Institution: University of East Anglia

Unit of Assessment:7 – Earth Systems and Environmental Sciences

Title of case study:

Halocarbons: Impacts on Ozone Depletion and Global Warming

1. Summary of the impact

Halocarbons in the atmosphere can be both ozone-depleting and greenhouse gases. Our halocarbon research has formed a vital part of the science that has underpinned the Montreal Protocol on 'Substances that Deplete the Ozone Layer'. Whilst this Protocol was originally ratified in 1987, it is amended at regular intervals based on the latest scientific evidence as reported through quadrennial World Meteorological Organisation (WMO) Ozone Assessments. Our research has contributed to the Assessments in 1994, 1998, 2002, 2006 and 2010, as well as IPCC (Intergovernmental Panel on Climate Change) assessments. These assessments have led directly to reductions in emissions of a large number of halocarbons and consequently major climate and health benefits worldwide; e.g. UEA research on methyl bromide and halons has led, via Montreal Protocol amendments, to a decline in atmospheric bromine between 2008-2013.

2. Underpinning research

The School is internationally renowned for measuring the abundance, and quantifying the sources, of atmospheric chlorine-, bromine- and fluorine-containing (halocarbon) trace gases that are highly significant for both ozone depletion and climate change. In line with the Montreal Protocol, which is aimed at protection of stratospheric ozone, we initially focussed our research on chlorofluorocarbons (CFCs) and the powerful bromine-containing **halons** and **methyl bromide** [e.g. 1, 2]. As 'replacement' compounds (hydrochlorofluorocarbons (**HCFCs**) and hydrofluorocarbons (**HFCs**)) were introduced, we shifted our focus towards these [e.g. 3, 4] and other highly potent greenhouse gases (i.e. **fully fluorinated compounds** [e.g. 5]). Subsequently we have gained international recognition for being the first to detect many of these compounds in the atmosphere (e.g. **Halon 1202** [1], **HFC-23** [4], **HFC-227ea** and **SF_5CF_3** [5]).

Research in this area started at UEA in 1985, but for the purpose of this impact case study when we refer to UEA research we mean that since 1993. This has been supported by over £3M from the Dept. of the Environment, EU and NERC, and has resulted in nearly 50 papers in international peer-reviewed journals. The work makes use of highly sensitive laboratory-based, and field-deployed mass spectrometers, allowing measurements from ground-stations, aircraft, stratospheric balloons, ships, deep polar snow (firn) and ice cores. The analyses we make allow us to track atmospheric temporal trends of halocarbons and to assess their origins, emission rates and atmospheric lifetimes. These parameters are crucial in the determination of policies for their regulation, and are fundamental to the calculation of metrics commonly used by policymakers such as Ozone Depletion Potentials and Global Warming Potentials.

By examining long-term records we have assessed the impact of human activities on the burden of gases in the atmosphere. We collaborate with CSIRO in Australia to make measurements on the Cape Grim, Tasmania air archive which dates from 1978 [e.g. 1, 3, 4, 5], and have extended this record backwards in time via measurements in firn and ice cores from the Arctic and Antarctic [e.g. 5], in part through UEA-led EU projects. Coupled to the observational work is a modelling capability from which we determine 'top-down' global emission estimates (i.e. constrained by atmospheric observations) for comparison with other emission estimates (including 'bottom-up' industrial estimates). This has identified large inaccuracies with industrial estimates for several halocarbons, including the **halons** [1], **HCFC-142b** [3]**, HFC-23** [4], perfluorocarbons (**PFCs**) and chloroform.

There has been intense political debate over the control, under the Montreal Protocol, of the man-made fumigant **methyl bromide** as it also has poorly constrained natural sources and sinks. We have undertaken modelling and measurement studies of specific sources of methyl bromide (e.g. marine, automobile) and of long-term trends of its atmospheric concentration leading to improved

understanding of its atmospheric budget and the anthropogenic contribution [e.g. 2].

Our measurements from balloons, research aircraft and commercial aircraft [e.g. 6] have allowed us to determine the important, but previously poorly known, contribution of the mostly unregulated halogenated '**very short-lived substances**' (**VSLS**) to the stratospheric bromine burden. This is vital in the quantification of the impact of controlled bromine substances.

This research has been led by **Penkett** (at UEA from 1985-2005, now emeritus), **Oram** (started 1987), **Reeves** (started 1989), **Sturges** (started 1993), and **Laube** (started 2008), with contributions from **Carpenter**, **Mills**, **Sturrock** and **Begley** as post-docs, and **Lee**, **Baker**, **McIntyre**, **Worton**, **O'Sullivan**, **Mani**, **Hogan** and **Newland** as PhD students.

3. References to the research

(UEA authors in bold) {citations from Scopus}

[1] Fraser P.J., D.E. **Oram**, C.E. **Reeves**, S.A. **Penkett** and A. McCulloch (1999) Southern Hemispheric halon trends (1978-1998) and global halon emissions, *J. Geophys. Res.* **104** 15985-15999 {67}
This is the first of 7 papers on halons (1998-2013). All of the 4 papers prior to 2010 are cited in WMO Assessments. 1 is also cited by IPCC.

[2] **Reeves** C.E. and S.A. **Penkett** (1993) An estimate of the anthropogenic contribution to atmospheric methyl bromide, *Geophys. Res. Letts.* **20** 1563-1566 {24}
This is the first of 10 papers on methyl bromide (1993-2003). 8 have been cited in WMO Assessments. 1 is also cited by IPCC.

[3] **Oram** D.E., C.E. **Reeves**, S.A. **Penkett** and P.J. Fraser (1995) Measurements of HCFC-142b and HCFC-141b in the Cape Grim air archive: 1978-1993, *Geophys. Res. Letts.* **22** 2741-2744 {36}
*This is 1 of 4 papers on **HCFCs** (1995-2013). Both of the 2 papers prior to 2010 are cited in WMO Assessments. 1 is also cited by IPCC.*

[4] **Oram**, D. E., W. T. **Sturges**, S. A. **Penkett**, A. McCulloch, and P. J. Fraser (1998) Growth of fluoroform (CHF_3, HFC-23) in the background atmosphere, *Geophys. Res. Letts.* **25** 35-38 1998 {42}
This is 1 of 6 papers on HFCs (1996-2011). 2 of the 4 papers prior to 2010 are cited in both WMO Assessments and IPCC reports.

[5] **Sturges**, W.T., Wallington, T.J. Hurley, M.D. Shine, K.P. Sihra, K. Engel, A. **Oram**, D.E. **Penkett**, S.A., Mulvaney, R. and Brenninkmeijer, C.A.M.(2000) A potent greenhouse gas identified in the atmosphere: SF_5CF_3, *Science* **289** 611-613 doi:10.1126/science.289.5479.611 {101}
This is 1 of 13 papers on fully fluorinated compounds (2000-2013). 4 of the 6 papers prior to 2010 are cited in WMO Assessments. 1 is also cited by IPCC.

[6] **Laube**, J.C., A. Engel, H. Bönisch, T. Möbius, D.R. **Worton**, W.T. **Sturges**, K. Grunow, and U. Schmidt (2008) Contribution of very short-lived organic substances to stratospheric chlorine and bromine in the tropics - a case study, *Atmos. Chem. Phys.* **8** 7325-7334 {23}
This is 1 of 19 papers on VSLS (1994-2013). 9 of the 14 papers prior to 2010 are cited in WMO Assessments. 1 is also cited by IPCC.

4. Details of the impact

Impacts on Ozone Depletion: Through emission controls of certain halocarbons, the Montreal Protocol on *'Substances that Deplete the Ozone Layer'* has been hugely successful in avoiding ozone depletion and has thus protected the global population from increased UV radiation and ozone-related climate change. The Montreal Protocol is an international agreement which was initially adopted in 1987, but is an on-going process by which the Parties are informed of the latest science through international WMO Assessments (hereafter referred to as Assessments) provided by a Scientific Assessment Panel of experts every 4 years, and, based on these, the Parties have agreed Amendments to the Protocol [7]. It is through inclusion of our results in this on-going

process of Assessments and Amendments that out research has had most impact.

This impact of our research has occurred in two forms. (i) Research in the earlier part of the REF research-period has fed through the Assessments into internationally agreed Amendments to the Protocol and subsequent national policies, which have in turn led to observable declines in emissions and atmospheric concentrations of ozone depleting substances during the REF impact-period. (ii) Our more recent research is impacting policy through the latest 2010 Assessment. Evidence (citations and authorship) of our contribution to the Montreal Protocol process is found in the Assessments [7, 8] and by the testimonial provided by the **Co-Chair of the Scientific Assessment Panel** [9].

In addition to impacting policy on ozone depleting substances through the established international process, we have also reported our research results directly to the UK Government. The **Head of the Global Atmosphere Division** in the UK Department of the Environment has provided a testimonial to confirm this [10].

Below are 2 examples where the impact of our research has been observable in the environment during 2008-13:

Example 1a - Halons:
UEA research contributed to the science which led to strengthening of the Montreal Protocol, resulting in an observable decline in bromine from halons during 2008-13, as corroborated by the **Co-Chair of the Scientific Assessment Panel**: "*Despite halon emission controls in developed countries, UEA research (Fraser et al, 1999) showed continuing increase in global emissions of the most abundant halon and alerted Parties to the growth in atmospheric concentrations of a previously undetected halon (1202). Consequently the Protocol resolved to identify the sources of halon-1202 and introduced controls on the other halons for developing countries. The impact has been that global emissions of all halons have fallen dramatically, with concentrations of all but one halon declining during the 2008-13 period (Newland et al, 2013).*" [9].

Example 1b - Methyl Bromide:
UEA research contributed to the science which led to methyl bromide becoming a controlled substance under the Montreal Protocol in 1997 and to subsequent Amendments and hence to lower atmospheric concentrations in 2008-13 [7, 11, 12]. This is corroborated by the **Head of the Global Atmosphere Division** in the UK Department of the Environment: "*UEA research during 1993-2003 helped to better constrain estimates of the anthropogenic contribution to atmospheric methyl bromide, which enabled the Parties to the Montreal Protocol to make informed decisions about its control. As a result of the controls introduced, atmospheric methyl bromide concentrations have decreased substantially.*" [10].

Below is an example where our research has informed policy-making during 2008-13:

Example 2: 2010 Scientific Assessment of Ozone Depletion:
The UEA research on halocarbons continues to have an on-going impact on international policy through the latest 2010 Assessment as corroborated by the **Co-Chair of the Scientific Assessment Panel**:

> "*I presented the scientific findings of the 2010 Assessment at the 23rd Meeting of Parties to the Montreal Protocol in 2011. UEA research contributed to these findings with the Assessment citing 11 papers where UEA scientists were authors, including Fraser et al (1999), Oram et al (1998) and Laube et al (2008). Halocarbon concentration data from UEA were also included in the Assessment.*" [9].

Impacts on Global Warming: Most long-lived halocarbon gases are also strong greenhouse gases, thus their control has also prevented a large contribution to climate forcing, including during the 2008-13 period [7]. The same UEA research that has underpinned the Montreal Protocol has therefore contributed to the climate forcing benefits of the Protocol.

However, the gain from reductions in the emissions of the CFCs and halons is threatened by the transition to other non-ozone-depleting halocarbons as replacement compounds, many of which are strong greenhouse gases (e.g. **HFCs**). These replacement halocarbons are therefore included in the WMO Ozone Assessments along with other fluorinated compounds that are potent greenhouse gases (i.e. **PFCs**) because of their climate impact even though they are not ozone-

depleting substances. UEA papers on **HFC-23**, **HFC-227ea**, CF_4 and C_2F_6 have been cited in the 2010 Assessment that was reported to the 2011 Meeting of the Parties to the Montreal Protocol.

Furthermore, the **HFCs** and **PFCs** are included in the Kyoto Protocol, which is an international agreement under the United Nations Framework Convention on Climate Change (UNFCCC), which commits its Parties by setting emission reduction targets. The Parties make decisions based on scientific information reported to them by the Intergovernmental Panel on Climate Change (IPCC). UEA research on the HFCs has been cited in several IPCC reports, for example in 2007.

The **Co-Chair of Working Group 1** of the **2007 IPCC** who has also been a regular member of the **Scientific Assessment Panel for the Montreal Protocol** has provided a testimonial [13] to confirm our contribution to the development of international policy on greenhouse gases:

> "*Over the last 20 years, scientists at UEA have made many valuable contributions to the understanding of the abundances of halocarbons in the atmosphere. Their research has been included in, and they have been co-authors of, many of the scientific assessments for the Montreal Protocol and the reports of the IPCC. UEA has therefore contributed to the success the Montreal Protocol has had in reducing greenhouse gas emissions. The UEA work on the trends in concentrations of the **HCFCs** and **HFCs** was also included in the 2007 IPCC report that better informed the UNFCCC of the climate-relevance of the key halocarbons during 2008-13. UEA has also identified and made first measurements of certain important halocarbons. These newly observed gases have thereafter become part of the growing number of gases reviewed in subsequent assessments of both the IPCC and the Montreal Protocol. E.g. **SF_5CF_3**, which has one of the highest radiative forcing efficiencies per molecule of any gas in the atmosphere. UEA has also made important contributions to the understanding of changing levels of HFC-23, an exceptionally strong greenhouse gas and a by-product of the manufacture of HCFC-22, and HFC-227ea.*"

5. Sources to corroborate the impact

[7] World Meteorological Organisation (2011) *Global Ozone Research and Monitoring Project Report No. 52:* ***Scientific Assessment of Ozone Depletion: 2010*** (co-chairs A-L. N. Ajavon, P.A. Newman, J.A. Pyle, A.R. Ravishankara)

[8] Report of the 2010 Assessment of the Scientific Assessment Panel

[9] Testimonial from the **Co-Chair of the Scientific Assessment Panel**, held on file at UEA and including the following:

> "*I can confirm that UEA research on atmospheric halocarbons since 1993 has formed a significant part of the science underpinning the Ozone Depletion Assessments. In addition, at least one of **Penkett**, **Reeves**, **Oram** and **Sturges** has served as an expert on all Panels since 1994, including leading chapters in the 1994, 2006 and 2010 Assessments. Consequently, UEA has made an extremely valuable contribution to the phasing-out of ozone-depleting substances, leading to major climate and health benefits experienced worldwide during the 2008-13 period. Furthermore the UEA research featured in the 2010 Assessment has been feeding into recent policy decisions.*"

[10] Testimonial from the **Head of the Global Atmosphere Division** in the **UK Department of the Environment**, held on file at UEA and including the following:

> "*UEA was contracted to provide scientific results required to inform development of UK policy on the control of ozone depleting substances. These results were delivered through contract reports in 1994, 1997, 1999 and 2001. Further their results were included in the science assessed in the UK Government commissioned Stratospheric Ozone Review Group (SORG) reports in 1993, 1996 and 1999. **Penkett** and **Reeves** also provided expert advice as members of SORG."*

[11] Yvon-Lewis *et al*, Recent trends in atmospheric methyl bromide: analysis of post-Montreal Protocol variability, Atmos. Chem. Phys., **9**, 5963-5974, 2009 doi:10.5194/acp-9-5963-2009

[12] NOAA CMDL website: ftp://ftp.cmdl.noaa.gov/hats/methylhalides/ch3br/flasks/

[13] Testimonial from the **Co-Chair of Working Group 1 of the 2007 IPCC** – held on file at UEA.