Atmospheric Environment 112 (2015) 196–207

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

European emissions of HCFC-22 based on eleven years of high frequency atmospheric measurements and a Bayesian inversion method

F. Graziosi [a, b], J. Arduini [a, c], F. Furlani [a, b], U. Giostra [a, b], L.J.M. Kuijpers [d], S.A. Montzka [e], B.R. Miller [e, f], S.J. O'Doherty [g], A. Stohl [h], P. Bonasoni [c], M. Maione [a, b, c, *]

[a] Department of Basic Science and Foundations, University of Urbino, Urbino, Italy
[b] CINFAI (National Inter-University Consortium for Physics of the Atmosphere and Hydrosphere, Tolentino), Italy
[c] Institute of Atmospheric Sciences and Climate, National Research Council, Bologna, Italy
[d] Technical University Eindhoven, The Netherlands
[e] Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO, USA
[f] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
[g] School of Chemistry, University of Bristol, Bristol, UK
[h] NILU – Norwegian Institute for Air Research, Kjeller, Norway

HIGHLIGHTS

- We found a reduction in HCFC-22 global atmospheric increasing trends.
- European emissions of HCFC-22 decreased significantly in the last decade.
- The efficacy of inverse modelling as an emission inventories verification tool is shown.
- European emissions of HCFC-22 will approach zero starting from 2025.

ARTICLE INFO

Article history:
Received 30 October 2014
Received in revised form
13 April 2015
Accepted 16 April 2015
Available online 18 April 2015

Keywords:
Hydrochlorofluorocarbons
Montreal Protocol
Stratospheric ozone protection
High frequency observations
Inverse modelling
Emission estimates

ABSTRACT

HCFC-22 ($CHClF_2$), a stratospheric ozone depleting substance and a powerful greenhouse gas, is the third most abundant anthropogenic halocarbon in the atmosphere. Primarily used in refrigeration and air conditioning systems, its global production and consumption have increased during the last 60 years, with the global increases in the last decade mainly attributable to developing countries. In 2007, an adjustment to the Montreal Protocol for Substances that Deplete the Ozone Layer called for an accelerated phase out of HCFCs, implying a 75% reduction (base year 1989) of HCFC production and consumption by 2010 in developed countries against the previous 65% reduction. In Europe HCFC-22 is continuously monitored at the two sites Mace Head (Ireland) and Monte Cimone (Italy). Combining atmospheric observations with a Bayesian inversion technique, we estimated fluxes of HCFC-22 from Europe and from eight macro-areas within it, over an 11-year period from January 2002 to December 2012, during which the accelerated restrictions on HCFCs production and consumption have entered into force. According to our study, the maximum emissions over the entire domain was in 2003 (38.2 ± 4.7 Gg yr^{-1}), and the minimum in 2012 (12.1 ± 2.0 Gg yr^{-1}); emissions continuously decreased between these years, except for secondary maxima in the 2008 and 2010. Despite such a decrease in regional emissions, background values of HCFC-22 measured at the two European stations over 2002–2012 are still increasing as a consequence of global emissions, in part from developing countries, with an average trend of ca 7.0 ppt yr^{-1}. However, the observations at the two European stations show also that since 2008 a decrease in the global growth rate has occurred. In general, our European emission estimates are in good agreement with those reported by previous studies that used different techniques. Since the currently dominant emission source of HCFC-22 is from banks, we assess the banks' size and their contribution to the total European emissions up to 2030, and we project a fast decrease approaching negligible emissions in the last five years of the considered period. Finally, inversions

* Corresponding author. Department of Basic Sciences and Foundations, University of Urbino, Piazza Rinascimento 6, 61029 Urbino, Italy.
E-mail address: michela.maione@uniurb.it (M. Maione).

http://dx.doi.org/10.1016/j.atmosenv.2015.04.042

conducted over three month periods showed evidence for a seasonal cycle in emissions in regions in the Mediterranean basin but not outside it. Emissions derived from regions in the Mediterranean basin were ca. 25% higher in warmer months than in colder months.

1. Introduction

HCFC-22 ($CHClF_2$) is a man-made stratospheric ozone depleting substance with an ozone depletion potential (ODP) of 0.04 (Daniel et al., 2011) and a powerful greenhouse gas with a Global Warming Potential (GWP) over 100 yr of 1760 (Myhre et al., 2013). Its relatively short lifetime of ca. 11.9 yr (SPARC, 2013) is mainly due to the reaction with OH radical. HCFC-22 is used primarily in refrigeration and air conditioning systems as the working fluid. Releases into the atmosphere occur partly when these systems are first filled, but mostly during maintenance, or as the result of accidental damage or when the equipment is finally removed from service, unless provisions are made to capture and destroy the material still in equipment (McCulloch et al., 2003). It is also used in foam blowing and as feedstock for the manufacture of fluoropolymers, but in this last use HCFC-22 is mostly destroyed during the process.

HCFC-22 was firstly introduced in the 1950s but its production and consumption have increased over time as it has been used as an interim replacement for several chlorofluorocarbons (CFCs), making it the third most abundant anthropogenic halocarbon, after CFC-12 and CFC-11, with a current atmospheric mixing ratio of about 220 ppt. A substantial growth of HCFC-22 global mixing ratio has been reported by O'Doherty et al. (2004) and Montzka et al. (2009), based on long term measurements conducted at remote sites across the globe in the frame of the AGAGE (Advanced Global Atmospheric Gases Experiment) and NOAA/ESRL (National Oceanic Atmospheric Administration/Earth System Research Laboratory) programmes, respectively. The acceleration in the growth rate observed in the last decade in the global atmosphere (Montzka et al., 2009) is consistent with the UNEP (United Nations Environmental Programme) data on production and consumption of the HCFCs. Such data also indicate that by 2004 the HCFCs production and consumption in developed countries exceeded the values reported from developed countries (UNEP, 2013). This reflects provisions within the Montreal Protocol for Substances that Deplete the Ozone Layer reported in Table 1, calling for an HCFCs phase-out with different schedules in Article 5 (A-5; or developing) countries and non A-5 (developed) countries (UNEP, 2009). In the European Union, the phase-out of HCFCs is covered by the European Regulation (EC) No 2037/2000 on substances that deplete the ozone layer that, among other things, declared illegal the use of virgin HCFCs to service refrigeration and air conditioning (RAC) equipment as of 1st January 2010.

Estimating emissions of HCFC-22 from atmospheric observations is important in order to ascertain the effectiveness of the Montreal Protocol in the protection of the ozone layer as well as of the climate (Velders et al., 2007). HCFC-22 is used in refrigerators and air conditioners (AC) and also as blowing agent. Therefore it released into the atmosphere over years to decades after production. The amount of HFCF-22 in equipment and foam represents a bank of produced but not yet emitted chemical. Currently, the dominant emission for HCFC-22 is from these banks (Montzka et al., 2011). The primary HCFC-22 banks are in existing refrigeration and air conditioning (AC) applications, from which it is released on a timescale of years to more than a decade (medium timescale). However, HCFC-22 has been also used for open-cell foam blowing having a short banking time (<1 years) and for closed-cell foam blowing, implying a long banking time (up to 20 years) (Midgley and Fisher, 1993; Velders et al., 2014). Relating emissions to the banks of non-released material is crucial for predicting future trends in stratospheric chlorine. In addition, reliable estimates of future trends imply a good understanding of production magnitudes, particularly from the past, in order to enable an accurate estimate of the size of the bank.

The main source of information on the production and consumption of HCFC-22 is from UNEP (United Nation Environmental Programme, Ozone Secretariat http://ozone.unep.org/new_site/en/ozone_data_tools_access.php) that makes available the aggregated HCFCs consumption and production data, expressed in ODP tons. In the UNEP database, data pertinent to the European Union Member States (EUMSs) are given in a grouped form.

The AFEAS (Alternative Fluorocarbons Environmental Acceptability Study, http://www.afeas.org/data.php) provides production and sales magnitudes of HCFC-22, expressed in metric tons. The sales data are split into three regions (Northern Hemisphere 0°–30° degrees north; 30°–90° degrees north; and Southern Hemisphere 0–90° degrees south) and into three categories corresponding to end uses with short, medium and long time scales ("banking time") before the substance is emitted. Several studies (Midgley and Fisher, 1993; Fisher and Midgley 1993, McCulloch

Table 1
HCFCs phase out schedule as decided during the 19th Meeting of the Parties to the Montreal Protocol, Montreal, Canada, 2007.

Non A-5 consumption		A-5 consumption		Non A-5 production		A-5 production	
Base level: 1989[a]		Base level: Average 2009–10		Base level: 1989[b]		Base level: Average 2009–10	
Freeze: 1996		Freeze: Jan 2013		Freeze: Jan 2004		Freeze: Jan 2013	
% reduction	Year	% reduction	Year	% reduction	Year	% reduction	Year
35	Jan 2004	10	Jan 2015	75	Jan 2010	10	Jan 2015
75	Jan 2010	35	Jan 2020			35	Jan 2020
90	Jan 2015	67.5	Jan 2025	90	Jan 2015	67.5	Jan 2025
99.5	Jan 2020[c]	97.5	Jan 2030[c]	99.5	Jan 2020[c]	97.5	Jan 2030[c]
100	Jan 2030	100	Jan 2040	100	Jan 2030	100	Jan 2040

[a] Average HCFC consumption +2.8% of 1989 CFC consumption.
[b] Average HCFC production +2.8% of 1989 CFC production.
[c] Thereafter, consumption restricted to the servicing of refrigeration and air conditioning equipment existing at that date.