Abstract. Higher atmospheric concentrations of methane are found in air samples from urban locations than in contemporary samples at the same latitude in remote locations. Higher concentrations of several trace chlorocarbon gases are also found in the same urban samples than in the corresponding remote samples. The "urban excess", i.e. urban concentration minus remote concentration, is generally 1000 to 2000 times larger on a molar basis for CH$_4$ than for CCl$_3$F. Because almost all CCl$_3$F is emitted in urban environments, the urban release of CH$_4$ is estimated from the observed molar ratios to be 30 to 60 megatons per year world-wide.

The fraction of world-wide methane release occurring in the urban environment can be estimated from the concentration ratios, urban to remote, for CH$_4$ vs. CCl$_3$F. About 8% to 15% of the atmospheric methane release is observed to occur in urban locations.

Introduction

Methane is the most abundant form of reduced carbon in the earth's atmosphere, participates in several important chemical cycles there, and functions as a greenhouse gas through its absorption of infrared radiation emitted by the earth. The realization that the world-wide tropospheric concentrations of methane have been increasing during the past several years [Rasmussen and Khalil, 1981a,b; Blake et al., 1982; Mayer et al., 1982; Khalil and Rasmussen, 1983; Rowland et al., 1984a] has focused attention on the problems of its sources, sinks and atmospheric lifetime, as well as on the question of how long such an increase has been occurring. Such rising concentrations can be important both for the direct effects through methane, but also because the reaction with tropospheric HO radicals, its primary sink, is an important atmospheric removal process for many other organic molecules.

The major methane sources identified by Ehhalt [1978, 1979] are biological in origin, including swamps, rice fields, cattle and other ruminant mammals, plus minor emissions from lakes, tundra, oceans, etc. Contributions from the activities of man include the managed biology of rice and cattle and direct emissions from non-agricultural activity such as the use of natural gas. In contrast to the biological sources, most of this non-biological anthropogenic activity occurs in urban environments, and can be expected to elevate the concentrations of methane there. The presence in Parisian air of combustible gases was established almost two centuries ago [deSaussure, 1804]; hydrocarbons were found soon after [Bous-...

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### TABLE 1. Urban Tropospheric Concentrations of CH$_4$ and CCl$_3$F

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<th>Concentrations $<a href="%5Ctext%7Bpptv%7D">\text{CCl}_3\text{F}</a>$</th>
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<th>Fractional $\text{CH}_4$ $\text{CCl}_3\text{F}$</th>
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(a) Concentrations of CH$_4$ in ppmv ($10^{-6}$) and of CCl$_3$F in pptv ($10^{-12}$).
(b) Ratio of absolute increase in CH$_4$ to absolute increase in CCl$_3$F.
(c) Ratio of fractional increase in CH$_4$ to fractional increase in CCl$_3$F.
(d) Ratio of (a) corrected by 10/15, the years required to emit the observed atmospheric burden for CH$_4$ divided by the years required for CCl$_3$F.

* U = urban ** R = remote

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**Results and Discussion**

The measured concentrations of methane and CCl$_3$F are shown in Table 1 for 22 urban air samples collected over a four year period from many different geographical locations. Each is a single individual sample and is not necessarily representative of its location except at that particular time. Nevertheless, the qualitative conclusion is obvious in Table 1 that there is a strong tendency to find in urban air samples excesses of both CH$_4$ and CCl$_3$F. Approximate background concentrations are given for contemporary samples collected away from these urban locations but otherwise representative.

We define an "urban excess" as the difference in concentration for a given trace species between an air sample measured in an urban location and the corresponding concentration at approximately the same latitude and date in nearby remote locations away from any recent urban input into the air parcels. Such urban excesses are calculated for both CCl$_3$F and CH$_4$ in Table 1. The urban excess in any particular sample is the complex result of the strengths of emission sources modified by local topography, weather conditions, etc. The major technological uses of CCl$_3$F assure that almost all of its release occurs in urban surroundings.

Calculation of the actual absolute emission strength for a particular source region is difficult to do for any atmospheric species, and...
estimates from atmospheric assay would require repeated measurements over an extensive period of time to obtain suitable averaging over variable transport conditions as well as for time variations in emission source strength. Measurement of the urban excess of CClF in any individual sample provides a normalization factor for all volatile gases emitted into it, responding to the complex conditions of weather and topography. In general the strengths of individual sources of CClF and CCl2F2 in a specific locality are not well-known, but the ubiquitous nature of many of their uses (aerosol sprays; refrigeration) tend to distribute such emissions very widely both in time and space, and in rough proportion to the population in technologically advanced countries.

Two alternative approaches can be used for the evaluation of these urban excess concentrations: (a) the ratios of the excess amounts on an absolute basis, and (b) ratios of the excesses relative to the accumulated remote background levels. Both of these approaches have been applied to the air samples of Table 1, as demonstrated for one of them in Table 2. The incremental increases in CH4 and CCl1F relative to contemporaneous remote north temperate concentrations are 0.41x10^6 pptv and 325 pptv, respectively. The CH4 increment is larger than that of CCl1F by a factor of 1260 on a molar basis, or 147 by tonnage. The atmospheric release of CCl1F during 1980 has been estimated as 265 kilotons [Cunnold et al., 1983]. If the world-wide ratio of urban atmospheric releases for CH4/CCl1F were typified during that year by this London observation, then the urban release of CH4 for 1980 could be estimated to be 147 times 265 kilotons, or 39 megatons. Comparable calculations in Table 2 based on CCl2F2 and CH3CCl3 provide estimates of 44 megatons and 48 megatons, respectively. This agreement (44±5 megatons) among these urban estimates is interesting, but is not typical of the majority of our data. For most of the air samples of Table 1 about ±50% agreement is found between estimates based on CCl2F2 and CCl1F. However, the urban excesses of CH4 and CH3CCl3 are much more variable, consistent with its release during industrial operations (e.g., degreasing of metals), in contrast to CCl2F2 whose emission is often caused by the actions of single individuals.

The molar emission ratios in Table 1 generally fall in the range from 1000-2000, although the values are as low as 200 in Copenhagen and Brussels, and as high as 5000 in Rio de Janeiro. The ratio of 4200 found in Cracow represents an especially massive increase in observed methane over that found in nearby remote locations. The emission levels of both CH4 and halocarbons are quite low in the densely populated Chinese cities of Beijing and Dalian. The measurements in Table 1 cover data over a four-year period, 1980-1983, throughout which the atmospheric release of CCl1F has been estimated yearly at about 270 kilotons/year [C.C.A., 1984b]. World-wide molar ratios of 1000 to 2000 for CH4/CCl1F correspond to tonnage ratios of 116 to 232, and therefore to world-wide emission estimates of 31 to 63 megatons of CH4. These numbers agree well with the source strength estimates made earlier for CH4 by Elhalt [1979].

Alternatively, the urban excesses for CH4 and CCl1F can each be considered through the ratio relative to its background concentrations, and then these "urban excess ratios" can be compared with one another, i.e., ratio of the fractional increases in concentration for species A and B in the same air parcel. Such comparisons require for each atmospheric species an estimate of the ratio of the atmospheric burden to the yearly emissions at the time of measurement. If both compounds have been emitted to the atmosphere at constant rates and are now in steady state, then the appropriate ratio in such a comparison is simply the observed atmospheric burden divided by the atmospheric lifetime in years. We have estimated the atmospheric lifetime of CH4 as about 10 years [Mayer et al., 1982; Rowland et al., 1984], and have used ten years as its average residence time in Table 2.

The situation is quite different for CCl1F, whose atmospheric lifetime is estimated to be 60-80 years [Cunnold et al., 1983; Rowland et al., 1984b], but which is many decades from a steady-state situation. The 1980 atmospheric burdens for CCl2F2 and CCl1F were only about 16 and 15 times the estimated yearly emissions respectively. The rapid rise in CH4/CCl1F production during the 1970’s and its much shorter atmospheric lifetime lead to much smaller accumulations of CH3CCl3 as the background level for a fixed tonnage release during 1980. This measured
ratio of excess ratios must then be corrected for the differing atmospheric residence times. After such corrections, the data of Table 2 show a consistent estimate of 0.10 to 0.12 for CH₄ versus all three halocarbons. As with the absolute tonnage estimates, the agreement shown in Table 2 is not typical — CCl₄F and CCl₃F regularly give similar results but CH₃CCl₃ is much more variable. If the London air sample were typical of the world, urban CH₄ emissions would constitute about 0.11 to 0.12 of the world total. The final column of Table 1 provides other estimates of the fractional contribution of urban methane to the world total, as though that individual sample were typical of the world. The values generally fall into the range of 0.08 to 0.15 for the fractional urban release of CH₄.

A world-wide average tropospheric CH₄ concentration of 1.6 ppmv corresponds to a total atmospheric burden of 4.5 x 10¹² megatons, and the ten years atmospheric lifetime adopted for CH₄ then implies that both sources and sinks must be in the vicinity of 450 kilotons per year. An increase of 1% per year in total CH₄ concentration implies an excess of sources over sinks of about 50 kilotons/year, so that the current source strength must be in the vicinity of 50 kilotons per year and the current rise in concentration is about 450-500 kilotons/year. The fractional release estimates of Table 1 show substantial scatter, but are reasonably consistent with urban atmospheric releases of 30-50 megatons per year, accounting for roughly 10% of the total world emission.

The primary implications of our results are: (a) the scattered measurements of our results are experimentally consistent with a yearly atmospheric release of 30 to 60 megatons of CH₄ in urban environments, in agreement with the source strength estimates of Ehhalt [1978, 1979]; (b) it should be possible through extended sets of such simultaneous measurements in a particular urban location together with evaluation of CCl₄F release for that area to obtain a good estimate of the yearly release of CH₄ there; (c) if needed, combinations of many such extended sets could provide better world-wide values for the magnitude of CH₄ releases in urban areas. The possibility further exists, especially with larger urban excesses, for determination of the Carbon-14 content of methane which discriminates most fossil fuel sources (C-free because of long isolation) from those of biological origin.

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References


CH4 (Chemical Manufacturers Association), Production, sales and calculated release of CFC-11 and CFC-12 through 1982, August 12, 1983.


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