Institution: University of Leeds

Unit of Assessment: Chemistry **(**UoA 8)

Title of case study 4:
Development of abatement strategies and policies for air pollutants facilitated by the Master Chemical Mechanism

1. Summary of the impact

Air pollution is a major health concern and government policy driver. Leeds researchers and colleagues have developed a detailed chemical mechanism which describes reactions in the lower atmosphere leading to the formation of ozone and secondary particulate matter, key air pollutants. The so-called 'master chemical mechanism' (MCM) is considered the 'gold standard' and has been used by the UK government and industry groups to inform their position on EU legislation and by the US EPA to validate and extend their regulatory models. The Hong Kong Environmental Protection Department has used the MCM to identify key ozone precursors and provide evidence for abatement strategies.

2. Underpinning research

Ozone and particulate matter (PM) are important atmospheric pollutants. Ozone is formed from the photo-oxidation, in the presence of nitrogen oxides (NO_x), of the large number of volatile organic compounds (VOCs) that are emitted both naturally and from man-made sources. Oxidation of VOCs also contributes substantially to PM formation. The **master chemical mechanism (MCM)** describes these complex mechanisms quantitatively. It is based on our current understanding of atmospheric oxidation chemistry; is traceable to experimental measurements and estimates of reaction rates and mechanisms; represents a synthesis of current knowledge; and provides a web-based resource for atmospheric chemistry modelling applications. Section 4 outlines the impact of the MCM on the development of air quality policies in the UK and internationally.

2.1 MCM creation – synthesis of knowledge. The development of the MCM was instigated by Dr R Derwent (Defra) in 1993 as the government recognised that it required more understanding of how different organic compounds in the atmosphere influence ozone formation. The project was initiated following collaboration between Defra and **Pilling** on VOC kinetics and ambient measurements of VOCs in cities. The MCM research was co-led by Prof Mike Pilling (University of Leeds, 1989-) (mechanism development and evaluation, website development) and Dr Mike Jenkin (UKAEA/AEA Technology 1981-2001, then Imperial College 2001-2008, then Atmospheric Chemistry Services, 2008-) (protocol and mechanism development, and application).

The mechanisms are based on a protocol (e.g. (1) from 1997), developed on the basis of a fundamental understanding of the detailed chemistry of atmospheric oxidation, and incorporate reaction rate and mechanism data from laboratory experiments. The project was funded by Defra (1993-2010), with funding for specific applications and subsequent development being secured through research grants (Grants: NERC(i), EU (ii)). The MCM is now supported by the National Centre for Atmospheric Chemistry (Dr Andrew Rickard), and may be accessed via a Leeds website (http://mcm.leeds.ac.uk/MCM/). In addition to representation of the mechanism, together with rate coefficients, the website provides output for incorporation into atmospheric models.

2.2 MCM as a basis for policy modelling. Derwent, Jenkin and the Leeds group also developed a predictive pollution model – the photochemical trajectory model (PTM) – published in 1998 that combines atmospheric transport and chemical reactions (2). The PTM models ozone formation in an air parcel, driven by winds from central Europe to the UK, and incorporates VOC and nitrogen oxide emissions from the surface. The MCM is a key component of the model, allowing the different contributions to ozone formation from specific VOCs to be quantified. A new VOC characteristic – the photochemical ozone creation potential (POCP) – provides a relative measure of the impact of different VOCs on ozone formation.

2.3 MCM evaluation and application. The complexity of the MCM demands direct experimental testing of its mechanistic predictions. Pilling has led developments in the use of atmospheric simulation chambers to evaluate the MCM in a series of European consortia (EXACT, 1999-2002; EUROCHAMP-1, 2004-2009; EUROCHAMP-2, 2009-2013, Integrated Infrastructures Initiative; grants ii) (3). Experimental field measurements, coupled with the MCM, have also been used to

develop and test our understanding of atmospheric chemistry. The construction in Leeds and application in the field of an instrument to measure OH and HO_2 radicals by Heard,(4) and modelling of their concentrations with the MCM (e.g. (5) published in 2006) have been central to these developments.

2.4 MCM: a validation tool for simplified models. The MCM is a very large mechanism that is too large and complex for use in global or even regional atmospheric models that include detailed atmospheric transport. The MCM is however widely used to validate models of atmospheric pollution that typically incorporate simpler, less fundamentally based chemical mechanisms. For example, in a collaboration between Leeds and US scientists in 2005-7, the MCM was used to evaluate the chemical mechanism in a 3D global model, to interpret satellite measurements of formaldehyde and to evaluate emissions of anthropogenic and biogenic VOCs in S E Asia (6).

Key personnel

Professor Mike Pilling, Professor of Physical Chemistry, 1989-2007 and Research Professor 2013.
Professor Dwayne Heard, University Research Fellow, 1994-2002 then Reader, 2002-4 then Professor of Atmospheric Chemistry, 2004-.
Dr Sandra Saunders, postdoctoral researcher, 1991-2002.
Dr V Wagner, postdoctoral researcher, 1999 - 2001.
Dr Roberto Sommariva, graduate student, 2000–2004 and postdoctoral researcher, 2011-2012.
Dr Claire Bloss, postdoctoral researcher, 2001-2003.
Dr Jenny Young (née Stanton), graduate student, 2002-2006 and postdoctoral researcher, 2007-.

Competitively-awarded funding following peer review

i. NERC: (a) "Highly instrumented reactor for atmospheric chemistry, HIRAC", NEC513493/1, PI: M. J. Pilling, £248k, 2004-2006; (b) "Integration and co-development of the MCM and IUPAC databases and websites", NE/E002668/1, PI: M. J. Pilling, £130k, 2006-2009; (c) "Laboratory measurements of photochemical and kinetic processes of atmospheric significance", RES20732, PI: M. J. Pilling, £118k, 2003-2006.
ii. EU: (a) EXACT, PI: M. J. Pilling, 1999-2002, €176k; (b) "Integration of EUROpean Simulation CHAMbers for Investigating Atmospheric Processes" (EUROCHAMP-1), PI: M. J. Pilling, 2004-2009, €279k; (c) "Integration of EUROpean Simulation CHAMbers for Investigating Atmospheric Processes" (EUROCHAMP-2), PI: M. J. Pilling, 2009-2013, Integrated Infrastructures Initiative, €422k.

Note: NERC and EU grants are awarded following extensive peer review on a competitive basis, provided the proposed research meets stringent quality criteria.

3. References to the research

1. "The tropospheric degradation of volatile organic compounds: A protocol for mechanism development", M. E. Jenkin, S. M. **Saunders**, and M. J. **Pilling**, *Atmospheric Environment,* 1997, **31**, 81 -104 (334 citations; Source: Scopus, 24/10/13) http://dx.doi.org/10.1016/S1352-2310(96)00105-7
2. "Photochemical ozone creation potentials for organic compounds in northwest Europe calculated with a master chemical mechanism", R. G. Derwent, M. E. Jenkin, S. M. **Saunders** and M. J. **Pilling**, *Atmospheric Environment* 1998, 32, 2429-2441 (194 citations; Source: Scopus, 24/10/13) http://dx.doi.org/10.1016/S1352-2310(98)00053-3
3. "Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons", C. **Bloss**, V. **Wagner**, M. E. Jenkin, R. Volkamer, W. J. Bloss, J. D. Lee, D. E. **Heard**, K. Wirtz, M. Martin-Reviejo, G. Rea, J. C. Wenger and M. J. **Pilling**, *Atmospheric Chemistry and Physics* 2005, **5**, 641-664. (143 citations; Source: Scopus, 24/10/13) http://dx.doi.org/10.5194/acp-5-641-2005
4. "Measurement of OH and HO_2 in the troposphere", D. E. **Heard** and M. J. **Pilling**, *Chem. Rev.*, 2003, **103**, 5163 – 5198 (145 citations; Source: Scopus, 24/10/13) http://dx.doi.org/10.1021/cr020522s
5. OH and HO2 chemistry during NAMBLEX: roles of oxygenates, halogen oxides and heterogeneous uptake R. **Sommariva**, W. J**.** Bloss, N. Brough, N. Carslaw, M. Flynn, A.-L. Haggerstone, D. E. **Heard**, J. R. Hopkins, J. D. Lee, A. C. Lewis, G. McFiggans, P. S. Monks, S. A. Penkett, M. J. **Pilling**, J. M. C. Plane, K. A. Read, A. Saiz-Lopez, A. R. Rickard, and P. I.

Williams, *Atmospheric Chemistry and Physics*, 2006, **6**, 1135 – 1153 (42 citations; Source: Scopus, 24/10/13)) http://dx.doi.org/10.5194/acp-6-1135-2006

6. "Space-based formaldehyde measurements as constraints on volatile organic compound emissions in east and south Asia and implications for o zone", T.-M. Fu, D. J. Jacob, P. I. Palmer, K. Chance, Y. X. Wang, B. Barletta, D. R. Blake, J. C. **Stanton** and M. J. **Pilling**, *Journal of Geophysical Research: Atmospheres* 2007, 112, D06312. (74 citations; Source: Scopus, 24/10/13)) http://dx.doi.org/10.1029/2006JD007853

All Leeds researchers in **bold**. Citation data from web of knowledge, accessed 03.09.2012. All papers are in internationally-leading peer-reviewed journals and are hence ≥2*, but references 1-3 are particularly highlighted by the UoA to demonstrate the quality of the underpinning research. Reference 1 was awarded the Haagen-Smit Prize in 2010 as an "outstanding publication".

4. Details of the impact

According to a 2010 report of the House of Commons Environmental Audit Committee *"Poor air quality reduces the life expectancy of everyone in the UK by an average of 7-8 months and up to 50,000 people a year die prematurely because of it.'* Defra estimates that poor health due to air pollution costs the UK ~£19 bn p.a. (http://www.defra.gov.uk/environment/quality/air/air-quality/eu/). The Health and Environment Alliance commented in 2013 *"For the first time, the Global Burden of Disease assessment has ranked an environmental* [health risk] *factor* [outdoor air pollution] *among the more widely discussed 'life-style' risk factors, such as tobacco and alcohol"* (Lin *et al*, *Lancet* 2012, **380**, 2224-60).

4.1 MCM informs policy. Action to manage and improve air quality in the UK is largely driven by EU legislation. The 2008 ambient air quality directive sets *legally binding* limits for concentrations in outdoor air of major air pollutants that impact public health. The EU also sets national emissions ceilings. VOC oxidation, to form ozone and secondary particulate matter (PM), presents particular problems because of its long range and therefore transnational nature. The Head of the Air Quality Programme at Defra (Department for Environment, Food and Rural Affairs) (2005-2010) (previously, Head of the Air Quality Science Unit, Defra, 1993-2005) stated that "*The MCM formed the core of the modelling research to inform policy related to ozone in Defra. As part of the PTM (Photochemical Trajectory Model), and as a benchmark against which other mechanisms were evaluated, it played a crucial role in ensuring that the UK's policy positions were founded on the basis of the best available science, on EU Directives such as the National Emissions Ceilings Directive and the Solvent Emissions Directive and the UNECE 'Gothenburg Protocol'. Over the period during which Defra supported the MCM it became a world-wide benchmark for chemical mechanisms and we in Defra were therefore able to feel great confidence in our international negotiations having based our positions on such excellent science*" (A). A detailed review for Defra provides a discussion of the MCM and of its application in policy related work (*A review of the Master Chemical Mechanism*, prepared for Defra, July 2007). Developments between 2007-2009 can be found in a 2009 project report to Defra (B) that outlines the use of the MCM to model the formation of secondary organic particulate matter (termed "secondary organic aerosol" in the report).

4.2 MCM as the gold standard to benchmark atmospheric pollution models. Because of the need to accommodate detailed atmospheric transport, models of air pollution for policy purposes simplify the chemistry and reduce the number of species involved to make the atmospheric modelling more manageable. Because of its fundamental nature, and the quality of its response to experimental evaluation, the MCM has contributed substantially to policy applications through its use as a **reference mechanism** that can be used to test the smaller, less fundamentally based mechanisms that are used in atmospheric policy models. In their report to Defra on modelling tools for policy applications (*Review of tools for modelling tropospheric ozone formation and assessing impacts on human health & ecosystems*, Report to Defra, November 2007), Monks et al. stated: "*the traceability of chemical schemes"* (i.e. mechanisms) "*to an explicit basis is a more robust methodology than the use of tuned generic schemes"* (i.e. mechanisms not directly linked to fundamental chemistry) "*and the MCM should be used as a reference benchmark for this process."* The Head of the Air Quality Programme at Defra (2005-2010) has stated that the impact of MCM has been sustained since 2008: "*The MCM has continued to provide a benchmark or standard*

against which other, simpler, mechanisms are judged. Models using these mechanisms are in continual use within Defra to inform and evaluate policy, as demonstrated by the revision of the UNECE/CLRTAP 'Gothenburg' Protocol in 2012 and the forthcoming negotiations on a revision of the EU National Emissions Ceilings Directive later this year" (A). This ongoing position was confirmed in 2013 by the current Head of the Air Quality Science and Evidence Team at Defra (A).

A similar recommendation has also been made in the United States where the Environmental Protection Agency now considers that the MCM "*is the 'gold standard' of chemical mechanisms. Both of the chemical mechanisms that US EPA recommends for regulatory actions since 2008 have drawn from the mechanism sequences in MCM. If our mechanisms are consistent with MCM, we are confident they will hold up to scrutiny"* (C).

4.3 PTM/MCM informs policy

Section 2.2 outlined the importance of the MCM in a photochemical trajectory model (PTM), which allowed the contribution of individual VOCs to ozone formation in Europe and the UK to be quantified through Photochemical Ozone Creation Potentials (POCPs). The PTM/MCM has been used since 2008:

- by Defra to ensure that the UK's policy positions are founded on the basis of the best available science. This included the evaluation of policy strategies based on VOC reactivity, implications of multiday ozone formation in Europe and the impacts of large VOC releases from industrial plant (A).
- by the Hong Kong Environmental Protection Department to identify key ozone precursors. *"Policy debate on the environment has been stimulated and informed by ... research evidence using the master chemical mechanism (MCM) as the chemical mechanism within a photochemical trajectory model (PTM). We are currently assessing the potential of using the MCM/PTM model as a new tool in the development of those policies"* (D).
- by the European Solvents Industry group in 2009 (E) to highlight the effectiveness of the Solvents Emissions Directive in reducing ozone since 1990, while also establishing that further restrictions under the 2004/42/EC Directive (Paints) would not contribute to a significant further ozone reduction in Europe.
- by Derwent et al. (F) to attribute improvements in peak episodic ozone concentrations in the UK 1990-2010 to EU Air Quality Policies. They also established that the upward trend in the annual mean daily maximum could be attributed to intercontinental transport of pollutants, emphasising the need for global policies to abate ozone, as discussed by the UNECE Task force on Hemispheric Air Pollution (G).

5. Sources to corroborate the impact

A. Letter, Head of the Air Quality Programme at Defra (2005-2010) (previously, Head of the Air Quality Science Unit, Defra, 1993-2005), 19th April 2013, and confirmation from current Head of Air Quality Science and Evidence Team at Defra, Sep 2013. Available on request from HEI.

B. "Modelling of Tropospheric Ozone: Project Summary Report", 2007-2009, AEA, 2009. http://uk-air.defra.gov.uk/reports/cat05/1003151144_ED48749_Final_Report_tropospheric_ozone_AQ0704.pdf

C. Letter, Physical Scientist and CMAQ Atmospheric Chemistry Workgroup Lead, US Environmental Protection Agency, April 26th 2013. Available on request from HEI

D. Letter, Senior Environmental Protection Officer, Hong Kong Environmental Protection Department. Available on request from HEI, 22nd April 2013. Available on request from HEI.

E. "The Ozone Challenge", European Solvents VOC Coordination Group, ESIG, Februrary 2009. http://www.esig.org/en/regulatory-information/ozone-modelling

F. "Ozone in Central England: the impact of 20 years of precursor emission controls in Europe", R. G. Derwent, C. S. Witham, S. R. Utembe, M. E. Jenkin and N. R. Passant, *Environmental Science and Policy* 2010, **13**, 195-204. http://dx.doi.org/10.1016/j.envsci.2010.02.001

G. UNECE Task force on Hemispheric Air Pollution. Report. http://www.htap.org/index.htm (2010)