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Tropospheric chlorine isotope measurements in CFC-11, CFC-12 and CFC-113

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In 2010, we reported the first measurements of chlorine isotope fractionation in stratospheric dichlorodifluoromethane (CF_2Cl_2, CFC-12) (Laube et al., Science 329:1167, 2010). We found an increase in the isotope delta, $\delta(^{37}\mathrm{Cl})$, with altitude and a tight correlation between $\ln[1 + \delta(^{37}\mathrm{Cl})]$ and ln(mixing ratio). The derived apparent isotope fractionation was $\epsilon_{\mathrm{app}} = (-12 \pm 2)$ ‰.

The stratospheric isotopic fractionation should lead to a continuous increase of the tropospheric chlorine isotope delta while CFC-12 is still emitted into the atmosphere. Provided the source signature has not changed, we predict a 2.5 to 3 ‰ increase since when CFC emissions started in the 1930s until 2010, with the strongest increase in recent years (about 1 ‰ per decade since the mid-1990s).

We have now measured the chlorine isotope delta of CFC-12 as well as CFC-11 (trichlorofluoromethane, $CFCl_3$) and CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane, $C_2F_3Cl_3$) in the Cape Grim Air Archive (1978 to 2010) and Arctic (NEEM, Greenland) and Antarctic firn samples (Fletcher, West Antarctica). The deepest firn samples include a significant proportion of older air from before 1978. The repeatability for individual samples was ± 2.6 ‰ for CFC-12 and ± 2.7 ‰ for CFC-11 and ± 3.7 ‰ for CFC-113. The results show no significant trends in $\delta(^{37}\mathrm{Cl})$ over the whole time period; however, there is a small positive trend for the latter period of the samples of (0.3 ± 0.1) ‰ per decade for CFC-12 since 1997, which explains at third of the predicted trend. The discrepancy between observed and predicted trends may be due to offsetting changes in the source isotope signature: If the there was decrease in the isotope delta of the emissions over time, this would reduce the predicted increase caused by downward transport of ^{37}Cl-enriched stratospheric air.