THE BUDGETS OF ETHANE AND TETRACHLOROETHENE: IS THERE EVIDENCE FOR AN IMPACT OF REACTIONS WITH CHLORINE ATOMS IN THE TROPOSPHERE?

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Abstract—In a number of recent papers evidence has been presented that reactions with Cl atoms substantially contribute to the turnover of organic compounds in certain regions of the marine atmosphere. However, the impact of this possible sink mechanism for organic compounds on global or hemispheric scales is still unknown. Based on the budgets of organic substances which react with Cl-atoms much faster than with OH-radicals it is possible to derive upper limits for the average tropospheric Cl-atom concentration. The rate constants for the ethane and tetrachloroethene reaction with Cl are by a factor of 200–300 higher than those with OH-radicals, this reaction being their only significant established sink in the troposphere. From several series of measurements in the remote troposphere we derived an estimate of mean tropospheric distributions and seasonal cycles of tetrachloroethene and ethane. Together with OH-fields from model calculations we calculated the removal of ethane and tetrachloroethene by OH-radicals. Within the uncertainties the calculated removal agrees with the known emissions of these substances. In spite of the substantial uncertainties of these budgets, the relatively high reactivity of these substances towards Cl-atoms allows to estimate useful upper limits of the removal rates by Cl-atoms and thus of the average tropospheric Cl-atom concentration. For the Northern Hemisphere a plausible upper limit of less than 1000 Cl-atoms cm^{-3} can be derived. Due to higher uncertainties in the budgets for the Southern Hemisphere, the upper limit of the Cl-atom concentration in the Southern Hemisphere is nearly 2000 Cl-atoms cm^{-3}. Nevertheless, these results show that on a global scale the Cl-atom-induced reactions for most organic trace gases are of minor importance.

Key word index: Chlorine chemistry, atmospheric removal, radical reactions, tetrachloroethene, ethane.

INTRODUCTION

There is increasing evidence that Cl-atoms may be important for the chemistry of the troposphere in certain regions (Singh and Kasting, 1988; Pszenny *et al.*, 1993; Jobson *et al.*, 1994; Hemming *et al.*, 1994; Finnlayson-Pitts, 1994; Blake *et al.*, 1995; Singh *et al.*, 1995). It has been speculated that Cl-atoms may be important for the tropospheric turnover of organic trace gases (Singh and Kasting, 1988; Finnlayson-Pitts, 1993; Blake *et al.*, 1995; Singh *et al.*, 1995). The existing evidence is indirect and either based on model calculations, laboratory studies of potential Cl-atom formation mechanisms, measurements of potential precursors, or the change in the pattern of nonmethane hydrocarbons (Singh and Kasting, 1988; Pszenny *et al.*, 1993; Finnlayson-Pitts, 1993; Jobson *et al.*, 1994; Blake *et al.*, 1995; Singh *et al.*, 1995). Sufficiently sensitive methods to measure Cl-atom concentrations in the range of a few 10^3–10^4 atoms cm^{-3} have yet to be developed. Moreover, the existing studies do not yet allow one to estimate annual, large-scale mean values for the tropospheric Cl-atom concentrations. Therefore, the actual impact of Cl-atoms on the tropospheric budgets of organic trace gases is still unknown. One possibility to look for the impact of Cl-atom chemistry in the troposphere is to investigate the budgets of trace gases which are only removed from the troposphere by reactions with OH-radicals or Cl-atoms but have much higher rate constants for the reaction with Cl-atoms than with OH-radicals. Suitable substances should be present in the troposphere at measurable levels, have atmospheric lifetimes of a few months or more to reduce the unsystematic variability in the troposphere, but still be reactive enough to be predominantly degraded in the troposphere. If the tropospheric distribution is sufficiently well known, the atmospheric removal by OH-radicals can be calculated from the rate constants for this reaction, the tropospheric OH-distribution (e.g. from model calculations) and the trace gas distribution. A comparison between the calculated removal and the emission rates into the atmosphere can be used to estimate the magnitude of a possible missing sink which may be caused by reactions with Cl-atoms. In principle the average Cl-atom concentration can then be derived from the unexplained atmospheric removal, the average

Table 1. Comparison of reaction rate constants ($cm^3 s^{-1}$ molecules$^{-1} \times 10^{13}$) for reactions with OH-radicals and Cl-atoms.

	298 K		280 K[a]	
	C_2Cl_4	C_2H_6	C_2Cl_4	C_2H_6
OH	1.67[b]	2.97[c]	1.29[b]	2.40[c]
Cl	413[d]	568[b]	413[e]	557[b]
Ratio Cl/OH	247	191	320	232

[a] Average tropospheric temperature suggested for reactions with OH-radicals by Warneck (1988).
[b] Rate constant from Atkinson *et al.* (1989).
[c] Rate constant from Atkinson *et al.* (1992).
[d] Rate constant from Atkinson and Aschmann (1987).
[e] Rate constant from Atkinson and Aschmann (1987), temperature dependence neglected according to the observations of Goldfinger *et al.* (1958) and Beadle and Knox (1974).

atmospheric concentration of the trace gas and the rate constant for the reaction of the selected substance with Cl-atoms.

However, the atmospheric budgets of most trace gases have substantial uncertainties and we cannot expect that it will be possible to determine the budget of a given trace gas precisely enough to obtain a budget which is, within its uncertainties, unbalanced. In reality we therefore can only hope to derive upper limits for the global Cl-atom concentration. In order to gain useful results the substances investigated should react with Cl-atoms much faster than with OH-radicals. Ethane and tetrachloroethene react by factors of 200–300 faster with Cl-atoms than with OH-radicals (Table 1). For most other organic trace gases in the atmosphere the relative differences in the reaction rates are much smaller. Thus the budgets of ethane and tetrachloroethene should show the largest impact from the contribution of Cl-atoms to the atmospheric removal of organic trace gases. Furthermore, the atmospheric lifetimes of both compounds are long enough to allow the determination of sufficiently representative tropospheric distributions from a reasonable number of measurements. Finally, both compounds also meet the condition that the reaction with OH-radicals in the atmosphere is the only established removal mechanism.

THE TROPOSPHERIC DISTRIBUTION OF ETHANE

Between 1980 and 1992 we made about 1500 measurements of ethane in the remote troposphere. The measurement methods, sampling procedures and calibrations are described in detail by Koppmann *et al.* (1992), Rudolph and Jebsen (1983), Rudolph *et al.* (1981, 1982, 1986, 1989a, b, 1992), Rudolph (1988) and Rudolph and Johnen (1990). Combined with several data sets from literature (see Rudolph, 1995, and references therein) these data were used to derive the latitudinal and seasonal distribution of ethane.

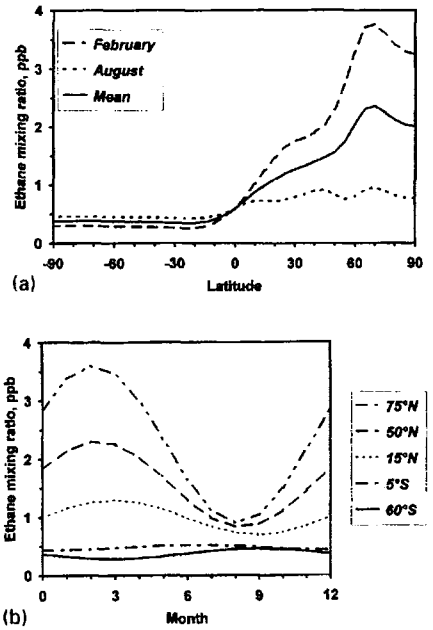

Fig. 1. Tropospheric distribution of ethane: (a) longitudinally averaged latitudinal profiles of the ethane mixing ratio for different seasons. The solid line represents the annual mean profile, (b) average seasonal variation of the ethane mixing ratio for different latitudes.

Details of the construction of the seasonal and latitudinal dependence of ethane are described and discussed by Rudolph (1995). The vertical gradients of ethane in the unpolluted troposphere are small, on the average the difference between the boundary layer and the upper troposphere is less than 10%. The longitudinal gradients are also assumed to be negligible (Hough, 1991; Isaksen *et al.*, 1985; Kanakidou *et al.*, 1991). In general, the ethane measurements made within one latitude belt fit, within their uncertainties, into the same seasonal pattern. However there are no systematic measurements of the longitudinal variability of ethane which adds some uncertainty to the overall distribution. We estimate that the uncertainty of the longitudinally averaged ethane distribution is on average about 30%. The latitudinal gradients for different seasons are shown in Fig. 1a, and examples for the seasonal variability at different latitudes are given in Fig. 1b.

THE TROPOSPHERIC DISTRIBUTION OF TETRACHLOROETHENE

Our data set of measurements of tetrachloroethene in the remote troposphere is somewhat smaller than for ethane and consists of roughly 1000 measurements

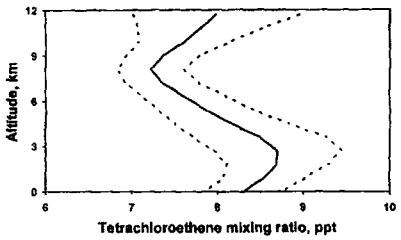

Fig. 2. Globally averaged vertical profile of the tetrachloroethene mixing ratio. The dashed lines represent the uncertainty of the mean mixing ratios.

made between 1983 and 1991. We did not include data from the literature since there has been no intercalibration or comparable activity to establish that the data sets from different groups are compatible. Thus the total available data set is about half the size of the ethane data set. Still the construction of a latitude/season dependence of the tetrachloroethene mixing ratio is justified because the average atmospheric lifetime of tetrachloroethene is about 4 months, nearly a factor of two longer than that of ethane and we can therefore expect a lower amount of unsystematic variability of the tetrachloroethene mixing ratio in the remote troposphere. For example, the globally averaged vertical profile for tetrachloroethene shows only a small variation of about $\pm 7\%$ (see example in Fig. 2).

Part of the results of the tetrachloroethene measurements have been published before (Rudolph *et al.*, 1984; Koppmann *et al.*, 1993, 1994). Details about the sampling procedure and the analytical techniques can be found in these papers. The longitudinally and vertically averaged latitudinal and seasonal variations of tetrachloroethene derived from our measurements are shown in Fig. 3a and b.

There are some recent measurement series of tetrachloroethene which can be compared with our distribution. Class and Ballschmiter (1986, 1987) derived from a limited number of measurements mean mixing ratios for the Northern- and Southern-Hemisphere of 15 ± 3 ppt and 2.3 ± 0.7 ppt, respectively. This is very similar to the values of 14.3 and 2.5 ppt, respectively, derived from our data set (Table 2). Makide *et al.* (1987) measured the seasonal cycle at a coastal station in Hokkaido. They report a late winter maximum of 25 ppt and a late summer minimum of about 13 ppt. Our distribution shows for the corresponding latitude belt (40–45°N) a nearly identical seasonal variation with a maximum of 23 ppt in March/April and a minimum of 10 ppt in September/October. During the ABLE 2B experiment in July 1990 Blake *et al.* (1994) measured the vertical profile of the tetrachloroethene mixing ratios at 51.5°N. Their mean value of 12.2 ± 1 ppt is very similar to our average of about 15 ppt for this time of the year at 50°N (Fig. 3a). From about 120 measurements in the troposphere

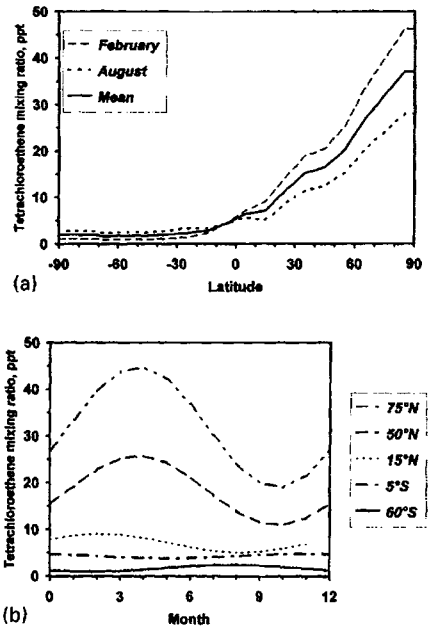

Fig. 3. Tropospheric distribution of tetrachloroethene: (a) longitudinally averaged latitudinal profiles of the tetrachloroethene mixing ratio for different seasons. The solid line represents the annual mean, and (b) average seasonal variation of the tetrachloroethene mixing ratio for different latitudes.

Wiedman *et al.* (1994) estimated the annual mean tetrachloroethene mixing ratios for three latitude ranges. For the southern hemisphere they found 2.2 ± 0.5 ppt, for the region between the equator and 30°N 7 ± 3 ppt, and for the latitudes north of 30°N 21 ± 5 ppt. This differs only marginally from the corresponding values of 2.5, 7.8 and 20.3 ppt which we calculate from our average tetrachloroethene distribution. Very recently Wang *et al.* (1995) presented measurements of the latitudinal profiles of the tetrachloroethene mixing ratios for four different months of the year. Each of the profiles was derived from 50–60 surface-based measurements. From these distributions they calculated an area weighted global mean tetrachloroethene mixing ratio of 7.3 ± 1.0 ppt which is in very good agreement with our mean value of 8.4 ppt. Also their mean southern hemispheric mixing ratio of 2.7 ppt compares favourably with our value of 2.5 ppt. Their global average surface mixing ratios for September, December, March and June are 4.3, 8.2, 9.5 and 7.0 ppt. Within the uncertainties expected for limited data sets they fully agree with the corresponding mean values of 6.5, 7.9, 11.2 and 9.8 ppt derived from our tetrachloroethene distribution. Also the shapes of the latitudinal profiles generally agree. The results of Wang *et al.* (1995) show a decrease from mid-northern latitudes to equatorial regions where mixing

Table 2. Ethane and tetrachloroethene in the troposphere

	Ethane			Tetrachloroethene		
	Whole troposphere	N. H.	S. H.	Whole troposphere	N. H.	S. H.
Mean mixing ratio, ppt	860 (600–1120)	1330 (1000–1700)	380 (290–490)	8.4 (6.5–11)	14.3 (11–19)	2.5 (2–3.3)
Removal by OH, $Tg\,yr^{-1}$	15 (9.4–23.6)	11 (7.2–18)	3.5 (2.3–5.7)	0.42 (0.27–0.68)	0.33 (0.2–0.53)	0.1 (0.06–0.15)
Exchange between Hemispheres, $Tg\,yr^{-1}$		−1.4 (1–2.1)	1.4 (1–2.1)		−0.1 (0.07–0.14)	0.1 (0.07–0.14)
Loss to stratosphere, $Tg\,yr^{-1}$	1.1 (0.8–1.6)	0.8 (0.6–1.2)	0.23 (0.17–0.35)	0.055 (0.04–0.08)	0.045 (0.03–0.07)	0.01 (0.006–0.013)
Total loss from domain, $Tg\,yr^{-1}$	15.8 (10–25)	13.4 (9–20)	2.4 (1–5)	0.48 (0.33–0.72)	0.47 (0.35–0.67)	0.01 (−0.034–0.082)

The values in parentheses give the range of uncertainty (1σ), the errors are calculated by Gaussian error propagation.

ratios around 6 ppt are observed. In the Southern Hemisphere very low mixing ratios with only small latitudinal gradients were observed. This is in excellent agreement with our findings (Fig. 3a). For high northern latitudes the amplitude of the seasonal cycle found in both studies is very similar, about 15 ppt. However, there is a significant disagreement in the mean values for these latitudes. Our results indicate an increase from 55°N to 80°N whereas the results of Wang *et al.* (1995) show constant mixing ratios between 35°N and 70°N. For high northern latitudes our distribution is mainly based on about 80 measurements made at Alert (81°N) in 1989 and 1990. The shape of the gradient between 55°N and 80°N is strongly influenced by the values at 80°N because we made only few other measurements in this latitude region. The exact shape of the gradient between 55°N and 80°N is therefore not known. Moreover, we made a rather unusual observation at Alert. About 20–25% of the measurements showed mixing ratios a factor of two or more above the mean value. These elevated mixing ratios were seen only during a few episodes and generally coincided with increased concentrations of other halocarbons. Wang *et al.* (1995) made similar observations for a limited number of measurements. They ascribed this to recent urban impact and excluded these values from the calculation of mean values. If we exclude the measurements with strongly elevated tetrachloroethene mixing ratios from our data set, we find a mean value of about 20 ppt which is very similar to the values found for mid northern latitudes. However, there is no indication that the elevated halocarbon concentrations we found at high northern latitudes are due to contaminations from local sources. Due to the very small number of such episodes it is not possible to identify the reasons for the elevated halocarbon mixing ratios. We also do not know how representative the observed number of such occurrences is and we therefore have to deal with a substantial uncertainty of the tetrachloroethene mixing ratios at high northern latitudes. Fortunately, this has only a small impact on the mean tetrachloroethene mixing ratio in the Northern Hemisphere. If we assume that the tetrachloroethene mixing ratio remains constant north of 55°N, the area weighted mean mixing ratio is 13 ppt. This corresponds to a reduction of 10%.

Based on the generally very favourable comparison with recent literature data we estimate that our tetrachloroethene distribution represents the average situation within a statistical uncertainty of about 30%. For the latitude range south of 55°N the very good agreement suggests that the uncertainties are probably lower.

THE ATMOSPHERIC REMOVAL OF ETHANE AND TETRACHLOROETHENE BY OH-RADICALS

The local removal rate of a trace gas X by reaction with OH-radicals can be calculated from its local atmospheric concentration, the local OH-radical concentration and the rate constant for this reaction:

$$d[X]_{OH}/dt = -{}^{X}k_{OH} * [OH] * [X] \qquad (1)$$

where $d[X]_{OH}/dt$ is the removal rate of X by reaction with OH-radicals, ${}^{X}k_{OH}$ is the rate constant for the reaction of X with OH-radicals, [OH] is the concentration of OH-radicals and [X] is the concentration of trace gas X.

The annual global tropospheric or hemispheric removal rate can then be calculated by integrating over longitude, latitude, altitude and season. For this calculation we used the rate constants and their temperature dependencies recommended by Atkinson *et al.* (1989, 1992), the global OH-radical field of Brasseur *et al.* (1990) as published by Taylor *et al.* (1991) and our ethane and tetrachloroethene fields. The global temperature fields were extracted from the GISS 3D model (Hansen *et al.*, 1983). We integrated numerically over intervals of 5° latitude, 1 km altitude and 1 month duration using the longitudinal averages.

The resulting global and hemispheric removal rates are presented in Table 2. Also included are the average tropospheric mixing ratios. The losses into the stratosphere are calculated from an average exchange time of 0.8 yr for the stratospheric air (cf. Warneck, 1988) and the average tropospheric mixing ratios. The exchange rates between the two hemispheres are estimated from the interhemispheric exchange rate of 1.5 yr (Mais and Levin, 1994) and the mean hemispheric mixing ratios.

The uncertainty ranges given in Table 2 are derived from the error of the rate constants (Atkinson *et al.*, 1989, 1992), the uncertainty of the ethane and tetrachloroethene distribution, respectively, and the uncertainties of the OH-field. The largest uncertainty in the tetrachloroethene distribution is observed at high northern latitudes (see above). Due to the rather low average OH-radical concentrations at high latitudes the turnover in this region is only small. Consequently, the relative error in the global turnover resulting from the uncertainties in the tetrachloroethene mixing ratios at high northern latitudes is below 2%. For the exchange times between troposphere and stratosphere and as interhemispheric exchange time we use an uncertainty (1σ) of 0.25 and 0.5 yr, respectively (Warneck, 1988).

It is claimed that the OH-fields which are able to give a reasonable description of the removal of certain trace gases with well-known atmospheric sources (e.g. 14-CO: Volz *et al.*, 1981; CH_3CCl_3: Taylor *et al.*, 1991) are reliable within an uncertainty of 20% (cf. Hough, 1991). However, presently there is evidence that the average global OH-radical concentration may be substantially higher than assumed before (Prinn *et al.*, 1994). To account for this possible systematic error we use an uncertainty for the average OH-radical concentration of -20% and $+50\%$. The corresponding range of the mean global OH-radical concentration is $5\text{–}10 \times 10^6$ cm^{-3}. This range includes the results of most estimates of mean global OH-radical concentrations since 1980 (Taylor *et al.*, 1991).

The uncertainty resulting from errors in the shape of the global OH-radical distribution is somewhat more difficult to assess. We have made a few sensitivity studies on the effect of changes of the shape of the seasonal, latitudinal and vertical distribution of the OH-radical concentration. On average the vertical profile of the OH-distribution we used (Taylor *et al.*, 1991) shows an increase of about 60% between ground level and 5 km altitude. In the upper troposphere the OH-radical concentrations decrease with increasing altitude. We varied the gradient between the boundary layer and 5 km altitude but scaled the profiles to the mean OH-radical concentrations of 6.4×10^5 cm^{-3}. The gradient was changed by a factor of two in both directions, replaced by a constant concentration and inverted. In all cases was the change in the global annual removal rates of both ethane and tetrachloroethene below 6%. A variation of the amplitude of the seasonal variation of the OH-radical concentrations by a factor of two in either direction causes changes of less than 3% in the annual turnover of ethane or tetrachloroethene. The extreme case of no seasonality of the OH-radical concentration or fourfolding the amplitude causes changes of less than 5%. Shifts in the phase of the seasonality of the OH-radical concentrations by ± 2 month results in changes of 2% and 6%. A change of the relative gradient of the OH-distribution between 40° and the equator by a factor of 2 or 0.5 changes the removal rates by 2–8%. Based on these sensitivity studies the uncertainties in the mean annual removal rates of ethane and tetrachloroethene resulting from errors of the shape of the OH-radical distribution are most probably below 10%.

THE ATMOSPHERIC BUDGET AND THE POTENTIAL CONTRIBUTION OF Cl-ATOM REACTIONS

In Table 3 the atmospheric budgets of ethane and tetrachloroethene are summarised. The ethane sources and their uncertainties are taken from Rudolph (1995). The tetrachloroethene emission rates published by SRI (1988, 1992) are 0.358 Tg yr^{-1} for 1990 and 0.386 Tg yr^{-1} for 1987. These data indicate a decrease in the tetrachloroethene production between 1987 and 1990 of about 8%. A recent production estimate (P. M. Midgley, personal communication) gave emission rates identical to those of SRI for 1990, but indicated a somewhat stronger decline of the emissions between 1988 and 1992. Since our tropospheric tetrachloroethene distribution is based on averages of measurements made between 1983 and 1991 this causes an uncertainty of about $\pm 10\%$. It has been speculated that there is an additional tetrachloroethene emission of up to 100×10^9 g yr^{-1} from residue processing in developing countries (Fisher *et al.*, 1994). On the other hand, Graedel and Keene (1995) state that solvent use is the principal global source of tetrachloroethene. Wiedmann *et al.* (1994) estimated that the average emission rate for the last decade is 0.48 Tg yr^{-1}. For our calculations we conservatively use a range (1σ) of 0.36–0.48 Tg yr^{-1} with a best estimate of 0.42 Tg yr^{-1}.

The source distribution of the ethane sources between the two hemispheres is calculated from the latitudinal source distributions of typical source types given by Hough (1991). For tetrachloroethene the hemispheric distribution of the emission rates is based on the sales data (P. M. Midgley, personal communication).

Basically, we can calculate the atmospheric removal by Cl-atoms analogous to the removal by OH.

$$d[X]_{Cl}/dt = -{}^{X}k_{Cl} * [Cl] * [X] \qquad (2)$$

with $d[X]_{Cl}/dt$ the removal rate of X by reaction with Cl-atoms, ${}^{X}k_{Cl}$ the rate constant for the reaction of X with Cl-atoms, [Cl] the concentration of Cl-atoms and [X] the concentration of trace gas X.

Table 3. Tropospheric budget of ethane and tetrachloroethene

	Ethane			Tetrachloroethene		
	Whole troposphere	N. H.	S. H.	Whole troposphere	N. H.	S. H.
Total atmospheric loss rate, Tg yr^{-1}[a]	15.8 (10.4–25)	13.4 (9.3–20)	2.4 (1.1–5)	0.48 (0.32–0.72)	0.47 (0.35–0.67)	0.01 (−0.03–0.08)
Sources, Tg yr^{-1}	13.3 (7–25)	10.5 (5–18)	2.8 (2–7)	0.42 (0.36–0.48)	0.42 (0.36–0.48)	0.004 (0.0–0.01)
Difference, Tg yr^{-1}	−2.5 (−14–10)	−2.9 (−11–6)	0.4 (−2.3–4.8)	−0.07 (−0.3–0.1)	−0.06 (−0.26–0.08)	−0.006 (−0.08–0.03)
Cl-atom concentration, molecules per cm^3 [b]						
(1) Uniform distribution in the troposphere	0 (0–1800)	0 (0–1300)	300 (0–3800)	0 (0–500)	0 (0–400)	0 (0–1000)
(2) in marine boundary layer only[c]	0 (0–8800)	0 (0–7000)	1200 (0–16000)	0 (0–2400)	0 (0–2400)	0 (0–4400)

[a] Includes losses to stratosphere and for the hemispheric values also interhemispheric exchange.

[b] If the budget estimates would require negative Cl-atom concentrations, zero is given as lowest possible value. The uncertainties given for the Cl-atom concentrations are calculated from the uncertainties of the budgets and the error of the rate constants for the reactions of Cl-atoms with ethane and tetrachloroethene, respectively.

[c] Assumes that the concentration of Cl-atoms outside the marine boundary layer is zero. The values in parentheses give the range of uncertainty (1σ), the errors are calculated by Gaussian error propagation.

Since, apart from the possible reaction with Cl-atoms, the removal by OH-radicals is the only established relevant sink for ethane and tetrachloroethene in the troposphere, the removal by Cl-atoms should be equal to the difference between source strength and removal by OH-radicals:

$$^{x}R_{Cl} = {}^{x}E - {}^{x}R_{OH} \tag{3}$$

where ^{x}E is the emission rate of ethane or tetrachloroethene, respectively; corrected for the loss into the stratosphere. For the hemispheric estimates also the contribution of the interhemispheric exchange has to be considered. $^{x}R_{OH}$ is the removal rate in domain by OH-radicals for ethane or tetrachloroethene, respectively, and $^{x}R_{Cl}$ is the removal rate in domain by Cl atoms.

The integration of equation (2) and combination with equation (3) gives:

$$^{x}E - {}^{x}R_{OH} = {}_{x}\int {}_{y}\int {}_{z}\int {}_{t}\int {}^{x}k_{Cl} * [Cl] * [X]\, dx\, dy\, dz\, dt. \tag{4}$$

The tropospheric distribution of Cl-atoms is essentially unknown and therefore equation (4) cannot be solved. As a first, simplified approximation we use a uniform Cl-atom concentration. As a further simplification we also use an average, temperature-independent rate constant for the reaction rate of ethane or tetrachloroethene with Cl-atoms. Equation (4) can then be written as

$$^{x}E - {}^{x}R_{OH} = {}^{x}k_{Cl} * [Cl]^{av} * [X]^{av} * M_d \tag{4}$$

with $[Cl]^{av}$ the average Cl-atom concentration in domain, $[X]^{av}$ the average concentration of trace gas X in domain and M_d the air mass in the considered tropospheric domain.

Equation (4) can be solved for $[Cl]^{av}$ and the Cl-atom concentrations calculated from the budget data in Table 3 and the rate constants in Table 1. The results and their plausible ranges (calculated from Gaussian error propagation) are included in Table 3. The assumption of a constant, temperature-independent rate constant for the reaction of Cl-atoms with ethane or tetrachloroethene introduces only a marginal error since the temperature dependence of this reaction is only small (see Table 1). This minor uncertainty is well within the error of the rate constants.

The required Cl-atom concentrations to balance the ethane and tetrachloroethene budgets are either zero or a few hundred molecules cm^{-3}. There still exist some uncertainties in the budgets. The ethane budget would still allow a few thousand Cl-atoms cm^{-3}. From the tetrachloroethene budget stricter constraints can be derived. The upper limits are a few hundred Cl-atoms cm^{-3} in the Northern Hemisphere and about 1000 Cl-atoms cm^{-3} in the Southern Hemisphere.

As mentioned, this simplified calculation assumes a uniform seasonal and latitudinal distribution of Cl-atoms. If the Cl-atom concentrations would be particularly high at latitudes and seasons with low ethane and tetrachloroethene concentrations, correspondingly higher Cl-atom concentrations might still be possible. From our present understanding it can be expected that in the troposphere Cl-atoms will be primarily found in the marine boundary layer. If we assume that the Cl-atom concentration is globally or hemispherically uniform in the marine boundary layer and zero in the troposphere outside the marine boundary layer, we can calculate the Cl- atom concentration by a procedure analogous to the one described above. The results are included in Table 3. The upper

limits derived from the tetrachloroethene budget range around a few thousand Cl-atoms cm^{-3}.

CONCLUSIONS

The budget estimates for ethane and tetrachloroethene allow to deduce reasonable upper limits for the average tropospheric Cl-atom concentrations. This is mainly due to a factor of several hundred higher rate constants for their reaction with Cl-atoms compared to reactions with OH-radicals. Based on our current understanding of the budgets, tetrachloroethene seems to be more suitable to derive meaningful limits for tropospheric Cl-atom concentrations. Although the budgets still allow a contribution to the atmospheric removal from reactions with Cl-atoms, the upper limits indicate that for the Northern Hemisphere on average Cl-atoms can only be of minor importance for the removal of most organic trace gases. The larger uncertainties for the Southern Hemisphere would still allow a Cl-atom contribution to the turnover of most organic trace gases of some 10%.

The upper limits of the mean Cl-atom concentration in the marine boundary layer indicates that on average reactions with Cl-atoms can only be important for those few organic substances which react nearly two orders of magnitudes (or more) faster with Cl-atoms than with OH-radicals. It should be noted that this does not exclude the possibility that the Cl-atom concentration may be significantly higher for limited areas or short periods of time.

As mentioned, the use of trace gases as indicators for reactions with Cl-atoms gives higher weight to regions with high trace gas concentrations. Since both ethane and tetrachloroethene have their highest concentrations at mid and high northern latitudes, relevant Cl-atom concentrations in these regions would have the most pronounced effect. It should be remembered that most of the existing evidence and the postulated formation mechanisms for significant tropospheric Cl-atom concentrations are for this region.

The still existing uncertainties are due to uncertainties in our knowledge of the atmospheric distributions of ethane and tetrachloroethene, of the sources of the trace gases and of the tropospheric OH-field. For ethane the largest error is due to the limited knowledge of its sources, for tetrachloroethene an improved data set of tropospheric measurements would reduce the overall uncertainties. Especially, the longitudinal distribution and the secular trend of tetrachloroethene is not yet sufficiently well-known. Finally, it should be noted that our calculations of the atmospheric removal by OH-radicals is based on an OH-field with a tropospheric average concentration of 6.5×10^5 molecules cm^{-3}, which is on the lower side of current estimates. If the average tropospheric OH-radical concentration indeed is substantially higher, the upper limits of the mean Cl-atom concentrations deduced from our budget calculations would have to be reduced even further.

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