

Atmospheric measurement and emission estimates of CFC-114 and CFC-114a

N. Mohd Hanif (1), C. E. Reeves (1), J. C. Laube (1), P. Martinerie (2), D.E. Oram (1,3), E. Gallacher (1), P. J. Fraser (4), J. Schwander (5), E. Witrant (6), J.-L Wang (7), C.-F Ou-Yang (8), L. J. Gooch (1), and W. T. Sturges (1)

(1) School of Environmental Sciences, University of East Anglia, Norwich, United Kingdom (N.Mohd-Hanif@uea.ac.uk), (2) CNRS/Univ. Grenoble Alpes, 38041, Grenoble, France, (3) National Centre for Atmospheric Science, School of Environmental Sciences, University of East Anglia, Norwich, United Kingdom, (4) Centre for Australian Weather and Climate Research, Oceans and Atmosphere Flagship, Commonwealth Scientific and Industrial Research Organisation, Aspendale, Australia, (5) Physics Institute, University of Berne, Bern, Switzerland, (6) Grenoble Image Parole Signal Automatique, Université Joseph Fourier/CNRS, Grenoble, France, (7) Department of Chemistry, National Central University, Taiwan, (8) Department of Atmospheric Sciences, National Central University, Taiwan

The prominent impact of chlorofluorocarbons (CFCs) on the Earth's climate through stratospheric ozone depletion and the greenhouse effect are well known and have attracted great attention in the past decades. The recent atmospheric concentrations, distributions and trends of CFC-114 have however received little attention in the peer-reviewed literature. Of particular interest here is the differentiation between CFC-114 and its isomeric form CFC-114a, as atmospheric measurements have been assumed to represent the total amount of both isomers.

This study has quantified CFC-114 and CFC-114a individually in unpolluted samples collected at Cape Grim, Australia and their changing concentrations from 1978 to 2014 have been determined. For CFC-114, the mixing ratio has doubled from 7.9 to 14.8 ppt and the mixing ratio of CFC-114a trebled from 0.35 to 1.03 ppt. Mixing ratios of both isomers were no longer increasing significantly at the end of that record. However we find that the fraction of CFC-114a mixing ratio relative to that of CFC-114 increased from 4.3% to 6.9% over the 37-year period. This is not in agreement with the current assumption that both isomers have been largely co-emitted. Complementary ground-based observations from air samples collected in Taiwan support this hypothesis with the latter pointing toward a persisting source of CFC-114a in East Asia. Time series of atmospheric derived from air extracted from deep polar firn suggest mixing ratios, and thus emissions, of both CFC-114 and CFC-114a were comparably small in 1960.

We also present top-down global annual emission estimates of CFC-114 and CFC-114a derived from these measurements using a two-dimensional atmospheric chemistry-transport model. In general, the emissions for both compounds grew from around 1960 into the 1980s, followed by a substantial reduction from the late 1980s onwards, which is consistent to the reduction of emission in response to the Montreal Protocol. However, we find that substantial emissions of both isomers remain in 2014. Moreover changes to the ratio of emissions of the two isomers since the 1990s confirm that the sources of the two gases are partly unrelated. In addition, our model-derived annual emissions were also compared with published emission inventories where available.

Finally we assess policy-relevant quantities such as atmospheric lifetimes, Ozone Depletion Potentials (ODPs), and Equivalent Effective Stratospheric Chlorine (EESC) from aircraft-based observations of the two isomers in the stratosphere.