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Tetrachloroethylene as an indicator of low Cl atom concentrations in the troposphere

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Abstract. Tetrachloroethylene (C_2Cl_4), a largely man-made chemical pollutant, is known to react with Cl atoms at a rate that is some 300 times faster than with OH radicals ($k_{Cl}/k_{OH} = 365$ at 275 K). Analysis of C_2Cl_4 data, with the help of a global 2-D model and in conjunction with the OH field derived from CH_3CCl_3 observations, has been used to provide a sensitive means for evaluating Cl atom abundance in the troposphere. In the "mean case" scenario, that employs best available measurements, emissions and kinetic parameters, it is found that OH oxidation is adequate to balance the C_2Cl_4 budget and significant removal by Cl is not indicated ($Cl \leq 10^2$ molec. cm^{-3}). An "upper limit" analysis that takes into account possible uncertainties in measurements, source emissions (man-made and natural), and reaction rates, is performed to estimate that annually averaged Cl atom concentrations in the troposphere are $<5 \cdot 10 \cdot 10^2$ molec. cm^{-3} . If we assume that nearly all (80-100%) of the Cl atoms reside in the marine boundary layer (MBL), mean MBL concentrations are estimated to be $<5 \cdot 15 \cdot 10^3$ molec. cm^{-3} . This analysis implies that mean Cl concentrations in the MBL are below or near the lower end of the values inferred in recent studies (10^4 - 10^6 molec. cm^{-3}). We conclude that despite their high reactivity, Cl atoms are too few to compete with OH radicals ($\approx 10^6$ molec. cm^{-3}) in influencing the oxidizing capacity of the global troposphere.

Introduction

Tetrachloroethylene is a well known chlorinated solvent, that finds a dominant use in the dry-cleaning industry, and has been measured in the atmosphere for more than two decades [Wiedmann *et al.*, 1994; Singh, 1995]. Due to its relatively rapid removal in the troposphere (lifetime ≈ 0.3 years), less than 1% of emissions are able to enter the stratosphere. An area of environmental concern has been its toxicity, and its ability to produce decomposition products such as phosgene and CCl_4 [Franklin, 1994]. Recently, accurate global emissions inventories for some of the more reactive halocarbon species (C_2Cl_4 , C_2HCl_3 and CH_2Cl_2) have been compiled for the period of 1988 to 1994 [McCulloch and Midgley, 1996; also private communication]. Kinetic studies [Nicolovich *et al.*, 1996], have shown that the rate of reaction of C_2Cl_4 with Cl is significantly larger than that with OH and the k_{Cl}/k_{OH} ratio is about 270 at 288 K and 365 at 275 K (Table 1), making the atmospheric concentrations of C_2Cl_4 extremely sensitive to the presence of Cl atoms. This is true of many other molecules as well (e. g. C_2H_6 , C_3H_8), but C_2Cl_4 is the only one where the sources are mainly anthropogenic and well-documented.

Chlorine atoms are of interest because they are up to 10^3 times more reactive than OH and may enhance the oxidizing capacity of the atmosphere. High concentrations of Cl could destroy ozone in certain regions of the troposphere, and greatly influence MBL chemistry of marine sourced chemicals such as dimethyl sulfide (DMS). Reactions of reactive halocarbons with Cl can also produce long-lived products ($C_2Cl_4 + Cl \rightarrow CCl_4$) that can impact stratospheric ozone [Franklin, 1994]. Singh and Kasting [1988] have suggested that Cl concentrations in the troposphere largely arise from HCl oxidation ($HCl + OH \rightarrow H_2O + Cl$) and other mechanisms of their formation are comparatively unimportant. Recent measurements show that HCl is present at typical mixing ratios of 35-70 ppt in the free troposphere and 150-350 ppt in the MBL [Graedel and Keene, 1995]. This would imply a corresponding mean Cl abundance of $1 \cdot 2 \cdot 10^2$ molec. cm^{-3} and $5 \cdot 10 \cdot 10^2$ molec. cm^{-3} , respectively. Inspired by chamber studies in Germany [Zetzsch and Behnke, 1992], a number of investigators have inferred that Cl concentrations in the 10^4 - 10^6 molec. cm^{-3} range, possibly resulting from sea salt

Table 1. Atmospheric Lifetimes and Reaction Rate Parameters of Selected Organic Chemicals

Chemicals	Reaction Rate Parameters*		k_{Cl}/k_{OH} (275 K, 800 mb)	τ (years) [#]
	k_{OH}	k_{Cl}		
C_2Cl_4	$9.40 \cdot 10^{-12} \times \exp(-1200/T)$	$k_0 = 1.40 \cdot 10^{-28}$, $n = 8.5$ $k_{\infty} = 3.97 \cdot 10^{-11}$, $m = 1.2$	365	0.31/0.26
CH_2Cl_2	$3.80 \cdot 10^{-12} \times \exp(-1050/T)$	$3.10 \cdot 10^{-11} \times \exp(-1350/T)$	3	0.41/0.41
CH_3CCl_3	$1.75 \cdot 10^{-12} \times \exp(-1550/T)$	$< 4 \cdot 10^{-14}$	< 6	4.95/4.94
CH_4	$2.65 \cdot 10^{-12} \times \exp(-1800/T)$	$1.1 \cdot 10^{-11} \times \exp(-1400/T)$	18	8.0/7.9
C_2H_6	$8.70 \cdot 10^{-12} \times \exp(-1070/T)$	$7.70 \cdot 10^{-11} \times \exp(-90/T)$	312	0.17/0.15
C_2H_2	$k_0 = 5.50 \cdot 10^{-30}$, $n = 0$ $k_{\infty} = 8.3 \cdot 10^{-13}$, $m = -2$	$k_0 = 5.4 \cdot 10^{-30}$, $n = 2.1$ $k_{\infty} = 2.1 \cdot 10^{-10}$, $m = 1.0$	31	0.05/0.06
C_3H_8	$10.0 \cdot 10^{-12} \times \exp(-660/T)$	$1.40 \cdot 10^{-10} \times \exp(40/T)$	178	0.043/0.04

* The $C_2Cl_4 + Cl$ three body rate parameters (in units of cm^6 molec. $^{-2}$ s $^{-1}$) are from Nicolovich *et al.* [1996]. All other rate parameters are from DeMore *et al.* (1994). The three body rate constant, $k(z,T)$, is calculated by using the Troe equation ($F_c = 0.6$) from DeMore *et al.* [1994]. [#] Model derived atmospheric lifetime with Cl=0 and 500.

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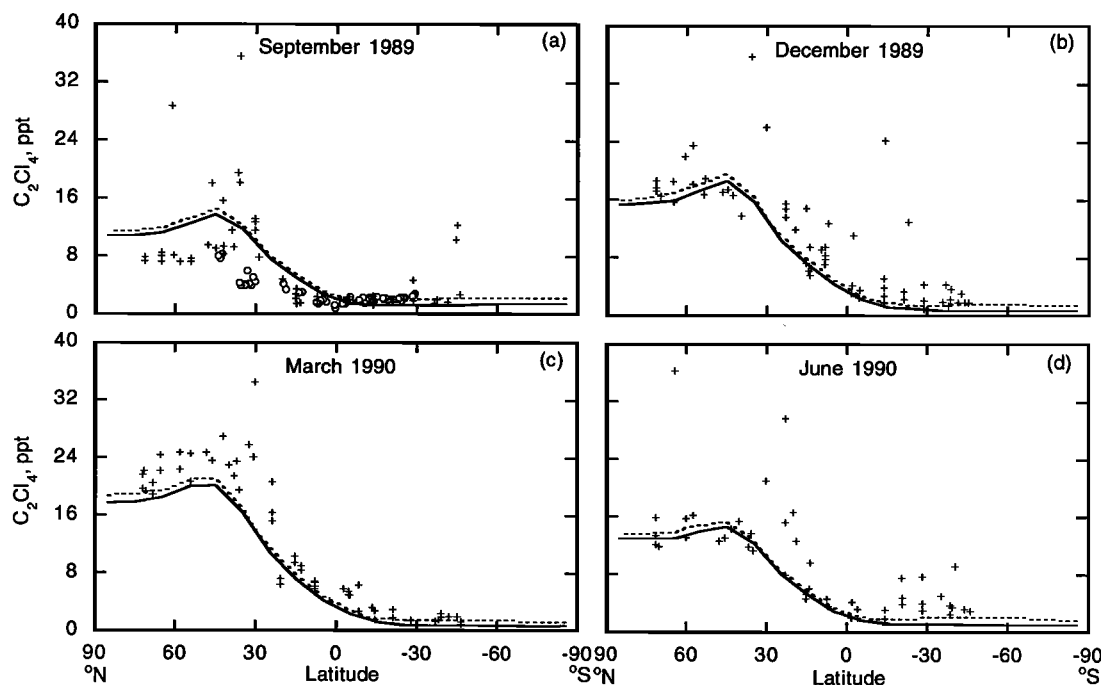


Figure 1. Measured and modeled surface mixing ratios of C_2Cl_4 in four seasons. Pluses (+) represent the 1989/90 data from Wang *et al.* [1995]. Open circles (o) are the August/September 1989 data from Koppmann *et al.* [1993]. Solid line is the prediction by the 2-D model based on the “industrial emissions only” scenario. The dashed line represents industrial emissions (395 Gg yr^{-1} 1989/1990 average) plus a 35 Gg yr^{-1} oceanic source. The C_2Cl_4 industrial source (92% in NH) is distributed according to McCulloch and Midgley [1996]. The oceanic source is distributed as 60% SH and 40% NH.

interactions with sun light, may be present in the MBL [Keene *et al.*, 1990; Pszenny *et al.*, 1993; Singh *et al.*, 1996; Wingenter *et al.*, 1996]. The potential significance of Cl in the MBL has been recently reviewed by Finlayson-Pitts [1993] and Graedel and Keene [1995]. By and large, the role of Cl atoms in tropospheric chemistry remains speculative.

A comparison of CH_3CCl_3 emissions with atmospheric observations has been successfully used to infer OH radical concentrations in the troposphere [Singh, 1977; Prinn *et al.*, 1995]. Because of its extremely high Cl reactivity, analysis of C_2Cl_4 in conjunction with the OH field fit to CH_3CCl_3 observations can provide an independent and sensitive means for evaluating Cl abundance. In this study we interpret the measurements of Wang *et al.* [1995] and Koppmann *et al.* [1993], with the help of a 2-D global photochemical model and a recently developed global source inventory, to estimate the abundance of Cl atoms in the troposphere.

Results and Discussion

Atmospheric C_2Cl_4 is largely removed by reaction with OH radicals; and loss to the oceans and to the stratosphere is negligible in comparison [Wiedmann *et al.*, 1994; Singh, 1995]. However, if Cl atoms were present they would cause additional removal due to their high reactivity with C_2Cl_4 . The basic premise of this study is that the atmospheric OH field can be defined accurately based on the budget and trend of CH_3CCl_3 [Prinn *et al.*, 1995]. If the predicted C_2Cl_4 mixing ratios, using this OH field alone, exceeded the measured ones, then removal by Cl atoms would be indicated. Although C_2Cl_4 has been measured extensively over the last two decades [Wiedmann *et al.*, 1994], there are few internally consistent and globally valid data sets available. To narrow the errors in the present analysis, we have used two independent data sets from the 1989–1990 period, when accurate emissions are known. These

are the Pacific data of Wang *et al.* [1995] where surface C_2Cl_4 was measured in four seasons from 71°N to 47°S latitudes, and the Atlantic shipboard data of Koppmann *et al.* [1993] who measured C_2Cl_4 during August/September 1989 from 45°N to 30°S latitudes. Absolute accuracy of better than $\pm 10\%$ at the 2 ppt level has been claimed in both studies. At the 40 ppt level, Wang *et al.* [1995] report errors to be $\pm 3\%$.

A 2-D model of the global troposphere, an improved version of Kanakidou *et al.* [1991], was used in this study. This model has a 10° horizontal resolution and 16 vertical layers extending from the surface to 24 km. The model contains detailed C_1 – C_3 HC/ NO_x / CO / O_3 gas phase chemistry including a limited number of heterogeneous reactions. The model contains no chlorine chemistry and is “tuned” to provide the best possible fit to the ALE/GAGE CH_3CCl_3 data. The model has a slight tendency to over-predict at northern latitudes ($>45^\circ N$) and under-predict at southern latitudes. The model-predicted mean CH_3CCl_3 tropospheric lifetime due to reaction with OH of 4.95 years (4.98 NH; 4.91 SH) can be compared with the 4.9 (± 0.3) years inferred from budget and trends [Prinn *et al.*, 1995]. The September 1991 mean vertical structure of C_2Cl_4 observed over the Pacific during PEM-A [Blake *et al.*, 1996], is in good agreement with that predicted by this model. Table 1 lists the rate constants and the atmospheric lifetimes of key species based on the OH distribution predicted by this model.

The industrial sources of C_2Cl_4 were input into this model according to the production/emission details provided by McCulloch and Midgley [1996]. Fully 92% of C_2Cl_4 is emitted in the NH. These emission data have errors of the order of $\pm 6\%$. Source inventories prior to 1988 are less accurate, but this has little effect on the 1989/1990 predictions due to the short lifetime of these species. The global emissions of C_2Cl_4 have declined (in Gg yr^{-1}) at an annual rate of about 35, from 454 in 1988 to 258 in 1994. At their peak in the early 1980's, C_2Cl_4 emissions may have been as high as 700 Gg yr^{-1} . The conventional view has been that C_2Cl_4 is purely man-made

with no natural sources. However, sea water supersaturations in coastal environments have been reported in the literature [Singh *et al.*, 1983]. Measurements by the NOAA CMDL group (J. Butler, private communication, 1996) indicate that tropical regions of the open oceans are supersaturated. Algae have been isolated that can form C_2Cl_4 in sea water [Abrahamsson *et al.*, 1993]. An estimated oceanic source of about 35 Gg yr^{-1} (upper limit of 70 Gg yr^{-1}) is consistent with the degree of supersaturation observed by the CMDL group. We note that the oceanic source of C_2Cl_4 , while highly uncertain, is probably small in comparison with its industrial emissions.

Figure 1 shows the measured and predicted latitudinal distribution of C_2Cl_4 at the surface in four seasons for the 1989/90 period. The solid line is the prediction by the 2-D model based on the industrial emissions alone. The dashed line represents an additional 35 Gg yr^{-1} oceanic source distributed as 60%SH and 40%NH. Although there is scatter in the data, both Wang and Koppmann measurements appear to be in reasonable agreement (Figure 1a). For Cl to be present, these predicted concentrations based on OH removal alone must exceed those measured. As is evident from Figure 1, this is not the case in any of the seasons except in September in the NH. We also note that while the measurements in the NH are distinctly lower in September they are also distinctly higher in March. A likely reason for these differences is the inability of the model to accurately simulate seasonal effects.

This SH C_2Cl_4 concentrations are extremely low and subject to greater measurement uncertainties (Figure 1). Wiedmann *et al.* [1994] collected a large body of data and reported an average surface mixing ratio of 2.2 ± 0.5 ppt. Koppmann *et al.* [1993] report a background of about 1 ppt over the south Atlantic in the spring of 1984. High scatter observed by Wang *et al.* in the SH is likely due to their sampling protocol which required them to be on islands and subject to nearby influences. The entire body of data is supportive of the view that SH concentrations of C_2Cl_4 are in the vicinity of 2 ppt. There are no indications that measured levels are lower than the predicted values.

To get around the difficulty of accurately simulating the seasonal variations, we compare model predictions and mea-

surements on an annualized basis. Figure 2 shows the mean annual distribution of C_2Cl_4 as measured (solid lines) and calculated (dashed lines) under a variety of scenarios. Solid line (solid circles) shows the annual average of the Wang and Koppmann data from Figure 1. High scatter in the Wang data was smoothed by removing obvious outliers in the NH and by restricting the SH ($>10^\circ\text{S}$) measurements to those below 4 ppt. Exclusion of these outliers would have the net effect of enhancing the estimated Cl abundances. Annual mean surface measured concentrations of 7.3 ppt (area integrated 4.4 ppt) can be determined from Figure 2. The model calculated values (industrial emissions + 35 Gg yr^{-1} oceanic source) are also shown in Figure 2 (dashed line open square) and correspond to a surface annual mean concentration of 7.4 ppt (area integrated 4.5 ppt). This implies that on average 98% of measured C_2Cl_4 is accounted for by OH and at best 2% loss can be attributed to Cl. In this "mean case" scenario removal by Cl can be inferred to be nearly negligible ($\tau_{Cl} \approx 15$ years; $Cl \leq 10^2 \text{ molec. cm}^{-3}$).

We recognize that emissions, measurements and kinetics data have uncertainties associated with them. Here we shall consider possible errors with the aim of obtaining a realistic "upper limit" on the atmospheric abundance of Cl. Thus we shall consider the possibility that measurements are high, emissions are low, and lifetimes are longer than calculated (Figure 2). All these will tend to deteriorate the agreement achieved in the "mean case" scenario and allow for the possible inference of Cl atoms. The lowest line in Figure 2 (solid line with solid triangles) is based on the assumption that the mean measurements are systematically too high by 10%. The dashed line (open diamonds) uses an industrial and an oceanic source that is respectively 6% ($\approx 420 \text{ Gg yr}^{-1}$) and 100% (70 Gg yr^{-1}) larger than the one used in the "mean case" scenario. The top most line in Figure 2 (open circles) further assumes that the kinetic uncertainties [Nicovich *et al.*, 1996 and references therein], are such that the C_2Cl_4 lifetime is 10% longer (0.34 years) than calculated in this model. The top and bottom lines in Figure 2 thus present a scenario of "reasonable extremes." When we consider the top and bottom lines in Figure 2, the mean concentrations of 9.3 ppt (area integrated 5.4 ppt) and 6.5 ppt (area integrated 3.9 ppt) do allow for a possible C_2Cl_4 loss that may be attributed to Cl. In this "upper limit" scenario, out of a total of $\approx 490 \text{ Gg yr}^{-1}$ C_2Cl_4 source some 70% is removed by OH and the remainder 30% by Cl ($\approx 147 \text{ Gg yr}^{-1}$). This would indicate a lifetime of C_2Cl_4 due to Cl (τ_{Cl}) of 0.8 years ($70 \times 0.34 / 30$) corresponding to a Cl inference of $\approx 10^3 \text{ molec. cm}^{-3}$ ($Cl = 1/k\tau_{Cl}$). In reality these errors are likely to be random rather than additive in nature. If we convert all these errors into equivalent source uncertainties (u_i in Gg yr^{-1}) of 25 in industrial source, 35 in oceanic source, 40 as equivalent measurement error, and 50 as equivalent lifetime uncertainty then the total uncertainty ($= \sqrt{\sum u_i^2}$) of about 77 Gg yr^{-1} is only about half as much. This level of uncertainty results in the inference of a Cl atom abundance of $\approx 5 \times 10^2 \text{ molec. cm}^{-3}$. While no clear signal is evident in the "mean case" analysis ($Cl \leq 10^2 \text{ molec. cm}^{-3}$), an "upper limit" annual mean tropospheric Cl of $< 5 \times 10^2 \text{ molec. cm}^{-3}$ cannot be ruled out.

An assessment of Cl abundance is also possible by using the C_2Cl_4/CH_2Cl_2 ratio, which should be largely insensitive to OH concentrations. Since CH_2Cl_2 does not react with Cl atoms to any appreciable degree (Table 1), removal by this process would be negligible. Figure 3 shows the measured and modeled distribution of CH_2Cl_2 for Aug./Sept. 1989. While industrial sources alone describe the NH distribution quite well, this is not the case in the SH. An oceanic source of about 180 Gg yr^{-1} (60% SH; 40% NH) is required to reconcile this difference in the SH. This is $\approx 30\%$ of the industrial source. The possibility of a somewhat large and uncertain oceanic source of CH_2Cl_2 and insufficient atmospheric data do not allow a reliable estimate of Cl with this ratio method at this time. However in the future, the ratio of C_2Cl_4 with halocarbons of comparable lifetimes

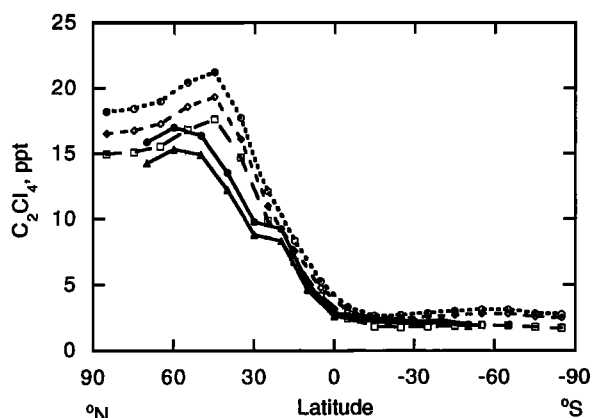


Figure 2. Annual mean measured and modeled surface mixing ratios of C_2Cl_4 . Solid lines (solid symbols) represent measurements and dashed lines (open symbols) represent model results. Solid circles show the mean data from Figure 1 and solid triangles are these data $\times 0.9$. Open squares represent mean industrial emissions plus a 35 Gg yr^{-1} oceanic source. Open diamonds show results when an industrial source that is 6% larger (419 Gg yr^{-1} 1989/1990 average) and an oceanic source that is 100% larger (70 Gg yr^{-1}), as compared to the "mean case" scenario, is used. The top most line (open circles) assumes that C_2Cl_4 lifetime is 10% larger (0.34 years) than calculated by the model (0.31 years).

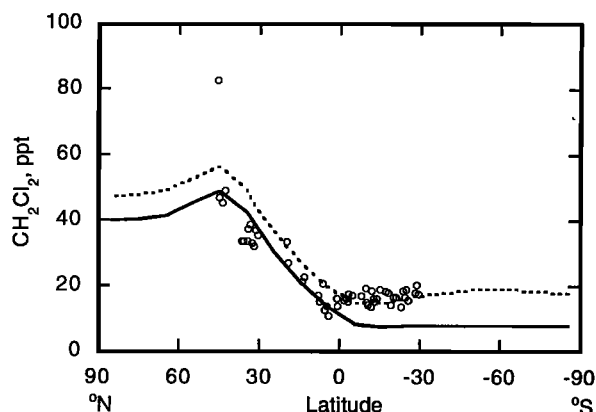


Figure 3. Measured and modeled surface mixing ratios of CH_2Cl_2 . Data are for August/September 1989 from Koppmann *et al.* [1993]. Model scenarios are as in Figure 1. A 180 Gg yr^{-1} oceanic source (60% SH ; 40% NH) is used.

and known sources (e. g. CF_3CHCl_2 or HCFC-123) may permit a more accurate estimate of Cl abundance.

The above analysis can be used to place reasonable constraints on the abundance of Cl in the MBL. Since free tropospheric concentrations of Cl are expected to be quite small, we assume that nearly all (80-100%) of the Cl atoms reside in the MBL. Given the scale height of the troposphere and the MBL of 7.5 km and 0.75 km respectively, and area ratio of earth to ocean of 1.4, MBL concentrations should be some 10-15 times $\{=(0.8-1.0) \times 1.4 \times 7.5/0.75\}$ those of the mean troposphere. Thus a Cl atom MBL mean of $\leq 10^3 \text{ molec. cm}^{-3}$ ("mean case") and $< 5 \times 10^3 \text{ molec. cm}^{-3}$ ("upper limit") can be estimated. Since Cl atoms are not expected to persist at night, daytime concentrations of $< 0.5 \times 10^4 \text{ molec. cm}^{-3}$ are indicated. This implies that on average, daytime MBL Cl concentrations are likely to be below or near the lower end of the values inferred (10^4 - $10^6 \text{ molec. cm}^{-3}$) in some recent studies [Graedel and Keene, 1995; Singh *et al.*, 1996; Wingenter *et al.*, 1996]. These few inferred values are not expected to provide a mean representation of the MBL. If sea salt is indeed associated with the release of active chlorine, then the presence of moderately high Cl atom concentrations ($> 10^4 \text{ molec. cm}^{-3}$) in the lower parts of the MBL are not ruled out from this analysis.

The conventional view that C_2Cl_4 is largely destroyed by reaction with OH radicals, appears to be basically correct. Present results support the suggestion of Singh and Kasting [1988] that low Cl atom concentrations, possibly from the oxidation of HCl, are present in the troposphere. We conclude that Cl atoms are not likely to play a major role in defining the oxidizing capacity of the atmosphere. For example, they are able to enhance methane oxidation by $< 2\%$ (Table 1). Even in the MBL, inferred Cl abundances would limit DMS oxidation to < 15 -30% ("best value" $\approx 3\%$) of that due to OH ($k_{\text{Cl}}/k_{\text{OH}} = 42$). Atmospheric processes that require Cl atoms, such as the conversion of C_2Cl_4 to CCl_4 $\{\text{C}_2\text{Cl}_4 + \text{Cl} (+\text{O}_2) \rightarrow \text{CCl}_3\text{COCl} (+h\nu) \rightarrow \text{CCl}_4 + \text{CO}\}$, are expected to be of minor importance.

Conclusions

The OH field derived from CH_3CCl_3 has been, over the years, greatly refined and is widely used in the validation of global photochemical models. We present here yet another extension of this concept to estimate Cl atom concentrations in the troposphere. We are able to show that Cl atom concentrations are extremely low and are not likely to play an important role in defining the oxidizing capacity of the troposphere. It is also unlikely that Cl abundances are unusually large in the marine boundary layer. These calculations can be further improved as more complete and accurate emissions data and atmospheric measurements become available. A better knowledge of the natural sources of C_2Cl_4 (and CH_2Cl_2) is needed.

Note added. During the Fall 1995 AGU Conference, and after the completion of this study, a presentation by J. Rudolph and co-workers (Jülich/Germany) made us aware that they have also interpreted their C_2Cl_4 data to infer low Cl concentrations.

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