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

TWO-DIMENSIONAL MODEL

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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.

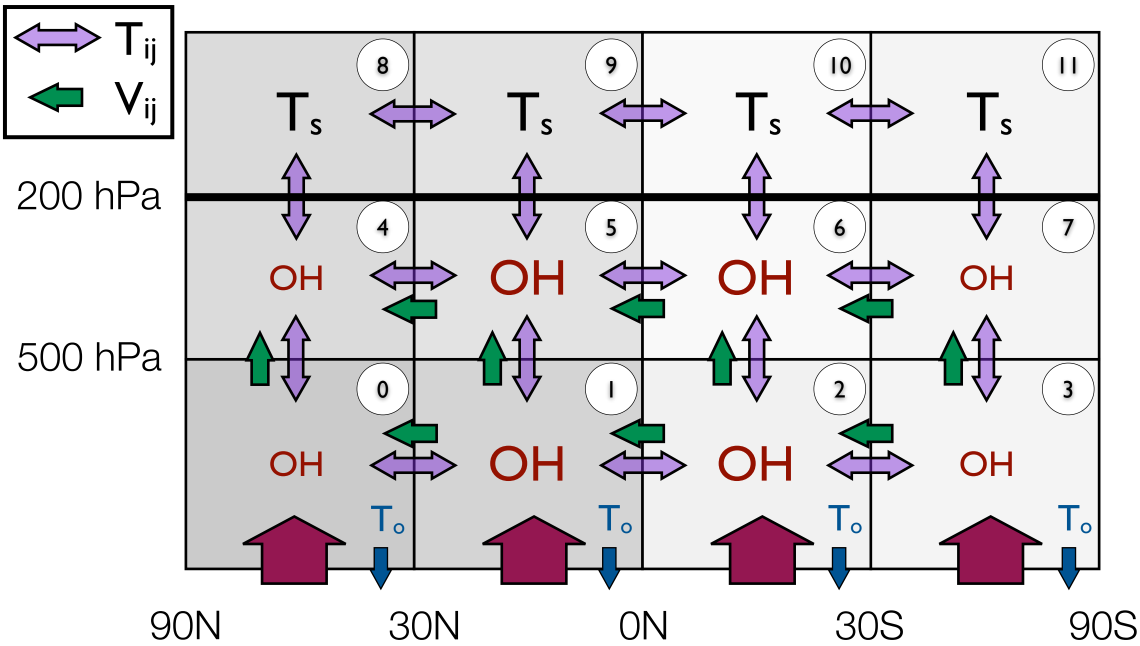

FIGURE 1. Two-dimensional model schematic. Eddy diffusion timescales between boxes i and j are given by T_{ij} and advection rates are given by V_{ij} and are enumerated in Table 1. Box indices are shown in circles. Instantaneous stratospheric lifetimes (T_s) are specified in the stratospheric boxes. 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 uptake is parameterized by the timescale T_o.

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 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. 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.

Table 1. Box model transport parameters

Parameter	Box i	Box j	Time scale (days) Winter	Spring	Summer	Fall
Eddy diffusion (T_{ij}^{-1})	0	1	116	116	261	139
	1	2	495	712	363	712
	2	3	167	167	116	116
	4	5	29	35	85	52
	5	6	124	178	124	178
	6	7	52	42	29	42
	4	0	38	38	38	38
	5	1	38	38	38	38
	6	2	38	38	38	38
	7	3	38	38	38	38
	8	4	1260	1260	1260	1260
	9	5	1260	1260	1260	1260
	10	6	1260	1260	1260	1260
	11	7	1260	1260	1260	1260
	8	9	100	100	100	100
	9	10	100	100	100	100
	10	11	100	100	100	100
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

Table 2. Box model *a priori* loss parameters

Model parameters	CFC-11	CFC-12	CFC-113	CH_3CCl_3
Stratospheric lifetime (years)	7.4	18.4	15.4	42.9[1]
Ocean uptake lifetime (years)				85[2]
OH: Arrhenius A[3] (cm^3 molecule^{-1} s^{-1})	1.00E-12	1.00E-12	1.00E-30	1.64E-12
OH: Arrhenius E/R[3] (K)	3700	3600	1600	1520

[1] Naik et al. [2000]
[2] Butler et al. [1991]
[3] Sander et al. [2011]

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