SCIENCE OF THE TOTAL ENVIRONMENT 391 (2008) 224–231

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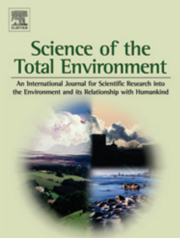

Observations of long-lived anthropogenic halocarbons at the high-Alpine site of Jungfraujoch (Switzerland) for assessment of trends and European sources

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ARTICLE INFO

Available online 26 November 2007

Keywords:
CFCs
HFCs
HCFCs
Emissions
GCMS
Montreal Protocol
Kyoto Protocol

ABSTRACT

Anthropogenic halocarbons, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), bromocarbons (halons) and long-lived chlorinated solvents have been measured continuously at the high-Alpine site of Jungfraujoch (Switzerland) since January 2000. Chloro- and bromo-containing halocarbons are responsible for the stratospheric ozone depletion and will be globally banned from usage within the next years. With the exception of the stable CFC-12 (CF_2Cl_2), all major CFCs and chlorinated solvents show a negative trend in recent years in their background concentrations at Jungfraujoch. HCFCs, as their first-generation substitute, are still increasing with a few percent per year. However, the frequency and the strength of HCFCs pollution events, which are caused by regional European emissions, are already declining. This can be seen as a sign of the impending ban of these gases within the next years in Europe. On the other hand, HFCs as the second-generation substitutes, are increasing with relative rates of at least 10% per year (e.g. almost 5 ppt per year for HFC-134a). An allocation of European sources was attempted by combining measured concentrations with trajectories of air masses reaching the Jungfraujoch during pollution events. Potential source regions could be detected in Italy, France, Spain and Germany.

1. Introduction

Anthropogenic halocarbons include important groups of industrially produced substances such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), bromocarbons (halons) and long-lived chlorocarbons (i.e. CCl_4 and CH_3CCl_3). In the last decades halocarbons have been used in large quantities for many applications such as foam blowing, refrigeration, industrial solvents and dry cleaning. Some of them exhibit a strong radiative forcing and have a share of 14% to the anthropogenic greenhouse effect (IPCC, 2001). In addition to their contribution to global warming, halocarbons containing chlorine and bromine lead to the depletion of stratospheric ozone (WMO, 2007). Therefore, their usage has been regulated under the Montreal Protocol and subsequent amendments, which will lead to the phase-out of their emissions. Thus, besides the reduction of the atmospheric chlorine content the Montreal Protocol also succeeded in alleviating global warming (Steinbacher et al., 2008-this issue). Hydrofluorocarbons (HFCs) are used as substitutes of the phased-out halocarbons, as they do not deplete the stratospheric ozone. They are part of the Kyoto Protocol to the

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doi:10.1016/j.scitotenv.2007.10.022

United Nations Framework Convention on Climate Change, which aims at reducing the world-wide emissions of anthropogenic greenhouse gases.

In order to follow the development of the atmospheric abundance of the halocarbons and to check for compliance with international treaties it is useful to analyse long-term observations (Montzka et al., 1999; Prinn et al., 2000; Montzka et al., 2003). The trends in the background concentrations can be used to derive global emissions of individual halocarbons (Clerbaux and Cunnold, 2007) and the peak values can be analysed for regional sources (Palmer et al., 2003; Hurst et al., 2004; Dunse et al., 2005; Li et al., 2005; Yokouchi et al., 2005; Hurst et al., 2006).

At the high-Alpine site of Jungfraujoch (3580 m asl) *in-situ* measurements of halocarbons have been performed quasi-continuously by gas chromatography-mass spectrometry (GCMS) since the beginning of the year 2000 (Reimann et al., 2004). These continuous measurements are a part of the European SOGE network (System for Observation of Halogenated Greenhouse Gases in Europe). Within SOGE, fully intercalibrated *in-situ* data have been acquired since 2001 with an almost identical technique at the four European background stations Mace Head (Ireland), Ny-Ålesund (Spitsbergen), Jungfraujoch (Switzerland) and Monte Cimone (Italy).

Ground-based infrared solar absorption spectroscopy has been used for measuring column abundances of atmospheric trace gases at Jungfraujoch as early as 1950–51. The quick accumulation of the anthropogenic halocarbons in the atmosphere during the second half of the last century has been recorded by the Fourier Transform Infrared Spectroscopy (FTIR) measurements at Jungfraujoch (Mahieu et al., 1997; Rinsland et al., 2000), which is part of the Network for Detection of Atmospheric Composition Change (NDACC, http://www.ndacc.org).

The goal of this publication is the analysis of the long-term *in-situ* measurements of halocarbons at Jungfraujoch to derive trends and identify European emission regions. The *in-situ* time series are compared with those from other world-wide networks (AGAGE and NOAA) and with those from the column abundances of the FTIR technique at Jungfraujoch.

2. Methods

2.1. *Analytical technique*

Every 4 h, 18 individual long-lived halocarbons are automatically analyzed by gas chromatography-mass spectrometry (GCMS, Agilent, 5793N) at Jungfraujoch (Reimann et al., 2004). Substances from 2 L of air are preconcentrated on a cooled micro trap (−50 °C), filled with 3 different adsorbents (Simmonds et al., 1995). After desorption by fast inductive heating to 235 °C, halocarbons are chromatographically separated by a 120 m × 0.32 mm CP-SIL 5CB capillary column with a film thickness of 5 μm (Varian). The temperature program starts at 37 °C and reaches 180 °C within 51 min. The individual compounds are quantified by single ion mass spectrometry (SIM) of selected characteristic ions and their individual chromatographic retention times.

Calibration is performed by bracketing each ambient air measurement with real-air standards within the concentration range of background air samples. The scale of the calibration (SIO 2005) is provided by the Scripps Institution of Oceanography (La Jolla, USA).

The vertical column abundances of the most important anthropogenic halocarbons, i.e. CFC-11, CFC-12 and HCFC-22 (expressed as the total number of molecules of a specific gas contained in a vertical column of 1 cm^2 extending through the entire atmosphere above the station) are retrieved routinely from the analysis of observed absorption features specific to each target gas (e.g. Rinsland et al., 1998). This analysis implies calculating synthetic spectra and fitting them to the observed ones by adjusting the amounts of the gases in the atmosphere. The uncertainty in the retrieved vertical column abundances depends essentially on the quality of the spectroscopic absorption parameters and the *a priori* concentration profiles adopted in the synthetic spectra calculations of the target and interfering gases (e.g. Rinsland et al., 2005; Zander et al., 2005).

2.2. *Statistical trajectory model for European source allocation*

3-dimensional (diabatic) backward trajectories have been calculated six times a day for the Jungfraujoch by the Swiss Meteorological Institute (MeteoSwiss) using the 3-dimensional TRAJEC model of the German Weather Service (DWD) (Fay et al., 1995). Wind fields have been provided by the alpine Local Model (aLMo, horizontal grid spacing of 7 km) and the arrival point of the trajectories was positioned 100 m above the model surface height. The arrival height of the trajectories is the most critical point arising from the usage of trajectories at a high mountain sides. Although the used model has a grid width of only 7 km × 7 km the average model surface height within the grid box is considerably lower than the actual height of Jungfraujoch. This is taken care of by using an arrival height of 100 m above the models surface, which has been evaluated to provide the best agreement of polluted events and trajectories having previously had contact with the European boundary layer. Furthermore, not only the trajectory arriving at the accurate location was used but also 4 trajectories being displaced by ±7 km in latitude and ±7 km in longitude, respectively.

For the assessment of European sources the trajectories were combined with measured concentrations at the Jungfraujoch, using the method of Seibert et al. (1994) and which has been described in detail by Reimann et al. (2004). In short, the domain of the calculated trajectories is separated into 0.22° × 0.22° grids. For these grid cells the mean concentrations are calculated related to measured concentrations during arrival of the trajectories at Jungfraujoch. Trajectories were only taken into account when they were over land and within the boundary layer. The boundary layer height was characterized by a pressure difference of not more than 120 hPa (in winter) and 200 hPa (in summer).

The allocation of the emissions is associated with potential errors because measured concentrations are distributed equally to all grid cells passed by the respective trajectory. Therefore, the diffusion of the pollutants during transport is taken into account only in a limited way. This short-coming could be avoided by the usage of a more sophisticated Lagrangian particle dispersion model (e.g. by Manning et al., 2003)