

## Tropospheric Observations of CFC-114 and CFC-114a

J.C. Laube<sup>1</sup>, N.M. Hanif<sup>1</sup>, P. Martinerie<sup>2</sup>, E. Gallacher<sup>1</sup>, P.J. Fraser<sup>3</sup>, C.A.M. Brenninkmeijer<sup>4</sup>, J. Schwander<sup>5</sup>, E. Witrant<sup>6</sup>, J.-L. Wang<sup>7</sup>, C.-F. Ou-Yang<sup>7</sup>, L.J. Gooch<sup>1</sup>, C.E. Reeves<sup>1</sup>, W.T. Sturges<sup>1</sup> and D.E. Oram<sup>1</sup>

<sup>1</sup>University of East Anglia, School of Environmental Sciences, Norwich NR4 7TJ, United Kingdom; +44 16 0359-3896, E-mail: j.laube@uea.ac.uk

<sup>2</sup>UJF-Grenoble / CNRS, Laboratoire de Glaciologie et Géophysique de l'Environnement, Grenoble, France

<sup>3</sup>Commonwealth Scientific and Industrial Research Organisation (CSIRO), Oceans and Atmosphere, Aspendale, VIC 3195, Australia

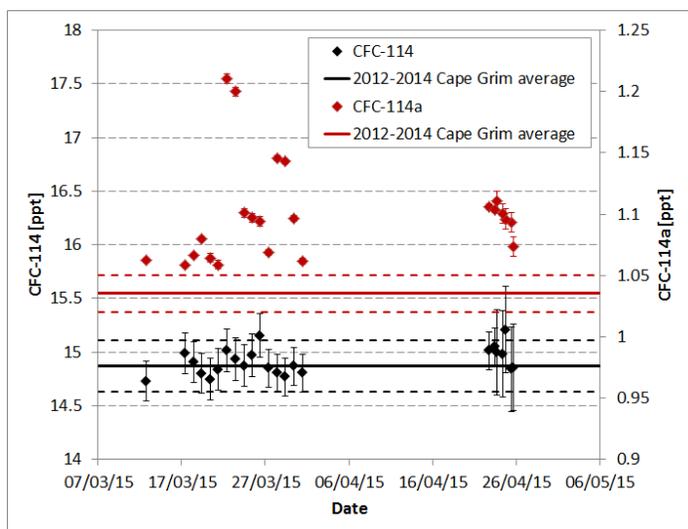
<sup>4</sup>Air Chemistry Division, Max Planck Institute for Chemistry, Jena, Germany

<sup>5</sup>University of Berne, Physics Institute, Bern CH-3012, Switzerland

<sup>6</sup>UJF-Grenoble / CNRS, Grenoble Image Parole Signal Automatique, Grenoble, France

<sup>7</sup>National Central University, Department of Chemistry, Taiwan

Chlorofluorocarbons (CFCs) are well known for their involvement in depleting stratospheric ozone and also their direct role in climate change as highly efficient greenhouse gases. Within the family of CFCs, one compound has received little attention in the literature, namely CFC-114 ( $C_2Cl_2F_4$ ). Of particular interest here is the differentiation between CFC-114 ( $CF_2ClCF_2Cl$ ) and its isomeric form CFC-114a ( $CF_3CFCl_2$ ) as atmospheric measurements so far have been assumed to represent the sum of both isomers. This study has quantified CFC-114 and CFC-114a 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, which agrees with aircraft observations of insignificant interhemispheric mixing ratio gradients. 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 extracted from deep polar firn as well as from air samples collected in Taiwan support this hypothesis with the latter pointing toward a persisting source of CFC-114a in East Asia. We also present top-down global annual emission estimates of CFC-114 and CFC-114a derived from these measurements and a two-dimensional atmospheric chemistry-transport model. In general, the emissions for both compounds grew steadily during 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 infer that 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.



**Figure 1.** Mixing ratios of CFC-114 and CFC-114a from samples collected during a ground-based campaign near Hengchun, Taiwan in early 2015 (diamonds) in comparison to mixing ratios observed at Cape Grim averaged from 2012 to 2014 (lines).