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# Global Distribution of Tetrachloroethene in the Troposphere: Measurements and Modeling

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The tropospheric concentrations of the anthropogenic trace compound tetrachloroethene (perchloroethylene, per, PCE,  $C_2Cl_4$ ) were measured over 8 years between 1982 and 1989 in both hemispheres at remote sampling sites representing the baseline level of tetrachloroethene. Air sampling was performed by adsorption on Tenax, thermal desorption, and gas chromatographic separation with electron capture detection (HRGC-ECD). The mean atmospheric concentrations of tetrachloroethene in both northern subhemispheres and the Southern Hemisphere are regarded as representative for these tropospheric boxes:  $21 \pm 5$  pptv ( $154 \pm 40$  ng/m<sup>3</sup>) for the box 90–30° N,  $7 \pm 3$  pptv ( $51 \pm 26$  ng/m<sup>3</sup>) for the box 30–0° N, and  $2.2 \pm 0.5$  pptv ( $16 \pm 4$  ng/m<sup>3</sup>) for the Southern Hemisphere. The measured atmospheric distribution of tetrachloroethene can be described by a simple two-box model of the troposphere. The measurements served for the optimization of the exchange parameters in a three-box model as well. Global fluxes of tetrachloroethene within the troposphere and in exchange with the stratosphere and the oceans are estimated.

## Introduction

In environmental chemistry, one major goal is to trace down the ultimate fate of stable and semistable anthropogenic compounds on regional and global scales (1–8). As part of our program of global environmental chemistry (9), we analyzed tetrachloroethene among other volatile organochlorine compounds in air samples at various remote sampling sites, which are representative for distinct well-mixed air masses of both hemispheres. Sampling covers the years 1982–1989. We used our analytical data to model the global distribution of tetrachloroethene and to demonstrate the accuracy of this model.

Tetrachloroethene ( $CCl_2=CCl_2$ ) is an atmospheric trace compound with well-known anthropogenic sources. It is a basic (key) chemical and is mainly used as a solvent for industrial degreasing and for dry cleaning. The occurrence of tetrachloroethene in the air from urban and rural areas in Europe and Japan is well established (10–16), whereas only a few attempts have been made to determine concentrations of tetrachloroethene in remote areas of the Northern and Southern Hemispheres and to describe its global distribution (Table 1 and references cited therein).  $C_2Cl_4$  represents a sensitive indicator for pollution from urban and industrial sources. Natural formation is not known. The ratios of hydrocarbons and CO relative to  $C_2Cl_4$  indicate whether there is a long-range transport of pollution (constant ratios) or a local input from natural sources, e.g., biomass fires (elevated ratios) (30).

The most simple model of the atmosphere is given by dividing it in two boxes (24, 32–35). According to its

physicochemical properties, tetrachloroethene is stable enough to pass the Intertropical Convergence Zone (ITCZ) and to reach the Southern Hemisphere. Figures for industrial production of tetrachloroethene, interhemispheric exchange rates, and its reaction rate constants for the various pathways of atmospheric degradation are reported in the literature (see Tables 3 and 4). These data allow us to predict tropospheric tetrachloroethene concentrations in the two-box model.

Comparing the predicted values with our analytical measurements led to an improved three-box model. Measured tropospheric concentrations of tetrachloroethene were used to calculate exchange rates and fluxes between the three compartments of this model. It has also been used to calculate the global distribution of further volatile organic compounds (VOC) on the basis of our measurements (36). In addition, we added the stratosphere and the global oceanic system as separated boxes resulting in numbers of global tetrachloroethene fluxes in and between the environmental relevant compartments.

## Experimental Section

The analytical procedure for the determination of tetrachloroethene and other volatile halocarbons at their baseline concentrations in air has been described in detail (2, 11, 28, 37). Sampling of defined air volumes is usually done by adsorption on Tenax TA in glass tubes of 6 mm diameter, which are kept flame-sealed to exclude any losses and contamination (37). The tubes were opened only during the times of precleaning, sampling, and analysis. Analysis involves thermal desorption, condensation in a capillary cold trap, high-resolution gas chromatography, and electron capture detection. External calibration with standard solutions in *n*-pentane was used for quantification. The limit of detection for tetrachloroethene achieved by this procedure depends on blank values of preparation, handling of the sampling tubes during the analysis, and impurities in the gas chromatographic system. Sample volumes of 5 L up to 25 L of air result in detection limits of 10 ng/m<sup>3</sup> (1 pptv) to 2 ng/m<sup>3</sup> (0.2 pptv), respectively. No breakthrough has been observed with sampling volumes up to 50 L using 200 mg of Tenax TA. Reproducibility of the analytical method is in the range of  $\pm 20\%$  at concentration levels of 1–10 pptv. The sampling sites and times are summarized in Table 2.

## Results

**Production, Use, and Emissions of Tetrachloroethene.** *Annual Production of Tetrachloroethene.* The industrial production of tetrachloroethene is well known. The U.S. production figures are published annually in *Chemical and Engineering News*. Production figures in the Federal Republic of Germany were available from the Statistisches Bundesamt (Wiesbaden, Germany) until 1987 (Table 3). The average annual U.S. production between

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**Table 1. Baseline Concentrations of Tetrachloroethene in the Troposphere As Reported in Literature**

references	sampling site	year	concentration (vol mixing ratio, pptv)
Northern Hemisphere			
Singh et al. (17)	California	1975	38.3 ± 11.1
	California	1975	43.1 ± 17.8
Singh (18); Singh et al. (19)	California	1976	30.7 ± 10.5
Cronn et al. (20)	Eastern Pacific	1976	15.6
Rasmussen and Khalil (21)	Hawaii (IBL) <sup>a</sup>	1981	60 ± 7
	Hawaii (ABL) <sup>b</sup>	1981	39 ± 7
Rasmussen and Khalil (22)	different sampling sites	1978	56 ± 11
Penkett (23)	North Atlantic	1981	34.2
Singh et al. (24)	Eastern Pacific	1981	29
Fabian and Gömer (25)	between 11.2 and 11.5 km altitude	1982	5
Rudolph et al. (26)		1982-83	19 <sup>c</sup>
Class and Ballschmiter (27)	North Atlantic	1984-85	15-30
Class and Ballschmiter (28)	different sampling sites	1982-85	15 ± 3
Tille and Bächmann (29)		1983	32
Wofsy et al. (30)	subarctic central and eastern Canada	1990	12
Southern Hemisphere			
Rasmussen and Khalil (22)	different sampling sites	1978	14 ± 4
Rasmussen et al. (31)	Eastern Pacific (IBL) <sup>a</sup>	1981	9 ± 1
	Eastern Pacific (ABL) <sup>b</sup>	1981	10 ± 1
Singh et al. (24)	Eastern Pacific	1981	5
Rudolph et al. (26)		1982-83	2.8
Class and Ballschmiter (27)	South Atlantic	1985	5-10
Class and Ballschmiter (28)	South Atlantic	1985	2.3 ± 0.7
Tille and Bächmann (29)		1983	15

<sup>a</sup> In the boundary layer. <sup>b</sup> Above the boundary layer. <sup>c</sup> Estimated.

the years 1978 and 1988 was 277 kt with an average decrease of about 4% or 11 kt/yr. This decline was partly compensated by West Germany, where the average annual production from 1978 to 1986 was 130 kt with a slight increase of 5% or 6.5 kt/yr. World production has been estimated to be 553 kt in 1984 (38) and 600-700 kt in 1985 (39). Assuming that a ratio of 1:2 of U.S. production to global production is maintained over the years leads to an average global production of about 600 kt of tetrachloroethene/yr in the time previous to our analysis.

**Use of Tetrachloroethene.** Tetrachloroethene is mainly used for dry cleaning and metal degreasing and as a technical solvent. A certain amount of 5% (40) to 20% worldwide (16) is converted to freons (F 113) and trichloroacetic acid. The trend of incorporating closed systems in dry-cleaning and extraction processes, the regeneration of the solvent after use, and the incineration of waste containing chlorinated solvents will reduce production and emissions. We conservatively assume that at least 80% of the annual worldwide production or 480 kt/yr has reached the troposphere in the last decade.

**Global Emission Pattern.** Bauer (43) proposed for the emissions of anthropogenic halocarbons a latitudinal distribution, i.e., 30-60° N, 95% of total emissions; 30° N-30° S, 2% of total emissions; and 30-40° S, 3% of total emissions. Golombek and Prinn (45) estimated for 1,1,1-trichloroethane that 2.4% of the global emissions take place in the Southern Hemisphere. Prinn et al. (46) also describe the distribution of sales for 1,1,1-trichloroethane in percentage of global production in 1985, i.e., for 90-30° N, 30-0° N, 0-30° S, and 30-90° S with 94.4%, 2.9%, 1.1%, and 1.6%, respectively. 1,1,1-Trichloroethane has a similar use pattern as tetrachloroethene. In analogy to these estimations, we assume the emissions of tetrachloroethene into the southern troposphere to be in the mean 12 ± 2 kt/yr or 2-3% of the annual global emissions with about 470 kt remaining in the Northern Hemisphere.

**Tropospheric Concentrations and Burdens.** *Sampling Sites and Variations in Concentrations.* Sampling sites for our Global Baseline Studies Program have been selected carefully in order to fulfill the following conditions: (i) they represent large and well-mixed air masses, (ii) they are influenced by long-range transport only, and (iii) they exclude any significant local or regional anthropogenic input. This is achieved mainly by air sampling on marine islands. Table 2 summarizes the sampling sites with the concentrations of tetrachloroethene determined in air masses which are characteristic for the northern and southern troposphere. Each value represents the mean of 2-9 individual samples collected during periods of 1-10 days of sampling at distinct weather conditions (Table 2).

Variations in concentrations of tetrachloroethene in air samples taken at different dates were within a factor of 2 in Moorea, in Hawaii, and in Porto Santo; within a factor of 3 in Reunion; and within a factor of about 4 in Tenerife and Madeira. The latter places were used to check for the vertical gradient in the Trade Wind Region.

**Tropospheric Burden in the Northern Hemisphere.** (A) *Northern Cell (90-30° N).* The pattern of the global mass flow in the troposphere as described by the general atmospheric circulation (47) divides the northern troposphere in two parts at about 30° N. The northern cell (30-90° N) covers two regions: First, the westerlies, where the major part of industrial anthropogenic compounds are emitted in global terms, and second, the polar region, where tropospheric degradation is considered to be moderate due to the lack of sunlight. Intense mixing in vertical and horizontal directions between 30° and about 80° N takes place within weeks. Particularly in the 5 hPa level of the troposphere (at about 5,000 m), global mixing is fast in both hemispheres (9).

Air samples were collected in this air belt over a period of six years (1982-1987) on the European continent, in the North Sea, and on various islands in the North Atlantic.

**Table 2. Concentrations of Tetrachloroethene in Air of the Northern and Southern Troposphere (Means of 2-9 Individual Samples)**

sampling site (altitude; wind direction)	latitude, longitude	month/year	no. of samples	mean concn (pptv)
Northern Troposphere; 90-~30° N				
Alps <sup>a</sup> (1800 m, SSE)	47N, 10E	1/82	4	15 <sup>x</sup>
Porto Santo <sup>b</sup> (100 m, NE)	33N, 16W	3/82	3	26 <sup>x</sup>
Azores <sup>c</sup> (0 m; 1800 m, NNW)	38N, 28W	6/82	3; 3	13 <sup>x</sup> ; 22
North Sea <sup>d</sup> (0 m, NW)	57N, 7E	7/82	3	20
Porto Santo <sup>b</sup> (100 m, NE)	33N, 16W	3/84	8; 8	25; 17
Madeira <sup>e</sup> (1800 m, NW)	32N, 17W	3/84	5	20
Porto Santo <sup>b</sup> (100 m, NE)	33N, 16W	8/84	8; 5	28; 18
North Atlantic <sup>f</sup> (0 m, W)	42N, 15W	3/85	5; 5	25; 20
North Atlantic <sup>f</sup> (0 m, NE)	35N, 21W	3/85	5; 5	19; 18
Bretagne <sup>g</sup> (0 m, W)	48N, 3W	9/85	2	19
Tenerife <sup>h</sup> (0 m; 800 m, NE)	28N, 16W	10/85	9; 3	20; 24
California <sup>i</sup> (700 m, NW)	38N, 123W	12/87	2	26
average concentration				21 ± 5 (154 ± 40 ng/m <sup>3</sup> )
Northern Troposphere; 30-0° N				
Pico Ariero <sup>k</sup> (1800 m, ESE)	32N, 17W	3/82	2; 2	9 <sup>x</sup> ; 4
Pico Ariero <sup>k</sup> (1800 m, NE)	32N, 17W	6/82	5	11 <sup>x</sup>
Pico Ariero <sup>k</sup> (1800 m, SSW)	32N, 17W	8/84	8	7
Bermuda <sup>l</sup> (0 m, SE)	32N, 64W	7/85	2	2
Teide <sup>m</sup> (2400-3400 m, WSW)	28N, 16W	10/85	6; 2	7; 11
Maldives <sup>n</sup> (0 m, NE; E)	3N, 73E	3/86	6; 4	8; 2
California <sup>i</sup> (700 m, NW)	38N, 123W	10/87; 7/88	2; 2	10; 8
Hawaii <sup>o</sup> (3000 m, NE)	20N, 156W	7/88	3	3
average concentration				7 ± 3 (51 ± 26 ng/m <sup>3</sup> )
Southern Troposphere; 0-30° S				
South Atlantic <sup>p</sup> (0 m, SE)	30S, 10E	3/85	6; 6	13; 8
South Atlantic <sup>q</sup> (0 m, ITCZ)	2S, 18W	3/85	7	2.3
Reunion <sup>r</sup> (0-1500 m, SE)	21S, 55E	3/87	8	2.2
Moorea <sup>s</sup> (0 m, E-NE)	17S, 150W	3/89	8	2.0
average concentration				2.2 ± 0.5 (16 ± 4 ng/m <sup>3</sup> )

<sup>a</sup> German Alps, Hochgrat, seventh day of a continuous inversion above southern Germany. <sup>b</sup> Island near Madeira, North Atlantic. <sup>c</sup> Sao Miguel, North Atlantic. <sup>d</sup> West of Denmark aboard SS *Soerlandet* (Norwegian full-rigged bark). <sup>e</sup> North Atlantic, Pico Ariero, no distinct trade wind inversion but after a snow storm. <sup>f</sup> West of Africa and Europe aboard RV *Polarstern*. <sup>g</sup> France, at the coast. <sup>h</sup> Canary Island, North Atlantic, north and south coast. <sup>i</sup> North of San Francisco at Mt. Tamalpais, Pacific Coast. <sup>k</sup> Madeira, North Atlantic, above the trade wind inversion. <sup>l</sup> North Atlantic, coast and aboard research vessel, distinct high-pressure situation. <sup>m</sup> Tenerife (meteorological station Izana and summit), Canary Islands, North Atlantic. <sup>n</sup> North Indic, second value was measured after a tropical thunderstorm. <sup>o</sup> North Pacific, Mauna Loa, well above trade wind inversion. <sup>p</sup> West of South Africa aboard RV *Polarstern*, air samples influenced by emissions from the vessel or, more likely, by the industrial Cape region. <sup>q</sup> Aboard RV *Polarstern*, approaching and in the intertropical convergence or doldrums. <sup>r</sup> South Indic, sampling at the coast and in the mountains. <sup>s</sup> South Pacific, island near Tahiti. <sup>x</sup> Kirschmer and Ballschmiter (10).

We have also collected samples onboard the German research vessel *FS Polarstern* in 1985 on its cruise from Cape Town to Bremerhaven (see Table 2). These samples describe the tetrachloroethene content in the northern subdivision of the troposphere.

The concentrations of tetrachloroethene in these source-remote parts of the Northern Hemisphere ranged from about 13 to 28 pptv (100-210 ng m<sup>-3</sup>) with a mean value of 21 pptv (154 ng m<sup>-3</sup>). This is equivalent to a tropospheric burden of 116 kt in the northern subdivision (30-90° N) of the northern troposphere. Investigations from Makide et al. in Hokkaido (40-45° N) over a time period of 7 years showed no increase but only seasonal variations in the tropospheric concentrations. The measured values were low in summer, were higher in winter, and always were in the range between 20 and 25 ± 3 pptv, respectively (13).

(B) *Subtropical/Tropical Cell (30-0° N)*. The subtropical and tropical belt (0-30° N) of the northern troposphere is equivalent to the so-called Hadley Cell System of the general atmospheric circulation. It represents the subtropical high-pressure areas over the oceans and the Trade Wind System with its prevailing easterly winds in the lower troposphere and westerly winds in the

upper part. It also represents the northern part of the Intertropical Convergence Zone (ITCZ) with its uprising air masses (48). We characterized this subdivision of the troposphere by air samples collected near Bermuda, in California, and on various islands at an altitude between 0 and 3400 m above sea level (see Table 2). The tetrachloroethene concentrations in these air samples range from 2 to 11 pptv (15-82 ng m<sup>-3</sup>).

Lowest values were observed in Bermuda at the center of a large and stable high-pressure area over the North Atlantic, which indicated descending air from the upper troposphere. In the Maldives and in Hawaii, low concentrations were measured demonstrating the occurrence of air parcels nearly depleted of tetrachloroethene. The same low levels were observed in air masses above the Trade Wind Inversion in the middle of the North Pacific and in the Indian monsoon region with its extreme sweep of the ITCZ to the north in the months of April to August.

Without any clustering of the values at different sampling sites, a mean tetrachloroethene concentration of 7 ± 3 pptv (51 ± 26 ng m<sup>-3</sup>) equivalent to a burden of 42 (± 20) kt is calculated for the 30-0° belt of the northern troposphere.

**Table 3. Annual Production of Tetrachloroethene in the United States and FRG and Estimated World Production (in kt)**

year	U.S.	FRG	world
1974	331 <sup>a</sup>	158 <sup>a,d</sup>	630 <sup>e</sup>
1975	308 <sup>a</sup>	108 <sup>a</sup>	586 <sup>e</sup>
1976	304 <sup>b</sup>	117 <sup>a,d</sup>	577 <sup>e</sup>
1977	279 <sup>b</sup>	128 <sup>a</sup>	570 <sup>e</sup>
1978	329 <sup>b</sup>	147 <sup>d</sup>	653 <sup>e</sup>
1979	351 <sup>b</sup>	127 <sup>d</sup>	693 <sup>e</sup>
1980	347 <sup>b</sup>	116 <sup>d</sup>	692 <sup>e</sup>
1981	313 <sup>b</sup>	108 <sup>d</sup>	628 <sup>e</sup>
1982	265 <sup>c</sup>	108 <sup>d</sup>	
1983	248 <sup>c</sup>	98 <sup>d</sup>	
1984	260 <sup>c</sup>	146 <sup>d</sup>	553 <sup>f</sup>
1985	308 <sup>c</sup>	167 <sup>d</sup>	600–700 <sup>g</sup>
1986	188 <sup>c</sup>	157 <sup>d</sup>	
1987	215 <sup>c</sup>	155 <sup>d</sup>	430, <sup>e</sup> 610 <sup>h</sup>
1988	226 <sup>c</sup>		450 <sup>e</sup>
1989	218 <sup>c</sup>		
1990	169 <sup>c</sup>	115 <sup>d</sup>	

<sup>a</sup> Schulze and Weiser (40). <sup>b</sup> C&EN, June 8, 1987 (41). <sup>c</sup> C&EN, June 28, 1993 (42). <sup>d</sup> Statistisches Bundesamt, Wiesbaden, FRG, 1992; in ref 16. <sup>e</sup> Under the assumption that world production is about twice the U.S. production (24, 43). <sup>f</sup> ECETOC 1989, estimated (38). <sup>g</sup> Ullmann's Encyclopedia of Industrial Chemistry, estimated (39). <sup>h</sup> Worldwide demand (44).

Altogether the tropospheric burden of tetrachloroethene in the Northern Hemisphere is estimated to be about  $116 + 42 = 158$  kt. A critical evaluation of this number reveals a range of uncertainty of about 20% based on the geographical distribution of the sampling sites and the significance of the concentrations determined in air as listed in Table 2 and discussed above.

**Tropospheric Burden in the Southern Hemisphere.** In the Southern Hemisphere, measurements of tetrachloroethene in air were performed by taking samples aboard the German research vessel *FS Polarstern* in the South Atlantic on a cruise from Cape Town to the equator (27). Some of these air samples were obviously influenced by industrial emissions of tetrachloroethene in South Africa. High concentrations close to Cape Town decreased with greater distance from the continent. Air samples from the ITCZ or doldrums were not influenced by direct continental input and resulted in an average concentration of tetrachloroethene of  $2.3 \pm 0.7$  pptv ( $17 \pm 5$  ng m<sup>-3</sup>) (mean of seven samples). This value is considered to be typical for the Trade Wind Region of the tropical South Atlantic.

Reunion, a French island in the Indian Ocean east of Madagascar in the southeast Trade Wind Region, allows air sampling at the coast as well as above the Trade Wind Inversion (about 1500 m above sea level). Its situation in the pattern of the general atmospheric circulation is similar to Madeira, Tenerife, and Hawaii in the Northern Hemisphere. Air samples were collected at different sampling sites on the island and at various times throughout the entire day. This resulted in an average tetrachloroethene concentration of  $2.2 \pm 0.6$  pptv ( $16 \pm 4$  ng m<sup>-3</sup>) (mean of eight samples).

Moorea is the neighboring island of Tahiti in the South Pacific. Air samples collected at the coast result in an average concentration of  $2.0 \pm 0.5$  pptv ( $15 \pm 4$  ng m<sup>-3</sup>) (mean of eight samples) of tetrachloroethene.

The tetrachloroethene concentrations in air obtained from these three very distant sampling series in the Southern Hemisphere are surprisingly reproducible con-

sidering the geographical distances and the period of four years (1985–1989) between the first and last sampling event. Taking them as representative for the entire Southern Hemisphere (0–90° S), we can assume an average concentration of tetrachloroethene in the southern troposphere of  $2.2 \pm 0.5$  pptv ( $16 \pm 4$  ng m<sup>-3</sup>) and thus calculate a southern tropospheric burden of  $26 \pm 6.5$  kt. This number represents the lower limit for the southern burden because all three sampling series took place at the end of the southern summer in very remote areas of the southern tropics. Most intense atmospheric degradation by hydroxyl radicals has to be expected in this region and during this time of the year.

Slightly higher tetrachloroethene concentrations in regions further south cannot be excluded. They could arise from a less effective degradation during the year. It is reasonable to give about 40 kt as an uppermost limit for the estimated southern burden, which would arise from an annually averaged tetrachloroethene concentration of 3.2 pptv in the entire Southern Hemisphere.

**Modeling of Atmospheric Distribution.** *Global Concentrations of Tetrachloroethene Using a Two-Box Model.* The intertropical convergence zone (ITCZ), a band of low pressure with rising air masses fed by the Trade Winds, reaches up to the stratosphere. It divides the troposphere into two equal parts. Each part contains a normalized volume of  $1.58 \times 10^{18}$  m<sup>3</sup> and has a mean tropospheric height of 11 km. Such a two-box model has been described by several authors (24, 32–35).

The concentration of a given trace compound in the atmosphere depends on its lifetime, which is defined as the reciprocal of the rate of disappearance (9). In the first approximation thermolysis, photolysis, hydrolysis, and its reaction with NO<sub>2</sub> molecules play a negligible role in the tropospheric fate of tetrachloroethene. Its reaction with OH radicals is fast compared to that with NO<sub>3</sub> radicals and ozone molecules, the latter one being in contrast to nonchlorinated alkenes. With the mean global concentrations of OH, O<sub>3</sub>, and NO<sub>3</sub> and the according reaction rate constants given in Table 4, it is possible to estimate the tropospheric tetrachloroethene lifetimes to be  $\tau_{OH} = 155$  days,  $\tau_{NO_3} = 7400$  days, and  $\tau_{O_3} = 9200$  days, respectively.

According to its high vapor pressure, tetrachloroethene does not adsorb on atmospheric particles in an appreciable amount. Therefore, the main part in the translocation process occurs by wind transport and, to a much lesser extent, by wet and dry deposition.

In the case of two-box modeling, the disappearance of tetrachloroethene thus is controlled by chemical degradation in the troposphere (sinks,  $\tau_{OH}^{-1}$ ) and the exchange between the tropospheric boxes (transport,  $\tau_T^{-1}$ ). Appearance is defined by the input level (sources). Kinetic equations containing the relevant terms are

$$\frac{dN}{dt} = I_N - k_{OH}[OH]_N - k_e(N - S) \quad (1)$$

$$\frac{dS}{dt} = I_S - k_{OH}[OH]_S - k_e(S - N) \quad (2)$$

where  $N$  and  $S$  are the tropospheric burdens of tetrachloroethene in the Northern and the Southern Hemisphere, respectively. The data used for the calculation, i.e., input in the atmosphere ( $I_N$  and  $I_S$ ), reaction rate

Table 4. Data Used for Two-Box Model Calculation

data	value	unit	ref
rate constant for the reaction of C <sub>2</sub> Cl <sub>4</sub> with OH radicals	9.44 exp(-1199/T) × 10 <sup>-12</sup>	cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	49
	9.64 (+2.85/-2.20) exp[(-1209 ± 88)/T] × 10 <sup>-12</sup>	cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	50
with O <sub>3</sub> molecules	2 × 10 <sup>-21</sup>	cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	51
with NO <sub>3</sub> radicals	<5.2 × 10 <sup>-17</sup>	cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	52
with Cl radicals	53 × 10 <sup>-13</sup> (298 K)	cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	53
mean global concn of OH radicals in the troposphere	7.7 × 10 <sup>5</sup>	radicals cm <sup>-3</sup>	46
for O <sub>3</sub> molecules	6.3 × 10 <sup>11</sup>	molecules cm <sup>-3</sup>	9
for NO <sub>3</sub> radicals	3 × 10 <sup>7</sup>	radicals cm <sup>-3</sup>	a
annual input of C <sub>2</sub> Cl <sub>4</sub> in the Northern Hemisphere, I <sub>N</sub>	470 ± 50	kt yr <sup>-1</sup>	b
annual input of C <sub>2</sub> Cl <sub>4</sub> in the Southern Hemisphere, I <sub>S</sub>	12 ± 2	kt yr <sup>-1</sup>	b
globally averaged tropospheric temp (relevant reaction temp)	262	K	54
interhemispheric exchange rate, k <sub>e</sub>	0.9 (+0.2/-0.1)	yr <sup>-1</sup>	24, 34, 55, 56

<sup>a</sup> Estimated upper limit of 10 pptv NO<sub>3</sub> for the remote troposphere. <sup>b</sup> See section on Global Emission Pattern.

Table 5. Averaged Tropospheric OH Radical Concentrations in 10<sup>5</sup> Radicals cm<sup>-3</sup> (Taken from Prinn et al.) (46)

	<i>S</i>		<i>N</i>	
0-12 km	90-30° S	30-0° S	0-30° N	30-90° N
4 boxes	5.7 ± 1.1	10.1 ± 1.9	10.2 ± 1.9	4.9 ± 0.9
both hemispheres	7.9 ± 1.9		7.6 ± 1.9	
global av	7.7 ± 1.4			

constant (k<sub>OH</sub>), and the interhemispheric exchange constant (k<sub>e</sub>), are given in Table 4.

Our modeling calculations for tetrachloroethene are based on the tropospheric OH concentrations given by Prinn et al. (46) (Table 5). Using a different approach of modeling OH radical concentrations based on the well-known pathways and reactions of atmospheric formation and disappearance, Lu and Khalil calculated the global averaged OH radical concentrations to be 8.2 × 10<sup>5</sup> radicals cm<sup>-3</sup> with little differences for the Northern (8.5 × 10<sup>5</sup>) and the Southern (7.8 × 10<sup>5</sup>) Hemisphere (57).

In the case of tetrachloroethene, no accumulation in the atmosphere could be observed between the years 1979 and 1986 (13). Thus, we assume a quasiequilibrium between emissions and loss by degradation, so far neglecting other pathways of disappearance and sinks such as transport into the stratosphere or into the oceans:

$$\frac{dN}{dt} = \frac{dS}{dt} = 0 \quad (3)$$

Solving eqs 1 and 2 results in concentrations of tetrachloroethene in the two hemispheres as a prediction: c<sub>N(pred)</sub> = 13 (+8/-5) pptv and c<sub>S(pred)</sub> = 3.7 (+3.8/-1.7) pptv. The averaged analytical values from our global baseline studies (Table 2) are c<sub>N(meas)</sub> = 14 (±5) pptv and c<sub>S(meas)</sub> = 2.2 (±0.5) pptv. The range of accuracy in the calculated values is derived from uncertainties of the individual data with the tropospheric input data having the greatest uncertainty.

Measured and predicted tetrachloroethene concentrations for the northern troposphere are nearly identical. For the southern troposphere, the calculated concentrations are higher than those of our measurements, though the range of precision is overlapping. Various possibilities could cause this discrepancy between c<sub>S(pred)</sub> and c<sub>S(meas)</sub>.

The Southern Hemisphere measurements took place in areas (0-30° S) and at times (March) when high levels of OH radical concentrations have to be expected (58). The

temporary concentration [OH]<sub>S</sub> was greater than the one given in Table 5.

In the southern subdivision of the Northern Hemisphere, we determined a tetrachloroethene concentration of 7 pptv or half the northern average (Table 2). Thus, we have to consider this compartment as a separate buffer zone decreasing the flux from the Northern Hemisphere to the southern one. The two-box model does not account for this. These reasons led us to a three-box model that includes the atmospheric transport processes in a more realistic way.

*Tropospheric Three-Box Model Derived from Tetrachloroethene Measurements.* The general circulation of the atmosphere makes it reasonable to divide the troposphere into four compartments (29, 46). The division of the Northern Hemisphere at 30° N agrees with the meteorological conditions. In the south, the situation seems to be more complex. Especially during the summer months in the Southern Hemisphere, the ITCZ expands south over the equator (58). As a result, the tropical zone of low pressure is situated at about 15° S in the boundary layer and goes further south with increasing altitude (35) (Figure 1). The sweeping of the ITCZ far to the north over the Indian Ocean is also not accounted for in a two-box model.

A three-box model describes the fluxes in the atmosphere with three subcompartments more accurately by approaching the mean meridional mass fluxes as depicted in Figure 1. The box N2 acts as a first dilution space for compounds coming out of the main source region N1. No exchange between troposphere and stratosphere was considered in this three-box model.

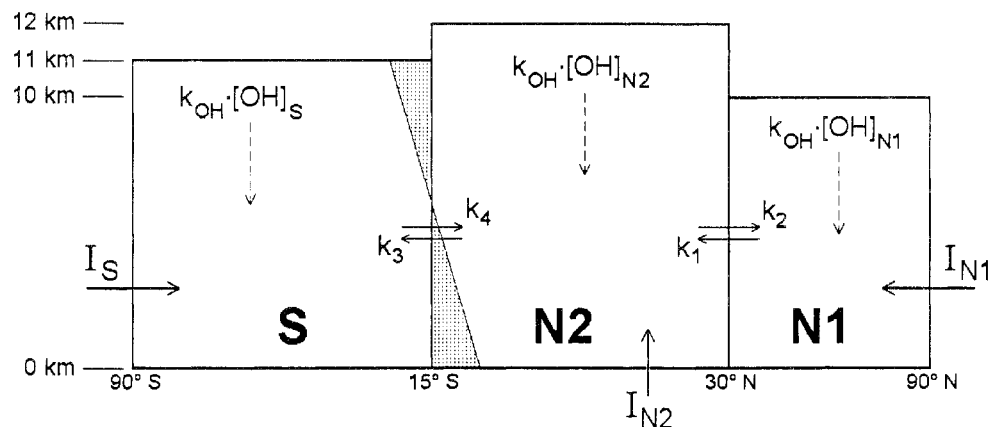
According to the different volumes, the exchange times between the boxes are different and depend on the direction of the exchange. From a large box, it will take longer for a compound to leave than from a smaller box.

Since accurate data of exchange rates for the three-box model are not available from literature, it is not possible to predict tetrachloroethene levels as was done in the two-box model. Therefore, we took our averaged analytical measurements of tetrachloroethene concentrations to calculate the exchange rates k<sub>1</sub>, k<sub>2</sub>, k<sub>3</sub> and k<sub>4</sub>, respectively.

The three-box model is described by

$$\frac{dN_1}{dt} = I_{N1} - k_{OH}[OH]_{N1}N_1 - k_1N_1 + k_2N_2 \quad (4)$$

$$\frac{dN_2}{dt} = I_{N2} - k_{OH}[OH]_{N2}N_2 + k_1N_1 - k_2N_2 - k_3N_2 + k_4S \quad (5)$$



**Figure 1.** Model of the atmosphere with three tropospheric boxes (the sloping line indicates the ITCZ; shaded areas have both the same volume). Box volumes (normalized to 1013 hPa and 273.15 K) are as follows:  $V_{N1} = 0.75 \times 10^{18} \text{ m}^3$ ,  $V_{N2} = 1.25 \times 10^{18} \text{ m}^3$ , and  $V_S = 1.19 \times 10^{18} \text{ m}^3$ .

**Table 6. Three-Box Model Calculation: Input Data and Results**

box	input data			direction of air exchange	varied parameters (best fitting values)		output data
	input (emissions) of $\text{C}_2\text{Cl}_4$ in the atmosphere <sup>a</sup> (kt/yr)	OH radical concn <sup>b</sup> ( $10^5$ radicals $\text{cm}^{-3}$ )	measured $\text{C}_2\text{Cl}_4$ levels (Table 2) (pptv)		exchange rates <sup>c</sup> ( $\text{yr}^{-1}$ )	corresponding exchange time <sup>c</sup> (months)	
N1 ↑↓	450	4.9	21	N1 → N2 N2 → N1	$k_1 = 3.3$ (2.2–8) $k_2 = 2.0$ (1.3–4.8)	3.6 (1.5–5.4) 6.0 (2.5–9)	22
N2 ↑↓	17	10.2	7	N2 → S S → N2	$k_3 = 0.69$ (0.4–1) $k_4 = 0.72$ (0.4–1)	17 (12–30) 16 (12–30)	7.8
S	12	7.2	2.2				2.3

<sup>a</sup> Estimated according to the assumptions made under Global Emission Pattern. <sup>b</sup> Calculated from Table 5 according to different box volumes. <sup>c</sup> The maximum range of uncertainty (in parentheses) is obtained by repeating the three-box model calculation with the extreme values of the measured analytical concentrations. Those are the data with the largest spreading.

$$\frac{dS}{dt} = I_S - k_{\text{OH}}[\text{OH}]_S S + k_3 N_2 - k_4 S \quad (6)$$

A computer program calculated tropospheric concentrations while varying the rates  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  to give the best fit. The volumes of the individual boxes are due to fixed ratios of the exchange rates; i.e.

$$k_1 = 1.67k_2 \quad (7)$$

$$k_3 = 0.95k_4 \quad (8)$$

Exchange rates that fit best with our experimental data for tetrachloroethene levels correspond to exchange times of 3.6–6 months for the northern intrahemispheric exchange ( $k_1$ ,  $k_2$ ) and 16–17 months for the interhemispheric exchange over the ITCZ ( $k_3$ ,  $k_4$ ) (Table 6). These values are comparable with meteorological data. The  $\text{C}_2\text{Cl}_4$  concentrations calculated with the best fitting  $k$  values do not exactly correlate with our measured concentrations. They are slightly higher. Nevertheless predicted and measured results are in the range of measurement accuracy (see output data in Table 6).

**Global Tetrachloroethene Fluxes.** (A) *Flux into the Stratosphere.* Tetrachloroethene entering the stratosphere will be totally degraded by short wavelength UV radiation, resulting in a negligible stratospheric burden. For most of the organic compounds, the stratosphere is a complete sink, and no flux downwards into the troposphere takes place. The transfer of tetrachloroethene from the

troposphere into the stratosphere is expressed as additional terms in the three-box model [eq 4 ( $-k_5 N_1$ ), eq 5 ( $-k_6 N_2$ ), and eq 6 ( $-k_7 S$ )].

Implementation of this stratospheric sink optimizes the three-box model, and the newly calculated tetrachloroethene concentrations can be brought into agreement with our measured values. Leaving the exchange rates  $k_1$ – $k_4$  constant and setting our measured data as fix points, we obtained exchange times for the flux from troposphere to stratosphere: 10 yr out of  $N_1$ , 2.5 yr out of  $N_2$ , and no flux out of the southern box.

Those values are in agreement with meteorological findings. The most intense mixing of air masses across the tropopause takes place in the subtropic/tropic compartment  $N_2$  that has the highest altitude. Particularly during the tropic thunderstorms, a regular crossing of the tropopause is observed. Junge reports of a mean global exchange time of 4 yr from the troposphere to the stratosphere (59).

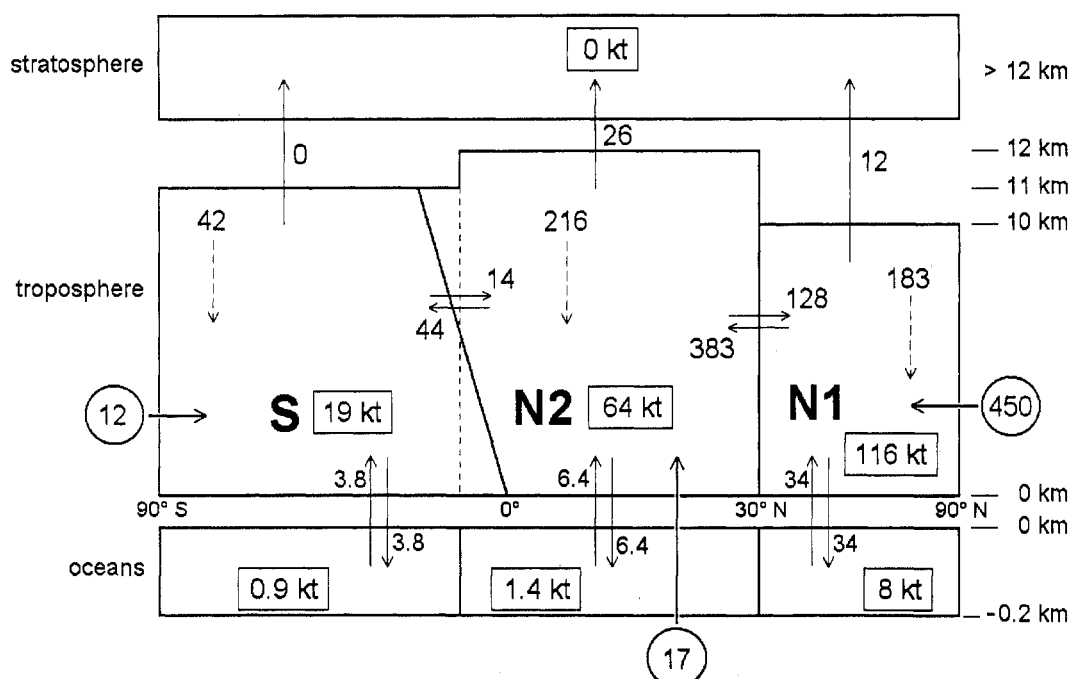
(B) *Tetrachloroethene Washout.* Washout of tetrachloroethene out of the troposphere has been neglected in our model calculation so far. An estimation of the amount of  $\text{C}_2\text{Cl}_4$  that is removed by this transport process occurs by calculating the washout fluxes according to Ballschmiter (9). Data used for this calculation are given in Table 7.

Resulting washout fluxes are smaller than  $0.05 \text{ kt yr}^{-1}$  for each tropospheric box. Thus,  $\text{C}_2\text{Cl}_4$  amounts removed by washout processes are negligible in comparison to the other tropospheric fluxes of tetrachloroethene (see Figure 2).

**Table 7. Data Used for Calculation of Washout and of Exchange over Air-Sea Interface of Tetrachloroethene in Three-Box Model**

surface area of oceans <sup>a</sup>	A (N1)	$77 \times 10^{12} \text{ m}^2$
	A (N2)	$130 \times 10^{12} \text{ m}^2$
	A (S)	$155 \times 10^{12} \text{ m}^2$
annual precipitation <sup>b</sup>	global	$511\,000 \text{ km}^3 \text{ yr}^{-1}$
	in N1	$90\,000 \text{ km}^3 \text{ yr}^{-1}$
	in N2	$253\,000 \text{ km}^3 \text{ yr}^{-1}$
	in S	$168\,000 \text{ km}^3 \text{ yr}^{-1}$
surface ocean water temp <sup>c</sup>	T (N1)	$8.5^\circ \text{C}$
	T (N2)	$25.7^\circ \text{C}$
	T (S)	$13.7^\circ \text{C}$
Henry's constant <sup>d</sup>	H	$101\,325 \times 10^{(12.45-4918/T)} \text{ Pa m}^3 \text{ mol}^{-1}$
exchange constant for liquid phase <sup>e</sup>	$k_1$	$10.3 \text{ cm h}^{-1}$
exchange constant for gas phase <sup>e</sup>	$k_g$	$988 \text{ cm h}^{-1}$
mass transfer coefficient expressed on liquid-phase basis <sup>e</sup>	$K_1$ at $8.5^\circ \text{C}$ (N1)	$872 \text{ m yr}^{-1}$
	$K_1$ at $25.7^\circ \text{C}$ (N2)	$890 \text{ m yr}^{-1}$
	$K_1$ at $13.7^\circ \text{C}$ (S)	$879 \text{ m yr}^{-1}$
	$K_g$ at $8.5^\circ \text{C}$ (N1)	$3005 \text{ m yr}^{-1}$
	$K_g$ at $25.7^\circ \text{C}$ (N2)	$1203 \text{ m yr}^{-1}$
	$K_g$ at $13.7^\circ \text{C}$ (S)	$2255 \text{ m yr}^{-1}$
mass transfer coefficient expressed on gas-phase basis <sup>e</sup>		$10, 12, 11 \text{ km}$
$d_T$ , mixing height of troposphere in N1, N2, and S		$200 \text{ m}$
$d_0$ , mixing depth of ocean		

<sup>a</sup> Calculated from numbers given in ref 9. <sup>b</sup> Calculated according to Sellers (60) and Blüthgen and Weischet (47). <sup>c</sup> From Blüthgen and Weischet (47). <sup>d</sup> Gossett (61). <sup>e</sup> Calculated according to Liss and Slater (62).



**Figure 2.** Estimations of global mass fluxes of tetrachloroethene (dashed arrows indicate loss by degradation; all numbers in  $\text{kt yr}^{-1}$  except burdens marked with kt).

**Table 8. Baseline Levels of Tetrachloroethene in Ocean Water**

authors (ref)	year	sampling site	ocean water concn of tetrachloroethene ( $\mu\text{g m}^{-3}$ )
Fogelquist (65)	1980	Arctic	0.68
Singh et al. (24)	1981	Eastern Pacific Ocean	$0.7 \pm 0.6$
Abrahamsson and Klick (66)		Skagerrak	0.26
		$52^\circ \text{S } 6^\circ \text{W}$	0.52

(C) *Exchange between Troposphere and Oceans.* Several investigations have been made to estimate the flux of organics across the air-water interface (63, 64). According to the method of Liss and Slater (62) and the applications of Neely (32) and Neely and Plonka (34), we calculated exchange constants for the liquid phase and the gas phase ( $k_1$  and  $k_g$ ), temperature-dependent mass transfer coef-

ficients ( $K_1$  and  $K_g$ ), and according exchange rates for each tropospheric box N1, N2, and S. These numbers, given in Table 7, are specific for the ability of tetrachloroethene to cross over the ocean surface.

If we assume that there is an equilibrium between the fluxes out of and into the oceans, it is possible to calculate the tetrachloroethene burdens of the oceanic boxes in the



200-m surface layer and thus to get mean water concentrations. Only few data of tetrachloroethene concentrations in the oceans are available from literature. They are summarized in Table 8. Our calculations result in concentrations of 0.5, 0.06, and 0.03  $\mu\text{g m}^{-3}$  for the ocean water in N1, N2, and S, respectively. These are rough estimations because the mixing of the oceanic subcompartments is neglected. Nevertheless, the calculated values are comparable with existing measurements of other authors and show that the assumptions of the three-box model are reasonable.

(D) *Estimation of Global Tetrachloroethene Fluxes.* All calculations and estimations mentioned above describe the mass fluxes of tetrachloroethene between several global compartments. Figure 2 shows that the numbers of input, exchange, and degradation are high in comparison to the tropospheric burden of tetrachloroethene. Because of a decrease in the emissions of this compound into the atmosphere due to chemical regulations during the last years, there will be a decrease in the tropospheric burden as well.

### Conclusions

Tetrachloroethene with its high industrial emission figures and its global atmospheric lifetime of about 150 d occurs in varying concentrations in the northern troposphere and with low but constant levels in the marine boundary layer of the tropic southern troposphere. Based on measurements over a period of 8 yr in remote areas of both hemispheres, the tropospheric burden of tetrachloroethene is calculated.

We assume that the tetrachloroethene content in air is in a pseudostationary equilibrium between emissions and atmospheric degradation. Then a simple two-box model with constant figures for global burdens and emissions leads to a prediction of global levels that compare well to the measured one.

A physically more realistic three-box model of the atmosphere is used to calculate exchange parameters between the modified compartments. With the stratosphere and the oceans as additional compartments, global mass fluxes of tetrachloroethene can be estimated. Neither the exchange with extratropospheric compartments nor the removal by washout are dominating factors for the tropospheric tetrachloroethene level. The stratosphere acts as a sink; the ocean acts as a depot for tetrachloroethene. The three-box model can be used to estimate the global fluxes of other persistent or semistable trace compounds in air (36).

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