



Longterm and seasonal variation in the isotopic composition of tropospheric CFC-12 and CFC-11

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Strong carbon isotope fractionation effects were recently discovered for the degradation of chlorofluorocarbons (CFC's) in landfills and for their photolytical destruction in the troposphere. Both results suggest an enrichment in ^{13}C in the residual fraction of these compounds over time. Thus the isotopic composition of these CFC's may improve our understanding of their fate and reduce uncertainties in current source estimates. Here we report carbon isotope ratios for CFC-11 (CFC13) and CFC-12 (CF2Cl2) in background air. The samples were taken during five sampling campaigns between September 2010 and July 2012 with the sample locations spanning from 10°N to 60°N .

For CFC-12 our data indicate a long term ^{13}C enrichment of $0.5\text{\textperthousand}$ per year corroborating very recent results from firn air measurements. The long term enrichment is superimposed by a seasonal cycle with an amplitude of $1.2\text{\textperthousand}$ with the most enriched $\delta^{13}\text{C}$ values occurring in June /July. We hypothesize the long term trend and the seasonal cycle to be driven by the stratosphere troposphere exchange (STE) of CFC-12. The mean $\delta^{13}\text{C}$ for CFC-11 was $-28.4 \pm 0.6\text{\textperthousand}$ ($n = 82$) without any significant spatial or temporal variation. The kinetic isotope effect for the photolytic degradation of CFC-11 in the stratosphere is substantially smaller as compared to that for CFC-12 resulting in a minor imprint of the STE on the isotopic composition of tropospheric CFC-11. Furthermore, in contrast to CFC-12, degradation of CFC-11 has been reported from a variety of oxygen deficient marine settings. This may result in small scale variations in the $\delta^{13}\text{C}$ of tropospheric CFC-11 superimposing any seasonal variability.