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Title
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Permalink
https://escholarship.org/uc/item/17m290ch

Journal
Geophysical Research Letters, 11(12)

ISSN
0094-8276

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Publication Date
1984-12-01

DOI
10.1029/gl011i012p01211

METHANE CONCENTRATIONS AND SOURCE STRENGTHS IN URBAN LOCATIONS

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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_3F. Because almost all CCl_3F 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_3F. 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-

singault, 1834]; and methane was identified as a constituent at the beginning of this century [Gautier, 1901]. Stephens and Burleson [1969] concluded from the concentration ratios among other light hydrocarbons that the major source of enhanced CH_4 concentrations in U.S. cities was the leakage of natural gas.

Ehhalt [1979] has placed the absolute releases from such non-biological anthropogenic activities at 25-60 megatons/year, while Sheppard et al. [1982] have estimated it to be about 100 megatons/year. However, such estimates have largely been source strength calculations with little quantitative confirmation by actual atmospheric measurement. In the present paper we describe our atmospheric measurements of trace gases in urban surroundings, and use these data to estimate the world-wide magnitude of urban methane emissions, and of the fractional importance of such emissions to its world-wide inventory.

During the past six years we have measured methane concentrations in tropospheric air samples collected in remote locations throughout the northern and southern hemispheres [Mayer et al., 1982; Rowland et al., 1984a]. We have also collected a smaller number of urban tropospheric air samples during that same period, and have assayed the methane concentrations in these as well. In most instances we have observed in these urban samples concentrations of methane elevated in comparison with those found in remote samples essentially coincident in latitude and date of collection.

Such quantitative data on elevated CH_4 concentrations measured for very specific localities and dates could be directly expanded into world-wide estimates of methane release only with a very large number of measurements because of the natural variability in climatic conditions governing atmospheric mixing, as well as from seasonal and/or diurnal variations in emission strengths. However, we have also measured in these same urban air samples several anthropogenic halocarbons (CCl_3F, CCl_2F_2, CCl_4, CH_3CCl_3) and such measurements are available for comparison with those of methane.

The concentration of trace atmospheric species in any urban environment represents the sum of the background contribution already present when the air parcel arrived in that location, plus the emissions added from local sources. The atmospheric concentrations of CCl_3F are entirely the result of anthropogenic activities, and its background concentrations measured in remote areas are then simply integral accumulations of such previous releases after world-wide distribution and mixing. For CH_4 and the four listed chlorocarbons, such a background is time and latitude dependent. With the approximate assumption that CCl_3F is emitted only in urban environments, comparison of the incremental increases in concentrations of CH_4 and of CCl_3F provides a basis for estimates of the urban release of

TABLE 1. Urban Tropospheric Concentrations of CH_4 and CCl_3F

Location	Date	Concentrations [CH_4] (a)		[CCl_3F] (a)		(b)	Urban Excesses Fractional CH_4	CCl_3F	(c)	(d)
		U*	R**	U*	R**					
Santiago, Chile	1/20/80	1.59	1.51	204	165	2100	0.053	0.24	0.22	0.15
Rio de Jan., Brazil	1/26/80	1.72	1.51	236	165	3000	0.14	0.43	0.32	0.22
Paramaribo, Surinam	2/01/80	2.44	1.61	474	165	2700	0.52	1.87	0.28	0.18
Cracow, Poland	5/08/80	3.42	1.65	599	180	4200	1.07	2.33	0.46	0.31
Warsaw, Poland	5/09/80	1.96	1.65	422	180	1300	0.19	1.34	0.14	0.09
London, England	7/25/80	2.02	1.62	564	184	1200	0.25	2.07	0.12	0.08
London, England	7/25/80	2.03	1.62	509	184	1300	0.25	1.77	0.14	0.09
Copenhagen, Denmark	8/01/80	1.68	1.60	455	182	300	0.05	1.50	0.03	0.02
Copenhagen, Denmark	8/01/80	1.69	1.60	570	182	200	0.06	2.13	0.03	0.02
Sao Paulo, Brazil	8/13/80	1.66	1.52	226	175	2700	0.09	0.29	0.32	0.22
Santiago, Chile	8/21/80	1.69	1.52	251	175	2200	0.11	0.43	0.26	0.17
Beijing, China	9/16/80	1.65	1.62	197	182	2000	0.02	0.08	0.25	0.16
Dalian, China	9/22/80	1.67	1.62	209	182	1900	0.03	0.15	0.02	0.13
Ketchikan, Alaska	11/22/80	1.92	1.63	329	189	2100	0.17	0.68	0.25	0.17
New York City	2/20/81	1.91	1.64	590	193	700	0.17	2.06	0.08	0.03
Rio de Jan., Brazil	6/14/81	1.62	1.53	192	175	5000	0.06	0.10	0.60	0.40
Hamburg, Germany	8/22/83	1.83	1.67	353	210	1100	0.10	0.68	0.14	0.10
Hamburg, Germany	8/24/83	1.82	1.67	317	210	1400	0.09	0.51	0.18	0.12
London, England	9/09/83	1.75	1.67	318	210	700	0.05	0.51	0.09	0.06
Brussels, Belgium	9/16/83	1.70	1.67	378	210	200	0.03	0.80	0.04	0.03
Rome, Italy	11/09/83	2.16	1.67	894	210	700	0.29	3.26	0.09	0.06
Rome, Italy	11/10/83	1.93	1.67	837	210	400	0.16	2.99	0.05	0.03

(a) Concentrations of CH_4 in ppmv (10^{-6}) and of CCl_3F in pptv (10^{-12}).
(b) Ratio of absolute increase in CH_4 to absolute increase in CCl_3F.
(c) Ratio of fractional increase in CH_4 to fractional increase in CCl_3F.
(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_3F.
* U = urban ** R = remote

methane, and of its fractional contributions to the total world emissions inventory.

Experimental

Tropospheric air samples have been collected in two-liter stainless steel canisters equipped with a single stainless steel valve. The canisters were evacuated in the laboratory and filled in open urban areas, usually in central parks within the cities. The measured trace concentrations of CH_4 varied from 1.5 to 3.5 parts per million by volume (ppmv), while those of CCl_3F were approximately 10^4 times smaller, from 160 to 900 parts per trillion by volume (pptv; 10^{-12}). The halocarbon content has been measured using electron capture gas chromatography as described for methylchloroform and for the perhalo compounds [Makide and Rowland, 1981; Rowland et al., 1984b]. The methane content has been measured in separate aliquots of the same samples using flame-ionization gas chromatography [Mayer et al., 1982; Blake et al., 1982] with a precision calculated as $\pm$ 0.006 ppmv.

The absolute calibration of the halocarbon measurements was carried out by successive dilutions on a vacuum line, and is accurate to about $\pm$ 5%. The natural variability in our data is large enough that the precision and/or accuracy of the halocarbon measurement is rarely a limiting factor in comparisons of incremental increases in CH_4 and CCl_3F concentrations in urban samples.

Results and Discussion

The measured concentrations of methane and CCl_3F 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_3F. 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_3F 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_3F 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

TABLE 2. Urban Excesses of CH_4 versus CCl_3F, CCl_2F_2, and CH_3CCl_3

Concentrations in pptv (10^{-12})	CH_4	CCl_3F	CCl_2F_2	CH_3CCl_3
London, England (7/25/80)	2.03×10^6	509	817	638
Remote Location Background	1.62×10^6	184	330	120
Absolute Concentration Excess	0.41×10^6	325	487	518
Molar Excess Ratio (CH_4/Halocarbon)		1260	840	790
Estimated 1980 Release (kilotons)		265	393	504
Estimated 1980 CH_4 Emissions (megatons)		39	44	48
Excess Ratio [Urban/Remote - 1.00]	0.25	1.77	1.48	4.32
Ratio of Excess Ratios [CH_4/X] (a)		0.14_3	0.17_1	0.05_9
Corrected Ratio of Excess Ratios (a)		0.10^3	0.11^1	0.12^9

(a) Corrected for total atmospheric burden divided by yearly release in 1980: CH_4, 10; CCl_3F, 15: CCl_2F_2, 16; CH_3CCl_3, 4.8.

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 CCl_3F 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 CCl_3F and CCl_2F_2 in a specific locality are not well-known, but the ubiquitous nature of many of their uses (aerosol sprays; refrigeration) tends 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 CH_4 and CCl_3F relative to contemporaneous remote north temperate concentrations are 0.41×10^6 pptv and 325 pptv, respectively. The CH_4 increment is larger than that of CCl_3F by a factor of 1260 on a molar basis, or 147 by tonnage. The atmospheric release of CCl_3F during 1980 has been estimated as 265 kilotons [Cunnold et al., 1983]. If the world-wide ratio of urban atmospheric releases for CH_4/CCl_3F were typified during that year by this London observation, then the urban release of CH_4 for 1980 could be estimated to be 147 times 265 kilotons, or 39 megatons. Comparable calculations in Table 2 based on CCl_2F_2 and CCH_3CCl_3 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 +25% agreement is found between estimates based on CCl_3F and CCl_2F_2. However, the urban excesses of CH_3CCl_3 are much more variable, consistent with its release during industrial operations (e.g. degreasing of metals), in contrast to CCl_3F and CCl_2F_2 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 CH_4 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 CCl_3F held at about 270 kilotons/year [C.M.A., 1983; Rowland et al., 1984b]. World-wide molar ratios of 1000 to 2000 for CH_4/CCl_3F correspond to tonnage ratios of 116 to 232, and therefore to world-wide emission estimates of 31 to 63 megatons of CH_4. These numbers agree well with the source strength estimates made earlier for CH_4 by Ehhalt [1979].

Alternatively, the urban excesses for CH_4 and CCl_3F 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 CH_4 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 CCl_3F, 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 CCl_2F_2 and CCl_3F were only about 16 and 15 times the estimated yearly emissions respectively. The rapid rise in CH_3CCl_3 production during the 1970's and its much shorter atmospheric lifetime lead to much smaller accumulations of CH_3CCl_3 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 CH_4 versus all three halocarbons. As with the absolute tonnage estimates, the agreement shown in Table 2 is not typical -- CCl_2F_2 and CCl_3F regularly give similar results but CH_3CCl_3 is much more variable. If the London air sample were typical of the world, urban CH_4 emissions would constitute about 0.11 ± 0.01 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 CH_4.

A world-wide average tropospheric CH_4 concentration of 1.6 ppmv corresponds to a total atmospheric burden of 4.5×10^3 megatons, and the ten year atmospheric lifetime adopted for CH_4 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 CH_4 concentration implies an excess of sources over sinks of about 50 kilotons/year, so that the current source strength consistent with a 10-year lifetime 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 30-60 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 CH_4 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 CCl_3F release for that area to obtain a good estimate of the yearly release of CH_4 there; (c) if needed, combinations of many such extended sets could provide better world-wide values for the magnitude of CH_4 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 (^{14}C-free because of long isolation) from those of biological origin.

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