

Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive Chlorine Emissions Inventory

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Abstract. Emission inventories for major reactive tropospheric Cl species (particulate Cl, HCl, ClNO₂, CH₃Cl, CHCl₃, CH₃CCl₃, C₂Cl₄, C₂HCl₃, CH₂Cl₂, and CHClF₂) were integrated across source types (terrestrial biogenic and oceanic emissions, sea-salt production and dechlorination, biomass burning, industrial emissions, fossil-fuel combustion, and incineration). Composite emissions were compared with known sinks to assess budget closure; relative contributions of natural and anthropogenic sources were differentiated. Model calculations suggest that conventional acid-displacement reactions involving S_(IV)+O₃, S_(IV)+H₂O₂, and H₂SO₄ and HNO₃ scavenging account for minor fractions of sea-salt dechlorination globally. Other important chemical pathways involving sea-salt aerosol apparently produce most volatile chlorine in the troposphere. The combined emissions of CH₃Cl from known sources account for about half of the modeled sink, suggesting fluxes from known sources were underestimated, the OH sink was overestimated, or significant unidentified sources exist. Anthropogenic activities (primarily biomass burning) contribute about half the net CH₃Cl emitted from known sources. Anthropogenic emissions account for only about 10% of the modeled CHCl₃ sink. Although poorly constrained, significant fractions of tropospheric CH₂Cl₂ (25%), C₂HCl₃ (10%), and C₂Cl₄ (5%) are emitted from the surface ocean; the combined contributions of C₂Cl₄ and C₂HCl₃ from all natural sources may be substantially higher than the estimated oceanic flux.

1. Introduction

The uses of reactive, chlorine-containing compounds by industry and in water purification are the focus of debate and

possible regulatory action by the U.S., Canadian, and European governments [e.g., Anderson, 1993; Hileman, 1993a, b; Abelson, 1994a, b]. In addition, emission controls implemented under the Montreal Protocol are reducing atmospheric loadings of chlorofluorocarbons and related, long-lived, Cl-containing compounds [e.g., Prinn et al., 1995; Montzka et al., 1996; Cunnold et al., 1997] and, thus, altering the relative mix of halogen fluxes to the stratosphere from natural and anthropogenic sources. However, large uncertainties in our understanding of the natural biogeochemistry of chlorine [Graedel and Keene, 1995, 1996; Singh, 1995] confound critical assessment of the potential environmental implications of changing emission scenarios. Although many experimental data exist concerning natural and anthropogenic emissions of reactive chlorine to the atmosphere (for example, see recent reviews by Graedel and Keene [1995, 1996], Singh [1995], and Khaliil [1999]), most of this information has not been synthesized and analyzed to produce integrated emission fields with which to assess the global atmospheric chlorine cycle or the role of natural processes.

To address this deficiency, we organized the Reactive Chlorine Emissions Inventory (RCEI) under the auspices of the International Global Atmospheric Chemistry Program's Global Emissions Inventory Activity (GEIA) [Graedel and Keene, this issue]. Our first objective was to develop and verify individual gridded global emission inventories as a function of source type for major reactive chlorine species in the troposphere, including particulate chlorine, hydrochloric

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acid (HCl), nitryl chloride (ClNO₂), methylchloride (chloromethane, CH₃Cl), chloroform (trichloromethane, CHCl₃), methyl chloroform (1,1,1-trichloroethane, CH₃CCl₃), perchloroethene (tetrachloroethene, C₂Cl₄), trichloroethene (C₂HCl₃), methylene chloride (dichloromethane, CH₂Cl₂), and the hydrochlorofluorocarbon (HCFC) chlorodifluoromethane (CHClF₂, HCFC-22). Tropospheric lifetimes for these compounds range from less than 1 day for ClNO₂ to about 13 years for chlorodifluoromethane; as described in more detail below, in the companion papers of this special section, and in the cited literature, the associated atmospheric impacts are varied. We restricted our analyses to species important to either the tropospheric burden of reactive Cl or to the rate of chlorine cycling. Compounds such as phosgene [Kindler *et al.*, 1995] and chloroacetic acids [Grimvall, 1995] which are produced from the chemical degradation of chlorinated precursors were not evaluated. Four major classes of source types were considered: oceanic and terrestrial biogenic emissions [Khalil *et al.*, this issue], sea-salt production and dechlorination [Erickson *et al.*, this issue], biomass burning [Lobert *et al.*, this issue], and exclusively anthropogenic emissions from industrial sources, fossil-fuel combustion, and incineration [Aucott *et al.*, this issue; McCulloch *et al.*, this issue (a), (b)].

Our secondary objectives were (1) to develop species-specific composite inventories by integrating the individual emission fields over source type, (2) to evaluate budget closure for each species by comparing composite emissions from major known sources with total fluxes inferred from inversion modeling and related approaches, (3) to differentiate the relative contributions of natural and anthropogenic sources, and (4) to assess associated uncertainties in the tropospheric chlorine cycle. Results of these analyses are reported herein.

2. Methods

2.1. Constituent Emission Inventories

Readers are referred to the companion papers of this special section for details of the methodologies used to generate the constituent inventories included in this analysis. Industrial CH₃CCl₃ emissions reported by Midgley and McCulloch [1995] were gridded using the same procedures employed by McCulloch *et al.* [this issue (a)] for C₂Cl₄, C₂HCl₃, and CH₂Cl₂. The chemical species included in this analysis, associated source types, and corresponding references are summarized in Table 1. All industrial emissions were derived from data for 1990. For some source types (e.g., mineral aerosol and volcanic emissions), insufficient information was available to produce credible emission inventories. For these cases, we incorporated previously published estimates of integrated global fluxes from the literature. In a few cases (e.g., Cl₂, HOCl, and BrCl emissions from sea-salt aerosol), fluxes were very poorly constrained and credible estimates unavailable; although perhaps important on a global scale, these compounds could not be included in the inventory. The analysis reported herein is based on the "best guess" estimates of the emission fluxes; associated uncertainties are assessed in the companion papers and cited literature. All global burdens and absolute and percentage fluxes reported herein are in units of Cl mass.

2.2. Inversion Modeling

The source deconvolution model used to infer the tropospheric sinks and corresponding lifetimes for selected species

is based on measured tropospheric concentrations, rates of oxidation by tropospheric OH, and losses to the stratosphere (see Khalil and Rasmussen [1999b] for a detailed description). Briefly, a low-resolution, two-dimensional (2-D) box model of the atmosphere was coupled with a detailed photochemical model of OH. The model included six tropospheric boxes spanning 0° to 30°, 30° to 60°, and 60° to 90° latitude north and south. Each tropospheric box was associated with a corresponding stratospheric box; transport within the stratosphere was neglected. Transport between tropospheric boxes was estimated on the basis of existing meteorological data [e.g., Newell *et al.*, 1972].

Uncertainties in modeled sinks arise from uncertainties in several aspects of the analysis including the accuracy and representativeness of ambient measurements, the modeled OH fields, the reaction-rate constants and associated temperature dependencies, transport, and tropospheric sinks not considered in the model (e.g., the presence of other significant oxidants, surface deposition). Absolute errors associated with the assumed OH field were probably small since the average OH in the model was consistent with the average OH inferred from CH₃CCl₃ [Prinn *et al.*, 1995]. The relative importance of other sources of uncertainty varied among species and are discussed below.

Simple calculations based on a modification of the above model were also applied for selected species (C₂Cl₄, C₂HCl₃, and CH₂Cl₂) to provide additional constraints on poorly characterized oceanic emissions inferred from observations. This model ignored troposphere-stratosphere exchange (a minor sink for these compounds, for example, Table 1) and assumed that measured concentrations in the southern hemisphere [Khalil *et al.*, this issue] were in steady state with respect to natural oceanic emissions and chemical destruction (i.e., anthropogenic emissions in the southern hemisphere were assumed to be insignificant). We assume further that the total oceanic source strength per unit area in the Southern Hemisphere was equal to that in the Northern Hemisphere; this assumption is supported by the similarity between estimated emission fluxes of CH₃Cl per unit area in the Northern and Southern Hemispheres [e.g.; Khalil and Rasmussen, 1999b]. On the basis of this approach we derived approximate integrated emission fluxes from the global oceans. Since finite anthropogenic sources exist in the Southern Hemisphere, these estimates probably represent upper limits for oceanic emissions.

3. Results and Discussion

3.1. Inorganic Chlorine

The production of sea-salt aerosol by wind stress at the ocean surface dominates the global emission flux of particulate Cl and of total inorganic Cl; on a global scale, other sources are relatively insignificant (Table 1). Most atmospheric sea salt is associated with supermicron aerosol and, consequently, has a relatively short lifetime against deposition (average of about 1.5 days [Erickson *et al.*, this issue]). Thus under most circumstances, sea-salt aerosol is not transported long distances over land. Although some sea-salt Cl is converted to volatile compounds (see below), most remains in the aerosol and is deposited back to the ocean surface. Concentrations of sea salt in the marine boundary layer over the open ocean vary over several orders of magnitude as an exponential function of wind velocity; average concentrations near the surface range from about 50 to 250 nmol Cl⁻ m⁻³ (1.8 to 8.9 μg

Table 1. Globally Integrated Annual Fluxes for Major Sources and Sinks of Reactive Chlorine in the Troposphere (Tg Cl yr⁻¹)

Species	Sources						Sinks			Transport to		Composite					
	Ocean Open ^a	Coastal ^b	Sea-salt Product and Dechlor. ^c	Terrestrial Ecosystems Fungi ^d	Soils ^e	Volcanos ^f	Biomass Burning ^g	Fossil-fuel Combust. ^h	Inciner- ation ^h	Industry ⁱ	Surface ^j	Chemical Reaction ^k	Stratos ^k	Sources ^l	Total	Sinks ^l	Sources minus Sinks ^l
Particulate Cl			1785	15		2	<6.3	4.6	2		1753	7.6		1803	1761	42	
HCl			7.6								62		-0.3	19	61	-42	
ClNO ₂			0.06									0.06		0.06	0.06	0	
Tot. Inor. Cl			1785	15		2	6.3	4.6	2		1815		-0.3	1815	1815	0	
CH ₃ Cl	0.46	0.0001		0.11			0.64	0.075	0.032	0.007	0.18	2.4	0.2	1.3	2.8	-1.4	
CHCl ₃	0.32	0.0002		0.18			0.002		0.062	0.572	0.04	0.41	0.002	0.56	0.41	0.15	
CH ₂ Cl ₂							0.013		0.313			0.30	0.05	0.59	0.39	0.20	
C ₂ H ₄	0.016							0.002		0.195		0.44	0.00	0.33	0.44	-0.11	
C ₂ H ₂ Cl ₂	0.020							0.003				0.35	0.00	0.22	0.35	-0.13	
CH ₂ Cl ₂	0.16	0.0003					0.049		0.487			0.49	0.01	0.70	0.50	0.20	
CHClF ₂									0.080			0.03	0.01	0.08	0.04	0.04	

^aKhalil *et al.* [this issue]; the CH₃Cl flux corresponds to the proxy approach (see text).

^bSturges *et al.* (unpublished manuscript, 1998).

^cErickson *et al.* [this issue]; the HCl flux corresponds to net production only from "conventional" acid-displacement reactions (see text).

^dWyating and Harper [1998].

^eParticulate Cl from Graedel and Keene [1996]; CHCl₃ from Khalil and Rasmussen [1999a] and Khalil *et al.* [this issue].

^fGraedel and Keene [1995].

^gLobert *et al.* [this issue]; CH₂Cl₂ is the average of estimates based on the emission-ratio approach (0.35 Tg Cl yr⁻¹) and the Cl-content approach (0.91 Tg Cl yr⁻¹).

^hMcCulloch *et al.* [this issue (a, b)].

ⁱCHCl₃ and CHClF₂ from Aucott *et al.* [this issue]; CH₃Cl from Midgley and McCulloch [1995]; other compounds from McCulloch *et al.* [this issue (a, b)].

^jFor particulate Cl and HCl, see text; CH₃Cl from Khalil and Rasmussen [1999b]; CH₂Cl₂ from Graedel and Keene [1995].

^kCH₃Cl from Khalil and Rasmussen [1999b]; CHCl₃ from Khalil and Rasmussen [1999a]; others from this work.

^lAssumes total inorganic Cl emitted from biomass burning is partitioned equally between particulate Cl and HCl.

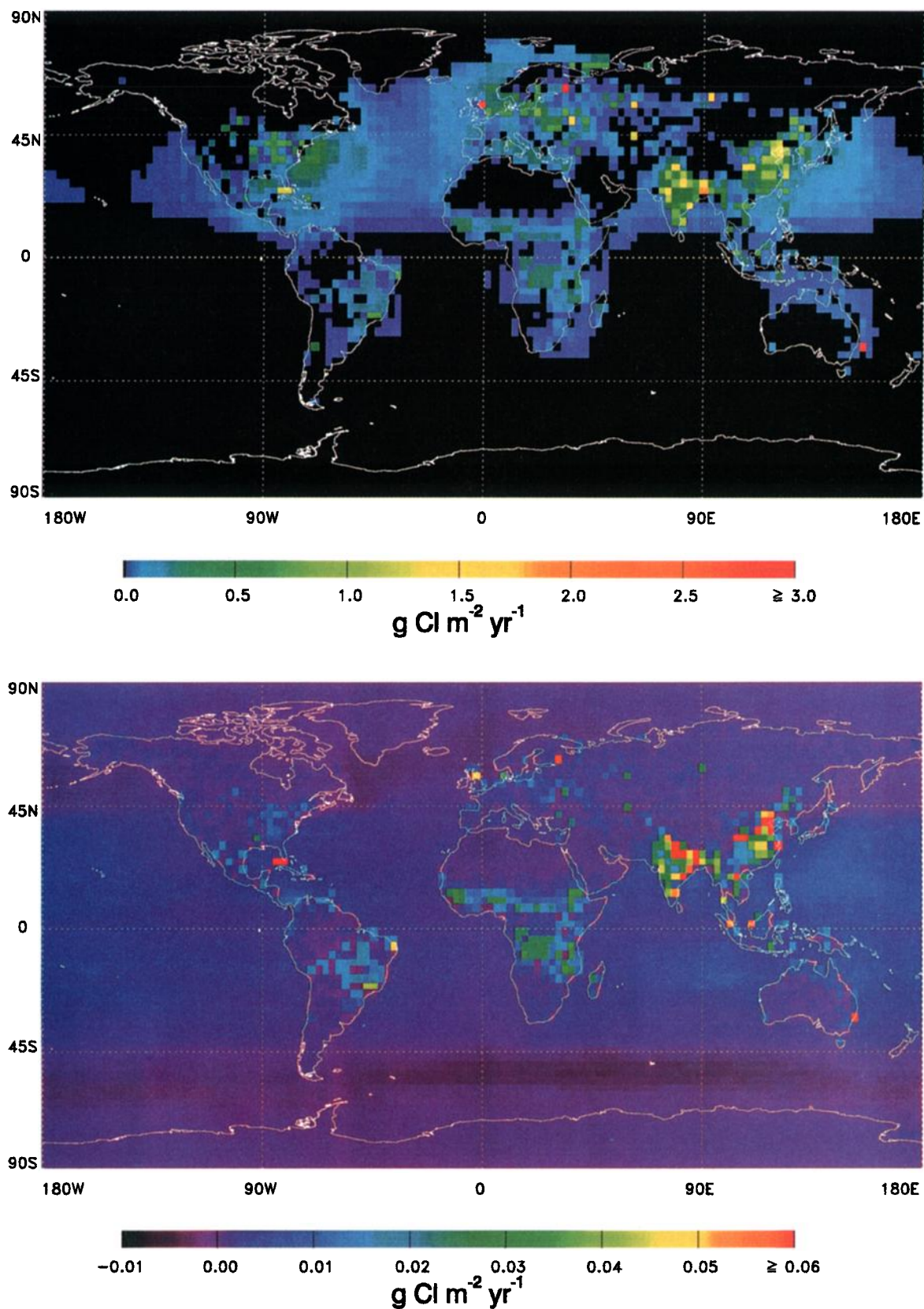


Plate 1. Composite gridded annual emissions of (a) total inorganic chlorine from sea-salt dechlorination, biomass burning, fossil-fuel combustion, and incineration (particulate Cl associated with atmospheric sea salt is not included) and (b) CH_3Cl from the surface ocean, biomass burning, fossil-fuel combustion, incineration, and industry (emissions from wood-rotting fungi have not been gridded).

Cl m⁻³) [Graedel and Keene, 1995 and references therein] yielding a tropospheric burden of about 15 Tg Cl. Concentrations decrease sharply above the marine boundary layer and over continents.

Chemical reactions in deliquesced sea-salt aerosol and on the surface of sea-salt crystals produce volatile inorganic Cl, including HCl, ClNO₂, Cl₂, HOCl, and BrCl [e.g., Pszenny et al., 1993; Graedel and Keene, 1995; Sander and Crutzen, 1996; Vogt et al., 1996; Keene et al., 1998; Oum et al., 1998; Spicer et al., 1998; Erickson et al., this issue]. These transformations are the major sources of reactive Cl gases in the global troposphere. At present, the direct production fluxes of Cl₂, HOCl, and BrCl are very poorly characterized and, thus, cannot be addressed explicitly as part of this analysis. Although possibly important as a source of Cl radicals in some polluted marine regions, production of ClNO₂ from N₂O₃ reactions involving sea salt are minor sources of reactive Cl on a global scale [Erickson et al., this issue].

Until recently, acid-displacement reactions involving H₂SO₄ (produced primarily from S_(IV) + O₃ in deliquesced aerosol) and HNO_{3g} scavenging were widely considered the dominant pathways for the dechlorination of atmospheric sea salt [e.g., Brimblecombe and Clegg, 1988; Chameides and Stelson, 1992; Sievering et al., 1995 and references therein]. On the basis of (1) measured Cl deficits in sea-salt aerosol and measured HCl concentrations in marine air and their respective lifetimes against deposition and (2) estimated amounts of NO_x and SO₂ incorporating into sea salt, Graedel and Keene [1995] infer a global net sea-salt dechlorination flux via acid-displacement reactions of 50 ± 20 Tg Cl yr⁻¹. However, the analysis of Erickson et al. [this issue] suggests that the "conventional" transformations incorporated in their model (including minor contributions from S_(IV) oxidation by H₂O₂ in the aerosol solutions and from H₂SO_{4g} scavenging) produce only about 7.6 Tg Cl yr⁻¹, a small fraction of the dechlorination flux estimated by Graedel and Keene [1995]. The modeled concentrations of particulate-phase reaction products {NO₃⁻ and non-sea-salt (nss) SO₄²⁻} from conventional acid-displacement reactions involving sea salt were also substantially less than observations suggesting that the Erickson et al. model was missing important chemical pathways for sea-salt dechlorination. In particular, the model consistently underestimates nss SO₄²⁻, suggesting that alternative production pathways, such as S_(IV) oxidation by hypohalous acids, may be significant on a global scale [e.g., Vogt et al., 1996; Keene et al., 1998]. Other transformations involving the photolysis of dissolved organic compounds [e.g., Keene et al., 1998], other free radical reactions [Oum et al., 1998], or cloud processing [Pszenny et al., 1998] may also dechlorinate sea salt. We conclude that the principal chemical transformations producing most volatile reactive Cl in the global troposphere are not known with confidence.

Although the absolute magnitude of the flux is poorly constrained, the production of mineral aerosol from the deflation of surface soils is a major source of particulate Cl over arid and semiarid continental regions. Graedel and Keene [1996] infer a global emission flux of about 15 Tg Cl yr⁻¹ based on reported atmospheric deposition of crustal Al and the reported Cl to Al ratios in atmospheric dust; to our knowledge, this is the only published estimate of this flux. Chemical processes involving mineral aerosol are also poorly understood [e.g., Dentener et al., 1996], but based on our knowledge of sea-salt-aerosol chemistry, it is likely that Cl associated with min-

eral aerosol would react in the atmosphere to form volatile inorganic Cl products. This process is virtually unexplored and no estimates of the hypothesized flux are currently available.

Rapid, multiphase chemical transformations in biomass burning plumes preclude the reliable differentiation of primary emissions of volatile inorganic Cl and particulate Cl from secondary products based on field measurements [Lobert et al., this issue]. Thus only total inorganic Cl emissions from this source type were considered in our analysis. About 6.3 Tg Cl yr⁻¹ of total inorganic Cl (particulate plus vapor) are emitted to the atmosphere from biomass burning globally [Lobert et al., this issue].

Volcanoes are important sources for tropospheric HCl, but emission fluxes vary interannually by large amounts [e.g., Symonds et al., 1988]. For the budget calculations herein, we adopt an average annual flux of 2 Tg Cl yr⁻¹ [Graedel and Keene, 1995]. HCl is also produced from coal combustion (4.6 Tg Cl yr⁻¹) and incineration (2 Tg Cl yr⁻¹) [McCulloch et al., this issue (a)]. Finally, on the basis of Prather et al. [1990] we infer a stratospheric Cl sink of 0.3 Tg Cl yr⁻¹ and assume that this corresponds to a net transport of HCl from the stratosphere to the troposphere. Although uncertain, this flux is small and has relatively little impact on the tropospheric HCl budget.

The global distribution of integrated annual emissions of total inorganic Cl from sources considered explicitly by the RCEI (sea-salt dechlorination [Erickson et al., this issue], biomass burning [Lobert et al., this issue], coal combustion, and incineration [McCulloch et al., this issue (b)]) is depicted in Plate 1a; because they would overwhelm other fluxes, emissions of particulate sea-salt Cl were excluded. Most inorganic Cl is emitted in the Northern Hemisphere. Maxima in China and India reflect significant direct emissions from both coal combustion and biomass burning. Secondary peaks in Europe and eastern North America are primarily associated with coal combustion. Reaction of combustion-derived S and N compounds with sea-salt aerosol produces significant HCl over the North Atlantic and western North Pacific Oceans. Emissions in equatorial regions and in the Southern Hemisphere originate primarily from biomass burning; coal combustion is an important additional source in some populated and industrial regions of South America, Africa, and Australia.

Global budgets of particulate Cl and of HCl based on the "best estimates" summarized above are depicted in Figures 1a and 1b. Following Graedel and Keene [1995] we assume a net global production (i.e., total production minus scavenging) of HCl via acid-displacement reactions involving sea-salt aerosol of 50 Tg Cl yr⁻¹. In addition, for purposes of budget closure, we arbitrarily assume that equal amounts of HCl and particulate Cl are emitted from biomass burning. The budgets are balanced by deposition to the surface. The inferred deposition fluxes of particulate Cl (Table 1) are consistent with sea-salt fluxes modeled by Erickson et al. [this issue], and those of HCl are consistent with budget calculations by Graedel and Keene [1995]. The relatively slow reaction of HCl with OH to produce atomic Cl [Singh and Kasting, 1988] may represent a significant flux in the HCl budget [Graedel and Keene, 1995]. However, most Cl atoms in the troposphere react rapidly with hydrocarbons via H abstraction [e.g., Keene et al., 1996], which would efficiently regenerate the precursor HCl. Thus this efficient gas-phase cycle is not a

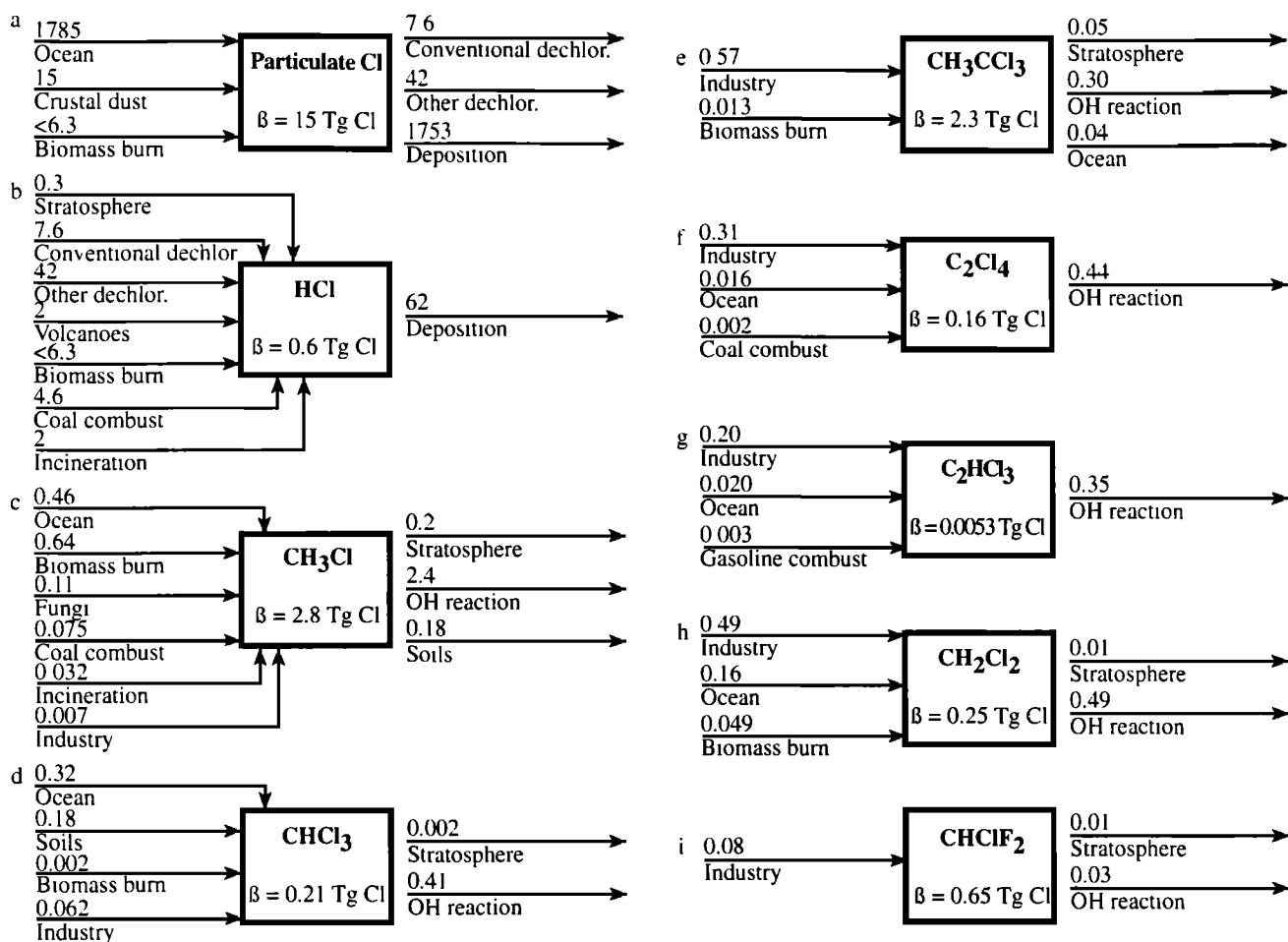


Figure 1. Global budgets of reactive Cl in the troposphere: (a) particulate Cl, (b) HCl, (c) CH₃Cl, (d) CHCl₃, (e) CH₃CCl₃, (f) C₂Cl₄, (g) C₂HCl₃, (h) CH₂Cl₂, (i) CHClF₂. Fluxes in Tg Cl yr^{-1} , burdens (β) in Tg Cl .

significant net sink for tropospheric HCl. The indicated sea-salt dechlorination fluxes represent net volatilization (total volatilization minus scavenging); recycling of volatile Cl (primarily as HCl) to the aerosol [e.g., Keene *et al.*, 1990; Keene and Savoie, 1998; Erickson *et al.*, this issue] is not explicitly considered in the budget evaluation; this recycling flux may be substantially greater than the net dechlorination flux [e.g., Graedel and Keene, 1995]. The HCl budget suggests that "other" as yet unresolved processes dechlorinate sea-salt aerosol; these "other" chemical transformations appear to be the most important sources of volatile Cl in the global troposphere. This conclusion is consistent with recent ion-balance analyses of the chemical composition of size-segregated marine measured over the open ocean, which indicate that "conventional" dechlorination processes involving H₂SO₄ (in particular the S_(IV) + O₃ pathway in supermicron sea salt) account for less than 25% of observed nss SO₄²⁻ in coarse marine aerosol [Pszenny *et al.*, 1998].

On a global scale, the production of particulate Cl is dominated by natural processes; the major anthropogenic sources (mineral-aerosol production associated with anthropogenic desertification and most biomass burning) account for substantially less than 1% of the total flux. Approximately half the HCl emitted directly from sea-salt aerosol via acid-displacement reactions involves precursors derived from

anthropogenic combustion [Graedel and Keene, 1996]. Assuming that (1) most stratospheric HCl originates from the degradation of long-lived, Cl-containing compounds of anthropogenic origin, (2) all inorganic Cl emitted from biomass burning is in the form of HCl (an upper limit), and (3) 90% of biomass burning is anthropogenic (J. S. Levine, personal communication, 1996), we estimate that greater than 50% of the total annual HCl emission flux involves anthropogenic sources or precursor compounds.

With regard to emissions of inorganic Cl (and Cl-containing organic compounds discussed below) from biomass burning, the relative contributions from natural and anthropogenic burns are highly uncertain and subject to debate. Extensive regions of the Earth's surface are burned each year through intentional and unintentional human intervention. However, many impacted ecosystems would burn naturally, albeit perhaps less frequently, in the absence of such influences. Thus extrapolating estimates for the current natural and anthropogenic contributions to biomass burning relative to the conditions that would exist in the absence of technologically capable humans is problematic.

3.2. CH₃Cl

With an average tropospheric mixing ratio of about 540 pptv and a global burden of about 2.8 Tg Cl, methylchloride

is the most abundant reactive Cl gas in the troposphere [Khalil *et al.*, this issue]. The major known sources are biomass burning, emissions from the open ocean, and production by wood-rotting fungi [Khalil *et al.*, this issue; Lobert *et al.*, this issue]; emissions from macrophytes (W. T. Sturges *et al.*, manuscript in preparation, 1998) and from coal combustion, incineration, and industrial processes [McCulloch *et al.*, this issue (a)] are of relatively minor importance. The major atmospheric sink for CH₃Cl is reaction with OH yielding a tropospheric lifetime of about 1.3 years [Khalil, 1999]. A relatively small but significant amount of tropospheric CH₃Cl (about 0.2 Tg Cl yr⁻¹) is transported to the stratosphere and subsequently destroyed by photo dissociation and reaction with OH. Although oceans are a net source globally, high-latitude ocean waters appear to be significant net regional sinks for tropospheric CH₃Cl [Lobert *et al.*, 1996; Moore *et al.*, 1996; Khalil *et al.*, this issue]. Available, albeit limited, experimental data reveal a consistent pattern of CH₃Cl uptake by soils over broad geographic regions [Khalil and Rasmussen, 1999b]. Although uncertain, this flux appears to be globally significant and is included in our budget assessment. CH₃Cl losses via oxidation by atomic Cl in the marine boundary layer may also be important [e.g., Keene *et al.*, 1996] but at present cannot be reliably quantified.

As discussed by Khalil *et al.* [this issue], the annual net global oceanic-emission flux estimated by direct extrapolation of experimental observations (0.31 Tg Cl yr⁻¹) and by the gridded proxy approach (0.46 Tg Cl yr⁻¹) is substantially less than those suggested by some previous assessments [e.g., Singh *et al.*, 1983a; Fabian, 1986; Tait *et al.*, 1994]. RCEI results indicate that oceanic emissions account for a relatively minor fraction (10% to 20%) of the total annual emission flux of CH₃Cl required to balance modeled atmospheric sinks. Moore *et al.* [1996] report similar results based on a subset of the information used to generate the RCEI oceanic-emissions inventory [Khalil *et al.*, this issue].

Biomass burning fluxes were estimated on the basis of both the emission-ratio approach and the Cl-content approach, which yielded integrated global fluxes of 0.35 and 0.91 Tg Cl yr⁻¹, respectively [see Lobert *et al.*, this issue, for detailed description]. We adopted the averages of these two approaches as our best estimates of actual emissions; on a global scale, the integrated flux (0.64 Tg Cl yr⁻¹) is near the lower limit of the range estimated by Andreae *et al.* [1996] (0.74 to 1.0 Tg Cl yr⁻¹).

Certain wood-rotting fungi produce significant quantities of CH₃Cl, which are emitted to the atmosphere. As part of the RCEI effort, Khalil *et al.* [this issue] [also see Watling and Harper, 1998] estimated a global flux from this source of 0.11 Tg Cl yr⁻¹. To our knowledge, no other global estimates for fungal emissions have been published.

The global distribution of integrated annual CH₃Cl emissions from major known sources considered explicitly by the RCEI is depicted in Plate 1b (emissions from wood-rotting fungi are not included). Peak emissions in southern Asia, central Africa, and central South America are primarily from biomass burning; emissions from biomass burning in the temperate Northern Hemisphere are relatively less important. More spatially diffuse oceanic emissions, which peak in western equatorial Pacific, are significant on a global scale.

The composite CH₃Cl budget based on our "best guess" estimates of the associated fluxes reveals a substantial imbalance

(1.4 Tg Cl yr⁻¹) between known sources and modeled sinks (Table 1), indicating a deficiency in our understanding of the tropospheric CH₃Cl cycle. Three possible explanations may account for the calculated imbalance: (1) One (or more) of the emission fluxes is substantially underestimated; (2) the atmospheric sink for CH₃Cl from OH oxidation is substantially overestimated (the combined sink from uptake by soils and transport to the stratosphere is small relative to the imbalance); or (3) a major unidentified source (or sources) for CH₃Cl is not included.

Overall uncertainties in CH₃Cl emissions from known sources are relatively large and if one or more is substantially underestimated may account for the apparent discrepancy (see uncertainty analyses in companion papers). Alternatively, as mentioned by Moore *et al.* [1996] and discussed in more detail by Khalil *et al.* [1999b], the modeled atmospheric sink from CH₃Cl + OH is also associated with substantial uncertainties. Largest among these is the uncertainty in the temperature dependence of the rate constant in the Arrhenius expression ($1400 \pm 250^\circ$) [DeMore *et al.*, 1997], which corresponds to a range in the atmospheric sink from 2.0 to 3.2 Tg Cl yr⁻¹. This uncertainty alone could account for much of the apparent discrepancy in the global budget.

The budget imbalance may also reflect significant unidentified sources for CH₃Cl. Direct emissions from many likely natural and anthropogenic sources have been critically evaluated by numerous investigators (e.g., see RCEI papers in this special section and references therein). However, the potential importance of emissions from higher plants is unknown. Some higher plants produce CH₃Cl from Cl⁻ in vitro but the emission flux from terrestrial vegetation in their natural habitat has not been quantified [e.g., Harper, 1997; Watling and Harper, 1998, and references therein]. In addition, the potential production of CH₃Cl from chemical transformations in the atmosphere has received relatively little attention. Laboratory studies demonstrate that CH₃Cl is produced in low yield from the oxidation of dimethylsulfide by atomic Cl [Langer *et al.*, 1996]. Although this pathway could account for less than 1% of total CH₃Cl inferred from inversion modeling, it does suggest the possibility that other atmospheric transformations, either in the gas phase or perhaps involving Cl in sea-salt aerosol, may produce significant CH₃Cl. In this regard, we note that Cl-addition reactions involving atomic Cl may also produce other chlorinated compounds in the troposphere, such as 1-chloro-3-methyl-3-butene-2-one from isoprene [Nordmeyer *et al.*, 1997] and chlorinated PAHs from PAH precursors [e.g., Keene *et al.*, 1996].

The latitudinal distributions of composite sources and modeled sinks are depicted in Figure 2. Relative to temperate and polar regions, OH concentrations are substantially higher and CH₃Cl concentrations may be somewhat higher in the tropics and subtropics (30°N to 30°S). Consequently, approximately 85% of CH₃Cl must be produced in these regions of the Earth to balance the modeled sink [Khalil, 1999]. Emissions from major known sources are concentrated in the tropics; thus if associated fluxes are underestimated, the largest discrepancies would be evident in the regions. Alternatively, if significant unidentified sources for CH₃Cl exist, they would be concentrated in these regions.

Resolution of the CH₃Cl budget imbalance has potentially important implications for understanding sources of stratospheric Cl. The Montreal Protocol has led to substantial reductions in emissions of the chlorofluorocarbons and related

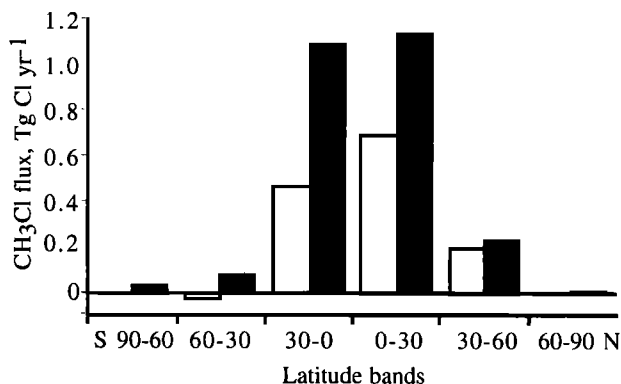


Figure 2. Latitudinal distribution of net composite annual emissions of CH_3Cl from major known sources considered by the Reactive Chlorine Emissions Inventory (ocean, fungi, biomass and fossil-fuel combustion, incineration, and industry) (open bars) compared with latitudinal distribution of modeled sinks for tropospheric CH_3Cl associated with OH oxidation and transport to the stratosphere (solid bars).

Cl-containing gases; consequently, fluxes of Cl to the stratosphere are beginning to decline [e.g., Prather and Watson, 1990; Prinn et al., 1995; Montzka et al., 1996]. Over the past two decades, CH_3Cl has contributed significant fractions (about 15% to 25%) of the total Cl flux to the stratosphere [Crutzen and Gidel, 1983; Prather and Watson, 1990; Montzka et al., 1996]. The percentage contribution of CH_3Cl is expected to increase in the future as emissions of long-lived anthropogenic compounds decline. Thus understanding the details of CH_3Cl cycling in the troposphere will become increasingly important in developing a predictive capability for stratospheric Cl chemistry.

In contrast to most previous studies [e.g., Graedel and Keene, 1995, and references therein], our results suggest that emissions from natural sources do not necessarily dominate the global CH_3Cl cycle. Assuming that biomass burning is 90% anthropogenic, about half the net CH_3Cl emissions from known sources evaluated as part of this investigation are of anthropogenic origin, most from biomass burning. Concentrations of CH_3Cl in ice cores would provide useful context for evaluating anthropogenic contributions. However, until the large budget imbalance is resolved, it will be impossible to reliably differentiate the relative importance of natural versus anthropogenic sources of CH_3Cl in the present-day atmosphere.

3.3. CHCl_3

The average mixing ratio of tropospheric CHCl_3 is about 18 pptv, yielding a tropospheric burden of about 0.21 Tg Cl [Khalil and Rasmussen, 1999a, and references therein]. CHCl_3 is nearly twice as abundant in the Northern Hemisphere as it is in the Southern Hemisphere. The major global sources for tropospheric CHCl_3 are poorly characterized but appear to be direct emissions from the surface ocean, soils, and fungi [Hoekstra et al., 1998a, b; Khalil and Rasmussen, 1999a; Khalil et al., this issue]; estimated emissions from industrial sources (primarily pulp and paper manufacturing and water treatment) [Aucott et al., this issue] and biomass burning [Lobert et al., this issue] contribute substantially smaller amounts (Figure 1d). Emissions from marine macro-

phytes appear to be insignificant (W. T. Sturges et al., unpublished manuscript, 1998, Table 1). The major tropospheric sink is reaction with OH yielding an average lifetime of about 0.5 years. A small amount of CHCl_3 (about 0.002 Tg Cl yr⁻¹) is transported to the stratosphere.

The latitudinal distribution of integrated annual CHCl_3 emissions from known sources considered explicitly by the RCEI is compared with modeled sinks in Figure 3. The large inconsistencies between estimated sources and sinks arise in part from the sparse observational data currently available. The oceanic flux of CHCl_3 estimated by Khalil et al. [this issue] (0.32 Tg Cl yr⁻¹) is sufficiently large to account for 78% of the global source required to balance modeled sinks (0.41 Tg Cl yr⁻¹). However, it is difficult to reconcile the apparent dominance of an oceanic source with the observed interhemispheric differences in CHCl_3 concentrations. These concentration distributions suggest substantially greater source strengths in the Northern Hemisphere, which contains only about 40% of the Earth's oceans. Since industrial CHCl_3 emissions are relatively low and reasonably constrained [Aucott et al., this issue], CHCl_3 emissions from soils or other components of terrestrial ecosystems [e.g., Hoekstra et al., 1995, 1998a, b] may be larger and oceanic emissions smaller than suggested by flux estimates reported herein. Additional experimental work is needed to resolve these apparent discrepancies in the global CHCl_3 budget.

Our results suggest that natural sources of CHCl_3 dominate its tropospheric cycle. Estimated emissions from anthropogenic sources account for only about 10% of the estimated combined total emitted from all sources (0.56 Tg Cl yr⁻¹). Although the calculated imbalance between globally integrated emissions and tropospheric sinks (0.15 Tg Cl yr⁻¹) is small relative to overall uncertainties in the analysis, latitudinal distributions of estimated sources and sinks reveal substantial discrepancies (Figure 3).

3.4. CH_2CCl_2

Virtually all atmospheric methylchloroform was produced by industry for use as a degreasing agent [Midgley and McCulloch, 1995]; small amounts of CH_2CCl_2 may also be emitted from biomass burning [Rudolph et al., 1995] although, on a global scale, this flux [Lobert et al., this issue] would

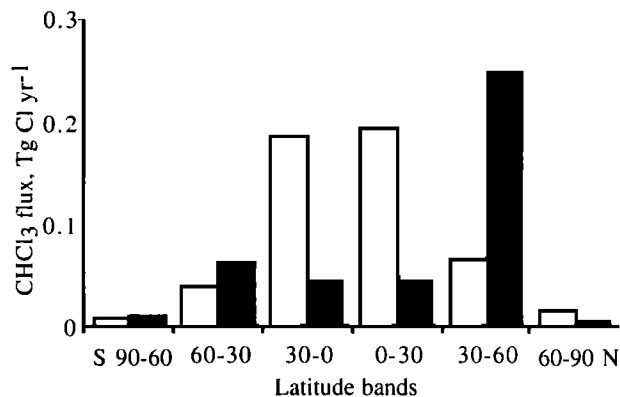


Figure 3. Latitudinal distribution of composite annual emissions of CHCl_3 from major known sources considered by the RCEI (ocean, soils, biomass burning, and industry) (open bars) compared with latitudinal distribution of modeled sinks for tropospheric CHCl_3 (solid bars).

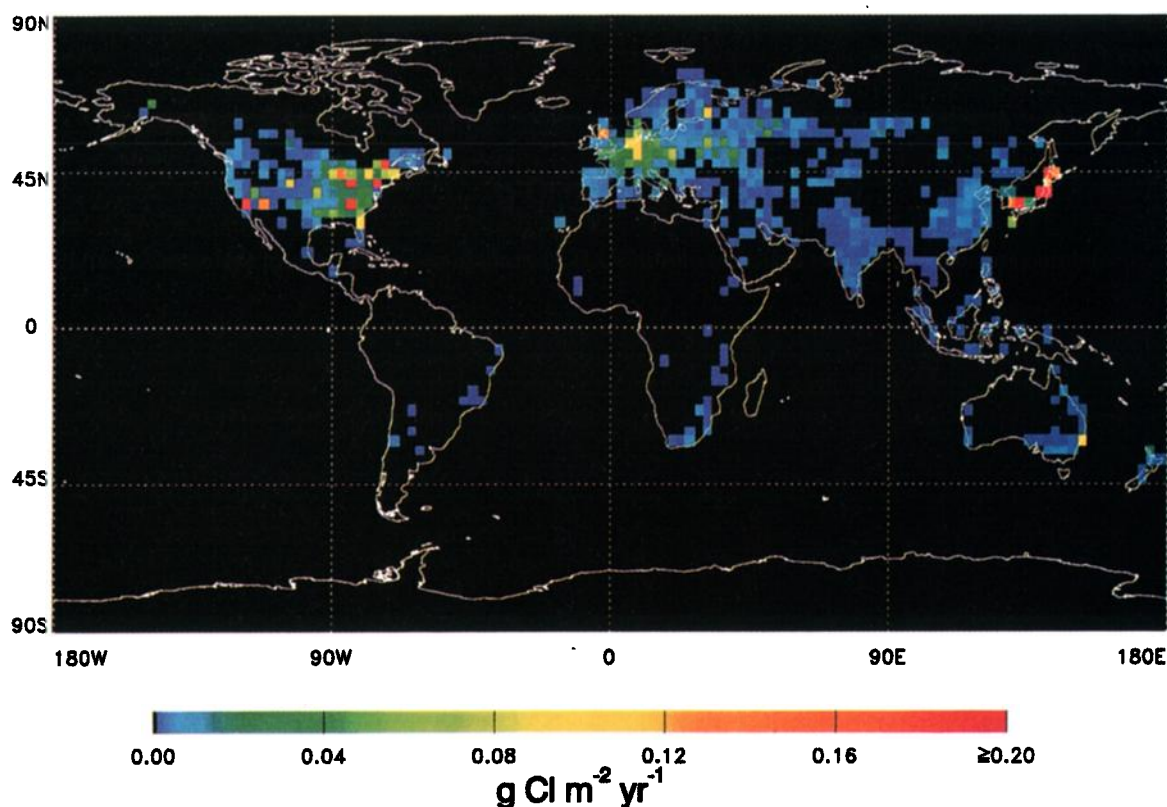


Plate 2. Composite gridded annual emissions of CH_2CCl_3 from industrial sources and biomass burning.

account for only about 2% of total emissions (Figure 1e). Tropospheric CH_2CCl_3 concentrations rose through the 1970s and 1980s as industrial production expanded but decreased sharply ($12.5\% \text{ year}^{-1}$) following implementation of the Montreal Protocols in the late 1980s and early 1990s [Prinn *et al.*, 1995; Khalil, 1999]. Atmospheric concentrations are now declining [e.g., Montzka *et al.*, 1996]. In 1990, ambient mixing ratios averaged about 125 pptv [Prinn *et al.*, 1995], yielding a tropospheric burden of about $2.3 \text{ Tg Cl yr}^{-1}$. At that time, concentrations were about 20% higher in the Northern than in the Southern Hemisphere; the interhemispheric difference decreased to about 4% by 1995 in response to decreased emissions [Khalil, 1999]. The lifetime of CH_2CCl_3 in the atmosphere is about 4.8 years [Prinn *et al.*, 1995]. Reaction with OH is the principal sink; losses to the stratosphere and to the surface ocean are also significant (Table 1, Fig. 1e). The budget imbalance between sources and sinks (Figure 1e) is consistent with increasing atmospheric concentrations during the 1990 reference year.

The global distribution of integrated annual CH_2CCl_3 emissions in 1990 is depicted in Plate 2; deposition fluxes to the ocean have not been gridded. Emissions peak in industrialized regions of North America, Europe, and Japan.

3.5. C_2Cl_4 , C_2HCl_3 , and CH_2Cl_2

Industrial production and subsequent emission to the atmosphere [McCulloch and Midgley, 1996; McCulloch *et al.*, this issue (b)] are major global sources of tropospheric perchloroethylene, trichloroethene, and methylene chloride. Mixing ratios of C_2Cl_4 in the Northern and Southern Hemispheres are

about 17 and 3 pptv, respectively; those for C_2HCl_3 are about 3 and 0.7 pptv, respectively; and those for CH_2Cl_2 are 40 and 17 pptv, respectively [Khalil, 1999; Khalil *et al.*, this issue; and references therein]. These large interhemispheric differences reflect the significant contributions of anthropogenic emissions to ambient concentrations in the Northern Hemisphere. The corresponding tropospheric burdens are approximately $0.16 \text{ Tg Cl C}_2\text{Cl}_4$, $0.0053 \text{ Tg Cl C}_2\text{HCl}_3$, and $0.25 \text{ Tg Cl CH}_2\text{Cl}_2$.

The potential importance of C_2Cl_4 , C_2HCl_3 , and CH_2Cl_2 production by biological processes in the surface ocean is uncertain; some incubation studies suggest significant production [e.g., Abrahamsson *et al.*, 1995a, b] and others do not (R. M. Moore, unpublished manuscript, 1998, and D. B. Harper, unpublished manuscript, 1998). Emissions from marine macrophytes appear to be insignificant on a global scale (W. T. Sturges *et al.*, unpublished manuscript, 1998, and references therein, Table 1). However, measured supersaturations of C_2Cl_4 , C_2HCl_3 , and CH_2Cl_2 in surface seawater [Singh *et al.*, 1983b; V. Koropalov, unpublished data, 1998; J. M. Lobert and J. H. Butler, unpublished data, 1998], indicate significant fluxes of all three compounds from the ocean to the atmosphere. Fossil-fuel combustion (C_2Cl_4 and C_2HCl_3) and biomass burning (CH_2Cl_2) represent additional minor sources (Table 1, Figures 1f, 1g, 1h). C_2Cl_4 , C_2HCl_3 , and CH_2Cl_2 are removed from the atmosphere primarily by reaction with OH yielding atmospheric lifetimes of about 113, 6, and 150 days, respectively. Significant C_2Cl_4 may also be oxidized by Cl atoms in the marine boundary layer although the magnitude of this flux is very poorly constrained [Singh *et al.*, 1996] and not considered in this analysis.

Production data provided by industry allow anthropogenic emissions to be estimated with a high degree of confidence (within about $\pm 6\%$) [McCulloch and Midgley, 1996]. In contrast, the corresponding natural emissions are based on very limited data and thus are considered preliminary. The oceanic flux of C_2Cl_4 estimated by Khalil *et al.* [this issue] (0.016 , Tg Cl yr^{-1} , Table 1) is within a factor of 2 of that inferred by Singh *et al.* [1996] (0.030 Tg Cl yr^{-1}) based on surface-water supersaturations, measured mixing ratios in surface marine air, and model calculations. Aucott [1997] applied an inversion modeling approach to explicitly solve for the natural emissions of C_2Cl_4 , C_2HCl_3 , and CH_2Cl_2 required to balance the global budgets. Those results suggest a somewhat higher combined flux of C_2Cl_4 (0.086 Tg Cl yr^{-1}) from all natural sources. Khalil *et al.*'s [this issue] estimate of the oceanic C_2HCl_3 flux (0.020 Tg Cl yr^{-1} , Table 1) is about a factor of 8 lower than natural emissions from all sources estimated by Aucott [1997] (0.16 Tg Cl yr^{-1}); the RCEI estimate of CH_2Cl_2 emitted from the surface ocean (0.16 Tg Cl yr^{-1} , Table 1) is within the tight range of previous estimates by Singh *et al.* [1996] (0.15 Tg Cl yr^{-1}) and Aucott [1997] (0.17 Tg Cl yr^{-1}).

On the basis of the RCEI results, oceanic emissions account for significant fractions of C_2Cl_4 (about 5%), C_2HCl_3 (about 10%), and CH_2Cl_2 (about 25%) emitted from known sources to the atmosphere on a global scale (Table 1, Figures 1f, 1g, 1h). Aucott's [1997] calculations suggest substantially higher relative contributions of C_2Cl_4 (22%) and C_2HCl_3 (44%) from all natural sources. Because anthropogenic sources are concentrated in the Northern Hemisphere, natural emissions are relatively more important sources for all three species in remote southern hemispheric regions.

As described in section 2.2, we applied simple model calculations to provide additional constraints on the contributions of oceanic sources to global burdens. This approach is based on the assumptions that (1) southern hemispheric concentrations are in steady state with respect to oceanic emissions and chemical destruction (i.e., anthropogenic sources in the Southern Hemisphere are insignificant) and (2) oceanic emissions per-unit area in the Southern Hemisphere are the same as those in the Northern Hemisphere. Resulting estimates are considered upper limits for the actual emissions from the surface ocean. These calculations yielded fluxes of 0.077 Tg Cl yr^{-1} of C_2Cl_4 , 0.073 Tg Cl yr^{-1} of C_2HCl_3 , and 0.21 Tg Cl yr^{-1} of CH_2Cl_2 corresponding to 18%, 21%, and 42%, respectively, of the total source strengths required to balance modeled sinks.

On the basis of RCEI results, modeled sinks exceed estimated sources for both C_2Cl_4 and C_2HCl_3 (Table 1). Decreasing atmospheric concentrations of C_2Cl_4 [e.g., McCulloch and Midgley, 1996] and greater oceanic (or other natural) emissions of both compounds may account for these discrepancies. However, apparent imbalances for all three compounds are within overall uncertainties for their respective budget-closure calculations.

3.6. $CHClF_2$

$CHClF_2$ is an interim replacement for some chlorofluorocarbons restricted under the Montreal Protocols; industrial production for use in air conditioning, refrigeration, and foam generation is the only known source [Houghton *et al.*, 1992; McCulloch, 1994]. Moderate increases in production of $CHClF_2$ (and associated leakage from equipment) coupled

with an atmospheric lifetime of about 13 years have led to rapidly increasing tropospheric concentrations (7% yr^{-1} [Montzka *et al.*, 1993]). Average northern hemispheric concentrations in 1990 were about 95 pptv; those in the Southern Hemisphere were about 12% lower [Montzka *et al.*, 1993, 1996]. The global burden in 1990 was about 0.65 Tg. The major tropospheric sinks are reaction with OH and transport to the stratosphere (Table 1, Figure 1g) [Khalil, 1999]. Although potentially important, losses to the surface ocean and soils have not, to our knowledge, been critically evaluated. The imbalance in the global tropospheric budget for $CHClF_2$ (Table 1) is approximately equal to that expected on the basis of increasing tropospheric concentrations.

4. Conclusions

1. Conventional acid-displacement reactions involving $S_{(IV)} + O_3$, $S_{(IV)} + H_2O_2$ and H_2SO_4 and HNO_3 gas scavenging account for minor fractions of sea-salt dechlorination globally. Other important chemical pathways involving sea-salt aerosol apparently produce most volatile chlorine in the global troposphere.

2. The combined contributions from biomass burning, oceanic emissions, wood-rotting fungi, coal combustion, incineration, and industrial emissions estimated by the RCEI account for about half the CH_3Cl emission source inferred from inversion modeling. These results suggest that either emissions from known sources have been substantially underestimated, the atmospheric sink from oxidation by OH has been substantially overestimated, or other as yet unidentified sources produce large fractions of tropospheric CH_3Cl . Anthropogenic emissions, primarily biomass burning, account for about 50% of known CH_3Cl sources considered in this analysis.

3. Anthropogenic emissions account for about 10% of tropospheric $CHCl_3$. Although relative magnitudes and associated distributions are uncertain, emissions of $CHCl_3$ from the surface ocean and soils appear to be the principal global sources.

4. Emissions from the surface ocean are very poorly constrained but apparently account for significant fractions of CH_2Cl_2 (25%), C_2HCl_3 (10%), and C_2Cl_4 (5%) in the global troposphere; the combined contributions of C_2Cl_4 and C_2HCl_3 from all natural sources may be substantially higher.

5. Access to On-Line Data

All gridded inventories generated by the RCEI are available online through the project web site at <<http://groundhog.sprl.umich.edu/geia/rcei>>. We plan to update these inventories as new information becomes available.

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