

Emissions of methyl chloroform (CH_3CCl_3) from biomass burning and the tropospheric methyl chloroform budget

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Abstract. The only known sources of atmospheric methyl chloroform are industrial production and biomass burning. With the phase-out of industrial methyl chloroform production the atmospheric burden of methyl chloroform is rapidly declining. Consequently the potential importance of non-industrial sources is increasing. Up to now only one experimental investigation of methyl chloroform emissions from biomass burning has been published. Here laboratory studies of methyl chloroform emission from wood burning are presented. The emission ratios relative to carbon dioxide and carbon monoxide are $12.7 \pm 2.6 \times 10^{-8}$ and $15.6 \pm 3.3 \times 10^{-7}$, respectively. Although based on a limited number of measurements, they strongly suggest that methyl chloroform emissions from biomass burning are at the lower end of previous estimates. The impact of these emissions on the chemistry of the atmosphere will be marginal. However, reliable knowledge of the biomass burning source strength will be essential for a detailed analysis of the trend of atmospheric methyl chloroform concentrations.

Introduction

Understanding the tropospheric distribution and budget of methyl chloroform (CH_3CCl_3 , 1,1,1-trichloroethane) is important for two reasons. Firstly, methyl chloroform is a source gas for stratospheric chlorine. Secondly, analysis of trends of tropospheric methyl chloroform concentrations has been used to derive average global and hemispheric values for OH-radical concentrations (Lovelock, 1977; Singh, 1977; Prinn et al, 1992, 1995). In the past the dominant source for atmospheric methyl chloroform was anthropogenic production (cf. Keene et al.; 1999). Based on field studies in Western Africa, Rudolph et al. (1995) reported evidence that methyl chloroform is emitted into the atmosphere by biomass burning. Their estimated source strength was in the range of 4-28 Gg CH_3CCl_3 /yr. Even the upper limit of this estimate would only contribute about 5% to the global budget of methyl chloroform during the last decades. However, due to the phase-out of man made emissions of methyl chloroform its tropospheric concentration has been decreasing since about 1993 (cf. Montzka et al., 1996, 1999) and the potential

importance of biomass burning for the global methyl chloroform budget is increasing.

Unfortunately, the magnitude of biomass burning emissions of methyl chloroform is highly uncertain. The estimate of Rudolph et al. (1995) does not only cover a large range but the authors also state that their emission ratios may only be an upper limit. Very recently Lobert et al. (1999) derived a global methyl chloroform source strength of 12.9 Gg Cl/yr. This corresponds to 16.2 Gg CH_3CCl_3 /yr., within the uncertainties identical to the best estimate given by Rudolph et al. (1995). However, this estimate is also based on the emission ratios of Rudolph et al. (1995).

In this paper we will present results of laboratory studies of methyl chloroform emissions from wood burning. The potential contribution of biomass burning emissions to the tropospheric budget of methyl chloroform will be discussed.

Experiment

Samples of tropical wood were burnt in a laboratory set up under controlled conditions in ambient air at the Max Planck Institute in Mainz, Germany, on January 19, 1998. The set-up used is described by Lobert et al. (1991). Three experiments were performed using different types of wood and amounts of fuel. Details about the burnt fuel are given in Table 1. In total seven samples of exhaust gas were collected cryogenically in aluminum cylinders of 10 L volume. The duration of sample collection ranged from about 10 to 45 minutes.

These whole air samples were analyzed in the laboratory for carbon dioxide (CO_2), carbon monoxide (CO), and a range of organic trace gases, including methyl chloroform. Carbon dioxide and carbon monoxide were determined by gas chromatography in combination with catalytic reduction to methane and flame ionization detection. Methyl chloroform was analyzed by gas chromatographic separation on a GSC-capillary column (30m length, 0.32 mm i.D.) and electron capture detection after cryogenic enrichment from sample volumes of 0.5 L (ambient samples) or 0.1 L (biomass burning exhaust). Parallel to the analysis of the biomass burning exhaust gas, ambient air samples collected in a semi-rural area (Research Center Jülich) in Germany were analyzed. The ambient samples were collected in September and October 1997. The relative accuracy of the CO and CO_2 analysis is around 1-2%. The estimated typical reproducibility of our methyl chloroform measurements, including sampling procedure, is about 6% for ambient samples and between 10 and 15% for biomass burning exhaust gas.

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Table 1. Composition, Type and Amount of Fuel Wood Used

| Experiment | Type | Amount [†] | Moisture | Carbon | Hydrogen | Nitrogen | Chlorine |
|------------|------------|---------------------|----------|----------|----------|----------|-----------|
| A | Eucalyptus | 1926 g | 75 g/kg | 485 g/kg | 62 g/kg | 4 g/kg | 540 mg/kg |
| B | Musasa | 1268 g | 68 g/kg | 480 g/kg | 61 g/kg | 12 g/kg | 29 mg/kg |
| C | Musasa | 1320 g [‡] | 68 g/kg | 480 g/kg | 61 g/kg | 12 g/kg | 29 mg/kg |

[†] Generally the fuel wood was cut into pieces of about 20 cm length and 2 cm diameter.

[‡] Nearly half the total amount of fuel wood consisted of one single piece.

Results

The results of the measurements are listed in Table 2. Also included is information on the sampled burning stage and the average composition of the ambient samples. The CO₂ and CO mixing ratios in the biomass burning samples (Table 2) are highly elevated. These elevated mixing ratios are due to the studied burning process. Thus a correlation between the concentrations of methyl chloroform and CO or CO₂ is an indicator for emission of this substance from the burning process and the slope of the regression represents the average emission ratio of the two substances. The regression coefficients for methyl chloroform mixing ratios versus carbon monoxide and carbon dioxide concentrations are 0.80 and 0.72, respectively. Thus about 50–65% of the observed methyl chloroform emissions can be described by systematic linear dependence between methyl chloroform and carbon monoxide or carbon dioxide. This demonstrates that methyl chloroform indeed is produced as part of the burning process. The emission ratios derived from the linear regressions are given in Table 3.

This procedure is independent from knowledge of the background of trace gas concentrations in the air that dilutes the exhaust gas. However, any random variability of the background concentrations will result in an increased uncertainty of the slope of the regression and thus the emission ratio. Calculation of emission ratios for individual measurements requires knowledge of the background concentration of CO, CO₂, and methyl chloroform in ambient air:

$$EM_{\text{CH}_3\text{CCl}_3/\text{X}} = \frac{([\text{CH}_3\text{CCl}_3]_s - [\text{CH}_3\text{CCl}_3]_b)}{([\text{X}]_s - [\text{X}]_b)} \quad (1)$$

Here $EM_{\text{CH}_3\text{CCl}_3/\text{X}}$ is the emission ratio of methyl chloroform relative to X (here CO or CO₂) and $[\]_s$ and $[\]_b$ indicate the

concentrations in sample and background air, respectively. For our calculations we use the average values of ambient measurements given in Table 2. The resulting emission ratios relative to CO and CO₂ are listed in Table 3. Obviously uncertainties in the background concentrations propagate into the calculated emission ratios. For CO and CO₂ the differences between sample and background are large compared to uncertainties in the background concentrations. For methyl chloroform several concentrations are very close to the ambient levels and uncertainties of the background values will influence the calculated emission ratios. The decrease of the northern hemispheric methyl chloroform concentrations is only in the range of 10–15 ppt/year (Montzka et al, 1995, 1999). The ambient and the biomass burning samples were collected within less than 4 months. Consequently the systematic trend of background methyl chloroform concentrations will only be a marginal source of uncertainty in the emission ratio calculations. However, our ambient samples were collected in a semi-rural area, the biomass burning experiments were conducted in a more urban environment. Although our measurements were made after the phase-out of methyl chloroform production and use in Western Countries it cannot be completely ruled out that our procedure might underestimate the methyl chloroform background mixing ratios and thus overestimate the calculated emission ratios. However, the lowest methyl chloroform mixing ratios in the biomass burning samples are very close to the ambient values (Table 2), consequently a major systematic bias seems unlikely. Moreover, the average of the individual emission ratios is, within the statistical uncertainties, identical to the average emission ratios derived from linear regression analysis. Since the linear regression procedure does not require use of background concentrations this gives us confidence that our results are not significantly biased by uncertainties in the background concentration.

Table 2. Composition of the Sampled Biomass Burning Exhaust

| Experiment | Sample ID | Burning stage [†] | CO ₂ (ppm) | CO (ppm) | CH ₃ CCl ₃ [‡] (ppt) |
|------------|-----------|----------------------------|-----------------------|------------|---|
| A | AF | Flaming | 1553 | 66 | 214 |
| A | AS | Smoldering | 921 | 111 | 119 |
| B | BC | Complete fire | 1292 | 119 | 376 |
| B | BF | Flaming | 544 | 17 | 93 |
| B | BS | Smoldering | 1642 | 256 | 396 |
| C | CF | Flaming | 1086 | 150 | 169 |
| C | CS | Smoldering | 1208 | 73 | 104 |
| Ambient* | | | 337 ± 13 | 0.58 ± 0.1 | 90 ± 7 |

[†] The definition of the burning stage is based on visual appearance.

[‡] The absolute calibration is based on an average value of 90 ppt for ambient northern hemispheric methyl chloroform mixing ratio in fall 1997, derived from the results published by Montzka et al., 1999).

* Error and average of eight whole air samples.

Table 3. Emission Ratios Calculated for the Samples Listed in Table 2.[†]

| Sample | CH ₃ CCl ₃ /CO | CH ₃ CCl ₃ /CO ₂ | CO/CO ₂ |
|------------|---|---|--------------------|
| AF | 19±4.1*10 ⁻⁷ | 10±1.7*10 ⁻⁸ | 5.4% |
| AS | 2.6±1.4*10 ⁻⁷ | 5±1.7*10 ⁻⁸ | 18.9% |
| BC | 24±3.9*10 ⁻⁷ | 30±3.5*10 ⁻⁸ | 12.4% |
| BF | 0.3±1.3*10 ⁻⁷ | 0.3±0.9*10 ⁻⁸ | 9.1% |
| BS | 12±1.9*10 ⁻⁷ | 23±2.9*10 ⁻⁸ | 19.6% |
| CF | 5±1.4*10 ⁻⁷ | 11±2.0*10 ⁻⁸ | 19.9% |
| CS | 2±1.9*10 ⁻⁷ | 1.7±1.2*10 ⁻⁸ | 8.3% |
| Average* | 14.3 [‡] ±3.8*10 ⁻⁷ | 17.6 [‡] ±4.5*10 ⁻⁸ | 13.4±2.5% |
| Regression | 12.7±2.6*10 ⁻⁷ | 15.6±3.3*10 ⁻⁸ | 12.1±2.7% |

[†] Values are in units of mol/mol.

[‡] Error weighted average

* Average and error of mean.

The emission ratios for different burning stages, fuel types etc. show a considerable variability with no statistically significant difference between smoldering and flaming stage, low and high chlorine content of the fuel, or fuel type. The small number of samples for the different categories does not allow a detailed analysis of the impact of the various parameters, obviously the methyl chloroform emission ratios for wood burning are not determined by a single parameter.

The average emission ratio of CO relative to CO₂ (Table 3) is with 12-14% at the upper end of emission ratios reported in literature (cf. Lobert et al., 1999; and references therein), an indication of a higher than average contribution of smoldering combustion in our study. Still, the range of CO to CO₂ emission ratios covers the range of values reported by other authors (cf. Lobert et al., 1999).

Our average methyl chloroform emission ratios relative to CO₂ and CO are about a factor of 4 and 6, respectively lower than the previously (Rudolph et al., 1995) reported values of $43.1 \pm 19 \times 10^{-8}$ mol/mol and $71.5 \pm 45 \times 10^{-7}$ mol/mol. All our individual values are lower than these average emission ratios. With one exception these differences are statistically significant at the 1 σ level, but only for two of our data points at the 2 σ level. This is consistent with the statement by Rudolph et al. (1995) that their methyl chloroform emission ratio might be biased to the high side. However, we also have to consider that Rudolph et al. (1995) studied Savanna fires, our results are for wood burning. Our measurements do not present any evidence for a systematic dependence of methyl chloroform emissions from the chlorine content of the fuel. Still, we cannot exclude that the higher emission ratios for Savanna burning are the consequence of the quite high chlorine content (several hundred to a few thousand ppm by weight) of Savanna type fuels (cf. Lobert et al., 1999).

Discussion

The two types of fuel wood studied are not sufficient to derive representative average values for wood burning, even if the studied types of wood, especially Eucalyptus, are abundant tree species. Moreover, the only existing Savanna study might be biased to the high side. Finally, the dependence of methyl chloroform emission ratios on parameters such as burning stage, moisture or chlorine content of fuel, fuel type etc. is essentially unknown. Obviously any extrapolation based on such limited knowledge will be highly uncertain. Nevertheless, even

Table 4. Comparison of Different Biomass Burning Emission Rate Estimates and Projected Atmospheric Turnover Rates of Methyl Chloroform.

| | Emission or Turnover Rate [†] |
|---------------------------------------|--|
| Specific emission ratios [‡] | 11 (18.7-3.8) Gg/yr. |
| Wood burning emission ratios only | 4.7 (1.2-8.2) Gg/yr. |
| Rudolph et al., 1995 | 14 (4-28) Gg/yr. |
| Lobert et al., 1999 | 16.2 Gg/yr. |
| Residual industrial turnover 2000 | 230 Gg/yr. |
| Residual industrial turnover 2010 | 28.6 Gg/yr. |
| Residual industrial turnover 2025 | 1.26 Gg/yr. |

[†] Given are the best estimates, the values in brackets indicate the estimated $\pm \sigma$ uncertainty range.

[‡] Based on emission ratios for Savannah type fires and wood burning.

uncertain estimates can be extremely important for the interpretation of atmospheric observations of methyl chloroform concentrations and trends and thus for realistic uncertainty estimates of information derived from such studies. As mentioned above, the continuing decrease of the atmospheric methyl chloroform concentrations (Montzka et al., 1999) results in an increasing relative impact of non-industrial methyl chloroform emission.

Table 4 presents a comparison of different estimates for global biomass burning emissions of methyl chloroform. Also included is the projected annual atmospheric loss rate of residual industrial methyl chloroform for different years. This estimate is based on an atmospheric residence time of 4.8 years for methyl chloroform, the present day average atmospheric mixing ratios published by Montzka et al. (1999) and a complete phase-out of industrial emissions. Previously published emission rate estimates are also shown in Table 4.

Two types of scenarios are used to derive plausible ranges for methyl chloroform emissions from biomass burning. In the first scenario we assume that the higher emission ratios

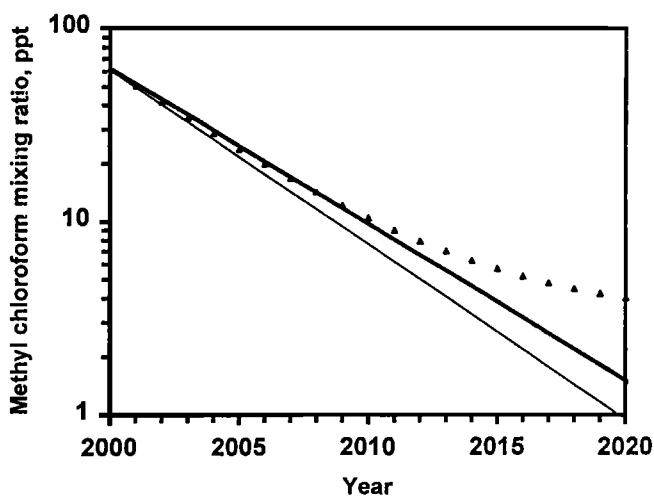


Figure 1. Projected development of average atmospheric methyl chloroform concentrations for different scenarios. Triangles show the development for an atmospheric residence time of 4.8 years and a biomass burning emission rates of 10 Gg/yr. The lines show the development in the absence of methyl chloroform emissions for different atmospheric residence times of 4.8 years (thick line) and 5.4 years (thin line).

reported by Rudolph et al. (1995) are primarily the result of the potential bias mentioned by the authors. In this case the emission ratios presented here are the only available data for an estimate of the global methyl chloroform emission from biomass burning. The total amount of carbon emitted from biomass burning is estimated by Logan and Yevich, (1998, unpublished manuscript cited from Lobert et al., 1999) to 3716 Tg/yr. We assume that this value has an uncertainty of 40% to reflect the range of estimates published by different authors (e.g. Seiler and Crutzen, 1980; Hao and Liu, 1994; Andreae, 1991). Using a CO₂/C molar emission ratio of 0.9 (cf. Lobert et al. 1999) we then obtain an annual emission rate of 5.3 ± 2.9 Gg CH₃CCl₃/yr. Based on the emission ratio relative to CO and an average CO/CO₂ ratio of 0.062 (cf. Lobert et al., 1999) we obtain a somewhat lower global emission rate in the range of 2.5 ± 1.4 Gg CH₃CCl₃/yr.

For the second scenario we assume that the emission ratios of Rudolph et al. (1995) are typical for Savanna fires. Consequently we have to differentiate between wood burning type and Savanna type fires. Based on the biomass burning feedstock characterization of Logan and Yevich (1998, unpublished manuscript cited from Lobert et al., 1999) the amount of carbon emitted from Savanna burning is 1410 Tg/yr. 569 Tg/yr. are emitted from grassland fires, burning in fields, etc. For these types of fires we use the Savanna fire emission ratios. For the remaining 1737 Tg/yr. (deforestation, forest wildfires, wood and charcoal burning, and slash and burn/shifting agriculture) wood burning emission ratios are more appropriate. The resulting source strength based on emission ratios relative to CO₂ and CO is 11.5 ± 7.2 and 10.5 ± 6.4 Gg CH₃CCl₃/yr., respectively.

From Table 4 it is obvious that presently biomass burning emissions only contribute marginally to the overall methyl chloroform budget. Nevertheless, due to the decrease of atmospheric methyl chloroform concentrations the biomass burning source of methyl chloroform will be an increasing fraction of the methyl chloroform budget and soon may be important. Still, the atmospheric concentrations that can be maintained by biomass burning alone are very low, between a fraction of a ppt and a few ppt. Thus any major impact of methyl chloroform emission from biomass burning on atmospheric chlorine content and stratospheric ozone depletion are unlikely. However, the analysis of atmospheric methyl chloroform measurements to deduce its atmospheric residence time will in future be more and more dependent on reliable knowledge of its biomass burning emission rates. E.g. between 2000 and 2010 a biomass burning source of 10 Gg CH₃CCl₃/yr. will, within experimental uncertainties, have the same effect on the atmospheric trend of methyl chloroform as a change of the atmospheric lifetime of methyl chloroform from 4.8 years to 5.4 years (Figure 1).

Conclusions

Our results support the concept that methyl chloroform is emitted from biomass burning. However, previous emission inventories most likely overestimate the magnitude of biomass burning emissions of methyl chloroform. Presently biomass burning is only a minor contribution to the atmospheric methyl chloroform budget. However, due to the continuing decrease of the atmospheric methyl chloroform burden, the relative importance of biomass burning emissions increases. Under the assumption of a 100% effective phase-out of industrial methyl chloroform emissions the

atmospheric methyl chloroform budget may well be dominated by biomass burning emissions by 2025. However, the atmospheric levels of methyl chloroform that might be maintained by biomass burning emissions are very low and will have no significant impact on the chemistry of the atmosphere. Nevertheless, already in the nearest future, reliable knowledge of the biomass burning source strength will be important for the analysis of the global methyl chloroform budget.

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