

METHANE AND CARBON DIOXIDE INCREASES IN THE URBAN BOUNDARY LAYER:  
INFERENCES FROM WHOLE-COLUMN INFRARED ABSORBANCE MEASUREMENTS

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*Abstract.* Using the sun as an infrared source, we determined the total atmospheric column absorbance of methane and carbon dioxide spectral lines in the 8- to 10- $\mu\text{m}$  infrared region. At our laboratory located in an urban region, these absorbances showed fluctuations larger than can be accounted for by known variabilities in the background atmosphere. We interpret these observations in terms of large changes in concentration of methane and carbon dioxide within the urban boundary layer. These increases could affect the radiative balance in urban locations and contribute to the urban heat island.

## Introduction

The transparency of the earth's atmosphere in the 8- to 10- $\mu\text{m}$  infrared region is affected strongly by the concentration of certain infrared absorbing gases. Increases in the concentration of these radiatively active gases could alter the radiation balance of the earth-atmosphere system and lead to global warming, the phenomenon commonly referred to as the "greenhouse effect" [e.g., Dickinson and Cicerone, 1986]. Measurements of radiatively active trace gases in the atmosphere have been performed extensively; however, the majority of such data report concentrations either above the planetary boundary layer or at ground level. Little information has been collected on trace gas concentrations within the planetary boundary layer or the urban boundary layer. In this report, we show that concentration increases in urban areas may be large, potentially leading to intensified local thermal trapping and contributing to the urban heat island. Existing literature on this topic describes sophisticated modeling but frequently underestimates pollutant concentrations.

Using a Fourier transform infrared spectrometer and a solar tracking coelostat at Lawrence Berkeley Laboratory, we measured whole-column infrared absorbances due to radiatively active gases using the sun as the source. We report here on results for carbon dioxide and methane. After correcting for path length differences, a time series of absorbances was generated, with a smallest time increment of 24 hr. The day-to-day fluctuations in whole-column absorbances due to carbon dioxide and methane in the San Francisco area were much greater than expected, suggesting substantial changes in the vertical distribution of these gases.

From calculations employing different boundary layer heights, the increase within the boundary layer can be estimated.

## Experimental Details

Infrared spectra were measured by a Fourier transform spectrometer capable of 0.125- $\text{cm}^{-1}$  resolution (Mattson Instruments, Sirius 100). A beam of solar radiation was brought into the laboratory by a solar tracking coelostat in conjunction with three 1-sq ft aluminum front-coated flat mirrors [Pasachoff and Livingston, 1984]. The ratio of solar beam to blocked beam signal was approximately 50 to 1, and the root mean square instrument noise level was about 0.1%.

Spectra were collected on 35 days spanning a 9-mo period and were taken primarily when the sky was cloudless. Intermittent cloudiness was acceptable if periods of clear beam path lasted long enough to perform a scan. The path length was the entire atmospheric column extending upwards from the elevation of the instrument (700 ft above sea level). Spectra were taken close to true solar noon, and path-length correction was performed each day to normalize absorption values. Scanning required 3 min, and the processing of the interferograms approximately 5 min at high resolution.

Spectral lines were identified by reference to a published atlas of IR solar spectra [Goldman et al., 1980]. Lines were chosen to minimize overlapping and saturation and were quantified by between 5 and 13 data points. Each line was fitted to a collision-broadened Lorentzian line shape given as

$$\ln I(\lambda) = k_b - (k_o \alpha^2)/(\lambda - \lambda_o)^2 + \alpha^2,$$

where  $\alpha$  is the half width,  $k_b$  is the background,  $\lambda_o$  is the central wavelength, and  $k_o$  is the absorbance at  $\lambda_o$  [Paltridge and Platt, 1976]. The fit was optimized with respect to all parameters. We then calculated the whole-column line absorbance—i.e., the integral of this line shape, given by  $A(\lambda_o) = \pi k_o \alpha$ .

To check the fit and the assignment of the background  $k_b$ , two or more spectral lines were located for each trace gas species. The absorbances for strong lines of the same species should correlate under changing conditions [D. Goorvitch, personal communication, 1986; H. A. Shugart, personal communication, 1986]. Differential line intensity changes due to temperature changes may occur, but this effect is on the order of a few percent for strong lines [Houghton, 1985]. A correlation coefficient of 0.81 was achieved for two methane lines located at 1228.78  $\text{cm}^{-1}$  and 1230.22  $\text{cm}^{-1}$ .

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TABLE 1. Scanning dates and whole column absorbance for methane and carbon dioxide lines located at  $1230.22 \text{ cm}^{-1}$  and  $938.64 \text{ cm}^{-1}$ , respectively. Whole column absorbance is the integral of the fitted absorbance peak, corrected for solar elevation.

Sequence #	Date	Whole column absorbance	
		CH <sub>4</sub>	CO <sub>2</sub>
1	10-4-85	0.296	0.207
2	10-11-85	0.306	0.175
3	10-13-85	0.273	0.186
4	10-16-85	0.223	0.194
5	10-25-85	0.270	0.179
6	11-6-85	0.293	0.185
7	11-18-85	0.227	0.152
8	3-17-86	0.285	0.205
9	3-18-86	0.250	0.172
10	3-19-86	0.274	0.168
11	3-20-86	0.261	0.179
12	3-21-86	0.267	0.201
13	3-24-86	0.272	0.162
14	3-25-86	0.256	0.186
15	3-26-86	0.299	0.171
16	3-27-86	0.319	0.165
17	4-2-86	0.274	0.190
18	4-3-86	0.271	0.161
19	4-4-86	0.261	0.173
20	4-9-86	0.315	0.196
21	4-10-86	0.274	0.175
22	4-11-86	0.249	0.181
23	4-14-86	0.271	0.169
24	4-17-86	0.249	0.165
25	4-21-86	0.271	0.188
26	4-23-86	0.278	0.194
27	5-8-86	0.268	0.186
28	5-9-86	0.296	0.179
29	5-13-86	0.290	0.198
30	5-16-86	0.274	0.202
31	5-21-86	0.298	0.190
32	7-7-86	0.323	0.216
33	7-9-86	0.326	0.211
34	7-10-86	0.329	0.206
35	7-31-86	0.297	0.212

### Results

Table 1 lists the observed vertical-column line absorbances of carbon dioxide and methane for lines centered at  $938.64 \text{ cm}^{-1}$  and  $1230.22 \text{ cm}^{-1}$  respectively. This absorbance is related to the total column concentration by Beer's law in the form

$$A_v(\lambda_0) = A(\lambda_0)/\sin \theta = \int c(x) a(\lambda_0, x) dx / \sin \theta,$$

where  $c(x)$  is the absorbing gas concentration at altitude  $x$ , and the integral is calculated from the laboratory to the top of the atmosphere along the beam path of elevation angle  $\theta$ . Figure 1 shows the same data, with the abscissa representing dates when scanning was per-

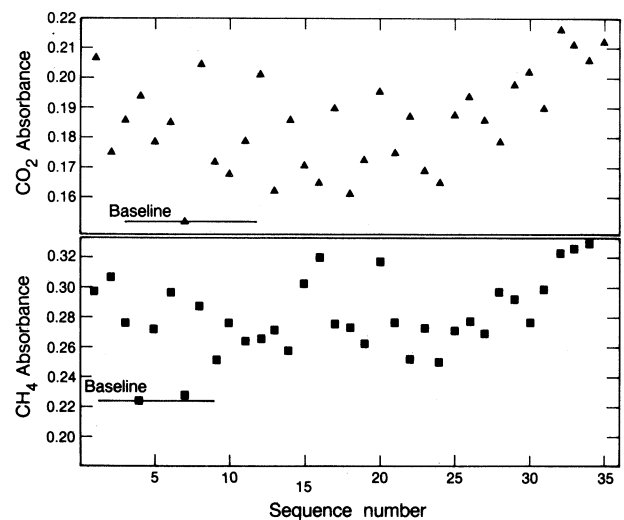
formed. (Note that not all days are consecutive.) The smallest values of  $A_{v0} = 0.223$  and  $0.152$  for methane and carbon dioxide represent the vertical-column line absorbances measured on the least polluted days when the local atmosphere most closely approached the background troposphere. Increases above these values represent increases in the total column loading of these gases. The largest value of  $A_v$  for methane was 1.48 times this minimum, and for carbon dioxide was 1.42 times greater. The greatest increases over a 24-hr period were 17% and 19%, respectively.

It is unlikely that the entire atmospheric column concentration varies by the above factors. Tropospheric methane and carbon dioxide have been widely monitored [e.g., Ehhalt and Heidt, 1973; Clark, 1982]. Methane varies by a maximum of 7-8% from mean values; carbon dioxide, by a maximum of 5%. The large changes shown in Figure 1 must therefore occur in a smaller region of the atmospheric column where concentrations of ground source pollutants are prone to fluctuate—the urban boundary layer.

This hypothesis is supported by measurements of the line half-width,  $\alpha$ . Collision broadening of the absorption line is a function of both the atmospheric pressure and absolute temperature as:

$$\alpha_L = \alpha_{L0}(P/P_0)(T_0/T)^{1/2},$$

where  $\alpha_{L0}$  is the Lorentzian half-width at standard atmospheric pressure  $P_0$  and temperature  $T_0$  [Houghton, 1985]. The absorption line observed at the earth's surface is the sum of absorbances by the particular gas species distributed throughout the atmospheric column. Absorbance contributions from higher altitudes will have line widths smaller than those from lower altitudes. Increases in the species concentration at the lowest altitudes (within the urban boundary layer) will therefore increase the width as well as the amplitude of the observed line relative to the background atmo-



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Fig. 1. Time series of methane and carbon dioxide whole column absorbance.

TABLE 2. Increase factors for methane and carbon dioxide in the given boundary layer height relative to the observed minimum. Nine-month maximum change and 24-hour maximum change are estimated. A range is given for methane representing calculations for two spectral lines. Single values for carbon dioxide estimates are given representing the strongest of a series of weak spectral lines.

Boundary layer height	Increase factors			
	Maximum change CH <sub>4</sub>	CO <sub>2</sub>	24-hr change CH <sub>4</sub>	CO <sub>2</sub>
0 to 0.5 km	2.1-6.0	6.0	1.3-1.7	2.4
0 to 1.0 km	1.6-3.5	3.6	1.2-1.3	1.7
0 to 2.3 km	1.3-2.1	2.1	1.1-1.14	1.3

sphere. This was observed in all of our data. The changes in line width were too large to be accounted for by changes in atmospheric pressure and temperature of a constant vertical distribution of the absorbing species and are therefore consistent with increases in concentration at low altitudes. With higher resolution spectra, it is possible to infer the column distribution of a gas from deconvolution of the absorption line shape [Goldman et al., 1983].

To estimate the changes of methane and carbon dioxide in the urban boundary layer, the vertical distribution of these gases was simulated in a multi-layer model. From published data, we calculated the vertical column infrared absorption for the background troposphere summed in 20 layers, and assigned this value to our minimum measured absorbances  $A_{v0}$ . Natural tropospheric fluctuations could then result in increases by factors of 1.08 and 1.05 for methane and carbon dioxide respectively. To account for the large increases actually observed (up to 1.48), we calculated the concentration increases required if the additional gas were added to the boundary layer only. These changes are amplified relative to the increase of the total vertical column absorbance: for a total column absorbance increase of 40% to be achieved by a concentration increase in the lowest 1 km layer, then that layer's concentration must approximately triple. Table 2 lists these increase factors for a range of possible boundary layer thicknesses. The two values shown for methane represent the results of this calculation performed for data from two methane lines. Increasing the smallest (i.e., "background") values of vertical-column line absorbance  $A_{v0}$  to 0.25 for methane and 0.165 for carbon dioxide reduces these factors in Table 2 by approximately 35% and 23%, respectively.

#### Discussion

The analysis calls for large concentration increases within the urban boundary layer. The most likely mechanism for producing these increases is the combination of ground-level sources and meteorological stag-

nation induced by topography and high pressure systems. The San Francisco Bay Area is prone to stagnation in spring and fall, with the mixed layer on average extending to approximately 1200 ft altitude [Lester, 1985]. Since our laboratory is located at an elevation of 700 ft, the observations were made through a depth of a few hundred feet of the urban boundary layer.

Ground-level measurements of methane concentrations are routinely performed by the Bay Area Air Quality Management District at several locations in the urban area. These concentrations vary typically from 1.6 ppm to a maximum of 5.3 ppm, with frequent day-to-day fluctuations by a factor of three [Bay Area Air Quality Management District, 1986]. The boundary layer methane variation estimates listed in Table 2 are therefore not unreasonable.

The estimates for carbon dioxide increases are considered to be less accurate than those for methane. Ground-level carbon dioxide in an urban situation has been observed to fluctuate by as much as 20% [A. D. A. Hansen, unpublished data, 1986] but not as much as the estimates in Table 2. A likely source of inaccuracy is the weakness of the carbon dioxide line used, resulting in width and amplitude parameters that are affected by temperature changes.

One result of large increases of these two gases would be increased infrared trapping in the polluted urban boundary layer, an important factor in the development of the urban heat island. Theoretical simulations of pollutant loading in urban areas have been conducted using sophisticated radiative transfer models [Bergstrom and Viskanta, 1973; Atwater, 1977]. The general conclusion of these studies was that thermal trapping due to pollutants added only small amounts of energy to urban areas. However, these models did not use actual pollutant compositions or concentrations. A simulation incorporating large changes in carbon dioxide, methane, and other radiatively active trace gases is necessary to determine the real effect such pollutant fluctuations may have on the urban climate.

#### Conclusions

Data collected on whole-column absorbances of methane and carbon dioxide imply large changes in their urban boundary layer concentrations when simulated in a vertical distribution model. Changes in methane concentration by up to a factor of 6 over background levels are suggested. Our estimates of boundary layer carbon dioxide changes, though presently prone to error, are an indication of possible increases within the lowest 1 or 2 km of the atmosphere. Increases in both these gases within the urban boundary layer could have definite ramifications for urban climate modeling.

Modeling of the effects of pollutants on urban radiative transfer does not appear to have taken adequate account of the concentrations of radiatively active trace gases. Simulations with concentrations approaching those observed here may show that these pollutants play important roles in urban heating.

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