

CHAPTER 2

Very Short-Lived Halogen and Sulfur Substances

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CHAPTER 2

VERY SHORT-LIVED HALOGEN AND SULFUR SUBSTANCES

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SCIENTIFIC SUMMARY

Definition of Very Short-Lived Substances

Very short-lived (VSL) substances are substances that have chemical lifetimes comparable with tropospheric transport time scales, with the result that the steady-state mixing ratio of the substance in the troposphere depends on where and when (time of the year) it is released. In practice, this happens for species with atmospheric lifetimes of a few months or less.

Ozone Depletion Potential (ODP) for Halogen Source Gases

- The Ozone Depletion Potential (ODP) of a halogen source gas X ($ODP(X, \bar{x}_e, t_e)$) is defined as the time-integrated effect on stratospheric ozone caused by emission of X at location \bar{x}_e and time t_e relative to the time-integrated effect on stratospheric ozone from the same mass emission of CFC-11 (CCl_3F) at the same location and time.
- In the general case, $ODP(X, \bar{x}_e, t_e)$ consists of two terms: $ODP_{SGI}(X, \bar{x}_e, t_e)$ and $ODP_{PGI}(X, \bar{x}_e, t_e)$. $ODP_{SGI}(X, \bar{x}_e, t_e)$ (source gas injection (SGI) term) and $ODP_{PGI}(X, \bar{x}_e, t_e)$ (product gas injection (PGI) term) represent the effects caused by inorganic halogen atoms that are transported to the stratosphere in the form of the source gas and in the form of degradation products, respectively.
- For long-lived source gases, the value for $ODP_{SGI}(X, \bar{x}_e, t_e)$ is independent of \bar{x}_e and t_e , and $ODP_{PGI}(X, \bar{x}_e, t_e)$ is negligible in comparison to $ODP_{SGI}(X, \bar{x}_e, t_e)$. Thus, a single value of ODP can be obtained based on the atmospheric lifetime of the source gas independent of location and time of emission. These are the traditional single-value ODPs reported in the literature.
- For VSL source gases, the $ODP_{SGI}(X, \bar{x}_e, t_e)$ value depends on the location and time of emission. The $ODP_{PGI}(X, \bar{x}_e, t_e)$ value depends also on the properties of the degradation products.
- If degradation of the VSL source gases gives rise to significant inorganic halogen concentration in the upper troposphere (UT), this may lead to ozone depletion in that region. The question then arises if this depletion should be added to the ODP value, which traditionally refers only to depletion in the stratosphere. It also points to the need to evaluate the role of halogen chemistry in the UT.

Transport from the Boundary Layer to the Stratosphere

- The most efficient route for irreversible transport of VSL source gases and their degradation products from the surface to the stratosphere is in the tropics, because the vertical transport times from the surface to the upper troposphere are short, and air that enters the stratosphere through the tropical tropopause remains there for more than a year.
- In the tropics, the transition from tropospheric to stratospheric air takes place in a “tropical tropopause layer” (TTL) between the secondary tropical tropopause (STT, 11-13 km) and the thermal tropical tropopause (TTT, 16-17 km). Transport of VSL source gases and degradation products from the surface to the UT and the lower part of the TTL is primarily through convection. From the TTL, a small fraction of the air enters the stratosphere via slow ascent through the tropical tropopause or via isentropic transport into the extratropical lower stratosphere.
- Current estimates indicate that air at the base of the TTL is replaced by convection from the tropical boundary layer on a time scale of 10-30 days. Thus, a significant fraction of the emitted VSL source gases can be expected to reach the TTL in regions of deep convection.
- In the extratropics, exchange across the tropopause maintains a “transition layer” of 1-2 km with chemical characteristics intermediate between those of the UT and LS (lower stratosphere). Frontal lifting can transport air on time scales of a few days to the UT or even occasionally into the LS. Through such mechanisms, VSL source gases are expected to enter the transition layer.

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Chemistry for VSL Halogens

- Inorganic chlorine, bromine, and iodine have the potential to destroy stratospheric ozone. For the same concentration in the stratosphere, iodine is most efficient in removing ozone, followed by bromine and chlorine. Laboratory data on iodine stratospheric chemistry have led to downward revision of the iodine efficiency in depleting ozone in the stratosphere. The estimated efficiency factor relative to chlorine (~150-300) is still higher than that of bromine (~45).
- The main uncertainties in estimating the impact of VSL halogen source gases on stratospheric ozone lie in the physical and dynamical processes transporting halogen into the stratosphere and the behavior of their intermediate degradation products; uncertainties in the gas-phase chemistry of the source gases are minor.
- The products expected from many of the bromine and iodine VSL source gases considered in this chapter are all rapidly converted to inorganic halogen. The inorganic halogen multiphase chemistry for bromine and iodine is not very well known. Heterogeneous processes that recycle reservoir species to reactive inorganic bromine and iodine may significantly increase the efficiency of halogen injection (via the PGI pathway) into the stratosphere.
- The odd-hydrogen (HO_x) chemistry in the upper troposphere is very critical both for the destruction/production of ozone and for the delivery of VSL source gases to the stratosphere. The understanding of this chemistry requires a better knowledge of the sources and processes for the oxygenated organics (carbonyl compounds, peroxides, etc.) and for the nitrogen oxides (NO_x) and total reactive nitrogen (NO_y) species.

VSL Halogen Source Gases in the Present-Day Atmosphere

- The observed concentrations of VSL halogen source gases are typically a few parts per trillion (ppt) for bromine and iodine VSL source gases, and up to 20 ppt for VSL chlorine source gases. The majority of these gases are of natural origin.
- Two model studies simulated the atmospheric distribution of bromoform (CHBr_3) assuming a simplified uniform (space and time) ocean source. The calculated atmospheric distributions indicate that an average surface mixing ratio of 1.5 ppt at the surface could maintain about 1 ppt of inorganic bromine in the stratosphere. The simulation shows that one-half to three-fourths of the bromine enters the stratosphere in the form of inorganic products. These results can be used as a guideline for estimating contributions from other source gases that have local photochemical lifetimes of about 10 days, no long-lived intermediate degradation product, and relatively uniform sources over the globe.
- Very short-lived bromine and iodine source gases with surface concentrations of a few ppt could have large effects on the current inorganic bromine and odd-iodine budget because the stratospheric concentrations of inorganic bromine and iodine are about 20 ppt and less than 1 ppt, respectively. The transfer of inorganic bromine from the UT may account for the current discrepancy in the stratospheric inorganic bromine budget (as discussed in this chapter and in Chapters 3 and 4).

Modeling Studies to Determine Values for the ODP of n-Propyl Bromide

- n-propyl bromide (n-PB; $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$) is removed by reaction with OH, with local photochemical lifetimes in the tropical troposphere of about 10-20 days. Laboratory data indicate that its degradation products, and particularly bromoacetone, have lifetimes shorter than a day.
- Given the complexity of atmospheric processes, three-dimensional numerical models are the preferred tool to evaluate the ODP for VSL source gases. Results for n-PB from three separate model studies that computed $\text{ODP}(\text{n-PB}, \bar{x}_e, t_e)$ were assessed. These results can be used as a guideline for other gases with similar local photochemical lifetimes (~10 days) and degradation schemes.

- Two of the three studies provided values only for $ODP_{SGI}(n\text{-PB}, \bar{x}_e, t_e)$. In the third study, which computed contributions from $ODP_{PGI}(n\text{-PB}, \bar{x}_e, t_e)$, the values of $ODP(n\text{-PB}, \bar{x}_e, t_e)$ are 0.04 for uniform emission over land. In this case, 0.5% of the bromine emitted as n-PB reaches the stratosphere, with about two-thirds entering in the form of degradation products. The model simulations also give 0.1 for tropical emission and 0.02-0.03 for emissions restricted to Northern midlatitudes.

VSL Sulfur Species and Stratospheric Sulfate

- A sulfur (S) source of 0.06-0.15 Tg (S) yr⁻¹ is needed to maintain the observed burden of the background stratospheric sulfate layer during periods with low volcanic activity. Current model estimates indicate that degradation of carbonyl sulfide (OCS) in the stratosphere can account for 20-50% of the needed source, with the balance from transport of sulfur VSL gases (dimethyl sulfide (DMS; CH₃SCH₃), hydrogen sulfide (H₂S), sulfur dioxide (SO₂)) and sulfate formed in the troposphere.
- Our current best estimates for the surface sources of sulfur are 10-30 Tg (S) yr⁻¹ for DMS, 1-2 Tg (S) yr⁻¹ for OCS, 0.5-1.5 Tg (S) yr⁻¹ for CS₂, 6-9 Tg (S) yr⁻¹ for H₂S, and 67-100 Tg (S) yr⁻¹ for SO₂. Emission from aircraft engines provides a source of 0.06 Tg (S) yr⁻¹ in the upper troposphere and lower stratosphere.
- Model simulations show that a few tenths of one percent of the SO₂ emitted at the ground reaches the stratosphere. This is consistent with estimates for VSL halogen source gases. For DMS, multiphase oxidation may occur and reduce its possible transfer to the UT.
- Previous climate calculations assumed that the change in stratospheric sulfate loading is proportional to changes in total SO₂ emission. Changes in the spatial distribution of the emission can have a large effect. Depending on how much of the sulfur gas is converted to small sulfate particles in the UT, the change in surface area per unit mass of sulfur transferred to the stratosphere could differ.

Model Evaluations

- In order to evaluate the contribution of VSL source gases to halogen and sulfur loading, global 3-D model simulations are required. Simulating aerosol microphysics in the troposphere with very short time constants in global-scale models presents a large challenge. Significant uncertainties exist in the treatment of dynamical and physical loss processes in such models.
- Further evaluation of model performance against observations is necessary, particularly relating to rapid transport processes and treatments of cloud scavenging. Various tracers can be used to test specific components: radon-222 and short-lived hydrocarbons for continental convection; methyl iodide, dimethylsulfide, and ozone for marine convection; lead and beryllium isotopes, and soluble gases for precipitation scavenging; and ozone for stratosphere-troposphere exchange.

2.1 INTRODUCTION

An important component of previous Assessments (e.g., WMO, 1999, 1995) is the discussion of the observed concentrations, budgets, trends, and atmospheric lifetimes of source gases that affect stratospheric ozone. These gases are mostly emitted at the surface. The source gas and its degradation products are transported to the stratosphere, where they could affect the ozone abundance. Examples of these include nitrogen species from nitrous oxide (N_2O); chlorine, bromine, and iodine species from organic halogen-containing chemicals; and methane (CH_4) reacting to produce water vapor in the stratosphere. Sulfur species found in the troposphere (e.g., carbonyl sulfide (OCS), carbon disulfide (CS_2), hydrogen sulfide (H_2S), dimethyl sulfide (DMS, CH_3SCH_3), sulfur dioxide (SO_2)) provide the source of sulfur to maintain the stratospheric sulfate layer. The sulfate aerosol particles provide sites for heterogeneous reactions that control the partitioning of the nitrogen and halogen radicals. One aim of the Assessments is to establish the tools that enable one to predict how changes in emissions of the various source gases would affect ozone. In the case of the halogen species, it is done in terms of the equivalent chlorine concentration estimated from emissions and lifetimes. A similar connection could be made for the sulfur source gases if one could predict how the stratospheric sulfate may change in response to changes in emissions. In this chapter, we restrict the discussion to halocarbons and the sulfur gases. Other species with similar lifetimes are affected by many of the same processes discussed in this chapter. One example is oxides of nitrogen released at the ground (from combustion and biomass burning) and produced in the free troposphere (by lightning or aircraft engines). They are not included in this chapter.

The purpose of this chapter is to discuss how very short-lived (VSL, defined later in this section) substances released at the surface or produced in situ in the troposphere could affect ozone in the stratosphere. Because the subject is relatively new, this chapter will deviate from the standard approach of providing a detailed review and assessment of the information in the published literature. The current state of our understanding does not provide concrete evaluations to assess the merit of the approaches and make recommendations for specific values, e.g., of Ozone Depletion Potentials (ODPs). Instead, the chapter focuses on outlining viable approaches with emphasis on how observations may be used in future evaluations. If certain simplifying assumptions are made, order-of-magnitude estimates for some of the parameters can be provided so that policymakers can start to consider how best to approach the problem. The emphasis of the chapter is on the issues needed to be resolved and the observations needed for evaluation.

In the discussion, it is often convenient to distinguish among the different forms in which the halogen atoms and sulfur atoms are transported to the stratosphere. Halogen atoms bound in the source gases and the intermediate degradation products are referred to here as organic halogen. The final products are referred to as inorganic halogen; these include, in the case of chlorine, the reservoir species (hydrogen chloride (HCl), chlorine nitrate (ClONO_2), hypochlorous acid (HOCl)) and the radical species (atomic chlorine (Cl), chlorine monoxide (ClO)). For sulfur, an analogous approach would identify OCS, CS_2 , H_2S , and DMS as source gases, and SO_2 and various forms of sulfate (SO_4) in gaseous, liquid, or solid form as the final product. As seen in Section 2.6, this turns out not to be desirable, because SO_2 and SO_4 are also released at the surface. We will refer to a sulfur species as sulfate or sulfate precursor in the discussion.

A major goal in the study of halogen source gases has been to track the life cycle of a source gas so that one can evaluate how its emission may affect the inorganic halogen budget in the present-day stratosphere. This is accomplished by combining the amount of the source gas emitted at the surface with the percentage of the emitted halogen atoms that is delivered to the stratosphere. It is important to provide values for the latter because it allows one to define the relative ODP of an individual source gas. Traditional methods for evaluating the contribution of organic halogen source gases with lifetimes of 1 year or longer have been reviewed and assessed in previous Assessments (e.g., WMO, 1995, 1999). However, such methods cannot be applied to VSL species. To understand why, we examine the processes that deliver the final products to the stratosphere. For ease of discussion, we will present the arguments in the context of the halogen species. It should be noted that many of the ideas are equally applicable to the sulfur species.

Figure 2-1 illustrates that there are two pathways for delivering the final products to the stratosphere. For the source gas injection (SGI) pathway, the source gas is transported to the stratosphere and then reacts to release the halogen atoms. For a given emission location and time, its efficiency depends mostly on the properties of the source gas (essentially its removal rate by chemical or physical processes in the troposphere as compared with the transport rate from the ground to the stratosphere). The product gas injection (PGI) pathway involves transport to the stratosphere of intermediate or final products produced in the troposphere. Its efficiency depends also on the properties of the degradation products.

To put things in perspective, we provide some rough numerical estimates for the two pathways for long-lived source gases that have uniform mixing ratios in the

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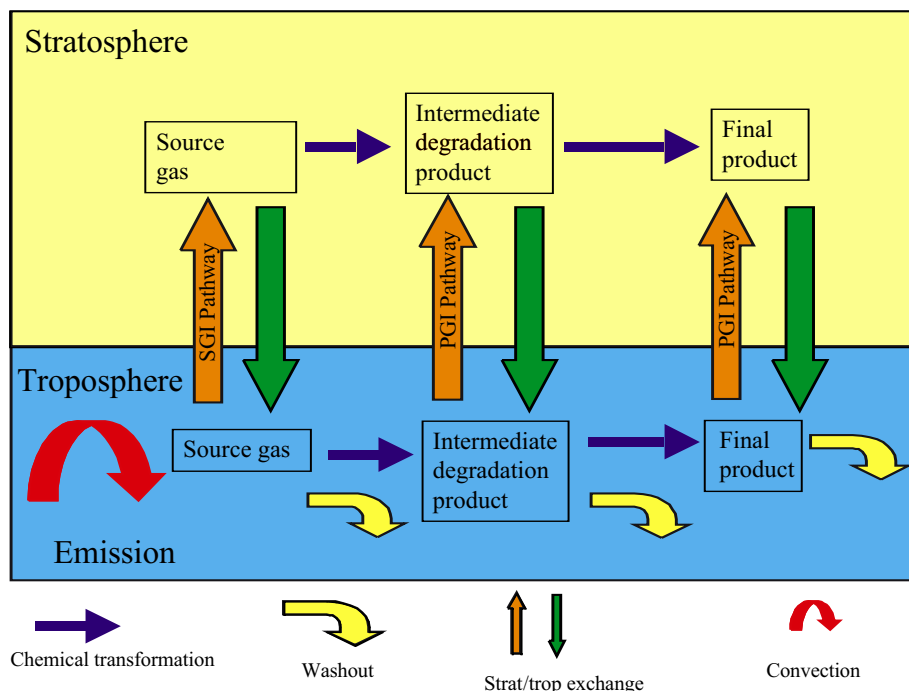


Figure 2-1. Schematic diagram showing the two pathways through which a source gas released at the surface delivers its degradation products to the stratosphere. The orange arrows and green arrows represent transport into and out of the stratosphere, respectively. The two pathways are labeled SGI for source gas injection and PGI for product gas injection.

troposphere. Long-lived source gases that are inert in the troposphere (most chlorofluorocarbons) are recycled between the troposphere and stratosphere until they are all removed via photochemical reactions in the stratosphere. Thus, 100% of the final product is delivered to the stratosphere via the SGI pathway. For long-lived source gases that are removed efficiently in the troposphere (most hydrogenated chlorofluorocarbons), at least 90% of the mass burden is found in the troposphere at steady state. If we assume that the local lifetimes in the troposphere and stratosphere are similar, this would imply that 90% of the final product is released in the troposphere. Thus, only 10% is delivered to the stratosphere via the SGI pathway. If one assumes that less than 1% of the degradation products (in the form of intermediate degradation products or inorganic halogen) released in the troposphere is transported to the stratosphere, then the supply from the PGI pathway (0.009 of emission) is a factor of 10 smaller than from the SGI pathway (0.1 of emission). This is why the contribution from the PGI pathway is usually ignored in considering the long-lived source gases.

We now explain the criteria for classifying a substance as VSL, as distinct from those discussed in Chapter 1 of this report. The established method for estimating inorganic halogen loading from the SGI pathway depends on the observed fact that the mixing ratio of the long-lived source gas is essentially uniform in the troposphere. [Note that the key issue is the difference in mixing ratio between

the boundary layer (BL) and the upper troposphere (UT). A small interhemispheric difference (~20%) in the BL will not affect the accuracy.] In these cases, the fraction of the emitted halogen atoms entering the stratosphere is independent of the location and time of emission. The inorganic halogen loading in the stratosphere can be estimated from the steady-state burden of the source gas, which is related to its atmospheric lifetime. Details of the transport processes in the troposphere play no role. As the local lifetime of the source gas gets shorter, its mixing ratio will no longer be uniform in the troposphere. The method used for long-lived species is no longer accurate when the mixing ratio in the UT is less than half of the mixing ratio in the BL. A survey of chemicals in the atmosphere indicates that this occurs when the local lifetime (inverse of the local removal rate) is 0.5 years or shorter. This will serve as the criteria for identifying VSL species.

The fraction of the emitted halogen atoms that are transported to the stratosphere via the PGI pathway depends on the properties of the intermediate and final products as well. Consider first the situation where the intermediate products are so short lived that, for practical purposes, the inorganic halogen species can be treated as being produced by the initial reaction experienced by the source gas. Many of the inorganic halogen species are water soluble or will react in solution to form water-soluble products. They are removed efficiently in the lower troposphere, with a local residence time of about 10 days.

In order for the PGI pathway to provide an effective source to the stratosphere, the products should be produced at least as fast as the washout rate (Ko et al., 1997). Thus, the PGI pathway will be important if the local photochemical lifetime of the source gas is of the order of 10 days or shorter.

The properties of the intermediate products could change the estimate in a significant way. If the intermediate products are long lived in the troposphere (i.e., with a photochemical lifetime longer than the source gas or the washout lifetime of the inorganic halogen), they could serve as a vehicle for transporting halogen atoms to the stratosphere and deliver much more of the degradation products via the PGI pathway. An example of an intermediate product having lifetime longer than the source gas is phosgene (COCl_2) formed from degradation of trichloroethene (C_2HCl_3). At the same time, if the local photochemical lifetimes of the intermediate products in the stratosphere are longer than their residence times in the stratosphere, they may be removed from the stratosphere before they release their halogen atoms. This will effectively decrease the efficiency of the SGI pathway (see Kindler et al., 1995).

Many of the same issues apply to the VSL sulfate precursor gases and how their fates in the troposphere would affect the stratospheric aerosol layer. In addition to the release of source gases at the surface, there is a direct way of injecting sulfur species into the stratosphere through explosive volcanic eruptions. In this chapter, we will briefly review the effects of volcanoes, building on work from the previous Assessment (Godin and Poole et al., 1999). The major emphasis here is on the role of the VSL precursor gases.

The structure of this chapter is as follows. Section 2.2 discusses the transport mechanisms in the troposphere and cross-tropopause exchange, and the chemical environment in the upper troposphere. Section 2.3 describes the removal mechanisms of the VSL halogen source gases and their degradation products. It also includes a brief discussion of the ozone removal efficiency of iodine in the stratosphere. Section 2.4 discusses how VSL halogen source gases may contribute to the inorganic halogen budget in the current stratosphere. The observations for these source gases are reviewed, with emphasis on our understanding of the budgets. Section 2.5 focuses on the issue of evaluating the inorganic halogen loading estimates and ozone depletion estimates of VSL halogen source gases. In addition to natural species, the discussion includes industrial species and the information that is needed on emission inventories to estimate their impact. Finally, Section 2.6 discusses the effects of sulfur-containing VSL gases and how they affect future trends in the stratospheric sulfate layer.

2.2 DYNAMICAL AND CHEMICAL CHARACTERISTICS OF THE UPPER TROPOSPHERE (UT) AND THE TROPICAL TROPOPAUSE LAYER (TTL)

The critical parameters for understanding the processes that control fluxes of key trace gases from the troposphere to the stratosphere are the mixing ratios of the trace gases in the upper troposphere (UT) and in the tropical tropopause layer (TTL) and the transport rates across the tropopause. We employ the following definitions in this chapter: the UT is the region from about 8-12 km, which is capped by the tropopause in the extratropics, and which overlaps with the lowest part (~1 km) of the TTL in the tropics. The TTL is bounded above by the thermal tropical tropopause (TTT; defined here as the cold point of the sounding) at about 16-17 km, and bounded below by a secondary tropical tropopause (STT) at 11-13 km. The STT is related to large-scale circulation in that it corresponds to the maximum Hadley-cell outflow (Highwood and Hoskins, 1998). At these levels, convection is no longer able to maintain a moist adiabatic temperature lapse rate, owing to the rapid decreases with height of the cumulus mass flux, and IR radiative cooling. Within the TTL there is a gradual transition from tropospheric to stratospheric dynamical and chemical characteristics. However, the rapid decrease with height of the convective outflow, and the rapid transition from clear-sky radiative cooling to radiative heating, combine to make the transition at the TTT fairly sharp (see, e.g., Folkins et al., 1999; Hartmann et al., 2001; Jensen et al., 2001; Thuburn and Craig, 2000). The TTL is a relatively new concept, and its nature and regional variations are still under investigation. The concentrations of trace gases in the UT and TTL are controlled by transport, physical and chemical removal processes in the troposphere and lower stratosphere, and the location and timing of emissions.

We consider two broad classes of transport mechanisms, illustrated in Figure 2-2. The first is deep moist convection, which transports air rapidly from the boundary layer to the UT, with a fraction detraining well into the TTL and some directly into the stratosphere. The second is large-scale stratosphere-troposphere exchange (STE), which transports air from the TTL upward into the stratospheric overworld, and laterally into the extratropical lower stratosphere. In addition, this section includes a discussion of extratropical STE, the chemical environment in the UT and TTL, and a survey of the database of observations that are needed to critically evaluate the results of models.

The numerical simulation of very short-lived substances is difficult because of the wide range of scales on

side convectively active regions, and nearly all air parcels have had recent contact with the tropical boundary layer. Convective clouds are often associated with the formation of precipitation (rain, snow, and graupel) and anvil cirrus clouds. This leads to efficient scavenging of soluble gases by precipitation where convection is active.

Convective events are highly stochastic. An individual cloud can transport air parcels (thermals) from the BL to the UT in less than an hour. However, the actual concentration of the source gases and degradation products in the UT and TTL depends on how quickly they are evacuated from the BL, how often thermals reach and penetrate the UT and the TTL, and how much old air from the midtroposphere (which has much smaller concentrations of the source gas) is entrained into the convective cores.

An estimate for the mean evacuation time for the BL in the tropics can be obtained using relatively well-defined values for the Hadley cell circulation and the clear-sky radiative cooling. The observed annual mean mass flux from the boundary layer in the Hadley circulation between 15°N and 15°S is about 10^{11} kg s⁻¹ (Hartmann, 1994). This, however, is the net mass flux arising from the difference between the upward flux in convection and the clear-sky subsidence. The clear-sky radiative cooling rate in the tropical lower troposphere is ~ 1.6 K day⁻¹ (e.g., Hartmann et al., 2001). Because convective disturbances cover less than 10% of the tropics, the above cooling rate implies a downward mass flux between 15°N and 15°S of about 2.0×10^{11} kg s⁻¹ (assuming descent along a dry adiabat). Thus the upward flux from the boundary layer in convection must be about 3.0×10^{11} kg s⁻¹. Assuming that the BL has a 100-hPa depth, then the mass between 15°N and 15°S is about 1.3×10^{17} kg. The upward flux from the BL then implies an evacuation time of about 5 days if one assumes that the material is taken from the whole BL rather than just from the top of the BL. On the basis of a 3-D general circulation model simulation, Prather and Jacob (1997) estimated a mean evacuation rate of the 130-hPa-deep BL in the tropics of 18% day⁻¹ (see the GISS results in Figure 2-3), which implies an e-folding removal time of 5.5 days, consistent with the above estimate. This estimate is at the low end of the 5-10 day estimate made in Kley et al. (1996) based on data from a different general circulation model, and is slightly longer than the estimate of 4 days made by Cotton et al. (1995). The actual evacuation rate will vary regionally, depending on the strength and frequency of convective events.

The GISS model results in Figure 2-3 show that the magnitude of the mass flux across the STT (1.4 g m⁻² s⁻¹) is about half that of the mass flux out the BL (2.8 g m⁻² s⁻¹). As indicated above, the latter mass flux implies a

replacement time for the BL of about 5 days. Since the TTL and BL have similar depths of about 100 hPa, the average replacement time for the whole TTL by air crossing the STT should be of the order of 10 days. However, the replacement time is not uniform with altitude. Much of the detrainment in the UT and TTL occurs near the STT, and within the TTL the mass flux decreases rapidly with height, but the precise height dependence has not yet been reliably determined. The local replacement time (defined as the replacement time of a layer of air by detrainment from convective clouds) can be estimated by assuming that the upward mass flux from convection is balanced by the clear-sky subsidence. Folkins et al. (2002) used this method to obtain replacement times of 5 days near the STT, and 100 days at 16 km. An alternative estimate can be obtained by using measured profiles of CO and O₃ (Dessler, 2002), yielding 10-30 days for the lower TTL and 50-90 days for the upper TTL. It is difficult to quantify the uncertainty in these estimates at present, but it is likely that global models with different contemporary convection parameterizations could produce numbers that differ by at least a factor of 2.

The replacement time can be used to estimate how much additional chemical transformation has occurred for the VSL species in air parcels since they have left the BL. The actual concentration of the species will depend also on the entrainment of old air as the convective column ascends the free troposphere. If the BL air has been diluted by 50% during the ascent, the replacement time for the TTL by BL air will be a factor of 2 larger than the estimates cited above. Cloud-resolving model simulations (Lu et al., 2000) indicate that only a very small amount of tracers that are produced in situ in the middle troposphere are entrained into the updrafts, but instead are forced aside and downward due to rising thermals. The wealth of literature on studies using cloud-resolving models (e.g., Lu et al., 2000; Redelsperger et al., 2000; Bechtold et al., 2000) reveals the immense complexity of transport in cumulus clouds and the difficulties of representing this in large-scale models.

The general transport characteristics of convection have also been studied using idealized tracers in a 3-D global chemistry-transport model, with a fixed uniform mixing ratio at the surface and a specified local decay rate (Crutzen and Lawrence, 2000). It was found that an insoluble gas with a lifetime of 30 days was 40-50% as abundant in the tropical UT as at the surface, whereas with a lifetime of 10 days the tropical UT abundance was 25-30% of the surface mixing ratio (see Figure 2-4). Lower values were computed in the UT outside the tropics: 25-35% and 10-15% for the 30- and 10-day lifetime tracers, respectively. As discussed above, these estimates depend

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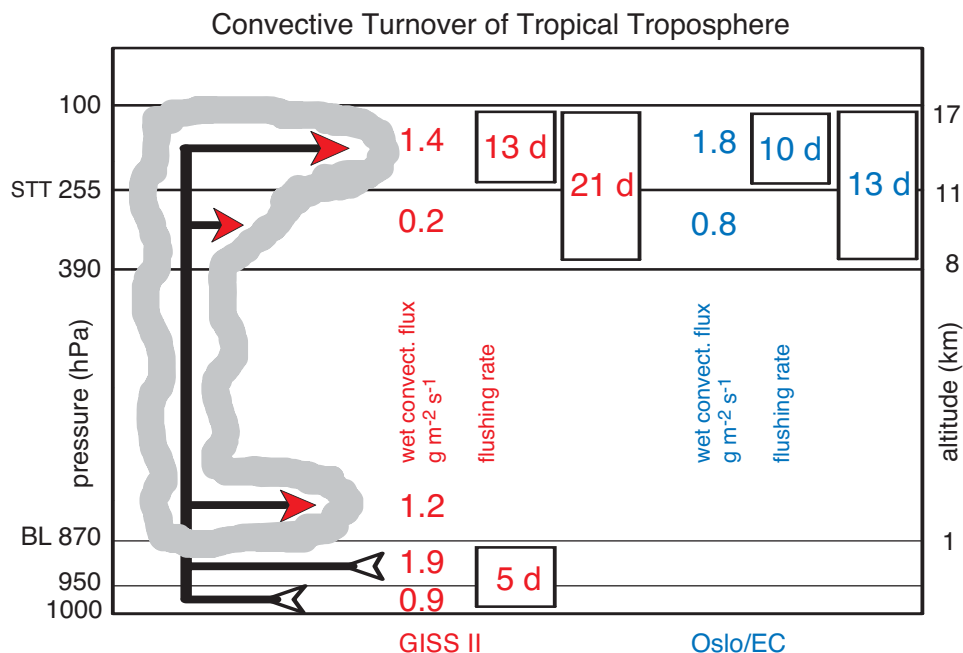


Figure 2-3. Convective turnover rates in the tropical troposphere. The results are from two models, GISS II (Goddard Institute for Space Studies), using winds generated by a general circulation model, and the Oslo CTM, driven by European Centre for Medium-Range Weather Forecasts (ECMWF) winds; based on Prather and Jacob (1997). The gray shaded outline provides a schematic representation of the structure of the convective cloud. The arrows represent entrainment fluxes (lower two arrows) and detrainment fluxes (top three arrows). The average convective mass fluxes (in $\text{g m}^{-2} \text{s}^{-1}$) and the implied turnover time constant (inverse of turnover rate; in days) of the reservoirs are given for each model (in red for the GISS II model and in blue for the Oslo model). The column mass densities in each reservoir are: $1.3 \times 10^6 \text{ g m}^{-2}$ for the boundary layer between 870 and 1000 hPa; $1.4 \times 10^6 \text{ g m}^{-2}$ for the upper troposphere located between 390 and 255 hPa; and $1.6 \times 10^6 \text{ g m}^{-2}$ for the tropical tropopause layer located between 255 and 100 hPa. The values from the GISS II model are calculated for the region between 12°S and 12°N for May-August conditions, whereas those for the Oslo model are for 22°S - 22°N for January-December 1997. Figure courtesy of M. Prather, University of California-Irvine, U.S.

strongly on the respective model formulations, and thus could differ significantly from the results obtained with other models. Such modeling studies, unfortunately, are rarely repeated once the first ones have been published.

The situation is even more complex for soluble gases because of the variable relationship between updraft mass flux and the amount of precipitation. Crutzen and Lawrence (2000) also examined this issue using idealized soluble tracers. Compared with the calculated concentration of an insoluble gas, they found that about 15%, 50%, and 85% of gases with Henry's Law solubility constants of 10^3 , 10^4 , and 10^5 M atm^{-1} , respectively, were scavenged by precipitation before they reached the UT (see Figure 2-5). This result was nearly independent of season, geographical location, and the decay rate applied to the tracers, but was strongly dependent on the assumptions made about whether tracers were rejected from, retained

in, or additionally scavenged by ice, snow, and graupel. Similar studies using cloud-resolving models (Barth et al., 2001; Yin et al., 2001) have also indicated that it is important to consider kinetic limitations to trace gas uptake in precipitation, because assuming Henry's Law equilibrium, as is generally done for the long time steps of global models, will lead to an overestimate of the amount of gases that can be taken up into precipitation, and thus to the scavenging loss of highly soluble gases. A promising approach for future studies is the use of observations of peroxides with various solubilities together with insoluble tracers like CO to test parameterizations of convective scavenging (e.g., Mari et al., 2000). At present it is difficult to apply these results to inorganic halogenated species because of a lack of observations, combined with the fact that they are also produced in situ in the UT and can have highly variable mixing ratios at the ground.

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such as variations in the BL height in association with non-zero large-scale vertical velocities, as well as topographical effects, can also contribute to the evacuation of the BL.

2.2.2 Stratosphere-Troposphere Exchange

Most air arriving in the lower stratosphere passes through the tropical tropopause (e.g., Holton et al., 1995), although net transport of chemical constituents across the subtropical and extratropical tropopauses is also known to take place. Because the net large-scale motion is upward in the tropical lower stratosphere and downward in the extratropical lower stratosphere, air entering the lower stratosphere via the tropical tropopause is believed to have a larger residence time (>1 year) in the stratosphere. The precise mechanisms of the cross-tropopause transport and their consequences for short-lived substances are still controversial. Furthermore, it is also important to know the form of halogenated gases in the UT, because soluble gases are subject to removal from the UT by precipitation (as discussed in the previous section), as well as by slower sedimentation of cirrus ice (Lawrence and Crutzen, 1998), both of which can occur at rates that can compete with the residence time of gases in the TTL. In this section, we discuss how one may obtain estimates of the flux across the tropopause by examining the mixing ratios of the species near the tropopause and the mass flux across the tropopause.

2.2.2.1 EXCHANGE ACROSS THE TROPICAL TROPOPAUSE

The transition from air having compositions typical of the troposphere to air typical of the stratosphere does not occur abruptly across the tropical tropopause (TT). Above the level where the clear-sky mass flux is mostly upward, air parcels are rising slowly into the stratosphere, driven by the Brewer-Dobson circulation (speed of order $30\text{--}50\text{ m day}^{-1}$). However, some deep convection penetrates deep into the TTL, and a small fraction of the air leaving the boundary layer (about 0.1%, based on Gettelman et al., 2002) is directly lofted across the TT. Thus, a small fraction of the air encountered directly above and below the TT may have a distinct “BL character.” At the same time, convective overshooting and breaking waves can mix material back downward (Fujiwara et al., 1998; Sherwood and Dessler, 2001), and therefore not all the air in the TTL is transported irreversibly into the stratosphere. Notably, the radiative properties of the TTL are sensitive to the stratospheric O_3 distribution (Thuburn and Craig, 2000), which is in turn sensitive to the transport of constituents through the TTL.

It is also likely that some of the air in the TTL has a stratospheric origin, entering via lateral mixing from the extratropical stratosphere (Figure 2-2). A 20-yr climatology of intrusions from the extratropics into the tropics (Waugh and Polvani, 2000) showed that Rossby wave-breaking events can result in transport of tongues of extratropical air deep into the tropics, and a more detailed look at four Rossby wave-breaking events (Scott et al., 2001) was used to “infer a potentially significant contribution to the global stratosphere-troposphere exchange from the wave-breaking processes.” Studies of mixing in the other direction also help give an indication of the time scales for two-way mixing, which can be comparable with convective time scales. For example, Dethof et al. (2000) reported a contour advection study using European Centre for Medium-Range Weather Forecasts (ECMWF) water vapor fields, in which they found that the isentropic transport of water vapor into the extratropical lower stratosphere is similar in magnitude to upward transport in tropical regions. Furthermore, the work of Strahan et al. (1998) also showed evidence of such isentropic transport based on the seasonal cycle of carbon dioxide simulated in a global chemical transport model.

Finally, according to Rosenlof and Holton (1993), the annual flux across the 100-hPa surface (i.e., TT) in the 15°N and 15°S latitude range is $8.5 \times 10^9\text{ kg s}^{-1}$. Because this is only $\sim 3\%$ of the flux of air out of the tropical BL computed above (Section 2.2.1), the vast majority of the air parcels in deep convection are circulated back down into the free troposphere to eventually re-enter the BL, or are transported isentropically into the extratropical lower stratosphere. A quantification of these fractions is not yet possible.

2.2.2.2 EXCHANGE ACROSS THE EXTRATROPICAL TROPOPAUSE

Exchange of air across the extratropical tropopause is accomplished by processes on a large range of temporal and spatial scales. Although the net (downward) mass exchange rates are controlled by global-scale processes as part of the Brewer-Dobson circulation (Holton et al., 1995), two-way exchange occurs on synoptic and sub-synoptic scales and may have important consequences for chemical species. Synoptic-scale frontal systems and to a lesser extent midlatitude deep convection frequently bring constituents from the boundary layer to the upper troposphere, leading to strong chemical contrasts across the tropopause. These processes may also transport trace constituents, including VSL substances, their degradation products and inorganic halogen into the lowermost stratosphere.

Previous analysis of observed and modeled carbon dioxide (CO_2) levels (Bolin and Bischof, 1970; Strahan et

al., 1998) suggested that there is not a large degree of communication between the UT and lower stratosphere (LS) in midlatitudes because of a clear separation in the seasonal cycle in these different regions. It was postulated that this is due to the bulk of air in the lower extratropical stratosphere originating either through the tropical stratosphere or possibly via lateral transport from the TTL. Analysis of CO₂ data from the Earth Resources (ER-2) high-altitude research aircraft (Hintsa et al., 1998) at 40°N also indicated that most of the air in the lower stratosphere must have entered laterally from the subtropics or tropics. However, there was also evidence that air entered the lower stratosphere directly from the midlatitude upper troposphere in conjunction with mixing processes near the tropopause.

Several more recent observational studies support the existence of a transition layer between the extratropical upper troposphere and lower stratosphere (see Figure 2-2). The layer exhibits chemical characteristics that are intermediate between these two regions. For example, ozone and carbon monoxide (CO) data collected as part of the Stratosphere-Troposphere Experiments by Aircraft Measurements (STREAM) program show the existence of a transition layer that varies in thickness between winter and summer (Hoor et al., 2001), being deeper in summer. A study of total reactive nitrogen (NO_y) and nitrous oxide (N₂O) relationships also showed that more exchange appears to occur in the summer months. This results in a deeper summertime transition layer with higher excess NO_y concentrations (i.e., in excess of what can be expected from photochemical destruction of N₂O) which may have been transported into the transition layer by deep convection (Fischer et al., 2000). Another study showed that frontal uplifting can be important for transporting trace gases (sulfur hexafluoride (SF₆), deuterated water vapor (HDO)) from the subtropics in the troposphere into the Arctic lower stratosphere during winter (Zahn, 2001).

These findings are consistent with seasonal variations in exchange predicted by model studies based on wind fields from large-scale meteorological datasets (Chen, 1995; Haynes and Shuckburgh, 2000). In effect, exchange at middle and high latitudes associated with synoptic eddies and frontal systems produces a transition layer in winter and summer that corresponds to potential temperatures between 310K and 330K. In winter at lower latitudes and higher levels the subtropical jet acts as an effective barrier to transport across the tropopause. Trajectory analyses point to frontal uplifting being a more effective exchange mechanism in the fall (Seo and Bowman, 2001) as well as the winter (Stohl, 2001). In summer the subtropical jet is a less effective barrier, and additional exchange results in a layer extending up to ~360 K. Deep convection at midlatitudes may also be important, but its effects are not yet well quantified.

In principle, the transition layer is a region in which concentrations of VSL substances and their degradation products may be relatively high and in which substantial in situ ozone depletion may take place. Clearly, further clarification of the mechanisms controlling the characteristics of the transition layer, the origin of air in this layer, and its seasonal evolution are needed. Also, time scales on which air parcels remain in this region, e.g., before returning to the troposphere, are unknown. All these factors have implications for the lifetimes and impact of VSL substances and their degradation products in this region.

2.2.3 Chemistry in the UT and TTL

Modeling the transport of VSL substances into the stratosphere requires an accounting of photochemical losses in the troposphere, particularly in the upper troposphere and tropical tropopause layer, where the VSL substances may reside for some time before ascent to the stratosphere. This section focuses mainly on the UT. Currently very few chemical observations of species other than ozone are available in the TTL, which is of critical importance for delivery of VSL substances to the stratosphere. Because the TTL is dry, sources other than water vapor are likely to dominate the supply of odd-hydrogen (HO_x) radicals there.

Loss by photolysis in the UT can be calculated with confidence if absorption cross section and quantum yield data are available, because observed ultraviolet (UV) actinic fluxes in the UT are typically within 15% of values computed from clear-sky radiative transfer models (Shetter et al., 2002). Loss by reaction with hydroxyl radical (OH) and possibly other radicals is more difficult to constrain. Work over the past 5 years has profoundly changed our understanding of HO_x (OH + HO₂) chemistry in the UT (Jaeglé et al., 2001). Aircraft measurements of HO_x radicals (Wennberg et al., 1998; Brune et al., 1998, 1999; Tan et al., 2002) and supporting photochemical models have shown that photolysis of acetone and of convected peroxides and aldehydes provides a large source of HO_x to the UT, comparable with or exceeding the source from oxidation of water vapor (Chatfield and Crutzen, 1984; Jaeglé et al., 1997, 1998a, 2000; Prather and Jacob, 1997; McKeen et al., 1997; Crawford et al., 1999; Müller and Brasseur, 1999; Collins et al., 1999; Wang et al., 2000; Ravetta et al., 2001). Current photochemical models constrained with aircraft observations reproduce observed HO_x concentrations in the UT to within the instrument accuracy (±40%), and account for 60-70% of the observed variance (Jaeglé et al., 2001). Large unresolved biases remain at sunrise and sunset, in cirrus clouds, and under high-NO_x conditions (Brune et al., 1999; Faloona et al., 2000; Jaeglé et al., 2000). The

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40% uncertainty in HO_x translates into errors in the computed concentrations of some VSL species in the UT and TTL.

Our ability to represent UT radical chemistry in global models remains weak, despite the constraints offered by HO_x and NO_x measurements from aircraft. Limitations are not so much in our understanding of the fast HO_x photochemistry as they are in defining the factors that control the concentrations of HO_x precursors and NO_x. Recognized uncertainties in models include (1) the sources of UT NO_x from lightning and from vertical transport of surface emissions, the chemical cycling between NO_x and nitric acid (HNO₃), and possible complications involving peroxyxynitric acid (HNO₄) chemistry (Lawrence et al., 1995; Folkins et al., 1998; Jaeglé et al., 1998b; Keim et al., 1999; Liu et al., 1999; Folkins and Chatfield, 2000; Schultz et al., 2000; Staudt et al., 2002); (2) the sources and chemistry of oxygenated species (peroxides; acetone and other carbonyls) and their deep convective transport to the UT (Zuo and Deng, 1999; Jaeglé et al., 2000; Jacob et al., 2002); and (3) low-temperature rate constants for critical reactions such as methylperoxy radical (CH₃O₂) plus hydroperoxyl radical (HO₂) (Tyndall et al., 2001; Ravetta et al., 2001). The possible role of halogen radicals themselves in influencing HO_x chemistry, and in turn the fate of other halogens, is another unresolved issue (Borrmann et al., 1996; Crawford et al., 1996; Davis et al., 1996; Solomon et al., 1997). These issues are particularly relevant in the presence of convective clouds, and studies with cloud-resolving models (e.g., Wang and Prinn, 2000) are providing additional insights.

2.2.4 Chemical Tracer Observations for Model Evaluation

Observations of chemical tracers offer valuable diagnostic information for testing atmospheric transport of VSL substances in global models. Of particular interest is the simulation of vertical transport from the BL to the UT and across the tropopause. An ideal chemical tracer for testing vertical transport in models should have the following properties: (1) well-defined boundary conditions (concentrations or fluxes) in the BL or in the LS; (2) well-defined production and loss rates within the atmospheric column; (3) an atmospheric lifetime such that the transport processes of interest translate into measurable concentration gradients; and (4) extensive observations for model evaluation statistics. No single tracer fully meets all these conditions, but several are sufficiently close to be helpful.

Table 2-1 summarizes the utility of various chemical tracers for global model evaluation of the key transport processes related to simulations of VSL substances. Current models can reproduce the vertical distributions of radon-222 (²²²Rn), nonmethane hydrocarbons, and CO without evident bias, providing some confidence in the simulation of convective transport from the BL to the UT at least in a global-mean sense (Jacob et al., 1997). Simulations of ozone and ⁷Be indicate that models often overestimate the downward transport of air from the LS to the UT (Bey et al., 2001; Liu et al., 2001). Aircraft observations of soluble gases in convective outflows suggest that the scavenging of these gases during deep convection from the BL to the UT can be successfully described on the basis of Henry's Law solubility and knowledge of gas retention upon cloud freezing (Mari et al., 2000). However, global models generally overestimate HNO₃ in the UT (Thakur et al., 1999), possibly because of insufficient scavenging, including neglect of cirrus precipitation (Lawrence and Crutzen, 1998). Overall, the suite of tracers in Table 2-1 provides important information for testing transport and scavenging processes of key relevance to VSL substances, and it is essential that any chemical transport model used to simulate VSL substances be first validated with an appropriate ensemble of these tracers.

Ozone is a particularly valuable tracer of vertical transport in the UT/LS region, but it has so far been underutilized for this purpose. It is the only gas sampled regularly enough in the UT (by both ozonesondes and aircraft) to provide data representative of actual monthly means (Logan, 1999; Thompson and Witte, 1999; Emmons et al., 2000; Lawrence, 2001). Ozone has a lifetime against chemical loss of months to years in the UT/LS; hence its vertical concentration gradient is primarily determined by transport and chemical production (Folkins et al., 1999). Vertical profiles of ozone across the tropopause region and correlations with water vapor provide an important test for evaluating the nature of the tropopause and cross-tropopause mass flux in global models (Law et al., 2000). Of particular relevance for VSL substances, ozonesonde profiles in the tropics can be used to diagnose vertical transport in the TTL and ascent into the stratosphere (Folkins et al., 1999). One difficulty with the use of ozone as a tracer of vertical transport is that its long lifetime in the UT allows for horizontal propagation of signals associated with vertical transport, and varying chemical production along these horizontal transport trajectories may have a major effect on concentrations (Pickering et al., 1992; Lawrence et al., 1999; Martin et al., 2002).

Table 2-1. Chemical tracers useful for evaluating simulations of vertical transport in the troposphere, scavenging in the troposphere, and stratosphere/troposphere exchange (STE) processes in global models.

| Tracer | Application | Source | Sink ^a | Selected References | Pros and Cons |
|---------------------------------------------------------------------------------------------------------|----------------------------------------|---------------------------------------------|----------------------------------------------------------------------------|-------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|
| ²²² Rn | Vertical transport over continents | Soils | Radioactive decay (lifetime 5.5 days) | Jacob et al. (1997); Dentener et al. (1999) | Pros: well-defined sink, relatively uniform continental source Cons: poor definition of source variability, sparse observations |
| Nonmethane hydrocarbons, CO | Vertical transport over continents | Anthropogenic and biogenic emissions | Reaction with OH | Blake et al. (1997); Bey et al. (2001) | Pros: extensive aircraft data, correlations between species provide additional constraints Con: poor source definition |
| CH ₃ I | Vertical transport over oceans | Oceans | Photolysis (lifetime ~5 days in tropics) | Blake et al. (1996); Bell et al. (2002) | Pro: extensive aircraft data Con: poor source definition |
| ²¹⁰ Pb | Vertical transport, aerosol scavenging | Decay of ²²² Rn | Wet deposition | Preiss et al. (1996); Rasch et al. (2000) | Pros: extensive surface data, good source definition Con: sparse aircraft data |
| ⁷ Be | STE, subsidence | Cosmic rays | Radioactive decay (lifetime 77 days), wet deposition | Dibb et al. (1997); Liu et al. (2001) | Pros: extensive surface data, good source definition Con: sparse aircraft data |
| ¹⁰ Be | STE (together with ⁷ Be) | Cosmic rays | Wet deposition (lifetime against radioactive decay ~10 ⁶ years) | Dibb et al. (1994); Koch and Rind (1998) | Pro: well-defined STE tracer Con: very sparse data |
| ¹⁴ CO | STE, OH | Cosmic rays | Reaction with OH (lifetime 1-3 months) | Jöckel et al. (1998); Jöckel et al. (2002) | Pro: well-defined source distribution Cons: uncertain total source strength, sparse aircraft data |
| O ₃ | Deep convection, STE | Photochemistry, transport from stratosphere | Photochemistry, deposition | Folkins et al. (1999); Logan (1999) | Pros: extensive sonde and aircraft data, correlation with water vapor provides additional constraints Con: complicated chemistry |
| Soluble gases: ^b CH ₃ OOH, HCHO, H ₂ O ₂ , HNO ₃ | Scavenging in deep convection | Boundary layer chemistry | Scavenging, chemistry | Mari et al. (2000); Crutzen and Lawrence (2000) | Pros: extensive aircraft observations Cons: difficulty of separating convective transport and scavenging processes |

^a All lifetimes are given as “e-folding” lifetimes, which are the inverse of the first-order removal rate.

^b CH₃OOH, methyl hydroperoxide; HCHO, formaldehyde; H₂O₂, hydrogen peroxide; HNO₃, nitric acid.

2.3 ATMOSPHERIC CHEMISTRY OF HALOGENATED VERY SHORT-LIVED (VSL) SUBSTANCES

This section presents an assessment of the state of knowledge of the kinetics and mechanisms of the chemical processes that determine the local lifetimes and distributions of the VSL organic halogen source gases and their degradation products in the atmosphere. The compounds to be considered are summarized in Table 2-2. They were selected because they have been either observed in the atmosphere or proposed for applications

that may lead to release. Fully fluorinated VSL substances are not covered in this Assessment, because the F-containing radicals produced in their degradation do not deplete ozone.

Section 2.3.1 deals with the kinetic data and reaction mechanisms for the organic source gases, which determine the efficiency of the SGI (source gas injection) pathway, as defined in Section 2.1. The efficiency of the PGI (product gas injection) pathway depends on the kinetic data and reaction mechanisms of the degradation products and the inorganic halogen species. These are discussed in Section 2.3.2. Some of the species were

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Table 2-2. VSL organic halogen source gases assessed in this report.

| Source Gas | Formula |
|----------------------------------------------------|----------------------------------------------------------------------------------------|
| Bromochloromethane ^a | CH ₂ BrCl |
| Dibromomethane (methylene bromide) ^a | CH ₂ Br ₂ |
| Dibromochloromethane ^a | CHBr ₂ Cl |
| Bromodichloromethane ^a | CHBrCl ₂ |
| Tribromomethane (bromoform) ^a | CHBr ₃ |
| 1-bromopropane (n-propyl bromide or n-PB) | n-C ₃ H ₇ Br; CH ₃ CH ₂ CH ₂ Br |
| Iodomethane ^a | CH ₃ I |
| Trifluoroiodomethane ^a | CF ₃ I |
| Iodoethane (ethyl iodide) ^a | C ₂ H ₅ I; CH ₃ CH ₂ I |
| 1-iodopropane (n-propyl iodide) ^a | n-C ₃ H ₇ I; CH ₃ CH ₂ CH ₂ I |
| 2-iodopropane (isopropyl iodide) ^a | i-C ₃ H ₇ I; CH ₃ CHICH ₃ |
| Chloriodomethane ^a | CH ₂ ClI |
| Bromiodomethane | CH ₂ BrI |
| Diiodomethane ^a | CH ₂ I ₂ |
| Dichloromethane (methylene chloride) ^a | CH ₂ Cl ₂ |
| Trichloromethane (chloroform) ^a | CHCl ₃ |
| Trichloroethene (trichloroethylene) ^a | C ₂ HCl ₃ ; CHClCCl ₂ |
| Tetrachloroethene (perchloroethylene) ^a | C ₂ Cl ₄ ; CCl ₂ CCl ₂ |
| 1,2-dichloroethane | C ₂ H ₄ Cl ₂ ; CH ₂ ClCH ₂ Cl |

^a Assessed in the 1999 Assessment (Kurylo and Rodríguez et al., 1999), which dealt only with the atmospheric observations of these species and their interpretation. The laboratory chemical data were not assessed in detail.

assessed in the most recent Assessment report (Kurylo and Rodríguez et al., 1999), and the current Assessment provides an update and extends that work to include the inorganic halogen chemistry in the UT/LS region. The degradation mechanism for n-propyl bromide is discussed in Section 2.3.3. Section 2.3.4 provides the state of knowledge of iodine chemistry in the stratosphere, which is used for the evaluation of the ozone removal efficiency of iodine.

2.3.1 Removal of the Halogen Source Gases

The atmospheric removal of the VSL halogen source gases under consideration is primarily initiated via reaction with the OH radical and/or by UV photodissociation. Removal via reactions with Cl atoms and nitrate radicals (NO₃) is expected to be of only minor importance. Table 2-3 summarizes the kinetic and photochemical parameters for the VSL halogen source gases. For larger molecules such as n-propyl bromide (n-PB, CH₃CH₂CH₂Br), the reaction rate constant with OH depends on the site of the OH reaction (see also Section 2.3.3).

Table 2-4 summarizes estimated values of the local lifetimes for some VSL halocarbons. For the chlorine- and bromine containing compounds, reaction with OH is the dominant loss process, apart from tribromomethane (CHBr₃) and dibromochloromethane (CHBr₂Cl), where photolysis contributes at least a comparable amount. For alkyl iodides (such as CH₃I, C₂H₅I, n-C₃H₇I, i-C₃H₇I, CH₂ClI, CH₂BrI, and CH₂I₂), photolysis is always the dominant loss process leading to prompt release of iodine atoms:



Local lifetimes for these iodides can be estimated from their absorption cross sections (Rattigan et al., 1997; Roehl et al., 1997; Mössinger et al., 1998): 4-12 days for CH₃I, 2-8 days for C₂H₅I, 1-3 days for i-C₃H₇I, 0.5-1.5 days for n-C₃H₇I, hours for CH₂ClI and CH₂BrI, and minutes for CH₂I₂. The ranges reflect variations with latitude, altitude, and seasons. Reaction with OH may also be a significant loss process for n-C₃H₇I and i-C₃H₇I, but I atoms are still believed to be released promptly (Cotter et al., 2001).

Table 2-3. Kinetic and photochemical parameters for the degradation reactions of halogenated VSL source gases.

| Species | OH Rate Constant, k ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) | $k_{300\text{K}}$ ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) | Photolysis Rate Constant, J^a (s^{-1}) | Comments and References ^b |
|--------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| CH ₂ BrCl | $2.0 \times 10^{-12} \exp(-870/T)$ | 1.1×10^{-13} | 7.7×10^{-10} | Sander et al. (2002) |
| CH ₂ Br ₂ | $2.0 \times 10^{-12} \exp(-840/T)$ | 1.2×10^{-13} | $<1 \times 10^{-8}$ | Sander et al. (2002); Kurylo and Rodríguez et al. (1999) |
| CHBr ₂ Cl | | 5.7×10^{-14} | 7.2×10^{-8} | Chiorboli et al. (1993); Kurylo and Rodríguez et al. (1999) |
| CHBrCl ₂ | | 1.2×10^{-13} | 5.2×10^{-8} | Bilde et al. (1998); Kurylo and Rodríguez et al. (1999) |
| CHBr ₃ | $1.35 \times 10^{-12} \exp(-600/T)$ | 1.8×10^{-13} | 1×10^{-6} | Sander et al. (2002); Kurylo and Rodríguez et al. (1999) |
| n-C ₃ H ₇ Br | $3.1 \times 10^{-12} \exp(-330/T)$ $6.6 \times 10^{-18} T^2 \exp(154/T)$ $k_\alpha = 1.44 \times 10^{-12} \exp(-450/T)$ $k_\beta = 2.5 \times 10^{-18} T^2 \exp(265/T)$ $k_\gamma = 2.9 \times 10^{-12} \exp(-957/T)$ | 1.0×10^{-12} 9.9×10^{-13} $k_\alpha/k = 0.32$ $k_\beta/k = 0.56$ $k_\gamma/k = 0.12$ | $<1 \times 10^{-8}$ | First rate constant value from Sander et al. (2002), second value and third set of values from Gilles et al. (2002) (see Figure 2-8 for explanation of α , β , and γ); J values from Herndon et al. (2001) and Kozlov et al. (2002) |
| i-C ₃ H ₇ Br | $1.75 \times 10^{-12} \exp(-260/T)$ $3.6 \times 10^{-12} \exp(-390/T)$ | 7.4×10^{-13} 9.7×10^{-13} | | Sander et al. (2002), Teton et al. (1996); no data |
| CH ₃ I | $2.9 \times 10^{-12} \exp(-1100/T)$ | 7.2×10^{-14} | 3×10^{-6} | Sander et al. (2002); Roehl et al. (1997) |
| CF ₃ I | $2.8 \times 10^{-11} \exp(-2100/T)$ | 2.4×10^{-14} | 8×10^{-6} | Sander et al. (2002), Gilles et al. (2000); Rattigan et al. (1997), Roehl et al. (1997), Solomon et al. (1994b) |
| C ₂ H ₅ I | | 3×10^{-13} 7.7×10^{-13} | 5×10^{-6} | Estimation based on correlation between Cl and OH abstraction rate coefficients from Cotter et al. (2001); Roehl et al. (1997) |
| n-C ₃ H ₇ I | | 1.47×10^{-12} | 2×10^{-5} | Carl et al. (1998); Roehl et al. (1997) |
| i-C ₃ H ₇ I | | 1.22×10^{-12} | 8×10^{-6} | Carl et al. (1998); Roehl et al. (1997) |
| CH ₂ ClI | | | 1×10^{-4} | No kinetic data; Rattigan et al. (1997), Roehl et al. (1997) |
| CH ₂ BrI | | | 3×10^{-4} | No kinetic data; Mössinger et al. (1998) |
| CH ₂ I ₂ | | | 4×10^{-3} | No kinetic data; Mössinger et al. (1998), Roehl et al. (1997) |
| CH ₂ Cl ₂ | $1.9 \times 10^{-12} \exp(-870/T)$ | 1.0×10^{-13} | | Sander et al. (2002); no data |
| CHCl ₃ | $2.2 \times 10^{-12} \exp(-920/T)$ | 1.0×10^{-13} | | Sander et al. (2002); no data |
| C ₂ HCl ₃ | $5.0 \times 10^{-13} \exp(445/T)$ | 2.2×10^{-12} | | Atkinson et al. (2001); no data |
| C ₂ Cl ₄ | $9.4 \times 10^{-12} \exp(-1200/T)$ | 1.7×10^{-13} | | Atkinson et al. (2001); no data |
| CH ₂ ClCH ₂ Cl | $1.05 \times 10^{-11} \exp(-1142/T)$ | 2.3×10^{-13} | | Qiu et al. (1992); no data |

^a The values for the photolysis rate constants are globally and seasonally averaged estimates for 5-km altitude based on cross sections and quantum yields measured in several laboratories (because different models were used, the values should be considered approximate).

^b References cited for photolysis follow semicolon. Rate constants, cross sections, and quantum yields that have been evaluated in International Union of Pure and Applied Chemistry (IUPAC) (Atkinson et al., 2001) and NASA Jet Propulsion Laboratory (NASA-JPL) (Sander et al., 2002) are indicated by the corresponding citations.

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Deposition of the source gases into the ocean would constitute a permanent removal if there are efficient chemical and/or biological pathways to transform the species in the water. Estimates for the ocean removal lifetime show that ocean removal has a negligible effect on the local photochemical lifetime of the VSL halogen source gases (Yvon-Lewis and Butler, 2002).

2.3.2 Production and Removal of Degradation Products

2.3.2.1 DEGRADATION MECHANISMS FOR SOURCE GASES

As stated, the atmospheric degradation of the source gas is primarily initiated via reaction with OH and/or by UV photodissociation. The radicals produced following the initiation reaction are rapidly converted into more stable products. Halogen atoms may be released in the initiation reaction or during the subsequent sequence of reactions occurring in the degradation mechanism.

The degradation mechanism for the halogen-containing compounds parallels that previously reported for the hydrochlorofluorocarbons (HCFCs) (Cox et al., 1995). However, many of the reactions and reaction intermediates in the degradation have not been studied or observed in the laboratory. In those cases, formulation of the elementary steps in the degradation mechanisms has been based on analogy with known mechanisms. Both OH reaction and UV photolysis loss processes will lead to the rapid formation of alkylperoxy radicals. The degradation of the halocarbons leads to the formation of carbonyl halides, peroxy nitrates, hydroxyhalomethanes, and haloperoxy acids. The yield of a specific degradation product will depend to some extent on the atmospheric conditions (temperature and pressure) as well as the atmospheric concentrations of nitric oxide (NO), nitrogen dioxide (NO₂), HO₂, and organic peroxy radicals (RO₂).

A general degradation mechanism for the halomethanes is shown in Figure 2-6, and a summary of the degradation products derived from the various source gases is given in Table 2-5. Upon photolysis, the singly iodinated compounds (alkyl iodides) and the dihalo-iodo compounds (CH₂CI, CH₂BrI, and CH₂I₂) eliminate an I atom with unit quantum yield. Photolysis therefore does not lead to the formation of iodine-containing organic degradation products, with the exception of CH₂I₂, which could form HIC(O) as a minor product. Photolysis also removes trifluoroiodomethane (CF₃I) rapidly from the atmosphere, with CF₃ and I as photolysis products. The atmospheric degradation of the CF₃ radical does not lead to significant ozone destruction, as discussed in Cox et al.

Table 2-4. Local photochemical lifetimes (in days) for halogenated VSL substances. The local lifetimes are estimated using the reaction rate constant with OH and estimated photolysis rates as indicated in the table.

| Compound | τ_{OH}^a | τ_J^b | τ_{local}^c |
|-----------------------------------------------|-----------------------|-----------------------------------------|------------------|
| CH ₂ BrCl | 150 | 15000 | 150 |
| CH ₂ Br ₂ | 120 | 5000 | 120 |
| CHBr ₂ Cl | 120 ^d | 161 | 69 |
| CHBrCl ₂ | 120 ^e | 222 | 78 |
| CHBr ₃ | 100 | 36 | 26 |
| n-C ₃ H ₇ Br (n-PB) | 13 ^f | >1200 ^f | 13 |
| i-C ₃ H ₇ Br | 17 ^f | ^g | 17 |
| CH ₃ I | 220 ^f | 7 ^h (4-12) ⁱ | 7 |
| C ₂ H ₅ I | 15-39 ^{e, f} | 5 ^h (2-8) ⁱ | 4 |
| n-C ₃ H ₇ I | 7.9 ^{e, f} | 0.6 ^h (0.5-1.5) ⁱ | 0.5 |
| i-C ₃ H ₇ I | 9.5 ^{e, f} | 1.4 ^h (1-3) ⁱ | 1.2 |
| CH ₂ CI | ^g | 0.1 | 0.1 |
| CH ₂ BrI | ^g | 0.04 | 0.04 |
| CH ₂ I ₂ | ^g | 0.003 | 0.003 |
| CH ₂ Cl ₂ | 140 | >15000 | 140 |
| CHCl ₃ | 150 | >15000 | 150 |
| C ₂ HCl ₃ | 4.6 ^f | >15000 | 4.6 |
| C ₂ Cl ₄ | 100 ^f | 1.2 × 10 ⁵ ^f | 99 |
| C ₂ H ₄ Cl ₂ | 70 ^f | | 70 |

^a Calculated for T = 275 K with reaction rate constants from *JPL 00-3* (Sander et al., 2000) and [OH] = 1 × 10⁶ molec cm⁻³ unless specified otherwise. Values are rounded to 2 significant figures.

^b Globally and seasonally averaged photolysis constant (*J*) value estimated for 5 km, unless specified otherwise.

^c From $(\tau_{local})^{-1} = (\tau_{OH})^{-1} + (\tau_J)^{-1}$, unless specified otherwise; the oceanic lifetime is not included (see text).

^d Estimated *T* dependence of reaction rate (Kurylo and Rodriguez et al., 1999).

^e Calculated for 300 K.

^f Calculated using OH rate constant from Table 2-3.

^g No data.

^h Surface value.

ⁱ Range for different altitudes and latitudes.

(1995). The photolysis of multiple-substituted halomethanes (CH₂BrCl, CH₂Br₂, CHBr₂Cl, CHBr₃) will lead to the direct elimination of a halogen atom and the formation of a formyl halide.

H-abstraction by OH is the primary loss process for several of the less photo-labile compounds (CH₂BrCl, CH₂Br₂, and CH₃CH₂CH₂Br (n-PB)) and is of secondary importance for the iodoalkanes (C₂H₅I, CH₃CHICH₃, and CH₃CH₂CH₂I). For CH₂BrCl and CH₂Br₂, upon reaction with OH, it is likely that carbonyls such as HC(O)Br, C(O)BrCl, and C(O)Br₂ will be produced and these may

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Table 2-5. Summary of the degradation products from halogenated VSL substances.

| Source Gas | Major Degradation Products | Minor Degradation Products |
|-------------------------------------------|----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|
| CH ₂ BrCl | HCIC(O), inorganic bromine | HClBrC(OOH) |
| CH ₂ Br ₂ | HBrC(O), inorganic bromine | HBr ₂ C(OOH) |
| CHBr ₂ Cl | HCIC(O), ClBrC(O), inorganic bromine | HBr ₂ C(OOH), ClBr ₂ C(OOH) |
| CHBrCl ₂ | HCIC(O), Cl ₂ C(O), inorganic bromine | Cl ₂ BrC(OOH), HCl ₂ C(OOH) |
| CHBr ₃ | HBrC(O), Br ₂ C(O) | Br ₃ C(OOH), HBr ₂ C(OOH) |
| n-C ₃ H ₇ Br (n-PB) | CH ₃ C(O)CH ₂ Br, inorganic bromine, CH ₂ BrCH ₂ C(O)H | Hydroperoxy compounds, peroxy carbonyl nitrates, peroxy nitrates |
| CH ₃ I | Inorganic iodine | — |
| CF ₃ I | Inorganic iodine | — |
| C ₂ H ₅ I | Inorganic iodine | CH ₂ IC(O)H |
| n-C ₃ H ₇ I | Inorganic iodine | CH ₃ C(O)CH ₂ I, CH ₂ ICH ₂ C(O)H |
| i-C ₃ H ₇ I | Inorganic iodine | CH ₃ CHIC(O)H |
| CH ₂ ClI | Inorganic chlorine and iodine | H ₂ CIC(OOH) |
| CH ₂ BrI | Inorganic bromine and iodine | H ₂ BrC(OOH) |
| CH ₂ I ₂ | Inorganic iodine | HIC(O), H ₂ IC(OOH) |
| CH ₂ Cl ₂ | HCIC(O) | HCl ₂ C(OOH) |
| CHCl ₃ | Cl ₂ C(O) | HCl ₂ C(OOH) |
| C ₂ HCl ₃ | Cl ₂ C(O), HCIC(O) | HCIC(OH)C(O)Cl, HCIC(OH)C(OOH)Cl ₂ , Cl ₂ C(OH)C(O)H, HCIC(OOH)C(OH)Cl ₂ |
| C ₂ Cl ₄ | Cl ₂ C(O), ClC(O)OH | Cl ₂ C(OH)CCl ₂ (OOH) |
| CH ₂ ClCH ₂ Cl | HCIC(O), inorganic chlorine | CH ₂ ClCHCl(OOH) |

to be small for all compounds. Current estimates give an upper limit of 10^{-3} (de Bruyn et al., 1995; George et al., 1994), which indicates that cloud removal may play a role if gas-phase reactions are slow. It must also be emphasized that, for the compounds with very low reactivity, cloud evaporation may re-inject these compounds into the air, possibly at a different altitude, before multiphase processing can occur.

2.3.2.3 INORGANIC BROMINE AND IODINE SPECIES

Br and I atoms released in the troposphere through the degradation of the source gases and their degradation products undergo a series of reactions in which they are

interconverted among the oxides (XO) and inorganic reservoirs: HX (hydrogen halides), XONO₂ (halogen nitrates), and HOX (hypohalous acids), where here X = Br or I. The partitioning reactions for the inorganic reservoirs are common to bromine and iodine, and are illustrated in Figure 2-7. Bromine does not form higher oxides but iodine monoxide (IO) can react with bromine monoxide (BrO) or IO at a rate competitive with HO₂ to form iodine dioxide (OIO) (Cox et al., 1999; Rowley et al., 2001). The chemical reactions of OIO are not well known. Photodissociation to the ground state of atomic oxygen (O(³P)) + IO is not favored thermodynamically in its main visible absorption band (Misra and Marshall, 1998) and is slow (Ingham et al., 2000). This photolysis

Table 2-6. Kinetic and photochemical parameters for the gas-phase reactions of the degradation products of halogenated VSL substances.

| Species | Radical ^a | k ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) | k_{300} ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) | Photolysis Rate Constant, J ^b (s^{-1}) | Comments and References ^c |
|----------------------------------------|----------------------|------------------------------------------------------------|------------------------------------------------------------------|----------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|
| Cl ₂ C(O) | OH | | $<5.0 \times 10^{-15}$ | 2×10^{-9} | Atkinson et al. (1997); Cox et al. (1995) |
| Br ₂ C(O) | | | | | No kinetic or photochemical data |
| BrClC(O) | | | | | No kinetic or photochemical data |
| HCIC(O) | OH | | $<5.0 \times 10^{-13}$ | 1×10^{-8} | Atkinson et al. (1997) (limited experimental data); Cox et al. (1995) |
| HCIC(O) | Cl | $1.2 \times 10^{-11} \exp(-820/T)$ | 7.9×10^{-13} | | Atkinson et al. (1997) |
| HBrC(O) | | | | 3×10^{-6} | No kinetic data; estimate |
| CH ₃ C(O)CH ₂ Br | | | | 1×10^{-4} | No kinetic data; Burkholder et al. (2002) |
| CH ₂ ClC(O)H | OH | | 3.1×10^{-12} | | Atkinson et al. (1997) |
| CCl ₃ C(O)Cl | | | | | No kinetic or photochemical data |
| HOI | | | | 1.2×10^{-2} | No kinetic data; Bauer et al. (1998) |
| HOBr | OH | | $<5 \times 10^{-13}$ | 3×10^{-3} | Kukui et al. (1996), upper limit; Ingham et al. (1998) |
| HOBr | Cl | | 8×10^{-11} | | Kukui et al. (1996), products are BrCl and OH |
| CH ₂ ClOOH | Cl ^d | | 5.9×10^{-13} | | Wallington et al. (1996), no kinetic data for OH reactions and photolysis |
| CCl ₂ BrOOH | | | | | No kinetic or photochemical data |
| BrONO ₂ | | | | $\sim 1 \times 10^{-3}$ | Burkholder et al. (1995) |
| IONO ₂ | | | | 4×10^{-2} | Mössinger et al. (2002) |
| OIO | | | | $<10^{-2}$ | No kinetic data; Ingham et al. (2000) (upper limit for O(³ P) channel), Ashworth et al. (2002) (products are I + O ₂) |

^a Cl atom reactions included if $k_{\text{Cl}} > 50 \times k_{\text{OH}}$ or no OH kinetic data available.

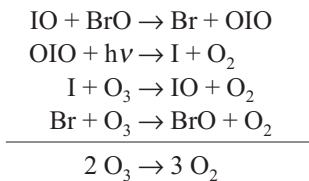
^b Atmospheric photolysis rate constants are globally and seasonally averaged estimates for 5-km altitude (because different models were used, the values should be considered approximate).

^c References cited for photolysis follow semicolon.

^d Strongly deactivating compared with reaction of Cl + CH₃OOH ($k_{300} = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) (Atkinson et al., 1997).

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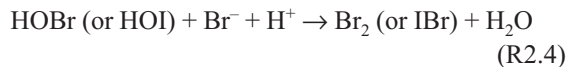
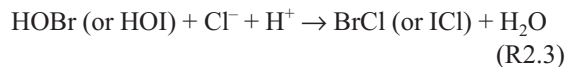
pathway would lead to a null cycle for ozone. However, photolysis to $I + O_2$ may occur (Ashworth et al., 2002), leading to an ozone loss cycle:



Thus OIO is a potentially significant atmospheric iodine species, and indeed has been detected in the marine boundary layer (Allan et al., 2001). Further oxidation of OIO, either by gas-phase or multiphase processes, to IO_3^- is a likely sink for tropospheric iodine, leading to the iodate observed in precipitation (Truesdale and Jones, 1996).

The relative importance of the halogen nitrates and HOX reservoirs depends on the local NO_2 and HO_2 concentrations, and on the presence of an aqueous phase where halogen nitrates may be hydrolyzed to form HOX. The inorganic reservoirs are removed from the troposphere by incorporation into aerosols, cloud droplets, and ice particles (cirrus clouds in the UT). However, the incorporation of the reservoirs into aerosols may not lead to permanent loss. Laboratory studies (Abbatt and Waschewsky, 1994;

Fickert et al., 1999; Holmes et al., 2001; Mössinger and Cox, 2001) show that HOX and $XONO_2$ species react very efficiently with Cl^- and Br^- on aerosols and ice particles, releasing the corresponding halogen or inter-halogen molecules, which all photodissociate to atomic halogens:



Reactions (R2.3) and (R2.4) are very efficient in acidic solutions or on HCl or hydrogen bromide (HBr)-doped surfaces. These reactions (and similar reactions involving $XONO_2$) have been the focus of many studies, especially in connection with their role in stratospheric halogen activation. They also play a role in tropospheric chemistry, particularly in the marine environment where sea salt aerosols contain Cl^- and Br^- ions. Additional reactive halogen is produced autocatalytically, leading for example to the so-called “bromine explosion” observed in the Arctic (e.g., Barrie and Platt, 1997). To be efficient, these reactions require cold conditions (such as frozen aerosols in the Arctic troposphere) and sustained levels of particles (such as ice or sulfuric acid aerosols in the stratosphere) that may be observed, for instance, under volcanic influence. Table 2-7 lists the required parameters for an assessment of the fate of some of the HOX and $XONO_2$ species.

Reactions similar to (R2.3) and (R2.4) efficiently recycle iodine and bromine into radical forms, thereby effectively increasing the lifetime of tropospheric halogens. This explains the relatively high abundance of IO in the marine boundary layer. There are also recent direct observations that show that BrO may be present in the upper troposphere at a concentration of 0.4-2 parts per trillion (ppt), which is much higher than predicted on the basis of known photochemical sources and heterogeneous removal rates (Fitzenberger et al., 2000). Such observations indicate that the recycling processes may be important, leading to a significant increase of the efficiency of the product gas injection (PGI) pathway in supplying inorganic halogen species to the stratosphere.

2.3.3 Degradation Mechanism for n-Propyl Bromide (n-PB)

The compound 1-bromopropane (or n-propyl bromide (n-PB), $CH_3CH_2CH_2Br$) has been suggested for use in a variety of applications that would lead to its release into the troposphere. A reliable estimate of the amount of inorganic bromine that will be delivered to the strato-

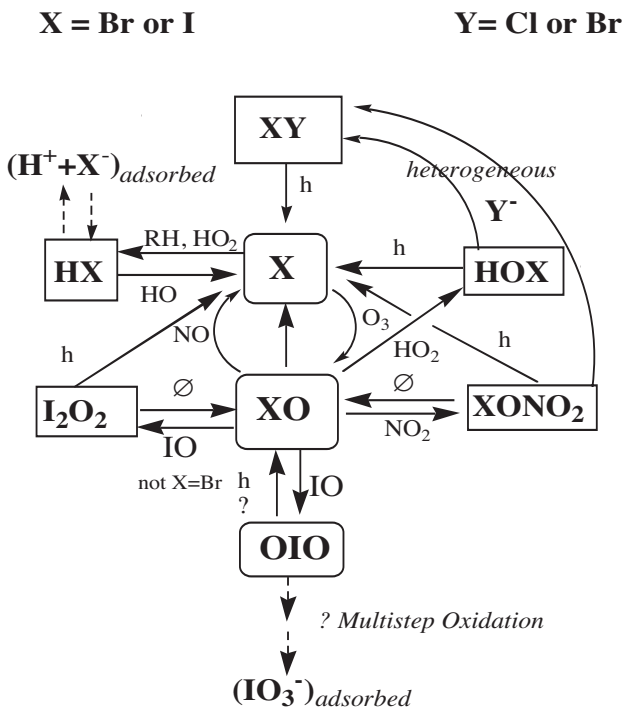


Figure 2-7. Inorganic halogen tropospheric chemistry.

Table 2-7. Data for the multiphase chemistry of some inorganic degradation products. The column for γ_{het} gives the reaction probability per collision with the surfaces.

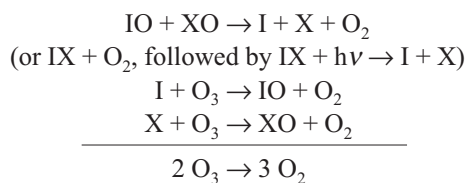
| Molecule | Henry's Law Constant (M atm ⁻¹) | Reaction | γ_{het} | Temperature (K) | References |
|-----------------------------------------|---------------------------------------------|---------------|-----------------------------------------------|-----------------|------------------------------|
| HOBr (hypo-bromous acid) | >1900 | Water | >0.01 | 274 | Blatchley et al. (1992) |
| | | NaCl | 6.5×10^{-3} | 300 | Atkinson et al. (2001) |
| | | NaBr | 0.18 | 300 | Atkinson et al. (2001) |
| | | HCl-doped ice | 4×10^{-3} to 0.3 | 180-222 | Chu and Chu (1999) |
| | | Sulfuric acid | >0.01 | 238 | Waschewsky and Abbatt (1999) |
| BrONO ₂ (bromine nitrate) | > 7.1×10^4 | Water | 0.06 | >273 | Aguzzi and Rossi (1999) |
| | | NaCl | 0.3 | – | Aguzzi and Rossi (1999) |
| | | NaBr | 0.3 | – | Aguzzi and Rossi (1999) |
| | | HCl-doped ice | >0.2 | 200 | Atkinson et al. (2001) |
| | | Sulfuric acid | >0.2 | 294 | Atkinson et al. (2001) |
| HOI (hypoiodous acid) | >45 | Water | – | – | Thompson and Zafiriou (1983) |
| | | NaCl | 1.6×10^{-2} | 278-298 | Atkinson et al. (2001) |
| | | NaBr | 3.4×10^{-2} | 278-298 | Mössinger and Cox (2001) |
| | | HCl-doped ice | 5×10^{-2} | 200 | Holmes et al. (2001) |
| | | Sulfuric acid | 1.5×10^{-2} to 7×10^{-2} | 195-252 | Holmes et al. (2001) |
| IONO ₂ (iodine nitrate) | – | Water | – | – | – |
| | | NaCl | >0.1 | 253 | Holmes et al. (2001) |
| | | NaBr | >0.1 | 253 | Holmes et al. (2001) |
| | | HCl-doped ice | >0.05 | 243 | Holmes et al. (2001) |
| | | Sulfuric acid | >0.3 | 253 | Holmes et al. (2001) |

sphere from release of n-PB requires better knowledge of its degradation mechanism and a guess as to the possible future quantities produced and emitted.

The degradation mechanism for n-PB is outlined in Figure 2-8. Recent laboratory measurements have determined the site-specific OH rate coefficients over the temperature range 230 to 360 K (Gilles et al., 2002). The kinetic data are reported in Table 2-3. The reaction rate constants reported by Gilles et al. (2002) and that recommended in Sander et al. (2002) give estimated local lifetimes of 13 days (Table 2-4).

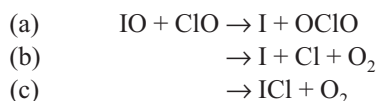
Bromoacetone (CH₃C(O)CH₂Br) was observed as a major degradation product following the OH reaction at the -CH₂- site of the n-PB molecule (β channel in Figure 2-8). Burkholder et al. (2002) have recently shown that CH₃C(O)CH₂Br will rapidly photolyze in the atmosphere (~hours). The photolysis products were not determined, but the possible bromine-containing products are expected to liberate bromine within days. The reaction of OH at the -CH₂Br group in CH₃CH₂CH₂Br (α channel) will lead

to the rapid elimination of Br and the formation of CH₃CH₂C(O)H. The reaction of OH at the CH₃- group in CH₃CH₂CH₂Br (γ channel) will predominantly lead to the formation of bromoaldehydes, (O)CHCH₂CH₂Br and (O)CHCH₂Br. These compounds are expected to degrade in the atmosphere (~days) through reaction with OH and UV photolysis. Minor reactions of the reaction intermediates can lead to the formation of peroxy nitrates (containing the OONO₂ group), peroxy carbonyl nitrates (PAN-type compounds, resulting from the further oxidation of the bromoaldehydes), and alkyl hydroperoxides (containing the OOH group). The peroxy nitrates will thermally decompose rapidly under all tropospheric conditions. The alkyl hydroperoxides will be removed via a combination of OH reaction, UV photolysis, and multiphase processing. The rates for these processes are not known but are expected to lead to atmospheric lifetimes on the order of days. The only possible degradation products of n-PB with atmospheric lifetimes longer than the parent compound are the peroxy carbonyl nitrates, but



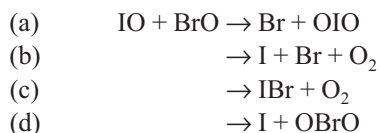
where here X is Br or Cl. At the time the study was done, rate data were not available for the reactions of IO with BrO and ClO. Solomon et al. (1994a) assumed a rate of $1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for both rate coefficients and estimated that the ozone removal efficiency for iodine is about 1000 times that of chlorine. It was suggested that the coupling of a low natural abundance of iodine species with increasing bromine and chlorine levels has contributed to the trend in ozone loss in the lowermost stratosphere.

Laboratory work in the past 5 years has significantly improved the knowledge of the relevant kinetic data. For the IO + ClO reaction, the rate coefficient has been found to be much lower than estimated by Solomon et al. (1994a), by a factor between 8 at 298 K and 5 at temperatures of the lower stratosphere (Bedjanian et al., 1997; Turnipseed et al., 1997). Furthermore, three product channels have been identified:



Channel (a), which leads to a null cycle for ozone depletion, is the major channel: $k_a/(k_a+k_b+k_c) = 0.55$. The channels that lead to ozone loss, (b) and (c), account for a significant fraction of the reaction: $(k_b+k_c)/(k_a+k_b+k_c) = 0.45$ at 298 K (Bedjanian et al., 1997; Turnipseed et al., 1997).

Several studies reported rate coefficients for the IO + BrO reaction ranging from 7×10^{-11} to $10 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Gilles et al., 1997; Laszlo et al., 1997; Bedjanian et al., 1998; Rowley et al., 2001). The possible channels for this reaction are:



The branching ratio for channel (a) here has been measured to be >0.65 (Bedjanian et al., 1998) while channels (b) and (c) account for less than 0.35 of the reaction at 298 K (Gilles et al., 1997; Bedjanian et al., 1998). The OIO molecule formed in channel (a) has been unambiguously

detected in this reaction (Cox et al., 1999). As discussed in Section 2.3.2.3, photolysis of OIO would efficiently produce I + O₂, and channel (a) could lead to an ozone loss cycle. However, uncertainties in OIO chemistry do not allow any firm conclusions regarding the ozone depletion efficiency of iodine in the stratosphere. The new data obtained for the IO + IO reaction are not discussed here, because this reaction, which also produces OIO, is not relevant to stratospheric iodine chemistry, but could be important in the marine boundary layer.

Laboratory investigations of the temperature dependence of the IO + HO₂ reaction (Maguin et al., 1992; Canosa-Mas et al., 1999; Cronkhite et al., 1999; Knight and Crowley, 2001) lead to a somewhat higher rate coefficient (up to a factor 3 at stratospheric temperatures) than that used in the calculations of Solomon et al. (1994a). This, associated with the reduced effect of the reactions of IO with both ClO and BrO, will increase the relative importance of the HO₂ cycle in the ozone loss due to iodine. Finally, in all reactions of IO with other radicals, the existence of a termolecular channel (similar to the ClO dimer-forming channel for ClO + ClO) was not observed.

The laboratory data in Sander et al. (2000) have been used for a recent re-evaluation of the ozone removal efficiency of iodine relative to chlorine; a value of 150-300 is used in this chapter (see Section 2.5) based on estimates provided by Bedjanian et al. (1998) and simulations using the Atmospheric and Environmental Research, Inc., model (see Ko et al., 1998). However, these estimates, which are lower than the value of 1000 initially suggested by Solomon et al (1994a), are still very uncertain because of the lack of knowledge about OIO chemistry, and also about the heterogeneous reactions that could be very important for iodine, since all the inorganic reservoirs are reactive toward stratospheric particles (both ice and sulfuric acid (H₂SO₄) surfaces). Many data are still missing for these heterogeneous processes, such as those needed to estimate the hydrolysis rate of IONO₂. When such data are available, a multidimensional atmospheric model should be used to perform a more rigorous calculation of the ozone removal efficiency of iodine.

2.4 CONTRIBUTION OF HALOGENATED VSL SUBSTANCES TO THE STRATOSPHERIC INORGANIC HALOGEN BUDGET

There are two independent ways to obtain the total local concentration of inorganic halogen species in the present-day stratosphere. The first method (inorganic method) is to add up the measured concentrations of each inorganic species (HCl, ClONO₂, HOCl, ClO, Cl₂O₂, etc., in the case of chlorine). A variant of this method uses

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measured concentrations of a subset of the inorganic halogen species (e.g., BrO) and derives the other concentrations using a photochemical model. The second method (the organic method) is to add the contributions from each source gas by taking the difference between the measured concentration of the source gas and its expected concentration in an air parcel based on when it first entered the stratosphere (see, e.g., Prather and Watson, 1990; Woodbridge et al., 1995; Wamsley et al., 1998). Contributions from transport of very short-lived (VSL) source gases, degradation products, and inorganic halogen species from the troposphere are usually ignored in the organic method. Agreement between the two methods provides some reassurance, but not irrefutable, that our understanding of the present-day halogen budget may be correct. For example, Woodbridge et al. (1995) carried out a study of the inorganic chlorine budget and concluded that inorganic chlorine (Cl_y) concentrations derived using the two methods are in reasonable agreement. However, the work of Wamsley et al. (1998) showed that derived inorganic bromine (Br_y) using the organic method is 30% smaller than the expected Br_y from the measured BrO, but that these differences are barely within calculated uncertainties. Recent analyses by Pfeilsticker et al. (2000) of a different dataset concluded that the two methods give values that agree within the estimated uncertainties (approximately ± 3 ppt) (see Chapters 3 and 4).

The measured concentrations of VSL source gases such as CH_3I and CHBr_3 are sufficiently high near the tropical tropopause that they could make a non-negligible contribution (see Table 2-8; review by Kurylo and Rodríguez et al., 1999; Sturges et al., 2000). This section summarizes the observations of the VSL halogen source gases and provides an estimate of their contribution to the present-day halogen budget in the stratosphere. Recent modeling studies are also reviewed and provide some estimates of the amount of Br_y entering the stratosphere from particular substances (CHBr_3 , n-PB) and their degradation products.

2.4.1 Observed Concentrations and Sources of Organic Chlorine, Bromine, and Iodine Compounds

The atmospheric distribution and sources of organic chlorine, bromine, and iodine compounds were reviewed in Kurylo and Rodríguez et al. (1999). Recent measured concentrations of the species in the tropical troposphere from Transport and Chemical Evolution over the Pacific (TRACE-P) and Pacific Exploratory Mission in the Tropical Pacific (PEM-Tropics) A and B are summarized in Table 2-8 and compared with values given in

the previous Assessment (Kurylo and Rodríguez et al., 1999). Burdens estimated using the numerator in the right-hand side of Equation (2.3) in Section 2.4.2 are given in Table 2-9. The estimated local lifetimes from Table 2-4 were used to calculate the sources for each species. These values were compared with previous estimates found in the literature. More recently, measurements taken from bottle samples collected on commercial aircraft as part of the European Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) project (<http://www.caribic-atmospheric.com/>) have also been analyzed for concentrations of halogen-containing source gases. These will prove useful in future studies. Reported measurements of degradation products or inorganic species in the troposphere are scarce, but include OIO (Allan et al., 2001), BrO (Fitzenberger et al., 2000), and phosgene (Kindler et al., 1995).

2.4.1.1 CHLORINE COMPOUNDS

Current measurements indicate that the mixing ratio of inorganic chlorine is about 3 parts per billion (ppb) in the upper stratosphere (based on measurement of HCl) and about 1.5 ppb in the lower stratosphere (based on the organic method). The VSL chlorine compounds have free-tropospheric concentrations in the range 1-50 parts per trillion (ppt). Many of them have an anthropogenic component in their sources. Methylene chloride (dichloromethane, CH_2Cl_2), trichloroethylene (trichloroethene, C_2HCl_3), and perchloroethylene (tetrachloroethene, C_2Cl_4) are mainly used as industrial solvents, and 1,2-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) is used as a lead scavenger in leaded gasoline. Concentrations of these gases in some urban areas reach ppb levels but their concentrations in the free troposphere are in the 1-30 ppt range (Blake et al., 1999a, 2001). Khalil et al. (1999) and references therein also suggested that natural emissions of chloroform (CHCl_3), predominantly from oceans, are important sources. This VSL also appears to have other small sources such as pulp and paper processing and water treatment. Biomass burning is thought to be a very minor source for CHCl_3 . Many of the VSL chlorine source gases exhibit significant seasonal and latitudinal variations in their concentrations (Wang et al., 1995; Yokouchi et al., 1996; Blake et al., 1999a). This could be due to variations in the emissions and variations in OH, because reaction with OH is the major removal process. Phosgene (COCl_2) is not emitted directly to the atmosphere but is a breakdown product of methyl chloroform and some of the gases listed above (Kindler et al., 1995). Its atmospheric concentration is in the 10-60 ppt range and its lifetime

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Table 2-8. Estimated values for f_{BL}^X (median tropical surface (<1 km) mixing ratios) and f_{UT}^X (median mixing ratios in the tropical upper troposphere (8-12 km)). The data for TRACE-P were collected over the Western Pacific and the South China Sea, 23.5°N to 8°N. The data for PEM-Tropics A and B were from over the remote Pacific, 15°N to 15°S.

| Species | Estimated Tropospheric Mixing Ratio ^a (pptv) | Estimated 10-km Tropical Mixing Ratio ^a (pptv) | f_{BL}^X and Range ^b from: TRACE-P ^c (331) ^d PEM-Tropics B ^c (572) ^d PEM-Tropics A ^c (337) ^d (pptv) | f_{UT}^X and Range ^b from: TRACE-P ^c (280) ^d PEM-Tropics B ^c (433) ^d PEM-Tropics A ^c (241) ^d (pptv) | Estimated $\frac{f_{UT}^X}{f_{BL}^X}$ from: TRACE-P PEM-Tropics B PEM-Tropics A |
|--------------------------------------|---------------------------------------------------------|-----------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| C ₂ HCl ₃ | NH, 1-5; SH, 0.01-0.1 | 0-0.1 | 1 (0.3-2.0) | 0.2 (0.02-0.28) | 0.2 |
| | | | N/A | N/A | N/A |
| | | | N/A | N/A | N/A |
| CH ₃ I | 0.1-2.0 | 0.05-0.2 | 0.6 (0.5-0.8) | 0.03 (0.02-0.08) | 0.05 |
| | | | 0.42 (0.3-0.5) | 0.09 (0.06-0.12) | 0.2 |
| | | | 0.445 (0.4-0.6) | 0.061 (0.04-0.09) | 0.15 |
| CHBr ₃ | 0.6-3.0 | 0.4-0.6 | 1.1 (0.9-1.5) | 0.3 (0.2-0.5) | 0.3 |
| | | | 1.82 (1.0-2.3) | 0.54 (0.4-0.7) | 0.3 |
| | | | 1.83 (1.4-2.2) | 0.42 (0.3-0.5) | 0.2 |
| CH ₂ ClCH ₂ Cl | NH, 20-40; SH, 5-7 | 14.9 ± 1.1 | 8.8 (5.7-14.5) | 2.9 (2.2-3.3) | 0.3 |
| | | | 1.53 (0.8-1.7) | 0.92 (0.7-1.3) | 0.6 |
| | | | N/A | N/A | N/A |
| CHBr ₂ Cl | 0.1-0.5 | 0.04-0.11 | 0.07 (0.06-0.08) | 0.04 (0.03-0.05) | 0.6 |
| | | | 0.20 (0.14-0.26) | 0.10 (0.08-0.12) | 0.5 |
| | | | 0.175 (0.14-0.21) | 0.08 (0.06-0.11) | 0.5 |
| CHBrCl ₂ | 0.12-0.6 | 0.04-0.11 | 0.19 (0.17-0.22) | 0.14 (0.12-0.15) | 0.7 |
| | | | 0.21(0.14-0.26) | 0.13 (0.11-0.14) | 0.6 |
| | | | 0.17 (0.15-0.20) | 0.08 (0.05-0.11) | 0.5 |
| C ₂ Cl ₄ | NH, 5-15; SH, 0.7-1.5 | 1-3 | 6.5 (4.5-10.3) | 2.1 (1.7-2.5) | 0.3 |
| | | | 2.34 (1.5-2.9) | 1.38 (1.2-1.7) | 0.6 |
| | | | 1.3 (1.2-1.16) | 1.4 (1.2-1.6) | 1.1 |
| CH ₂ Br ₂ | 0.8-3.4 | 0.6-0.9 | 1.15 (1.0-1.2) | 0.9 (0.7-1.0) | 0.8 |
| | | | 1.33 (1.1-1.5) | 0.92 (0.85-1.0) | 0.7 |
| | | | 1.07 (0.93-1.18) | 0.81 (0.77-0.85) | 0.8 |
| CH ₂ Cl ₂ | | | 34 (27-39) | 17 (16-19) | 0.5 |
| | | | 13.9 (9-16) | 10.1 (9-12) | 0.7 |
| | | | 11.4 (10.9-13) ^e | 13.1 (12.4-14) ^e | 1.1 |
| CHCl ₃ | NH, 10-15; SH, 5-7 | 3.1 ± 0.7 | 11.4 (9.0-13.3) | 6.9 (6.3-7.5) | 0.6 |
| | | | 6.6 (5.2-7.1) | 5.1 (4.8-5.6) | 0.8 |
| | | | 6.0 (5.7-6.4) | 5.8 (5.6-6.1) | 1.0 |

In columns 4-6, for each species, the first value is for data from TRACE-P; the second, from PEM-Tropics B; and the third, from PEM-Tropics A. N/A denotes data not available.

^a From Kurylo and Rodríguez et al. (1999).

^b Range is 25th-75th quartile.

^c The results for PEM-Tropics A and B can be found in Blake et al. (1999a,b, 2001, 2002). For a description of the campaigns and data availability, go to http://www-gte.larc.nasa.gov/gte_fld.htm.

^d Number of samples.

^e Data from a subset of cans (BL, n = 89; UT, n = 41) analyzed by E. Atlas, NCAR, U.S.

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Table 2-9. Estimated local lifetimes, burdens, removal rates, and sources for some halogenated VSL compounds.

| Compound | τ_{local} (days) | Estimated Burden (Gg) | Estimated Removal Rate (Gg yr ⁻¹) | Estimated Source from Inventory or Estimate of Biogeochemical Cycle (Gg yr ⁻¹) |
|--------------------------------------|---------------------------------|-----------------------------|------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|
| CH ₂ BrCl | 150 ^a | 1.2 (Br) ^{*1} | 2.9 (Br) ^c | |
| CH ₂ Br ₂ | 120 ^a | 18-22 (Br) ^b | 55-67 (Br) ^c | |
| | 120 ^a | 19 (Br) ^{*1} | 58 (Br) ^c | |
| CHBrCl ₂ | 78 ^a | 1.3-1.5 (Br) ^b | 6.1-7.0 (Br) ^c | |
| | 78 ^a | 1.2 (Br) ^{*1} | 5.5 (Br) ^c | |
| CHBr ₂ Cl | 69 ^a | 0.8-2.2 (Br) ^b | 4.2-12 (Br) ^c | |
| | 69 ^a | 2.3 (Br) ^{*1} | 12 (Br) ^c | |
| CHBr ₃ | 26 ^a | 11-18 (Br) ^b | 150-250 (Br) ^c | |
| | 26 ^a | 14 (Br) ^{*1} | 200 (Br) ^c 285 ^{*2, d} | 209 (47-370) (Br) ^{*3} |
| CH ₃ I | 5 ^e | 1.7-2.2 ^b (I) | 120-160 (I) ^c | 90-450 (I) ^{*4} |
| | 6 ^f | 4.8 (I) ^f | 214 (I) ^f | |
| C ₂ H ₅ I | 4 ^a | 0.5 (I) | 46 (I) ^c | |
| CH ₂ Cl ₂ | 140 ^a | 83-250 (Cl) ^b | 220-650 (Cl) ^c | 583 (or 487 (Cl)) ^{*5} (industrial) |
| | 140 ^a | 250 (Cl) ^{*6} | 650 (Cl) ^c | 160 (Cl) ocean ^{*6} |
| | 180 ^{*6, e} | 250 (Cl) ^{*6} | 500 (Cl) ^{*6, d} | 49 (Cl) biomass burning ^{*6} |
| CHCl ₃ | 150 ^a | 66-130 (Cl) ^b | 160-320 ^c | 564 (Cl) ^{*6} |
| | 150 ^a | 210 (Cl) ^{*7} | 511 ^c | |
| | 183 ^{*7, e} | 210 (Cl) ^{*7} | 470 (350-600) ^{*7, e} 412(Cl) ^{*6, d} | |
| C ₂ Cl ₄ | 99 ^a | 17-85 (Cl) ^b | 63-310 (Cl) ^c | 366 (or 313 (Cl)) ^{*5} (industrial) |
| | 99 ^a | 160 (Cl) ^{*6} | 590 (Cl) ^c | 16 (Cl) ocean ^{*6} |
| | 133 ^{*6, e} | 160 (Cl) ^{*6} | 440 (Cl) ^{*6, e} | 2 (Cl) fossil fuel ^{*6} |
| C ₂ HCl ₃ | 4.6 ^a | 3.1 (Cl) ^b | 260 (Cl) ^c | 241 (or 195 (Cl)) ^{*5} (industrial) |
| | 4.6 ^a | 5.30 (Cl) ^{*6} | 440 (Cl) ^c | 20 (Cl) ocean ^{*6} |
| | 5.5 ^{*6, e} | 5.30 (Cl) ^{*6} | 350 (Cl) ^{*6, e} | 3 (Cl) fossil fuel ^{*6} |
| COCl ₂ | 70 ^g | 250 (Cl) ^{*1} | 1000 ^c | |
| CH ₂ ClCH ₂ Cl | 70 ^a | 5-26 (Cl) ^b | 26-130 (Cl) ^c | 700 ^{*8} |

References: ^{*1} Kurylo and Rodríguez et al. (1999); ^{*2} Dvortsov et al. (1999); ^{*3} Carpenter and Liss (2000); ^{*4} Singh et al. (1983), Liss and Slater (1974), Moore and Groszko (1999); ^{*5} McCulloch et al. (1999); ^{*6} Keene et al. (1999); ^{*7} Khalil et al. (1999); ^{*8} Khalil (1998).

^a From Table 2-4.

^b Burden estimated using Equation (2.3) with the median BL mixing ratios from Table 2-8 and estimated scale height given in Table 2-10. The range reflects the three different median mixing ratios from TRACE-P, PEM-Tropics A, and PEM-Tropics B.

^c From estimated lifetime and estimated burden, i.e., (column 3)/(column 2). The range reflects range in estimated burden.

^d From 2-D model.

^e From 12-box model as calculated in reference 3.

^f From 3-D model simulation from Bell et al. (2001).

^g Wet-removal lifetime.

from wet deposition is about 2 months. Textor et al. (2002) revisited the issue of volcanic injection of chlorine to the stratosphere. However, reliable numerical estimates are not yet available.

2.4.1.2 BROMINE COMPOUNDS

Based on measured concentrations of BrO in the lower stratosphere, the concentration of Br_y is estimated to be about 20 ppt. The observed concentrations of VSL bromocarbons in the BL are in the 0.02-5 ppt range. Most have higher concentrations in the marine BL in regions with high ocean productivity. This indicates a possible marine source, although the exact mechanism for production is not well understood in most cases. Dibromomethane (CH₂Br₂; methylene bromide) is reasonably well mixed throughout the troposphere, compared with other bromocarbons, in part because of its widespread marine emissions and also because its lifetime is about 4 months (Table 2-4). Blake et al. (2002) reported mixing ratios of 0.8-1.2 ppt to altitudes of 12 km in tropical regions, and Schauffler et al. (1999) observed concentrations of 0.3-0.7 ppt at altitudes of 15-19 km in the tropics. The lower values from Schauffler et al. (1999) are consistent with the fact that Stratospheric Tracers of Atmospheric Transport (STRAT) data were obtained in the regions and seasons when convection was less prevalent. Bromoform (CHBr₃) is mainly emitted from marine source(s), but it has recently been reported that it may also have a minor source from industrial processes (Blake et al., 2002). Photolysis dominates its removal (Table 2-4). Blake et al. (2002) reported average marine boundary layer (MBL) mixing ratios of 0.7-1.9 ppt from their Pacific airborne samples collected between 35°N and 50°S. Higher marine boundary layer concentrations were observed in equatorial regions. Average mixing ratios for the 8-12 km region for all latitudes were 0.4-0.6 ppt, with the highest concentrations observed again in the equatorial latitudes. Halomethanes CH₂BrCl, CHBrCl₂, and CHBr₂Cl are thought to be produced by similar mechanisms and therefore have similar source distributions (Carpenter et al., 1999). CH₂BrCl has the longest average lifetime (Table 2-4) of the three gases and thus the highest overall concentrations. Schauffler et al. (1999) reported CH₂BrCl mixing ratios of 0.15-0.25 ppt at 10 km in the tropics, decreasing to about 0.01 ppt at 20 km. CHBrCl₂ concentrations were 0.1-0.15 ppt at 10 km and dropped to below 0.03 ppt at 15 km. Tropical concentrations of CHBr₂Cl were 0.05-0.2 ppt at 10 km and decreased to below 0.02 ppt above 15 km. These observations are consistent with photolysis being a significant removal process for CHBr₂Cl and CHBrCl₂ (see Section 2.3).

2.4.1.3 IODINE COMPOUNDS

Iodocarbons are mainly emitted from marine sources, and their generally very short lifetimes are reflected in their concentrations, typically 0.01-1 ppt. Methyl iodide (CH₃I) is the most prevalent iodocarbon in the atmosphere. CH₃I concentrations in the MBL are higher at low latitudes and midlatitudes, and show clear seasonal variations at midlatitudes with the highest concentrations in summer (Blake et al., 1999a; Yokouchi et al., 2001). Continental CH₃I concentration measurements are scarce. Bell et al. (2002) simulated the distribution of CH₃I in the troposphere using a 3-D model and an ocean source parameterized in terms of ocean productivity. The model calculated a mean atmospheric lifetime (defined as atmospheric burden divided by photochemical loss) of CH₃I against photolysis of about 6 days. The ratio of upper tropospheric (8-12 km) to lower tropospheric (0-2 km) concentrations in the tropical marine environment ranges from 0.11 in subsiding regions to 0.40 in upwelling regions (Bell et al., 2002). In the upper troposphere and lower stratosphere, CH₃I has been observed at concentrations of 0.0-0.2 ppt (Blake et al., 1999a; Sturges et al., 2001). Bell et al. (2002) calculated a net sea-to-air flux of 210 Gg yr⁻¹, which falls within the range of previous estimates (100-500 Gg yr⁻¹). Photochemical production of CH₃I in the seawater is consistent with the recent MBL observations (Yokouchi et al., 2001). Biomass burning (<10 Gg yr⁻¹; Andreae et al., 1996), rice fields (90 Gg yr⁻¹; Redeker et al., 2000; Muramatsu and Yoshida, 1995), wetlands (7.3 Gg yr⁻¹), and peatlands (1.4 Gg yr⁻¹; Dimmer et al., 2001) are the main continental sources. However, higher emissions from biomass burning of 20 Gg yr⁻¹ have also been reported (Muramatsu and Yoshida, 1995).

Carpenter et al. (2000) reported the automated measurements of biogenic alkyl halides at Mace Head, Ireland, including the detection of CH₂BrI and the first non-Arctic measurements of CH₂I₂ and CH₂ClI. The atmospheric mixing ratios of CH₂I₂ (<0.02-0.36 ppt), CH₂ClI (<0.02-0.21 ppt), CH₂BrI (<0.02-0.32 ppt), C₂H₅I (<0.02-0.21 ppt), and CH₃I (0.12-1.47 ppt) were used to calculate iodine atom emissions. The largest contribution of iodine atoms to the marine boundary layer was from CH₂I₂ (lifetime on the order of a few minutes). Annual global atmospheric input of 0.04 Gg yr⁻¹ by macroalgae was estimated by Giese et al. (1999). Thus, polyhalogenated iodine compounds released from macroalgae make a very small contribution to the global iodine budget (only 0.01-0.05% of total CH₃I emission), but are likely a significant source of iodine to coastal atmospheres (Bassford et al., 1999; Baker et al., 2000).

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Current estimates of total inorganic iodine concentrations in the stratosphere are based on column measurements of IO (Wennberg et al., 1997; Pundt et al., 1998; Wittrock et al., 2000). The estimated range is from less than 0.05 ppt to 0.7 ppt.

2.4.2 Estimates of Contributions from VSL Halogen Source Gases

In this section, we describe a simple method for estimating the percentage of halogen atoms (emitted as organic source gases at the surface) that are transported to the stratosphere via the two pathways identified in Figure 2-1. Numerical estimates can be obtained using observed concentrations of the source gases and their degradation products, or using model output. The paucity of observations limits this analysis to providing an order-of-magnitude estimate. The exercise also helps to identify useful diagnostics for comparing model results. For simplicity, we assume that the intermediate products are sufficiently short lived that their contributions to the PGI pathway are small.

Consider a source gas X that contains $n_X^{h_X}$ halogen atoms and is emitted at \mathcal{E} moles (h_X) yr^{-1} , where h_X is inorganic halogen species (Cl, Br, or I) found in compound X . The fractions of the emissions that enter the stratosphere via the SGI pathway ($\mathcal{J}_{\text{SGI}}^X$) and the PGI pathway ($\mathcal{J}_{\text{PGI}}^X$) are given by

$$\begin{aligned}\mathcal{J}_{\text{SGI}}^X &= \frac{n_X^{h_X} \times f_{\text{TT}}^X \times |wM_{\text{TT}}| \times A}{\mathcal{E}} \\ \mathcal{J}_{\text{PGI}}^X &= \frac{f_{\text{TT}}^{h_X} \times |wM_{\text{TT}}| \times A}{\mathcal{E}} = \frac{f_{\text{TT}}^{h_X}}{n_X^{h_X} \times f_{\text{TT}}^X} \times \mathcal{J}_{\text{SGI}}^X\end{aligned}\quad (2.1)$$

where f_{TT}^X and $f_{\text{TT}}^{h_X}$ are the mixing ratios for X and h_X near the tropical tropopause, w is the large-scale upward velocity across the tropopause, M_{TT} is the air density at the tropical tropopause in moles per unit volume, and A is the area of the Earth. To get a numerical value for $|wM_{\text{TT}}|$, we note that

$$|wM_{\text{TT}}| = \frac{M_{\text{surf}} \times \int_0^{Z_T} e^{-\frac{z}{H_0}} dz}{\tau_{\text{res-trop}}^{\text{air}}}\quad (2.2)$$

where $\tau_{\text{res-trop}}^{\text{air}}$ is the replacement time for tropospheric air against transport out of the troposphere, z is altitude, H_0 is the atmospheric scale height of air, M_{surf} is the air density (in moles per unit volume) at the surface, and Z_T is the altitude of the tropopause. Rosenlof and Holton (1993) provided an estimate of the mass flux across 100 mb that can be used to give a value of 17 years for $\tau_{\text{res-trop}}^{\text{air}}$.

The emission \mathcal{E} is equal to the removal rate of X in the stratosphere and troposphere. We derive an expression for the removal rate assuming that the removal in the stratosphere can be ignored and that the local lifetime is uniform in the troposphere:

$$\begin{aligned}\mathcal{E} &= n_X^{h_X} \times \iiint \frac{M(\bar{x}) \times f^X(\bar{x})}{\tau_{\text{local}}^X(\bar{x})} dV \\ &\approx \frac{n_X^{h_X} \times M_{\text{surf}} \times f_{\text{BL}}^X \times A \times \int_0^{Z_T} e^{-\frac{z}{H_0}} \times f_{\text{norm}}^X(z) dz}{\tau_{\text{local}}^X}\end{aligned}\quad (2.3)$$

where $M(\bar{x})$, $f^X(\bar{x})$, and $\tau_{\text{local}}^X(\bar{x})$ are the air density, mixing ratio, and local lifetime of X as a function of \bar{x} . The local photochemical lifetime of X is taken from Table 2-4 and assumed to be approximately uniform in the troposphere, f_{BL}^X is the mixing ratio of X in the boundary layer, and $f_{\text{norm}}^X(z)$ is the normalized altitude profile of $f^X(\bar{x})$ and has the value 1 in the 1-km-thick BL and falls off with the assumed scale height H_f^X given in Table 2-10. Note that although $f_{\text{norm}}^X(z)$ is used to estimate the burden of the source gas, f_{TT}^X is expected to be larger than

$$f_{\text{BL}}^X \times \exp\left[-(Z_T - 1)/H_f^X\right]$$

because convection will carry additional source gas to the TTL. Model results in Figure 2-4 clearly show that the mixing ratio between 500 and 200 hPa do not follow a simple exponential decrease with height. The contribution to the burden from the extra source gas carried by convection to the TTL is ignored in this estimate. Combining Equations (2.1), (2.2), and (2.3) gives

$$\mathcal{J}_{\text{SGI}}^X = \frac{f_{\text{TT}}^X}{f_{\text{BL}}^X} \times \frac{\tau_{\text{local}}^X}{\tau_{\text{res-trop}}^{\text{air}}} \times K(H_0, H_f^X)\quad (2.4)$$

where $K(H_0, H_f^X)$ is a simple quadrature in terms of the scale heights (see footnote b in Table 2-10).

Table 2-8 gives the observed median surface concentrations and the median concentrations at 10 km in the tropics for several VSL source gases from the TRACE-P and PEM-Tropics A and B campaigns. In lieu of values for f_{TT}^X , it is assumed that X is well mixed in the TTL and $f_{\text{TTL}}^X \sim f_{\text{UT}}^X$. Using the $f_{\text{UT}}^X / f_{\text{BL}}^X$ values in Equation (2.4) gives estimated values of $\mathcal{J}_{\text{SGI}}^X$ (see Table 2-10) ranging from 0.03% to 3% for source gases with local lifetimes of 5 days to 150 days. The values derived for the VSL source gases with 100-day lifetimes are comparable with previous

Table 2-10. Values used to estimate the fraction of halogen atoms transported to the stratosphere via the SGI pathway (\mathcal{F}_{SGI}^X) (see Section 2.4.2).

| Species | Local Lifetime ^a (days) | Estimated H_f^X (km) | $K(H_0, H_f^X)^b$ | Estimated $\frac{f_{UT}^X}{f_{BL}^X}$: ^c | | | \mathcal{F}_{SGI}^X Calculated Using Eq. (2.4): | Model Estimate of \mathcal{F}_{SGI}^X |
|--------------------------------------|------------------------------------|------------------------|-------------------|------------------------------------------------------|---------------|---------------|---------------------------------------------------|-----------------------------------------|
| | | | | TRACE-P | PEM-Tropics B | PEM-Tropics A | | |
| C ₂ HCl ₃ | 4.6 | 1 | 4.8 | 0.2 | | | 0.0008 | |
| | | | | N/A | | | N/A | |
| | | | | N/A | | | N/A | |
| CH ₃ I | 7 | 1 | 4.8 | 0.05 | | | 0.00026 | |
| | | | | 0.2 | | | 0.0011 | |
| | | | | 0.15 | | | 0.000803 | |
| CHBr ₃ | 26 | 2 | 3.3 | 0.3 | | | 0.0042 | |
| | | | | 0.3 | | | 0.0042 | |
| | | | | 0.2 | | | 0.0028 | |
| CH ₂ ClCH ₂ Cl | 70 | 5 | 2.0 | 0.3 | | | 0.0065 | |
| | | | | 0.6 | | | 0.013 | |
| | | | | N/A | | | N/A | |
| CHBr ₂ Cl | 69 | 5 | 2.0 | 0.6 | | | 0.013 | |
| | | | | 0.5 | | | 0.011 | |
| | | | | 0.5 | | | 0.011 | |
| CHBrCl ₂ | 78 | 10 | 1.5 | 0.7 | | | 0.013 | |
| | | | | 0.6 | | | 0.011 | |
| | | | | 0.5 | | | 0.0093 | |
| C ₂ Cl ₄ | 99 | 10 | 1.5 | 0.3 | | | 0.0071 | 0.01 ^{*1} |
| | | | | 0.6 | | | 0.014 | |
| | | | | 1.1 | | | 0.032 | |
| CH ₂ Br ₂ | 120 | 15 | 1.3 | 0.8 | | | 0.020 | |
| | | | | 0.7 | | | 0.018 | |
| | | | | 0.8 | | | 0.020 | |
| CH ₂ Cl ₂ | 140 | 15 | 1.3 | 0.5 | | | 0.015 | 0.014 ^{*2} , |
| | | | | 0.7 | | | 0.021 | 0.02 ^{*3} |
| | | | | 1.1 | | | 0.033 | |
| CHCl ₃ | 150 | 15 | 1.3 | 0.6 | | | 0.019 | 0.004 ^{*4} , |
| | | | | 0.8 | | | 0.025 | 0.02 ^{*1} |
| | | | | 1.0 | | | 0.031 | |

In columns 5 and 6, for each species, the first value is for data from TRACE-P; the second, from PEM-Tropics B; and the third, from PEM-Tropics A. References: ^{*1} Kindler et al. (1995); ^{*2} Keene et al. (1999); ^{*3} Graedel and Keene (1995); ^{*4} Khalil (1998), results are from 12-box model.

^a From Table 2-4.

^b

$$K(H_0, H_f^X) = \int_0^{Z_T} e^{-\frac{z}{H_0}} dz \bigg/ \int_0^{Z_T} e^{-\frac{z}{H_0}} \times f_{\text{normal}}^X(z) dz, \text{ where } f_{\text{normal}}^X(z) = 1 \text{ for } z \leq 1 \text{ km; } f_{\text{normal}}^X(z) = e^{-\frac{z-1}{H_f^X}} \text{ for } z \geq 1 \text{ km.}$$

The integral is calculated assuming that areas in the tropics and extratropics are equal and Z_T is 15 km and 10 km for the tropics and the extratropics, respectively. See Section 2.4.2 for definitions of other terms.

^c From Table 2-8.

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results derived using a 12-box numerical model (see reference cited in Table 2-10).

For $\mathcal{J}_{\text{PGI}}^X$, we use the following estimate:

$$\mathcal{J}_{\text{PGI}}^X = \frac{f_{\text{TT}}^{h_X}}{n_X^{h_X} \times f_{\text{TT}}^X} \times \mathcal{J}_{\text{SGI}}^X \approx \frac{\tau_{\text{PG-X}}}{\tau_{\text{local}}^X} \times \mathcal{J}_{\text{SGI}}^X \quad (2.5)$$

where $\tau_{\text{PG-X}}$ is the local residence time (against chemical degradation, transport, and washout) for the product gas from the degradation of X . If there is no long-lived intermediate product for species X , $\tau_{\text{PG-X}}$ will correspond to the washout lifetime of the inorganic halogen species. Using a nominal value of 10 days would indicate that $\mathcal{J}_{\text{PGI}}^X$ is comparable with $\mathcal{J}_{\text{SGI}}^X$ for source gases having local lifetimes of about 10 days, and a tenth of $\mathcal{J}_{\text{SGI}}^X$ for source gases having lifetimes of order 100 days. If there is a long-lived intermediate ($\tau_{\text{PG-X}}$ longer than half a year), the value for $\mathcal{J}_{\text{PGI}}^X$ could approach $(1 - \mathcal{J}_{\text{SGI}}^X)$.

It is important to recognize the assumptions that were used to obtain these estimates. In the procedure, we assumed that the flux through the tropopause is governed by the large-scale circulation with uniform f_{TT}^X and $f_{\text{TT}}^{h_X}$ along the tropopause and that the concentrations of X or h_X are uniform within the TTL so that observations collected in the upper troposphere can be used. In addition, we did not include transport along isentropic surfaces in the subtropics or sub-synoptic-scale stratosphere-troposphere exchange events that occur in the extratropics. In estimating the chemical removal rate of the source gas, it is assumed that the local photochemical lifetime is uniform in the troposphere. A similar assumption is made for the washout rate of the inorganic halogen. However, these two parameters are likely to vary strongly with latitude and season and to be very dependent on the location of emissions.

To relate the concentration of inorganic halogen in the stratosphere ($f_{\text{Strat}}^{h_X}$) to the concentration of the source gas at the surface (f_{BL}^X), one can proceed as follows. For simplicity, it is assumed that the source gas contains one halogen atom. Take the case in which the concentration of the source gas is 1 ppt in a 1-km layer above the surface and the lifetime of the gas is 10 days. The emission needed to balance the removal in the BL is estimated to be 8×10^8 moles yr^{-1} . If one assumes that 0.1 to 1% of the flux emitted in the troposphere enters the stratosphere as odd halogen, the flux is 0.8×10^6 to 8×10^6 moles yr^{-1} . Taking a stratospheric residence time of 2 years (see, e.g., Holton, 1990) would mean that the average mixing ratio for inorganic halogen in the stratosphere is about 0.1 to 1

ppt. The typical concentrations for VSL halogen source gases are of order several ppt for bromine and iodine source gases, and up to 50 ppt for chlorine source gases. The current inorganic chlorine concentration in the stratosphere is about 3 ppb. It is thus unlikely that VSL chlorine source gases will make a significant contribution to the chlorine budget in the middle and upper stratosphere. However, they may still make a contribution close to the tropopause. In the case of bromine (with inorganic bromine concentration at 20 ppt and iodine at <1 ppt), it is likely that the effects from VSL halogen source gases will be important throughout the stratosphere.

2.4.3 Modeling Studies

We now review some of the modeling work on the contribution of VSL source gases to the stratospheric inorganic halogen budget. There have been two recent model studies on bromoform (CHBr_3). In both studies it was assumed that the degradation products immediately released their Br atoms. Dvortsov et al. (1999) used a global two-dimensional (2-D) model with parameterized convection and washout prescribed as a function of altitude, resulting in washout time constants ranging from about 9 days at the ground to 17 days just below the tropopause. Emissions were assumed to be uniform over the ocean and were adjusted to give a surface concentration of 1.5-2 ppt CHBr_3 . In their model simulation, sufficient bromine atoms (in its organic and inorganic form) were transported to the stratosphere to maintain ~ 1 ppt Br_y . Note that 75% of the flux came through the tropical tropopause as Br_y . Nielsen and Douglass (2001) ran an offline 3-D model using assimilated winds to simulate CHBr_3 and Br_y . Their washout time constant was fixed at ~ 6 days throughout the troposphere. Surface fluxes and mixing ratios were treated in a manner similar to that of Dvortsov et al. (1999). Figure 2-9 shows their average modeled tropical CHBr_3 profile again compared with PEM-Tropics data, plus measurements in the tropical tropopause layer (TTL) from the STRAT campaign. Nielsen and Douglass (2001) also calculated that ~ 1 ppt Br_y is derived from CHBr_3 in the lower stratosphere, with 50% of this amount transported as inorganic bromine.

Although both model studies agree well with data up to about 10 km, both studies overestimate CHBr_3 in the TTL compared with the STRAT data. Because the models maintain too much CHBr_3 in the TTL, Nielsen and Douglass (2001) estimate that CHBr_3 contributes to maintaining, at most, 15% of the Br_y in the stratosphere. The relative effect of this contribution is likely to be greatest in the layer immediately above the tropopause, where Br_y from CHBr_3 would increase total Br_y by $\sim 45\%$. These

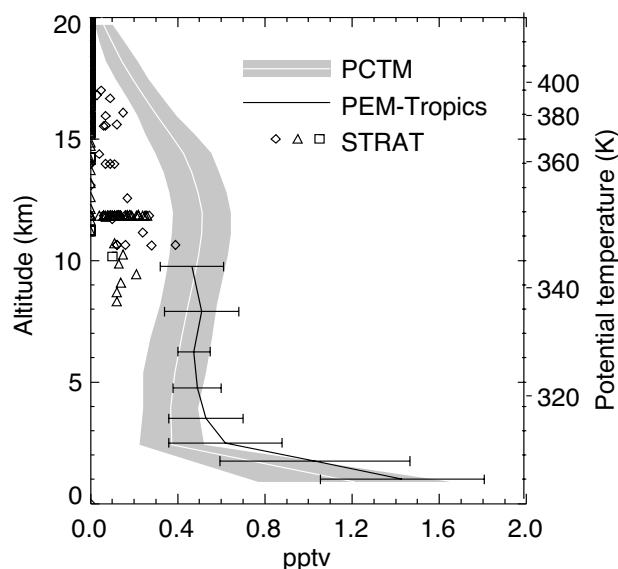


Figure 2-9. Results from 3-D model simulations (PCTM, parameterized chemistry and transport model) of tropical CHBr_3 and comparison with PEM-Tropics and STRAT data within 30° of the equator. The different symbols denote data taken at different times (diamonds for data taken in January and February, triangles for July and August, and squares for December). The model overestimates the transport of CHBr_3 to the tropical upper troposphere (see Nielsen and Douglass, 2001). Figure courtesy of A. Douglass, NASA GSFC, U.S.

modeling studies, together with the observationally based studies of Wamsley et al. (1998) and Pfeilsticker et al. (2000), suggest the importance of including shorter lived species in the stratospheric bromine budget.

Several recent studies provide estimates for the impact of 1-bromopropane (n-PB) on stratospheric bromine levels (Olsen et al., 2000; Bridgeman et al., 2000; Wuebbles et al. 2001) (see Section 2.5.3). They all noted that the idea of a single lifetime is flawed for VSL species and that mixing ratios of n-PB reaching the tropical upper troposphere depend strongly on the latitude and season of the emissions. The Wuebbles et al. (2001) study used a global 3-D model with a parameterized chemistry scheme to investigate transport of n-PB and its degradation products across the tropical tropopause. They found that tropical emissions were twice as likely to enter the stratosphere as high-latitude emissions, in qualitative agreement with the other two studies. Wuebbles et al. (2001) showed that up to 0.5% of the Br emitted as n-PB at the surface entered the stratosphere, with only one-third of Br in the form of n-PB (the SGI pathway). The remainder was mostly in the form of inorganic bromine (the PGI

pathway). However, these values are likely to change as more reliable information on the degradation of n-PB becomes available.

All the modeling studies emphasize that the lack of knowledge about the fate of the degradation products limits our ability to quantify their contribution to halogen loading in the stratosphere. Up to now, little attention has been paid to evaluation of model simulations of the processes and time scales necessary to understand the transport and chemistry of VSL substances. For example, cross-tropopause transport rates are very important for determining the effects of Br_y on O_3 loss in the lowermost stratosphere, yet neither observations nor models are able to fully agree on the degree of communication between the troposphere and stratosphere (see Section 2.2.2.2). Furthermore, few models had their transport evaluated in this region against observations. Examples of such studies include the analyses by Strahan et al. (1998) and Douglass et al. (1999). These studies evaluated the tropopause behavior of different models participating in the Global Modeling Initiative by comparisons with the known phase lag between UT and LS CO_2 . Clearly more studies of this type are required.

2.4.4 Information Needed for Future Evaluation

In summary, it can be concluded that the effects of VSL halogen source gases on halogen loading in the stratosphere are likely to be limited to bromine and iodine budgets in the present-day atmosphere. It is unlikely that VSL chlorine compounds will make a significant contribution to the chlorine budget.

It is clear that more observations of VSL substances, their degradation products, and inorganic halogen species are required in the troposphere and the stratosphere if we are to reduce the uncertainties surrounding our estimates of the contribution of these compounds to the present halogen loading in the stratosphere. In particular, measurements are needed in the TTL and the lowermost stratosphere. This could be particularly challenging if the sequestration of halogen ions in aerosol particles turns out to be important (Murphy and Thomson, 2000). It is encouraging that several independent models simulate similar amounts ($\sim 0.5\%$) of Br_y input into the stratosphere from n-PB, although this cannot be easily verified using available observations. The observed $f_{\text{UT}}^X / f_{\text{BL}}^X$ ratios as defined in Table 2-8 for specific source gases could provide useful constraints although one must also have a good knowledge of the distribution of surface source strengths. Improved estimates will be brought about by improvements in modeling capabilities

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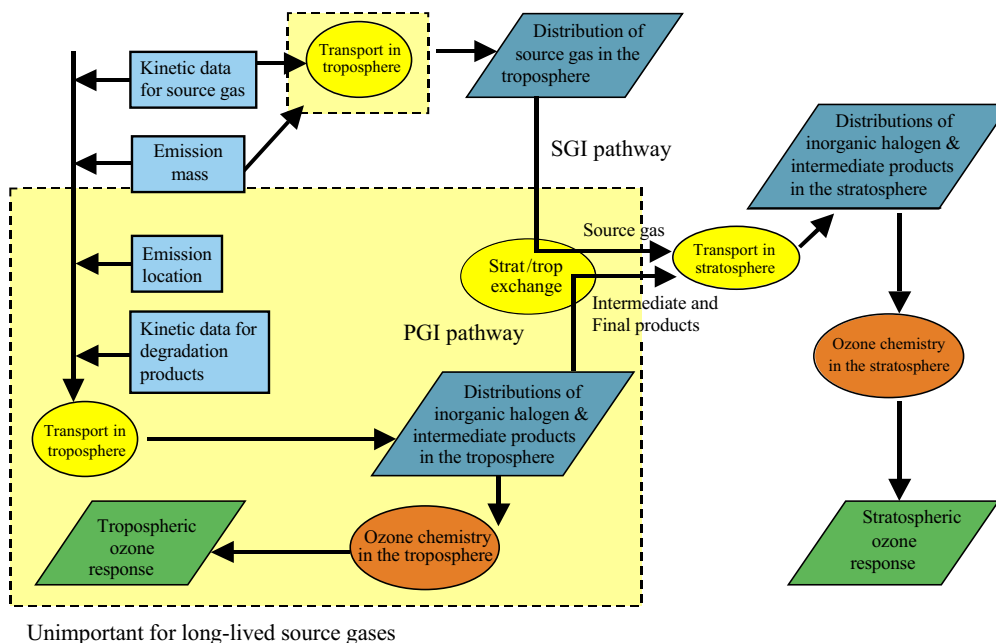


Figure 2-10. Schematic showing information needed to assess the ozone depletion estimate of halogen source gases. Items in rectangles are species specific. Items in ovals are common to all species. Items in parallelograms are model predictions. Several processes are highlighted in two yellow-colored boxes with heavy dashed outlines. The simulation of these processes in numerical models has not been fully evaluated.

and parameterization of processes like convection and washout. Cross-tropopause transport in the tropics, through the TTL region, also requires thorough evaluation in global models including tests of tropical ascent rates and exchange with the extratropics. These studies need to be coupled to better understanding of degradation products, their local lifetimes and solubilities (also see Section 2.3).

2.5 ESTIMATES FOR THE POTENTIAL IMPACT OF HALOGENATED VSL SUBSTANCES ON COLUMN OZONE

An operational definition for the Ozone Depletion Potential (ODP) of a species X is given by

$$\text{ODP}(X, \bar{x}_e, t_e) = \frac{\Delta O_3(X, E)}{\Delta O_3(\text{CFC-11}, E)} \quad (2.6)$$

where $\Delta O_3(X, E)$ is the steady-state percent change in stratospheric ozone burden due to emission of X at the rate of $E \text{ g yr}^{-1}$ at a specific location (\bar{x}_e) and time (t_e) of the year. The ODP value is defined relative to the ozone-depleting efficiency of CFC-11 (CCl_3F). An equivalent definition for ODP is the cumulative ozone depletion for the same mass pulse emission (same location and time of

year) of X versus that of CFC-11 (Prather, 1996, 1997, 2002). This latter definition leads naturally to using the ODP values in equivalent effective stratospheric chlorine (EESC) calculations (Daniel et al., 1995; Madronich and Velders et al., 1999).

Figure 2-10 shows the information needed and the procedure for calculating the change in column ozone from emission of a halogen source gas at the Earth's surface. The procedure for calculating ODP was originally developed for halocarbons (Wuebbles, 1981, 1983) with lifetimes sufficiently long (more than 1 year) that their mixing ratios are uniform in the troposphere and the increase in inorganic halogen in the troposphere is expected to be small. For those gases, the processes in the yellow boxes in Figure 2-10 are unimportant, and thus the ODP value is independent of location and time of emission. The methods (either using results from numerical models or using measured quantities in semiempirical approaches) for calculating ODP values for long-lived source gases have been reviewed in previous reports, and they are judged to give reliable results. However, many of the processes in the yellow boxes and how well they are simulated in models have not been evaluated. Thus, assessing the reliability of the ODP values for very short-lived (VSL) halogen source gases emitted at the Earth's surface requires further evaluations.

Several recent efforts to address these issues include a workshop on VSL compounds in March 1999 sponsored by the U.S. Environmental Protection Agency (EPA) and the National Aeronautics and Space Administration (NASA) (Wuebbles and Ko, 1999); the findings of a special United Nations Environment Programme (UNEP) report (UNEP, 2000); and several recent publications (Bridgeman et al., 2000; Olsen et al., 2000; Wuebbles et al., 2001). We review the methods used to compute ODP for long-lived source gases in Section 2.5.1, and in Section 2.5.2 we contrast them with the new method needed for the VSL source gases. Some of the results for ODP based on numerical models are reviewed in Section 2.5.3. A brief discussion on performing the chlorine loading calculation is presented in Section 2.5.4.

2.5.1 Review of Methodology for Calculating ODPs for Long-Lived Source Gases

Because the ODP value of a long-lived source gas is independent of the location and time of emission, we will suppress the \bar{x}_e and t_e notations in this section. Solomon et al. (1992) provided an expression for computing a semiempirical value for the ODP ($ODP_{s-e}(X)$) of a long-lived source gas. This is useful for relating ODP values to measured quantities that could be used to evaluate the model-calculated results. We will follow a similar procedure here and express $\Delta O_3(X, E)$ as a product of two factors:

$$\Delta O_3(X, E) = HL_X(E) \times \delta_X \quad (2.7)$$

where $HL_X(E)$ is the steady-state stratospheric inorganic halogen loading (chlorine, bromine, or iodine mixing ratio in mole fraction) associated with emission of X at E g yr⁻¹ and δ_X is the ozone-removal efficiency per unit inorganic halogen loading from X . Note that the definitions for $HL_X(E)$ and δ_X are related in that there is more than one way to quantify the halogen loading. One could either use the average mixing ratio of the inorganic halogen in the stratosphere ($HL_X^{Avg}(E)$) or the mixing ratio at the stratopause ($HL_X^{Strp}(E)$), where Strp means stratopause). Depending on which definition one chooses, δ_X will take different values. Using this notation,

$$\begin{aligned} ODP_{s-e}(X) &= \frac{HL_X(E)}{HL_{CFC-11}(E)} \times \frac{\delta_X}{\delta_{CFC-11}} \\ &= CLP(X) \times \zeta_X \end{aligned} \quad (2.8)$$

where $CLP(X)$ is the chlorine loading potential and ζ_X is the ratio of the ozone-removal efficiency factors. For long-lived source gases where the contribution from the PGI pathway to the inorganic halogen loading in the stratosphere is small compared with that from the SGI pathway, the steady-state mixing ratio of h_X at the stratopause (that results from a constant emission of X) is approximately equal to the mixing ratio of X in the troposphere (see Prather and Watson, 1990). Now

$$HL_X^{Strp}(E) = \frac{1}{M} \times \frac{E \times \tau_X}{\mu_X} \times n_X^{h_X} \quad (2.9)$$

where μ_X is the gram molecular weight, τ_X is the atmospheric lifetime of X , $n_X^{h_X}$ is the number of halogen atoms in X , and M is the number of moles of air in the atmosphere. Thus, for long-lived species like those treated in Chapter 1,

$$\begin{aligned} CLP^{Strp}(X) &= \frac{HL_X^{Strp}(E)}{HL_{CFC-11}^{Strp}(E)} \\ &= \frac{\mu_{CFC-11}}{\mu_X} \times \frac{\tau_X}{\tau_{CFC-11}} \times \frac{n_X^{h_X}}{n_{CFC-11}^{Cl}} \end{aligned} \quad (2.10)$$

The efficiency factor ζ_X^{Strp} has two components: $\zeta_X^{Strp} = \zeta^S \times \zeta_X^D$. The values for the first component (ζ^S , S for speciation) depend on whether the halogen is chlorine, bromine, or iodine. The other factor (ζ_X^D , D for distribution) has to do with the distribution of the inorganic halogen in the stratosphere. Equation (2.8) corresponds to the same definition used in Chapter 1, with ζ^S identified with the α factor, and ζ_X^D is the fractional release factor. When a numerical model is used to calculate $ODP(X)$ via Equation (2.6), one can identify the value for $\zeta^S \times \zeta_X^D$ with the $ODP(X)/CLP^{Strp}(X)$ ratio. From this perspective, the value for $\zeta^S \times \zeta_X^D$ corresponds to a spatial and seasonal average weighted by the ozone response in the lower stratosphere. Thus, it is not possible to pick values for ζ^S and ζ_X^D at a specific location and time to represent the $ODP(X)/CLP^{Strp}(X)$ ratio. A way to proceed is to pick a conventional value for ζ^S and define ζ_X^D as $ODP(X)/CLP^{Strp}(X)$ divided by ζ^S . The value for ζ^{Cl} is 1 by definition. Based on the $ODP(X)/CLP^{Strp}(X)$ ratios for chlorine species (see Table 1-5), the value for ζ_X^D ranges from 0.35 for HCFC-22 (CH_2ClF_2) to 1.08 for methyl chloroform (CH_3CCl_3). Model simulations by Ko et al. (1998) gave a value of 58 for $\zeta^{Br} \times \zeta_{CH_3Br}^D$ for CH_3Br . The con-

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vention is to take τ_{Br}^{D} to be 45, implying that $\tau_{CH_3Br}^{D}$ has the value of 1.3. The kinetic data are less complete for iodine. Solomon et al. (1994a) provided an estimate of 100-2000 for τ_{I}^{D} based on estimated reaction rate constants. Bedjanian et al. (1998) gave 150 using updated rate data. A more recent study using JPL-2000 rates (Sander et al., 2000) from the Atmospheric and Environmental Research, Inc. (AER) model (Ko et al., 1998) gave a value of 300 for $\tau_{CH_3I}^{D}$ for CH_3I . This could be interpreted as 150 for τ_{I}^{D} and 2 for $\tau_{CH_3I}^{D}$. However, considering the missing data on some of the reservoir species (see Section 2.3.4), we will use a range of 150-300 for τ_{I}^{D} . A useful guideline for τ_{X}^{D} is that τ_{X}^{D} is greater or smaller than 1 depending on whether the local lifetime τ_{X}^{D} in the lower stratosphere is shorter or longer than the local lifetime of CFC-11 (~2 years). From the values of fractional release measured for CFC-11 in the lower stratosphere, τ_{X}^{D} should generally not be much larger than 2. Thus, the estimate for long-lived source gases is

$$ODP_{se}^{long\ lived}(X) = \frac{CFC11}{X} \frac{X}{CFC11} \frac{n_X^{hx}}{3} \quad (2.11)$$

| | | |
|----|-----|-----------------|
| Cl | 1 | |
| Br | 45 | τ_{Br}^{D} |
| I | 150 | 300 |

2.5.2 Modified Approach for Estimating ODP for Halogenated VSL Substances

The inorganic halogen loading from a VSL source gas is maintained by the transport of halogen atoms affected by the SGI and PGI pathways. Solomon et al. (1994b) suggested a method to estimate the contribution from the SGI pathway based on the observed concentration of the VSL source gas near the tropopause. We will restrict the discussion in this subsection to emissions at the Earth's surface. Thus τ_{e}^{D} can be represented by τ_{e}^{D} and τ_{e}^{D} , corresponding to the latitude and longitude of the emission location. It should be noted that certain applications (e.g., inerting fuel tanks in aircraft) involve release of the chemical in the atmosphere above the surface. In those cases, the ODP value will also depend on the altitude at which the VSL substance is released. In this section, using the notation from Section 2.4 (Equation (2.1)) and $\mathcal{L} = E n_X^{hx} / X$, we obtain

$$HL_X^{Avg}(E(\tau_e, \tau_e, t_e)) = \frac{HL_{X-SGI}^{Avg}(E(\tau_e, \tau_e, t_e))}{HL_{X-PGI}^{Avg}(E(\tau_e, \tau_e, t_e))} \frac{E(\tau_e, \tau_e, t_e) n_X^{hx}}{M_{Strat} X} \frac{h_{res\ strat}^{hx}}{(\mathcal{J}_{SGI}^X(\tau_e, \tau_e, t_e) \mathcal{J}_{PGI}^X(\tau_e, \tau_e, t_e))} \quad (2.12)$$

where M_{Strat} is the number of moles of air in the stratosphere, and \mathcal{J}_{SGI}^X and \mathcal{J}_{PGI}^X are functions of $\tau_e, \tau_e,$ and t_e . The residence time for the inorganic halogen in the stratosphere is designated $h_{res\ strat}^{hx}$. Strictly speaking, $h_{res\ strat}^{hx}$ could also be a function of $\tau_e, \tau_e,$ and t_e because material that enters the tropical lower stratosphere has residence times different from material that enters the extratropical lower stratosphere. We do not consider this for now.

The expression for $HL_{CFC11}^{Avg}(E)$ is much simpler:

$$HL_{CFC11}^{Avg}(E) = \frac{1}{M_{Strat}} \frac{E}{CFC11} \frac{3}{h_{res\ strat}^{CFC11}} \quad (2.13)$$

where we used the facts that for CFC-11, $\mathcal{J}_{SGI}^X = 1$, $\mathcal{J}_{PGI}^X = 0$, and it contains three chlorine atoms. We left off the explicit $\tau_e, \tau_e,$ and t_e dependence because the loading for CFC-11 will only depend on the averaged annual tropospheric emission independent of location.

Using Equations (2.12) and (2.13) in Equation (2.8), we obtain

$$ODP_{se}^{VSL}(X, \tau_e, \tau_e, t_e) = \frac{ODP_{se-SGI}^{VSL}(X, \tau_e, \tau_e, t_e)}{ODP_{se-PGI}^{VSL}(X, \tau_e, \tau_e, t_e)} \frac{CFC11}{X} \frac{n_X^{hx}}{3} \frac{h_{res\ strat}^{hx}}{h_{res\ strat}^{CFC11}} \left(\frac{Avg}{X-SGI} \mathcal{J}_{SGI}^X(\tau_e, \tau_e, t_e) \right) \left(\frac{Avg}{X-PGI} \mathcal{J}_{PGI}^X(\tau_e, \tau_e, t_e) \right) \quad (2.14)$$

Similar to the discussion in Section 2.5.1, we use the expression

$$\frac{Avg}{X-SGI/PGI} \mathcal{J}_{SGI/PGI}^D(\tau_e, \tau_e, t_e)$$

where $\mathcal{J}_{SGI/PGI}^D$ is the distribution factor for X maintained by either the SGI or PGI pathway. Thus, for VSL com-

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Table 2-11. Summary of existing studies that have determined a range of ODP values for the case of n-propyl bromide (n-PB), updated from the evaluation in UNEP (2000).

| Study | Range of ODP Values ^a | Effects of Halogen Loading from the PGI Pathway |
|-------------------------|----------------------------------|-------------------------------------------------|
| Bridgeman et al. (2000) | 0.0033-0.0109 | No |
| Olsen et al. (2000) | 0.0002-0.06 | No |
| Wuebbles et al. (2001) | 0.016-0.105 | Yes |

^a Range for the different set of calculations performed in each study. The extreme range of values in Olsen et al. (2000) was due to calculating separate results for individual seasons.

three-dimensional chemical-transport model ($5^{\circ} \times 5^{\circ} \times 34$ levels) in combination with their two-dimensional model to compute ODPs for n-PB. An effort was made to quantify the effects of degradation products. With then-available information, bromoacetone was considered to be the intermediate degradation product with the largest concentration, having a local lifetime of about 1 day. The three-dimensional model was used with simplified chemistry having bromoacetone as the only intermediate degradation product. For n-PB emitted uniformly over global land masses north of 60°S and south of 70°N , their three-dimensional model calculations suggest that about 0.44% of the emitted bromine enters the stratosphere. About 33% of the bromine reaching the stratosphere results from the direct transport of n-PB to the stratosphere and about 19% due to the transport of bromoacetone to the stratosphere. The rest (48%) is from transport of inorganic bromine. Calculated ODP values for other emission scenarios are given in Table 2-12.

Recent data (Burkholder et al., 2002) suggest that the lifetime of bromoacetone is of the order of hours rather than days. Thus, the contribution from bromoacetone may be considerably smaller in evaluating the ODPs for n-PB. As an estimate of the effects of the newly evaluated much shorter atmospheric lifetime, Table 2-12 uses the model results in the Wuebbles et al. (2001) paper to estimate the resulting ODPs if no bromoacetone had reached the stratosphere. The resulting ODP values are reduced, but only slightly. However, the estimate did not account for the likely increase in the amount of inorganic bromine that would reach the stratosphere if the bromoacetone lifetime was reduced to a few hours, and the different distribution in inorganic bromine in the two cases.

Table 2-12. Estimated ODP for n-PB as a function of location of emissions based on Wuebbles et al. (2001).

| Emission Scenario | Derived ODP Range | Modified ODP Range (Reduced Bromoacetone) |
|-------------------------------|-------------------|-------------------------------------------|
| Global | 0.033-0.040 | 0.027-0.038 |
| North America | 0.018-0.019 | 0.015-0.017 |
| United States | 0.016-0.019 | 0.013-0.018 |
| North America + Europe + Asia | 0.021-0.028 | 0.017-0.026 |
| Indonesia + Southeast Asia | 0.087-0.105 | 0.071-0.100 |

Estimates are based on combined results from analyses with the University of Illinois at Urbana-Champaign (UIUC) two-dimensional model and the MOZART2 three-dimensional model. Emissions were evenly distributed over the land masses based on their representation in the three-dimensional model. The range represents different assumptions on the degradation chemistry. In the simulation, bromoacetone is the major intermediate degradation product that is transported to the stratosphere. The last column gives the estimated ODPs assuming that bromoacetone does not reach the stratosphere.

In summary, the existing studies for n-PB have shown that the ODP for a VSL source gas does vary with location and season of the emissions, by more than a factor of 5 for this particular gas, with the largest values for tropical emission. However, there remain significant uncertainties in the existing studies. Better treatments of tropospheric convection processes and wet scavenging processes could be particularly important to reducing the uncertainties for ODPs.

2.5.4 Information Required for Evaluating Ozone Impact from VSL Source Gases

As discussed above, unlike for the longer lived compounds, the ODP for the VSL source gases cannot be viewed as an intrinsic property of the substance that is equally applicable worldwide. The location and timing of the emissions are important to determine a meaningful set of ODP values for VSL halogen source gases. Figure 2-10 shows the different steps needed in estimating the ozone depletion effects of long-lived species and VSL halogen source gases. Future studies of ODPs for VSL substances require careful consideration of the following parameters:

- Determination that the vapor pressure of the substance, at atmospheric temperatures at the point of emission, is sufficient to generate a significant gas-phase concentration in the atmosphere.
- Determination of the atmospheric reactivity of the VSL substance (with OH, through photolysis, etc.) and its water solubility.
- Evaluation of the degradation products, their water solubility, and their chemical behavior in the troposphere.
- Determination of the potential uses of the VSL substance, where the VSL substance will be used and likely emitted, and the likely seasonal variations in the emissions (see, e.g., data compiled for n-PB by the UNEP Technology and Economic Assessment Policy (TEAP) task force (UNEP, 2001)).

Given the complexity of the processes in the troposphere, it is unlikely that they could be treated in 2-D models. Three-dimensional models of the global troposphere and stratosphere are necessary to determine accurately the resulting set of ODPs for a newly considered VSL substance.

As discussed in Section 2.5.1, the ODP represents the cumulated effects from the same mass pulse emission relative to CFC-11. The time evolutions of the effects are distinctly different for long-lived species and VSL source gases. For long-lived species, the full effect is realized after a few years' delay and then decreases exponentially according to the atmospheric lifetime of the source gas. For CFC-11, this means that the cumulative effect is spread over about 100 years. For VSL source gases, the effect lasts about 5 years. Thus, the short-term (5 years after emission) effects from a VSL source gas can be 20 times larger than indicated by its ODP value. For fully analyzing the potential effects on ozone, it is important to consider the projected amount of future use and resulting emissions of the VSL substances and evaluate the time-dependent effects (e.g., Wuebbles and Calm, 1997; Calm et al., 1999). One approach often used for evaluating future emissions is the concept of equivalent chlorine loading, or more appropriately for determining stratospheric ozone loss, its variation, equivalent effective stratospheric chlorine (EESC) (e.g., Solomon and Wuebbles et al., 1995; Daniel et al., 1995; Madronich and Velders et al., 1999; Calm et al., 1999). As demonstrated in Chapter 1, EESC can be very useful for evaluating the effects on ozone from long-lived halocarbons. However, given that the halogen loading from VSL source gases as given by Equation (2.13) is very different from Equation (2.8), one cannot use the normal EESC formulation for VSL source gases. A modified procedure is needed for such calculations.

2.6 VSL SULFUR SPECIES AND STRATOSPHERIC AEROSOLS

2.6.1 Introduction

Stratospheric aerosol consists mainly of super-cooled hydrated H_2SO_4 particles with a sulfuric acid mass fraction in the range of 50-80%. At very low temperatures in the wintertime polar stratosphere, nitric acid can be taken up on sulfuric acid particles to form a ternary solution $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$. Stratospheric aerosols can stay liquid to very low temperatures. Other aerosol components can also be present (Carslaw et al., 1997; Murphy et al., 1998; Murphy and Thomson, 2000). The presence of soot in the lower stratosphere has been observed and documented (Pueschel et al., 1992, 1997; Strawa et al., 1999), although measurements remain scarce. Smoke from boreal forest fires has also been observed in some occasions in the lower stratosphere (Fromm et al., 2000).

The particles form a persistent aerosol layer, the stratospheric sulfate aerosol (SSA) layer or Junge layer, which extends from the tropopause up to ~25 km altitude. This layer shows strong variability at annual or longer time scales due to the dominant influence of explosive volcanic eruptions that inject sulfur compounds into the stratosphere (see, e.g., Godin and Poole et al., 1999). For example, satellite observations from the Stratospheric Aerosol and Gas Experiment (SAGE) II show that it took 6 years for the stratospheric aerosol concentrations to return to their pre-Pinatubo-eruption levels of 1991 (Kent et al., 1995, 1998; Thomason et al., 1997a,b) after a 100-fold increase in mass loading. It is generally believed that the observed sulfate loading after the year 2000 is representative of the background sulfate aerosol unaffected by large explosive volcanic eruptions.

Changes in stratospheric aerosols will affect stratospheric ozone in at least two ways. First, heterogeneous reactions occurring on the aerosol surface affect the partitioning of chemical species between reservoirs and free radicals. This is primarily due to the heterogeneous conversion of active NO_x to NO_y reservoirs, which significantly alters the partitioning of HO_x and halogen species. Thus, an increase in the aerosol surface area tends to convert more of the halogen reservoirs to radicals and hence affects the catalytic cycles leading to ozone depletion. Second, changes in aerosol loading change the radiative balance, and therefore the temperature, in the lower stratosphere. This in turn changes the transport circulation, resulting in a redistribution of ozone. Effects from both mechanisms were evident after the Mt. Pinatubo eruption (see, e.g., Pitari and Mancini, 2002).

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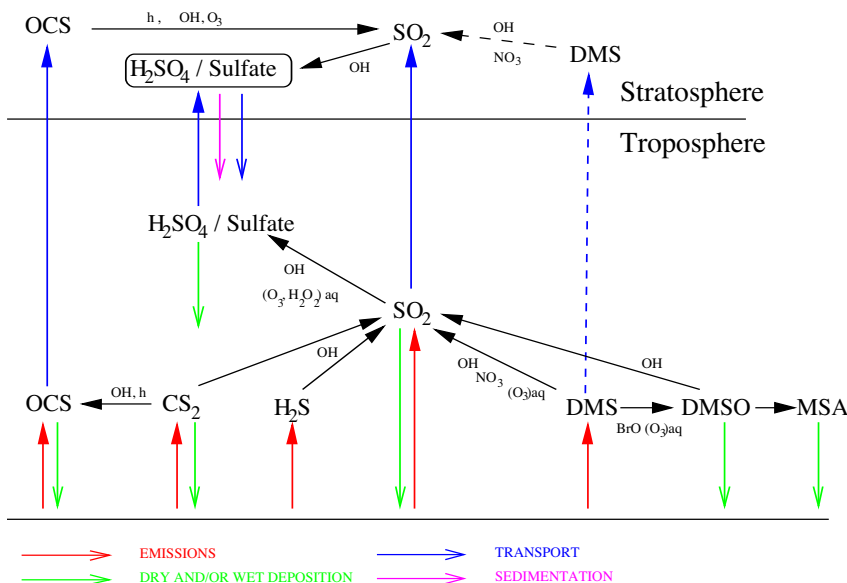


Figure 2-11. Schematic diagram of the tropospheric and stratospheric sulfur cycles. The contributions from oxidation of DMS in the stratosphere have not been quantified. Those processes are indicated by dashed arrows. Production of SO_2 from OCS in the troposphere and direct emission of H_2SO_4 are not shown because their effects on the budget in the troposphere are small compared with the other processes.

The purpose of this section is to examine the processes that determine how injection of sulfur from large explosive volcanic eruptions and release of VSL precursor gases in the troposphere might affect the SSA. Stratospheric aerosol is maintained by the supply of sulfur (in gas and liquid forms) to the stratosphere that is balanced with removal by transport out of the stratosphere. The residence time for aerosols in the stratosphere is of the order of 1 year. It is not possible to define a single residence time for aerosols, because it changes with the size distribution of the aerosol particles and it also depends on where the aerosol particles are formed in the stratosphere. The supply to the stratosphere could be in the form of sulfate (Brock et al., 1995) or gas-phase sulfate precursors. Figure 2-11 summarizes the processes that control the gas-phase sulfate precursor gases. Sulfate precursors released from the Earth's surface include sulfur dioxide (SO_2), hydrogen sulfide (H_2S), and organic gases such as dimethyl sulfide (DMS, CH_3SCH_3), carbonyl sulfide (OCS), and carbon disulfide (CS_2). DMS, H_2S , and SO_2 can be oxidized in the lower troposphere via gas-and/or aqueous-phase processes with a lifetime of a few days or less, forming sulfate aerosol as the main final product. Thus they behave like the VSL halogen source gases discussed earlier in this chapter. The present emission rates have been estimated as 10-30 Tg (S) yr^{-1} for DMS, 1-2 Tg (S) yr^{-1} for OCS, 0.5-1.5 Tg (S) yr^{-1} for CS_2 , 6-9 Tg (S) yr^{-1} for H_2S , and 67-100 Tg (S) yr^{-1} for SO_2 (see recent review in Watts, 2000; Penner et al., 2001). The dominant natural source of sulfur is DMS, of which

about 80-95% is emitted from the oceans. The source for SO_2 consists mostly of anthropogenic sources from fossil fuel use (~ 70 Tg (S) yr^{-1}), with volcanic outgassing (including small eruptions) and biomass burning contributing 8-20 Tg (S) yr^{-1} (Graf et al., 1997; Andres and Kasgnoc, 1998) and 2.5 Tg (S) yr^{-1} (Hao et al., 1990), respectively. Note that portions of the latter sources are deposited directly into the free troposphere and can reach the stratosphere more efficiently. The amount of sulfur emitted by aviation in the upper troposphere and lower stratosphere was estimated to be 0.06 Tg (S) yr^{-1} in 1992 (see Fahey and Schumann et al., 1999). The Mt. Pinatubo eruption is estimated to have injected 20 Tg (S) directly into the lower stratosphere.

2.6.2 Chemistry of the VSL Sulfur Species

Here we discuss briefly the chemistry of each of the VSL sulfur species and some of the current uncertainties. Oxidation of H_2S in the troposphere is well understood. It reacts with OH and produces mainly SO_2 . Oxidation of CS_2 occurs by reaction with OH and possibly by a mechanism involving direct photoabsorption by CS_2 , both mechanisms occurring at comparable rates (Jones et al., 1983). Both routes form OCS and SO_2 as the main stable products. DMS reacts in the gas phase with OH during the day and with NO_3 at night. Figure 2-12 shows the DMS degradation mechanism. SO_2 is the major oxidation product, with dimethyl sulfoxide (DMSO, $\text{CH}_3\text{S(O)CH}_3$) and methanesulfonic acid (MSA,

CH₃SO₃H) as minor products. The specific yields of DMS oxidation products, which depend on temperature and other environmental conditions, are still under debate (Williams et al., 2001; de Bruyn et al., 2002). Recent laboratory measurements have shown that DMS can also react with ozone in solution with a rate that is a factor of about 10⁶ faster than the corresponding homogeneous gas-phase reaction (Gershenson et al., 2001). Such a fast reaction may, under certain conditions, compensate for the small DMS solubility so that the liquid-phase reactions may be significant in clouds.

The basic chemistry of SO₂ oxidation to form H₂SO₄ is well understood. It occurs mainly by liquid-phase oxidation in clouds or aerosols, involving hydrogen peroxide (H₂O₂), O₃, or HOX (X = Cl or Br) as oxidizing agents. The other loss processes for SO₂ in the troposphere are dry and wet deposition, and gas-phase oxidation by OH. The gas-phase oxidation represents only about 10-20% of SO₂ loss (e.g., Koch et al., 1999; Barth

et al., 2000; Chin et al., 2000). The combined residence time of SO₂ against all removal processes in the troposphere is estimated to be 1 to 2 days, with a large fraction of SO₂ being removed via deposition and liquid-phase oxidation. In the stratosphere, SO₂ is transformed to H₂SO₄ by gas-phase oxidation by OH with a lifetime of approximately 35 days (Bluth et al., 1992). The sulfate vapor will either form new particles by homogeneous nucleation of sulfuric acid and water vapor or condense on existing aerosol particles.

It is important to keep track of formation of new particles because smaller particles have longer residence times in the stratosphere and will lead to a larger mass loading. There are some indications that the upper troposphere can be a source of new particles, which can then be transported to the stratosphere where they grow in size (Brock et al., 1995; Hamill et al., 1997; de Reus et al., 1999). Transport of small sulfate aerosol particles to the stratosphere will result in a larger increase in surface area

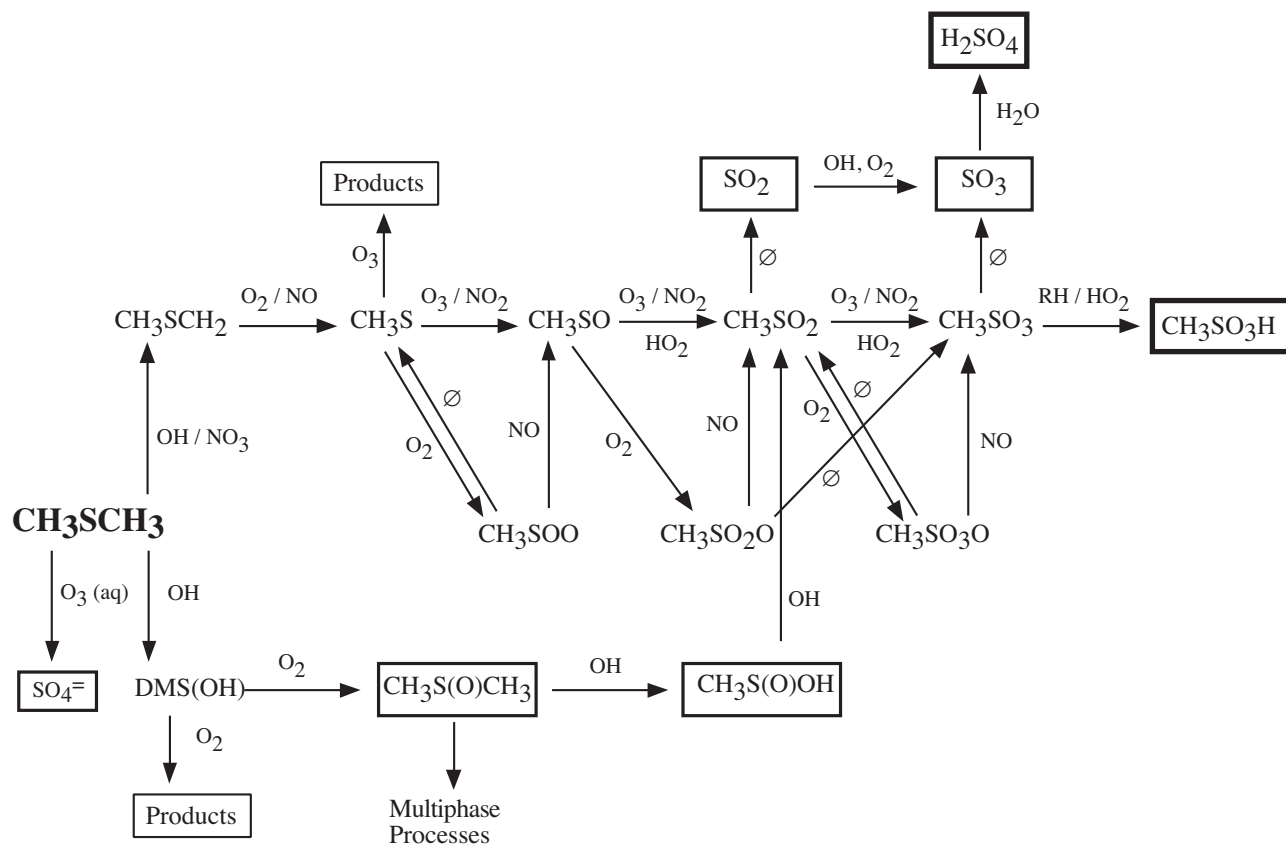


Figure 2-12. Degradation mechanisms for dimethylsulfide (DMS, CH₃SCH₃).

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than transport of the same mass of sulfur in gaseous form, which will preferentially condense on existing sulfate particles. The mechanisms and conditions necessary for new particle formation are still not well understood (de Reus et al., 2000).

2.6.3 Sources for the Stratospheric Sulfate Layer

2.6.3.1 DIRECT INPUT FROM EXPLOSIVE VOLCANIC ERUPTIONS

Direct injections of volcanic sulfur into the stratosphere are sporadic and unpredictable. Explosive volcanic eruptions reach the stratosphere in general at least once every 2 years (Simkin, 1993). Typically, sulfur gases, mainly SO_2 and H_2S , contribute 2 to 35% (in volume) to the volcanic gas emissions. OCS and CS_2 contribute only a small fraction (10^{-4} to $10^{-2}\%$ in volume).

Most models simulate the aerosol evolution after a volcanic eruption assuming that all the sulfur is injected in the form of SO_2 . This will not lead to a large error for the sulfur species because H_2S oxidizes to SO_2 within 2 days in the troposphere and within 10 days in the stratosphere. The Mt. Pinatubo eruption is estimated to have deposited 20 Tg (S) in the stratosphere. After the Mt. Pinatubo eruption, 98% of the observed stratospheric aerosol was volatile (Deshler et al., 1992; Sheridan et al., 1992), indicating that homogeneous nucleation is the most important process for stratospheric aerosol formation in the disturbed atmosphere. Within the volcanic layers, Deshler et al. (1992) found an increase of 1-2 orders of magnitude in the concentration of condensation nuclei. Model calculations that successfully reproduced Mt. Pinatubo sulfate aerosol (Timmreck and Graf, 2000; Weisenstein et al., 1997) were based on homogeneous nucleation.

Observations (Russell et al., 1996) and model studies (Zhao et al., 1995; Timmreck and Graf, 2000) show that it takes about 3 months to build up the sulfate peak. The volcanically enhanced stratospheric aerosol layer can be observed for several years after major eruptions. The aerosol optical depth at 550 nm first peaked to >0.2 three months after Mt. Pinatubo, and then reduced within 6 years to the background value of 0.003. This represents an e-folding time of approximately 17 months (McCormick and Veiga, 1992; Ansmann et al., 1997). The relatively faster removal of large compared with small particles from the stratosphere leads to a more rapid decrease in aerosol mass than in aerosol surface (Ansmann et al., 1997; Godin and Poole et al., 1999).

The presence of the volcanic aerosol would change the transport circulation in the lower stratosphere (see, e.g., Kinne et al., 1992; Schoeberl et al., 1993). Most of the model studies do not take this into account. Questions have also been raised whether a sufficiently large volcanic injection could also affect the HO_x cycle in the stratosphere. From simple consideration of stoichiometry, it can be assumed that one molecule of H_2O is produced per H_2S oxidized. For SO_2 , it is assumed that no net gain or loss of HO_x results from SO_2 oxidation (Read et al., 1993; McKeen et al., 1984). Finally, approximately three molecules of H_2O are needed to oxidize SO_2 and condense sulfuric acid to sulfate aerosols (Bekki, 1995). Two-dimensional model simulations (Bekki et al., 1996) showed that a hypothetical injection of 6000 Tg SO_2 could dehydrate the stratosphere. Given that most large eruptions inject about several tens of teragrams of sulfur, this effect is probably not important under most conditions.

2.6.3.2 VSL PRECURSORS EMITTED IN THE TROPOSPHERE

It has been long recognized that oxidation of OCS in the stratosphere is an important source of stratospheric background sulfate aerosol (Crutzen, 1976). Carbonyl sulfide is emitted at the Earth's surface by natural and anthropogenic sources, and is also formed by the oxidation of CS_2 (Chin and Davis, 1993, and the references therein; Watts, 2000). Chin and Davis (1995) used available OCS atmospheric observations and improved laboratory reaction-rate data to show that oxidation of OCS produces $0.03 \text{ Tg (S) yr}^{-1}$ in the stratosphere. This corresponds to 5% of the OCS emission from the surface and is only 20-50% of the recently revised estimates of the sulfur flux ($0.06\text{-}0.15 \text{ Tg (S) yr}^{-1}$) needed to maintain the background stratospheric sulfate layer (Chin and Davis, 1995). Later model studies seem to support these conclusions and attribute the other major source to SO_2 supplied from the troposphere. For example, Weisenstein et al. (1997) found in their 2-D model, which includes a microphysical treatment of the particles, that OCS oxidation could account for $0.049 \text{ Tg (S) yr}^{-1}$ of sulfate production in the stratosphere, and that convective transport of SO_2 in the tropical troposphere could provide 50% of the background sulfate aerosol. Kjellström (1998) estimated that the sulfate production from OCS was 3 to 12 times smaller than the stratospheric background source of sulfate aerosols, and that the transport of SO_2 from the troposphere was the major supplier for the background sulfate aerosol. A very recent global 3-D model study (Pitari et al., 2002) estimated that OCS photochemical oxidation could account for about 43% of the total background strat-

ospheric sulfate aerosol, whereas the upward transport of tropospheric sulfate and SO₂ contribute 30% and 27%, respectively. There are important uncertainties in such model results because of uncertainties in the model description of how transport processes control the amount of VSL substances such as SO₂ and sulfate delivered to the stratosphere (see Section 2.2).

Of particular interest is how changes in anthropogenic SO₂ emissions would affect the sulfate loading in the stratosphere. Chin et al. (2001) and Pitari et al. (2002) performed simulations to compute the sulfate loading from anthropogenic SO₂ emission. Using the most recent estimate of emission of 69 Tg (S) yr⁻¹ from the Intergovernmental Panel on Climate Change *Special Report on Emissions Scenarios* (IPCC-SRES) (Nakićenović et al., 2000), they calculated burdens of 0.7-0.8 Tg (S) sulfate in the troposphere and 0.07-0.09 Tg (S) sulfate in the stratosphere. A residence time for sulfate in the stratosphere of 1-2 years would imply that about 0.05-0.15% of the SO₂ surface emission enters the stratosphere. No study has been done for SO₂ emissions from volcanic degassing and biomass burning. It is important to remember that because of different emission locations, the effect will not necessarily scale with the emission strengths. Kjellström et al. (1999) estimated that aircraft emissions contribute less than 1% of the total sulfate mass in regions of high air traffic.

2.6.4 How Can We Predict Future Changes in the Stratospheric Sulfate Layer?

If anthropogenic SO₂ emissions can account for more than half of the stratospheric background sulfate aerosol, future changes in anthropogenic SO₂ emission could have an important impact on stratospheric sulfate aerosol loading. One can ask whether the past secular trend in anthropogenic SO₂ emission has caused an

increase in the loading of stratospheric aerosol. This question cannot be easily answered from the limited existing set of observations. Analysis of time series related to the stratospheric aerosol layer does not show any evidence of a trend in the nonvolcanic aerosol loading between the late 1970s, the late 1980s, and the late 1990s to the present (see Chapter 4). The average global anthropogenic SO₂ emission strength has probably been fairly constant between 1980 and 1990, the increases in some regions being compensated by decreases in other regions (Boucher and Pham, 2002). However, changes in the geographical distribution of anthropogenic SO₂ emissions may also modify the fraction of surface SO₂ emissions that contribute to the stratospheric sulfate aerosol layer. Finally, since the contribution of tropospheric volcanic emissions to the total atmospheric sulfate burden is nearly equal to that from anthropogenic sources (Graf et al., 1997), the climatological stratospheric aerosol levels are also determined by outgassing associated with volcanic activity that is highly variable in space and time and unpredictable.

Future changes in the stratospheric sulfate layer have been estimated by performing model simulations using the IPCC projected emission scenarios for years 2030 and 2100 (Nakićenović et al., 2000). Table 2-13 summarizes the model results of Chin et al. (2001). The first simulation, SC1, is taken from the IPCC SRES (scenario A2) to represent the anthropogenic emissions in year 2000. Simulations 2 and 3 (SC2 and SC3) are based on the SRES preliminary emission scenario A2p, which projects a regionally inhomogeneous economic development for years 2030 and 2100, respectively. Simulation 4 (SC4) is from another SRES preliminary emission scenario (B1p) for year 2100, which assumes a convergent world with a rapid introduction of new and more efficient technologies. It can be deduced from the values in Table 2-13 that every 1 Tg (S) yr⁻¹ increase in anthropogenic SO₂

Table 2-13. Estimated sulfur emission rates in years 2000, 2030, and 2100 and the model-calculated corresponding tropospheric and stratospheric sulfate burdens. The cited values for the simulated burdens are from Chin et al. (2001).

| Emission Rates and Stratospheric Sulfate Burdens | SC1 2000 | SC2 2030 | SC3 2100 | SC4 2100 |
|-------------------------------------------------------------------|---------------------|---------------------|---------------------|---------------------|
| Anthropogenic emission, SO ₂ (T (S) yr ⁻¹) | 69.0 | 111.9 | 60.4 | 28.7 |
| Oceanic emission, DMS (Tg (S) yr ⁻¹) | 16.1 | 16.1 | 16.1 | 16.1 |
| Volcanic emission, SO ₂ (Tg (S) yr ⁻¹) | 4.8 | 4.8 | 4.8 | 4.8 |
| Tropospheric burden (Tg (S)) | 0.656 | 1.124 | 0.647 | 0.372 |
| Stratospheric burden (Tg (S)) | 0.069 | 0.143 | 0.068 | 0.044 |

Volcanic emissions are for the continuously erupting volcanoes only and are from Andres and Kasgnoc (1998). Anthropogenic emissions are from four scenarios in the IPCC SRES (Nakićenović et al., 2000).

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emission could roughly result in 9 Gg (S) of sulfate burden increase in the troposphere and 1 Gg (S) in the stratosphere. Using the emission rates of SC2, Pitari et al. (2002) have estimated that the stratospheric non-OCS sulfate burden will be 0.14 Tg (S) in 2030, a value similar to that in Table 2-13.

Using a coarse-grid model with simple chemistry, Pitari et al. (2002) showed the increase in surface emission of SO₂ between year 2000 (SC1) and 2030 (SC2) will result in an increase in aerosol surface area of up to 0.5 μm² cm⁻³ in the Northern Hemisphere, at altitudes between 100 and 200 hPa. The increase in the stratospheric surface area would cause a slowdown of the stratospheric ozone recovery rate expected from the reduction in the CFCs.

Overall it can be concluded that representation of the processes controlling the SSA budget in models is very much simplified and the calculations of impacts of future changes in nonvolcanic sulfur emissions are therefore very uncertain. More studies are needed to understand the relative contributions of surface emission of VSL sulfur substances to the present and future stratospheric sulfate aerosol burden. In addition to the general problems of transport of VSL species in the troposphere (discussed in Section 2.2), areas of uncertainty are the role of aerosol nucleation in the upper troposphere; the mechanism of gas-phase DMS oxidation; the heterogeneous reactions of VSL sulfur substances on aerosol surfaces; the induced changes in the radiation balance and circulation in the lower stratosphere; and the magnitude of future emissions. The attempts by several modeling groups (e.g., Pitari and Mancini, 2002; Timmreck, 2001; Pitari et al., 2002) represent promising starts. However, such models must be extended to include a more complete treatment of the processes in the troposphere and be thoroughly evaluated with measurements (see, e.g., Lohmann et al., 2001).

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