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Sulfuryl fluoride in the global atmosphere

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[1] The first calibrated high-frequency, high-precision, in situ atmospheric and archived air measurements of the fumigant sulfuryl fluoride (SO2F2) have been made as part of the Advanced Global Atmospheric Gas Experiment (AGAGE) program. The global tropospheric background concentration of SO2F2 has increased by 5 ± 1% per year from ~0.3 ppt (parts per trillion, dry air mol fraction) in 1978 to ~1.35 ppt in May 2007 in the Southern Hemisphere, and from ~1.08 ppt in 1999 to ~1.53 ppt in May 2007 in the Northern Hemisphere. The SO2F2 interhemispheric concentration ratio was 1.13 ± 0.02 from 1999 to 2007. Two-dimensional 12-box model inversions yield global total and global oceanic uptake atmospheric lifetimes of 36 ± 11 and 40 ± 13 years, respectively, with hydrolysis in the ocean being the dominant sink, in good agreement with 35 ± 14 years from a simple oceanic uptake calculation using transfer velocity and solubility. Modeled SO2F2 emissions rose from ~0.6 Gg/a in 1978 to ~1.9 Gg/a in 2007, but estimated industrial production exceeds these modeled emissions by an average of ~50%. This discrepancy cannot be explained with a hypothetical land sink in the model, suggesting that only ~2/3 of the manufactured SO2F2 is actually emitted into the atmosphere and that ~1/3 may be destroyed during fumigation. With mean SO2F2 tropospheric mixing ratios of ~1.4 ppt, its radiative forcing is small and it is probably an insignificant sulfur source to the stratosphere. However, with a high global warming potential similar to CFC-11, and likely increases in its future use, continued atmospheric monitoring of SO2F2 is warranted.

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1. Introduction

[2] Sulfuryl fluoride (SO2F2) is used increasingly as a fumigant to replace methyl bromide, which, owing to its large ozone depletion potential, is being partially phased out (consumption for nonquarantine/preshipment uses) under the Montreal Protocol on Substances that Deplete the Ozone Layer and its subsequent amendments [United Nations Environment Programme, 2006]. During structural fumigation several thousand ppm (parts per million) of SO2F2 are applied over 24 h. Owing to its acute toxicity, SO2F2 levels within the fumigated structure must be reduced to less than 1 ppm prior to reentry by venting excess SO2F2 to the atmosphere (the exposure limit is 5–10 ppm). In addition, SO2F2 has been approved for postharvest fumigation of dried fruits, tree nuts, grains, and flours [Environmental Protection Agency, 2004, 2005]. SO2F2 has also been released in stack air (TRI Explorer, 2006, Environmental Protection Agency, http://www.epa.gov/triexplorer) (hereinafter Environmental Protection Agency online data, 2006), probably as a byproduct from certain manufacturing processes (M. Krieger, Dow AgroSciences, personal communication, 2008). Further emissions to the atmosphere may result from the use of SO2F2 in the semiconductor industry as a plasma cleaning gas [Hobbs and Hart, 2005] and in the magnesium industry as a blanketing gas to replace sulfur hexafluoride (SF6), which has an exceptionally large global warming potential. Trace amounts of SO2F2 are also formed from SF6 by electrical discharges in transformers [Köréh et al., 1997; Pradayrol et al., 1997]. Symonds et al. [1988] concluded that SO2F2 emissions from volcanoes are probably extremely small. It is possible, however, that certain fluorite minerals may be a natural source of SO2F2 to the atmosphere [Kranz, 1966], similar to their roles as small sources of atmospheric carbon tetrafluoride (CF4) and SF6 [Harnisch et al., 2000].
From a recent European Union report [Swedish Chemicals Agency, 2005] a global anthropogenic release of 1.8 Gg/a can be deduced for 1992 to 2000, on the basis of estimates of global SO$_2$F$_2$ production and release provided by Dow AgroSciences. This report also estimates that more than 88% of SO$_2$F$_2$ emitted to the atmosphere, more than 1.62 Gg per year, results from fumigant use and that the atmospheric lifetime of SO$_2$F$_2$ is at most 4.5 years. This lifetime estimate is an upper limit obtained from a global mass balance calculation, based on a steady state assumption for an SO$_2$F$_2$ mixing ratio of at most 0.5 ppt (the detection limit of earlier measurements which failed to detect SO$_2$F$_2$ in background air). It is assumed in this report that SO$_2$F$_2$ does not react with the OH radical, that wet and dry deposition are negligible, that uptake and degradation by vegetation and soils are possible but unquantified sinks, and that hydrolysis in surface waters and photodissociation in the stratosphere are likely significant sinks of SO$_2$F$_2$ [Swedish Chemicals Agency, 2005].

According to the California Pesticide Use Reports (1989–2006, from California Environmental Protection Agency, http://www.cdpr.ca.gov/docs/pur/purmain.htm) (hereinafter California Environmental Protection Agency online reports, 1989–2006), the pesticide use of SO$_2$F$_2$ in California has increased from 0.44 to 1.30 Gg/a from 1989 to 2006, and was used mostly for structural pest control (S. Orme and S. Kegley, PAN Pesticide Database, 2006, http://www.pesticideinfo.org; see also California Environmental Protection Agency online reports, 1989–2006) and was therefore eventually emitted into the atmosphere [Swedish Chemicals Agency, 2005]. For 2000, this report [Swedish Chemicals Agency, 2005] states that 1.1 Gg of SO$_2$F$_2$ were used in California as pesticide, corresponding to 60% of the global anthropogenic estimate given above.

SO$_2$F$_2$ is registered for fumigation use in the United States, Canada, the Caribbean, Japan, Australia (in 2008), Switzerland, and the European Union [e.g., Derrick et al., 1990; United Nations Environment Programme, 2004], so that future emissions will most likely increase. SO$_2$F$_2$ is currently produced in the United States (Dow AgroSciences), China (Zhejiang Linhai Liming Chemical Co. and LongKou City Chemical Plant), Germany (Solvay), and Poland (Fluorochemika).

The environmental fate of SO$_2$F$_2$ is poorly known. In the troposphere it is likely removed very slowly by reaction with OH or NO$_3$ radicals or O$_3$, as SO$_2$F$_2$ is highly oxidized and much more chemically inert than other oxidized sulfur gases such as SO$_2$Cl$_2$ [Holleman and Wiberg, 1985]. Motivated by our initial atmospheric measurements [Mühle et al., 2006], kinetic studies of SO$_2$F$_2$ have been performed by Dillon et al. [2008] and, in a collaborative effort with us, by Papadimitriou et al. [2008]. These studies confirm that gas-phase reactions of SO$_2$F$_2$ with Cl, O$_3$, and O($^1$D) are unimportant, and that the reaction with OH is, at most, marginally important.

The solubility of SO$_2$F$_2$ in water per atmosphere (atm) partial pressure is 0.529 cm$^3$ (STP)/mL at 0°C and 0.215 cm$^3$ (STP)/mL at 23.3°C [Cady and Misra, 1974], which equates to 2.41 g/L and 0.978 g/L, respectively. (Published solubility constants ~16 times lower likely resulted from the incorrect use of the vapor pressure of SO$_2$F$_2$ (15.6 atm) in the calculation, even though the experiment was performed at 1 atm (M. Krieger, Dow AgroSciences, personal communication, 2007).) Holleman and Wiberg [1985] report that SO$_2$F$_2$ does not decompose in the presence of water up to 150°C, while Cady and Misra [1974] state that SO$_2$F$_2$ hydrolyzes slowly in water and quickly in basic solutions. Therefore hydrolysis in acidic environments such as most precipitation [Whelpdale and Miller, 1989; Collett et al., 1994; Seinfeld and Pandis, 1997] and many lakes and rivers is likely unimportant, while hydrolysis in the slightly basic surface ocean waters [Orr et al., 2005] could affect the atmospheric lifetime of SO$_2$F$_2$ significantly [Cady and Misra, 1974].

SO$_2$F$_2$ does not photolyze in the lower atmosphere, but in the upper atmosphere it will eventually be photolyzed by hard UV radiation or removed by ion and radical processes [Pradayrol et al., 1996; Dillon et al., 2008; Papadimitriou et al., 2008] similar to those that remove trifluoromethyl sulfur pentafluoride (SF$_3$CF$_3$) [Takahashi et al., 2002a] or SF$_6$ [Ravishankara et al., 1993; Morris, 1995].

SO$_2$F$_2$ can be a source of stratospheric sulfur [Crutzen, 1976] and a “greenhouse gas” [California Environmental Protection Agency, 2005; Pest Management Regulatory Agency, 2006] owing to its infrared absorption in the “atmospheric window” [Perkins and Wilson, 1952; Hunt and Wilson, 1960; Heise et al., 1997; Dillon et al., 2008; Papadimitriou et al., 2008].

In this paper we present the first calibrated high-frequency, high-precision, in situ ambient and archive air measurements of SO$_2$F$_2$, reconstruct the global atmospheric history, discuss the sink processes, estimate the atmospheric lifetime, quantify the source flux, and discuss the importance of SO$_2$F$_2$ as a sulfur source to the stratosphere and as an infrared-absorbing “greenhouse gas.”

2. Experimental Method

2.1. Instrumentation and Calibration

Sulfuryl fluoride and ~35 other halogenated compounds are measured by the Advanced Global Atmospheric Gases Experiment (AGAGE) in 2-L air samples with the newly developed Medusa instrument, a cryogenic preconcentration system custom-fitted to a gas chromatograph (GC, Agilent 6890) with a quadrupole mass selective detector (MSD, Agilent 5973) [Miller et al., 2008].

For this work, data from seven Medusa GC/MSD instruments at seven sites were used. The La Jolla (33°N, 117°W, California) site at the Scripps Institution of Oceanography (SIO) serves as the main calibration site. Archived air tanks (see section 2.3) were measured at SIO and at the Commonwealth Scientific and Industrial Research Organisation (CSIRO, Aspendale, Australia). Routine ambient air measurements began at SIO in August 2004, and subsequently at the five remote AGAGE field stations: at Mace Head, Ireland (53°N, 10°W) in November 2004; at Trinidad Head, California (41°N, 124°W) in April 2005; at Cape Grim, Tasmania (41°S, 145°E) in May 2005; at Ragged Point, Barbados (13°N, 59°W) in July 2005; and at Cape Matatula, American Samoa (14°S, 171°W) in June 2006.

Each ambient or archived air sample was alternated with reference gas measurements [Prinn et al., 2000], resulting in up to 12 fully calibrated air measurements per
day. The reference gases at each site were calibrated relative to parent standards at SIO. Details of the calibration method and hierarchy are given by Miller et al. [2008].

14 SO$_2$F$_2$ is reported on the SIO-2007 scale, which is based on gravimetric SO$_2$F$_2$/nitrous oxide (N$_2$O) mixtures prepared via a stepwise dilution technique with large dilution factors for each step in the range of 10$^3$ to 10$^5$ [Prinn et al., 2000, 2001] to reduce systematic uncertainties. The SIO-2007 SO$_2$F$_2$ scale is based on four stable primary calibration standards in zero air with prepared values of 3.30–3.41 ppt, each containing ∼20 torr water vapor. Each zero air/water vapor primary was measured on the Medusa GC/MSD to verify insignificant SO$_2$F$_2$ blank levels before being spiked with one of the SO$_2$F$_2$/N$_2$O mixtures. For further calibration details, see Prinn et al. [2000].

The pure SO$_2$F$_2$ (99.8%, Dow AgroSciences) and N$_2$O (99.99%, Matheson or 99.9997%, Scott Specialty Gases) used to prepare the primary standards were further purified by repeated cycles of freezing (at −196°C), vacuum removal of noncondensable gases, and thawing. Zero air (Ultra Zero Air, Matheson or 99.9999%, Scott Specialty Gases) used to further calibrate traps showed no blanks for SO$_2$F$_2$. Mass spectra obtained in scan mode during an SO$_2$F$_2$ measurement at SIO were compared with parent standards at SIO. Details of the calibration method and time period of up to almost 4 years typically agree within ±20 ppm range [2000], who reported a detection limit of 3.30–3.41 ppt, each containing 0.02–0.03 ppt showing that SO$_2$F$_2$ mixing ratios were lower than expected SO$_2$F$_2$ mixing ratios. These tests directly show that measurements at the two sites are in agreement. On the basis of two sigma deviations from a fit through all 70 (64 at CSIRO and 6 at SIO) SH samples, four samples with lower than expected SO$_2$F$_2$ mixing ratios were rejected, and one sample with higher than expected mixing ratios was rejected, leaving 65 SH samples (93%). The 112 unique NH samples, all 33 samples with mixing ratios below the detection limit were rejected, and 28 samples were recursively rejected as being outside of two sigma deviations from of a fit through all NH data. Before 1999 the uncertainties of the resulting NH fits were so large that they were not suitable for the modeling and all NH data before 1999 were rejected, leaving 51 unique NH samples (46%).

2.3. Archived Air Samples of the Northern and Southern Hemisphere

17 To reconstruct the atmospheric history of SO$_2$F$_2$, 108 unique archived Northern Hemisphere (NH) air samples were measured at SIO, and 64 Southern Hemisphere (SH) air samples (Cape Grim air archive (CGAA) samples [Krummel et al., 2007] were measured at CSIRO. Six additional SH samples were measured at SIO, of which five were in good agreement with the SH samples of similar age measured at CSIRO (ΔSO$_2$F$_2$ = 0.02–0.03 ppt, Δt = 0–12 days). One sample was rejected as an outlier with lower than expected SO$_2$F$_2$ mixing ratios. Similarly, four additional NH samples were measured at CSIRO, of which three were in good agreement with NH samples of the same age measured at SIO (ΔSO$_2$F$_2$ = 0.02–0.03 ppt, Δt = 0–12 days). One sample was rejected as an outlier with higher than expected SO$_2$F$_2$ mixing ratios. These tests directly show that measurements at the two sites are in agreement. On the basis of 20-torr water vapor. Each of these tanks, except for 33 samples with mixing ratios below the detection limit were rejected, and 28 samples were recursively rejected as being outside of two sigma deviations from of a fit through all the NH data. Before 1999 the uncertainties of the resulting NH fits were so large that they were not suitable for the modeling and all NH data before 1999 were rejected, leaving 51 unique NH samples (46%).

3. Model Studies

3.1. Two-Dimensional 12-Box Model

18 A flexible 2-D 12-box model has been widely used in AGAGE for inverse studies of gases with lifetimes longer than interhemispheric exchange times [e.g., Prinn et al., 2005; Xiao et al., 2007]. For this purpose, the model provides semihemispheric average concentrations, and accuracy in inverse problems, that are remarkably similar to those in observationally driven 3-D models [Bousquet et al., 2005; Prinn et al., 2005]. Its computational efficiency and flexibility enables explicit estimation of uncertainties due to
modeling and other errors. The AGAGE measurement sites have been specifically chosen to be representative of the four equal-mass semihemispheres in the lower troposphere, which are the four lowest boxes of the 2-D model. The model has horizontal divisions at 90°N, 30°N, 0°N, 30°S, and 90°S and vertical divisions at 1000, 500, 200, and 0 hPa. The model thus contains eight tropospheric boxes and four stratospheric boxes. Tests with a high-resolution 3-D model with interannually varying and observationally constrained meteorology confirm that the monthly mean mixing ratios and standard deviations at a particular AGAGE station define well the large volume averages corresponding to our 2-D model for gases whose lifetimes are much longer than the approximately few-month-long mixing times in a given semihemisphere [Prinn et al., 2005]. The numeration of the boxes from north to south is: 1, 3, 5, and 7 for the lower troposphere (NH extra tropics, NH tropics, SH tropics, and SH extra tropics); 2, 4, 6, and 8 for the upper troposphere; and 9, 10, 11, and 12 for the stratosphere. The equation governing the mixing ratio \( \chi_i \) of SO\(_2\)F\(_2\) in each box \( i \) is given by

\[
\frac{\partial \chi_i}{\partial t} = \frac{qP_i}{M_i} + T_i - \frac{\chi_i}{\tau_{\text{surface},i}} - \frac{\chi_i}{\tau_{\text{OH},i}}, \quad \text{for} \quad i = 1, 3, 5, \text{and} \ 7, \quad (1)
\]

\[
\frac{\partial \chi_i}{\partial t} = T_i - \frac{\chi_i}{\tau_{\text{OH},i}}, \quad \text{for} \quad i = 2, 4, 6, \text{and} \ 8, \quad (2)
\]

\[
\frac{\partial \chi_i}{\partial t} = T_i - \frac{\chi_i}{\tau_{\text{strat},i}}, \quad \text{for} \quad i = 9, 10, 11, \text{and} \ 12. \quad (3)
\]

[19] Here \( P_i \) is the emission rate (or source strength) of SO\(_2\)F\(_2\) in box \( i \), \( M_i \) is the total air mass in box \( i \), \( q \) is the molecular weight ratio of SO\(_2\)F\(_2\) to air, and \( T_i \) is the net convergence of the flux of SO\(_2\)F\(_2\) into the box parameterized by using time-varying zonally averaged velocities and eddy diffusion coefficients (details given by Cunnold et al. [1983, 1994]). These parameters are based on observed circulation rates and have been tuned for the model to optimally predict the observed distributions of long-lived species. Thus the model is expected to be suitable for simulations of long-lived gases whose lifetimes much exceed interbox transport times. SO\(_2\)F\(_2\), with a lifetime of decades (see sections 3.2, 3.3, 3.4, and 4.3), easily satisfies this requirement.

3.2. Gas Phase Loss Processes in the Troposphere

[20] The SO\(_2\)F\(_2\) lifetime in the troposphere results from possible reactions with OH, Cl, and \( \text{O}_3 \). The lifetime due to reaction with OH in the eight tropospheric boxes is \( \tau_{\text{OH},i} \). In a collaborative effort with us, Papadimitriou et al. [2008] determined the upper limit of the OH rate constant \( k_{\text{OH-SO}_2\text{F}_2} < 1.0 \times 10^{-16} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1} \), which is used as a priori initial estimate in the inversion. The resulting global tropospheric lifetime \( \tau_{\text{OH}} \) is at least \( >300 \) years. Papadimitriou et al. [2008] also determined that the reaction with Cl atoms is negligible, as the corresponding global tropospheric lifetime is \( >10,000 \) years. SO\(_2\)F\(_2\) reacts with \( \text{O}_3 \) in the troposphere even more slowly than with OH or Cl according to Dillon et al. [2008], who calculated a corresponding global tropospheric lifetime of \( >24,000 \) years. Thus, tropospheric destruction of SO\(_2\)F\(_2\) due to reactions with \( \text{O}_3 \) and Cl is negligible, and destruction due to reaction with OH is at most marginally important.

3.3. Loss Processes in the Stratosphere

[21] SO\(_2\)F\(_2\) destruction in the stratosphere results from photolysis and reaction with O(\(^{1}\)D). The lifetime in the four stratospheric boxes is \( \tau_{\text{strat},i} \). Dillon et al. [2008] suggest long stratospheric lifetimes on the basis of their measurements of the reaction of SO\(_2\)F\(_2\) with O(\(^{1}\)D) and UV absorption cross sections from Pradayrol et al. [1996] and comparisons with N\(_2\)O. Papadimitriou et al. [2008] calculate lifetimes with respect to reaction with O(\(^{1}\)D) and UV photolysis of 700 years and \( >4700 \) years, respectively, and report a combined stratospheric lifetime of 630 years on the basis of a rigorous calculation with a 2-D model. The total global stratospheric lifetime used here is therefore 630 years. The latitudinal distributions of the stratospheric destruction are assumed to be the same as for N\(_2\)O, which also has a long lifetime with respect to stratospheric destruction.

3.4. Dissolution and Hydrolysis of Tropospheric SO\(_2\)F\(_2\) in the Oceanic Mixed Layer

[22] At the baseline station Mace Head, Ireland, we found no indication of loss of SO\(_2\)F\(_2\) in the continental boundary during stagnant meteorological conditions, and Dillon et al. [2008] concluded that uptake of SO\(_2\)F\(_2\) on aerosols is not important. However, the ocean’s upper mixed layer, which is on the order of 100 m thick, is turbulently mixed on a short enough timescale that it can be considered well-mixed with respect to gas exchange. For decades, oceanographers have modeled air-sea exchange of slightly soluble gases such as SO\(_2\)F\(_2\) as being controlled by wind speed—dependent diffusion in the surface boundary layer between atmosphere and ocean, with rapid mixing within the mixed layer below [Broecker and Peng, 1974; Wanninkhof, 1992]. Factoring in the fast hydrolysis of SO\(_2\)F\(_2\) under oceanic pH (see below) [Cady and Misra, 1974; Holleman and Wiberg, 1985], it is likely that dissolution followed by hydrolysis in the basic ocean upper mixed layer, which covers 71% of the planet, is an important factor controlling the lifetime of SO\(_2\)F\(_2\). In contrast, hydrolysis in acidic environments such as much precipitation [Whelpdale and Miller, 1989; Seinfeld and Pandis, 1997], many lakes and rivers, and cloud water droplets is slow [Cady and Misra, 1974; Holleman and Wiberg, 1985] and likely unimportant.

[23] On the basis of the solubility and hydrolysis data of Cady and Misra [1974] it can be estimated that the hydrolysis of SO\(_2\)F\(_2\) in basic waters occurs in minutes to hours (Tables 1 and 2), while the lifetime of dissolved slightly soluble gases with respect to exchange with the atmosphere is on the order of 1 month [Broecker and Peng, 1974]. Even in the unlikely event that the hydrolysis of SO\(_2\)F\(_2\) is 5 times slower than measured by Cady and Misra [1974], SO\(_2\)F\(_2\) would still hydrolyze within a few hours to a day, so that all SO\(_2\)F\(_2\) entering the ocean will be hydrolyzed much more rapidly than it can exchange back with the atmosphere. Thus the transfer velocity across the air-sea boundary layer is the rate limiting step and the modeling of
the atmospheric lifetime is highly insensitive to the oceanic hydrolysis lifetime. This makes a rough estimate of the lifetime of SO$_2$F$_2$ with respect to dissolution and hydrolysis in the ocean, $\tau_{\text{ocean}}$, possible. On the basis of an oceanic transfer velocity, $v_i$ of 3.2–4.25 m/d (Table 3), a scale height of the troposphere, $Z$, of ~7000 m, a volume ratio Henry’s Law coefficient, $H_i$, of 5.24–3.91 mL/mL (Table 1), and the fraction of Earth’s surface area covered by ocean $f_{\text{ocean}}$, of 0.708, the e-folding time, $\tau_{\text{ocean}}$, of SO$_2$F$_2$ can be estimated using

$$
\tau_{\text{ocean}} = \frac{Z \cdot H}{f_{\text{ocean}} \cdot v_i},
$$

with error propagation of the uncertainty ranges of $v$ and $H$, to be 35 ± 14 years. This is much shorter than the lifetimes due to the tropospheric and stratospheric loss processes discussed in sections 3.2 and 3.3, indicating that dissolution and hydrolysis in the ocean surface is in fact the most important loss process for SO$_2$F$_2$. It should be stressed that Dillon et al. [2008] did not include this classical representation of the air-sea exchange process and oceanic mixed layer hydrolysis in their treatment of this problem and therefore obtained a much lower estimate of the oceanic SO$_2$F$_2$ destruction rate.

[24] In our 12-box model, air-sea exchange of SO$_2$F$_2$ is described using conventional oceanic uptake calculations following the method outlined above [Broecker and Peng, 1974; Wanninkhof, 1992]. The oceanic fluxes $\phi$ and the corresponding lifetimes $\tau_{\text{ocean},i}$ (which replaces $\tau_{\text{surface},i}$ in equation (1)) due to the oceanic destruction in the lowest four boxes are calculated on the basis of the following equations:

$$
\phi = \frac{v_i}{H_i}[\text{SO}_2\text{F}_2]_{\text{air},i}; \left(1 - \frac{v_i \cdot \tau_{\text{hydro},i}}{\tau_{\text{ocean},i}}\right)
$$

$$
\tau_{\text{ocean},i} = \frac{Z_{\text{air},i} \cdot H_i}{f_{\text{ocean},i} \cdot v_i \left(1 - \frac{v_i \cdot \tau_{\text{hydro},i}}{\tau_{\text{ocean},i}}\right)}.
$$

For each lower tropospheric box $i = 1, 3, 5,$ and 7, $v_i$ is the gas transfer or “piston” velocity which is estimated optimally in the inversion, $H_i$ is the volume ratio Henry’s Law coefficient [Cady and Misra, 1974] (Table 1), $\tau_{\text{hydro},i}$ is the SO$_2$F$_2$ oceanic hydrolysis lifetime calculated from the rate constant given by Cady and Misra [1974] (Table 2), $f_{\text{ocean},i}$ is the fraction of planetary surface area covered by ocean, $Z_{\text{ocean},i}$ is the ocean mixed layer depth, $Z_{\text{air},i}$ is the atmospheric height, and $[\text{SO}_2\text{F}_2]_{\text{air},i}$ is the atmospheric molar concentration. The a priori initial estimates of these parameters for the model are listed in Table 3. The role of exchange of SO$_2$F$_2$ between the ocean mixed layer and the deep ocean is negligible on the timescales of interest here considering the relatively rapid rate of SO$_2$F$_2$ hydrolysis in the mixed layer, and is therefore not included in the calculation.

### 3.5. Inversion Approach for SO$_2$F$_2$

[25] To solve the inverse problem of deducing the sources or sinks of SO$_2$F$_2$ from the observed concentrations, a discrete recursive weighted least squares Kalman filter is used in the 12-box model. This approach has been used in a number of studies to estimate the atmospheric lifetimes or global sources of trace gases [Prinn et al., 2000; Prinn, 2000]. The 12-box model SO$_2$F$_2$ reference case, covering the period 1942–2007, is described in section 4.2. The AGAGE SO$_2$F$_2$ measurements began in 1978, which allows sufficient model spin-up time.

[26] In the Kalman filter, the state vector contains eight factors which are optimally estimated during the inversion: $F_{\text{ocean}}$, $F_{\text{OH}}$, and six emission coefficients $f_i$. The basic approach for the SO$_2$F$_2$ sink and source estimation is to multiply the reference inverse oceanic lifetime $1/\tau_{\text{ocean},i}$ and the tropospheric lifetime $1/\tau_{\text{OH},i}$ (see sections 3.4 and 3.2) by the dimensionless factors $F_{\text{ocean}}$, and $F_{\text{OH}}$. Because of the fast hydrolysis (i.e., short hydrolysis lifetime $\tau_{\text{hydro},i}$), $F_{\text{ocean}}$ is approximately proportional to the transfer velocity $v_i$ (see equations (4) and (6)). $F_{\text{OH}}$ is proportional to the reaction rate constant $k_{\text{OH-SO}_2\text{F}_2}$. The total global emissions in the model are essentially determined by the six emission coefficients $f_i$ and described with the emission function

$$
E(x) = f_0 + f_1N^2P_1(x) + \frac{f_2}{3}N^2P_2(x) + f_3NP_3(x)
$$

$$
+ \frac{f_4}{10}N^2P_4(x) + f_5NP_5(x)
$$

$$
E(x) \left[ \frac{\text{Gg}}{\text{yr}} \right], \quad N = \frac{t_{\text{end}} - t_0}{2} \text{[years]}, \quad x = \frac{t - t_0}{N} - 1,
$$

where $P_n(x)$ is the Legendre polynomial of the order $n$, with its argument normalized to $N$ and measured from the midpoint of the 2N yearlong interval from $t_0 = 1960$ to $t_{\text{end}} = 2007.96$. Likely latitudinal distributions of emissions are assessed on the basis of available industrial data as discussed in section 4.3.

[27] To avoid inconsistencies during the inversion, regular monthly means of the observed mixing ratios are needed as input data. However, only sparse data are available before in situ measurements began. Therefore polynomial functions

$$
x(t) = p_0 + p_1t + p_2t^2 + p_3t^3 \text{ [ppt]}
$$
with \( t \) in years were fitted to the observational data and used as model input. For the SH extratropics (30°S–90°S, box 7) the SH CGAA tank data (section 2.3) and the background monthly mean in situ values with pollution events removed for Cape Grim, Tasmania were combined. Similarly, for the NH extra tropics (30°N–90°N, box 1) the NH tank data (section 2.3) and the background monthly mean in situ values with pollution events removed for Trinidad Head, California, and Mace Head, Ireland, were combined. The NH tropics (0°–30°N, box 3) contain Ragged Point, Barbados, data and the SH tropics (0°–30°S, box 5) contain Cape Matatula, American Samoa, data. Coefficients \( p_i \) for the polynomial fits are listed in Table 4. The derived atmospheric histories for the SH and NH are discussed in section 4.2. Uncertainties of each polynomial fit were calculated as the root sum square of the measurement standard deviations and the deviations of the measurements from the polynomial fit for periods with similar deviations. These uncertainties are compared to the differences between the measurements and the model to assess the quality of the inversions in section 4.3. Only monthly mean in situ data until May 2007 are used, since later in situ data are referenced against working standards which were still in use at the field stations and had thus not been returned to SIO for recalibration.

[28] Owing to the semilinear nature of the inversion problem, several iterations of the filtering runs are needed. The iteration ends when the final estimates of the state vector converge with the initial estimate from that particular filtering run. For every inversion iteration, 100% error was assigned to the initial estimate of each factor \( F_{\text{ocean}} \), \( F_{\text{OH}} \), and \( f_c \). In addition to the measurement errors, we also included errors resulting from transport uncertainties in the inversion results discussed below.

4. Results and Discussion

4.1. Observations

[28] At the Mace Head, Ireland, and Cape Grim, Tasmania, AGAGE remote stations, baseline conditions are generally observed with mean mixing ratios for January 2007 of ~1.53 ppt at Mace Head and ~1.35 ppt at Cape Grim (Figure 1). Sporadic pollution events have been observed at Mace Head, pointing to small local or regional emissions.

[30] No pollution events above background were observed at Cape Grim (Figure 1), Cape Matatula, American Samoa (not shown), and at urban Aspendale, Australia (38°S, 145°E, preliminary data), during the period of the study. The first above-baseline events were observed at Cape Grim and Aspendale in mid-2008 after SO\(_2\)F\(_2\) was registered for use in Australia (M. Krieger, Dow Agro-Sciences, personal communication, 2008). Australian regulatory agencies are not aware of any use prior to 2008 (P. J. Fraser, CSIRO, personal communication, 2008). SO\(_2\)F\(_2\) has not yet been registered for use in other Southern Hemisphere countries and we are not aware of any sales in that region (M. Krieger, Dow AgroSciences, personal communication, 2008). We conclude therefore that SO\(_2\)F\(_2\) has been used almost entirely in the NH.

[31] At Trinidad Head on the Northern California coast, background conditions similar to Mace Head are observed when air originates offshore or from colder areas of Northern California, while SO\(_2\)F\(_2\) pollution events are generally associated with air originating from Southern California where furnigation with SO\(_2\)F\(_2\) for termite control is common (air history maps demonstrating this were provided by the UK Met Office using the NAME 3-D Lagrangian dispersion model [Manning et al., 2003; Jones et al., 2007]). In urban La Jolla on the Southern California coast, several hundred to several thousand ppt are frequently observed owing to

### Table 2. Hydrolysis Lifetimes \( \tau_{\text{hydro},i} \) of SO\(_2\)F\(_2\) in the Ocean Surface Mixed Layer

<table>
<thead>
<tr>
<th>Region</th>
<th>Average Annual Temperature(^a) (°C)</th>
<th>Average Annual pH(^b)</th>
<th>( \tau_{\text{hydro},i} ) (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tropics (0°–30°N/0°–30°S)</td>
<td>23–29</td>
<td>8.05–8.01</td>
<td>0.017–0.029</td>
</tr>
<tr>
<td>Extratropics (30°N–90°N/30°S–90°S)</td>
<td>−2–23</td>
<td>8.1–8.3</td>
<td>0.023–0.203</td>
</tr>
</tbody>
</table>

\(^a\) Annual average temperatures from Locarnini et al. [2006].

\(^b\) Annual average pH from Orr et al. [2005].

### Table 3. Initial Estimates of Oceanic Transfer Velocity \( v_i \), Henry’s Law Coefficient \( H_i \), Ocean Hydrolysis Lifetime \( \tau_{\text{hydro},i} \), Fraction of Total Surface Area Covered by Ocean \( f_{\text{ocean},i} \), Atmospheric Box Height \( Z_{\text{atm},i} \), and Ocean Mixed Layer Depth \( Z_{\text{ocean},i} \) for Each Lower Troposphere Box

<table>
<thead>
<tr>
<th>Parameter</th>
<th>30°N–90°S</th>
<th>0°–30°N</th>
<th>0°–30°S</th>
<th>30°S–90°S</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_i ) (m/d)</td>
<td>4.00</td>
<td>3.22</td>
<td>3.20</td>
<td>4.25</td>
</tr>
<tr>
<td>( H_i )</td>
<td>3.906</td>
<td>5.256</td>
<td>5.236</td>
<td>3.906</td>
</tr>
<tr>
<td>( \tau_{\text{hydro},i} ) (days)</td>
<td>0.042</td>
<td>0.013</td>
<td>0.021</td>
<td>0.042</td>
</tr>
<tr>
<td>( f_{\text{ocean},i} )</td>
<td>0.504</td>
<td>0.711</td>
<td>0.779</td>
<td>0.850</td>
</tr>
<tr>
<td>( Z_{\text{atm},i} ) (m)</td>
<td>150</td>
<td>30</td>
<td>100</td>
<td>5495.5</td>
</tr>
<tr>
<td>( Z_{\text{ocean},i} ) (m)</td>
<td>3599.6</td>
<td>5799.68</td>
<td>5799.68</td>
<td>5495.5</td>
</tr>
</tbody>
</table>

\(^a\) Ocean transfer velocities \( v_i = 0.31 \times (660/\text{Sc})^{0.5} \times U_{10}^{0.5} \) for SO\(_2\)F\(_2\) were estimated for each lower tropospheric box using area, sea surface temperature (SST), and Schmidt number (\( \text{Sc} \)) data from the Takahashi et al. [2002b] carbon dioxide climatology (on a \( 4° \times 5° \) grid) and QSCAT winds for 1999–2004 (\( U_{10} \)) over the ocean, assuming that the diffusion coefficient of SO\(_2\)F\(_2\) in seawater is ~40% less than that of carbon dioxide. The estimated absolute uncertainty for each \( v_i \) is ~50% to reflect differences among the various parameterizations for \( v_i \) with wind speed. The estimated uncertainty for the ratios of \( v_i/v_j \) for any two boxes i and j is ~20%. That is, the relative latitudinal distribution of \( v_i \) is better constrained than each \( v_i \) (R. Wanninkhof, personal communication, 2008).

\(^b\) Volume ratio Henry’s Law coefficient \( H_i = 1/(\text{Ostwald coefficient}) \); see Table 1.

\(^c\) The oceanic hydrolysis lifetime \( \tau_{\text{hydro},i} \) is calculated in Table 2.

\(^d\) Land and ocean fractions from NASA Goddard Institute for Space Studies (http://data.giss.nasa.gov/landuse/soilunit.html).

\(^e\) Climatology oceanic mixed layer depth from National Center for Environmental Prediction (http://www.cpc.ncep.noaa.gov/cgi-bin/godas_parameter.pl).

The 1000- to 500-hPa atmospheric height is calculated using 287·T/9.81·log(1000/5000), where \( T \) is the temperature in each box.
nearby fumigation with SO$_2$F$_2$, but the lowest observed values agree well with the baseline Mace Head and Trinidad Head records. Preliminary results from the new AGAGE-affiliated station at Gosan, Jeju Island, Korea (33°N, 126°E) operated by Seoul National University show frequent pollution events (not shown), pointing to SO$_2$F$_2$ sources in eastern Asia, in agreement with the presence of Chinese SO$_2$F$_2$ production and emissions.

4.2. Reconstruction of the Atmospheric History of SO$_2$F$_2$

[32] The atmospheric history of SO$_2$F$_2$ in the SH was reconstructed from analysis of archived SH air from the Cape Grim air archive (CGAA) [Krummel et al., 2007] (section 2.3) and background monthly mean in situ for Cape Grim, Tasmania. SO$_2$F$_2$ mixing ratios in Antarctic firm air samples measured in our laboratory (J. E. Shields, unpublished data, 2008) agree well with our recent SH measurements at the top of the firm profile and showed no detectable SO$_2$F$_2$ at the bottom of the profile which predate industrial SO$_2$F$_2$ production. We therefore assume that there is negligible natural SO$_2$F$_2$ in the atmosphere and that the history of SO$_2$F$_2$ in the atmosphere began with the onset of its industrial production in 1960 (see section 4.3). The atmospheric history of SO$_2$F$_2$ in the NH was reconstructed from analysis of archived NH air and background monthly mean in situ values for Mace Head, Ireland, and Trinidad Head, California. In contrast to the SH tanks, the NH tanks were collected from various sources and show a larger scatter in SO$_2$F$_2$ and other trace gases as discussed in section 2.3. Nevertheless, after filtering of outliers, a clear atmospheric trend from 1999 to 2007 was obtained for the NH. The excellent quality of the CGAA enabled the reconstruction of the atmospheric trend from 1978 to 2007 for the SH. The resulting measured SO$_2$F$_2$ values and fitted baseline trends for both hemispheres are plotted in Figure 2. SO$_2$F$_2$ has been accumulating in the global atmosphere with a growth rate of 5 ± 1% per year since 1978 and the interhemispheric concentration ratio has been 1.13 ± 0.02 over the 1999–2007 period.

4.3. Emission and Lifetime Estimates

[33] Since no significant pollution events were observed at either SH AGAGE station (SO$_2$F$_2$ was not registered for fumigation use in Australia or other Southern Hemisphere countries prior to 2008), and since we found no other evidence of SO$_2$F$_2$ use in the SH (see section 4.1), we assumed that all emissions have been in the NH. To account for possible emissions in Hawaii (M. Krieger, Dow AgroSciences, personal communication, 2008), two emission

![Figure 1](image_url). In situ observations of SO$_2$F$_2$ at Mace Head, Ireland, and Cape Grim, Tasmania. Sporadic pollution events have been observed at Mace Head, Ireland, pointing to local or regional emissions. No pollution events were observed at Cape Grim, Tasmania, and Cape Matatula, American Samoa (not shown), indicating that SO$_2$F$_2$ has as of yet mostly been used in the Northern Hemisphere.
scenarios were investigated. Scenario a assumes 100% of the emissions in the NH extratropics (30°N–90°N) and scenario b assumes 90% of the emissions in the NH extratropics (30°N–90°N) and 10% in the NH tropics (0°–30°N).

The quality of the inversions can be assessed by comparing the residual differences between the measurements and the model to the uncertainties of the polynomial fits to the measurements (see section 3.5). As seen in Figure 3 for scenario a, the residuals are small (<0.02 ppt), randomly distributed around zero, and within the uncertainties of the polynomial measurement fits for the NH extratropics (30°N–90°N), the NH tropics (Cape Matatula, American Samoa, 0°–30°S), and the SH extra tropics (Cape Grim, Tasmania, 30°S–90°S), which reflects a good inversion as the time averaged state vector is estimated. The residuals for scenario b (not shown) are very similar. For the NH tropics (Ragged Point, Barbados, 0°–30°N) the residuals are larger and mostly positive, albeit still within the uncertainties of the polynomial measurement fits, except for a short period in late 2006. This could be related to the shifting of the intertropical convergence zone (ITCZ) which complicates the inversion for Ragged Point. Inversions of other species have resulted in similar differences for Ragged Point as the complex meteorology which would be needed to fully describe the observations at Barbados is not included. Also, the fit of the Ragged Point data has the lowest correlation coefficient ($R^2 = 0.758$; see Table 4) reflecting that the fit smoothed out some of the observed variability in the record.

During the inversions of the SO$_2$F$_2$ observations, the dimensionless factors $F_{\text{ocean}}$ (proportional to the inverse oceanic lifetimes $1/\tau_{\text{ocean,i}}$) and $F_{\text{OH}}$ (proportional to the inverse tropospheric lifetimes owing to reaction with the OH radical $1/\tau_{\text{OH,i}}$) and the six coefficients $f_i$ (describing the emission function) were estimated optimally to best explain the observations. The results are shown in Tables 5 and 6. The final estimates (last iteration) and the error reduction from the first iteration do not differ significantly between emission Scenarios a and b, showing that we cannot distinguish between these two scenarios.

The resulting modeled $F_{\text{ocean}} = 1.3–1.4$ with an error of $\sim$30%. Owing to the fast hydrolysis of SO$_2$F$_2$, $F_{\text{ocean}}$ is approximately proportional to the transfer velocity $v_i$ (see equation (6)). The estimated uncertainty of the a priori initial $v_i$ (and thus $F_{\text{ocean}}$) is $\sim$50% (R. Wanninkhof, personal communication, 2008) to reflect differences among various parameterizations of air-sea exchange rates with
wind speed. The 30–40% deviation of the inverted $F_{\text{ocean}}$ from unity represents reasonable agreement within the expected uncertainty of ~50%. A different parameterization with higher (lower) values of $v_i$ will result in a lower (higher) $F_{\text{ocean}}$, but inversion results are similar, as long as the relative latitudinal distribution of $v_i$ is similar. Note that the estimated uncertainty for the ratios of $v_i/v_j$ for any two boxes $i$ and $j$ is ~20%. That is, the relative latitudinal distribution of $v_i$ is better constrained than each $v_i$ (R. Wanninkhof, personal communication, 2008). We have verified that perturbations of the latitudinal distribution of $v_i$ by 20% have no significant effect on the inversion results.

The modeled $F_{\text{OH}} = 0.2–0.3$ with an error of more than 100%, which means that the inversion is insensitive to the OH sink.

The resulting average total global lifetime for both inversions $\tau_{\text{total}} = 36 \pm 11$ years (Table 7). The average atmospheric lifetime for oceanic loss $\tau_{\text{ocean}}^G = 40 \pm 13$ years and the average atmospheric lifetime due to reaction with OH $\tau_{\text{OH}}^G = 1604–999$ years (with more than 100% error) assuming a stratospheric lifetime $\tau_{\text{stratos}} = 630$ years based on our collaborative work with Papadimitriou et al. [2008]. This confirms that hydrolysis of SO$_2$F$_2$ in the oceanic mixed layer is the overwhelmingly dominant global sink and that reaction with OH is unimportant. This also explains why the error of $F_{\text{OH}}$ (and $\tau_{\text{OH}}^G$) could not be reduced during the inversion. The agreement between the inversion result of $\tau_{\text{ocean}}^G = 40 \pm 13$ years, which is based on a full air-sea exchange description, and the rough estimate of $\tau_{\text{ocean}}^G = $...
35 ± 14 years (section 3.4), which is based on a simple oceanic uptake calculation using transfer velocity and solubility, and assumes instant hydrolysis, is striking. In contrast, as noted above, Dillon et al. [2008] did not consider the air-sea exchange of slightly soluble gases in their assessment of the lifetime of SO₂F₂ in the marine boundary layer.

The Legendre coefficients fi for the emission function are well defined with errors of 9–18% and error reductions of 82–91% for the first four coefficients f₀−f₁ (the importance of f₂ decreases with i). The resulting global emissions for both scenarios (Figure 4) agree within the uncertainties of ~0.14 Gg/a (shown as dotted lines). Modeled emissions rose from ~0.6 Gg/a in 1978 to ~1.1 Gg/a in 1995 and ~1.9 Gg/a in 2007.

Owing to the increasing fraction of total surface area covered by ocean from north to south, lifetimes tend to decrease and emission trend to increase when larger fractions of emissions are allowed to occur farther to the south. However, the two emission scenarios a and b are reasonable assumptions of the most likely latitudinal distribution based on available industrial data, which are likely to be reasonably accurate because SO₂F₂ is a highly toxic compound that is strictly regulated. If 33% of the emissions are allowed to occur in the NH tropics (0°–30°N), the resulting global lifetime of 29 years still agrees with the τ⁰ total = 36 ± 11 years for scenarios a and b, although the resulting emissions are ~0.1 Gg/a (1990) to ~0.2 Gg/a (2007) higher than the emissions for scenarios a and b.

For comparison to the modeled emissions, a global industrial estimate (M. Krieger, Dow AgroSciences, personal communication, 2008) and a U.S. industrial estimate (Dow AgroSciences internal production and sales data and TRI Explorer (Environmental Protection Agency, online data, 2006)) are included in Figure 4. Note that the global industrial estimate is more uncertain because production, sales, and usage data are generally trade secrets. Also note that SO₂F₂ was produced from 1960 to 1975, but detailed production data for this period are unavailable, and that stack emissions of SO₂F₂ have only been accounted for since 1995 (TRI Explorer (Environmental Protection Agency, online data, 2006)). Also shown in Figure 4 is the reported SO₂F₂ pesticide use in California based on the Pesticide Use Report (California Environmental Protection Agency online reports, 1989—2006) which represents for ~37–56% of the global usage estimate and ~41–75% of the U.S. usage estimate.

The reported California pesticide use is 0.1–0.5 Gg/a lower than the modeled emissions and global industrial estimates are on average 1.5 ± 0.3 times the modeled emissions, that is ~50 ± 30% higher. Discrepancies of such a magnitude between measurement based and industrial emission estimates are common for many anthropogenic atmospheric trace gases, and could be caused by accounting errors in the industrial estimate. However, because SO₂F₂ production prior to about 1997 was mostly by one company (Dow AgroSciences) which has provided their production estimate, the discrepancy is surprising. A calibration error of such magnitude is very unlikely given the proven AGAGE calibration methods.

Initial inversions of the atmospheric SO₂F₂ observations using the global industrial estimate as an initial estimate were unsuccessful in yielding a simple calibration scaling factor. Assuming that a smoothed global industrial estimate is correct (to avoid inconsistencies during the inversion caused by the fluctuations in the industrial estimate) leads to lifetimes which are not in agreement with the observed interhemispheric gradient and the release pattern. A simple calibration scaling factor cannot therefore explain the discrepancy.

A delay between production and emission (stockpiling) of several years would be required to bring the industrial estimate and the modeled emissions in closer agreement, but this seems very unlikely even though some degree of stockpiling may have taken place causing the strong fluctuations in reported production values.

There is no experimental evidence for a significant terrestrial sink. For example, mixing ratios do not drop at the Mace Head, Ireland, AGAGE remote station during stagnant meteorological conditions. We nevertheless carried out modeled inversions including a hypothetical terrestrial sink proportional to ice-free land surface areas as a possible explanation for the discrepancy between the global industrial estimate and the modeled emission estimates without such a land sink. If the a priori initial lifetime with respect to a hypothetical land sink is chosen to be the same as the initial oceanic sink (~50 years), the inversion yields a negative land sink. If the initial lifetime with respect to a

| Table 7. Total Global Lifetime of SO₂F₂ and Atmospheric Lifetimes for Oceanic Loss, OH Reaction, and Stratospheric Loss for Both Emission Scenarios

<table>
<thead>
<tr>
<th>Emission Scenario</th>
<th>τG^° total</th>
<th>τG^° ocean</th>
<th>τG^° OH</th>
<th>τG^° stratos</th>
<th>τG^° total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario a</td>
<td>37 ± 11</td>
<td>41 ± 13</td>
<td>1604</td>
<td>630</td>
<td>630</td>
</tr>
<tr>
<td>Scenario b</td>
<td>34 ± 10</td>
<td>38 ± 11</td>
<td>999</td>
<td>630</td>
<td>630</td>
</tr>
<tr>
<td>Average</td>
<td>36 ± 11</td>
<td>40 ± 13</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The inversion is insensitive to the reaction of SO₂F₂ with OH and the error of τG^° total is more than 100%.

The stratospheric lifetime τG^° stratos has been taken from our collaborative work with Papadimitriou et al. [2008] and has not been estimated optimally in the inversion.
hypothetical land sink is chosen to be ∼100 years, the inverted global and oceanic lifetimes are the same as without a land sink (scenario a, Table 7), the lifetime with respect to the hypothetical land sink is long and undefined (∼1800 years, 100% error), the lifetime with respect to the OH reactions remains long and undefined (∼1260 years, 100% error), and the emissions are not statistically different from scenario a. This means that no significant land sink is allowed by the data and the model. Thus we conclude that a missing land sink is extremely unlikely to explain the observed discrepancy.

Besides a yet unknown or underestimated known sink, a possible explanation is that ∼1/3 of SO$_2$F$_2$ is destroyed during the fumigation process and only ∼2/3 is vented to the atmosphere. Similarly large fractions of methyl bromide are known to be destroyed during fumigation [Yagi et al., 1995; Yates et al., 1998], although direct evidence of SO$_2$F$_2$ destruction during fumigation, such as correspondingly high residual fluoride ion, is so far lacking (M. Krieger, Dow AgroSciences, personal communication, 2008). This question should be addressed with further experimental work.

5. Conclusions

The atmospheric history of SO$_2$F$_2$ in both hemispheres was reconstructed from in situ measurements and archived air, showing that SO$_2$F$_2$ has been accumulating in the global atmosphere with growth rates of 5 ± 1% per year since 1978. Mixing ratios of ∼0.3 ppt (SH) in 1978, ∼0.95 ppt (SH) and ∼1.08 ppt (NH) in early 1999, as well as ∼1.35 ppt (SH) and ∼1.53 ppt (NH) in early 2007 were observed. The SO$_2$F$_2$ interhemispheric concentration ratio has been 1.13 ± 0.02 over the 1999–2007 period.

Sporadic pollution events were seen at the Mace Head, Ireland, AGAGE remote station, while remote and urban Southern Hemisphere AGAGE stations (Cape Grim, Tasmania; Aspendale, Australia; and Cape Matatula, American Samoa) showed baseline conditions since the beginning of in situ measurements with no pollution events. This
indicates that SO$_2$F$_2$ has been mostly used in the NH. SO$_2$F$_2$ pollution events seen at the Trinidad Head AGAGE station on the Northern California coast are generally associated with air originating from Southern California where fumigation with SO$_2$F$_2$ is common, while background conditions similar to Mace Head are observed at other times. At urban La Jolla on the Southern California coast, several hundred to several thousand ppt of SO$_2$F$_2$ are frequently observed owing to nearby fumigation with SO$_2$F$_2$, but the lowest observed values agree well with the Mace Head and Trinidad Head baseline records.

[49] Inversions with a 2-D 12-box model lead to a global total lifetime $\tau_{\text{total}}^{G}$ = 36 ± 11 years for SO$_2$F$_2$ which is substantially longer than previous estimates of less than 4.5 years given in a recent European Union report on the environmental fate and behavior of SO$_2$F$_2$ [Swedish Chemical Agency, 2005]. Dissolution and hydrolysis in the ocean is the overwhelmingly dominant global sink with an atmospheric lifetime for oceanic loss $\tau_{\text{ocean}}^{G}$ = 40 ± 13 years. Other tropospheric and stratospheric sinks processes are only marginally important in agreement with kinetic studies [Dillon et al., 2008; Papadimitriou et al., 2008].

[50] Modeled SO$_2$F$_2$ emissions rose from ~0.6 Gg/a in 1978 to ~1.1 Gg/a in 1995 and ~1.9 Gg/a in 2007. But global industrial production estimates based on assumptions about global industrial activity (M. Krieger, Dow AgroSciences, personal communication, 2008) have averaged ~50% higher than the modeled emissions. We have attempted to model this discrepancy as being due to a hypothetical land sink that is proportional to ice-free land surface area, but the discrepancy persisted in the new inversion results. Although no confirming experimental evidence exists, we conclude that besides a yet unknown or underestimated known sink, a possible explanation is that ~1/3 of SO$_2$F$_2$ is destroyed in the fumigation process and only ~2/3 is vented to the atmosphere.

[51] At a mean global mixing ratios of ~1.4 ppt, the radiative forcing of SO$_2$F$_2$ is small and SO$_2$F$_2$ is probably an insignificant source of sulfur to the stratosphere compared to carbonyl sulfide (COS) with a lifetime of 3–6 years and a mixing ratio of ~500 ppt [Chin and Davis, 1995; Kettle et al., 2002; Montzka et al., 2007]. However, given a SO$_2$F$_2$ global warming potential similar to that of CFC-11 (~4780, 100-year time horizon, based on measured infrared cross sections and the modeled lifetime of 36 ± 11 years Papadimitriou et al. [2008]) and in view of likely increases in its future use, continued atmospheric monitoring of SO$_2$F$_2$ is highly warranted.

[52] Acknowledgments. This work was carried out as part of the international AGAGE research program, which is supported in the United States by the Upper Atmospheric Research Program of NASA, in Australia by CSIRO and the Bureau of Meteorology, and in the UK by DEFRA and NOAA. We thank E.J. Dlugokencky, J.W. Elkins, B.D. Hall, and S.A. Montzka at NOAA/GMD; C.D. Keeling and R.F. Keeling at SIO; O. Hermansen, C. Lunder, and N. Schmidbauer at NILU; and R.C. Rhew at University of California, Berkeley, for air samples. We are grateful to D. Barnekow and M. Krieger at Dow AgroSciences for approval to obtain a sample of pure SO$_2$F$_2$ (Vikane) with which we made primary standards. We thank the anonymous reviewers for their comments and questions. We particularly thank M. Krieger for providing the global industrial SO$_2$F$_2$ emission estimates given in this paper and for his feedback. We especially thank J.B. Burkholder at NOAA/CSD for valuable discussions and collaboration on kinetic studies of SO$_2$F$_2$. R. Wanninkhof at NOAA/AOML for providing the initial estimates of the oceanic transfer velocities for the four tropospheric model boxes and for valuable input regarding the modeling of SO$_2$F$_2$ sea-air exchange, and J.E. Shields at SIO for access to her unpublished modeling of our firn air measurements. D.M. Cunnold at GaTech and P.J. Crutzen at SIO provided valuable discussions.

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