions

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Hydrofluorocarbons (HFCs) are synthetic halocarbons that are used in refrigeration and cooling, aerosols, fire-extinguishing equipment, and solvents. Emissions of these chemicals have risen since the mid-1990s as they increasingly replaced chlorofluorocarbons (CFCs) (Figure 1). HFCs reflect the long-wave radiation emitted from the Earth back to the Earth surface, causing a warming effect. They have a global warming potential (GWP) of up to 40,000 and an atmospheric lifetime of up to 260 years. Efforts are underway in the European Union and beyond to reduce HFC use and emissions as part of climate change mitigation policies.

The identification of the ozone hole in 1974 led to international efforts to restrict the use of ozone-destroying chemicals. These efforts culminated in the signing of the Montreal Protocol on Substances that Deplete the Ozone Layer, which was agreed in 1987 and entered into force in 1989. The Protocol aimed to phase out chlorofluorocarbons (CFCs), halons, and other chlorinated gases with high ozone-depleting potentials (ODPs) by 2000. The Montreal Protocol is thought of as one of the most successful pieces of environmental legislation, having been signed by 197 countries. As a direct result of the Protocol, 97% of ozone depleting substances had been phased out by 2010.

Prior to HFCs, CFCs were used in refrigeration and air conditioning. CFCs have an overall climate cooling effect, because their high ODP of 0.8 to 1.0 (relative to the ODP of CFC11), offsets their high GWP of around 15,000. HFCs replaced CFCs because they have an ODP of less than 0.001; however, this means that the impact of their GWP is significant, resulting in an overall warming effect. Industries favored the replacement of CFCs with HFCs, because they are chemically similar to each other and HFCs could thus be used in existing refrigerant systems. However, concern about the contribution of HFCs to global warming has led to efforts to restrict their use.

Policy controls on HFCs

The MAC Directive – EU (2006) (*1*). This directive aims to ban the use of fluorinated greenhouse gases (including HFCs) in mobile air conditioning (MAC) units in new vehicles by 2017 (Directive 2006/40/EC). However, the directive only includes fluorinated gases (F-gases) that have a GWP higher than 150. It thus allows warming

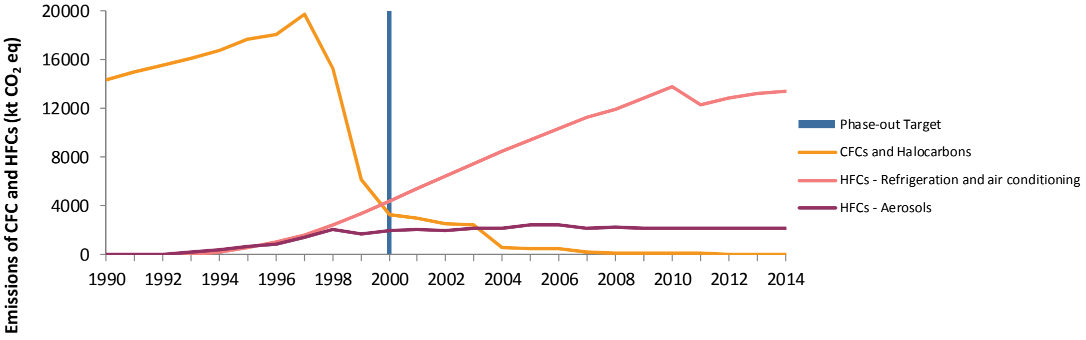

Figure 1. *Decline in CFC emissions after the Montreal Protocol signing in 1987, phase-out target, and rise in HFC emissions. Data from (5).*

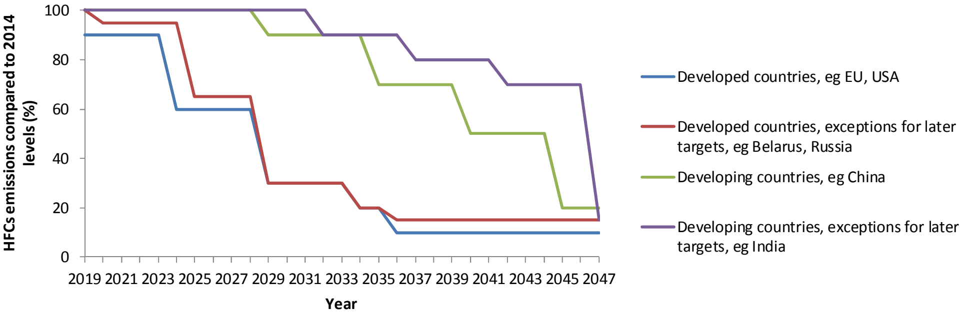

Figure 2. HFC emission reduction targets, compared to 2014 levels, in the Kigali Amendment, 2016. Data from (3).

agents up to 150 times more powerful than CO_2 to continue to be used. It also fails to account for existing MAC units that use F-gases with a GWP above 150.

Regulations on F-gases – EU (2006, amended 2014) (*2*). Policies were set out to reduce production and consumption of F-gases throughout the EU. The policies aim to reduce emissions from leakages and faulty equipment. The 2014 amendments aim to reduce F-gas emissions to 33% of 2014 emission levels by 2030 (Regulation No. 517/2014).

Kigali Amendment on HFC uses (2016) (*3*). The Kigali Amendment of the Montreal Protocol is a global agreement to limit and reduce HFC emissions. It is estimated that this agreement will prevent emission of ~70 billion tonnes of CO_2-equivalents to the atmosphere by 2050. Under the agreement, developed countries must start to reduce HFC emissions by 2019, with HFC levels of just 10% of current levels by 2036. However, developing countries do not have to start reducing HFCs until 2028, or 2031 for some countries (Figure 2).

Do international policies work?

The success of the Montreal Protocol shows that international policies can work. However, China and India are resisting the rapid implementation of the Kigali amendment. Both countries produce large amounts of HFCs, and their resistance is thus likely to impede the success of phasing out HFCs.

The impacts of HFCs on the climate were identified in the mid-2000s. The delay in politicising these issues internationally, combined with the delayed target reduction schedule, mean that more HFCs will be emitted. This could have serious impacts on keeping global warming below a 2 °C temperature rise, the limit decided on in the 2015 Paris Agreement.

Furthermore, there is a need for suitable alternatives to HFCs. These replacements need to be thoroughly analysed for long-term impacts on the environment to prevent any unintended consequences. Potential alternatives to HFCs for refrigeration include hydrofluoroolefins (HFO), which are unsaturated HFCs with a lower GWP and a short atmospheric lifetime (*4*); hydrocarbons, which have low GWPs of less than 5.5, but raise safety concerns over flammability; and CO_2, with a GWP of 1. However, production of CO_2 refrigerants ultimately comes from fossil fuels.

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