Institution: University of York		
Unit of Assessment: 8 - Chemistry		
Title of case study: Halogens, stratospheric ozone and the Montreal Protocol		
Period when the underpinning research was undertaken: 2007-2018		
Details of staff conducting the underpinning research from the submitting unit:		
Name(s): Lucy Carpenter	**Role(s) (e.g. job title):** Professor	**Period(s) employed by submitting HEI:** Sep 2000 to present
Period when the claimed impact occurred: 2014-2020		
Is this case study continued from a case study submitted in 2014? N		

1. Summary of the impact (indicative maximum 100 words)

Research on atmospheric halogen chemistry has supported the continued development and ratification of the Montreal Protocol and subsequent treaty extensions for the protection and recovery of the stratospheric ozone layer. The impact arises from research into natural sources of organohalogens and their role in controlling tropospheric and stratospheric ozone. The impact is achieved through inclusion of this science in atmospheric models and analysis used to underpin the quadrennial United Nations Scientific Assessments of Ozone Depletion, part of the international treaty ratification process. Carpenter co-led the International Policy Conclusions chapter within the 2018 Assessment and the Ozone Depleting Substances chapter within the 2014 Assessment.

2. Underpinning research (indicative maximum 500 words)

Stratospheric ozone protects humankind and crops from harmful ultraviolet radiation. Ozone destruction is caused mainly by long-lived chlorine-containing molecules such as chlorofluorocarbons (CFCs) and bromine molecules including halons and methyl bromide. The Montreal Protocol (1987) on substances that deplete the ozone layer, and the Protocol's subsequent amendments (including most recently the 2019 Kigali Amendment), resulted in the phasing-out of many halogen-containing ozone depleting substance (ODS) – preventing millions of cases of skin cancer deaths and cataracts, and reducing emissions of halogenated greenhouse gases.

Over the last decade **Carpenter** has made a leading contribution to the body of knowledge relating to chemicals of relevance to stratospheric ozone depletion. Research on the atmospheric emissions and chemistry of bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2) demonstrated that they are the principal VSL (very short lived) bromine source gases to the stratosphere, of significance in ozone depletion chemistry, and that they are predominately of natural marine origin, with ocean phytoplankton and macroalgae being the largest global sources [e.g. 3.1, 3.2]. Using observations made from ground, from ships and research aircraft, Carpenter has provided new evidence on the abundance of VSL source gases that can be transported from the marine boundary layer to the tropical tropopause layer. Accounting fully for natural VSL gases has resulted in an improved estimate of reactive bromine source gas injection (SGI) to the stratosphere, and particularly the size of the contribution arising from natural sources [3.3 - 3.5]. This information is a critical input into models of stratospheric ozone and is essential if forecasts of ozone recovery are to be credible and accurate.

Separate research on iodine containing compounds (both organic and inorganic) has discovered new chemical mechanisms that lead to the oceanic release of iodine into the atmosphere. By accounting for these ocean and biogeochemical processes it has been demonstrated that global iodine emissions increased over the 20th century [3.6], the research indicating a likely higher iodine content in the stratosphere than was previously thought.

Whilst the majority of Carpenter's outputs have been in academic publications, significant primary research has also been produced as part of the United Nations Environment Programme (UNEP) / World Meteorological Organization (WMO) Scientific Assessments of Ozone Depletion. The Scientific Assessments not only act as the vehicle for creating impact on policymakers from already published research, but also allow the Lead authors of the

Assessments to undertake new analyses and data syntheses from multiple sources. These can be highly influential, revealing emerging issues that then focus the research community towards important evidence gaps that are critical for policymakers and governments.

Carpenter and Reimann (Chapter 1 in the 2014 Assessment – see section 5) identified marked increases in surface concentrations and likely stratospheric source gas injection of CH_2Cl_2, highlighting that VSL chlorinated compounds were becoming more relevant for stratospheric O_3, leading to a landmark study on the same subject which was published three years later. Analysis by Carpenter and Daniels (in Chapter 6 in the 2018 Assessment – see section 5) showed that if the growth in CH_2Cl_2 emission rate seen during the first decade of the 21st century were to continue, this uncontrolled anthropogenic chlorine compound could deplete as much stratospheric ozone between 2020 and 2060 as the controlled ozone depleting substances (ODSs) emitted during that period.

3. References to the research (indicative maximum of six references)

3.1. **Carpenter, L.J.**, Wevill, D.J., Hopkins, J.R., Dunk, R.M., Jones, C.E., Hornsby, K.E., and McQuaid, J.B. (2007) Bromoform in tropical Atlantic air from 25 degrees N to 25 degrees S. Geophysical Research Letters, **34** (11). doi.org/10.1029/2007GL029893

3.2. **Carpenter, L.J.,** Jones, C.E., Dunk, R.M., Hornsby, K.E., and Woeltjen. J. (2009) Air-sea fluxes of biogenic bromine from the tropical and North Atlantic Ocean. Atmospheric Chemistry and Physics, **9** (5), 1805-1816. doi: 10.5194/acp-9-1805-2009

3.3. Andrews, S. J., **Carpenter, L.J.**, Apel, E.C., Atlas, E., Donets, V., Hopkins, J.R., Hornbrook, R.S., Lewis, A.C., Lidster, R.T., Lueb, R., Minaeian, J., Navarro, M.S., Punjabi, S., Riemer, D. and Schauffler, S. (2016) A comparison of very short lived halocarbon (VSLS) and DMS aircraft measurements in the tropical west Pacific from CAST, ATTREX and CONTRAST. Atmospheric Measurement Techniques, **9**, 5213-5225. doi:10.5194/amt-9-5213-2016.

3.4. Hossaini, R., Patra, P.K., Leeson, A.A., Krysztofiak, G., Abraham, N.L., Andrews, S.J., Archibald, A.T., Aschmann, J., Atlas, E.L., Belikov, D.A., Bönisch, H. and **Carpenter, L.J.** (2016) A multi-model intercomparison of halogenated very short-lived substances (TransCom-VSLS): linking oceanic emissions and tropospheric transport for a reconciled estimate of the stratospheric source gas injection of bromine. Atmospheric Chemistry and Physics, **16**, 9163-9187. doi:10.5194/acp-16-9163-2016.

3.5. Pan, L.L., **Carpenter, L.J.** and 42 others. (2017) The Convective Transport of Active Species in the Tropics (CONTRAST) Experiment. Bulletin of the American Meteorological Society, **98**, 106–128. doi:10.1175/ bams-d-14-00272.1.

3.6. Sherwen, T., Evans, M.J., **Carpenter, L.J**., Schmidt, J.A., and Mickley, L.J. (2017) Halogen chemistry reduces tropospheric O_3 radiative forcing. Atmospheric Chemistry and Physics, 17, 1557–1569. doi.org/10.5194/acp-17-1557-2017.

All references have been peer reviewed.

4. Details of the impact (indicative maximum 750 words)

The Montreal Protocol on Substances that Deplete the Ozone Layer is widely acknowledged to have been the most successful global cooperation to protect the environment and public health. It has resulted in striking reductions in the global emissions of ozone depleting substances (ODSs) which has led recently to an upturn in upper stratospheric ozone levels. There is now confidence in projections that stratospheric ozone will recover sometime around mid-century at mid-latitudes and the Arctic, and somewhat later for the Antarctic. Since many ODSs are also potent greenhouse gases, the Montreal Protocol and its Amendments and Adjustments have contributed more to climate change mitigation than any other existing international agreement.

The Scientific Assessment Panel of the United Nations Montreal Protocol is charged with updating the state-of-scientific-understanding regarding the depletion of stratospheric ozone every 4 years, under the auspices of the United Nations Environment Programme (UNEP) and the World Meteorological Organization (WMO). These periodic assessments are written and reviewed at the request of The Parties to the UN Montreal Protocol and are the official scientific evidence that guides policymakers in ratifying and strengthening the provisions of the Montreal

Protocol with regard to the phase-out of ozone-depleting chemicals such as the chlorofluorocarbons ("CFCs") and other matters related to the long-term protection of the stratospheric ozone layer. The Montreal Protocol has been ratified by all 196 members of the United Nations and all decisions have been based on the findings of these Scientific Assessments.

Carpenter's body of research into atmospheric halogens led to her appointment by the Scientific Assessment Panel as one of the two Lead Authors of Chapter 1, "Update on Ozone-Depleting Substances and Other Gases of Interest to the Montreal Protocol" of the 2014 Assessment [5.1] and of Chapter 6, "Scenarios and Information for Policymakers" of the 2018 Assessment [5.2]. Only a handful of scientists world-wide have served as Ozone Assessment lead authors more than once. This role has facilitated the translation of York research directly into the Assessment.

Carpenter has contributed work that has been repeatedly cited and used in successive ozone assessments, and influenced Assessment conclusions and subsequent global policy changes and actions. Research on VSL halogens (with atmospheric lifetimes typically less than 6 months) showed they were emitted predominantly from the oceans [3.1, 3.2]. Emissions of VSL halocarbons are not restricted by the Montreal Protocol, but they are now included in evaluations in order to reconcile observed stratospheric measurements of inorganic or "active" bromine with the reported anthropogenic bromine emission sources. The research from York into natural sources of VSL provided a framework for international model studies that have explored whether future increases in VSL halocarbons, as a result of climate change, could counteract the effect of halogen reductions under the Montreal Protocol. Measurements made by Carpenter and co-workers [3.1-3.3] contributed to a reduction in the uncertainty range of total VSL bromine in the stratosphere (Chapter 1, WMO 2018, [5.3]). This was central to providing signatory governments with more reliable predictions of changes in stratospheric O_3, and greater confidence that natural variability in VSL was fully accounted for in the Montreal Protocol.

Carpenter and Reimann provided an early warning of a global rise in dichloromethane (CH_2Cl_2) an emission which is not controlled by the Montreal Protocol (Ozone Assessment 2014, p75, [5.1]). This led to a number of high profile studies of the potential impact of VSL chlorine (e.g. Hossaini *et al*., *Nature Communications*, 2017) and widespread media reporting. In the 2018 Ozone Assessment Carpenter and Daniels [5.2] provided key information to policymakers highlighting the potential future impact of CH_2Cl_2 on stratospheric ozone depletion. They showed that global growth in CH_2Cl_2 emissions, if it continued unabated, could deplete as much stratospheric ozone between 2020 and 2060 as that by controlled ODSs emitted during that period. This led to the inclusion of CH_2Cl_2 into the suite of compounds which the Parties to the Montreal Protocol request information on (WMO, 2018, [5.4]). Carpenter and Daniels research for the Assessment overturned the conclusions of a previous white paper on CH_2Cl_2 from the European Chlorinated Solvent Association which had stated that "CH_2Cl_2 is believed not to have a significant impact on stratospheric ozone depletion."

The discovery of a new mechanism by Carpenter which indicated that there had been higher iodine emissions over the 20th century [3.6] than previously thought allowed a re-assessment of the potential for iodine to impact the stratosphere. New calculations showed that the levels of total reactive iodine injected into the stratosphere were between two and five times larger than previously assumed upper limits, and exert an ozone-depletion potential similar to, or even larger than, that of VSL bromine. This new insight into the role of iodine was presented to the Parties to the Treaty for the first time in the WMO (2018) Ozone Assessment [5.2, 5.3].

The research outputs from Carpenter have been used to develop improved projections of future scenarios for emissions of ozone depleting substances. These projections are central to informing the key policy messages of the Assessment. Future theoretical scenarios have been developed and used to predict the recovery of the ozone layer (both within the Assessment [5.2] and used by independent studies worldwide) and to compare and evaluate the impacts of various future policy options for reducing emissions of ODSs. The work has therefore had a significant influence on national and international decision making, and policy decisions made by the Parties to the Montreal Protocol. "*Science has always informed decisions taken by governments for the protection of ozone and climate under the Montreal Protocol…. scientific research, analysis and observations provide the basis for policy actions. You are at the heart of the interface between science and policy*" Letter to Carpenter from UN-Environment Ozone Secretariat [5.5].

5. Sources to corroborate the impact (indicative maximum of 10 references)

5.1. Carpenter, L.J. and S. Reimann (Lead Authors), J.B. Burkholder, C. Clerbaux, B.D. Hall, R. Hossaini, J.C. Laube, and S.A. Yvon-Lewis, Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1 in *Scientific Assessment of Ozone Depletion: 2014*, Global Ozone Research and Monitoring Project–Report No. 55, World Meteorological Organization, Geneva, Switzerland, 2014. Link to document at: http://www.esrl.noaa.gov/csd/assessments/ozone/2014/chapters/chapter1_2014OzoneAssessment.pdf

5.2. Carpenter, L.J. and J.S. Daniel (Lead Authors), E.L. Fleming, T. Hanaoka, J. Hu, A.R. Ravishankara, M.N. Ross, S. Tilmes, T.J. Wallington, D.J. Wuebbles, Scenarios and Information for Policymakers, Chapter 6 in *Scientific Assessment of Ozone Depletion: 2018*, Global Ozone Research and Monitoring Project–Report No. 58, World Meteorological Organization, Geneva, Switzerland, 2018.

5.3. Engel, A. and M. Rigby (Lead Authors), J.B. Burkholder, R.P. Fernandez, L. Froidevaux, B.D. Hall, R. Hossaini, T. Saito, M.K. Vollmer, and B. Yao, Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1 in Scientific Assessment of Ozone Depletion: 2018, Global Ozone Research and Monitoring Project — Report No. 58, World Meteorological Organization, Geneva, Switzerland, 2018.

5.4. WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion*: 2018, Global Ozone Research and Monitoring Project – Report No. 58, 588 pp., Geneva, Switzerland, 2018.
https://csl.noaa.gov/assessments/ozone/2018/downloads/2018OzoneAssessment.pdf

5.5. Letter from UN-Environment to Carpenter, 13/2/19, (Executive Secretary, Ozone Secretariat, UNEP, Nairobi, Kenya.)