

Global chlorine emissions from biomass burning: Reactive Chlorine Emissions Inventory

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Abstract. Emissions of reactive chlorine-containing compounds from nine discrete classes of biomass burning were estimated on a 1° latitude by 1° longitude grid based on a biomass burning inventory for carbon emissions. Variations on approaches incorporating both emission ratios relative to CO and CO₂ and the chlorine content of biomass burning fuels were used to estimate fluxes and associated uncertainties. Estimated, global emissions are 640 Gg Cl yr⁻¹ for CH₃Cl; 49 Gg Cl yr⁻¹ for CH₂Cl₂; 1.8 Gg Cl yr⁻¹ for CHCl₃; 13 Gg Cl yr⁻¹ for CH₃CCl₃; and 6350 Gg Cl yr⁻¹ for the sum of volatile-inorganic and particulate chlorine. Biomass burning appears to be the single largest source of atmospheric CH₃Cl and a significant source of CH₂Cl₂; contributions of CHCl₃ and CH₃CCl₃ are less than 2% of known sources.

1. Introduction

Biomass burning is a major source for many atmospheric trace constituents [Crutzen *et al.*, 1979; Crutzen and Andreae, 1990; Levine, 1996]. Today's burning of vegetation appears to be about 90% human-induced (J. S. Levine, NASA Langley, personal communication, 1998); only a minor fraction is considered to be entirely natural, caused by events such as lightning and volcanic lava efflux. Although early publications on biomass burning have identified methyl chloride (CH₃Cl) as one of its smoke constituents [Crutzen *et al.*, 1979], only recently was the global magnitude of this and other chlorine compounds to the atmosphere constrained [Lobert *et al.*, 1991; Manö and Andreae, 1994; Andreae *et al.*, 1996; Rudolph *et al.*, 1995; Blake *et al.*, 1996].

This publication is part of a series on emissions of chlorine-containing compounds to the atmosphere from major, known sources; the Reactive Chlorine Emissions Inventory (RCEI) is an activity of the Global Emissions Inventory Activity (GEIA) conducted under the auspices of the International Global Atmospheric Chemistry (IGAC) project. Other papers in this series have been published for industrial emissions [McCulloch *et al.*, this issue (a,b); Aucott *et al.*, this issue], oceanic and terrestrial biogenic sources [Khalil *et al.*, this issue], sea-salt dechlorination [Erickson *et al.*, this issue] as well as a composite overview paper [Keene *et al.*, this issue] and an introduction to the series [Graedel and Keene, this issue].

Here we present the first global inventory of reactive chlorine emissions from biomass burning at the standard GEIA 1°

latitude by 1° longitude grid resolution, which is unique both in its geographical breakdown and global approach. The inventory is based on work by J. A. Logan and R. Yevich (unpublished manuscript, 1998) and R. Yevich and J. A. Logan (unpublished manuscript, 1998), who compiled global emissions of carbon from biomass burning. We implemented measured and estimated emission factors of chlorine compounds into this database to derive the emission grids.

2. Database: Basics and Implementation

2.1. Compounds

Only few chlorine-containing compounds have been measured in biomass burning plumes, the most important one and best studied is methyl chloride (CH₃Cl). CH₃Cl is the largest, natural contributor to organic chlorine in the atmosphere and is currently present at about 540 ppt (10⁻¹² mols per mol). Other organic gases considered in this publication are dichloromethane (methylene chloride, CH₂Cl₂), trichloromethane (chloroform, CHCl₃), and 1,1,1-trichloro-ethane (methyl chloroform, CH₃CCl₃).

A few studies have estimated emissions of inorganic chlorine (or enrichments in associated aerosol) from biomass burning [Echalar *et al.*, 1995; Gaudichet *et al.*, 1995]. Although poorly constrained, these investigations suggest substantial fluxes. HCl and particulate Cl are probably the dominant forms of inorganic Cl emitted from biomass burning. However, temperature, aerosol surface area and liquid water content, and concentrations of other soluble acids influence the phase partitioning of HCl and particulate Cl in air [Keene and Savoie, 1998; Keene *et al.*, 1998]. We anticipate significant temporal variability in Cl phase partitioning within aging plumes because burning plumes cool rapidly, constitu-

ent water vapor condenses, and other chemical transformations proceed. As such, primary emissions of HCl and particulate Cl cannot be reliably differentiated from secondary products based on the assumption that measured concentrations within plumes are conservative. Therefore, the analysis reported herein will assess only the emissions of total (particulate plus vapor) inorganic Cl. In addition, the particulate fraction probably contains minor amounts of organically bound chlorine. We will refer to the combined fraction of volatile-inorganic and particulate chlorine as $Cl_{p,i}$. Emissions of other Cl-containing compounds appear to be insignificant [Hegg et al., 1990; Rudolph et al., 1995].

2.2. Underlying Database

GEIA specifies emissions inventories with 1° latitude by 1° longitude grid resolution, a fixed base year of reference, and global coverage. The only published database that describes global biomass burning in a gridded implementation is from Hao and Liu [1994]. However, this database is based on information from the Food and Agriculture Organization (FAO) from the late 1970s, is limited in geographical extent to the tropical and subtropical areas of the world, and has a resolution of $5^\circ \times 5^\circ$. Recent efforts by Sproles [1996] demonstrate how high-resolution biomass burning inventories can be implemented in publicly available models, but emission data are currently still based on data of Hao and Liu [1994].

J. A. Logan and R. Yevich (unpublished manuscripts, 1998) have established a biomass burning inventory that satisfies the geographical spread and high, spatial resolution and, although not based on a single year, incorporates a multitude of input data from 1980 to early 1990s; thus it is the most current inventory available. As biomass burning is thought to increase at a rate of a few percent per year, this database is more representative for today's biomass burning emissions. The database is separated into nine different feedstock categories and covers all continents and vegetation zones (Table 1).

The amount of savanna burning (SVH) is based on the methodology of Menaut et al. [1991] which assumes that the biomass loading and the burning frequency are related to the annual precipitation. The vegetation map of Matthews [1983]

was used to locate the savanna, and the gridded rainfall data of Legates and Willmot [1990] were used.

The amount of burned biomass as a result of tropical deforestation (DEF) is based on a similar approach as in Hao and Liu [1994], but on more recent data. Estimates of the mean, burned area for each country for 1980-1990 were taken from publications of the Food and Agriculture Organization [FAO, 1993] except for Brazil, and the aboveground biomass loadings are based on the same source except for Brazil and Asia; loadings for Asia are based on Brown et al. [1993]. The burned area is spatially desegregated within a country using the land-use map of Matthews [1983]. For Brazil, the deforestation rate is from Fearnside [1993], and loadings are from Brown and Lugo [1992]; the burned area is spatially desegregated using the results of Skole and Tucker [1993].

The burned area in the tropics as a result of slash and burn/shifting cultivation (SBS) is based on estimates of the rural population that practice this form of agriculture. A clearing rate of 0.15 ha per person per year is used as in the work of Logan et al. [1981]; the regions for shifting cultivation are taken from Grigg [1974].

The areas of forest wildfires in temperate and high latitudes (FOR) are taken from surveys of national statistics [e.g., FAO, 1992, 1993, 1994, 1995], and are several-year averages, representative of the decade of the 1980s. The amount of burned biomass is based on data obtained from forestry experts on fuel consumption in mid- and high-latitude fires.

Biofuels, such as fuel wood, charcoal, and agricultural residues including dung (CMB), and open field burning of unusable crop residues (BIF) provide a considerable portion of the biomass combustion in the developing world [Crutzen and Andreae, 1990]. Earlier estimates of the amount of burned crop residues were based on simple assumptions, for example, the assumption of a uniform fraction of the residue being burned. The estimates used by R. Yevich and J. A. Logan (unpublished manuscript) are based on regional differences in burning practices of biofuels and field residues derived from a combination of energy assessments from the World Bank; government statistics; discussions with experts in agronomy, forestry, agro-industries; and technical reports.

Table 1. Biomass Burning Feedstock Categories

Database Acronym	Category	Global Extent	Global Emissions		NH Emissions, %		
			Tg C yr ⁻¹	%	5°S	Equator	5°N
SVH	savanna fires	tropical	1410	37.9	56.1	50.8	44.7
WDF	wood and charcoal burning	uniform	876	23.6	85.6	81.7	77.7
DEF	deforestation	tropical	365	9.8	77.1	49.5	35.1
CMB	agro-industrial and dung burning	(sub) tropical	323	8.7	90.9	89.0	87.7
FOR	forest wildfires	temperate/boreal	265	7.1	72.5	71.3	71.3
SBS	slash and burn/ shifting cultivation	tropical	232	6.2	72.0	61.7	50.7
BIF	burning in fields	(sub) tropical/ temperate	214	5.8	75.3	71.1	66.7
SHB	shrubland, heath, tundra fires	temperate/boreal	22	0.6	32.2	32.2	32.2
GRS	grassland fires	midlatitudes	10	0.3	89.8	89.8	89.8
TOT	total	global	3716	100.0	71.3	64.6	58.9

Data are taken from J. A. Logan and R. Yevich (unpublished manuscript, 1998) and R. Yevich and J. A. Logan (unpublished manuscript, 1998). "Global extent" describes the approximate, areal extent of each category. Northern hemispheric (NH) emissions assume a hemispheric split at 5°S, the equator, or 5°N. DEF, FOR, GRS, and SHB were originally established in units of g fuel yr⁻¹; all others in units of g C yr⁻¹; fuel was converted to carbon with a factor 0.45.

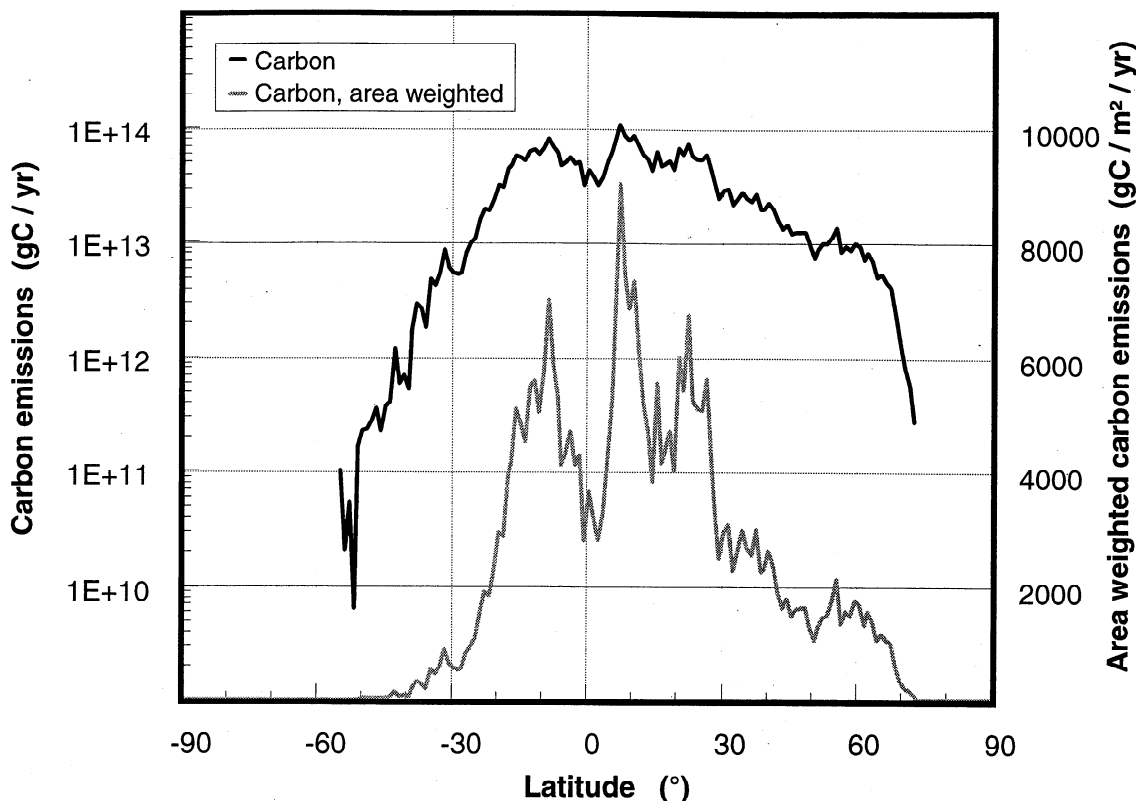


Figure 1. Global carbon emissions from biomass burning binned into 1° latitudinal bands. The absolute amounts are plotted in logarithmic scale (black line); the gray line delineates the area-weighted emissions (linear scale).

Fuel wood consumption (WDF) was estimated from country specific estimates of per-capita fuel wood and charcoal consumption and population statistics from the United Nations. Estimates of crop residue availability were based on statistics of crop production [FAO, 1986] and production to residue ratios. Estimates of crop residues and dung used as biofuels come primarily from surveys of residue use and information on extent of the fuel wood deficit. Residue that does not have another use, such as biofuel, mulch, fodder for livestock, or construction materials, and that does not decompose quickly is frequently burned to clear the fields for planting (or harvesting, in the case of sugar cane). The fraction of residue burned in the fields was estimated by subtracting estimates of residue needed for other purposes from the available residue and then burning the remainder at a level consistent with information on the local field burning customs. The estimates for wood fuels, charcoal, agricultural residue, and dung biofuel and data on the residue burned in the fields were spatially desegregated using a map of rural population density based on the cultivation map of Matthews [1983] and other maps of agricultural intensity.

All nine categories taken together show that the geographical extent of biomass burning is ubiquitous over most of the world's land area; significant lacks of fire activity are found only in extended desert and mountainous regions of the world. Categories SVH, DEF, CMB, SBS, and BIF are located mostly in the tropical and subtropical regions, while FOR, GRS, and SHB fires are predominantly found in temperate/boreal regions. Only WDF, the wood and charcoal burning, can be found in low and high latitudes.

The latitudinal breakdown of global emissions from the Logan and Yevich study reveals maximum emissions in the tropics (Figure 1). Globally, about 35% of all emissions are in the Southern Hemisphere, 65% in the Northern Hemisphere. In contrast, the study from Hao and Liu [1994] estimated almost equal contributions from both hemispheres, but that study considered only tropical sources. For informal purposes, we also considered the hemispheres to be separated by the average Interhemispheric Tropical Convergence Zone (ITCZ) at 5°N; hemispheric emissions would then split to 41% and 59% for the southern and Northern Hemisphere, respectively. However, in some regions, the ITCZ moves south before or during the burning (dry) season and may actually increase northern hemispheric (NH) emissions. This ITCZ movement needs to be considered both regionally and temporally, as most biomass burning occurs in the tropics where the movement is of largest impact.

Relative, global emissions, weighted by the land mass in each latitude band, peak at about 10° in each hemisphere, the northern peak reflecting large emissions from southern India, Southeast Asia, and the northern part of South America. The peak in the Southern Hemisphere is due to emissions from central Africa and central South America (Amazon Basin).

2.3. Inventory Approaches

The work by J. A. Logan and R. Yevich (unpublished manuscript, 1998) and R. Yevich and J. A. Logan (unpublished manuscript, 1998) considered some of the burning characteristics such as type of fuel that is burned or the effi-

Table 2. Published, Molar Emission Ratios for CH₃Cl Relative to CO₂ and CO

Category/Fuel	CH ₃ Cl/CO _x			N ^b	CO/CO ₂		Reference
	Median, ×10 ⁻⁵	Min., ^a ×10 ⁻⁵	Max., ^a ×10 ⁻⁵		Mean, %		
<i>CH₃Cl/CO₂</i>							
SVH							
Miscellaneous savanna grasses	17.7	5.7	32.9	4	7.01		<i>Lobert et al.</i> [1991] ^c
African savanna	4.30	3.34	5.26		8.67		<i>Rudolph et al.</i> [1995]
	2.00	1.80	2.20	173	5.30		<i>Andreae et al.</i> [1996]
	2.7	2.3	3.1		6.20		<i>Blake et al.</i> [1996]
Median for approach 1A	4.00				6.60		
WDF							
Wood	N/A	N/A	N/A	N/A	3.63		<i>Lobert et al.</i> [1991] ^c
	4.00	2.17	5.83	3	N/A		<i>Rasmussen et al.</i> [1980]
Charcoal	0.40	0.25	0.54	2	N/A		<i>Rasmussen et al.</i> [1980]
Median for approach 1A	4.00				3.63		
DEF, FOR, SBS							
Temperate forest	2.34	0.44	5.72	7	14.0		<i>Crutzen et al.</i> [1979]
Oak leaves, pine needles	10.8	8.50	13.0	2	N/A		<i>Rasmussen et al.</i> [1980]
Coniferous litter	8.61	3.61	13.6	2	7.48		<i>Lobert et al.</i> [1991] ^c
Temperate forest	1.33	0.64	2.02	11	5.53		<i>Laurson et al.</i> [1992]
Miscellaneous fuels	8.52	N/A	N/A	N/A	N/A		<i>Manö and Andreae</i> [1994]
Boreal forest	6.84	N/A	N/A	N/A	N/A		<i>Manö and Andreae</i> [1994]
Tropical forest	2.7	2.3	3.1	N/A	3.70		<i>Blake et al.</i> [1996]
Median for approach 1A	6.84				6.51		
FOR/AUS							
Leaf litter, eucalypt	28.9	5.60	52.2	10	N/A		<i>Tassios and Packham</i> [1985]
	40.3	34.6	46.0	4	N/A		<i>Tassios and Packham</i> [1985]
Median for approach 1A	34.6				6.51 ^c		
CMB							
Corn stalks, straw	21.9	21.0	31.3	4	N/A		<i>Rasmussen et al.</i> [1980]
Straw	7.25	3.27	12.5	3	6.57		<i>Lobert et al.</i> [1991] ^c
Median for approach 1A	14.6				6.57		
BIF							
Corn stalks, straw	21.9	21.0	31.3	4	N/A		<i>Rasmussen et al.</i> [1980]
Straw	7.25	3.27	12.5	3	6.57		<i>Lobert et al.</i> [1991] ^c
Sugar cane	1.90	1.60	2.20	10	1.80		<i>Andreae et al.</i> [1996]
Median for approach 1A	7.25				4.18		
SHB, GRS							
Chaparral	6.31	N/A	N/A		N/A		<i>Manö and Andreae</i> [1994]
Grass and bushes	9.9	9.2	10.6	15	10.5		<i>Andreae et al.</i> [1996]
Median for approach 1A	8.1				10.5		
Overall median for approach 1B	6.58	6.32 ^d	14.3 ^d		6.38		All sources
<i>CH₃Cl/CO</i>							
African savanna	49.6	46.1	53.1	N/A	8.67		<i>Rudolph et al.</i> [1995]
	95.0	94.0	96.0	176	5.30		<i>Andreae et al.</i> [1996]
	57.0	54.0	60.0	N/A	6.20		<i>Blake et al.</i> [1996]
Tropical forest	85.0	79.0	91.0	N/A	3.70		<i>Blake et al.</i> [1996]
Temperate forest	28.9	6.9	50.9	11	5.53		<i>Laurson et al.</i> [1992]
	11.8	2.8	22.8	7	19.90		<i>Crutzen et al.</i> [1979]
Miscellaneous fuels	79.2	8.7	302	13	7.30		<i>Lobert et al.</i> [1991] ^c
Overall median for approach 1B	57.0	46.1	60.0		6.20		All sources

N/A means not available.

^a If minimum and maximum ranges were reported by the authors, we used them for our purposes. If no range was given, we derived it from the mean plus or minus one standard deviation of all measurements.^b The number of observations (N) is as reported by the authors, either the number of experiments or the number of individual samples.^c Revised or extracted values as described in the text.^d Means instead of median.^e Adopted from DEF, FOR, SBS category.

ciency of pyrogenic conversions. Knowledge of burning efficiencies, in particular, is important because emissions of most compounds vary as a function of fuel type and fire conditions. For example, total mass emissions of CH_3Cl during the inefficient smoldering phase of fires were found to be three times greater than those during the flaming stage. This behavior is consistent with many other, reduced organic compounds [Lobert *et al.*, 1991]. However, reliable information about burning efficiencies of categories is lacking due to the high variability of fuel type, moisture, density, and arrangement [Lobert and Warnatz, 1993, and references therein]. Additionally, emissions of chlorine-containing gases are also dependent on the Cl content of the biomass, similar to the case of nitrogen containing compounds [Lobert *et al.*, 1991].

We employed two basic approaches for estimating emission fluxes. Approach 1 (hereafter referred to as the emission-ratio approach) was based on reported emission ratios between the compound of interest and a tracer species (CO or CO_2), the amount of the tracer emitted during combustion, and the corresponding amount of burned biomass. As described in more detail below, this approach was implemented in two different scenarios. For approach 1A, representative, mean emission ratios were applied to each burning category (variable ratio). Available data limited application of this scenario to CH_3Cl with CO_2 as the tracer species. For approach 1B, a constant, mean emission ratio for each organic compound was applied across all burning categories (static ratio). Approach 2 (hereafter referred to as the chlorine-content approach) was based on the reported Cl content of each fuel category, the corresponding fraction of Cl emitted as a given species during combustion, and the amount of fuel burned.

2.4. Emission Ratios

In order to derive a compound-specific emission factor, we combined two relative emission ratios. One is the commonly published, molar emission ratio for the compound in question (y) relative to the emitted amount of tracer CO or CO_2 (X_y/X_{CO_x}), where X is the molar, excess mixing ratio of the gas above ambient background concentration (mol per mol). The other necessary, molar emission ratio is that of CO or CO_2 relative to the amount of volatilized carbon (X_{CO_x}/X_C). The latter ratio also directly reflects the burning efficiency, with a high CO/C ratio or low CO_2/C ratio indicating low burning efficiency (with associated high CH_3Cl emissions). The global chlorine emissions Cl_y^i (in g Cl yr^{-1}) of compound y for each grid cell i of the $1^\circ \times 1^\circ$ database were computed from

$$\text{Cl}_y^i = \frac{C_V}{M_C} M_{\text{Cl}} N_{\text{Cl}} \frac{X_y}{X_{\text{CO}_x}} \frac{X_{\text{CO}_x}}{X_C} \quad (1)$$

where C_V is the volatilized amount of carbon from the database (g C yr^{-1}) and M and N are the molecular weights of the compound (g mol^{-1}) and number of chlorine atoms per molecule, respectively (subscript C for carbon, Cl for chlorine). The sum over all 360×180 grid cells yields the global emission of compound y from biomass burning.

2.4.1. CH_3Cl . We draw our best estimate of CH_3Cl emissions from a mean of approach 1B and approach 2. For approach 1B, we used a median, relative, molar emission ratio $\text{CH}_3\text{Cl}/\text{CO}$ of 5.7×10^{-4} and a global, mean CO/CO_2 emission ratio of 5.5% (Tables 2 and 3). The minimum and maximum estimates for this approach are medians computed from all

Table 3. Best-Estimate Emission Ratios for All Gases

	CH_3Cl	CH_2Cl_2	CHCl_3	CH_3CCl_3
	$X/\text{CO}, \times 10^{-5}$			
Median	57.0	2.48	0.069	0.72
Minimum	46.1	1.84	0.046	0.27
Maximum	60.0	3.12	0.091	1.17
CO/C	5.5%	5.5%	5.5%	5.5%
	$X/\text{CO}_2, \times 10^{-6}$			
Median	65.8	3.45	0.077	0.43
Minimum	63.2	2.83	0.056	0.24
Maximum	143	4.07	0.099	0.63
CO_2/C	89.5%	89.5%	89.5%	89.5%
	$\text{Combined Factor}, \times 10^{-6}$			
Median		2.23	0.054	0.39
Minimum		1.77	0.038	0.18
Maximum		2.69	0.070	0.60

Ratios for CH_3Cl were used individually for different approaches. For all other gases, only one approach was utilized with the combined factor.

reported minimum and maximum emission ratios, respectively. We would have preferred to utilize approach 1A with variable $\text{CH}_3\text{Cl}/\text{CO}$ ratios; but, in many earlier publications on CH_3Cl emissions, the better correlation of CH_3Cl with CO compared to CO_2 was not considered, hence data coverage for a breakdown by burning category is insufficient. Data availability is marginally sufficient for emission ratios relative to CO_2 , which we have used and compared to the estimates from static emission ratios (approach 1B, Table 2).

Most of the available data were adopted as published in form of a median of all measurements. Some publications contain results for different fuels and some allowed for a breakdown and extraction of certain fuel types from the data. The mean emission ratio $\text{CH}_3\text{Cl}/\text{CO}$ published by Lobert *et al.* [1991] was skewed by one experiment that resulted in very large, overall CH_3Cl emissions. We revised their emission ratio by using a median instead of a mean, which we consider more appropriate for non-normally distributed data. The revised emission ratios are 1.2×10^{-4} for $\text{CH}_3\text{Cl}/\text{CO}_2$ and 7.9×10^{-4} for $\text{CH}_3\text{Cl}/\text{CO}$, both within the range of other published data. Furthermore, in order to match measurements with burning categories, we extracted individual experiments of the Lobert *et al.* database and binned them for similar fuels.

Data of Tassios and Packham [1985] for Australian fires are amongst the highest reported ratios. However, Australian forest fuels contain high concentrations of chlorine (Table 4) and are likely to emit more CH_3Cl than other fuels, particularly in low-efficiency forest fires. Consequently, we separated the FOR category in Australia from the rest of the world and matched it with these data. We were not able to distinguish emission ratios for different forest fuels or different types of forest fires; such as prescribed fires, slash and burn, or wildfires, or to distinguish between the burning of tree canopies, stemwood, or forest litter due to a lack of data for each of these fire types. Hence categories DEF, SBS, and FOR were considered to be the same and were represented by emissions from forested areas.

Enhanced atmospheric deposition of sea-salt-derived Cl leads to higher concentrations of Cl in foliage, bark, and litter (but not wood) of coastal forests relative to those inland

Table 4. Chlorine Content of Biomass Fuels and Associated Burning Categories

Cl content	N	Location	Biomass/Ecosystem	Reference
<i>Savanna: SVH</i>				
1260	5	South Africa	grass	Andreae et al. [1996]
855	6	Zambia	grass	McKenzie et al. [1996]
490	3	Zambia	litter;	McKenzie et al. [1996]
830	3	Zambia	dicots	McKenzie et al. [1996]
539	1	Venezuela	Trachypogon grass	D. B. Harper (unpublished)
3025	1	Africa	undefined savanna grass	D. B. Harper (unpublished)
1913	1	Unspecified	Sorghum intrans grass	D. B. Harper (unpublished)
1035	1	Venezuela	Calobozo grass	D. B. Harper (unpublished)
1900	1	Cote d'Ivoire, Africa	Hyparrhenia grass	D. B. Harper (unpublished)
888	1	Cymbia, Africa	Hyparrhenia grass	D. B. Harper (unpublished)
<i>Agro-Industrial and Dung Burning: CMB</i>				
1820	13	Rio Grand Valley	avocado, grapefruit, orange, and mango leaves	Cooper and Gordon [1950]
1200	5	Texas	citrus leaves (aboveground) grown	Cooper et al. [1952]
9000	3	Southern California	citrus leaves	Harding et al. [1956]
657	2	Southern California	grapefruit (leaves)	Pearson et al. [1957]
6911	26	Victoria, Australia	Sultana vines from irrigated fields	Woodham [1956]
4360	1	India	cow dung	D. B. Harper (unpublished)
<i>Agricultural Fuels: BIF</i>				
4012	1	Unspecified	cotton	Ergle and Eaton [1949]
5290	1	Riverside, CA	Rhodes grass	Gauch and Wadleigh [1951]
3124	1	Riverside, CA	Dallis grass	Gauch and Wadleigh [1951]
4200	13	Unspecified	mixed crops	Cram [1976]
2741	3	Northern Japan	rice straw	Saito et al. [1994]
6800	1	Texas	switchgrass - leaves and grass from fertilized field	Agblevor and Besler [1996]
1333	1	Manitoba, Canada	wheat straw	Amiro et al. [1996]
9422	1	Germany	hay	D. B. Harper (unpublished)
5605	1	Indonesia	rice straw	D. B. Harper (unpublished)
7575	1	South Africa	sugar cane	D.B. Harper (unpublished)
<i>Wood - Temperate (except Australia): WDF, FOR</i>				
12	4	Maine	red maple, white birch, white pine, and red spruce	Young and Guinn [1966]
28	4	Oklahoma (U.S.)	eastern cottonwood, white oak, basswood, white ash	Osterhaus et al. [1975]
11	18	Unspecified (U.S.)	white oak	Slocum et al. [1978]
50	7	Unspecified (U.S.)	white oak, basswood, hard maple, southern pine, Douglas fir, redwood western red cedar,	Cutter et al. [1980]; Young and Guinn [1966]
90	8	New Jersey	pitch pine	Hall and Naumann [1984]
50	1	West Canada	Lodgepole-Jack pine (without polluted samples)	Legge et al. [1984]
2.4	60	Ohio	Tulip trees; plantation grown	McClenahan et al. [1989]
37	3	Washington State	Douglas fir	Reinhardt and Ward [1995]
123	4	North Carolina	Bald cypress; Cl intrusion not included	Yanosky et al. [1995]
9	3	Oregon	Douglas fir;	McKenzie et al. [1996]
185	130	North Ireland, Scotland, China	130 different species	Watling and Harper [1998]
<i>Bark and Phloem - Temperate (not considered)</i>				
58	1	Oklahoma	eastern cottonwood bark	Osterhaus et al. [1975]
170	8	New Jersey	pitch pine; bark and phloem	Hall and Newmann [1984]
37	6	Oregon	douglas fir	McKenzie et al. [1996]

Table 4. (continued)

Cl Content	N	Location	Biomass/Ecosystem	Reference
<i>Leaves - Temperate Forest: FOR</i>				
2428	45	Oklahoma	leaves from six species impacted by oil-field drainage; data excluded from category statistics	Harper [1946]
373	3	Massachusetts	oak, hickory, and maple leaves and twigs; only untreated trees included	Holmes [1961]
567	3	Massachusetts	sugar maple; data for trees adjacent to salted roads were excluded	Baker [1965]
592	3	Massachusetts	sugar maple; data for trees adjacent to salted roads were excluded	Button [1965]
760	5	Massachusetts	sugar maple; data for trees adjacent to salted roads were excluded	Holmes and Baker [1966]
9	3	Washington State	slash - Douglas fir	Reinhardt and Ward [1995]
296	18	Oregon	Douglas fir; author reports multiple samples at six sites	McKenzie et al. [1996]
259	1	Germany	pine needles	D. B. Harper (unpublished)
<i>Litter/Duff - Temperate Forest: FOR</i>				
121	4	Washington State	douglas fir	Reinhardt and Ward [1995]
127	18	Oregon	douglas fir	McKenzie et al. [1996]
139	1	Unspecified	top soil layer; deciduous forest	D. B. Harper (unpublished)
<i>Charcoal: WDF</i>				
12	18	Unspecified (U.S.)	commercial charcoal from white oak	Slocum et al. [1978]
50	9	Unspecified (U.S.)	charcoal (from various species)	Cutter et al. [1980]
<i>Wood (Eucalypt) (applied only to Australia): FOR</i>				
606	20	Australia, Tasmania, North Ireland, Scotland	20 different species	Watling and Harper [1998]
<i>Wood - Tropical/Subtropical (except Australia): WDF, SBS, DEF</i>				
498	3	Venezuela	3 different species	Osterhaus et al. [1975]
105	2	Brazil	upland evergreen forest	McKenzie et al. [1996]
50	1	Zambia	moist savanna	McKenzie et al. [1996]
249	48	Cameroon, Borneo, Malaysia	48 different species	Watling and Harper [1998]
<i>Leaves - Tropical/Subtropical Forest: SBS, DEF</i>				
230	3	Brazil	foliage	McKenzie et al. [1996]
830	6	Zambia	dicots	McKenzie et al. [1996]
1600	3	Zambia	foliage	McKenzie et al. [1996]
<i>Litter - Tropical/Subtropical Forest: SBS, DEF</i>				
83	6	Brazil	multiple samples at two sites	McKenzie et al. [1996]
490	3	Zambia	multiple samples at one site	McKenzie et al. [1996]
321	1	Philippines	pine needle litter	D. B. Harper (unpublished)
<i>Grasslands - No Data - Temperate Forest Leaves Used as Proxy: GRS</i>				
<i>Shrubland, Heath, Tundra Fires - No Data - Temperate Forest Leaves Used as Proxy: SHB</i>				

D. B. Harper (unpublished data, 1998) describes data obtained from biomass samples used by Lobert et al. [1991]. Units in the first column are mg Cl kg⁻¹ dry fuel.

[McKenzie et al., 1996]. In this study, Cl concentrations decreased roughly exponentially with distance inland; most of the decrease occurred within the first few kilometers and about 90% within 60 km. Available information is limited and precludes a detailed evaluation of the associated impact on Cl emissions from biomass burning. On the basis of the limited areal extent of the effect, however, we infer that it is probably of minor importance on a global scale.

For wood and charcoal burning (WDF), we did not distinguish between the two processes, even though CH₃Cl emission ratios can be different by an order of magnitude for the two fuels [Rasmussen et al., 1980]. However, the charcoal-making process exhibits very high CO/CO₂ ratios of about 0.24 [Brocard et al., 1996], indicating that CH₃Cl emissions may be high during this initial process. Therefore we have assumed the same emissions ratio as for wood for the entire

WDF category and ignored the ratio for charcoal. For agro-industrial (CMB), burning in fields (BIF), shrub (SHB), and grass (GRS) fires, we have adopted data for grassy and crop-like fuels. For SHB and GRS, we used emission ratios from *Manö and Andreae* [1994] and *Andreae et al.* [1996].

It should be noted that savanna fires were associated with CH_3Cl emission ratios that are slightly higher than those from forest fires even though the burning efficiency is much higher than that of forest burns. However, savanna grasses contain much higher amounts of chlorine than wood or forest fuels (Table 4) and hence would be expected to emit more chlorine per unit of burned biomass. This indicates that molar emission ratios in Table 2 reflect the dependency of emissions on fuel-Cl content at least to some extent.

2.4.2. CH_2Cl_2 , CHCl_3 , and CH_3CCl_3 . For the remaining organic compounds, CH_2Cl_2 , CHCl_3 , and CH_3CCl_3 , only one publication reported emission ratios relative to CO and CO_2 [*Rudolph et al.*, 1995]. Thus it was impossible to use approach A and only one emission factor was implemented into the database to derive global emissions. In analogy to CH_3Cl , we expect all three of these compounds to correlate better with CO than with CO_2 , as they all are reduced compounds and hence should be ratioed to CO for best results. However, the data of *Rudolph et al.* do not exhibit a clear correlation for CHCl_3 and CH_3CCl_3 with either tracer species, perhaps due to the limited number of observations and also, in case of CH_3CCl_3 , because of the low, measured excess mixing ratios. Thus we decided to use both published emission ratios, relative to CO and CO_2 , to derive estimates of emissions. We multiplied each mean emission ratio with the associated ratio of CO_x/C and averaged the two factors to derive our best emissions estimate (Table 3). No information is available on how much of the volatilized chlorine is emitted as these compounds; hence we were not able to apply the chlorine content approach.

2.4.3. CO and CO_2 emissions, burning efficiency. Virtually all reported CO/CO_2 emission ratios from biomass burning fall in the range of 0.02 to 0.25 (2-25%), most are within 3 to 15%. Data summarized in Table 2 span a range of 1.8% for very hot, efficient sugar cane fires to 20% for mixed fuel, inefficient smoldering fires. We consider the variability of these data to be primarily natural and not a result of instrumental uncertainty. For our calculations, we used the actually measured CO/CO_2 emission ratios, which are included in Table 2. As mentioned, some publications do not contain any information on these ratios, and hence data coverage is not as good as it is for the $\text{CH}_3\text{Cl}/\text{CO}_2$ ratios. For SVH, DEF, SBS, FOR, and BIF, averages of available data were taken. For Australian forest fires, we had to assume the same CO/CO_2 ratio as for the general FOR category; for WDF, we adopted a ratio from *Lobert et al.* [1991], even though these authors did not measure the CH_3Cl emissions in their wood experiments. CMB, GRS, and SHB categories are not well represented with respect to CO/CO_2 ratios but contribute less than 20% to the total emissions in this approach. Assuming that about 5% of all fuel carbon is emitted as particulate matter and hydrocarbons [*Lobert*, 1989], then CO plus CO_2 account for the remaining 95% of emitted carbon. This was considered when calculating ratios of CO_2/C (Table 3).

2.5. Chlorine Content of Biomass Burning Fuels

Approach 2 estimates emissions based on fuel Cl as follows

$$\text{Cl}'_y = F_{\text{Cl}} \text{Cl}_z \frac{C_{\text{fuel}}}{0.45} \text{Cl}_{\text{fuel}} \times 10^{-6} \quad (2)$$

where Cl'_y is the emitted mass of chlorine from compound y in each grid cell i (in g Cl yr^{-1}), F_{Cl} is the fraction of the total fuel Cl being emitted to the atmosphere, and Cl_z is the fraction of F_{Cl} associated with compound y . $C_{\text{fuel}}/0.45$ is the total, dry mass of burned fuel (in g yr^{-1}), which we back-calculated from emitted carbon amounts of the database by J. A. Logan and R. Yevich assuming that all biomass contains 45% carbon; Cl_{fuel} is the fuel-chlorine content (in $\text{mg Cl per kg dry weight fuel}$).

For F_{Cl} and Cl_z , we draw our information from only four publications. According to measurements of *Andreae et al.* [1996], F_{Cl} is 83%; 95% of that was estimated to be $\text{Cl}_{\text{p},i}$ and 3.0% was measured to be $\text{Cl}_{\text{CH}_3\text{Cl}}$. *McKenzie et al.* [1996] reported two sets of measurements with 73 (± 43)% and 79 (± 39)% for F_{Cl} . *Lobert et al.* [1991] did not directly publish such data, but we were able to utilize some of the unpublished material to derive such values from three experiments in which Cl content of the fuel was determined. According to those experiments, an average of $36.9 \pm 23.9\%$ of the fuel Cl was emitted and a fraction of $22.6 \pm 13.8\%$ of the emitted Cl (4.7% of the fuel Cl) was released in form of CH_3Cl , a substantially larger fraction than reported by *Andreae et al.*, whereas the total emitted chlorine was significantly smaller. *Amiro et al.* [1996] report volatilization rates of 91, 89, and 64% in three straw fires and also indicate that Cl volatilization may be a function of fire temperature with higher Cl emissions at higher temperatures.

The average of the reported means for F_{Cl} is $72 \pm 22\%$. The mean for the fraction of emitted CH_3Cl relative to the total emitted Cl ($E_{\text{CH}_3\text{Cl}}$) of $12.8 \pm 13.9\%$ is based on data from *Lobert et al.* [1991] and *Andreae et al.* [1996]. Assuming that no other Cl compound is emitted in significant quantities, we adopt the residual 87% for the respective fraction of $\text{Cl}_{\text{p},i}$ ($E_{\text{Cl}_{\text{p},i}}$). The ratio $\text{Cl}_{\text{p},i} : \text{CH}_3\text{Cl}$ is 6.81, which we applied to the global emissions of CH_3Cl from all scenarios to estimate the corresponding $\text{Cl}_{\text{p},i}$.

Table 4 contains all individual fuel-Cl data, Table 5 summarizes the weighted means that were applied to the database. For the SVH category, we took a mean of all data for various savanna grasses. For WDF, we ignored the charcoal data for similar reasons as for emission ratios. However, we distinguished temperate from tropical areas and also from the area of Australia because of significantly different Cl content in the respective types of wood. We divided tropical/ subtropical from temperate regions at 30° of latitude wherever applicable.

Both DEF and SBS burning categories are mainly located in the tropical/subtropical regions (Australia does not have any SBS/DEF), hence we separated them from the FOR category even though all three consist of similar principal types of vegetation. Most of the burning described in these categories are fires with forest fuels that are made up of stemwood, branches, green parts of plants, and ground litter. Accordingly, we compiled data into four bins of plant parts: wood, leaves, litter, and bark/phloem. We ignored the bark/phloem

Table 5. Statistics of Table 4

	Temperate; WDF, FOR									Tropical; SBS, DEF		
	SVH	CMB	BIF	Wood	Bark, Phloem	Leaves	Litter	Charcoal	Wood Austral.	Wood	Leaves	Litter
Mean fuel Cl	1275	3991	5010	54	88	408	129	31	606	226	887	298
Weighted mean ^a	1022	4840	4416	109	109	389	126	25	606	254	873	229
Median	962	3090	4745	37	58	373	127	31	606	177	830	321
Standard deviation	789	3092	2314	54	58	232	7	19		119	561	167
N (observations) ^b	18	50	24	242	15	36	23	27	20	54	12	10
N (studies)	3	5	7	11	3	7	3	2	1	3	1	2

Fuel Cl in mg Cl kg⁻¹ dry fuel.

^a The weighted mean, which was used for implementation into the database, is the sum of the products of the concentration and the corresponding number of observations for each study divided by the total number of observations from Table 4.

^b Repetitive measurements on the same sample were counted as one observation.

data because this fuel is probably a negligible portion of the overall biomass and also has Cl content similar to that of wood. We further estimated that about 50% of the burned biomass is stemwood, 45% is green parts (tree crowns), and 5% is ground litter, which is partially decomposed biomass. We applied the same factors to all three forest type categories, but separated the published data into temperate/boreal (FOR) and tropical/subtropical (SBS, DEF) bins of wood, green parts, and litter.

For CMB, the agro-industrial and dung burning, we used fuels that become available during agricultural processes and one cow dung sample from the database of experiments by *Loberet et al.* [1991]. All of these fuels contain large amounts of chlorine, much higher than those for green foliage. Similarly, we used crop fuels for the BIF category, which should be somewhat similar to the CMB type burning, except that the former is practiced in situ while the latter is done in oven/furnace arrangements. For the final two categories GRS and SHB, we assumed that temperate forest foliage/green plants are representative of those burning categories.

In order to derive a range of possible emissions, we calculated the following minimum and maximum emission factors. For the variable emission-ratio approach 1A, we used the total amount of emissions and applied a sample standard deviation of all best emission ratios from Table 2. For the static emission-ratio approach 1B, we used the median value ± one sample standard deviation and applied it to the carbon database. Finally, for the fuel-Cl approach 2, we varied the fraction of the emitted Cl relative to the fuel Cl by adding or subtracting one sample standard deviation from the mean value of 72% before applying it to the carbon database.

3. Results and Discussion

3.1. Results

We consider approach 2 to yield the best estimates for Cl_{p,i} because (1) the Cl content appears to have a greater influence on emissions than the burning efficiency and (2) detailed

information on fuel Cl is available for a wide variety of fuels; no directly measured emission ratios are available for Cl_{p,i}. For CH₃Cl, however, we need to consider two emission-ratio scenarios. Both reflect the Cl content to a certain extent, but we favor the approach with a static emission ratio (1B) relative to CO over that of a variable emission ratio (1A) relative to CO₂ because the CH₃Cl/CO ratio should be largely independent from burning efficiency, which is known to influence CH₃Cl emissions. More importantly, the lack of sufficient CH₃Cl/CO_x and/or associated CO/CO₂ data does not warrant the implementation of any variable emission ratios into an emissions grid for CH₃Cl at this point. The results from this approach in Table 7 and Figure 2 are for informal purposes only and are too uncertain to be considered.

Our best estimate for Cl_{p,i} emissions is 6.3 (4.4 - 8.3) Tg Cl yr⁻¹; other emission scenarios, linked in the same way to CH₃Cl emissions, deliver similar, albeit generally lower, results (Table 6). For CH₃Cl, we employed five different scenarios and the resulting emissions vary between 0.3 and 1.4 Tg Cl yr⁻¹. We believe that none of the scenarios is certain enough to be used exclusively. However, the CH₃Cl/CO emission-ratio approach 1B and the Cl-content approach 2 appear to be equally useful, both exhibit tight and symmetric ranges. The CH₃Cl/CO approach results in the tightest range of all scenarios and is somewhat independent of burning efficiency, whereas the Cl-content approach has the best input data with respect to fuel variability, but it does not represent burning efficiency at all. Our best estimate for CH₃Cl emissions of 0.64 (0.46 - 0.79) Tg Cl yr⁻¹ is an average of these two approaches. For the three minor chlorine gases CH₂Cl₂, CHCl₃, and CH₃CCl₃, we derived emissions of 49, 1.8, and 13 Gg Cl yr⁻¹ based on the combined, static factor approach. We consider the estimated CH₃CCl₃ and CHCl₃ emissions as upper limits, based on uncertainties discussed by *Rudolph et al.* [1995].

The 1° latitude by 1° longitude emissions grids for CH₃Cl and Cl_{p,i} in Plate 1 represent both the Cl-content approach (for Cl_{p,i}) and the emission-ratio approach (as part of our best estimate for CH₃Cl, which is a mean of approaches 1B and 2).

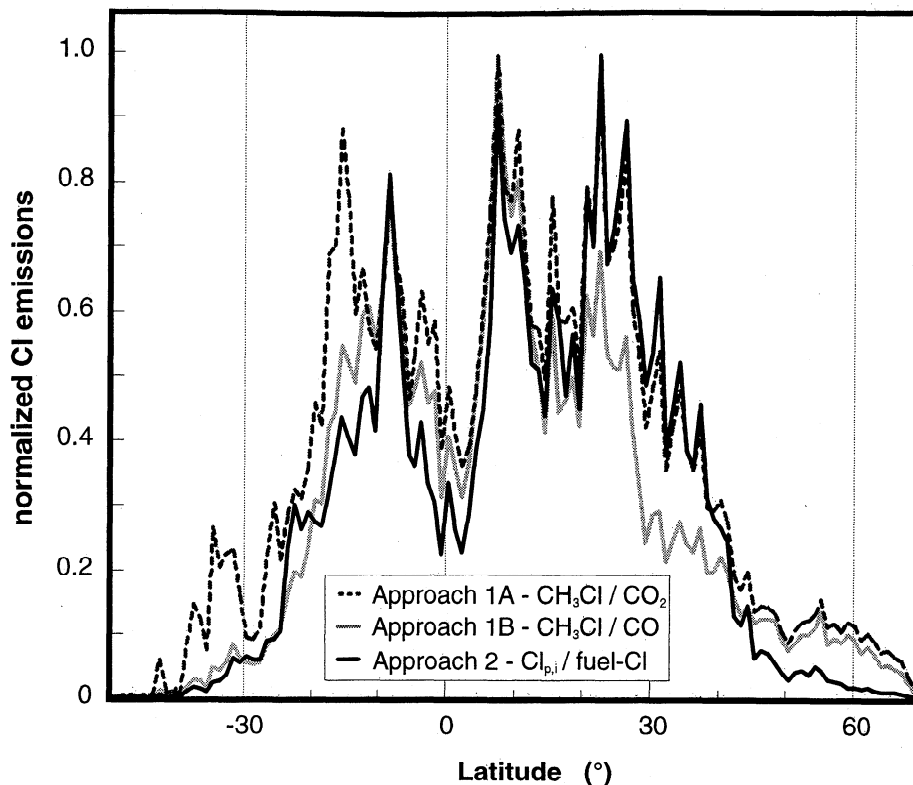


Figure 2. Comparison of normalized emissions from the three main approaches.

The basic distribution pattern is similar for both, emission hot spots are located in the regions of Southeast Asia, India, tropical Africa, and South America. Regional emission differences between the two color plates are due to differences in the emissions from the two approaches 1B and 2. SVH is one of the two largest contributors in the Cl-content approach (Table 7). CMB is the other large contributor (34.4%) but is only a minor fraction in the emission-ratio implementation; the same applies for BIF (20.7%) because of the large quantities of Cl in the associated fuels. Although WDF is the second largest carbon category, it is only a minor contributor to Cl emissions in approach 2 (3.9%) because of the low Cl content of wood. This fact and the high burning efficiency of wood and charcoal fires and expected low emissions of CH_3Cl do not seem to be reflected in any of the emission-ratio approaches (15.2 and 23.6%).

Figure 2 depicts the relative, latitudinal emissions and reveals that NH temperate areas are more important sources in the Cl-content approach than they are in the fixed emission-ratio approach 1B. Again, this is mostly due to the very high fuel-Cl content of the CMB and BIF categories, which contribute much more to the total in this approach than in any of the fixed emission-ratio approaches (Table 7). On the other hand, high NH latitudes and southern hemispheric (SH) tropics contribute more in approach 1B, probably because of the low Cl content of the FOR category, which is predominant in the NH high latitudes. The same reason applies to the SBS and DEF categories, which are significant in the SH tropics and also show low Cl content, hence the higher emissions in those regions in approach 1B.

Compared to the relative distribution of CH_3Cl from the static emission-ratio approach 1B, which is identical to that of

carbon in Figure 1, the variable approach 1A ($\text{CH}_3\text{Cl}/\text{CO}_2$) is very similar only between 10°S and 20°N and north of 50°N but generally higher everywhere else and even higher than the fuel-Cl approach south of 10°S (Figure 2). Significant differences of approach 1A also occur at 15°S and $30^\circ\text{--}40^\circ\text{S}$. Both are caused by very high emission ratios from CMB and FOR for Australia. Compared to approach 1B, approach 2 results in somewhat lower, relative emissions in the Southern Hemisphere and significantly larger, relative emissions between 20°N and 45°N . Overall, relative NH emissions (split at the equator) are larger when using the Cl-content approach (70%) compared to the static emission-ratio approach (64%). However, absolute CH_3Cl emissions of approach 2 are about twice as large and also significantly higher than those of approach 1A (Figure 3).

Estimated emissions by continent are summarized in Table 8. SE Asia appears to be the largest contributor with more than one third of the total chlorine emissions, followed by Africa. South and Central America and NE Asia together contribute another 30%; the remaining continents represent only minor fractions. This distribution of global Cl emissions is primarily driven by fluxes of $\text{Cl}_{p,i}$, hence by the fuel-Cl approach because $\text{Cl}_{p,i}$ dominates the combined emissions. However, global emissions based on a static factor approach would yield similar rankings.

3.2. Comparisons

The global carbon emissions of $3716 \text{ Tg C yr}^{-1}$ from biomass burning from the studies of J. A. Logan and R. Yevich (unpublished manuscript, 1998) and R. Yevich and J. A. Logan (unpublished manuscript, 1998; both combined in

Table 6. Global Emissions From Various Approaches

Approach	Scenario	CH ₃ Cl	Cl _{p,i} ^a	CH ₂ Cl ₂	CHCl ₃	CH ₃ CCl ₃
Emission-ratio approach 1A	variable X/CO ₂	614	4180			
		590	4020			
		1330	9060			
Emission-ratio approach 1B/CO ₂	fixed X/CO ₂	645	4390			
		620	4220			
		1400	9540			
Emission-ratio approach 1B/CO	fixed X/CO	347	2360			
		280	1910			
		365	2490			
Emission-ratio approach 1B/CO and CO ₂	fixed, combined X/CO _x	496	3380	49.0	1.77	12.9
		384	2620	39.0	1.24	5.9
		1056	7190	59.0	2.29	19.9
Fuel Cl-content approach 2	variable content	932	6350			
		645	4390			
		1219	8300			
Best estimate		640	6350	49.0	1.77	12.9
		460	4390	39.0	1.24	5.9
		790	8300	59.0	2.29	19.9

The three values are best, minimum, and maximum estimates and were derived from the range of published emissions data. All units in Gg Cl yr⁻¹.

^a Cl_{p,i} was derived from the emissions of CH₃Cl multiplied with a factor of 6.81, see text. CH₃Cl best estimates were derived from an average of approach 1B/CO and 2.

Table 1) are very similar in magnitude to estimates by *Andreae* [1991] of 3940 Tg C yr⁻¹, but the methodology is often different and the approach is considerably more detailed. Estimates by *Seiler and Crutzen* [1980] (five categories) and *Hao and Liu* [1994] (four categories) are considerably lower at 1500-3000 and 2400 Tg C yr⁻¹, respectively. In addition,

estimates of the relative contributions of individual categories have changed over time. Whereas *Seiler and Crutzen* estimated tropical forest fires (here SBS plus DEF) to be the largest category of burning (1090 Tg C yr⁻¹), followed by savanna fires with 540 Tg C yr⁻¹, both *Hao and Liu* and *J. A. Logan* and *R. Yevich* list savanna fires as the predominant source

Table 7. Chlorine Emissions for Individual Compounds and Relative Contributions by Category

Approach	CH ₃ Cl				CH ₂ Cl ₂ , 1B/CO _x	CHCl ₃ , 1B/CO _x	CH ₃ CCl ₃ , 1B/CO _x	Cl _{p,i} , 2 ^a	Contribution to Global, %		
	1A/CO ₂	1B/CO	2	Best ^a					1A	1B	2
SVH	147	132	295	213	18.6	0.67	4.89	2008	24.0	37.9	31.6
WDF	92.4	81.8	36.8	59.3	11.5	0.42	3.03	251	15.1	23.6	3.9
DEF	65.3	34.1	39.2	36.6	4.8	0.17	1.27	267	10.6	9.8	4.2
CMB	123	30.2	320	175	4.3	0.15	1.12	2180	20.1	8.7	34.4
FOR	96.2	24.8	20.0	22.4	3.5	0.13	0.92	137	15.7	7.1	2.2
SBS	41.4	21.6	25.2	23.4	3.1	0.11	0.80	171	6.7	6.2	2.7
BIF	41.5	20.0	193	107	2.8	0.10	0.74	1315	6.8	5.8	20.7
SHB	4.5	2.0	1.7	1.9	0.29	0.01	0.08	11.7	0.7	0.6	0.2
GRS	2.0	0.9	0.8	0.9	0.13	0.005	0.03	5.4	0.3	0.3	0.1
TOT	614	347	932	640	49.0	1.77	12.9	6346	100.0	100.0	100.0
SH ^b	229	124	283	203	17.5	0.63	4.6	1847	37.4	35.7	30.3
NH ^b	384	223	649	436	31.5	1.14	8.3	4498	62.6	64.3	69.7

All emissions in Gg Cl yr⁻¹.

^a For CH₃Cl, we averaged columns 3 and 4 for the best, global estimate.

^b SH and NH emissions are the amounts or percentages of chlorine emitted in the southern and Northern Hemisphere (equator split).

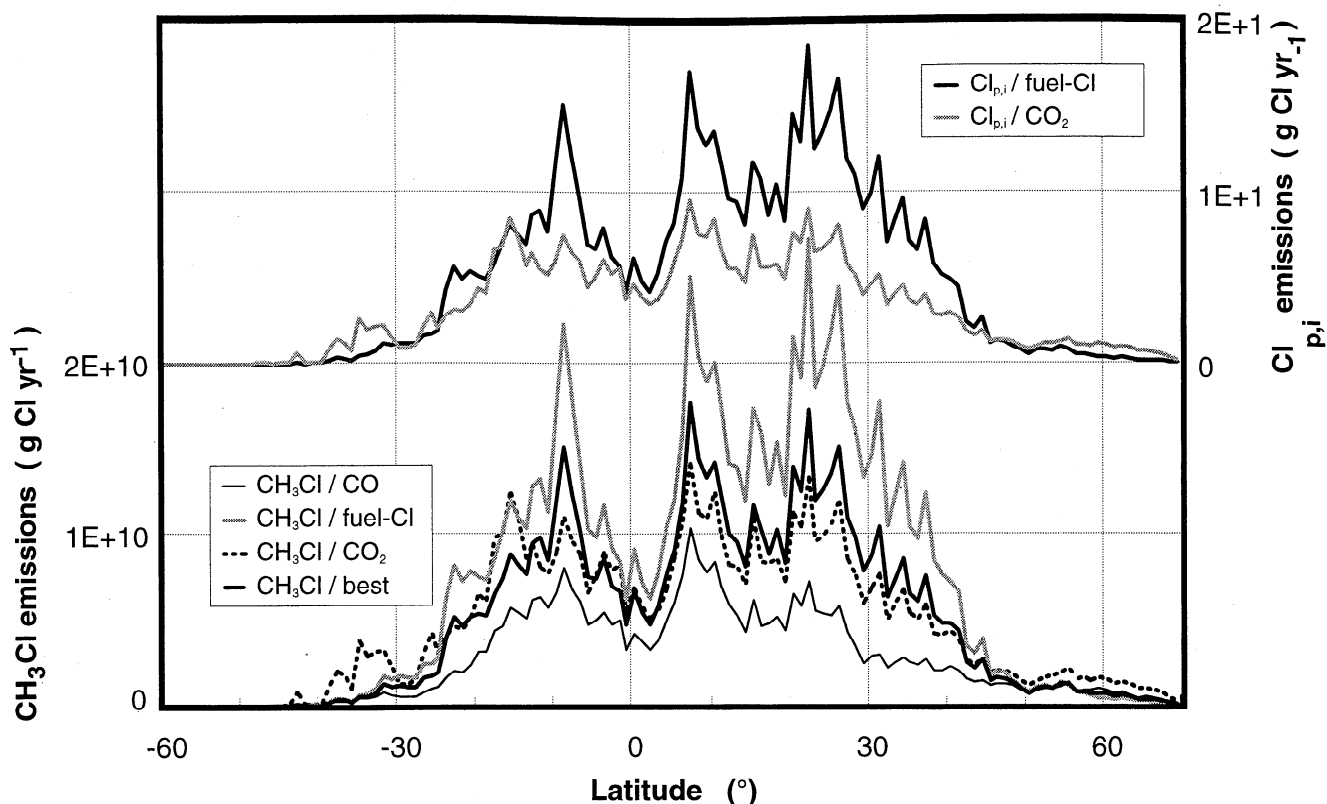


Figure 3. Latitudinal distribution of (bottom) CH_3Cl and (top) $\text{Cl}_{\text{p},i}$ emissions. The shown data represent the different approaches of Table 6. In addition, we have plotted the other variable approach for $\text{Cl}_{\text{p},i}$ derived from the $\text{CH}_3\text{Cl}/\text{CO}_2$ scenario. The thick, black, solid lines are our best estimates; the best CH_3Cl estimate was derived from the thick, gray and the thin, black line.

(1700 and 1400 Tg C yr^{-1}) with 2 to 3 times as much in emissions as tropical forest fires (570 and 600 Tg C yr^{-1}). Estimates of emissions from fuel wood have also changed between these studies from 470 to 280 to 640 and 880 Tg C yr^{-1} (Crutzen and Seiler, Hao and Liu, Andreae, J. A. Logan and R. Yevich), emissions from temperate and boreal forest fires changed from 130 to 265 Tg C yr^{-1} between Crutzen and Seiler and J. A. Logan and R. Yevich. Another significant difference is found in the burning of agricultural wastes, which was estimated at 855, 300, and 910 Tg C yr^{-1} (Crutzen and Seiler, Hao and Liu, Andreae) and now is estimated at 540 Tg C yr^{-1} (J. A. Logan and R. Yevich, Table 1, CMB+BIF). Hao and Liu considered only tropical burning categories and is based on data from 1975 to 1980 and hence is expected to yield a somewhat lower, global estimate. Considering differences in spatial coverage and an increase in burning activity with time and the overall uncertainties in such estimates, the global emissions in the mentioned reports are quite consistent. However, regional differences may be significant, but can only be compared between Hao and Liu and the Logan and Yevich effort, which are the only two spatially segregated databases.

Global CH_3Cl emissions have also been estimated previously. Starting with Crutzen *et al.* [1979], the first global estimate for CH_3Cl was between 0.19 and 0.42 Tg Cl yr^{-1} ; data from Lobert *et al.* [1991] result in a global source of 0.52 (0.22-1.8) Tg Cl yr^{-1} using their revised emission ratio;

Rudolph *et al.* [1995] estimated 0.52 (0.23-0.90) Tg Cl yr^{-1} ; Andreae [1993] estimated 0.65 to 2.6 Tg Cl yr^{-1} ; and Andreae *et al.* [1996] estimated 1.1 to 1.5 Tg Cl yr^{-1} . Blake *et al.* [1996] published a range of 0.7 to 1.0 Tg Cl yr^{-1} based on their measurements of CH_3Cl relative to CO but also report another range of 0.26 to 0.41 based on their $\text{CH}_3\text{Cl}/\text{CO}_2$ ratio. The overall minima of reported data are similar to those in our new estimate. The maxima, however, vary over a wide range and exceed our best-estimate maxima by significant amounts. According to our calculations, biomass burning does not contribute more than 1.4 Tg Cl yr^{-1} to the atmosphere. Our best, global estimate of CH_3Cl of 0.64 Tg Cl yr^{-1} is within the previously reported data. This does not necessarily confirm one another, but we believe that we have constrained the global amounts with various scenarios to an overall tighter range of emissions (0.46 - 0.79 Tg Cl yr^{-1}).

Only one publication has previously estimated global emissions of CH_2Cl_2 , CHCl_3 , and CH_3CCl_3 [Rudolph *et al.*, 1995], and their emission ratios are the basis of our results. Thus global estimates are very similar; Rudolph *et al.* calculated 70 (32-118), 2 (0.9-4), and 14 (4-28) Gg yr^{-1} for the three compounds, respectively. On the basis of a simple extrapolation from data for savanna fires reported by McKenzie *et al.* [1996] and Andreae *et al.* [1996], Graedel and Keene [1996] estimated a global flux of inorganic Cl from biomass burning of about 27 Tg Cl yr^{-1} . This flux is about 4-5 times greater

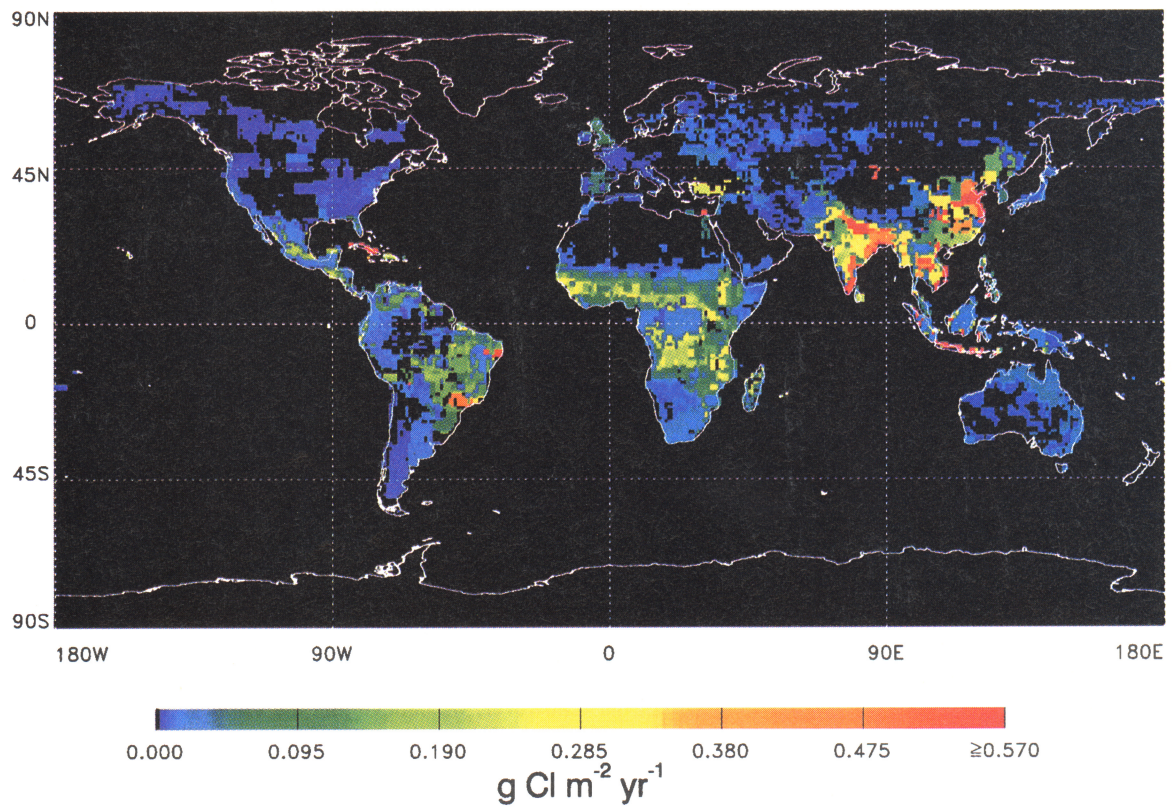
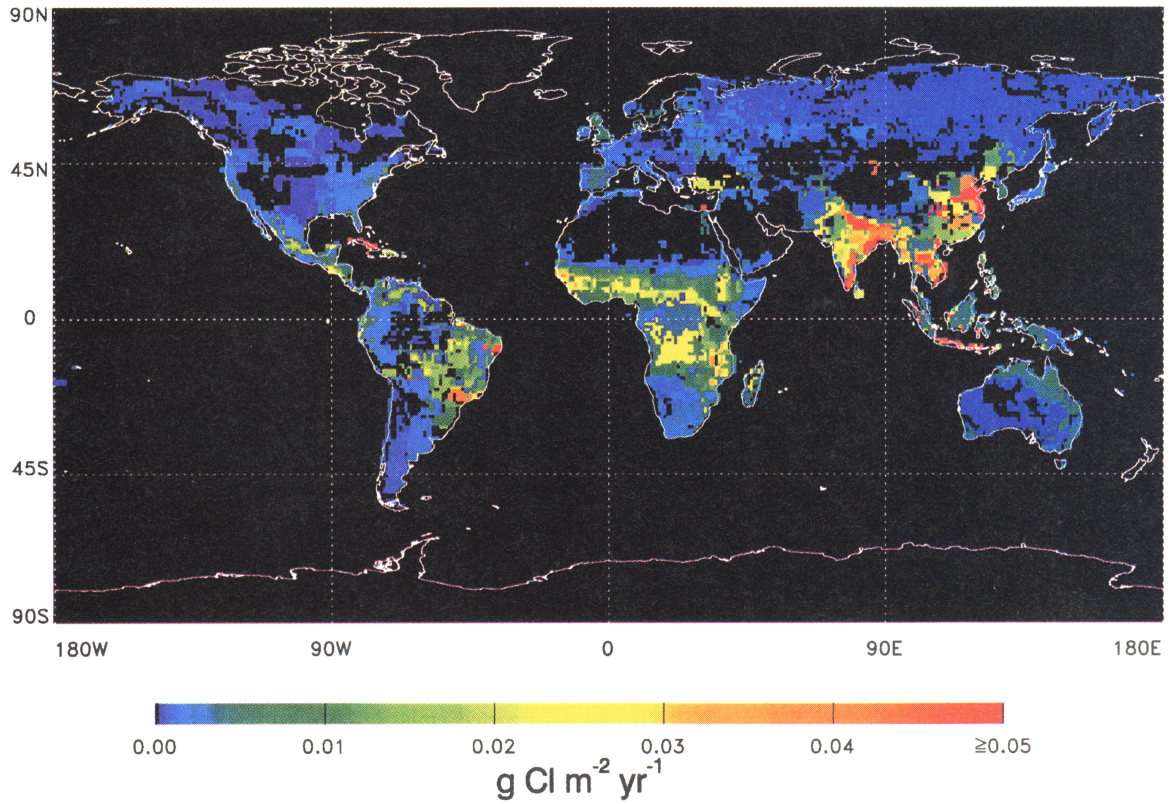


Plate 1. Emissions grid for for (top) CH_3Cl and (bottom) $\text{Cl}_{p,i}$ with a resolution of 1° latitude by 1° longitude. The color scale was compressed toward lower emissions to deemphasize hot spots, which appear in white.

Table 8. CH₃Cl and Cl_{p,i} Emissions by Continent

	Emission			Contribution to Global
	CH ₃ Cl	Cl _{p,i}	Sum Cl	
Southeast Asia	219	2307	2526	36.2
Africa	190	1759	1949	27.9
South and Central America	111	1104	1215	17.4
Northeast Asia	78	856	934	13.4
Europe	18	173	191	2.7
Australia	12	94	106	1.5
North America	10.6	54	65	0.9
Global	639	6346	6985	100.0

Emissions are in Gg Cl yr⁻¹ (% for contributions) and were based on our best estimate approaches. We estimated emissions by rectangular, continental areas: Africa includes Mauritius; southeast Asia is constricted to the east at 54°E, to the south at 11°N, and to the north at 30°N and includes Japan; South and Central America includes everything south of 28°N; northeast Asia is between 30° and 90°N and between 54°E and 180°E; Europe includes Asia to 54°E and Iceland; Australia includes New Zealand and New Caledonia; North America is the United States and Canada above 28°N.

than that suggested by the more detailed analysis reported herein. We know of no other global estimates for this flux.

3.3. Budget Analysis

A comprehensive overview and budget analysis for the compounds considered in this work is given by Keene *et al.* [this issue] and will not be discussed in detail here. Briefly, biomass burning contributes a significant fraction, probably the single largest amount, to the global budget of CH₃Cl. The amount is almost twice as large as the oceanic source reported by Khalil *et al.* [this issue], which traditionally was thought to be the largest contributor for this gas. The budget of CH₃Cl is still largely imbalanced, estimates suggest that biomass burning contributes about 25% to the global source strength inferred from inversion model calculations.

Biomass burning also contributes a significant portion of about 10% to the globally combined sources of CH₂Cl₂. Assuming that the estimated emissions of CHCl₃ and CH₃CCl₃ are realistic, the amounts emitted from fires represent only 0.4% and 2%, respectively, of their global source strengths.

The amounts of inorganic and particulate chlorine from biomass burning are highly uncertain. Depending on the relative contribution of HCl to the combined Cl_{p,i} emissions, biomass burning may contribute as much as 25% to the total sources of HCl but is an insignificant source for particulate Cl on a global scale.

3.4. Uncertainties

Uncertainties for the emission grids can be categorized into three main aspects: limitations of the underlying database, uncertainties in the measured or estimated emission factors, and inadequacies of our implementation of the emission factors. With respect to the database, we can identify the input data as a major uncertainty but it is beyond the scope of our

analysis to address specifics concerning the types of uncertainties herein. However, forthcoming manuscripts (J. A. Logan and R. Yevich, unpublished manuscript, 1998; R. Yevich and J. A. Logan, unpublished manuscript, 1998) will include a detailed assessment of uncertainties in the underlying database for biomass burning. Estimates of how much biomass is burned are most useful if they represent long-term averages. However, such long-term observations of burning frequency have just begun and only limited information is available to date. Although the location of fires can be monitored from space [e.g., Justice *et al.*, 1996], the areas burned are not readily derived from these data. Furthermore, quantifying the aboveground biomass that is available and consumed in the fire remains a challenge to the scientific community; highly variable burning frequencies add to overall uncertainty and cannot easily be averaged.

The second category of uncertainties can be attributed to the available emission factors such as the measured emission ratios of compounds relative to each other and the emission ratios of compounds relative to the carbon or chlorine content of the fuel. The precision of these measurements is quite good, whereas the accuracy is often less defined because of a lack of method intercalibration and intercomparison, which have not been carried out until recently. Although measurement errors contribute to overall uncertainty, the large ranges of reported emissions are typical for biomass burning measurements and not necessarily a result of analytical bias. Increased numbers of observations over a range of fire conditions will improve the confidence in mean values and thereby enhance the overall accuracy of future analyses such as ours.

The third category of major uncertainties is our implementation of emission factors. In the case of the fuel chlorine measurements, we believe that the available data are reliable and represent a wide variety of fuels and ecosystems. One obvious shortcoming is the implementation of various fuel contents into the overall category of, for example, forest fires. We assumed an apportionment of 50%, 45%, and 5% for the contribution of stemwood, canopy parts, and forest litter. The actual percentage breakdown varies substantially and applies only if the entire fuel is burned with the same efficiency at the same time. Some burning practices do not burn the entire fuel at the same time (SBS) and even in highly efficient, wild forest fires, the canopy is expected to burn at a higher efficiency than the stemwood, which sometimes does not get burned at all. In addition, the extrapolation from a small quantity, the fraction of Cl_{CH₃Cl} in equation (2), to a large fraction of emitted Cl_{p,i} is very uncertain due to a complete lack of reliable emission data for Cl_{p,i}. With respect to emission-ratio approaches, it is not satisfactory to average all available data into one static factor, but unless more emission ratios for a wider variety of burning systems become available, a more detailed breakdown cannot be done.

Considering the above, we estimate that our calculated fluxes are reliable to within a factor of 2 to 3. Despite this large range and the shortcomings of the presented approach, however, we believe that the effort is still an advancement in the understanding of the distribution and global flux of chlorine emissions from biomass burning.

3.5. Seasonality and Trends

The global emission grids presented here do not have any temporal resolution. In general, we can expect a seasonality pattern that follows climatological rainfall statistics. Thus a

first proxy for seasonality could be implemented by using regional, long-term rainfall statistics. Changes in the overall emissions of both carbon and chlorine can be expected with varying burning frequency and efficiency. *Hao and Liu* [1994] report a general pattern with emission peaks around March-June in the NH and September-December in the SH. The database of J. A. Logan and R. Yevich will ultimately contain some information about the seasonality of biomass burning emissions; this information may be implemented as part of a future RCEI effort.

Very little quantitative information is available about the long-term trend of biomass burning. We can safely assume that several thousand years ago global emissions were dominated by natural fires and the contribution of anthropogenic burning was small. With an exponentially growing population in developing countries, however, this scenario has changed and today biomass burning is viewed as an anthropogenic source of trace compounds to the atmosphere. In fact, many estimates of global biomass burning are based on population statistics (including parts of the underlying database for this study) and project that biomass burning will increase at a similar rate as the future population. Although ice core records can give reliable information about the amounts of black carbon in the prehistoric atmosphere, the quantitative link between black carbon in ice and the associated biomass burning activity has not been established. However, a substantial increase in biomass burning activity should be reflected in the trends of, for example, atmospheric CH_3Cl , which does not seem to show a significant change over the past 10 years [*Khalil and Rasmussen*, 1999] and only a small trend of about 5-10% can be seen in firn air samples dating back about 80 years (J. H. Butler, NOAA/CMDL, unpublished data, 1998). Recent changes in the trends of atmospheric CO could indicate that biomass burning may currently not be increasing at all [*Novelli et al.*, 1994, 1998]. Clearly, more research is needed to resolve these issues.

3.6. Tobacco Smoke as a Source for Atmospheric CH_3Cl

Another type of biomass burning, also of anthropogenic origin, is the consumption of smoking tobacco, which is known to release measurable amounts of CH_3Cl [*Stedman*, 1968; *Elmenhorst and Schultz*, 1968, and references therein]. We briefly investigated this source and estimated that annual emissions of CH_3Cl could be as much as 1.3 Gg Cl. This estimate is based on several different, numerical approaches that correlate data from various sources. If we consider the amount of worldwide tobacco leaf production [*FAO*, 1998] and assume 30% leaf moisture, we calculate the availability of 5.77 Tg dry matter tobacco per year. If we apply emission factors $\text{Cl}_{\text{CH}_3\text{Cl}}$ and F_{Cl} from equation (1), we estimate a global emission of 0.05 Gg Cl yr^{-1} from CH_3Cl in tobacco smoke. If, instead, we use an emission factor of 0.109 mg Cl kg^{-1} dm [*Norman*, 1977] and the same tobacco production, we arrive at 0.6 Gg Cl yr^{-1} . Finally, we can utilize a third estimate based on the amount of emitted smoke of 0.28 L g^{-1} tobacco [*Griest and Guerin*, 1977], a measured mixing ratio for CH_3Cl of 495 ppm in smoke [*Elmenhorst and Schultz*, 1968], and the FAO tobacco production to arrive at an emission of 1.3 Gg Cl yr^{-1} . The mean of all three estimates is 0.66 Gg Cl yr^{-1} , a factor 1000 below the biomass burning estimate (Table 6).

These estimates are based on assumptions that (1) the annual production of tobacco is completely consumed in the

form of standard U.S.-type cigarettes, (2) a standard cigarette contains about one gram of tobacco [*Griest and Guerin*, 1977], and (3) all of the formed CH_3Cl is ultimately released to the atmosphere. We further assumed that emission factors do not change significantly with the type of tobacco and the type of smoke. Although highly uncertain, these estimates suggest that CH_3Cl emissions from tobacco smoke are insignificant for the global budget of this gas.

4. Availability of On-Line Data

All gridded inventories generated by the RCEI are available on-line through the project website at <<http://groundhog.sprl.umich.edu/geia/rcei>>. We refer to the website for detailed information on available data, download options, and contacts. We plan to update these inventories as new information becomes available. Briefly, the RCEI database for biomass burning emissions from this publication consists of one inventory grid, 360° of longitude \times 180° of latitude, for each compound for all nine categories combined: CH_3Cl , CH_2Cl_2 , CHCl_3 , CH_3CCl_3 , and $\text{Cl}_{\text{p.i.}}$. For consistency with other GEIA databases, we divided the global flux in each grid cell according to equations (1) and (2) with the surface area of each grid cell and calculated fluxes in grams of chlorine per m^2 per year ($\text{g Cl m}^{-2} \text{yr}^{-1}$). A grid with the surface area of each cell is supplied on-line.

5. Summary

As part of the Reactive Chlorine Emissions Inventory, we estimated emissions of organic and inorganic Cl-containing compounds from nine different categories of biomass burning on a 1° by 1° global grid. Fluxes and associated uncertainties were derived from the burning inventories developed by J. A. Logan and R. Yevich (unpublished manuscript, 1998) and R. Yevich and J. A. Logan (unpublished manuscript, 1998) using several approaches including emission ratios referenced to CO and CO_2 and the Cl content of fuel feedstock categories. Results from most approaches agreed within a factor of 2. The largest Cl emissions were associated with savanna fires (SVH), wood and charcoal burning (WDF), agro-industrial and dung burning (CMB), and burning in fields (BIF), which together account for 66% to 91% of the total Cl flux from all categories. Although CMB and BIF together account for only about 15% of global carbon emissions from biomass burning, the high Cl contents of these fuels result in substantial fluxes. Cl emissions are concentrated in the tropics and subtropics; SE Asia accounts for about 36% of total Cl emissions, followed by Africa (~30%); South and Central America and NE Asia combine for another 30%. Biomass burning appears to be the single largest, known source of atmospheric CH_3Cl and a major source of inorganic Cl in many continental regions.

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