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First atmospheric observations of three chlorofluorocarbons

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Abstract

We report the first atmospheric observations of the Chlorofluorocarbons (CFCs) trifluorochloroethene, 3-chloropentafluoropropene and 4,4-dichlorohexafluoro-1-butene by means of Gas Chromatography with Electron Capture and Mass Spectrometric detection (GC-ECD-MS) in air samples taken at the Taunus Observatory operated by the University of Frankfurt (Main) and the Jungfraujoch High Altitude Research Station in Switzerland. These substances belong to a class of CFCs containing a double bond and are suspected to originate from the production and thermal degradation of widely used fluoropolymers like polychlorotrifluoroethene (PCTFE). Their atmospheric lifetimes are expected to be rather short. As a quantitative calibration is not available for these species by now we use a relative sensitivity method to estimate the observed atmospheric abundances. Identification was possible because of an air plume containing high concentrations of these substances. We suggest that the abundances found on this occasion originated from a local source. However, we have also observed the novel CFCs in air masses representative of background conditions, though with much lower concentrations. These species and some of their degradation products are toxic and could also be relevant for stratospheric and tropospheric ozone depletion.

1 Introduction

The production and use of many halocarbons is regulated by the Montreal Protocol and its subsequent amendments (see http://ozone.unep.org/ for details), because if these substances are transported into the stratosphere, they can release chlorine and/or bromine. The inorganic chlorine/bromine released from the halocarbons enhances the efficiency of catalytic ozone destruction cycles. This has led to both global ozone depletion and strong loss of nearly all ozone in an altitude layer between 15 and 25 km above Antarctica during austral spring; a phenomenon known as the ozone hole. See Solomon (1999) for a detailed review on this subject. Up to date only seven Chlorofluorocarbons (CFCs) have been observed in the atmosphere (e.g. Montzka and Fraser, 2003). All of them have rather long atmospheric lifetimes of more than 40 yr. Five of them are decreasing in the global background atmosphere due to their regulation under the Montreal Protocol. For CF_3Cl (CFC-13) there is no up-to-date trend data available. The only exception is C_2F_5Cl (CFC-115) which is still increasing slowly because of its very long lifetime (see Table 1.2 of Clerbaud and Cunnold, 2007 for details). Here we report the first atmospheric observations of three CFCs which are expected to have short atmospheric lifetimes relative to atmospheric transport times i.e. below half a year. Nevertheless considerable amounts of short-lived substances are able to reach the stratosphere. Law and Sturges (2007) estimated about 55 ppt (range: 52–60 ppt) of chlorine from 10 short-lived substances in the main stratospheric entrance region, the tropical upper troposphere. Thus, although their ozone depletion potential might be small, the newly observed short-lived CFCs are potential contributors to stratospheric chlorine. But none of them is covered by the Montreal Protocol.

2 Analytical procedure

Air samples were taken at the Taunus Observatory at the Kleiner Feldberg (50°13′29.6″ N, 8°26′28.7″ E) near Frankfurt (Main) between October and December 2007. Stainless steel and also silanized stainless steel canisters were used for sampling. The canisters were tested prior to use and none of them showed a blank signal in any CFC. The canisters were evacuated using a turbo pump which was also checked to be free of CFCs. They were filled by simply opening them in order to avoid effects from a compressor or a drying agent. A CFC-free and preconditioned sampling line was used to avoid breath contaminations. For analysis trace gases out of 500 ml of air were pre-concentrated cryogenically on porous glass beads by using liquid nitrogen. Separation was carried out with a Siemens Si1 Gas Chromatograph on a micro packed PorasilC/n-Octane column with a temperature programme from −40°C to 120°C. Samples were not dried before measuring. Two detectors were used simultaneously: an

Electron Capture detector (ECD) from Siemens and a quadruple Mass Spectrometer from Agilent (MSD 5975) run in electron impact selected ion monitoring (EI-SIM) mode. MS detection limits were below 1 ppt for almost every halocarbon and below 0.3 ppt for CFCs (ECD: below 0.1 ppt). None of the detectors showed a blank signal in any CFC.

3 Results and discussion

On the 2 October 2007 an air sample was taken at the Taunus Observatory. During analysis using the system described above the ECD showed some large additional signals. Figure 1 shows the zoom of the ECD chromatogram in comparison with a “normal” clean air sample. Several large signals occurred in addition to the known peaks belonging to CF_2Cl_2 [CFC-12, (1)], CF_2ClBr/CF_2ClCF_2Cl [Halon-1211/CFC-114, coeluting, (2)], $CFCl_3$ [CFC-11, (3)], $CF_2ClCFCl_2$ [CFC-113, (4)] and CCl_4 (5). This was a strong indication towards halocarbons as the ECD is very sensitive to these substances. Our MSD is usually operated in Selected Ion Monitoring (SIM) mode measuring only a few ions at a time to get enhanced detection limits. To identify the unknown signals the sample was measured again, this time pre-concentrating about one litre of air and operating the MSD in Scan mode scanning all mass fragments from 15 to 300 atomic mass units (amu). Figure 2 shows the mass spectrum at 8.4 min retention time. The background was subtracted in order to remove peaks originating from air entering the system through small leaks. The result of a search in the NIST mass spectral library was an excellent match with C_2F_3Cl (chlorotrifluoroethene) as all important mass fragments are present in the expected relative abundances. The substance eluted just after CFC-12 which had a retention time of 8.1 min. As the chromatographic system separates primary via boiling points this substance should have a boiling point of about −20°C. C_2F_3Cl boils at −28.4°C. The mass spectra at 11.1 and 16.2 min retention time also agreed perfectly with the library spectra of CF_2CFCF_2Cl (3-chloropentafluoropropene) and $CF_2CFCF_2CFCl_2$ (4,4-dichlorohexafluoro-1-butene). Both substances boiling points also fit very well with their retention times. 3-chloropentafluoropropene boils at 8°C and eluted 0.45 min after CF_3CFCl_2 (CFC-114a) which boils at 3°C. For 4,4-dichlorohexafluoro-1-butene boiling points between 67 and 71°C have been reported (source: Beilstein Crossfire database) and it coeluted with CCl_4 which boils at 77°C. To our knowledge none of the three substances has been reported in the atmosphere before. All other unknown signals are likely to be caused by halocarbons, too. However, they could not be identified yet due to the fact that comparison with the library gave no exact match. Possible explanations are the coelution of two or more substances or simply missing reference mass spectra.

As no calibration is available for the identified substances we derived a method for a minimum and maximum concentration estimate. We inferred the sensitivity relative to CFC-12 for six different halocarbons: $CFCl_3$, $CF_2ClCFCl_2$, CHF_2Cl (HCFC-22), CF_2ClBr, CH_3Br and $CHCl_3$. First the substances sensitivity s_i was calculated according to Eq. (1).

$$s_i = h_i/(a * \rho_i) \tag{1}$$

$$S_i = s_i/s_{\text{CFC}-12} \tag{2}$$

The signal height h of the substance i is divided by the sample amount a and the substance mixing ratio ρ_i. The relative sensitivity S_i is then given by division of s_i with $s_{\text{CFC}-12}$ (Eq. 2). Values of S_i were between 0.10 and 1.20 and remained constant for each species within ±6% over a period of two years. To consider the fact that we are using only one mass fragment to quantify a substance we introduced a fragmentation correction factor according to Eq. (3).

$$f_i = r_q/\sum_{j=1}^{j=10} r_j \tag{3}$$

$$C_i = S_i/f_i \tag{4}$$

This factor f_i is given by r_q – the relative abundance of the mass fragment used to quantify the substance – divided by the sum of the relative abundances r_j of all major

mass fragments. Only fragments with an abundance of more than 10% relative to the main fragment are used and 10 fragments included at most. The corrected relative sensitivity C_i is then given by the relative sensitivity S_i divided by the fragmentation factor f_i (Eq. 4). Derived values for C_i ranged from 0.62 to 3.26. We then calculated minimum and maximum mixing ratios for the new CFCs via the CFC-12 mixing ratio of the sample and derived a mixing ratio range of 5–29 ppb for C_2F_3Cl, 3–14 ppb for CF_2CFCF_2Cl and 3–15 ppb for $CF_2CFCF_2CFCl_2$ in the plume observed on 2 October.

Trichlorofluoroethene is also known as R-1113 and is toxic. Cook and Pierce (1973) reported an LC_{50} (i.e. the concentration which kills 50% of a sample population) of 1000 ppm and its ERPG-3 (i.e. the maximum airborne concentration below which individuals could be exposed for up to 1 h without life-threatening health effects) is 300 ppm (source: http://cameochemicals.noaa.gov). Like most fluoroalkenes 3-chloropentafluoropropene and an isomer of dichlorohexafluorobutene are also reported to be highly toxic (Thun and Kimbrough, 1981; Clayton, 1977). Considering the fact that C_2F_3Cl carries a double bound and is highly flammable its atmospheric lifetime is expected to be very short. Thus we suggest the plume we observed originated from a local source which is supported by the low wind speed (~1m/s) on the sampling day. However, concentrations close to the source could have been much higher – especially if that source was located indoors. We observed other large unknown signals which are likely to be chlorofluoroalkenes due the occurrence of characteristic fragments like m/z 147 and 149 or m/z 197 and 199. Both pairs showed an abundance ratio of 3:1 which is a strong indication towards the C_2F_4Cl and the C_3F_6Cl fragment. Thus it is also possible that the sum of the chlorofluoroalkenes could have reached concentrations which affect human health. Backward trajectories showed that air masses had been advected from the southwest sector with rather low wind speed probably originating from the densely populated Rhein-Main area.

We took six more air samples at the Taunus observatory and one at the High Altitude Research Station Jungfraujoch (Switzerland) and measured them by running the MSD in SIM mode monitoring C_2F_3Cl on m/z 116, CF_2CFCF_2Cl on m/z 131 and

$CF_2CFCF_2CFCl_2$ on m/z 147. The substances were present all the time except for the sample taken directly at the exhaust of the observatories air conditioning system which was free of short-lived CFCs. An indoor sample taken at our institute contained no C_2F_3Cl and no CF_2CFCF_2Cl but a very small amount of $CF_2CFCF_2CFCl_2$. The estimated mixing ratios for the six outdoor samples were in the lower ppt range and can be found in Table 1. Data is too few to see a correlation with wind speed or wind direction. All three short-lived CFCs were also present at the Jungfraujoch though we can not rule out that they were emitted from the station itself. We also checked several of our air standards for the substances. All of them contained low amounts of the substances and two even showed contaminations with C_2F_3Cl probably originating from the pressure regulator or the cylinder valve. The properties of C_2F_3Cl are very similar to those of CFC-12 (boiling point and several main fragments). Thus, coelution is very likely to occur in other chromatographic systems. Contaminations could cause falsified calculations of CFC-12 mixing ratios if an ECD or MSD is used for detection.

We believe the observed substances are very likely to be connected with chlorofluoro(co)polymers – particularly polychlorotrifluoroethene (PCTFE, tradenames are Kel-F, Neoflon or Aclar). PCTFE was first commercialized in 1934 by Hoechst (Utracki, 1995) and is still widely used in equipment manufacturing because of its excellent thermoplastic properties, chemical resistance and good impermeability to gases and vapours (Abusleme and Manzoni, 2004). The main precursor for PCTFE production is chlorotrifluoroethene. Birnbaum et al., 1968 studied the toxicity of the pyrolysis of PCTFE and found it to increase rapidly with rising temperature. The thermal degradation of PCTFE and copolymers of it were studied by Zulfiqar et al. (1994) who found the monomer (i.e. chlorotrifluoroethene) to be the major product and amongst others chloropentafluoropropene in traces. Long et al. (1984) carried out infrared multiphoton dissociation experiments and found the toxic substances COF_2, COFCl, and CF_2ClCOF to be the exclusive products in the presence of oxygen. We checked the MS scan chromatogram of the plume sample but could not detect any of these product gases. The microbial biodegradation of $CF_2ClCFCl_2$ (CFC-113) and

$CHClFCClF_2$ (HCFC-123a) are also possible sources of chlorotrifluoroethene. A nice overview on that topic was given by Field and Sierra-Alvarez in 2004. But as 3-chloropentafluoropropene and dichlorohexafluorobutenes are also used for the production of copolymers (e.g. Robb et al., 1962; Lo et al., 1959) our suggestion is, that the observed plume was generated by the thermal degradation of a fluoropolymer blend.

4 Conclusions

We have shown that chlorotrifluoroethene, 3-chloropentafluoropropene and 4,4-dichlorohexafluoro-1-butene are present in the atmosphere. The substances were identified through their mass spectra and their retention times are in agreement with the expectation based on the boiling point. We have also found other substances which we believe to be chlorofluoroalkenes but were not able to identify them up to now. The identified CFCs showed high mixing ratios in the lower ppb range in a plume but the substances were also observed to be present in background ambient air with mixing ratios in the lower ppt range. These CFCs are not listed in the Scientific Assessment of Ozone Depletion 2006 of the World Meteorological Organisation/United Nations Environment Programme (WMO/UNEP) (see Tables 1–4 of Clerbaux and Cunnold, 2007) or the Montreal Protocol and its subsequent amendments. But as these substances are most probable of anthropogenic origin it is important to find out more about their sinks and sources. The newly observed substances are expected to be short-lived. However, if emitted in the tropics they could reach the stratosphere and have an impact on ozone depletion. Furthermore all known CFCs are strong greenhouse gases. Thus we suggest to establish continuous measurements of these substances and to investigate their atmospheric lifetimes in order to assess their possible influence on the global background atmosphere. Considering human health it is also important to find out if plumes containing high amounts of the CFCs can occur again – outdoor as well as indoor.

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Table 1. Wind data and mixing ratio estimates of the novel detected CFCs for different air samples taken at the Taunus Observatory.

	Wind Speed	Wind	Estimated mixing ratio range (ppt)		
Date 2007	(1 h mean, m/s)	Direction	C_2F_3Cl	C_3F_5Cl	$C_4F_6Cl_2$
2 October	1	NW	5000–29 000	3000–14 000	3000–15 000
6 November	6	NW	1.7–9.1	0.6–3.0	0.4–2.3
21 November	4	S	0.9–4.5	0.3–1.5	0.2–1.1
5 December	5	SW	1.3–6.9	1.1–5.8	0.4–2.3
12 December*	~10	NE	0.3–1.7	0.2–1.1	0.2–1.0
21 December	5	SE	0.4–2.2	0.3–1.8	0.3–1.4

* sample taken at the Jungfraujoch High Altitude Research Station. (Switzerland).

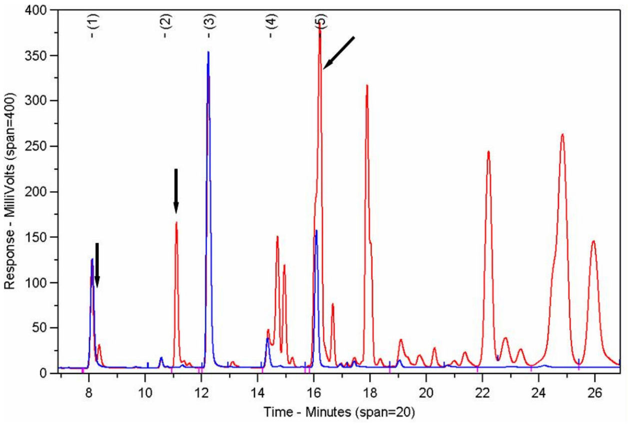

Fig. 1. Comparison of the chromatograms from two air samples taken at the Taunus Observatory operated by the University of Frankfurt. Trace gases were concentrated cryogenically from 1 l of air and detected using an ECD. The blue line represents "normal" air while the red line is the plume sample taken on the 2 October 2007 which showed a number of unidentified large signals. The known large peaks are CF_2Cl_2 [CFC-12, (1)], CF_2ClBr/CF_2ClCF_2Cl [Halon-1211/CFC-114, coeluting, (2)], $CFCl_3$ [CFC-11, (3)], $CF_2ClCFCl_2$ [CFC-113, (4)] and CCl_4 (5). Three of the unknown substances could be identified by now and are labelled with black arrows: trifluorochloroethene at 8.4 min, 3-chloropentafluoropropene at 11.1 min and 4,4-dichlorohexafluoro-1-butene at 16.2 min.

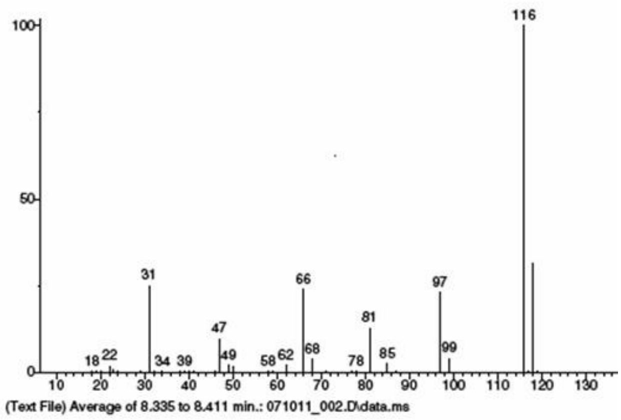

Fig. 2. The mass spectrum belongs to a chromatogram of an air sample taken at the Taunus Observatory near Frankfurt. The background spectrum was subtracted in order to remove peaks originating from air entering the system through small leaks. Trace gases were concentrated cryogenically from 1 l of air and measured by means of GC-MS (EI-Scan mode).The averaged spectrum at about 8.4 min retention time belongs to a substance eluting near CF_2Cl_2 (CFC-12) and gave an excellent match with that of C_2F_3Cl as listed in the NIST mass spectral library. Expected relative abundances for C_2F_3Cl were 100% for mass/charge ratio (m/z) 116, 87% for m/z 31, 38% for m/z 66, 33% for m/z 85, 33 % for m/z 118, 31% for m/z 97, 26% for m/z 47, 17% for m/z 81, 13% for m/z 68 and 11% for m/z 87.