RE-EVALUATION OF THE LIFETIMES OF THE MAJOR CFCS AND CH_3CCL_3 USING ATMOSPHERIC TRENDS

TWO-DIMENSIONAL MODEL

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1. Theoretical framework

The two-dimensional model of trace gas chemistry and transport used in this work is based on the original 9-box model of Cunnold et al. (1983), augmented with three extra stratospheric boxes in Cunnold et al. (1994). In the resulting 12-box model, the atmosphere is divided into four equal-mass latitudinal sections with divisions at 30N, 0N and 30S, and three vertical layers, divided at 500hPa and 200hPa (see Figure 1). The stratosphere is defined as the four boxes in the highest layer.

Cunnold et al. (1983) calculated constituent transport between the boxes by parameterizing bulk advection and eddy diffusion. Advection was calculated by considering the rate of trace gas movement across box intersections. Down-gradient diffusion was calculated by assuming that air was exchanged between neighboring boxes with a characteristic diffusion timescale. For both of these processes, timescales were specified in the troposphere in each season based on Newell et al. (1969). It was assumed that no advection occurred across the tropopause, and stratosphere-troposphere exchange was determined by a single mixing time-scale. This timescale was estimated as 4 years in Cunnold et al. (1983), but subsequently reduced to 3.5 years in Cunnold et al. (1994). Surface mole fractions were found to be relatively insensitive to the chosen mixing timescales between the four stratospheric boxes, so these parameters were arbitrarily set to 100 days (Cunnold et al., 1994). The *a priori* parameters used in the current model are summarized in Table 1.

In Cunnold et al. (1983, 1994) and many subsequent papers that used the 12-box model, the diffusion parameters given in Table 1 were subsequently adjusted to optimally match the observed gradients of CFC-11 at surface sites. Scaling parameters were estimated that multiplied the mid-latitude diffusion rates, stratosphere-troposphere exchange and cross-equatorial mixing. Some advection parameters were also adjusted non-optimally to match the observed gradients. In this paper, we adjust all of the 17 diffusion parameters for each month of the year in a multi-species inversion, using the original (non-optimized or adjusted) values given in Cunnold et al. (1983, 1994) as *a priori* constraints. Uncertainties were not provided for the Newell et al. (1969) timescales used, so we estimated *a priori* uncertainties on all parameters as the mean seasonal standard deviation of those parameters that have a seasonal cycle (36%). Advection timescales were not adjusted in the inversion since transport is dominated by eddy diffusion in the model (Cunnold et al., 1983).

Emissions to the model are specified in each month of the simulation for each of the surface boxes. Emissions are assumed to be instantaneously mixed throughout the lowest boxes.

There are three major loss processes in the model, an instantaneous loss rate in any box (parameterizing, for example, photolysis), reaction with a fixed OH field in the troposphere, and oceanic uptake. The instantaneous loss is specified as a time-scale in each box. In Figure 1, loss timescales are indicated in the stratosphere, parameterizing photochemical losses in the upper-most boxes. An OH field is specified in each of the tropospheric boxes, based on monthly averages from the 3-dimensional model output from Spivakovsky et al. (2000). This OH field can be adjusted in each box in the model. Temperatures are also specified in each tropospheric

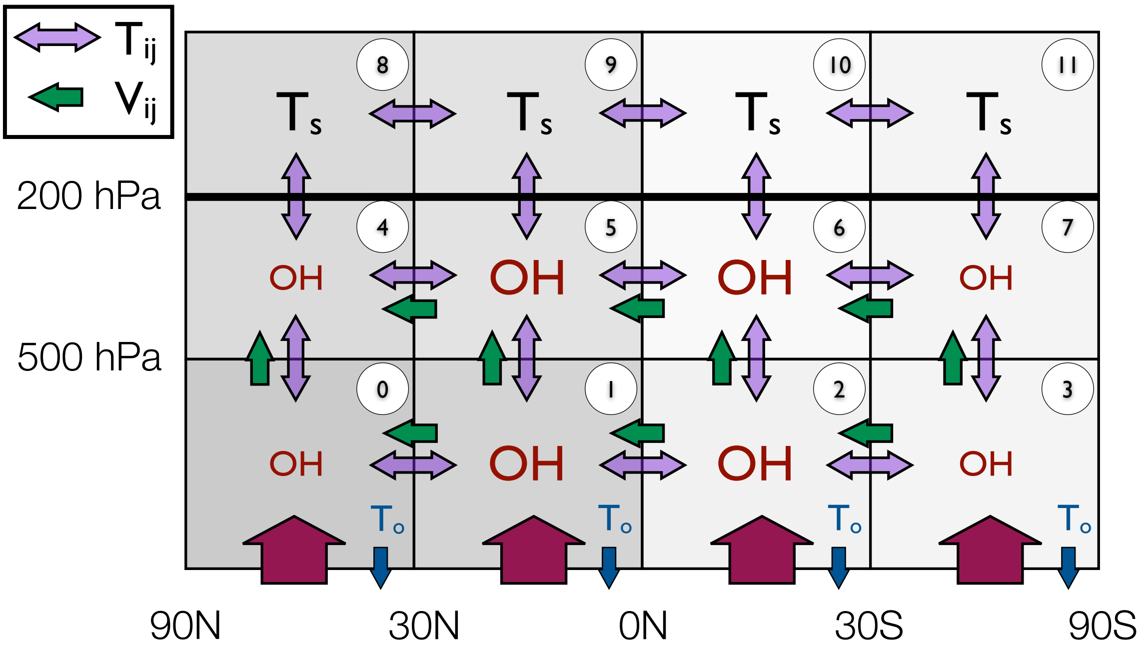

FIGURE 1. Two-dimensional model schematic. Eddy diffusion timescales between boxes i and j are given by T_{ij} and advection rates are given by V_{ij} and are enumerated in Table 1. Box indices are shown in circles. Instantaneous stratospheric lifetimes (T_s) are specified in the stratospheric boxes. Seasonally varying OH levels and temperatures are specified in each of the tropospheric boxes and OH reaction rates are input to the model to calculate trace gas loss through OH oxidation. Emissions are input to the lowest model levels, and oceanic/soil uptake is parameterized by the timescale T_o.

box during each month, based on the 1990 - 2010 average temperature from the NCEP/NCAR reanalysis (Kalnay et al., 1996). Temperature-dependent reaction rates are then input to the model. The final loss process parameterized in the model is uptake by the ocean and/or soils. This is again parameterized as a first-order loss timescale in the lowest boxes. *A priori* estimates of each loss parameter are given in Table 2 for the four species investigated here.

2. Optimized transport

Eddy diffusion parameters were optimised in each season of the simulation. The mean optimised values are shown in Table 2. The table shows that the optimised values are relatively similar to the prior for most parameters. Some of the largest changes to the prior values are found for the parameters that represent stratosphere-troposphere exchange. This may be expected for the gases investigated here, three of which are primarily destroyed in the stratosphere and whose trends are therefore sensitive to stratosphere-troposphere exchange. Future studies will use a combination of reactive and relatively inert tracers to further constrain these parameters. Further constraints would also be provided by simultaneous assimilation of surface and vertical-profile measurements.

TABLE 1. Box model advection and eddy diffusion parameters. Note that advection timescales are mass conserving when the mass of air passing between boxes is accounted for (Cunnold et al., 1983).

Parameter	Box I	Box J	Prior (days)				Optimized (days)			
			Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
Eddy diffusion (T_{ij}^{-1})	0	1	116	116	261	139	84	83	165	80
	1	2	495	712	363	712	244	568	187	560
	2	3	167	167	116	116	165	165	117	124
	4	5	29	35	85	52	22	26	51	40
	5	6	124	178	124	178	81	105	103	109
	6	7	52	42	29	42	60	40	31	43
	4	0	38	38	38	38	26	26	23	30
	5	1	38	38	38	38	45	39	31	38
	6	2	38	38	38	38	29	39	36	37
	7	3	38	38	38	38	31	36	37	37
	8	4	1260	1260	1260	1260	895	775	694	897
	9	5	1260	1260	1260	1260	1011	1123	1349	1198
	10	6	1260	1260	1260	1260	1645	1722	1806	1668
	11	7	1260	1260	1260	1260	1306	1688	1674	1398
	8	9	100	100	100	100	95	94	94	95
	9	10	100	100	100	100	95	95	97	96
	10	11	100	100	100	100	99	99	100	99
Advection (V_{ij})	0	1	-1506	581	1882	-442				
	1	2	-69	-376	50	126				
	2	3	1506	1075	753	1506				
	4	5	1506	-581	-1882	442				
	5	6	69	376	-50	-126				
	6	7	-1506	-1075	-753	-1506				
	4	0	-1506	581	1882	-442				
	5	1	-72	-228	52	98				
	6	2	65	279	-54	-137				
	7	3	-1506	-1075	-753	-1506				

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Table 2. Box model *a priori* loss parameters

Model parameters	CFC-11	CFC-12	CFC-113	CH_3CCl_3
Stratospheric loss frequency ($years^{-1}$)	0.135	0.054	0.065	0.159[1]
Ocean uptake loss frequency ($years^{-1}$)				0.023[2]
OH: Arrhenius A[3] (cm^3 $molecule^{-1}$ s^{-1})	1.0×10^{-12}	1.0×10^{-12}	1.0×10^{-30}	1.64×10^{-12}
OH: Arrhenius E/R[3] (K)	3700	3600	1600	1520

[1] Based on stratospheric lifetime of Naik et al. (2000)
[2] Based on oceanic lifetime of Butler et al. (1991)
[3] Sander et al. (2011)

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