

1 **Newly detected ozone depleting substances in the atmosphere**

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5

6 **Summary paragraph**

7 Ozone-depleting substances emitted through human activities cause large-scale damage to the
8 stratospheric ozone layer, and influence global climate. Consequently, the production of many
9 of these substances has been phased out; prominent examples are the chlorofluorocarbons
10 (CFCs), and their intermediate replacements, the hydrochlorofluorocarbons (HCFCs). So far,
11 seven types of CFC and six types of HCFC have been shown to contribute to stratospheric
12 ozone destruction^{1,2}. Here, we report the detection and quantification of a further three CFCs
13 and one HCFC. We analysed the composition of unpolluted air samples collected in Tasmania
14 between 1978 and 2012, and extracted from deep firn snow in Greenland in 2008, using gas
15 chromatography with mass spectrometric detection. Using the firn data, we show that all four
16 compounds started to emerge in the atmosphere in the 1960s. Two of the compounds continue
17 to accumulate in the atmosphere. We estimate that, before 2012, emissions of all four
18 compounds combined amounted to more than 74,000 tonnes. This is small compared with
19 peak emissions of other CFCs in the 1980s of more than one million tonnes each year².
20 However, the reported emissions are clearly contrary to the intentions behind the Montreal
21 Protocol, and raise questions about the sources of these gases.

22

1 Letter

2 Since the discovery of the “ozone hole” over Antarctica³ much progress has been made in
3 understanding the causes and implications of this phenomenon. Decomposition products of
4 mostly anthropogenic halogenated organic compounds such as the chlorofluorocarbons
5 (CFCs) have been confirmed as the main cause for ozone depletion in the stratosphere⁴. The
6 “Montreal Protocol on Substances that Deplete the Ozone Layer” came into force in 1989
7 and, including a number of subsequent amendments, has since been very successful in
8 reducing the production of many of these compounds on a global scale². The first-stage
9 replacements for CFCs were hydrochlorofluorocarbons (HCFCs). HCFCs are more
10 susceptible to chemical break down in the lower atmosphere before reaching the stratosphere,
11 but are still able to deplete ozone. The production of CFCs has been phased out in both
12 industrialised and developing nations, with a total global ban on production (except for some
13 exempted purposes and intermediate products) achieved by 2010. Continued production of
14 HCFCs is allowed under transitional arrangements within the Montreal Protocol.

15 Our observations on air samples collected in remote regions of the atmosphere show the
16 presence of four previously undetected Ozone Depleting Substances (ODSs). We have
17 identified and quantified CFC-112 (CFC₁₂CFC₁₂), CFC-112a (CF₂CICCl₃), CFC-113a
18 (CF₃CCl₃) and HCFC-133a (CF₃CH₂Cl) in the atmosphere (Figure 1). We have reconstructed
19 their past abundances from air extracted from deep polar firn which can provide a “natural
20 archive” of atmospheric composition up to about a century back in time⁵. Our firn air
21 measurements suggest that all four newly reported compounds are anthropogenic (see also
22 Supplementary Information), with insignificant atmospheric abundances before the 1960s.
23 More recent information comes from analyses of archived samples collected since 1978 at the
24 remote observatory at Cape Grim, Tasmania^{6,7}. In late 2012, CFC-113a was the most

1 abundant of the four gases at 0.48 parts per trillion molar (ppt), followed by CFC-112 at 0.44
2 ppt, HCFC-133a at 0.37 ppt and CFC-112a at 0.07 ppt. Also apparent from Figure 1 is that
3 the increases observed in Tasmania lag behind those inferred from firm air collected in
4 Greenland (NEEM project⁸). This lag reflects that the dominant source for these gases is in
5 the northern hemisphere where most industrialised countries are located. Because mixing of
6 old and more recent air in the firm smoothes out short term variations⁹, a more quantitative
7 evaluation of hemispheric differences is difficult. Nevertheless the firm data suggest entirely
8 anthropogenic origins of the four compounds as they are not detectable in air dated from
9 before the 1960s.

10 It is evident from Figure 1 that CFC-112 and CFC-112a show a similar evolution, suggesting
11 that they might have been produced conjointly. Their atmospheric abundances increased from
12 the 1960s until the mid 1990s; subsequently we find a slow decrease in global abundances,
13 similar to previously reported CFCs where production has been increasingly reduced under
14 the Montreal Protocol. Between around 2005 and 2010 we have observed a temporary
15 slowing in the rate of decline for CFC-112 and CFC-112a. This period was however followed
16 by a renewed decrease in 2011 and 2012.

17 Most notable is the temporal evolution of CFC-113a (Figure 1) as it contrasts with those of
18 CFC-112 and CFC-112a as well as those of all other CFCs with known atmospheric histories.
19 This compound has continuously grown in abundance from the 1960s to 2012. It is
20 particularly interesting as its behaviour is dissimilar to that of its isomer CFC-113
21 ($\text{CF}_2\text{ClCFCl}_2$) which has been decreasing in abundance for more than a decade².

22 The fourth ODS in Figure 1, HCFC-133a, also exhibits an unusual behaviour. It appeared in
23 the atmosphere before CFC production was being replaced on a large scale by HCFCs. It is
24 thus likely that its sources are to some degree unrelated to CFC replacement. Also notable is

1 an accelerated increase starting in 2004, which was then interrupted from mid-2008 to mid-
2 2010. These variations may be due to one or few large industrial emitters changing production
3 procedures and/or product ranges. In more recent years we observe a strong growth and
4 atmospheric abundances of HCFC-133a increased by 45 % in the last 2.5 years of the record.

5 The estimation of global emissions of these ODSs from the inferred time trends requires
6 knowledge of their atmospheric lifetimes. Only in the case of HCFC-133a has an estimate
7 been published (4.3 years²). Stratospheric lifetimes of CFCs are essentially identical to their
8 total atmospheric lifetimes². We use measurements of these gases in air samples collected in
9 the stratosphere and apply a previously described methodology^{10,11}. This method allows the
10 estimation of the stratospheric lifetime of an unknown compound to be inferred from its
11 correlation with a compound of known stratospheric lifetime. We utilise the correlations of
12 the newly reported compounds with that of CFC-11 assuming a recommended lifetime of 45
13 years for the latter². The resulting lifetimes are similar to that of CFC-11 with 51 years for
14 CFC-112 (uncertainty range from 37 to 82 years), 44 years for CFC-112a (28 – 98 years), 51
15 years for CFC-113a (27 – 264 years), and 35 years (21 – 92 years) for HCFC-133a. In
16 agreement with ² the stratospheric lifetime of HCFC-133a is much longer than its overall
17 atmospheric lifetime. As with other HCFCs its loss is dominated by the reaction with the OH
18 radical which occurs mainly in the troposphere.

19 Another important quantity that can be inferred from stratospheric measurements is the Ozone
20 Depletion Potential or ODP which “represents the global ozone loss due to release of a
21 particular molecule relative to a reference molecule (generally CFC-11)”¹². We infer semi-
22 empirical ODPs of 0.88 (uncertainty range 0.62-1.44) for CFC-112, 0.88 (0.50-2.19) for CFC-
23 112a, and 0.68 (0.34-3.79) for CFC-113a. Taking into account that CFC-11 is a strong ODS,
24 this implies that the three new CFCs are comparably dangerous to stratospheric ozone on a

1 per kg basis. For HCFC-133a we determine an ODP of 0.02 (0.00-0.12) which does not
2 significantly differ from zero within uncertainties, but agrees with the range listed in the
3 Montreal Protocol (0.02-0.06). We conclude that its ODP is comparatively low (i.e. < 0.12) as
4 is expected for an HCFC.

5 The estimates of the lifetimes, in combination with the Cape Grim observations and a 2-D
6 chemical transport model¹³, enable us to infer the global emissions (Figure 1). Compared to
7 other ODSs, which can have mixing ratios of up to hundreds of ppt, the abundances of these
8 gases have remained small. Their temporal evolution however reveals that emissions of up to
9 3,100 tonnes per year are required to explain their individual atmospheric abundances in
10 recent years. Apart from the apparent small rise in the mid-2000s, emissions of CFC-112 and
11 CFC-112a have fallen continuously since the early 1990s. This contrasts with CFC-113a, for
12 which emissions did not decline and in fact more than doubled from 2010 to mid-2012, as
13 well as for HCFC-133a, for which emissions approximately tripled after 2009. Summing all
14 emissions inferred from the Cape Grim record until mid-2012, we find that at least 19,600
15 tonnes of CFC-112, 20,500 tonnes of CFC-113a, and 30,500 tonnes of HCFC-133a must have
16 entered the atmosphere. For CFC-112a no Cape Grim data are available prior to 1999 because
17 of storage problems with the type of canisters used. We therefore combined emissions
18 inferred from firm air trends with the available Cape Grim record to estimate cumulative
19 emissions of at least 3,600 tonnes.

20 These four ODSs all fall under the Montreal Protocol. Some production has been reported to
21 the United Nations Environment Programme (UNEP) Ozone Secretariat but publicly available
22 data on these particular gases are exceedingly sparse or non-existent. It is notable that there
23 are a number of caveats to the Montreal Protocol. In addition to officially granted exempted
24 uses, reporting does not have to include intermediate species, as well as estimates of fugitive

1 emissions or trace amounts released in the production of other ODSs. And although it is
2 mandatory to report production for chemical feedstock, UNEP is not allowed to release the
3 feedstock component to the public.

4 CFC-113a, for example, has been listed as an "agrochemical intermediate for the manufacture
5 of synthetic pyrethroids" in a list of Montreal Protocol exemptions in 2003. This is possibly
6 related to its use in the production of the insecticides cyhalotrin and tefluthrin¹⁴. There have
7 however been no publicly accessible reports of actual CFC-113a production to UNEP.
8 Another possible explanation here is that the Montreal Protocol does not require isomeric
9 compounds to be reported separately. Therefore its production could have been reported as
10 "CFC-113". CFC-113a and HCFC-133a are also intermediates in two of the processes to
11 produce the widely-used refrigerants HFC-134a¹⁷ and HFC-125¹⁸.

12 CFC-112 and -112a may have been used as feedstock chemicals for the production of
13 fluorovinyl ethers¹⁵ and also as solvents for cleaning electronic components¹⁶. For CFC-112
14 some production has been reported but only small quantities and only between 1989 and
15 2001. No reports have been released for the production of CFC-112a (or it may have been
16 reported as CFC-112) and only one report for HCFC-133a production in 2010.

17 It cannot be concluded whether the observed atmospheric abundances of these ozone
18 depleting gases are due to their use as feedstock and chemical intermediates and subsequent
19 fugitive emissions, or even due to production that is not sanctioned by the Montreal Protocol.
20 Given that emissions of two of these gases have been increasing considerably in recent years,
21 it may be time to both investigate the origins of these compounds. To ensure the long-term
22 efficacy of the Montreal Protocol it might be worth reconsidering its reporting regime,
23 including the differentiation of isomeric forms.

24

1 **Methods summary**

2 All samples were processed by cryogenically extracting and pre-concentrating the trace gases,
3 followed by their gas chromatographic separation and detection with a high-sensitivity mass
4 spectrometer. The system has been described in detail⁹ as have the collection details of the
5 samples originating from Cape Grim (from 1978 to 2012 in this study), Greenland (firn air
6 from the NEEM project, collected in 2008¹⁹), and the extra-tropical stratosphere (2009 and
7 2010, between 9 and 20 km). Storage problems of CFC-112a were overcome by the use of
8 SilcoTM-treated sample containers after 1999.

9 The physics of trace gas transport in the NEEM firn was modelled with a multi-gas approach
10 as previously described²⁰. This model was inter-compared satisfactorily with other state of the
11 art models⁸. The atmospheric time trends were then inferred from firn air concentration data
12 using a recently improved inverse method²¹ which accurately reconstructs long-term trends in
13 past atmospheric abundances from firn air measurements.

14 The exact methodology for the estimation of stratospheric lifetimes and ODPs includes a
15 correction for the slower vertical transport in the stratosphere as compared to the troposphere,
16 which influences the spatial distribution of the reported compounds. For instance, an air
17 parcel at an altitude of 21 km may have entered the stratosphere some years before the
18 collection date, and tropospheric abundances of trace gases could have changed during that
19 period. We here apply corrections using mean stratospheric transit times derived from
20 measurements of sulphur hexafluoride¹⁰. For more information on methods, calibrations, firn
21 and emission modelling and additional data please see the Supplementary Information.

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21 **Supplementary Information** is linked to the online version of the paper at
22 www.nature.com/nature.

23

24 **Acknowledgements**

1 We are grateful for the contributions of the anonymous reviewers as well as funding from the
2 UK Natural Environment Research Council (Research Fellowships NE/F015585/1 &
3 NE/I021918/1, Research Award NE/F021194/1 and the National Centre for Atmospheric
4 Science). We thank the staff at the Cape Grim station and at CSIRO GASLAB Aspendale for
5 collecting and maintaining the Cape Grim air archive and preparing the UEA flask and sub-
6 samples. We also acknowledge CSIRO and the Bureau of Meteorology for funding these
7 activities. NEEM is directed and organized by the Center of Ice and Climate at the Niels Bohr
8 Institute and US NSF, Office of Polar Programs. It is supported by funding agencies and
9 institutions in Belgium (FNRS-CFB and FWO), Canada (GSC), China (CAS), Denmark
10 (FIST), France (IPEV, CNRS/INSU, CEA and ANR), Germany (AWI), Iceland (RannIs),
11 Japan (NIPR), Korea (KOPRI), The Netherlands (NWO/ALW), Sweden (VR), Switzerland
12 (SNF), United Kingdom (NERC) and the USA (US NSF, Office of Polar Programs). The
13 Geophysica flights from Oberpfaffenhofen were funded by ESA under the PremieEx project
14 and by Forschungszentrum Jülich. The Geophysica flights from Kiruna were funded by the
15 EC as part of the FP7 project RECONCILE (Grant number: RECONCILE-226365-FP7-ENV-
16 2008-1). Air sampling during these campaigns was funded by the Dutch Science foundation
17 (NWO, grant number 865.07.001). The research leading to these results has received funding
18 from the European Community's Seventh Framework Programme (FP7/2007-2013) in the
19 InGOS project under grant agreement 284274. In addition we are grateful for contributions
20 from Gerald Mutisya (Ozone Secretariat), Paul A. Newman (NASA), Samuel Allin (UEA),
21 Thijs F. Duindam & Michel Bolder (Utrecht University), all CARIBIC partners, the
22 Geophysica team (discussions, software help, sample collection and campaign organisation)
23 as well as from the NOAA-ESRL GMD, AGAGE and WMO GAW teams (provision of
24 publicly available data).

25

1 **Author contributions**

2 J.C.L. and C.H. performed the measurements, M.J.N. and C.E.R. modelled the emissions and
3 P.M. and E.W. the firm air data. C.A.M.B., P.J.F., D.E.O., T.R. and J.S. collected and
4 provided air samples and all authors contributed to the interpretation and the writing of the
5 manuscript.

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1 **Competing financial interests**

2 The authors declare no competing financial interests.

3

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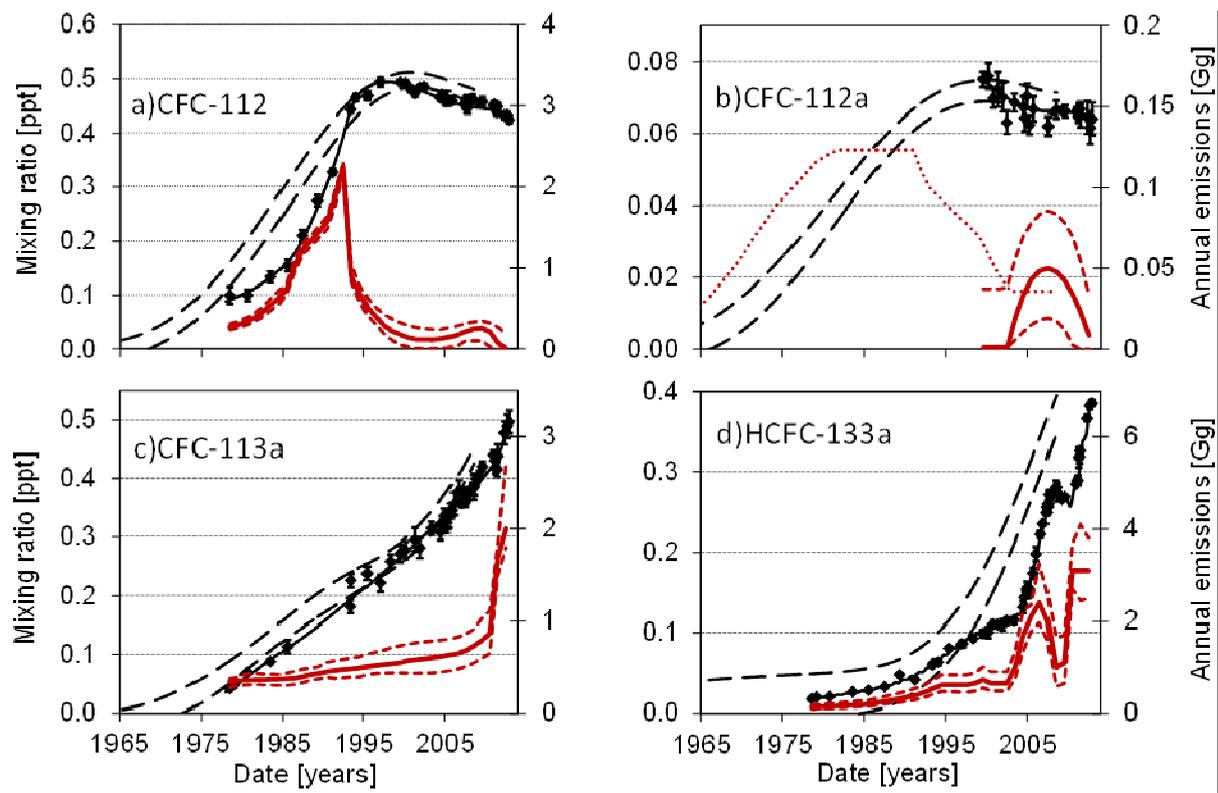
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7 **Figure legends**

8 Figure 1. Atmospheric histories and global emissions of CFC-112 (A), CFC-112a (B), CFC-
9 113a (C), and HCFC-133a (D). The range from northern hemispheric trend reconstructions
10 (originating from firn air collected in Greenland in summer 2008, see supplement for further
11 information) is displayed as dashed lines. Diamonds represent averages of measurements of
12 individual samples (collected at Cape Grim between 1978 and 2012) with 1σ standard
13 deviations as error bars. The black solid line is the model fit through this southern
14 hemispheric time series that was used to infer the emissions (red line, right-hand axis) and
15 their 1σ uncertainties (red dashed lines). CFC-112a was found to be unstable in the type of
16 storage canisters used for Cape Grim samples before 1999 and the temporal trend and
17 emissions for the earlier part of the record were inferred using firn data (red dotted line). As
18 mixing of air in the firn smoothes out short term variations these CFC-112a emissions are not
19 directly comparable to the Cape Grim data but both estimates agree within the uncertainties
20 for the overlap period.

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1

2 Figure 1.