Using box models to quantify zonal distributions and surface emissions of halocarbons in the background atmosphere.

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The NOAA Measurement Network

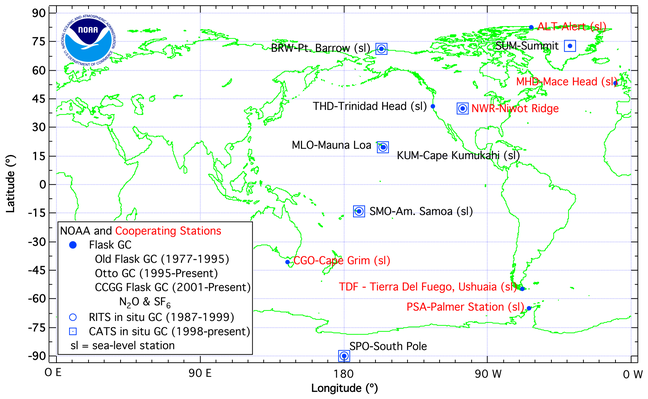

Figure 1 Map of Stations

1. Introduction: The Halocarbons and other Atmospheric Trace Species (HATS) of NOAA's Global Monitoring Division started measurements of the major chlorofluorocarbons and nitrous oxide in 1977 from flask samples collected at five remote sites around the world shown in **Figure 1**. Our program has expanded to measure over 40 compounds at twelve sites including in situ measurements at six sites. The Montreal Protocol for Substances that Deplete the Ozone Layer and its subsequent amendments has helped to decrease the concentrations of many of the ozone depleting compounds in the atmosphere. Our goal is to estimate global and zonal emissions and global lifetimes from our measurements of these trace gases and make these estimates available on our web site. Here, we present emissions for several long-lived, ozone depleting substances without tropospheric sinks that were estimated from two 2-D box models. The measurements of SF_6, N_2O, and four halocarbons regulated by the Montreal Protocol are shown in **Figure 2**. We use combined datasets (unless otherwise noted) available from http://www.esrl.noaa.gov/gmd/hats/combined/X.html, where X is the gas, e.g. SF6, CFC11, CCl4, etc.

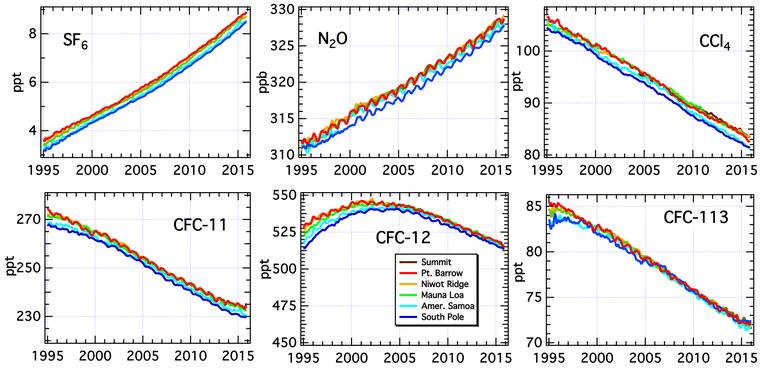

Figure 2 Concentrations of SF_6, N_2O, & Four Halocarbons

The Models

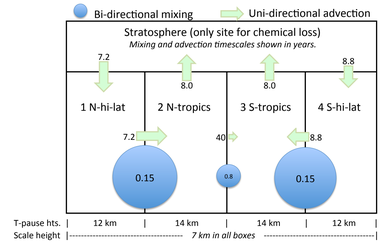

Figure 3 Diagram of the Harvard 5-box Model

2. 5-box Model (Harvard): This model consists of 4 equal area, semi-hemispheric, tropospheric boxes (N-hi-lat, 90-30° N; N-tropics, 0-30° N; S-tropics, 0-30° S; S-hi-lat, 30-90° S) and one stratospheric box shown in **Figure 3**. Uni-directional advection timescales are based on a 4 year stratospheric turnover time with troposphere-to-stratosphere flow divided equally between N and S tropics boxes. The stratosphere-to-troposphere return flow is unequally split at 55% N to 45% S in the high latitude boxes. Bi-directional mixing timescales were tuned with the advection scheme in place by minimizing the difference between concentrations computed from scaled (+10%), bottom-up, EDGAR emissions estimates for SF_6 and surface measurements of SF_6 from NOAA.

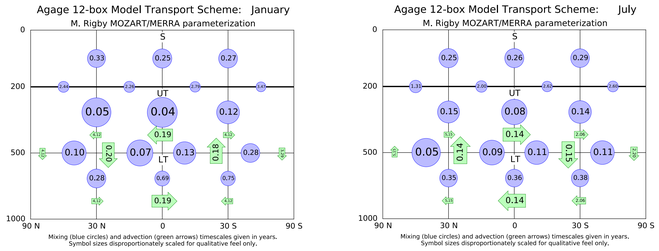

Figure 4 Diagram of AGAGE 12-box Model in January and July

3. 12-box Model (AGAGE): This model consists of 4 equal area, semi-hemispheric tropospheric surface boxes, 4 upper tropospheric boxes, and 4 stratospheric boxes (see original work, *Cunnold et al.*, 1983). Default transport parameters, tuned (by M. Rigby) in reference to the MOZART/MERRA 3D chemical transport model, were used with a Kalman filter inversion technique to model emissions that were simultaneously constrained by NOAA/ESRL/GMD atmospheric measurements and a set of "prior" emissions estimates. Mixing parameters vary on a monthly basis, while advection parameters vary seasonally. Examples are shown in **Figure 4** for January and July. Priors were either derived from AFEAS sales inventories and or taken from estimates published previously elsewhere (e.g.Scientific Assessment of Ozone Depeletion 2014). **Table 1** shows the global lifetime inputs for the 5-box model (SAOD 2014) and the stratospheric partial lifetime inputs for the 12-box model (*Rigby et. al.* 2013), as well as the global lifetime estimates from the 12-box model. Lifetimes for CCl_4 are based on WMO values, with recently revised numbers reflecting weaker ocean and soil losses shown in parentheses.

Table 1 Lifetimes of Gases

Long-lived Gas	Global Lifetime: 5-box Input	Stratospheric Partial Lifetime: 12-box Input	Global Lifetime: 12-box Output
N_2O	120 years	5.4 years	116 years
SF_6	3200	10^{12}	$> 10^{12}$
CFC-11	52	2.5	57
CFC-12	102	4.4	95
CFC-113	93	4.1	88
CCl_4	26 (37)	1.9 (4.2)	26 (37)

The Results for Emissions

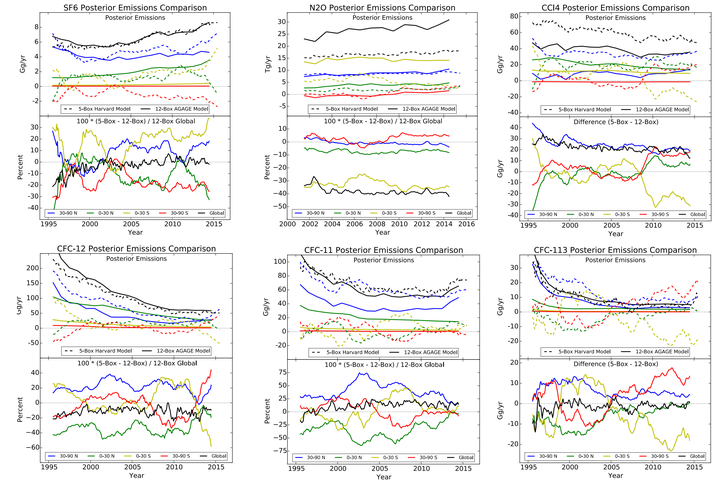

Figure 5 Comparison of emission results from the Harvard 5-box and AGAGE 12-box models.

4. Results: We have used NOAA/GMD data to calculate emissions for atmospheric SF_6, N_2O, CCl_4, CFC-11,-12 and -113 using a 5-box model and a 12-box model (**Figure 5**). For all gases, except for the last 5 years of CFC-113 emissions, the 5-box model places the strongest source region in the N hi-lat box. Note that CCl_4 emissions are shown here under the 37 year global lifetime scenario. By contrast, the 12-box model places the strongest source region in one of the tropics boxes for 3 of the 6 gases studied (N_2O, CCl_4, CFC-12) . These differences are believed to stem primarily from the differing transport schemes and the influence of the priors and other constraints at work in the 12-box model but absent from the 5-box model.

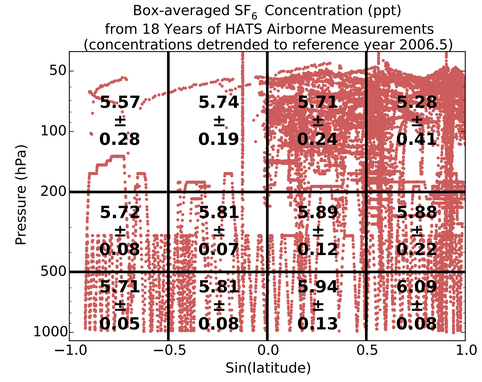

Figure 6 Density weighted SF_6 airborne measurements to calibrate transport in AGAGE model.

5. Future Work: Convenient methods are needed for tuning transport parameters – especially in the 12-box model, where a default scheme derived from MOZART/ MERRA 3D CTM data was used. We expect that our airborne data will be useful in this regard. Also, a convenient means of loosening the 12-box model's added priors and other constraints, along with the flexible addition of these constraints to the 5-box model, are needed to facilitate more meaningful comparisons between the two.