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Methyl chloride and other chlorocarbons in polluted air during INDOEX

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[1] Methyl chloride (CH_3Cl) is the most abundant, natural, chlorine-containing gas in the atmosphere, with oceans and biomass burning as major identified sources. Estimates of global emissions suffer from large uncertainties, mostly for the tropics, partly due to a lack of measurements. We present analyses of whole-air canister samples for selected nonmethane hydrocarbons and chlorocarbons. The samples were collected from an aircraft during the Indian Ocean Experiment (INDOEX) campaign over the northern Indian Ocean in February and March 1999. The CH_3Cl results are correlated to selected nonmethane hydrocarbons and in situ measurements of carbon monoxide (CO) and acetonitrile (CH_3CN). We relate high mixing ratios of $\sim 750 \text{ pmol mol}^{-1}$ of CH_3Cl to biomass burning, as observed in polluted air masses from India and Southeast Asia. We infer a relatively high enhancement ratio relative to CO, $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO} \approx 1.74 \pm 0.21 \times 10^{-3} \text{ mol mol}^{-1}$. The CH_3Cl levels relate to the extensive biofuel use in India and Southeast Asia, notably the burning of agricultural waste and dung with a comparatively high chlorine content. It appears that CH_3Cl emissions from biofuel consumption in India and Southeast Asia have been underestimated in the past. Furthermore, we observed enhanced dichloromethane (CH_2Cl_2) and trichloromethane (CHCl_3) levels, correlating with high CO, acetylene (C_2H_2) and CH_3Cl , indicating that biomass burning is a small but significant source of these species.

INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); **KEYWORDS:** methyl chloride, chlorocarbons, biomass burning, biofuel use, biosphere-atmosphere interactions, Southeast Asia

1. Introduction

[2] Recently, extensive surveys on the abundance and importance of chlorocarbons for atmospheric chemistry have been published [Keene *et al.*, 1999; Khalil and Rasmussen, 1999; Lobert *et al.*, 1999; McCulloch *et al.*, 1999]. They highlight the importance of methyl chloride (CH_3Cl) as the most abundant halocarbon, estimated to be about 43% of the total reactive chlorine in the troposphere [Khalil and Rasmussen, 1999]. The known sources of CH_3Cl , as described by Keene *et al.* [1999], include about 48% from biomass burning, $\sim 35\%$ by oceans and $\sim 8\%$ by wood rotting fungi. Furthermore, emissions from urban/industrial activity (including coal burning) contribute about 9%. The main sink of CH_3Cl in the troposphere is the reaction with OH radicals ($\sim 86\%$), resulting in an average atmospheric lifetime of about 1.3 years [Khalil, 1999]. A

minor but significant loss mechanism is transport to the stratosphere, where CH_3Cl is destroyed by photo-dissociation and reaction with OH [Keene *et al.*, 1999], from which the reactive chlorine contributes to ozone loss. The relative contribution of CH_3Cl to the total recent Cl flux to the stratosphere has been estimated at 15–25% [Montzka *et al.*, 1996]. This fractional contribution is likely to increase in the near future due to the decline of long-lived anthropogenic halocarbons in response to the Montreal Protocol. The composite budget for CH_3Cl by Keene *et al.* [1999], however, suggests a substantial underestimation of sources ($1.32 \text{ Tg Cl yr}^{-1}$) as compared to modeled sinks ($2.78 \text{ Tg Cl yr}^{-1}$), i.e., about $1.45 \text{ Tg Cl yr}^{-1}$ ($\text{Tg} = 10^{12} \text{ g}$). Three possible explanations may account for the imbalance. Keene *et al.* [1999] state that the relatively large uncertainties of the emissions from known sources allow the possibility that one or more emission fluxes have been significantly underestimated. Second, a considerable uncertainty in the temperature dependence of the rate constant of the CH_3Cl oxidation by OH (described by DeMore *et al.* [1997]) could contribute to the discrepancy. Thirdly, the emissions from higher plants, which are not taken into account due to the lack of field measurement, may represent a major unidentified source of CH_3Cl . According to Khalil and Rasmussen [1999], 85% of CH_3Cl from known sources

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is produced in the tropics and subtropics in the 30°S–30°N latitude band.

[3] Here we focus on biomass burning, which is estimated to be the largest global source of CH_3Cl and a significant source for dichloromethane (methylene chloride, CH_2Cl_2). Biomass burning appears to be mainly human-induced, with savanna fires and the burning of biofuels as major contributors [Lobert *et al.*, 1999]. Present estimates indicate that the use of biofuels, such as fuelwood, charcoal, agricultural residues waste and dung, and open field burning of unusable crop residues, contributes more than half ($\sim 53\%$) to the CH_3Cl emissions (and about 38% of both the CH_2Cl_2 and trichloromethane (chloroform, CHCl_3) emissions) from biomass burning [Lobert *et al.*, 1999]. India and neighboring countries, have the comparatively largest consumption of biofuel, which contributes about 25% to the global biofuel emissions [Olivier *et al.*, 1996]. Biomass burning emissions in Southeast Asia are responsible for about a third of all CH_3Cl emissions from biomass burning of $0.64 \text{ Tg Cl yr}^{-1}$, as estimated by Lobert *et al.* [1999].

[4] We present hydrocarbon and chlorocarbon measurements from air samples, with emphasis on CH_3Cl , collected over the tropical Indian Ocean in February/March 1999 during the Indian Ocean Experiment (INDOEX). The measurement area was affected by pollution outflow from India and Southeast Asia, inhabited by about half the world's human population. The measurements encompass air samples both with a strong continental influence and from the pristine southern Indian Ocean atmosphere. Enhancement ratios relative to carbon monoxide (CO) for CH_3Cl and other chlorocarbons, notably CH_2Cl_2 and CHCl_3 , are inferred from the measurements, which we compare to available emission factors for biomass burning from the literature. We will use the CH_3Cl enhancement ratio to estimate emissions from biomass burning in India and Asia. Finally, we discuss the uncertainties in presently estimated source contributions from biomass burning for CH_3Cl .

2. Field Campaign and Measurement Techniques

2.1. The INDOEX Campaign

[5] The INDOEX field campaign was an international collaboration between institutes from the United States, Europe, India and the Maldives, involving various measurement platforms on land, sea and in the air. The main purpose of INDOEX was to characterize the pollutant outflow from India and Southeast Asia and to study the effect on atmospheric chemistry and solar radiation attenuation by aerosols. We present measurements performed on-board a Cessna Citation-II twinjet aircraft operated by the Delft University of Technology, Netherlands. The aircraft was operated from the international airport of Malé, the capital of the Maldives. A total of 23 flights was performed up to 12.5 km altitude between 7°S and 8°N over the Indian Ocean. A detailed description of the flights, measurement payload during INDOEX, as well as an overview of the results is given by de Gouw *et al.* [2001]. Here we only summarize the measurement techniques relevant for this paper. For an overview of the main results from the different measurement platforms operating during INDOEX, focusing on the chemical composition of

the outflow from South and Southeast Asia, we refer to Lelieveld *et al.* [2001].

2.2. Measurements of Hydrocarbons, CH_3Cl , and Other Chlorocarbons

[6] Air samples were collected with an automated air-borne sampling system in 2.5-L stainless steel electropolished canisters for postcampaign analysis of hydrocarbons and chlorocarbons, including CH_3Cl . Precleaned pure nitrogen-containing canisters were evacuated and flushed for about 5 min prior to pressurizing with ambient air to 2.5 bars overpressure by a MB-602 metal bellows pump. The collection of a boundary layer sample took about 5 s, while in the upper troposphere (at ambient pressures less than 0.2 bar) sampling up to 3 min was necessary. Between 20 and 45 days after sampling, the canisters were analyzed in the laboratory. The analysis was performed with a gas chromatograph (Varian star 3600 CX) equipped with a CP-SilicaPLOT column (0.53 mm I.D.; 60 m long) and detection by Flame Ionization Detection (hydrocarbons and CH_3Cl) and Electron Capture Detection (chlorocarbons). CH_3Cl is detected by both the ECD and the FID for quantitative evaluation. No interference could be observed in both the FID and the ECD peak. We chose the FID quantitative results for CH_3Cl for its higher precision due to larger peak areas and better stability than the ECD output. The detection limit of the peak integration for CH_3Cl is about 10 pptv (FID). The detection limit for hydrocarbons is <3 pptv, for CH_2Cl_2 <5 pptv, and for the other chlorocarbons <0.1 pptv. Preconcentration of a 1-L sample was done with a Varian Sample Preconcentration Trap (SPT) at a freeze-out temperature of -170°C . The reproducibility of the SPT with standard gas was better than 2% (1σ). A commercial gravimetrically prepared standard gas mixture (PRAXAIR) was used as reference air, with an absolute accuracy of 3% for hydrocarbons and 2% for chlorocarbons, as indicated by the supplier. CH_3Cl showed excellent linearity ($N = 20$; $R = 0.998$ at the 99% confidence level) with the FID response over a concentration range of 50 to 650 pptv, yielding a uniform and stable response factor. A comparison of eight canister sample analyses, prior to the INDOEX campaign, was performed between the laboratory of J. Rudolph (Centre for Atmospheric Chemistry, York University, Toronto, personal communication, 1999) and our laboratory. The comparison indicated an overestimation of our CH_3Cl results based on the PRAXAIR standard by a factor of 1.17 ± 0.07 ($N = 8$) relative to their results. Our quantification was based on a commercial chlorocarbon standard (PRAXAIR), whereas J. Rudolph used a standard mixture prepared by the American National Institute of Standards and Technology (NIST) for quantification. To check the absolute concentrations in our PRAXAIR standard, an additional comparison was arranged with S. A. Montzka (NOAA/CMDL, Boulder, CO, personal communication, 2000) (about 18 months after INDOEX). The analysis of our standard by S. A. Montzka, indicated a significantly lower amount of CH_3Cl (by a factor of 0.76 ± 0.04) than stated by the manufacturer, in accordance with the earlier comparison with J. Rudolph. Good agreement, within the uncertainty of the measurements, was obtained between the NOAA/CMDL and the PRAXAIR standard for the other

Table 1. Average Trace Gas Mixing Ratios During INDOEX (1999)^a

	INDOEX ~6.5°S Flight 11 Indian Ocean N = 3 ^b	INDOEX 0°S–8°N Flight 13 to 16 Arabian Sea N = 11 ^b	INDOEX 0°S–8°N Flight 1 to 10 Bay of Bengal N = 16 ^b	INDOEX 8°S–8°N All Flights Indian Ocean N = 71 ^b
Species	<0.5 km alt.	<0.5 km alt.	<0.5 km alt.	1.2–12.5 km alt.
CO, ppbv	47 (7)	131 (14)	206 (35)	114 (22)
CH ₃ Cl, pptv	542 (6)	666 (35)	757 (62)	639 (31)
CH ₃ CN, pptv	194 (65)	257 (70)	273 (71)	126 (62)
ethane, pptv	195 (37)	467 (107)	817 (243)	542 (139)
acetylene, pptv	2 (3)	102 (44)	291 (173)	109 (51)
propane, pptv	6 (1)	36 (33)	50 (35)	48 (22)
n-butane, pptv	3 (1)	10 (8)	10 (7)	14 (11)
benzene, pptv	3 (2)	47 (18)	99 (40)	35 (17)
toluene, pptv	3 (1)	14 (19)	6 (2)	15 (12)
isoprene, pptv	21 (6)	29 (15)	15 (16)	10 (8)
C ₂ Cl ₄ , pptv	0.8 (0.02)	1.8 (0.4)	2.8 (0.4)	2.7 (0.7)
CH ₃ CCl ₃ , pptv	66 (0.1)	67 (2)	65 (3)	70 (3)
CH ₂ Cl ₂ , pptv	8 (0.5)	22 (5)	26 (5)	29 (12)
CHCl ₃ , pptv	3.3 (0.1)	6.6 (0.9)	7.9 (1.2)	9.4 (1.1)

^aThe CO and CH₃CN data are averages for the flight levels during which the canisters samples were collected. The 1σ standard deviation is indicated between parentheses.

^bDenotes the number of air samples.

chlorocarbons. The comparison of the standards with S. A. Montzka suggested a slight declining trend of the CH₃Cl concentration in our standard. Hence, we corrected our CH₃Cl results by a factor of 0.85 from the earlier comparison with J. Rudolph, resulting in an additional uncertainty of about 5% (total accuracy 7%).

[7] The precision (1σ) of CH₃Cl and nonmethane hydrocarbons (for concentrations >5 pptv detected by FID) and chlorocarbons (for concentrations >1 pptv detected by ECD), determined as the average relative standard deviation of duplicate analyses of up to 9 different samples, was as follows: CH₃Cl 1%, ethane (C₂H₆) 4%, acetylene (C₂H₂) 3%, propane (C₃H₈) 10%, n-butane (n-C₄H₁₀) 30%, isoprene (C₅H₈) ~50%, benzene (C₆H₆) 10%, toluene (C₇H₈) 14%, CH₂Cl₂ 21%, CHCl₃ 7%, 1,1,1-trichloroethane (methyl chloroform, CH₃CCl₃) 2%, and tetrachloroethylene (C₂Cl₄) 2%. The relatively low analytical precisions (deviation >15%) of some species are due to low ambient concentrations (in case of n-butane and isoprene) or a weak detector response (in case of CH₂Cl₂) resulting in a low signal-to-noise ratio (<3) and poor peak integration. To test the stability of the chloro- and hydrocarbons in the canisters, we performed a reanalysis on five samples up to 43 days after the first analysis (and up to 75 days after sampling). The average of the relative standard deviations of the means of the first and the second analyses (N = 5) was found to be ±3%, within the 1σ precision for all compounds except for benzene and CHCl₃. For the latter two compounds the mean of the relative standard deviations were about ±8% within the (1σ) precision. Hence our tests indicate no significant storage effect up to 75 days after sampling for the hydrocarbons and chlorocarbons described in this study.

2.3. CO Measurement

[8] Tunable diode laser absorption spectroscopy (TDLAS) was applied to measure the CO mixing ratios in situ during the flights at a frequency of 1 Hz [Wienhold et al., 1998]. For the INDOEX data the calibration accuracy was 2.8% and the average precision 3.6% (1σ). The CO results from the Citation aircraft during INDOEX are further

discussed by *de Gouw et al.* [2001] and *Williams et al.* [2002].

2.4. Acetonitrile (CH₃CN) Measurements

[9] CH₃CN measurements, among many other compounds, were carried out with a Proton-Transfer-Reaction Mass-Spectrometer (PTR-MS) on-board the measurement aircraft [*de Gouw et al.*, 2001]. The technique is described in detail by *Lindinger et al.* [1998]. Measurements were performed on-line every 12 s and finally smoothed over 5 points resulting in a measurement frequency of 1 min. CH₃CN was detected with a precision of ±30% and a calibration uncertainty better than ±20%. The results from the PTR-MS instrument during INDOEX are described by *de Gouw et al.* [2001].

3. Measurement Results

3.1. Overview of Results

[10] Table 1 presents an overview of the average concentrations of CH₃Cl, selected hydrocarbons, chlorocarbons, CO and CH₃CN measured in the marine boundary layer and in the free troposphere during the INDOEX flights. Mixing ratios are given in parts per billion by volume (ppbv, 10⁻⁹ mol mol⁻¹) for CO and parts per trillion by volume (pptv, 10⁻¹² mol mol⁻¹) for hydrocarbons, chlorocarbons and CH₃CN. We compare CH₃Cl results with CO and C₂H₂, propane, n-butane and benzene, because they are all released from combustion processes involving either biomass or fossil fuels. We include the biogenically emitted isoprene, which has a very short lifetime (a few hours), as tracer for nearby natural emissions. C₂Cl₄ and CH₃CCl₃ are included as tracers for urban/anthropogenic pollution. Furthermore, we show boundary layer results of CH₂Cl₂ and CHCl₃, of which emission ratios relative to CO and CO₂ from biomass burning have been reported as well [*Rudolph et al.*, 1995].

[11] In this study we present CH₃CN data because it has been proposed as a distinct marker of biomass burning [*Lober et al.*, 1991; *Holzinger et al.*, 1999]. Laboratory measurements of biomass burning emissions by *Holzinger*

Figure 1. Composite of ECMWF 5-day back-trajectories for each boundary layer flight track over the Maldives area. During flights 1 to 10 (performed between 14 February to 2 March; black lines) polluted air masses originating from the Bay of Bengal were encountered. On flight 11 (4 March; gray line) a boundary flight track was flown behind the ITCZ in pristine southern hemispheric air. Flights 13 to 16 (15 to 21 March; dotted lines) correspond to less polluted air masses coming from the Arabian Sea area. The fat arrows indicate the general flow directions.

et al. [1999] showed a strong correlation between CO and CH_3CN (among many other organics) leading to the conclusion that biomass burning dominates the global budget of CH_3CN . The subdivision in Table 1 for the northern Indian Ocean marine boundary layer measurements indicates the different source areas as distinguished on the basis of back-trajectories provided by the Royal Netherlands Meteorological Institute (KNMI) [de Gouw *et al.*, 2001; Verver *et al.*, 2001]. The trajectories were calculated on the basis of archived 3D wind data from the European Center for Medium Range Weather Forecasts (ECMWF) model [Stohl *et al.*, 2001]. Figure 1 shows a compilation of 5-day back-trajectories representative for the marine boundary layer flight tracks. The marine boundary layer height over the Maldives area was generally between 0.5 and 1 km altitude. The trajectories end in the marine boundary layer at the ~ 150 m flight altitude of the Cessna Citation. During the first part of the campaign, from 14 February to early March (flights 1 to 10), a steady northeasterly monsoon carried polluted air masses from northern India and the Bay of Bengal region. During the second part of the campaign (flights 13 to 16) from early to late March, the flow shifted toward a more northwesterly direction, carrying relatively cleaner air masses from the Arabian Sea to the measurement area (Figure 1). The trajectories from the Bay of Bengal region indicate travel times of the encountered air masses between about 2 and 5 days from potential source regions around the Bay of Bengal. In most cases the ITCZ (Inter Tropical Convergence Zone) was too far south (between 5°S

and 12°S) to be reached by the Citation. Only on 4 March (flight 11; Figure 1), when the ITCZ was located at $1\text{--}3^\circ\text{S}$, the aircraft was able to cross the ITCZ and to reach pristine southern hemispheric air masses in the marine boundary layer at $\sim 6.5^\circ\text{S}$. For an extensive survey of the meteorology during INDOEX we refer to Verver *et al.* [2001].

3.2. Boundary Layer Results

[12] The marine boundary layer measurements are, as explained before, subdivided into three regimes based on the meteorology during INDOEX. The most polluted conditions (i.e., highest CO) were encountered during the first part of the campaign (February to early March) when a steady northeasterly flow from the highly populated Bay of Bengal region dominated the measurement area near the Maldives. All tracers that characterize biomass combustion processes, including CH_3Cl (Table 1), were strongly enhanced. The flow from the Arabian Sea region carried cleaner air masses (lower CO) but still high CH_3Cl , originating from the less densely populated Middle East and the Arabian peninsula. Cleanest conditions were encountered during a boundary layer track on 11 March at $\sim 6.5^\circ\text{S}$, when our aircraft crossed the ITCZ at about 1°S .

[13] As expected, the tracer for natural terrestrial emissions (isoprene) was low levels throughout the campaign. The lifetime of isoprene (by reaction with the OH radical) in the marine boundary was on the order of one hour (based on a reaction coefficient $k_{[\text{OH}]}$ of $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Atkinson [1990], and a diurnal average OH concentration of $2.5 \times 10^6 \text{ molecules cm}^{-3}$, from de Laat *et al.* [2001]). Thus, within a day, high concentrations ($\sim 1\text{--}2$ ppbv) from the continent would be depleted. The low, though nonnegligible, background concentration may have originated from the ocean. A marine source of isoprene related to phytoplankton activity has been reported earlier by several investigators [e.g., Bonsang *et al.*, 1992; Milne *et al.*, 1995; Broadgate *et al.*, 1997].

[14] The tracer C_2Cl_4 is an indicator of urban/industrial activity. This chlorocarbon has almost no natural sources and is used as an industrial solvent. Its atmospheric lifetime is about 150 days, mainly due to reaction with the OH radical [Khalil, 1999]. We measured rather low and homogeneously distributed concentrations of C_2Cl_4 over the northern Indian Ocean, which underscores the low level of urban/industrial emissions from South and Southeast Asia. CH_3CCl_3 measured at the PEM-West A campaign (Pacific Exploratory Mission) over the western Pacific, proved to be a good tracer for coastal East-Asian industrial activity [Blake *et al.*, 1996]. During INDOEX we found no significant difference in the CH_3CCl_3 concentration between polluted and pristine air masses. In fact, the average CH_3CCl_3 concentration of about 66 pptv in polluted air masses resembles closely the global tropospheric mean for 1999 of about 65 pptv [Montzka *et al.*, 1999], which emphasizes the minor contribution of urban/industrial activity. A recent laboratory study by Rudolph *et al.* [2000] indicated that the release of CH_3CCl_3 from biomass burning is of marginal importance, being even much smaller than previously assumed. Our results agree with this. CH_2Cl_2 and CHCl_3 , on the other hand, were slightly enhanced in polluted air masses during INDOEX, correlating with high CH_3Cl , C_2H_2 and CO concentrations (further discussed in section 4.2). This strongly suggests that these compounds

Table 2. Comparison of the Average INDOEX Data With the PEM-West A Hydrocarbon Results^a

Species	INDOEX 6.5°S–8°N Indian Ocean N = 34 ^b <2 km alt.	PEM-West A ^c 0.5°S–59.5°N Western Pacific N = 421 ^b <2 km alt.
CO, ppbv	173 (45)	N.A.
CH ₃ Cl, pptv	711 (65)	N.A.
CH ₃ CN, pptv	260 (71)	N.A.
ethane, pptv	677 (248)	758 (414)
C ₂ H ₂ , pptv	207 (153)	172 (265)
propane, pptv	46 (33)	150 (318)
n-butane, pptv	10 (7)	70 (290)
benzene, pptv	73 (39)	53 (98)
toluene, pptv	9 (12)	49 (367)
isoprene, pptv	21 (16)	<3
C ₂ Cl ₄ , pptv	2.4 (0.6)	9 (21)
CH ₃ CCl ₃ , pptv	66 (3)	176 (75)
CH ₂ Cl ₂ , pptv	25 (6)	N.A.
CHCl ₃ , pptv	7.3 (1.2)	N.A.

^aAverage INDOEX (February/March 1999) data for altitudes <2 km with the PEM-West A (September/October 1991) hydrocarbon results are shown. The CO and CH₃CN data are averages for the flight levels during which the canisters samples were collected. The standard deviation (1σ) is given between parentheses.

^bDenotes the number of air samples.

^cFrom *Blake et al.* [1996].

have biomass burning sources, in agreement with earlier findings by *Rudolph et al.* [1995].

3.3. Comparison with Other Measurements

[15] To our knowledge there are no other reports of extensive hydrocarbon and chlorocarbon measurements performed in the INDOEX region to compare with. Hence, we compare average results from INDOEX with results from the Pacific Exploratory Mission over the Western Pacific (PEM-West A), which took place in September and October 1991 in Southeast Asia [*Blake et al.*, 1996]. The PEM-West results were strongly influenced by outflow of highly polluted air masses from large urban centers in Eastern Asia, resulting in relatively high mean concentrations. In Table 2 the average concentrations from canisters samples collected below 2 km altitude from INDOEX and PEM-West A are shown. The PEM-West source regions in eastern Asia, which include East China, South Korea and Japan, are characterized by a higher level of economic and industrial development than the INDOEX region. We find the most prominent differences for propane, n-butane, CH₃CCl₃ and C₂Cl₄. Notably, these hydrocarbon species are expected to be more abundant in more developed urban/industrialized regions sampled during PEM-West A, for which fossil fuel use was a primary source. The INDOEX concentrations of these species were considerably lower, whereas other combustion tracers like C₂H₂ were fairly similar, as these gases are less specific, being emitted from both fossil and biofuel use. The relatively high CH₃CCl₃ concentrations measured during the PEM-West A campaign in 1991 correspond to the global average around 150 pptv at the time [*Montzka et al.*, 1999]. Since the beginning of 1990, its concentrations have declined to around 65 pptv in 1999, due to the Montreal Protocol for halocarbons [*Montzka et al.*, 2000].

[16] We compare average boundary layer CH₃Cl mixing ratios measured during INDOEX with average observed CH₃Cl based on monthly means of January to April 1999

from selected NOAA/CMDL remote surface stations (Mauna Loa, Hawaii, USA (19°N); Samoa, USA (14°S); Cape Grim, Tasmania, Australia (40°S)), and a global mean for the same period (based on all seven NOAA/CMDL remote sampling locations; see *Montzka et al.* [1999]) provided by S. A. Montzka (personal communication, 2000) from NOAA/CMDL (Table 3). *Khalil et al.* [1999] report a global average atmospheric mixing ratio for CH₃Cl of about 540 pptv, slightly lower than the global mean of 553 pptv for January to April 1999 (S. A. Montzka, personal communication, 2000).

[17] The latitudinal variation from the data provided by S. A. Montzka (personal communication, 2000) shows a positive gradient toward the tropics where the highest concentrations are measured, in agreement with results from *Khalil et al.* [1999]. Compared to the average concentration of 590 ± 20 pptv CH₃Cl, representative for the remote northern hemispheric tropics, the average marine boundary layer concentration of 720 ± 69 pptv during INDOEX is significantly higher. In the relatively clean air south of the ITCZ (see Table 1), encountered on 4 March, the lowest CH₃Cl concentration of 542 pptv was observed, similar to the southern hemispheric tropical average of Montzka.

3.4. Photochemical Age of Polluted Air Masses in the Boundary Layer

[18] Back-trajectory analysis by the ECMWF-model [*Verver et al.*, 2001] indicated that the air masses from the Indian continent had traveled over the Bay of Bengal and the Indian Ocean for about 2 to 5 days to the measurement area over the Maldives. A further diagnostic of the (photochemical) age of air masses away from continental sources is provided by the NMHC composition and concentrations. Mixing ratios of NMHCs such as ethane, C₂H₂, propane, n-butane, benzene and toluene, originating from combustion sources over the continent, can be used to mark the photochemical age of an air mass, because they have no significant oceanic sources, and their sink is mainly reaction with OH radicals. Estimated photochemical lifetimes of these species in the marine boundary layer during INDOEX are 18.6, 5.1, 4.2, 3.8, 2.1 days and 0.7 day for ethane, C₂H₂, propane, benzene, n-butane and toluene, respectively, based on reaction coefficients (KOH) by *Atkinson et al.* [1992], an average boundary layer temperature of 298 K and a diurnal average OH concentration of 2.5 × 10⁶ molecules cm⁻³, according to *de Laat et al.* [2001]. Thus, significant mixing ratios above background level (generally >10 pptv) of short-lived compounds, like n-butane and toluene, can only be present in relatively fresh plumes (<2 days old), whereas

Table 3. Comparison of INDOEX Mean CH₃Cl Mixing Ratios (or Concentration) With Average Observed CH₃Cl Mixing Ratios^a

Year	1999	Global	Northern Hemisphere	Southern Hemisphere	
			Tropical ^a	Tropical ^b	Temperate ^c
NOAA/CMDL	553 (3)		590 (20)	541 (13)	516 (4)
INDOEX			720 (69)	542 (6)	

^aMixing ratios are in parts per trillion by volume. Mixing ratios are based on monthly means of January to April 1999 from selected NOAA/CMDL surface stations: Mauna Loa^a (19°N), Samoa^b (14°S), Cape Grim^c (40°S); provided by S. A. Montzka, NOAA/CMDL, Boulder, CO. The 1σ standard deviation of four monthly means (in parentheses) indicates the atmospheric variability.

Figure 2. Correlation of CH_3Cl with CO, C_2H_2 , benzene, and n-butane in the free troposphere during INDOEX (all data between 1.2 and 12.5 km altitude, R at the 99% confidence level). The error bars denote the measurement uncertainty (sum of the absolute accuracy and measurement precision), which is 6.4% for CO, 8% for CH_3Cl , 6% for C_2H_2 , 13% for benzene, and 33% for n-butane.

longer-lived compounds like benzene, C_2H_2 and propane can still be enhanced in aged plumes (<5 days). When applying this simple diagnostic to the mean results for the Bay of Bengal data, as presented in Table 1, we find that toluene and n-butane were both close to their background as found in aged air masses (Indian Ocean, $\sim 6.5^\circ\text{S}$), while benzene was still significantly enhanced. This implies that the polluted air masses advected from the Bay of Bengal had a photochemical age between 2 and 4 days from continental sources.

3.5. Free Tropospheric Results

[19] The mean results of 71 air samples, collected during INDOEX in the free troposphere between 1.2 and 12.5 km altitude over a latitude range of 6.5°S to 8°N , are presented in Table 1 (last column). Back-trajectory analysis did not clearly indicate dominant source areas, as was the case for the marine boundary layer air masses. Furthermore, the travel distances of the air masses were, as can be expected, much longer due to higher wind speeds in the free troposphere. As a result, air mass mixing and plume dilution is more efficient, so that the absolute concentrations and the variability (1σ standard deviation) are generally smaller in the free troposphere compared to the boundary layer. Nevertheless, compared to the pristine conditions encountered during the southern hemispheric flight track, average trace gas concentrations in the free troposphere, notably of CH_3Cl , were significantly

enhanced, being comparable to the boundary layer conditions of the air masses from the Arabian Sea region (Table 1). In general, it appears that the free troposphere was influenced by biomass burning emissions either from distant source regions or local convection of polluted boundary layer air. This significance of biomass burning sources in the free troposphere is underscored by the correlation of CH_3Cl with the combustion tracers C_2H_2 and benzene (R of 0.72 and 0.73 for $N=71$, respectively, at a 99% confidence level), shown in Figure 2. The correlation with CO (Figure 2) is weaker ($R=0.46$; 99% confidence level), indicating the influence of other combustion sources. The very poor correlation ($R=0.19$; 99% confidence level) between CH_3Cl and n-butane (Figure 2) is due to the very short atmospheric lifetime of n-butane relative to CH_3Cl . As a result, most of the n-butane measurements are at background levels.

3.6. Vertical Distributions

[20] In Figures 3a and 3b we show vertical profiles from all canister data collected between about 6.5°S and 8°N for CH_3Cl , CH_3CCl_3 and the combustion tracers C_2H_2 , propane and benzene, and the short-lived tracer n-butane. We included n-butane as an indicator of fresh continental pollution transported upwards by deep convection. We observed a large variability for all compounds in the boundary layer related to different source areas, source strengths and ages of the air masses (Figure 3a). Furthermore, there appears to be a

3a.

Figure 3. Altitude profiles of CH_3Cl , CH_3CCl_3 , C_2H_2 , propane, and n-butane canister data. Panel 3a shows the canisters from 150 m in the boundary layer up to about 3.5 km altitude. Panel 3b shows vertical profiles from 3.5 to about 12.5 km altitude. The error bars denote the measurement uncertainty.

3b.

Figure 3. (continued)

Figure 4. Correlations between CH_3Cl , CO, and other trace gases in the marine boundary layer during INDOEX. The CO data correspond to the in situ CO measurement at the time of the air canister sampling. The linear fit and correlation coefficient R (95% confidence level) correspond to the Bay of Bengal data (most polluted case). Measurement uncertainty is indicated by error bars.

local maximum at about 1.5 km altitude for the combustion tracers C_2H_2 , propane and n -butane, just above the marine boundary layer (<1 km altitude), which is less prominent for the other compounds. This might be related to a pronounced maximum, which was found between 1 and 3 km altitude in profiles of ozone and pollutants like CO, measured from various platforms over the Maldives area [Lelieveld *et al.*,

2001]. It is hypothesized by Lelieveld *et al.* [2001] that such a polluted layer is related to a sea breeze circulation at the Indian coast, which adds pollution from the deep continental boundary layer (~ 2 km altitude) to a residual layer above the marine boundary layer. Figure 3b shows the altitude profiles of the same species as in Figure 3a in the free troposphere up to about 12.5 km altitude. As expected, the long-lived tracers

Figure 5. Correlations between CH_2Cl_2 and biomass burning tracers (CO , C_2H_2 , CH_3CN , and CH_3Cl) and urban/industrial tracers (CH_3CCl_3 and C_2Cl_4) in the marine boundary layer during INDOEX. The linear fit and correlation coefficient R (95% confidence level) corresponds to polluted Bay of Bengal data. The error bars denote the measurement uncertainty.

CH_3Cl and CH_3CCl_3 show less variability in the free troposphere as compared to the short-lived hydrocarbons. This is in agreement with the concept, first explored for the global distribution of long-lived tracer species by Junge [1974], that the atmospheric variability of a species is inversely proportional to its atmospheric lifetime. Recently, Jobson *et al.* [1998], showed that an inverse variability-lifetime relationship applied for short-lived hydrocarbons on a regional scale as well. In addition, Jobson *et al.* [1999] reported inverse relationships between the measured variability and the OH lifetime for hydrocarbons and halocarbons for various tropospheric data sets.

[21] Enhanced hydrocarbon mixing ratios and a high variability, most clearly seen in benzene and n-butane, were measured in air masses in the upper troposphere above 8 km. Here, outflow of pollutants from the boundary layer by convective clouds is expected [de Gouw *et al.*, 2001]. Hence, enhancements at higher altitudes, notably of species with relatively short chemical lifetimes such as benzene and n-butane (on the order of 10 and 5 days in the upper free troposphere, respectively), point to the influence of deep convection in the region and rapid long-range transport. The absence of enhanced CH_3Cl above 8 km altitude indicates that source regions are dominated by fossil fuel emissions rather than by emissions from biofuel burning. Indeed, ten-day back-trajectories indicate that rapid long-range transport of pollutants, which originated from more industrialized

distant source regions in southeastern Asia and China, could play a role as well. Additional indications of convective transport during INDOEX are discussed by de Gouw *et al.* [2001] and Williams *et al.* [2002].

4. Sources of CH_3Cl and Other Chlorocarbons

4.1. Sources of Enhanced CH_3Cl

[22] Reports in the literature of high CH_3Cl concentrations (up to ~ 1 ppbv), as observed during INDOEX, relate to measurements in biomass burning plumes [e.g., Blake *et al.*, 1996, 1999] or terrestrial sources in coastal areas, notably salt marshes [Li *et al.*, 1999; Yokouchi *et al.*, 2000]. During the PEM-tropics A campaign [Blake *et al.*, 1999] over the remote South Pacific Ocean in 1996, for example, up to 700 pptv of CH_3Cl was measured in biomass burning plumes from South America. Li *et al.* [1999] report CH_3Cl concentrations of 647 ± 52 at a remote coastal site (Okinawa, Japan) during August 1996. They suggest that the elevated CH_3Cl concentration (and the high variability), as compared to what is found over the remote ocean (e.g., see Table 3), might be due to large emissions from coastal areas (either from coastal waters or a nearby land source). Yokouchi *et al.* [2000] measured strongly enhanced CH_3Cl concentrations up to 1.5 ppbv at a remote subtropical coastal site, which they relate to a presently unknown land source, due to its strong correlation with terrestrial plant-related

Figure 6. Correlations between CHCl_3 and biomass burning tracers (CO , C_2H_2 , CH_3CN , and CH_3Cl) and urban/industrial tracers (CH_3CCl_3 and C_2Cl_4) in the marine boundary layer during INDOEX. The CO data relate to the in situ measurement periods during the air canister sampling. The linear fit and correlation coefficient R (95% confidence level) correspond to the Bay of Bengal data. Note that the outlier in the CHCl_3 data is not included in the correlations and the linear fits. The error bars denote the measurement uncertainty.

α -pinene. *Rhew et al.* [2000] show that CH_3Cl is released to the atmosphere from vegetation zones of coastal salt marshes in southern California. They do not present concentrations but their flux estimate of 0.17 Gg per year (range: 0.065–0.44) emphasizes the potential importance of this source.

[23] Nevertheless, in polluted air masses affected by biomass burning, elevated CH_3Cl is always found together with high CO and hydrocarbon concentrations. As a result of their common sources, hydrocarbons and CH_3Cl are generally well correlated with CO in biomass burning plumes [e.g., *Blake et al.*, 1996]. Enhanced continental boundary layer concentrations of CH_3Cl over Brazil and Southern Africa up to 1.3 ppbv were measured during the NASA TRACE-A project (Transport and Atmospheric Chemistry near the Equator-Atlantic) [*Blake et al.*, 1996], together with strongly enhanced hydrocarbons as well as CO from biomass fires in these regions. In the TRACE-A study correlation coefficients (R^2) between CO and CH_3Cl of ~ 0.9 (99% confidence level) were found ($N = 25$ over Brazil; $N = 33$ over Southern Africa).

[24] In Figure 4 we present correlations between CH_3Cl ($N = 16$) and CO ($N = 15$; the CO measurement is missing for 1 canister), hydrocarbons ($N = 16$) and CH_3CN ($N = 9$; the CH_3CN measurement is not available for 7 canisters) for the marine boundary layer measurements during INDOEX. We show the correlation coefficients between CH_3Cl and the

selected tracers only for the data from the most polluted Bay of Bengal region. We find that CH_3Cl is highly correlated with CO , C_2H_2 and benzene ($R > 0.9$ for $N = 16$; 95% confidence level), all important products of incomplete combustion of fossil and biofuels. A weaker and no correlation at all was found with *n*-butane and toluene, respectively, because they were mainly detected at background levels due to their short atmospheric lifetimes. Furthermore, an excellent correlation with CH_3CN of $R = 0.98$ ($N = 9$; 95% confidence level) was found, in spite of the lower number of measurements. CH_3CN is a strong indicator of biomass burning activity.

[25] Here we focus on biomass burning emissions, notably from the use of biofuels, from India and neighboring countries (includes Bangladesh, Sri Lanka, Myanmar, Nepal and Pakistan), which have the largest potential to have influenced our measurements. The domestic energy consumption pattern in Asia, and in particular in India, has been studied extensively, focusing on the domestic use of biofuels [*Ravindranath and Ramakrishna*, 1997; *Sinha et al.*, 1998; *Streets and Waldhoff*, 1999]. *Streets and Waldhoff* [1999] made a detailed emission database, RAINS-Asia (Regional Air Pollution Information and Simulation Model for Asia), which contains estimates of CO and CO_2 emissions from 23 countries in Asia (including India). They present an estimate of biofuel and fossil fuel use in Asia for

Figure 7. Correlations between C_2Cl_4 and combustion biomass burning tracers (CO , C_2H_2 , CH_3Cl , and CH_3CN) in the marine boundary layer during INDOEX. The linear fit and correlation coefficient R (95% confidence level) correspond to polluted Bay of Bengal data. The error bars denote the measurement uncertainty.

1990 in Tg C per year, indicating that biofuels comprise 28% of the total energy consumption. For India alone, *Streets and Waldhoff* [1999] estimate that 54% of all anthropogenic carbon emissions originates from the use of biofuels. In close agreement with the RAINS-Asia database, the EDGAR (Emission Database for Global Atmospheric Research) database estimates that about 60% of all the anthropogenic CO_2 emissions emitted in India and neighboring countries is related to the use of biofuels [*Olivier et al.*, 1996]. The biofuel consumption in India is mainly residential in rural areas. *Ravindranath and Ramakrishna* [1997] report that about 93% of the Indian rural energy use depends on biofuels. The remaining 7% is made up of fossil fuels (e.g., kerosene, LPG). In urban areas the estimated fossil fuel component increases to about 56%, whereas the remaining 44% of biofuels is dominated by firewood [*Ravindranath and Ramakrishna*, 1997], in agreement with estimates by *Streets and Waldhoff* [1999]. They found for India and neighboring countries that 59% of the used biofuel consists of firewood, the remaining part being divided between dung (17%) and agricultural waste (24%).

4.2. Sources of Other Chlorocarbons

[26] Sources of CH_2Cl_2 are dominated by natural emissions from oceans and soils (together about 90%) [*Aucott et al.*, 1999], whereas sources of $CHCl_3$ are mainly industrial (70%) and oceanic (23%) [*Khalil et al.*, 1999;

McCulloch et al., 1999]. CH_3CCl_3 and C_2Cl_4 are almost entirely produced by industry (98% and 95%, respectively) [see *Keene et al.*, 1999, and references therein]. In addition, *Rudolph et al.* [1995] showed that CH_2Cl_2 , and to a much lesser extent $CHCl_3$ and CH_3CCl_3 , might have small but significant emissions from biomass burning. No biomass burning emissions have been reported for C_2Cl_4 , although this urban/industrial tracer might have a small biological source in the surface ocean, contributing <5% [see *Keene et al.*, 1999, and references therein]. *Lobert et al.* [1999] used emission ratios relative to CO and CO_2 from *Rudolph et al.* [1995], to estimate that biomass burning contributes a significant portion of about 10% to the globally combined sources of CH_2Cl_2 . For $CHCl_3$ and CH_3CCl_3 , the emissions from biomass burning appear to play only a minor role, representing about 0.4% and 2%, respectively, of their global source strength. On a regional scale, however, the emission from biomass burning might play a relatively larger role.

[27] To determine the significance of the above mentioned emission sources for CH_2Cl_2 and $CHCl_3$ levels during INDOEX we investigated correlations with biomass burning tracers (CO , C_2H_2 , CH_3Cl , and CH_3CN) and urban/industrial tracers (C_2Cl_4 and CH_3CCl_3) presented in Figure 5 and Figure 6, respectively. We show correlation coefficients, R ($N = 15$ for CO , $N = 16$ for C_2H_2 and CH_3Cl and $N = 9$ for CH_3CN ; 95% confidence level), for the Bay of Bengal

Figure 8. Correlations between CH_3CCl_3 and biomass burning tracers (CO , C_2H_2 , CH_3CN , and CH_3Cl) and C_2Cl_4 in the marine boundary layer during INDOEX. The linear fit and correlation coefficient R (95% confidence level) correspond to polluted Bay of Bengal data. The error bars denote the measurement uncertainty.

measurements, where the highest level of pollution was encountered. CH_2Cl_2 and CHCl_3 show weak correlations ($R \approx 0.4$) with increasing concentrations of CO , C_2H_2 , as well as CH_3Cl , suggesting an influence by biomass burning sources beside the ocean surface as a diffuse large-scale source. There is a positive but very poor correlation between CH_2Cl_2 and CH_3CN ($R \approx 0.2$; upper right panel in Figure 5), whereas the correlation between CHCl_3 and CH_3CN is comparable to the other biomass burning tracers for CHCl_3 ($R \approx 0.4$; upper right panel in Figure 6). The latter corroborates the indication of biomass burning emissions as a source of CHCl_3 during INDOEX. No correlation of CH_2Cl_2 and CHCl_3 with CH_3CCl_3 ($R \approx 0$) and a very poor correlation of both species with C_2Cl_4 ($R = 0.1$ to 0.2) is found for the Bay of Bengal measurements, suggesting no significant common

sources originating from urban/industrial activities. Variable oceanic sources of CH_2Cl_2 and CHCl_3 are the most probable cause of the high variability in the data and the weak correlations with the biomass burning tracers in Figures 5 and 6. Nevertheless, our data seem to confirm that biomass burning emissions are a minor source of enhanced CH_2Cl_2 and CHCl_3 beside the oceans as major source.

[28] In Figure 7 we show correlations between C_2Cl_4 and biomass burning tracers (CO , C_2H_2 , CH_3Cl and CH_3CN). The positive correlations between C_2Cl_4 and CO , as well as C_2H_2 and CH_3Cl of $R \approx 0.5$, 0.7 and 0.5 (Bay of Bengal measurements; 95% confidence level), respectively, together with the lack of correlation with CH_3CN ($R \approx 0$), show that biomass burning and urban/industrial emissions are to some extent coincident. In Figure 8, finally, we present correla-

tions of CH_3CCl_3 with CO, C_2H_2 , CH_3CN , CH_3Cl , and C_2Cl_4 , which appear to be all negative for the Bay of Bengal measurements ($R = -0.2$ to -0.8 ; 95% confidence level), pointing to the absence of CH_3CCl_3 sources in Bay of Bengal area.

5. Enhancement Ratios for CH_3Cl and Other Chlorocarbons

5.1. Determination of Enhancement Ratios

[29] We have shown that CO, as the most important product of incomplete combustion, was highly elevated in polluted air masses originating from the Bay of Bengal area. A high correlation between CO and other combustion related species, such as CH_3Cl , is an indication of their common sources and can be used to obtain a source specific enhancement or emission ratio. Enhancement ratios can be determined as the slope of the linear regression relating the molar mixing ratio of species X to the corresponding molar mixing ratio of the reference gas CO ($\Delta X/\Delta \text{CO}$). We obtained enhancement ratios from an orthogonal distance regression (ODR) analysis, a linear regression technique in which errors are allowed in both variables [Press *et al.*, 1992]. We used the most polluted Bay of Bengal measurements to obtain an enhancement ratio for CH_3Cl and selected chlorocarbons, assuming that these are representative of pollution from India and surrounding countries. Enhancement ratios for a number of nonmethane hydrocarbons from the INDOEX marine boundary layer measurements are discussed in the paper of *de Gouw et al.* [2001].

[30] Linear regression avoids possible errors due to the derived emission ratios by wrongly defined background concentrations. A limitation of the use of enhancement ratios is, however, imposed by the occurrence of variable background mixing ratios. The use of linear regression to determine emission ratios from field measurements therefore assumes that one relevant trace gas source is dominant, e.g., biomass burning. Furthermore, the effect of photochemical aging and dilution of an air mass has to be considered. The marine boundary layer during INDOEX was characterized by a stable northeasterly flow (winter monsoon) throughout the campaign, induced by strong subsidence over the Bay of Bengal region that minimized vertical mixing. As a result a strong vertical gradient was observed in the mixing ratios of chemically active tracer species between the marine boundary layer and the free troposphere (see Figure 3a).

[31] The ratio of species X versus CO will evolve as function of its removal rate from the atmosphere relative to that of CO. We have estimated that the polluted air masses from the Bay of Bengal during INDOEX had aged about 3 ± 1 days on average. However, the atmospheric lifetimes of the chlorocarbons are so large (>100 days [Khalil, 1999]), as compared to the travel time from the source regions, that their concentrations remain virtually unaffected by photochemical loss. For example, the chemical lifetime of CH_3Cl in the Indian ocean boundary layer is about 110 days (for a daily mean OH concentration of 2.5×10^6 molecules cm^{-3} in the marine boundary layer [de Laat *et al.*, 2001], and the reaction coefficient ($k_{[\text{OH}]}$) of 4.27×10^{-14} cm^3 molecule $^{-1}$ s $^{-1}$ at 298 K by Atkinson *et al.* [1992]). Thus, within 3 ± 1 days travel time from the source, the CH_3Cl concentration

decreases less than 1% by chemical loss. However, due to the relatively short chemical lifetime of CO in the tropical boundary layer of ~ 19 days ($k_{[\text{OH}]}$: 2.0×10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$, at 298 K by Atkinson *et al.* [1997]), the $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ ratio is expected to increase by 10 to 20% over the period considered. Hence the above arguments suggest that photochemistry was more important than vertical mixing in altering the concentrations, and thus the enhancement ratios during transport.

5.2. Enhancement Ratio of CH_3Cl

[32] The ODR method was applied to the measurements of the most polluted marine boundary air masses from the Bay of Bengal (Figure 4; upper left panel). This resulted in a molar enhancement ratio (slope) $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ of $1.98 \pm 0.24 \times 10^{-3}$ with a correlation coefficient of $R = 0.93$ (95% confidence level). We have argued that the mixing effects on chemically active trace gas concentrations in the marine boundary layer during INDOEX were probably small compared to chemical decay on a timescale of several days. Hence, taking only chemical destruction of CO by the OH-radical into account and assuming an average transport time of 3 days, we derive a $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ "source" enhancement ratio of $1.74 \pm 0.21 \times 10^{-3}$ mol mol $^{-1}$.

[33] We can compare the INDOEX $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ "source" ratio to enhancement ratios of various wood and agricultural waste burning emissions reported in the literature. A ratio of $0.57 \pm 0.28 \times 10^{-3}$ mol mol $^{-1}$ is the overall median enhancement ratio from various natural and anthropogenic wood and savanna burning sources used in the global emission inventory by Lobert *et al.* [1999]. It includes, for example, the mean enhancement ratios of $0.57 \pm 0.03 \times 10^{-3}$ mol mol $^{-1}$ from African savanna burning and $0.85 \pm 0.06 \times 10^{-3}$ mol mol $^{-1}$ from Brazilian forest fires derived from the "Transport and Atmospheric Chemistry Near the Equator-Atlantic" aircraft expeditions (TRACE-A) by Blake *et al.* [1996]. Very few directly observed $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ ratios for agricultural waste burning are available in the literature and none for dung to our knowledge. A laboratory study by Lobert *et al.* [1991] of the emission of CH_3Cl from the burning of different types of grass, hay, straw, and one type of wood, resulted in a range of 0.18 to 4.4×10^{-3} mol mol $^{-1}$ for $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ and a median of 1.6×10^{-3} mol mol $^{-1}$. Rasmussen *et al.* [1980] performed laboratory studies of the emissions from the burning of straw, cornstalk and dead oak leaves relative to CO_2 . They inferred $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}_2$ ratios between 8.5 and 30×10^{-5} mol mol $^{-1}$. From this range and the mean ratio of CO/CO_2 of $\sim 6.6\%$ for this fuel category reported by Lobert *et al.* [1999], we can infer a $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ ratio between 1.3 and 4.5×10^{-3} mol mol $^{-1}$, which agrees very well with Lobert *et al.* [1991]. From the results of both laboratory studies we calculate a mean $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ ratio of $\sim 2.5 \pm 1.4 \times 10^{-3}$ mol mol $^{-1}$, representative of agricultural waste burning. Since cattle dung has a similar chlorine content as agricultural waste, as earlier mentioned, we expect a similar enhancement ratio for dung burning. Relatively high emission ratios for agricultural waste and dung are consistent with the high Cl contents of these fuels as compared to wood fuels [Lobert *et al.*, 1999]. The Cl content measured in various biofuels varied between 650 (grapefruit leaves) and 9500 (hay) mg Cl kg $^{-1}$ of dry fuel,

Table 4. Enhancement Ratios of Chlorocarbons Relative to CO ($\Delta X/\Delta \text{CO}$)^a

Species	$\Delta X/\Delta \text{CO} \times 10^{-5}, \text{mol mol}^{-1}$				
	FOS/DECAFE 1991 Savanna Fires ^b	<i>R</i>	Laboratory Study Wood Burning ^c	INDOEX Bay of Bengal	<i>R</i>
CH ₂ Cl ₂	2.5 (0.6)	0.78	NA	4.4 (4.7)	0.39
CHCl ₃	0.07 (0.02)	0.87	NA	0.9 (0.5)	0.43
CH ₃ CCl ₃	0.72 (0.45)	0.64	0.127 (0.026)	−5.3 (2.1)	−0.59

^aRatios from the INDOEX polluted boundary layer were compared to results from the FOS/DECAFE 91 campaign [Rudolph *et al.*, 1995] and a laboratory study by Rudolph *et al.* [2000]. Ratios are in (mole per mole) $\times 10^{-5}$. Standard deviation (1σ) of enhancement ratios in parentheses. The regression coefficient is given by *R* (95% confidence level). Note that the outlier in the INDOEX CHCl₃ measurements has not been included in the regression analysis.

^bFrom Rudolph *et al.* [1995].

^cFrom Rudolph *et al.* [2000].

with a median value of 4840 mg Cl kg^{−1}, close to the 4360 mg Cl kg^{−1} that has been found for Indian dung [see Lobert *et al.*, 1999, and references therein]. Tropical and subtropical wood, tree litter and leaves have a much lower Cl content of 50 to 1600 mg Cl kg^{−1}, and a median value of 530 mg Cl kg^{−1} of dry fuel [Lobert *et al.*, 1999]. Note that these estimates are quite uncertain, as they are based on only a few measurements.

[34] The burning efficiency, or the phase of a fire, is also a significant factor for the release of CH₃Cl. In the smoldering phase, during which many reduced compounds are released, the CH₃Cl emission can be a factor of three larger than during the flaming phase [Lobert *et al.*, 1999]. Lobert *et al.* [1991] and Rudolph *et al.* [1995] showed that CH₃Cl was better correlated with CO than with CO₂ because CO is primarily a product of smoldering combustion as well. Since biomass combustion in India predominantly involves smoldering fires in ovens or furnaces [Ravindranath and Ramakrishna, 1997], a relatively high CH₃Cl emission can be expected.

[35] We infer that the $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ ratio for the polluted INDOEX marine boundary layer of $1.74 \pm 0.21 \times 10^{-3} \text{ mol mol}^{-1}$ lies in between the high derived mean emission ratio for agricultural waste (and dung) of $2.5 \pm 1.4 \times 10^{-3} \text{ mol mol}^{-1}$ and the low mean emission factor for various wood fuels of $0.57 \pm 0.28 \times 10^{-3} \text{ mol mol}^{-1}$, pointing to a mixture of various biomass burning sources. It appears that the enhanced $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ ratio of CH₃Cl measured in polluted air masses from the Bay of Bengal relates to the extensive use of biofuels in the region, with emphasis on the low burning efficiency of residential fires and the high fraction of chlorine rich fuels like agricultural waste and dung.

5.3. Enhancement Ratios for Other Chlorocarbons

[36] We calculate weak correlations ($R \approx 0.4$; 95% confidence level) between both CH₂Cl₂ and CHCl₃ and CO as well as with C₂H₂ and CH₃Cl in polluted air masses originating from the Bay of Bengal area, suggesting some influence from biomass burning sources (Figures 5 and 6). Negative correlations with CO, C₂H₂, CH₃CN and CH₃Cl, were found for CH₃CCl₃ ($R \approx -0.6$ to -0.8 ; 95% confidence level). Enhancement ratios for CH₂Cl₂, CHCl₃, and CH₃CCl₃ relative to CO were determined as the slope of orthogonal distance regression for the Bay of Bengal measurements ($N = 15$) and compared with results from the FOS/DECAFE 91 (Fire Of Savannas/Dynamique Et Chimie de l'Atmosphère en Forêt Equatorial) experiment, which was conducted dur-

ing February 1991 in Equatorial Africa (Table 4). In this experiment about 20 air samples were collected in plumes of savanna fires to derive enhancement ratios (in their study referred to as emission ratios) of halocarbon species versus CO (and CO₂). Contrary to the FOS/DECAFE 91 results, the INDOEX enhancement ratios relate, most probably, to a mixture of emissions from biofuel burning with different fuel and burning characteristics, as well as other unidentified potential sources (e.g., oceanic or industrial). Hence, this allows only a qualitative comparison. The negative correlation between CH₃CCl₃ and CO (and other tracers) indicates that biomass burning was not a significant source.

[37] As mentioned before, a recent laboratory study of CH₃CCl₃ emissions from wood burning by Rudolph *et al.* [2000] emphasized the marginal importance of biomass burning as a global source (the enhancement factor is given in Table 4). We derive enhancement ratios for CH₂Cl₂ and CHCl₃, which are roughly two to ten times higher, respectively, than the savanna fire estimates (taking the effect of photochemical aging (~ 3 days) on the CO concentration into account). Since biomass burning is a relatively small source, we cannot rule out that other (notably industrial) sources are responsible for the discrepancy. The high uncertainty in both emission estimates ($\sim 30\%$) and the weaker correlation of the INDOEX data contributes to the difference as well. Nevertheless, our results suggest a contribution of biomass burning to sources of CH₂Cl₂ and CHCl₃ in the INDOEX measurement area. The uncertainty of the calculated enhancement ratios is, however, too large to reasonably estimate biomass burning emissions.

6. CH₃Cl Biofuel Burning Emission Estimate

6.1. Approach

[38] To estimate CH₃Cl emissions (in 10⁹ g per year or Gg Cl yr^{−1}) from biomass burning, notably from India and Southeast Asia, we apply the $\Delta \text{CH}_3\text{Cl}/\Delta \text{CO}$ “source” enhancement ratio (ER) of $1.74 \times 10^{-3} \text{ mol mol}^{-1}$ from the INDOEX measurements. The amount of emitted CH₃Cl in Gg Cl yr^{−1}, as a function of the CO-emissions from biomass burning of the source region of interest, is then described by:

$$\text{Cl}_{\text{CH}_3\text{Cl}} = (\text{C}_{\text{CO-biofuel}}/12) \times \text{ER} \times 35.5 \quad (1)$$

where $\text{Cl}_{\text{CH}_3\text{Cl}}$ is the amount of Cl emitted as CH₃Cl in Gg yr^{−1}; $\text{C}_{\text{CO-biofuel}}/12$ is the amount of C emitted as CO

Table 5. Emission Estimate of CH₃Cl From Biofuel Consumption in India+ and Southeast Asia^a

Source Region	EDGAR Database		CO Method		Cl Method ^b	Mean Cl and CO Method	
	Tg C-CO	Tg C	Lobert-ER	INDOEX-ER		Lobert-ER	INDOEX-ER
India+	20	356	34	103	153	94 (60)	128 (25)
SE Asia	28	510	47	144	259	153 (106)	202 (58)

^aEstimates are in gigagrams Cl per year on the basis of carbon emission estimates from the EDGAR database for the year 1990, the $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$ for biofuels from Lobert *et al.* [1999] of $0.57 \pm 0.28 \times 10^{-3} \text{ mol mol}^{-1}$ (Lobert-ER), and the $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$ from this work of $1.74 \pm 0.21 \times 10^{-3} \text{ mol mol}^{-1}$ (INDOEX-ER). India+ includes Bangladesh, Sri Lanka, Myanmar, Nepal, and Pakistan; Southeast Asia includes India+, S. Korea, Indonesia, Malaysia, Philippines, and Thailand. The standard deviation (1σ) of the mean of the Cl and CO method is given in parentheses.

^bWe adopted 4.84 g Cl kg⁻¹ dry fuel for agricultural waste and dung and 0.205 g C kg⁻¹ dry fuel for wood from Lobert *et al.* [1999]. Furthermore, for the Cl method we applied the biofuel partitioning from Streets and Waldhoff [1999] for India+ and Southeast Asia (India+: 41% agricultural waste and dung and 59% woodfuel; S-E Asia: 49% agricultural waste and dung and 51% woodfuel).

from biofuel consumption in Gg yr⁻¹ divided by the molar mass of C (g), ER $\times$ 35.5 is the enhancement ratio for CH₃Cl over CO in mol mol⁻¹ multiplied by the molar mass of Cl (g). This method is referred to as the “CO method” similar to that of Lobert *et al.* [1999]. Clearly, Cl estimates based on the CO method are directly proportional to the enhancement ratio for CH₃Cl over CO. Lobert *et al.* [1999] used a $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$ of $0.57 \times 10^{-3} \text{ mol mol}^{-1}$ for global biofuel emission estimates. Thus the higher $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$ enhancement ratio of $1.74 \times 10^{-3} \text{ mol mol}^{-1}$ from INDOEX implies that emissions from biofuel consumption in India and Southeast Asia could have been underestimated by a factor of three based on the CO method alone.

[39] Besides the CO method, Lobert *et al.* [1999] apply a second method to estimate CH₃Cl emissions based on the Cl-content of biofuels and the estimated release of Cl as CH₃Cl during the burning process. This method, referred to as the “Cl method,” describes the release of CH₃Cl in Gg Cl yr⁻¹ as follows:

$$\text{Cl}_{\text{CH}_3\text{Cl}} = (\text{C}_{\text{biofuel}}/0.45) \times \text{Cl}_{\text{biofuel}} \times \text{F}_{\text{Cl}} \times \text{F}_{\text{Cl-CH}_3\text{Cl}} \quad (2)$$

where $\text{Cl}_{\text{CH}_3\text{Cl}}$ is the emitted mass of chlorine from CH₃Cl in Gg Cl yr⁻¹; $(\text{C}_{\text{biofuel}}/0.45)$ is the total dry mass of burned biofuel (wood fuel, crop residues and dung) in Tg/yr, assuming that all biomass contains 45% of carbon; $\text{Cl}_{\text{biofuel}}$ is the biofuel chlorine content in g per kg dry fuel; F_{Cl} is the fraction of total fuel Cl being emitted, estimated at $72 \pm 22\%$ [Lobert *et al.*, 1999]; $\text{F}_{\text{Cl-CH}_3\text{Cl}}$ is the fraction of Cl emitted as CH₃Cl, estimated at $12.8 \pm 13.9\%$ [Lobert *et al.*, 1991; Andreae *et al.*, 1996]. The Cl biofuel used by Lobert *et al.* [1999] for wood fuel and agricultural waste (and dung) is 0.205 g Cl and 4.84 g Cl per kg dry fuel, respectively. These values comprise the weighted means for these fuel categories from an overview of chlorine content of biomass fuels by Lobert *et al.* [1999]. In our estimates we applied the biofuel use partitioning from Streets and Waldhoff [1999] for India+ (includes Bangladesh, Sri Lanka, Myanmar, Nepal, Pakistan) of 41% agricultural waste and dung, and 59% wood fuel, and for Southeast Asia (includes India+, S. Korea, Indonesia, Malaysia, Philippines, Thailand) of 49% agricultural waste and dung and 51% woodfuel.

[40] Lobert *et al.* [1999] argue that the Cl method is based on the best input data with respect to fuel variability, however, neglecting burning efficiency, whereas the CO method results in estimates with the lowest variability, being

less dependent on burning efficiency. As a result, their best estimate for biofuel burning emission of CH₃Cl (in Gg Cl yr⁻¹) is based on the average of the CO- and the Cl method. For their estimates Lobert *et al.* [1999] use a global carbon emission inventory valid for the year 1990 from J. A Logan and R. Yevich (unpublished manuscript, 1998), which specifies biomass burning emissions on a 1° latitude by 1° longitude grid. According to this inventory, carbon emissions from agricultural waste and dung burning, and wood-fuel burning are 323 Tg C yr⁻¹ and 876 Tg C yr⁻¹, respectively. We apply the EDGAR database [Olivier *et al.*, 1996], because it provides detailed carbon emissions estimates from biofuel use in Asia on a country and regional basis. The EDGAR-database, developed partly in support of the Global Emission Inventory Activity (GEIA), contains detailed CO₂, CO and CH₄ emission inventories for the year 1990. The biofuel use has been divided between residential and industrial use, and is separated into different fuel categories (includes wood, crop residues and dung). The emission estimates for Asia are in close agreement with the RAINS-Asia database [Streets and Waldhoff, 1999]. The uncertainty in the EDGAR global carbon emissions from biofuel use is estimated to be $\pm 100\%$ [Olivier *et al.*, 1996]. We note that global carbon emissions from biofuel burning from EDGAR of 1599 Tg C yr⁻¹ appear to be about 33% higher than the emission estimates used by Lobert *et al.* [1999]. Such considerable discrepancies between emission inventories, which are within the uncertainty of these databases, might explain part of the missing sources of CH₃Cl described by Keene *et al.* [1999].

6.2. Emission Estimates

[41] The global CH₃Cl emission estimate by Lobert *et al.* [1999] for biofuel burning (sum of all fuel categories) results is 112 Gg Cl yr⁻¹ with the CO method and 357 Gg Cl yr⁻¹ by the Cl method. The mean of both methods is 234 Gg Cl yr⁻¹ (with a 1σ standard deviation of 122 Gg Cl yr⁻¹), which amounts to about 37% of all biomass burning sources in the emission inventory of Lobert *et al.* [1999]. All CH₃Cl biomass burning emissions (including a large fraction from biofuel burning) for Southeast Asia were estimated at 219 Gg Cl yr⁻¹ by Lobert *et al.* [1999], which is about one-third of the global CH₃Cl emission from biomass burning. They estimated that their calculated fluxes are reliable to within a factor of 2 to 3. The INDOEX enhancement factor for CH₃Cl of $1.74 \times 10^{-3} \text{ mol mol}^{-1}$ enables revision of the emission estimates of CH₃Cl (in Gg Cl yr⁻¹) from biofuel

burning, notably of the India region and Southeast Asia. We estimated the emission of CH_3Cl from biofuel use from India+ and Southeast Asia on basis of the EDGAR database and the INDOEX CH_3Cl enhancement ratio. We derive CH_3Cl emissions of $103 \text{ Gg Cl yr}^{-1}$ for India+ and $144 \text{ Gg Cl yr}^{-1}$ for Southeast Asia with the CO method. By means of the Cl method (equation 2), we derive CH_3Cl emissions of $153 \text{ Gg Cl yr}^{-1}$ for India+ and $259 \text{ Gg Cl yr}^{-1}$ for Southeast Asia. The combined error in these estimates (apart from the uncertainty in the carbon emissions from the EDGAR database) is of the order of 60%. Table 5 gives an overview of emission estimates in Gg Cl yr^{-1} per year from biofuel burning from the CO- and the Cl method for India+ and Southeast Asia, as well as the mean values for both methods. Interestingly, the estimates on the basis of the INDOEX enhancement ratio are much closer to the results from the Cl method than the CO method estimate by *Loibert et al.* [1999]. Furthermore, taking the uncertainty of the mean estimates in Table 5 into account, there appears to be reasonable agreement between the mean estimate based on CH_3Cl enhancement ratio from *Loibert et al.* [1999] and the one from this work. We infer that our mean emission estimates are 30–35% higher than estimates with the $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$ enhancement ratio from *Loibert et al.* [1999] (based on the EDGAR carbon emissions). Applying the enhanced INDOEX ER to the global biofuel burning emission estimate (CO method) from *Loibert et al.* [1999], the global CH_3Cl emission of $112 \text{ Gg Cl yr}^{-1}$ increases by a factor of 3.05 to $342 \text{ Gg Cl yr}^{-1}$. Thus, the mean with the $357 \text{ Gg Cl yr}^{-1}$ from the Cl method estimate from *Loibert et al.* [1999] (which remains unchanged) becomes $350 \text{ Gg Cl yr}^{-1}$ (with a 1σ standard deviation of 8 Gg Cl yr^{-1}), which corresponds to a mean increase of $116 \text{ Gg Cl yr}^{-1}$ (range 0–247 Gg) or +50% globally.

[42] Although enhancement ratios can be determined with reasonable accuracy (<20%), global biofuel CO_2 and CO emission estimates suffer from considerable uncertainties, as indicated earlier by significant differences between various emission inventories. For example, the annual global carbon (CO and CO_2) emissions from biofuel burning applied by *Loibert et al.* [1999] of $1199 \text{ Tg C yr}^{-1}$ is 400 Tg C yr^{-1} lower than the EDGAR (Emission Database for Global Atmospheric Research) database estimate by *Olivier et al.* [1996] ($1599 \text{ Tg C yr}^{-1}$). Applying the EDGAR annual global carbon emissions in the Cl emission estimate by *Loibert et al.* [1999] leads to a mean CH_3Cl emission of $300 \text{ Gg Cl yr}^{-1}$. Thus, an increase of 66 Gg Cl yr^{-1} , as compared to the global estimate by *Loibert et al.* [1999] ($234 \text{ Gg Cl yr}^{-1}$) can arise from the higher carbon emissions estimate alone. Combining the global carbon emission estimates from EDGAR with the INDOEX $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$ factor, results in a global mean of $435 \text{ Gg Cl yr}^{-1}$ (with a 1σ standard deviation of 33 Gg Cl yr^{-1}) from biofuel consumption. Up to now, about 1.45 Tg of Cl from CH_3Cl emissions is “missing” due to underestimated sources, uncertainties in emission ratios, and uncertainties in the chlorine content of fuels [*Keene et al.*, 1999]. Our global estimate might account for about 200 Gg Cl or $\sim 14\%$ of the “missing” sources suggested by *Keene et al.* [1999]. We speculate that other biomass burning sources, notably the burning of crop

residues in fields ($\sim 214 \text{ Tg C yr}^{-1}$ according to *Loibert et al.*, [1999]), of which sparse or no measurements are reported in the literature, could be underestimated as well from applying a too low $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$ emission ratio.

7. Conclusions

[43] We present measurements of CH_3Cl and selected hydrocarbons and chlorocarbons from analyses of canister samples collected on-board an aircraft during the INDOEX campaign over the Indian Ocean in February/March 1999. We measured strongly enhanced CH_3Cl and related combustion tracers (CO, hydrocarbons and CH_3CN) in polluted air masses originating from India and Southeast Asia. We attribute the enhanced CH_3Cl levels to extensive biofuel use, notably the burning of agricultural waste and dung with a comparatively high chlorine content. We infer a high emission ratio relative to CO ($\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$) of $1.74 \pm 0.21 \times 10^{-3} \text{ mol mol}^{-1}$. The recent emission inventory by *Loibert et al.* [1999] applied a mean value of $0.57 \times 10^{-3} \text{ mol mol}^{-1}$ to estimate global CH_3Cl emissions from biofuel use. On the basis of our measurements we suggest that the contribution to CH_3Cl emissions from the use of biofuels may previously have been underestimated by 30–35% for India and Southeast Asia. According to *Keene et al.* [1999], the combined emissions of CH_3Cl from known sources account only for half the modeled sinks. By extrapolating the INDOEX $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$ enhancement ratio to a global scale, our higher emission estimate might account for about 14% of the “missing” source. In accord with earlier findings by *Rudolph et al.* [1995] we infer small biomass burning sources for CH_2Cl_2 and CHCl_3 . Future work should, in particular, provide improved estimates of the chlorine content of biofuels and the release of CH_3Cl and other chlorocarbons as a function of burning efficiency.

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