

## Natural emissions of chlorine-containing gases:

### Reactive Chlorine Emissions Inventory

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**Abstract.** Although there are many chlorine-containing trace gases in the atmosphere, only those with atmospheric lifetimes of 2 years or fewer appear to have significant natural sources. The most abundant of these gases are methyl chloride, chloroform, dichloromethane, perchloroethylene, and trichloroethylene. Methyl chloride represents about 540 parts per trillion by volume (pptv) Cl, while the others together amount to about 120 pptv Cl. For methyl chloride and chloroform, both oceanic and land-based natural emissions have been identified. For the other gases, there is evidence of oceanic emissions, but the roles of the soils and land are not known and have not been studied. The global annual emission rates from the oceans are estimated to be 460 Gg Cl/yr for CH<sub>3</sub>Cl, 320 Gg Cl/yr for CHCl<sub>3</sub>, 160 Gg Cl/yr for CH<sub>2</sub>Cl<sub>2</sub>, and about 20 Gg Cl/yr for each of C<sub>2</sub>HCl<sub>3</sub>, and C<sub>2</sub>Cl<sub>4</sub>. Land-based emissions are estimated to be 100 Gg Cl/yr for CH<sub>3</sub>Cl and 200 Gg Cl/yr for CHCl<sub>3</sub>. These results suggest that the oceans account for about 12% of the global annual emissions of methyl chloride, although until now oceans were thought to be the major source. For chloroform, natural emissions from the oceans and lands appear to be the major sources. For further research, the complete database compiled for this work is available from the archive, which includes a monthly emissions inventory on a 1° x 1° latitude-longitude grid for oceanic emissions of methyl chloride.

## 1. Introduction

There has been a sustained interest in natural emissions of chlorine-containing gases driven by the discovery that man-made chlorofluorocarbons can deplete ozone in the stratosphere [Molina and Rowland, 1974]. Only a few natural chlorine-containing gases significantly affect stratospheric ozone, or global atmospheric chemistry.

We surveyed the atmospheric concentration data for all known chlorinated organic gases in the atmosphere with concentrations greater than a few parts per trillion. We classified these gases

according to their lifetimes as reactive, if the globally averaged lifetime is less than 2 years; moderately reactive if the lifetime is between 2 and 10 years, and unreactive if the lifetime is longer than 10 years. Available data indicate that only the reactive gases have natural sources [Khalil, 1998]. This paper deals with the emissions of chlorine-containing gases from natural sources including the oceans, soils, plants and fungi. Not included are emissions from natural forest and grass fires since these are discussed by Lobert *et al.* [1999] and possible atmospheric production of chlorine-containing gases from natural precursors because we have no data on such processes.

Methyl chloride is the most abundant chlorine-containing gas in the atmosphere with a global average concentration of about 540 pptv (1 pptv = 1 molecule gas/ 10<sup>12</sup> molecules air). The average concentration of chloroform, integrated over the troposphere, is at about 16 pptv. These two gases appear to have large natural sources with some contributions from anthropogenic activities including small emissions from industrial processes [Aucott *et al.*, 1999; McCullough *et al.*, 1999]. Other reactive chlorine-containing gases are present in even lesser amounts and include dichloromethane, chlorinated ethylenes, and ethanes.

We bring together the results of a substantial recent research program to delineate the natural sources of the most abundant organic chlorine-containing trace gases in the Earth's atmosphere. As a guide to the detailed discussions in this paper, we list the noteworthy results from this research: (1) Current data on the ocean-air exchange of methyl chloride suggest that the global emissions are about 460 Gg Cl/yr which is only about 12% of the global emissions needed to account for the observed concentrations based on our current understanding of its oxidation in the atmosphere by reaction with hydroxyl radical. Until now the oceans were considered to be the major source of methyl chloride. (2) A source of methyl chloride, not previously considered in global budgets is its production during fungal decomposition of woody material in natural forest ecosystems. While the current data are highly uncertain, we estimate that this source is about 100 Gg Cl/yr with a possible range between 30 and 330 Gg Cl/yr. We also discuss the possibility of release of methyl chloride from higher plants but sufficient data are not available to

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Paper number 1998JD100079.  
0148-0227/99/1998JD100079\$09.00

estimate global emissions, if any, from this source. (3) On the basis of our estimates the known natural sources are insufficient to account for most of the methyl chloride present in the atmosphere. (4) We show that there are substantial global emissions of chloroform from the land and the oceans. These natural emissions may be sufficient to explain most of the observed abundance of chloroform in the atmosphere, which is ubiquitous and represents the next most abundant source of natural chlorine in the troposphere (about 47 parts per trillion by volume (pptv) Cl). In the past it was thought that atmospheric chloroform was primarily from anthropogenic sources [*National Academy of Sciences (NAS)*, 1978]. (5) Dichloromethane, trichloroethylene and tetrachloroethylene are the three next most abundant chlorine-containing gases for which there is evidence of natural emissions from the oceans. Although we have estimated the global emission rates, the data establish only that natural oceanic sources may exist. This has not been shown before for tri- and perchloroethylenes. (6) We have described a method by which we can use the underlying empirical relationship between saturation level and water temperature to estimate the flux of methyl chloride from the oceans at any desired spatial and temporal resolution, with some limitations. Using this method we have calculated the emissions of methyl chloride from  $1^\circ \times 1^\circ$  longitude-latitudinal cells over the oceans. This is a standard resolution adopted by the Global Emission Inventory Activity (GEIA) program under which this work was conducted. We believe that this estimate is accurate since it is founded on a relationship that has been replicated by three independent studies and it produces flux estimates over time scales and space scales that are most useful for the analysis of global budgets.

While there are many uncertainties, our work offers the opportunity to test the regional distributions of emissions of methyl chloride and the budgets of the other chlorine-containing gases with natural sources. The underlying data and results are available to

readers from the archive.

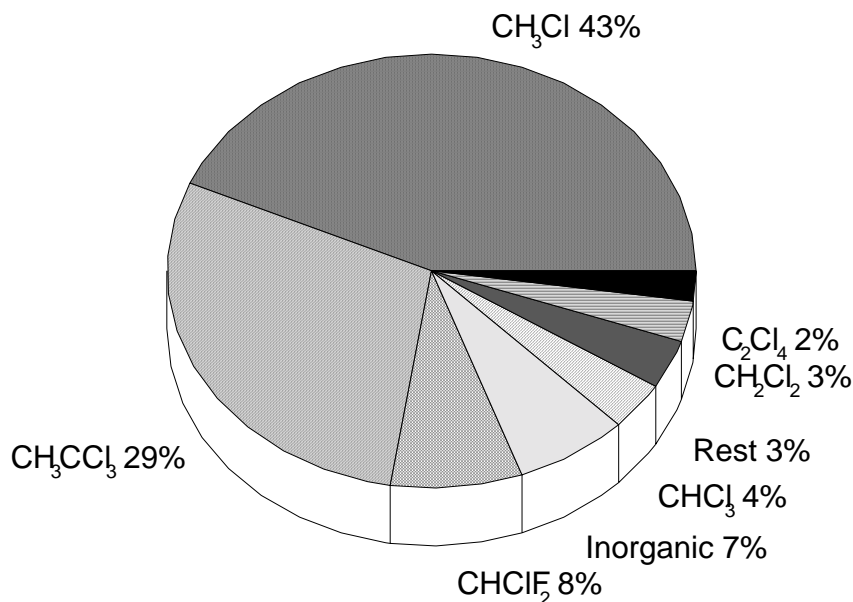
We will focus more attention on methyl chloride than the other gases, not only because we have the most information on its natural emissions, but also because it represents a major fraction of the known natural organic chlorine pool in the atmosphere. A summary of the atmospheric distribution of gaseous organic chlorine is given in Figure 1 showing the significance of methyl chloride and the other gases that have natural sources.

## 2. Concentration Distribution of Reactive Chlorine Gases

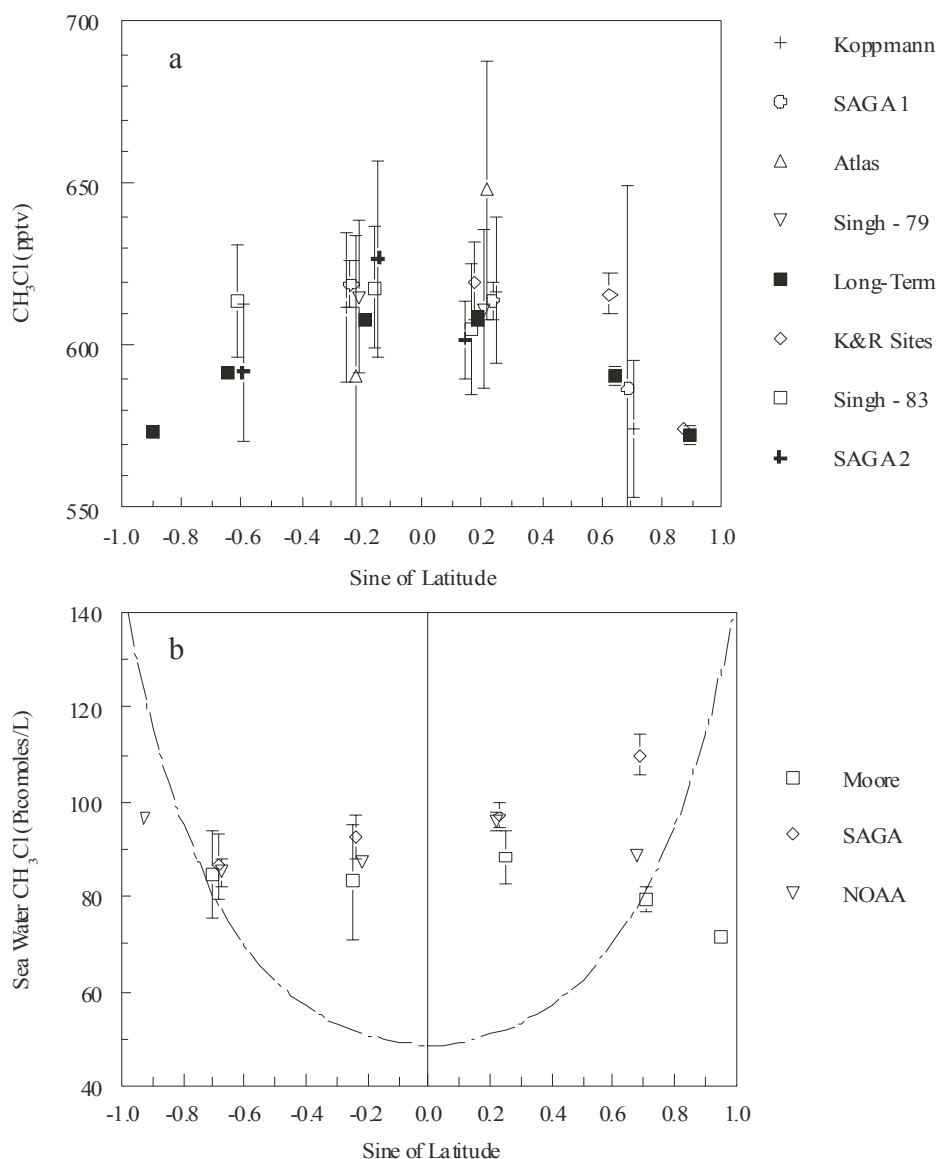
The global balance of a gas in the atmosphere consists of three components: the sum of emissions from all sources (S) (usually expressed in giga grams/yr = 1 Gg/yr =  $10^9$  g/yr or tera grams/yr = 1 Tg/yr =  $10^{12}$  g/yr), less the losses due to all processes (L) equals the trend (dC/dt). We will use units of GgCl or TgCl throughout the paper. The total loss term (L) is used to define the lifetime as the ratio of the amount in the atmosphere (C) over the losses. Of these three variables, the atmospheric concentration is often the best known, as is the case for the gases included here. We will discuss these components for each of the chlorine-containing gases of interest [see also *Keene et al.*, 1990; *Graedel and Keene*, 1995; *Khalil*, 1998].

### 2.1 Methyl Chloride: Air and Seawater Concentrations

The global concentration of methyl chloride in the air and in seawater has been reported in several studies [*Khalil and Rasmussen*, 1998a, b, c, d; *Moore et al.*, 1996, 1998; *Lober et al.*, 1996, 1998; *Khalil*, 1998, and references therein]. In Figure 2a, the solid squares represent the average of 16 years of data (1981-1997) from six land-based sites in the marine boundary layer at polar, middle, and tropical latitudes of each hemisphere (Point Barrow, Alaska,  $71.16^\circ\text{N}$ ; Cape Meares, Oregon,  $45.5^\circ\text{N}$ ; Cape Kumukahi and Mauna Loa, Hawaii,



**Figure 1.** The contribution of gases (as Cl) to the total reactive chlorine concentration in the troposphere. Only gases with atmospheric lifetimes around 10 years or less, classified as reactive and moderately reactive, are shown here. There are about 23 Tg of chlorine in the atmosphere, with about 14.8 Tg as unreactive or long-lived gases, 2.7 Tg as moderately reactive gases, and 5.7 Tg as reactive gases. Natural emissions are observed only for the reactive class.



**Figure 2.** (a) The latitudinal distribution of methyl chloride in the marine boundary layer. The bars represent 90% confidence limits of the data. The points are representative of latitudinal bands between 0°-30°, 30°-60°, and 60°-90° in each hemisphere. They are plotted here slightly offset from the center so that the points can be distinguished. Solid squares are averages over 1-3 years from marine sites [Khalil and Rasmussen, 1998a]. The data from various publications are adjusted for absolute calibration differences to the Rasmussen Scale, as discussed in the text. This graph illustrates the replication of the latitudinal pattern by various studies. One high value of 945 pptv in the data reported by Atlas *et al.* [1993] was omitted as it appeared to be an outlier. (b) Average concentrations of methyl chloride in sea water based on shinboard measurements.

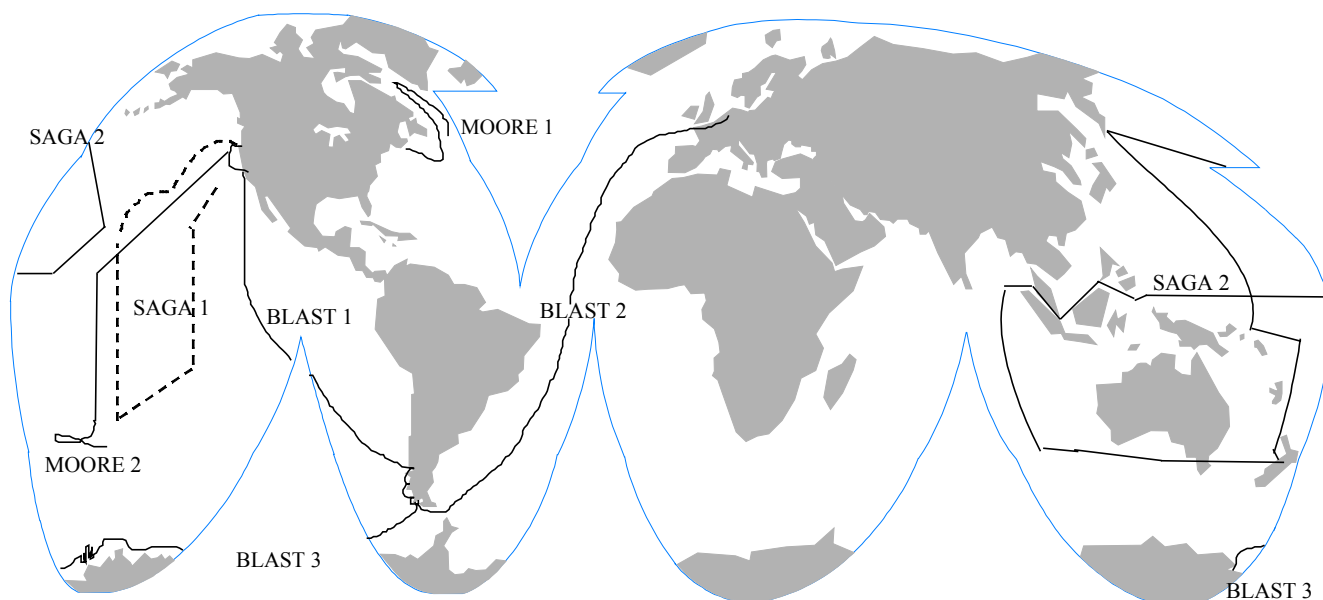
19.3°N; Samoa, 14.1°S; Cape Grim, Tasmania, 42°S; Palmer Station, 65.46°S; South Pole at 90°S). These data and their analyses are reported elsewhere [Khalil and Rasmussen, 1998a].

The other data shown are mostly from ship cruises [Koppman *et al.*, 1993; Singh *et al.*, 1979, 1983a, b; Atlas *et al.*, 1993; Khalil and Rasmussen, 1998b, d). These data have been averaged over latitudes from 0°-30°, 30°-60°, and 60°-90° in each hemisphere and represented as regional averages to make them comparable with the data from the long-term sites.

The measured latitudinal distributions consist of two components: the absolute concentration and the latitudinal pattern. The measured absolute concentration is affected by the experimental process since each laboratory has created an independent calibration standard.

While we expect that the various experimenters will generally agree on the absolute concentration, experience has shown that substantial systematic differences exist in independent calibrations for gases at such low levels as the ones discussed here. The latitudinal pattern however, is the property of the global cycle of the gas and should be independent of the measurement process. We have therefore put data from different experimenters on the same absolute scale to see if they agree on the latitudinal pattern and to quantify the differences of absolute concentrations between observers.

The data of Koppmann *et al.* [1993], as shown in the graph, were multiplied by 1.12 (data were 12% lower relative to long-term sites). Data from Moore *et al.* [1996] and Moore [1998] for northern latitudes are about 10% lower than the long-term average (not shown,



**Figure 3.** Cruise tracks where flux measurements were taken for  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$  and other gases. Only methyl chloride was measured on all cruises. The tracks represent three main studies by Khalil and Rasmussen (SAGA 1,2 1983, 1987), R. Moore (Atlantic cold water and long transect 1995), and NOAA/CMDL (J. Lobert: BLAST 1,2,3 cruises 1994 and 1995).

because there are only three measurements). These comparisons suggest that the Rasmussen scale, on which the long-term concentrations are based, may be about 10% high [Rasmussen *et al.*, 1980; Edgerton, 1985; Khalil and Rasmussen, 1998a]. Additional research is needed to reduce this absolute calibration uncertainty. While this difference is important, it is not large enough to contribute significantly to the present uncertainties in the global budget of methyl chloride. The numerical results on the sources and sinks presented here are adjusted to 90% of the Rasmussen scale to be consistent with the more recent absolute calibration values.

The main feature of the long-term ambient levels is a higher concentration in the tropical regions compared with concentrations at high latitudes. This feature was observed in earlier data reported by Rasmussen *et al.* [1980]. Subsequent data are consistent with this observation. Since there are seasonal variations of methyl chloride at middle and higher latitudes, and the equatorial bulge is small, it can be obscured in data obtained from ocean cruises that span a short time, usually less than one season [Khalil and Rasmussen, 1998a]. This latitudinal pattern, however, has implications for the emissions of methyl chloride from various sources as we will discuss later.

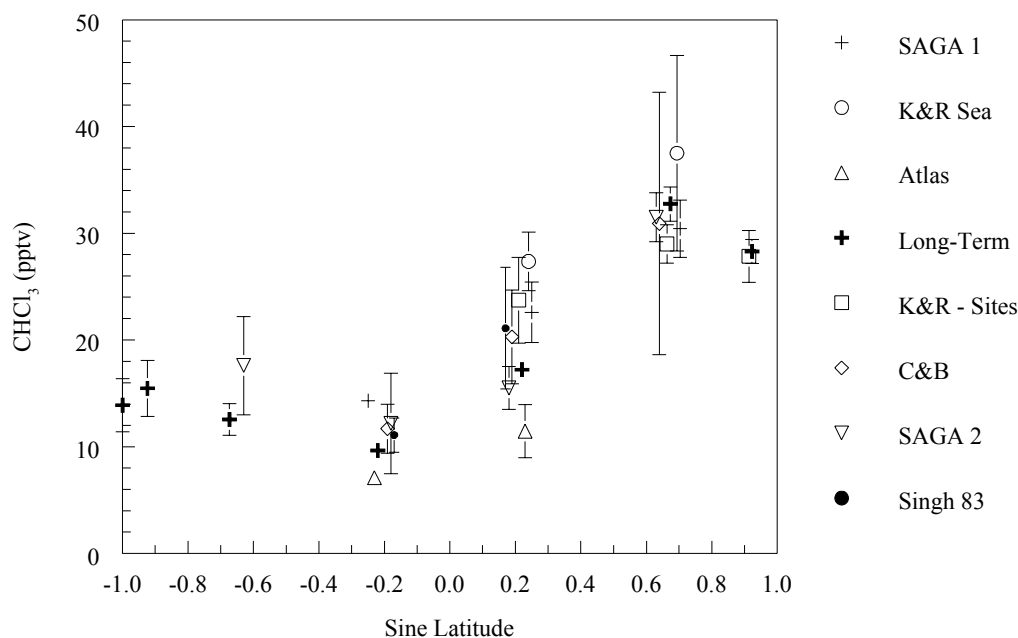
The shipboard data are expected to be more variable when compared with the long-term climatology partly because of the systematic seasonal cycle that is difficult to remove from the “instantaneous” data collected on board ships or aircraft. Moreover, there is substantial short-term random variability of concentrations at any location. The fixed site samples on the other hand represent an integration time of an hour or more for each weekly data point. These are combined to form a monthly average which is commonly used in the analysis of time series. The fixed site data therefore have small residual variability as monthly averages, while the aircraft and ocean cruise data have larger variability because samples are taken over a few minutes. A measure of the spread of average mixing ratios for methyl chloride, between the different available data sets, is the standard deviation of the averaged measurements at each location (as in Figure 2a) after adjusting the data to a common absolute scale. Such standard deviations for methyl chloride are quite small at

between 10–20 pptv depending on the latitude considered, or about 2%–4% of the mean values. It can be concluded that there is good agreement between observers on the latitudinal pattern of methyl chloride concentrations.

The concentrations measured in seawater are shown in Figure 2b. The main cruise tracks where these measurements were taken are shown in Figure 3. Also shown in Figure 2b is the concentration ( $C_{w\text{-eq}}$ ) in seawater that would be expected if it were in equilibrium with atmospheric concentrations measured at the long-term stations. This curve is constructed by assuming that  $C_{w\text{-eq}} = C_a / H$  where  $C_a$  is the air concentration at the long-term sites and  $H$  is the Henry's law constant. The measured sea surface temperatures are expressed as third-order polynomials in the sine of latitude, and so is the concentration  $C_a$ , based on the long-term averages shown in Figure 2 ( $C_a(\text{pptv}) = 611.4 + 5.2\mu - 41.3\mu^2 - 8.1\mu^3$  and  $T(\text{C}) = 28.3 - 0.11\mu - 3.1\mu^2 + 0.32\mu^3$  where  $\mu$  is sine of latitude). The Henry's law constant is calculated as  $H = \exp(8.75 - 2834/T)$  with  $T$  in degrees K. If measured values of the seawater concentrations are higher than the equilibrium value, then there is a supersaturation of methyl chloride in seawater and there should be a net flux out of the ocean, and if it is less than the equilibrium, the ocean is a net sink. A curious feature of the seawater concentration is that it is more or less constant with latitude. The figure shows clearly that the difference between equilibrium concentrations and actual concentrations are largest in the equatorial regions, and least at higher latitudes. At latitudes above about  $50^\circ$ , in either hemisphere, the observed seawater concentrations represent an undersaturation, and hence the oceans are a sink in these regions. This net sink at these latitudes is relatively small, and on the whole the oceans are a sizable source of methyl chloride, particularly in the tropics. We will discuss this source in more detail later.

## 2.2. Chloroform: Air and Seawater Concentrations

The measured atmospheric concentrations of chloroform are shown in Figure 4a [Khalil and Rasmussen, 1998b; Atlas *et al.*, 1993; Class and Ballschmiedt, 1986, 1987; Singh *et al.*, 1983a, b] The



**Figure 4.** The latitudinal distribution of chloroform in the atmosphere at the surface based on long-term flask sampling and measurements on ocean cruises.

long-term measurements are from the same sites as for methyl chloride [Khalil and Rasmussen, 1998b]. The time series of chloroform has considerable variability, but large seasonal cycles are not observed despite its short lifetime. This may be due to either a lack of sufficient measurements or the seasonal coincidence of high emissions with high destruction rates. The data from many independent observations (Figure 4) are consistent with each other and show a standard deviation of 2-5 pptv depending on latitude or about 20% between different studies. The main feature of the latitudinal distribution is the clear peak in the middle northern latitudes and also a slight peak in the southern middle latitudes suggesting land-based sources. There are very few data for concentrations in seawater [Khalil *et al.*, 1983; Baker *et al.*, 1999]. These data show a supersaturation suggesting that the oceans are a source of chloroform to that atmosphere.

### 2.3. Other Chlorine-Containing Gases

There are progressively fewer data for the remaining compounds, dichloromethane, perchloroethylene, and trichloroethylene. There is evidence of natural emissions for all three, but the magnitudes of the fluxes are extremely uncertain at present. The evidence is in the form of slight supersaturations in seawater, but there is some question as to whether these may be caused by transport of these gases from higher latitude cold waters rather than natural production. More work is needed to resolve these issues. The available data are summarized in Figure 5 [Koppman *et al.*, 1993; Khalil, 1998; Atlas *et al.*, 1993; Singh, 1983a, b; Wang *et al.*, 1995; Youkouchi *et al.*, 1996; Class and Ballschmiedt, 1986, 1987; Wiedman *et al.*, 1994; Rasmussen and Khalil, 1982]. For the chloroethylenes particularly, the natural oceanic source is expected to be a small fraction of the global emission rates. This inference is based on the fact that the concentrations of these gases are very small in the southern hemisphere, and it is supported by the measurements of the concentrations in seawater. Evidence of supersaturations of dichloromethane in seawater were first reported by Singh *et al.* [1983a, b] and more recently by Baker *et al.* [1999]. Supersaturations of perchloroethylene and trichloroethylene are discussed by Khalil

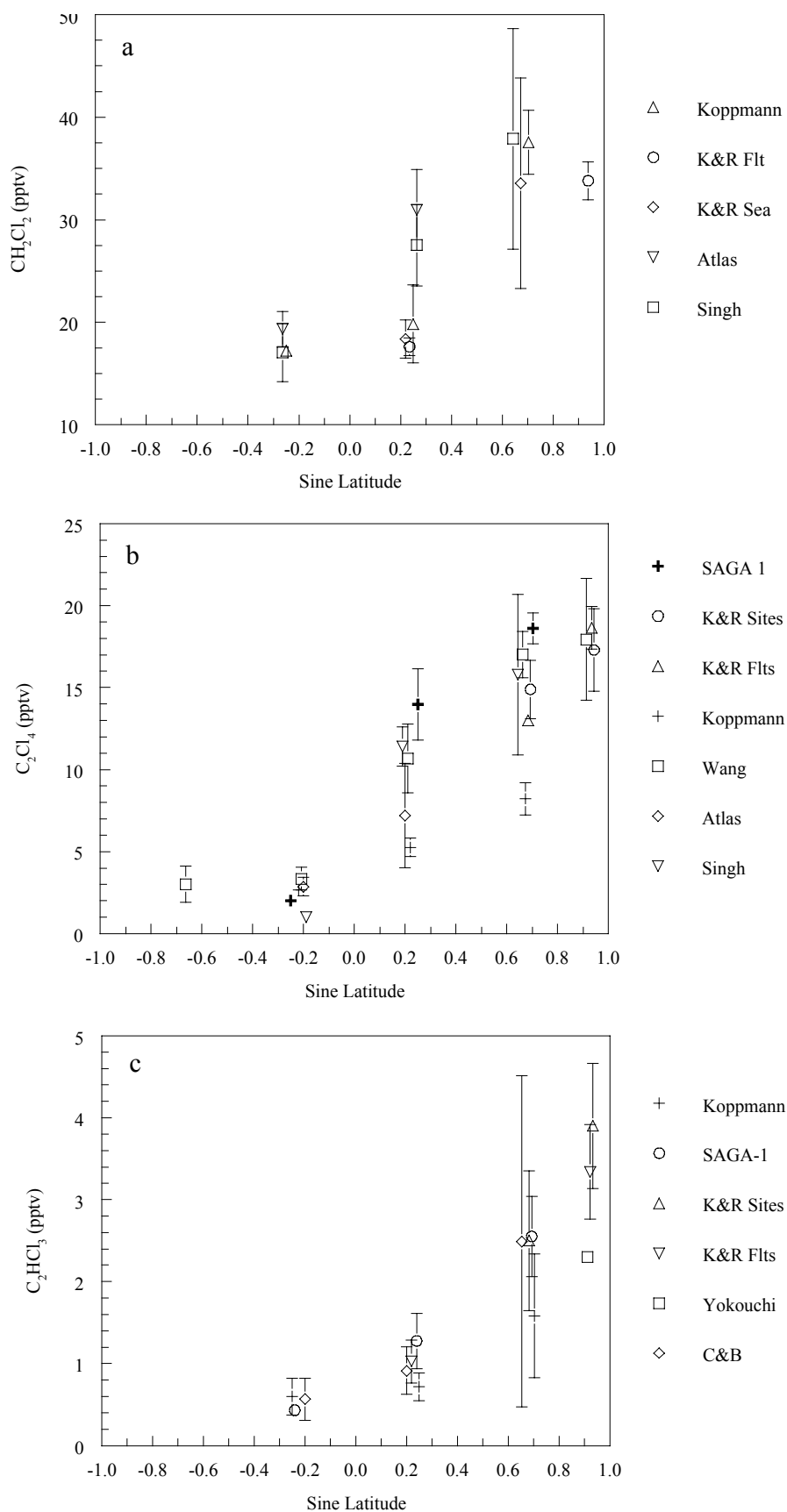
and Rasmussen [1998d].

### 3. Sources and Sinks

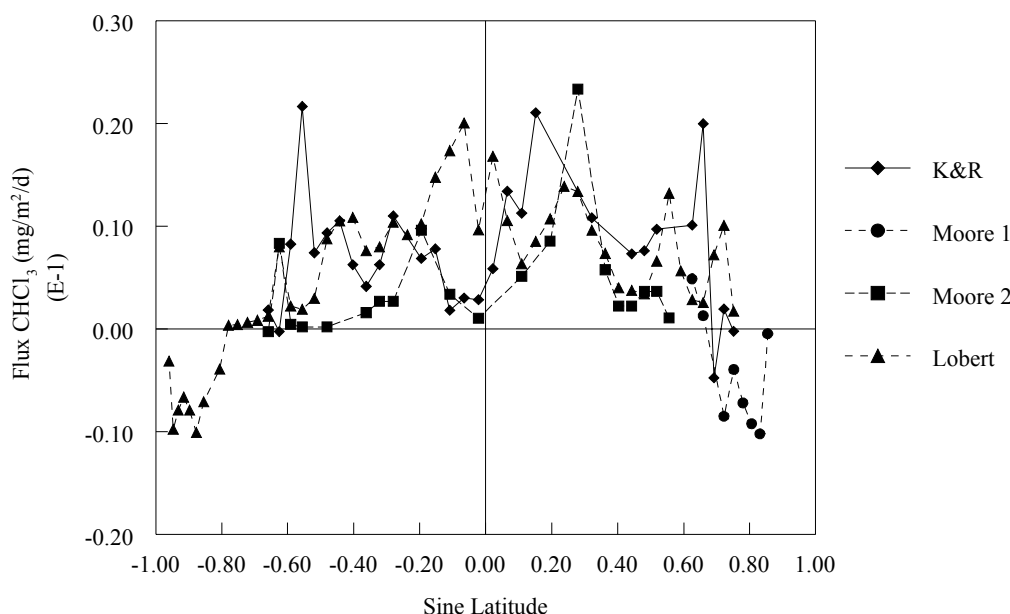
The major sink for the reactive chlorine-containing gases is reaction with hydroxyl radicals in the troposphere. For methyl chloride, which is the longest-lived, stratospheric sinks are also significant which include photo-dissociation and reactions with stratospheric OH. In addition to these atmospheric processes, it is expected that the oceans, soils, and other terrestrial ecosystems could also be sinks in some locations and sources in other regions. The magnitude of these sinks is likely to be much smaller than the reaction with tropospheric OH radicals. On the basis of the existing atmospheric concentrations and the measured reaction rate constants, the sink due to OH is estimated to be 2.6 Tg Cl/yr for  $\text{CH}_3\text{Cl}$ , 500 Gg Cl/yr each for  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{C}_2\text{HCl}_3$  and 400 Gg Cl/yr for  $\text{C}_2\text{Cl}_4$  [see Khalil and Rasmussen, 1998a, b, and references therein]. The photochemical model to estimate OH concentrations is described by Lu and Khalil [1991] and is consistent with most other recent estimates of OH distributions. The globally averaged model value is about  $10^6$  molecules/ $\text{cm}^3$ . These estimates of expected total emissions based on losses by reaction with OH, are provided for comparison with the emissions from specific natural sources estimated here. The overall budgets of these gases and the imbalances will be discussed by Keene *et al.* [1999].

The sources of these gases are both anthropogenic and natural. Industrial emissions, emissions from biomass burning, and other anthropogenic activities are discussed in companion papers [Lobert *et al.*, 1999; McCullough *et al.*, 1999]. For all the reactive chlorine gases mentioned here, there are identified oceanic net emissions. The case is unequivocal for methyl chloride, strong for chloroform, but progressively weaker dichloromethane and the chloroethylenes. This is a reflection of the shortage of relevant data as well as issues related to the measurements of these gases dissolved in seawater.

Aside from the oceans, there is strong evidence for the production of chloroform in soils and the production of methyl chloride from the activity of certain white rot fungi. A number of studies have been conducted to measure fluxes of gases from bare or vegetated soils. In all such studies, emissions of chloroform have been observed. In



**Figure 5.** The latitudinal distributions of (a) dichloromethane, (b) perchloroethylene, and (c) trichloroethylene at the Earth's surface based on data from short-term sampling at various locations.



**Figure 6.** The fluxes of methyl chloride from the oceans based on three independent recent experiments by Khalil and Rasmussen, R. Moore, and NOAA/CMDL (J.M. Lobert et al.) with cruise tracks as shown in Figure 3.

needed to evaluate the role of biogenic emissions in the global budget of methyl chloride. We consider next the estimates of terrestrial-biogenic and oceanic fluxes that can be estimated with the available data.

### 3.1. Oceanic Emissions

The oceanic emissions are estimated using the following standard model for the exchange of gases between the ocean and the atmosphere.

$$F = K C_a S (n_o/N_o M) \quad (1)$$

$$S = 1 - HC_w / C_a \quad (2)$$

where  $F$  is the flux in  $\text{mg m}^{-2} \text{h}^{-1}$ ,  $K$  is the transfer velocity ( $\text{m/h}$ ),  $H$  is the dimensionless Henry's constant,  $C_a$  is the atmospheric mixing ratio,  $C_w$  is the equivalent mixing ratio in the water, " $n_o$ " is the number density of air at the sea surface ( $\text{molecules/m}^3$ ),  $N_o$  is Avogadro's number ( $\text{molecules/mol}$ ), and  $M$  is the molecular weight of the gas under study ( $\text{g/mol}$ ).  $S$  is the dimensionless saturation anomaly that can also be expressed in percent.

Additional calculations are needed to estimate  $H$  and  $K$  as follows:

$$H = \exp(A - B/T) \quad (3)$$

where  $A$  and  $B$  are constants specific to each gas and are obtained from compiled values [see Moore, 1998; Khalil and Rasmussen, 1998d, and references therein] (values adopted are  $A=8.75$ ;  $B=2834$  K).  $T$  is the temperature of the seawater, or often the sea surface temperature (in K), as measured in the experiments.

Following the treatment by Wanninkhof [1992],  $K$  ( $\text{cm/h}$ ) is represented as

$$K = 0.31 u^2 (Sc/660)^{-1/2} \quad (4)$$

$$Sc = 335.6 M^{1/2} (1 - 0.065 T + 0.002043 T^2 - 2.6 \times 10^{-5} T^3) \quad (5)$$

where  $u$  ( $\text{m/s}$ ) is the local wind measured at 10 m along with the air and water concentrations,  $T$  is in  $^{\circ}\text{C}$ , and  $Sc$  is the Schmidt number estimated using (5) [Khalil and Rasmussen, 1998d]. Alternative methods for estimating  $K$  have been suggested by Liss and Merlivat [1986] that would give somewhat lower results for emissions.

**3.1.1. Methyl chloride.** The fluxes of methyl chloride estimated by these methods are shown in Figure 6 for the four sets of recent experiments (with cruise tracks shown in Figure 3). For convenience, we have averaged the data over  $2.5^{\circ}$  latitudinal bands. The results are in good agreement with each other, and the global emission rate based on these studies is  $310 \text{ Gg Cl/yr}$  (120 data points [Moore et al., 1996, 1998], 164 data points [Khalil and Rasmussen, 1998d], 1200 data points [Lobert, 1998]). This is considerably lower than previous estimates of about  $2.1 \text{ Tg Cl/yr}$  based on the work of Singh et al. [1979], who reported some of the earliest global measurements of methyl chloride in seawater. The low emissions from the oceans leave a considerable gap between the emissions expected from the mass balance and those that can be accounted for by known sources and emission rates [see Keene et al., 1999]. It is also noteworthy that the oceanic emissions are higher in the tropics compared with middle latitudes, and there is observational evidence that in the cold waters of the higher latitudes beyond about  $50^{\circ}$ , the oceans are a net sink (seawater concentrations are undersaturated relative to atmospheric concentrations; see Figure 2b). These findings are consistent with the observed latitudinal distribution of methyl chloride from the long-term sites (Figure 2) which requires large emissions from the tropical areas to balance the higher tropical concentrations of methyl chloride and the large tropical concentrations of hydroxyl radicals which remove methyl chloride from the atmosphere [Khalil and Rasmussen, 1998a].

**3.1.2. Other gases.** For the other gases in this group, the data are much fewer. For  $\text{CHCl}_3$  the only global data available are from the Khalil et al. [1983], which give oceanic emissions of about  $320 \text{ Gg Cl/yr}$ . Recent measurements by Baker et al. [1999] for coastal seawater also show super-saturations confirming a source from the oceans to the atmosphere.

Seawater data for  $\text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{HCl}_3$  are from a cruise in 1981 with

about 40 measurements of the flux between latitudes 40°N and 30°S [Khalil and Rasmussen, 1998d]. These measurements show a persistent supersaturation of these gases in seawater and can be taken to mean that the oceans are likely to be a net source. The estimated emissions are highly uncertain and are of the order of 20 Gg Cl/yr for each gas. For CH<sub>2</sub>Cl<sub>2</sub>, there are measurements in 1983 [Khalil and Rasmussen, 1998d; Singh *et al.*, 1983a, b], which result in a flux of 160 Gg Cl/yr. These estimates are tabulated later in this paper in semi-hemispherical regions.

**3.1.3. Uncertainties.** The uncertainties fall into two broad categories, measurements and extrapolation. As shown in (1), the oceanic flux estimate is the product of several independent variables that are based on laboratory or field measurements, namely, the transfer velocity, Henry's law constant, and the saturation anomaly, all of which are subject to measurement errors. Errors in the transfer velocity, as expressed in (4), are mostly related to wind speed and are of the order of plus or minus a factor of 2 [Butler *et al.*, 1991; Wanninkhof, 1992; Lobert *et al.*, 1998]. Since the method we use is particularly sensitive to wind speed, the uncertainty is greatest when high wind speeds are measured and used in the calculation. Errors in the Henry's constant produce additional uncertainties. Together these uncertainties could lead to errors between plus or minus factors of 2 to 3 in individual flux estimates.

Uncertainties in the measurements of the concentrations are both systematic, related to absolute calibration, and random, related to the combined precision of experimental setup. For methyl chloride, which is the most studied of these gases, we believe that the systematic "error" is of the order of 10% due to differences in absolute calibration, as discussed earlier. For other gases, this is more difficult to assess, but different groups agree to within 20% for chloroform, chloroethylenes, and dichloromethane. These uncertainties are correctable by laboratory re-calibration. Imprecision can come from the combined effects the instruments used to measure the gases, the effects of the sampling devices and the storage of air for long periods before analysis. For most of the gases of interest here, we expect this uncertainty to be small.

Another, more insidious set of uncertainties, arise from the experimental design itself. We want to estimate the emissions during a month or season and from relatively large regions that constitute the grid cells required by the accepted resolution of the Global Emissions Inventory Activity (GEIA). The measurements for estimating emissions from the oceans that we have on hand are "instantaneous." We have no measure of how representative these measurements are for estimating the monthly or annual emission rates. For instance, if a high wind is encountered during the cruise, generally a large flux is calculated. This flux may be valid for the period of observation. When the estimated fluxes are extrapolated to obtain the annual emission rate, this high wind velocity is also effectively assumed to be representative of the whole year, which is unlikely to be true. Similarly, low wind conditions encountered during a particular experiment may underestimate the annual flux. As we reduce the grid size, it is difficult to say how representative the results are even if we had measurements over the whole year because in the next year the environmental situation in that cell may be quite different and result in different emissions. This problem is greatly reduced if we make the areas of the cells large, or if we take them to be latitudinal bands. Representing seasonal or annual emissions based on instantaneous measurements remains a major source of uncertainty because the data do not satisfy the assumptions that are made in deriving the seasonal or annual fluxes from the oceans. These issues are resolved to a significant extent by estimating the average fluxes from the oceans based on the proxy method described later and used to create the gridded RCEI emission inventory.

### 3.2. Land-Based Biogenic Emissions

**3.2.1. Methyl chloride.** The full extent of the land-based sources of methyl chloride is not known at present. One piece of evidence for the existence of such sources is that long-term annual concentrations of methyl chloride over continental areas (590-770 pptv) are generally higher than at the sites representing the marine boundary layer (about 520-560 pptv) [Khalil and Rasmussen, 1998a]. The bare or vegetated soils that have been sampled show an uptake of methyl chloride at substantial rates [Khalil and Rasmussen, 1998c]. These facts suggest that land-based sources are not ubiquitous and probably exist only in specific ecosystems. The identified land-based sources of methyl chloride are wood rotting fungi, and certain plants. While there is insufficient information on the role of plants in the global cycle of methyl chloride, some data are available for the fungal sources that we will use to estimate global emission rates.

The estimates of the flux of CH<sub>3</sub>Cl from wood-rotting fungi are based on the calculations of Watling and Harper [1998] and are derived as follows. Some 10-18 peta grams (Pg = 10<sup>15</sup> g) of carbon are fixed in the form of woody tissue per year in the terrestrial biosphere [Fung, 1993]. Assuming a mean value of 14 Pg and a carbon content of wood of 47% [Atjay *et al.*, 1979] gives 30 Pg dry weight of wood that is formed globally per year. The tropical and subtropical forests comprise 60% of annual global production of dry matter by forest ecosystems so that total wood production in the tropical and subtropical environments is of the order of 18 Pg and the remaining 12 Pg is expected to be produced in the temperate forests [Atjay *et al.*, 1979]. Satellite data indicate that Australian tropical/subtropical and temperate forests represent 1.9 and 1.2%, respectively, of the global totals for each of these categories [De Fries and Townshend, 1994]. Therefore the annual production of woody biomass (variable W in equation (6) below) by tropical and subtropical (excluding Australia), temperate (excluding Australia), and Australian forests are 17.7, 11.9, and 0.5 Pg, respectively. Wood from Australian forests is treated as a separate category because of

the high content of Cl<sup>-</sup> in *Eucalyptus*, the dominant woody genus in Australia. The flux of methyl chloride from Australian forests is therefore expected to be greater than forests in similar latitudinal bands elsewhere.

If it is assumed that the biosphere is in a state of approximate equilibrium, then the quantities of wood decomposed annually must be similar to those produced. The main agency responsible for such decay are the polypore basidiomycetes comprising both white and brown rot fungi [Cooke and Rayner, 1984; Watling and Harper, 1998]. However, a proportion of above ground litter in forest ecosystems is destroyed by insect attack particularly in the tropics. In addition, water-logged timber can be attacked, albeit only superficially by soft rot fungi of the Ascomycotina, and mineralization of wood by forest fires can also occur. To allow for these other routes of decomposition, Watling and Harper [1998] assumed that the proportion of woody tissue available for attack by polypore Basidiomycetes (variable A in equation (6)) is 75% for tropical/sub-tropical, 85% for the Australian, and 95% for temperate forests.

For each category of wood, the concentration (variable C in equation (6)) of chloride (Cl<sup>-</sup>) employed in calculations is based on the mean of the values reported in the literature and those measured by Watling and Harper [1998] for tree species of each category weighted for the number of experimental observations reported in the different investigations. The mean Cl<sup>-</sup> concentrations assigned to tropical/subtropical, temperate, and Australian wood were 254, 109, and 606 mg/kg dry weight, respectively.

Within the total polypore population, the ability to volatilize Cl<sup>-</sup> as

CH<sub>3</sub>Cl appears to be largely confined to the poroid genera of the hymenochaetaceae [Harper, 1985; Harper and Kennedy, 1986; Harper et al., 1988]. Accordingly, in calculating CH<sub>3</sub>Cl emissions, a factor is employed to reflect the proportion of hymenochaetaceous species relative to the total polypore species. This percentage (variable G in equation (6) varies from 16 to 30% for the various geographical regions for which published data exist. A global average of 20% is adopted, since there were no systematic differences between the percentages recorded in the various forest categories [Watling and Harper, 1998].

Poroid hymenochaetaceous species fall into two general groups based on the percentage of Cl<sup>-</sup> converted to CH<sub>3</sub>Cl during growth, namely, *Phellinus*, (group 1) and *Inonotus* plus other genera (group 2) [Harper et al., 1988]. Hence, for each type of forest, the proportion of species of each group relative to the total poroid hymenochaetaceous species present is an important parameter which must be considered in any estimate of CH<sub>3</sub>Cl emission. The ratio of the number of species in group 1 to that in group 2 was calculated from published records as 70:30 for tropical/subtropical and Australian forest and 60:40 for temperate forests [Watling and Harper, 1998].

The mean percentage conversions (variable E in equation (6)) of Cl<sup>-</sup> to CH<sub>3</sub>Cl by species of the two groups of hymenochaetaceous fungi were calculated from a survey of CH<sub>3</sub>Cl emission by 35 species of *Phellinus* and 16 species *Inonotus* and other hymenochaetaceous genera when growing on a cellulose-based medium containing 10 mM Cl<sup>-</sup>. Mean conversion efficiencies of 15% for *Phellinus* species and 5% for species of *Inonotus* and other genera were observed [Harper et al., 1988].

The magnitude of CH<sub>3</sub>Cl emissions by each of the two groups of hymenochaetaceous fungi in each forest type can be estimated in Gg Cl/yr per year using the following formula (terms are in the order discussed above) and are summed to get the global emissions:

$$S = \sum_i W_i \cdot A_i / 100 \cdot C_i \cdot 10^{-6} \cdot H_i / 100 \cdot G_i / 100 \cdot E_i / 100 \quad (6)$$

where i indexes the various ecosystems considered, W is the annual woody biomass production in Gg dry weight, A is the percentage of wood decomposed by polypore basidiomycetes in the forest type under consideration, C is the concentration of Cl<sup>-</sup> in wood of the forest type in mg/kg dry weight, H is the number of poroid hymenochaetaceous species present as a percentage of the total number of polypore species recorded for the area, G is the number of species of the hymenochaetaceous group under consideration (i.e., *Phellinus* or *Inonotus* plus other genera) in the area as a percentage of all poroid hymenochaetaceous species present, and E is the mean percentage conversion of Cl<sup>-</sup> to CH<sub>3</sub>Cl by species of the hymenochaetaceous group under consideration. The results are summarized in Table 1.

**3.2.2. Uncertainties.** There are two types of uncertainties in these estimates. The first type arises from the uncertainty in the values of the variables used to estimate the global flux in (6). The second concerns the assumptions that have been made in deriving these estimates mainly with regard to the growth habitat of wood rotting fungi.

The uncertainty in the global emission rate deduced above, can be estimated by using the range of values of each parameter in (6) (expressed as  $S = W \times A \times C \times H \times G \times E / 10^8$ ). We assume that the effective value of each parameter is equally likely to be anywhere within the observed range. We then assign each of the six variables in (6) an equally spaced set of values ranging from the minimum to the maximum observed. We calculate the expected global emission rates for all possible combinations of the values in these six sets. The distribution of these possible values is approximately lognormal. The

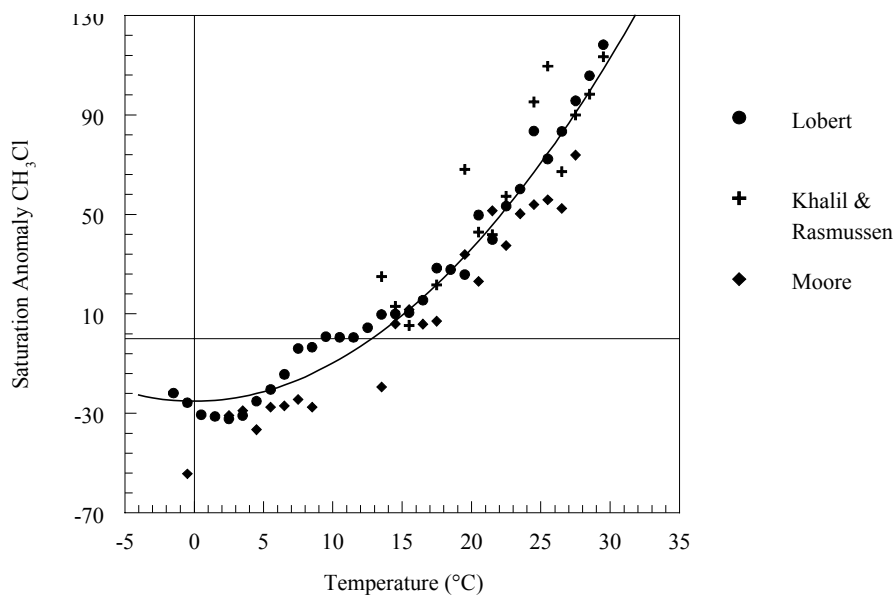
**Table 1.** Emission of CH<sub>3</sub>Cl From Fungi in Different Forest Types

Forest Type	Fungal Genera	CH <sub>3</sub> Cl Emission, Gg Cl/yr
Temperate (excluding Australia)	<i>Phellinus</i>	22
	<i>Inonotus</i> plus other genera	5
	Total	27
Tropical/sub-tropical (excluding Australia)	<i>Phellinus</i>	71
	<i>Inonotus</i> plus other genera	10
	Total	81
Australia	<i>Phellinus</i>	5
	<i>Inonotus</i> plus other genera	1
	Total	6
All forest types	Total	114

From Watling and Harper [1998].

result of the calculation is that the geometric mean is 110 Gg/yr and 90% of the values for the global emissions lie between 30 Gg/yr and 330 Gg/yr. We interpret this to mean that while our best estimate is 100 Gg/yr as shown in Table 1, the uncertainty range, or the 90% confidence limit, is 30-330 Gg/yr. This calculation shows that with the data available, there is a large uncertainty of about a factor of 10 in the estimate of global emissions from fungal processes. The method we have used was reported by Khalil [1992] for estimating uncertainties of the sum of a number of uncertain variables, instead of the product, as is the case here. Taking the natural logarithms of each side of (6) transforms it into the case of adding ranges. The calculated values of the confidence range are then transformed back by exponentiation allowing us to use the previously established method [Khalil, 1992].

New uncertainties arise from the assumptions concerning the growth habitat of wood-rotting fungi and the distribution of the CH<sub>3</sub>Cl-releasing trait amongst polypore fungi [Watling and Harper, 1998]. Possibly the most critical parameter governing the potential flux of CH<sub>3</sub>Cl from wood-rotting fungus is the availability of Cl<sup>-</sup> in the fungal growth substrate. In calculations of fungal CH<sub>3</sub>Cl emissions it has been assumed that the only chloride accessible to wood-rotting fungi is that normally present in the unrotted wood. Most estimates of the litter composition on the forest floor indicate that about 25% of detritus is woody [Bray and Gorham, 1964]. Fungi decomposing wood in such an environment will have access to higher concentrations of Cl<sup>-</sup> than those attacking wood in standing trees. Not only will Cl<sup>-</sup> present in soil water be readily absorbed into such rotting timber, but Cl<sup>-</sup> released during decomposition of leaf litter by other fungi and contained in leaf leachate from the forest canopy will also be available. Soil in non-saline areas can contain up to 40mg/g



**Figure 7.** The relationship between saturation of methyl chloride in seawater and the water temperature. The relationship is replicated by three studies.

extractable  $\text{Cl}^-$ , and freshwater in general has a  $\text{Cl}^-$  concentration between 2 and 100 mg/L [Grimshaw *et al.*, 1989]. Leaf litter in forests normally contains between 500 and 1500 mg/kg dry weight  $\text{Cl}^-$  [Lobert *et al.*, 1999]. These sources represent a substantial reservoir of  $\text{Cl}^-$ , which, if available to  $\text{CH}_3\text{Cl}$ -producing fungi attacking woody detritus on the forest floor, could significantly increase the flux of  $\text{CH}_3\text{Cl}$  from forest environments.

Another related area of uncertainty in estimating the flux of  $\text{CH}_3\text{Cl}$  from fungi is the extent to which hyphae of such fungi spread beyond the woody substrate with which their fruiting bodies are associated. It is conceivable that hyphae of wood-rotting fungi extensively penetrate the leaf litter layer and indeed the upper layer of the soil in forest ecosystems. Although such colonization of sterile soil and litter by cultures of white rot fungal hyphae is widely observed in the laboratory [see Watling and Harper, 1998], competition with other fungi and microorganism is likely to restrict this process in nature, but nevertheless some proliferation of white rot fungal hyphae in nonwoody substrates is almost certain to occur with consequent increase in the size of the pool of  $\text{Cl}^-$  available for conversion to  $\text{CH}_3\text{Cl}$ .

An area of uncertainty of critical importance is the number of fungal species capable of  $\text{CH}_3\text{Cl}$  release. The premise employed by Watling and Harper [1998] in deriving emission fluxes was that  $\text{CH}_3\text{Cl}$  release is restricted to species of the hymenochaetaceae. However, only a small proportion (approximately 30) of the 1250 nonhymenochaetaceous polypore species known to exist globally have been screened for  $\text{CH}_3\text{Cl}$  emission. It is therefore quite conceivable that there are other major genera of  $\text{CH}_3\text{Cl}$ -releasing polypores yet to be discovered.

Higher plants represent yet another terrestrial biological source of  $\text{CH}_3\text{Cl}$ . Tubers of the potato, *Solanum tuberosum*, were reported by Varns [1982] to release  $\text{CH}_3\text{Cl}$  at rates of up to 17 ng/g fresh weight/day for a short period after harvest and a survey of 60 cultivars by Harper *et al.* [1998] has demonstrated  $\text{CH}_3\text{Cl}$  emissions by tubers of up to 600 ng/g fresh weight/day within 48 h of harvest.  $\text{CH}_3\text{Cl}$  release by species of the Pinaceae was noted but not quantified by Isidorov [1990]. A survey of 118 species of herbaceous plant showed that leaf discs of the majority of species representing a broad range of plant orders released halomethanes when incubated in

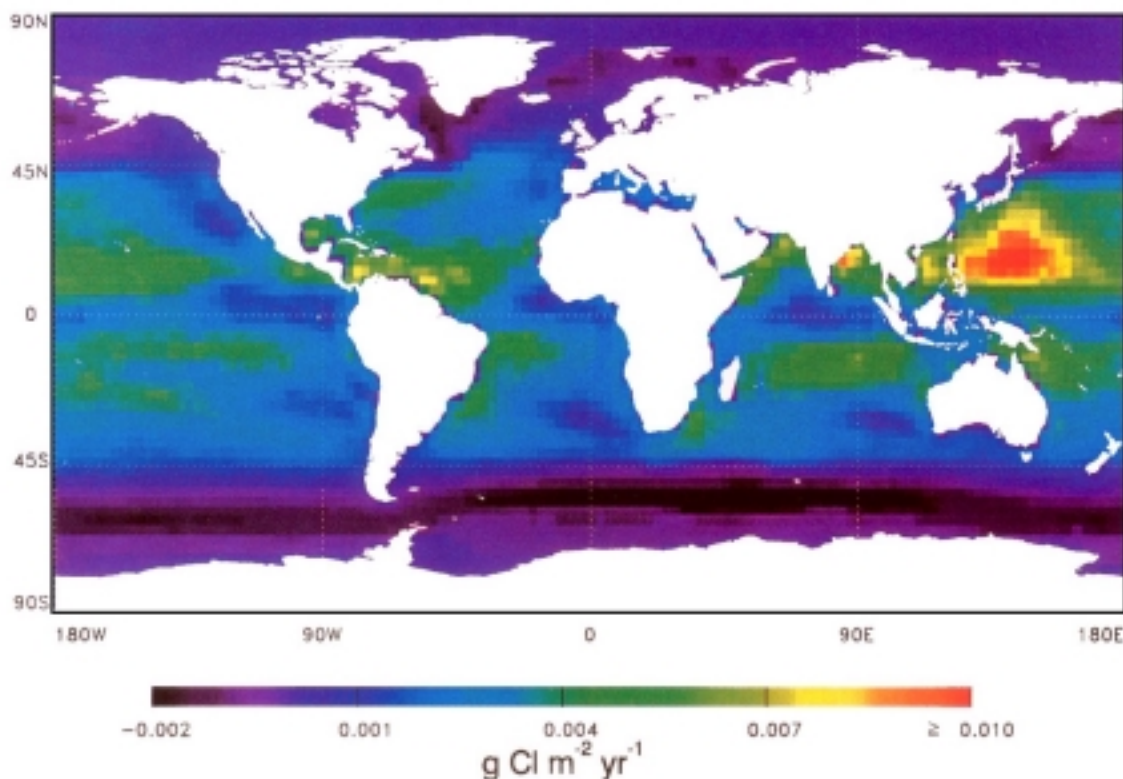
the presence of 100 mM halide ion [Saini *et al.*, 1995]. However, the methyltransferase enzyme responsible for halide methylation was isolated by Attieh *et al.* [1995] from *Brassica oleracea* and was found capable of methylating  $\text{HS}^-$  at a rate 1000-fold greater than  $\text{Cl}^-$ . It therefore seems likely that  $\text{HS}^-$  is the normal physiological substrate for the enzyme in plant tissue. Nevertheless, the relatively high  $\text{Cl}^-$  content of plant sap [Cram, 1976] renders it unlikely that methylation in vivo is entirely restricted to  $\text{HS}^-$ , and it is quite conceivable that trace amounts of  $\text{CH}_3\text{Cl}$  are released. Accurate estimation of the global  $\text{CH}_3\text{Cl}$  flux, if any, from higher plants must await measurement of  $\text{CH}_3\text{Cl}$  emission by intact plants in situ under normal growing conditions.

**3.2.3. Other chlorine-containing gases.** There is substantial evidence that chloroform is emitted from various soils, although the mechanisms are still not fully understood [Frank and Frank, 1990; Khalil *et al.*, 1990; Khalil and Rasmussen, 1998c]. The data obtained from direct flux measurements from the soils using chamber methods show a median value of  $8 \mu\text{g m}^{-2} \text{d}^{-1}$  with a 90% confidence range 4–13  $\mu\text{g m}^{-2} \text{d}^{-1}$ . An extrapolation of the median value to the global land area (excluding the polar regions), gives about 200 Gg/yr (100–400 Gg/yr). Whether the true value is within this range cannot be stated unequivocally because so few data are available. Nonetheless, these values are consistent with the global source needed to balance the losses. Natural land-based sources are particularly important in explaining the observed atmospheric distribution shown in Figure 4 since industrial emissions are estimated to be relatively small at about 60 Gg/yr [Aucott *et al.*, 1999].

For the other gases considered here,  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_2\text{Cl}_4$ , and  $\text{C}_2\text{HCl}_3$ , land-based sources are needed to explain the observed latitudinal distributions. Budget analyses suggest that industrial emissions are the major global sources for these gases [McCullough *et al.*, 1999; Keene *et al.*, 1999].

#### 4. Gridded Emissions Inventory for Methyl Chloride

There are several methods by which emissions can be distributed over the oceans and land consistent with the measured fluxes and



**Plate 1.** Annual emissions of methyl chloride from the oceans in cells  $1^\circ \times 1^\circ$  in latitude and longitude, based on the relationship between saturation and sea surface temperature shown in Figure 6. A pocket of high emission rates as an annual average is predicted for the middle Pacific latitudes. This is due to high wind speeds and warm waters that result in large emissions in our model. Monthly emissions at the same resolution are available from the archive.

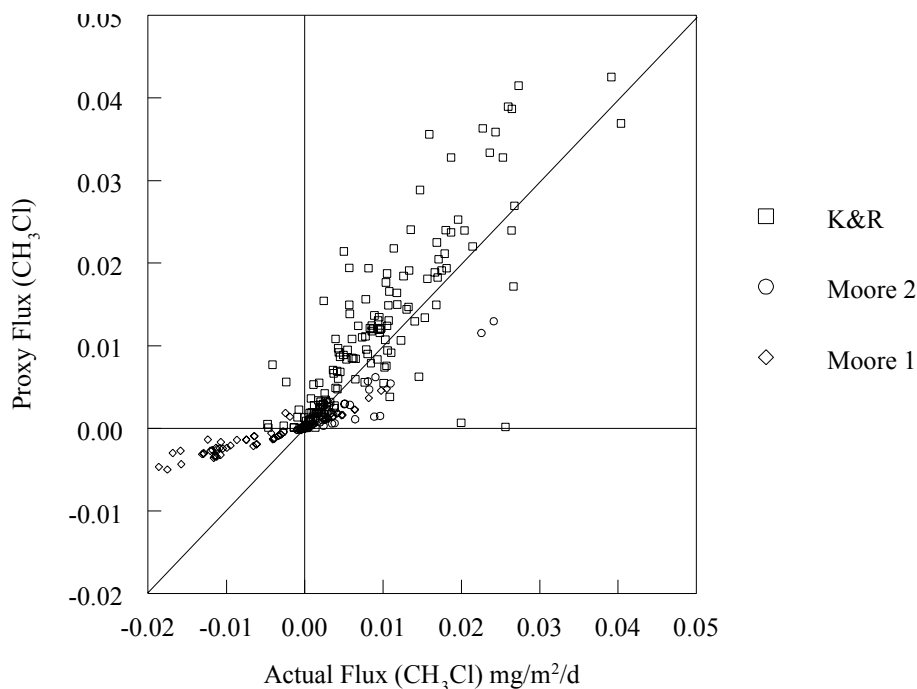
emission rates from fungi. Since actual emissions data are quite limited, these methods rely on using factors that affect or control emissions. For the case of methyl chloride we have found that the saturation in seawater is closely related to the temperature. The data on the oceanic saturation of methyl chloride can be used to establish an empirical relationship between saturation and sea surface temperature. This relationship is shown in Figure 7 for all three main studies on flux measurements. It is summarized by a simple quadratic formula as  $\%S = -24.1 + 0.159 T^2$ , ( $T$  in  $^\circ\text{C}$ ), which fits with a correlation of 0.94 (using CMDL data only).

Having established this relationship from experimental data, we can map the super-saturation of methyl chloride in each  $1^\circ \times 1^\circ$  (latitude by longitude) grid for the GEIA emission inventory. For each grid point, we take the 10-year monthly mean winds generated by NCAR Community Climate Model (CCM3 [Kiehl *et al.*, 1996]). The sea surface temperature (SST) data are derived from *Shea et al.* [1990]. The air concentrations are taken from the climatology established by *Khalil and Rasmussen* [1998a]. The flux is estimated using (1) with the saturation anomaly determined by the SST and  $K$  determined by (4) and (5). The emissions in each cell are calculated for each month of the year. The monthly results are not shown here to save space but are available to readers on the  $1^\circ \times 1^\circ$  grid from the GEIA archive (see instructions later on how to obtain the data). The annual average emissions are shown in Plate 1.

We tested the empirical relationship between temperature and saturation by the following procedure: We used only the data from the NOAA/CMDL experiments to establish the relationship (as shown above). We then calculated the proxy fluxes for the conditions of the other two data sets shown in Figure 6 (Moore data set and SAGA 2 cruises). The proxy fluxes and the actual fluxes are plotted

in Figure 8. Quantitatively, for perfect agreement, we expect the slope of the relationship between the proxy and actual measurements to be 1 and the intercept 0 for each experiment. The proxy and actual fluxes have correlations of 0.9 to 0.95, the slopes (dimensionless) and intercepts ( $\text{mg m}^{-2} \text{d}^{-1}$ ) are (1.18, 0.002), (0.3, 0.00042 cold water), and (0.5, -0.00001) for the SAGA 2, and the two Moore data sets, respectively (shown in Figure 6). The proxy does well in representing fluxes from warm waters but tends to underestimate the uptake in colder waters. The integrated fluxes over the regions of the measurements are within +30% for the SAGA 2 data and -50% for Moore data set 2. For Moore's cold water data set (data set 1), representing mostly an uptake of  $\text{CH}_3\text{Cl}$ , the difference between actual and proxy fluxes is -80%. For the individual flux measurements, 80% of the proxy calculations are within a factor of 2 of the measured fluxes for the SAGA 2 data. We believe therefore that the proxy can reproduce instantaneous fluxes to about a factor of 2. This uncertainty is about the same as the uncertainty among the three main experiments discussed earlier, namely, about a factor of 2.

It should be noted that the estimate of the global flux based on direct measurements may not be more reliable than the estimates based on the proxy flux estimated here. This is because the individual cruises represent instantaneous fluxes that may not be adequate for obtaining accurate estimates of annual emissions as discussed earlier in Section 3.1, whereas the proxy estimate using the sea surface temperature exploits an underlying relationship that may be valid throughout the year and may therefore lead to a more accurate estimate. Moreover, the proxy estimates are averaged over each month, and then over the year, taking into account the changes of sea surface temperature and winds from month to month, while the



**Figure 8.** Comparison of emissions calculated by a sea surface temperature proxy method and measured emissions of methyl chloride from the oceans. This figure shows the performance of the proxy method in reproducing the fluxes of methyl chloride.

annual estimates from direct measurements use instantaneous temperatures and winds that are not representative of the annual averages and may therefore bias the annual average estimate. The global emissions estimate based on the sea surface proxy is about 460 Gg Cl/yr. This is in good agreement with the 310 Tg Cl/yr estimated from the extrapolation of the direct flux measurements (Table 2).

## 5. Conclusions

The emissions of chlorine-containing gases from biogenic and oceanic sources have been collected and documented. The gases selected are methyl chloride, chloroform, dichloromethane, trichloroethylene, and perchloroethylene. Although there may be natural emissions of other gases, a compilation of existing data by *Khalil* [1998] suggests that their contribution to total gas phase chlorine in the atmosphere is likely to be small.

For methyl chloride, the oceanic emissions have been distributed over a  $1^\circ \times 1^\circ$  (latitude, longitude) grid. The estimates of emissions

**Table 2.** Biogenic and Oceanic Emissions of Organic Chlorine-Containing Gases

	$S_n$ (90°N-30°N) <sup>a</sup>	$S_{nt}$ (30°N-0°)	$S_{st}$ (0°-30°S)	$S_s$ (30°S-90°S)	Total <sup>b</sup>
CH <sub>3</sub> Cl <sub>oc</sub> eanicLand	-130	20050	28050	-70	460 <sup>c</sup> 100 <sup>d</sup>
CHCl <sub>3</sub> <sub>oc</sub> eanicLand	1860	13460	13450	3610	320 <sup>e</sup> 180 <sup>f</sup>
CH <sub>2</sub> Cl <sub>2</sub> <sub>oc</sub> eanic	20	42	42	60	160 <sup>g</sup>
C <sub>2</sub> HCl <sub>3</sub>	10	4	4	4	20 <sup>g</sup>
C <sub>2</sub> Cl <sub>4</sub> <sub>oc</sub> anic	3	3	5	5	16 <sup>g</sup>

Units in Gg Cl/yr.

<sup>a</sup> The regions are four equal areas: “n” and “s” refer to northern and southern hemispheres; the “t” refers to “tropical regions,” which are taken to include the surface up to 30°.

<sup>b</sup> The numbers are rounded to 2 significant digits or fewer as appropriate.

<sup>c</sup> This work, based on sea surface proxy method.

<sup>d</sup> *Watling and Harper* [1998] as discussed in the text.

<sup>e</sup> From *Khalil et al.* [1983].

<sup>f</sup> *Khalil and Rasmussen* [1998c].

<sup>g</sup> *Khalil and Rasmussen* [1998d].

of all gases considered are summarized in Table 2 in which we provide annual emissions over each quarter of the Earth's surface.

The purposes of this work were to assemble the existing observational data bases on key chlorine-containing trace gases in the atmosphere, to evaluate the role of natural processes in the global production of these gases and subsequent release to the atmosphere, and to produce a 1° x 1° database for emissions from individual sources. This work therefore brings the reader to the current state of the knowledge of the natural emissions of these gases to the atmosphere. The databases and the calculations of the fluxes can be readily modified with the addition new data. We want to stress that there are many remaining uncertainties as discussed in preceding sections. These uncertainties are so large that we cannot say that we understand the budgets of the natural chlorine-containing gases well enough to assess their role in the environment. This work points to new directions for research to address the remaining questions that are important to obtain an understanding of the global cycles of natural chlorine-containing gases. The gridded inventory is available from <http://groundhog.sprl.umich.edu/geia/rcei>. The inventories will be brought up to date as new results become available.

**Acknowledgments.** We thank R. A. Rasmussen for his contributions and advice. We thank Don Stearns, Jim Mohan, Bob Dalluge (OGI), and Martha Shearer (PSU) for their contributions to this project. We thank the staffs of the NOAA CMDL program, the Baseline Cape Grim Station, and CSIRO for collecting air samples that provide data for this paper. Major financial support for this work was provided by the [Chemical Manufacturers Association](#) via the [Chlorine Chemistry Council](#) and by the [European Chemical Industry Council](#) (CEFIC) via [Euro Chlor](#). Additional support was provided by the resources of Andarz Co.

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(Received June 2, 1998; revised November 11, 1998; accepted November 13, 1998.)