Determining the atmospheric mixing ratio of CFC-11 from firn air samples.

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The goal of this study is to characterize the most likely atmospheric mixing ratio of CFC-11 (CCl_3F) for the years between 1900 and 1940. We also wish to estimate the uncertainty in the value we determine. We choose this time interval because is it accessible with our firn air samples, and because it was only in 1940 that industrial activity began to measurably increase the atmospheric burden of CFC-11 (Gamlen *et al.*, 1986).

Our starting point is the set of air samples extracted from the firn at South Pole in January 1995. The collection and analyses of these samples is described by Battle *et al.* (1996) and Butler *et al.* (1999). Also described in these papers is the 1-dimensional forward model of diffusion in the firn that we use in this study.

To get an estimate of the CFC-11 ages of our deepest firn air samples, we use our firn model to assign CO_2-based ages. These ages are determined as follows: We use a known atmospheric history of CO_2 (Etheridge *et al.* 1996) as a boundary condition for the model. The model is run with the molecular diffusivity of CO_2 adjusted to the value appropriate for CFC-11. We then use the model output to determine the time in the forcing history that the CO_2 mixing ratio equaled the values predicted by the model at the depths we sampled. Based on this methodology, we conclude that our deepest 6 samples reflect the atmospheric mixing ratio of CFC-11 between the years 1900 and 1940. These dates are only approximate, since CFC-11 and CO_2 have different atmospheric growth histories, but they are close enough for the purpose of this work.

To quantify the uncertainties associated with both collection of firn air and analytical methods, we assume that the atmospheric mixing ratio of CFC-11 between 1900 and 1940 was constant. Thus, all the variation in the values of our 6 deepest samples must be a result of artifacts. The measured values of CFC-11, after correcting for gravitational enrichment using $\delta^{15}N$ of N_2 (Battle *et al.*, 1996) are given in Table 1, below. Based on these data, we conclude that the firn air samples have a mean value of 5.2 ± 3.1 ppt (all uncertainties quoted here are 1 σ).

Next, we assume that the anthropogenic atmospheric burden of CFC-11 was accurately predicted by the production/emission model of Gamlen *et al.* (1986). We add a pre-industrial background level of 5.0ppt to every annual value of the Gamlen scenario, and use this as the boundary condition for a forward model run referred to hereafter as "baseline". In this baseline run, the atmospheric mixing ratio between 1900 and 1940 is 5.0 ppt. We characterize the agreement between model predictions and our firn air measurements by calculating χ^2 for the 6 deep samples (using σ = 3.1 ppt). For this baseline model run, χ^2= 6.0 (by construction). We then varied the pre-industrial background level from 1.0 to 10.0 ppt in successive model runs, and found that χ^2 increased to 7.0 when the background level differed from the baseline value by ±1.4 ppt

(with 1 degree of freedom, a 1 σ excursion will lead to an increase of χ^2 by 1 above its minimum value).

Based on this exercise, we conclude that the atmospheric mixing ratio of CFC-11 in the years from 1900-1940 (approximately) was 5.2 ± 1.4 ppt.

We believe this estimate of the background mixing ratio is a conservative upper limit for two reasons.

First, the calculation is substantially influenced by the samples collected at 119.88 and 122.08 mbs (see Table 1). Based on values of other species measured in these flasks, we find equivocal evidence of contamination in these samples. If we were to discard them from our analysis, the central value would drop to 3.3 ppt with an error of less than 1.0 ppt.

Secondly, the simple method we have used for determining χ^2 ignores the fact that our measured values are not distributed normally, but instead are asymmetric (since mixing ratios cannot fall below zero). A more rigorous treatment of the errors is beyond the scope of this work, but would almost certainly reduce the central value significantly.

Table 1.

Collection depth (meters below surface)	Measured mixing ratio (ppt)	Gravitationally corrected mixing ratio (ppt)
116.06	4.65	4.35
117.06	4.11	3.83
118.95	2.48	2.32
119.88	11.11	10.41
121.32	2.89	2.72
122.08	7.91	7.33

Note that the "measured" mixing ratios (i.e. uncorrected for gravitational enrichment) are available as supplementary on-line material associated with the publication of Butler *et al.* (1999). They also are available at ftp://ftp.cmdl.noaa.gov/hats/firnair/.

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