Institution: University of York
Unit of Assessment: 8, Chemistry
Title of case study: Ozone-depleting halogens in the atmosphere

1. Summary of the impact

The international Montreal Protocol limits the production of stratospheric-ozone depleting substances that contain chlorine and bromine. York researchers used the Atmospheric Chemistry Experiment (ACE) satellite to monitor the decay of halogen-containing molecules in the stratosphere and to re-evaluate their atmospheric lifetimes. This York research also determined that oceans represent a vast reservoir of organohalogens, which are released to air and impact significantly on ozone destruction. The research results have been incorporated into the conclusions of the World Meteorological Organization/United Nations Environment Programme (WMO/UNEP) Scientific Assessments on Ozone Depletion, the pre-eminent knowledge base used for international policy and domestic legislation. Experimental infrastructure created in this York research now contributes to UK Government obligations under the United Nations Framework Convention on Climate Change (UNFCCC) and informs it of long-term atmospheric change.

2. Underpinning research

Stratospheric ozone protects humankind and its crops from harmful ultraviolet radiation. Anthropogenic stratospheric ozone destruction is caused mainly by long-lived chlorine-containing molecules such as CCl_4 and chlorofluorocarbons (CFCs), and bromine molecules such as halons (brominated fluorocarbons) and methyl bromide. The 1987 Montreal Protocol on substances that deplete the ozone layer and its subsequent amendments have resulted in the phasing-out of the production of many such chlorine-and bromine-containing species – preventing not only millions of cases of skin cancer deaths and cataracts, but also reducing emissions of halogenated greenhouse gases by the equivalent of more than 10 billion tonnes of CO_2 at the end of 2008. In view of the steady progress made under the Protocol, former UN Secretary-General Kofi Annan called it in 2003 *Perhaps the single most successful international agreement to date* (ozone.unep.org/Publications/MP_Key_Achievements-E.pdf).

It is crucial to assess the performance of the Montreal Protocol in reducing the concentrations of ozone-depleting substances (ODSs) and to monitor the recovery of the ozone layer. Therefore, every four years the WMO and UNEP publish a report on the ''Scientific Assessment of Ozone Depletion'', carried out by the Scientific Assessment Panel (SAP). The York-based group, led by Bernath, contributed to the WMO ozone report by measuring global concentration distributions of many chlorine-containing molecules using data from the ACE satellite[1] (www.ace.uwaterloo.ca).

- UV photodissociation of these molecules forms intermediates such as phosgene (Cl_2CO) and ClFCO [1,2] and leads ultimately to the formation of HCl. ACE satellite measurements tested the accuracy of chemical models and showed the anticipated decline in HCl and other halogenated gases due to the implementation of the Montreal Protocol.
- Atmospheric lifetimes are crucial parameters in models and the research group determined the relative stratospheric lifetime of CCl_4 by the method of tracer-tracer correlations; there are surprisingly large uncertainties in these lifetimes (see 2010 WMO ozone report).
- CCl_4 is destroyed mainly by photolysis in the stratosphere giving phosgene. Fu *et al.* measured the first global distribution of phosgene[2] and found that concentrations had declined from earlier *in situ* measurements owing to decline in the parent source gases CH_3CCl_3 and CCl_4.
- The York group found that the global distribution of FClCO,[1] produced by photolysis of the parent CFC-11 (CF_3Cl) molecule, agreed well with that calculated by an atmospheric model, giving confidence in the reliability of the emissions projections and the model.

Conventionally, it was thought that anthropogenic bromine compounds in the form of halons and CH_3Br were the sole carriers of bromine into the stratosphere. However, calculated stratospheric Br_y concentrations from measurements of BrO were too high by 15-40% to be explained by these halocarbons alone. The oceanic and atmospheric measurements of Carpenter in York showed that emissions of natural bromine compounds including $CHBr_3$ and CH_2Br_2 from the marine biosphere, especially macroalgae, represent a major global source of bromine.[3] Subsequent model studies

showed that these emissions were sufficient to explain the discrepancy between modelled and measured stratospheric BrO concentrations. The York group demonstrated that ozone in the troposphere was also controlled over wide oceanic areas by natural halogen emissions,[4] and this has led to public and policy debate on the potential contribution of such processes to the reduction of ground level ozone, a key pollutant (in contrast to the essential nature of stratospheric ozone).

Both the ACE and the tropospheric research are part of multi-centre programmes involving collaboration of York with other institutes in Canada, USA, Belgium, UK, Germany and France.

Key researchers:

Peter F. Bernath: Appointed 01/07/2006 as Professor,

Lucy J. Carpenter: Appointed 01/09/2000 as Lecturer A, Promotion to Chair 01/10/09

3. References to the research

This research exceeds the quality threshold as is evident from the journal quality, the number of citations (citation data from Scopus, November 2013) and recognition in prizes.

Peer-reviewed publications –- Authors at York in bold

1. D. Fu, C. D. Boone, **P. F. Bernath**, D. K. Weisenstein, C. P. Rinsland, G. L. Manney, and K. A. Walker, First global observations of atmospheric COClF from the Atmospheric Chemistry Experiment mission, *J. Quant. Spectrosc. Radiat. Transfer*, 2009, **110**, 974. DOI: 10.1016/j.jqsrt.2009.02.018. *5 citations*

2. D. Fu, C. D. Boone, **P. F. Bernath**, K. A. Walker, R. Nassar, G. L. Manney, and S. D. McLeod, Global phosgene observations from the Atmospheric Chemistry Experiment (ACE) mission, *Geophys. Res. Lett*., 2007 **34**, L17815. DOI: 10.1029/2007GL029942. *7 citations*

3. **L. J. Carpenter,** P. S. Liss and S. A. Penkett, Marine organohalogens in the atmosphere over the Atlantic and Southern Oceans, *J. Geophys. Res.- Atm.,* 2003, **108**, DOI: 10.1029/2002JD002769. *49 citations*

4**. K. A**. **Read,** , A. S. Mahajan, **L. J. Carpenter**, **M. J. Evans**, B. V. E. Faria, D. E. Heard, **J. R. Hopkins**, **J. D. Lee**, **S. J. Moller**, **A. C. Lewis**, L. Mendes, J. B. McQuaid, H. Oetjen, A. Saiz-Lopez, M.J. Pilling, and J. M. C. Plane, Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, *Nature*, 2008, **453**, 1232. DOI: 10.1038/nature07035. *133 citations*

Other evidence of quality:

2012 Benedict Spectroscopy Award to P. Bernath: (from Elsevier Press on behalf of the *Journal of Quantitative Spectroscopy and Radiative Transfer*) The citation states that Bernath “has also been at the forefront of satellite remote sensing experiments, particularly as the mission scientist for the ACE (Atmospheric Chemistry Experiment) satellite”

2009 Alouette Award of Canadian Aeronautics and Space Institute (CASI) to P. Bernath for developing the ACE satellite and the resulting observations (shared with V. Wehrle, G. Rumbold, I. Walkty, T. McElroy and M.-A. Soucy)

2006 Philip Leverhulme prize to L. J. Carpenter – citation: "Not only has she made pioneering measurements [on the chemistry of atmospheric bromine and iodine compounds], but she has also contributed substantially to the interpretation of the observations to shed light on the underlying chemistry. These results are of great significance in understanding the Earth’s climate."

Selected research grants:

Bernath, 2008-2011, 'VOCs in the Troposphere Retrieved from ACE Satellite Measurements', NERC, £364,058.

Bernath, 2011-2013, 'Satellite Observations of Halogen-Containing Molecules', NERC, £349,740.

Carpenter and Lewis, 2005-2008, 'UK SOLAS Atmospheric Observatory at Cape Verde', NERC SOLAS contract, £572,220.

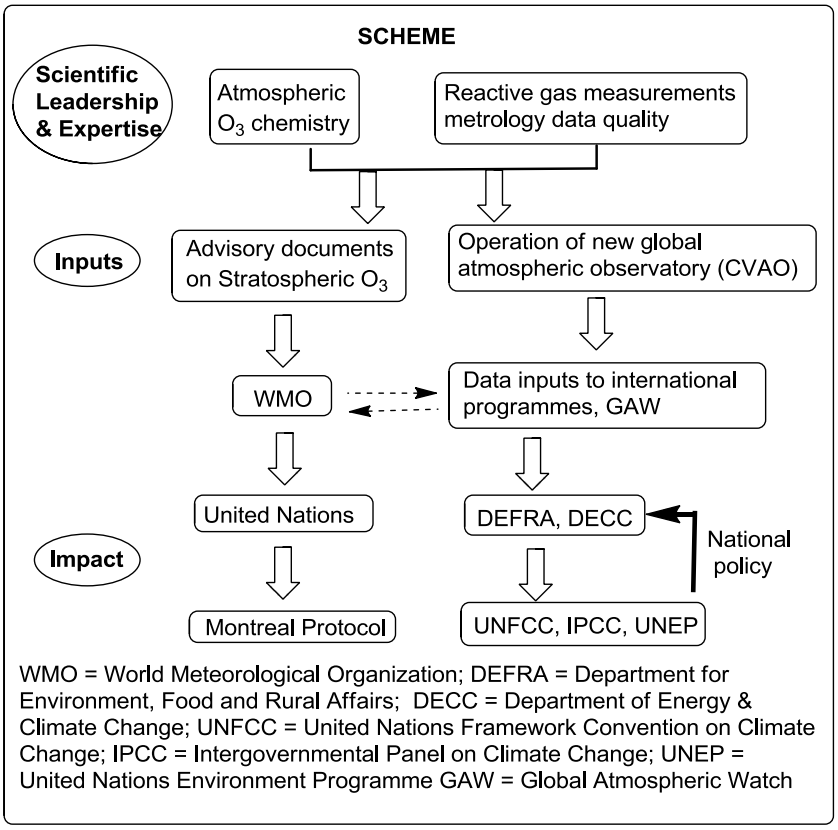
Carpenter, 2006-2009, Philip Leverhulme Prize in ‘Earth Ocean and Atmospheric Sciences’, Leverhulme Trust, £70,000.

4. Details of the impact

The York research created impact by: (a) measuring changes in stratospheric atmospheric composition and determining lifetimes of ozone-depleting substances; these results are needed by

UNEP in order to make decisions, especially to provide evidence of policy effectiveness and a more robust prediction of the likely timescales for ozone hole recovery; (b) revealing natural halogenated emissions that close the gap between modelled and measured stratospheric BrO concentrations, providing confidence in the models used to inform UNEP of stratospheric halogen changes; (c) by serving on the Scientific Assessment Panel (SAP) that advises UNEP; (d) by proving the value to the UK of long-term background tropospheric measurements of trace gases and enabling the UK to fulfil its international obligations.

The SAP is charged with the periodic updating of the scientific understanding of the depletion of stratospheric ozone as summarised by A.R. Ravishankara (co- Chair of SAP). "*The assessment is written and reviewed by leading experts in the international atmospheric sciences community at the request of the Parties to the U.N. Montreal Protocol* [197 countries]. *It forms the scientific basis for decisions that the Parties reach with regard to the phaseout of ozone-depleting chemicals such as the CFCs and other matters related to the long-term protection of the stratospheric ozone layer. As you may know, all previous Montreal Protocol decisions have been based on the science findings of the Scientific Assessment Panel.... For previous assessments, it has proven true that the participants have found their efforts rewarded with increased stature and recognition in the scientific community. Likewise, their supporting institutions have received recognition for their leadership in providing world-class scientific expertise to the international effort."*[5] The Assessment process involves scientific research and stakeholders including governments and their agencies, research managers, industries and the public.



The 2010 Ozone Assessment,[6] and two earlier reports, make significant reference to the original underpinning research undertaken in York, which contributed to a better understanding of the observed behaviour of ODSs and ozone in the stratosphere and thus to continued international acceptance of the Montreal Protocol. Bernath and Carpenter also contributed substantially as both reviewers of the 2010 report and members of the 2010 Scientific Assessment Panel.

York impact on Scientific Assessment Panel - stratospheric ozone. The projections of different ozone depleting gases restricted by the Montreal Protocol including CCl_4, CH_3CCl_3 and CFC-11, and their photochemical products have been evaluated through the ACE measurements.

- In the 2010 report[6] it was noted that CCl_4 declined more slowly than predicted in the 2006 report; these predictions are very sensitive to the assumed atmospheric lifetime. The new stratospheric lifetime contributed to the assessment that the problem is due to unreported emissions, rather than an erroneous lifetime.
- The end product of the destruction of chlorinated gases in the stratosphere and lower mesosphere is HCl. Observations of HCl reduction in the lower mesosphere by ACE contributed to the overall assessment of the success of the Montreal Protocol in the 2010 report.[6]
- In relation to natural brominated compounds, the research provided emissions estimates, hitherto unidentified species, and new understanding of the halogen composition and chemistry of the stratosphere and troposphere.[3,4] The major impact is that inclusion of such natural

bromine species and their chemistry in global models has led to better agreement of the model with inorganic bromine measurements in the stratosphere, as detailed in the 2010 report.[6] This provides evidence that the policy is effective and improves the robust prediction of the timescales for ozone hole recovery.

York impact - tropospheric ozone. Whilst the role of halogen chemistry in controlling stratospheric ozone has been well known for several decades, the impact on tropospheric ozone has been less understood. Ozone in the troposphere is important for several reasons; it is an air pollutant, a greenhouse gas in its own right, and indirectly it controls the lifetime of methane, another important greenhouse gas. The roles of both ozone and methane as greenhouse gases are increasing in importance. The new knowledge of halogen-tropospheric ozone processes reported by the York scientists[4] has contributed to policy recommendations; the Royal Society Ozone report (2009)[7] used the research to highlight the need to understand and control background ozone concentrations in relation to air quality. The research was also reported widely in the media and led to public debate on the potential of natural processes to mitigate against air pollution.[8]

The research programme[4] has achieved long-term impacts through the building of experimental infrastructure. The proposal for a tropical ocean atmospheric observatory was driven by Carpenter (York) with Leeds colleagues and resulted in the construction of an observatory in Cape Verde (www.ncas.ac.uk/cvao). The research demonstrated the value of long-term monitoring of the tropical atmosphere.[4] As a result, the observatory is now supported as a permanent UK contribution to the World WMO Global Atmospheric Watch programme (www.wmo.int/gaw); it is one of 28 stations worldwide and the only station supported by the UK Government. It employs two permanent Cape Verdean technicians (one of whom is now enrolled on an MSc in Chemistry at York) as well as UK researchers. The data generated from it now form part of the UK capability to meet its obligations on climate change detection under UNFCCC. The research continues to generate long-term observations of trends in ozone and other gases, and these data are disseminated to academic and Government users *via* agencies such as the Department of Energy and Climate Change (DECC), UNFCCC and WMO. The data alerts the government to changes in the Atlantic atmosphere arising from pollution episodes or long-term changes.

Quotation from L. Jalkanen Chief, Atmospheric Environment Research Division, World Meteorological Organization,[9] *"The University of York, with support from other UK and German and Cape Verdean partners, created in 2006 a new observatory in Cape Verde. This observatory helped GAW fill in an important gap in global observations, providing information on changes occurring in the tropical North Atlantic marine boundary layer, a region sensitive to both natural and anthropogenic change. ... The global reach of the GAW programme, and its contributor scientists, allows it to also influence governmental understanding and policy on atmospheric change*.

5. Sources to corroborate the impact

Reports related to policy

5. Letter from Co-chair Montreal Protocol Scientific Assessment Panel

6. WMO/UNEP Assessment Report on Stratospheric Ozone 2010, Chapter 1 Ozone-Depleting Substances (ODSs) and Related Chemicals, http://ozone.unep.org/Assessment_Panels/SAP/Scientific_Assessment_2010/00-SAP-2010-Assement-report.pdf

7. Royal Society report "Ground-level ozone in the 21st century: future trends, impacts and policy implications" 2008. http://royalsociety.org/policy/publications/2008/ground-level-ozone

References to public debate (not exhaustive) relating to reference 4*:*

8. BBC World Service interview given by Prof L J Carpenter (26.06.08, Science In Action, "Low level ozone pollution". http://worldservice.prototyping.bbc.co.uk/programmes/X0901226 (sign up required); *The Guardian* newspaper online (http://www.guardian.co.uk/environment/2008/jun/26/climatechange.pollution?INTCMP=SRCH); *New Scientist* Online (http://www.newscientist.com/article/dn14211-tropical-ocean-sucks-up-vast-amounts-of-ozone.html); A solicited *Nature* News and Views article (von Glasow, *Nature*, 2008, **453**, 1195-1196), *Nature Reports Climate Change* (Newton, "A natural detox", DOI: 10.1038/climate.2008.67)

9. Letter from Chief, Atmospheric Environment Research Division, WMO, Geneva