# Newly detected ozone depleting substances in the atmosphere

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## Summary paragraph

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

## Letter

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

Our observations on air samples collected in remote regions of the atmosphere show the presence of four previously undetected Ozone Depleting Substances (ODSs). We have identified and quantified CFC-112 ($CFCl_2CFCl_2$), CFC-112a ($CF_2ClCCl_3$), CFC-113a ($CF_3CCl_3$) and HCFC-133a ($CF_3CH_2Cl$) in the atmosphere (Figure 1). We have reconstructed their past abundances from air extracted from deep polar firn which can provide a "natural archive" of atmospheric composition up to about a century back in time[5]. Our firn air measurements suggest that all four newly reported compounds are anthropogenic (see also Supplementary Information), with insignificant atmospheric abundances before the 1960s. More recent information comes from analyses of archived samples collected since 1978 at the remote observatory at Cape Grim, Tasmania[6,7]. In late 2012, CFC-113a was the most abundant of the four gases at 0.48 parts per trillion molar (ppt), followed by CFC-112 at 0.44 ppt, HCFC-133a at 0.37 ppt and CFC-112a at 0.07 ppt. Also apparent from Figure 1 is that the increases observed in Tasmania lag behind those inferred from firn air collected in Greenland (NEEM project[8]). This lag reflects that the dominant source for these gases is in the northern hemisphere where most industrialised countries are located. Because mixing of old and more recent air in the firn smoothes out short term variations[9], a more quantitative evaluation of hemispheric differences is difficult. Nevertheless the firn data suggest entirely anthropogenic origins of the four compounds as they are not detectable in air dated from before the 1960s.

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

Most notable is the temporal evolution of CFC-113a (Figure 1) as it contrasts with those of CFC-112 and CFC-112a as well as those of all other CFCs with known atmospheric histories. This compound has continuously grown in abundance from the 1960s to 2012. It is particularly interesting as its behaviour is dissimilar to that of its isomer CFC-113 ($CF_2ClCFCl_2$) which has been decreasing in abundance for more than a decade[2].

The fourth ODS in Figure 1, HCFC-133a, also exhibits an unusual behaviour. It appeared in the atmosphere before CFC production was being replaced on a large scale by HCFCs. It is thus likely that its sources are to some degree unrelated to CFC replacement. Also notable is an accelerated increase starting in 2004, which was then interrupted from mid-2008 to mid-2010. These variations may be due to one or few large industrial emitters changing production procedures and/or product ranges. In more recent years we observe a strong growth and atmospheric abundances of HCFC-133a increased by 45 % in the last 2.5 years of the record.

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

Another important quantity that can be inferred from stratospheric measurements is the Ozone Depletion Potential or ODP which “represents the global ozone loss due to release of a particular molecule relative to a reference molecule (generally CFC-11)”[12]. We infer semi-empirical ODPs of 0.88 (uncertainty range 0.62-1.44) for CFC-112, 0.88 (0.50-2.19) for CFC-112a, and 0.68 (0.34-3.79) for CFC-113a. Taking into account that CFC-11 is a strong ODS, this implies that the three new CFCs are comparably dangerous to stratospheric ozone on a per kg basis. For HCFC-133a we determine an ODP of 0.02 (0.00-0.12) which does not significantly differ from zero within uncertainties, but agrees with the range listed in the Montreal Protocol (0.02-0.06). We conclude that its ODP is comparatively low (i.e. $< 0.12$) as is expected for an HCFC.

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

These four ODSs all fall under the Montreal Protocol. Some production has been reported to the United Nations Environment Programme (UNEP) Ozone Secretariat but publicly available data on these particular gases are exceedingly sparse or non-existent. It is notable that there are a number of caveats to the Montreal Protocol. In addition to officially granted exempted uses, reporting does not have to include intermediate species, as well as estimates of fugitive emissions or trace amounts released in the production of other ODSs. And although it is mandatory to report production for chemical feedstock, UNEP is not allowed to release the feedstock component to the public.

CFC-113a, for example, has been listed as an "agrochemical intermediate for the manufacture of synthetic pyrethroids" in a list of Montreal Protocol exemptions in 2003. This is possibly related to its use in the production of the insecticides cyhalotrin and tefluthrin[14]. There have however been no publicly accessible reports of actual CFC-113a production to UNEP. Another possible explanation here is that the Montreal Protocol does not require isomeric compounds to be reported separately. Therefore its production could have been reported as “CFC-113”. CFC-113a and HCFC-133a are also intermediates in two of the processes to produce the widely-used refrigerants HFC-134a[17] and HFC-125[18].

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

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

## Methods summary

All samples were processed by cryogenically extracting and pre-concentrating the trace gases, followed by their gas chromatographic separation and detection with a high-sensitivity mass spectrometer. The system has been described in detail[9] as have the collection details of the samples originating from Cape Grim (from 1978 to 2012 in this study), Greenland (firn air from the NEEM project, collected in 2008[19]), and the extra-tropical stratosphere (2009 and 2010, between 9 and 20 km). Storage problems of CFC-112a were overcome by the use of Silco$^{TM}$-treated sample containers after 1999.

The physics of trace gas transport in the NEEM firn was modelled with a multi-gas approach as previously described[20]. This model was inter-compared satisfactorily with other state of the art models[8]. The atmospheric time trends were then inferred from firn air concentration data using a recently improved inverse method[21] which accurately reconstructs long-term trends in past atmospheric abundances from firn air measurements.

The exact methodology for the estimation of stratospheric lifetimes and ODPs includes a correction for the slower vertical transport in the stratosphere as compared to the troposphere, which influences the spatial distribution of the reported compounds. For instance, an air parcel at an altitude of 21 km may have entered the stratosphere some years before the collection date, and tropospheric abundances of trace gases could have changed during that period. We here apply corrections using mean stratospheric transit times derived from measurements of sulphur hexafluoride[10]. For more information on methods, calibrations, firn and emission modelling and additional data please see the Supplementary Information.

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

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## Author contributions

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

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## Competing financial interests

The authors declare no competing financial interests.

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## Figure legends

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

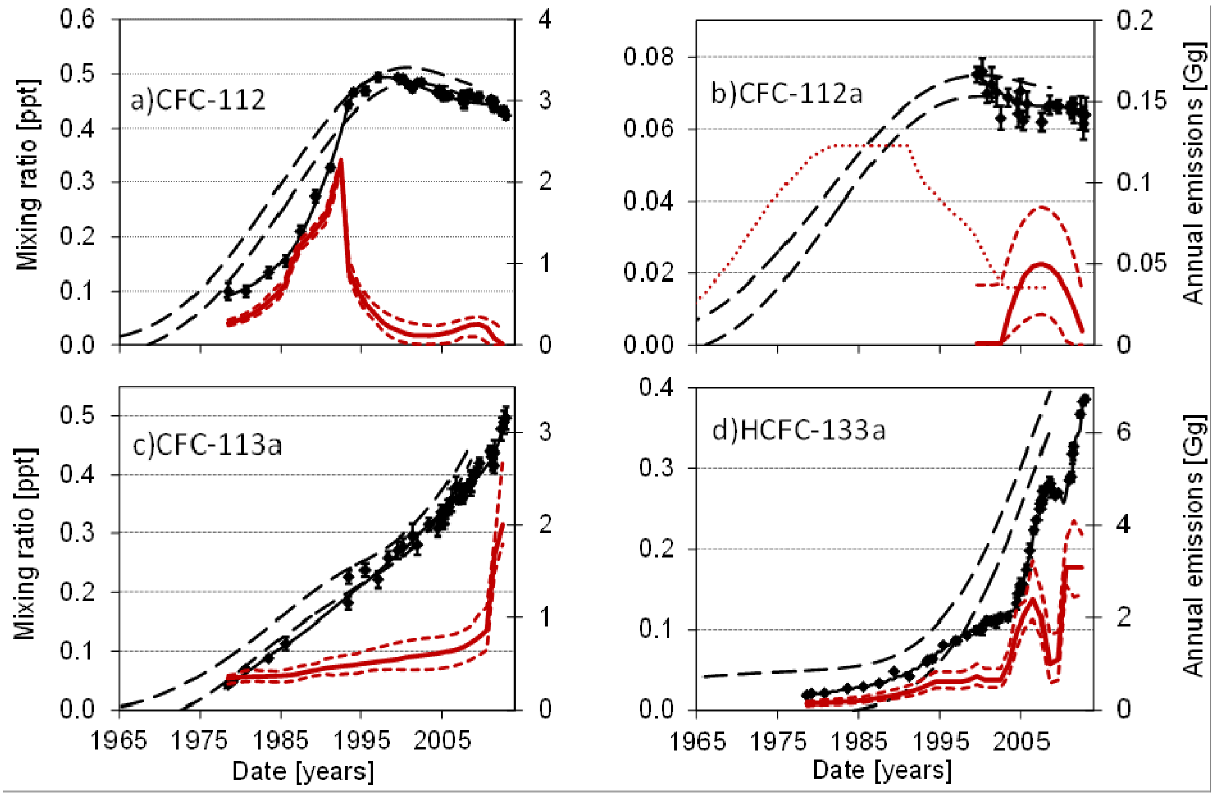
a)CFC-112
b)CFC-112a
c)CFC-113a
d)HCFC-133a
Mixing ratio [ppt]
Annual emissions [Gg]
Date [years]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
1
2
3
4
0.00
0.02
0.04
0.06
0.08
0.05
0.1
0.15
0.2
6
1965
1975
1985
1995
2005

Figure 1.