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Development of Atmospheric Tracer Methods To Measure Methane Emissions from Natural Gas Facilities and Urban Areas

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A new, integrated methodology to locate and measure methane emissions from natural gas systems has been developed. Atmospheric methane sources are identified by elevated ambient CH_4 concentrations measured with a mobile laser-based methane analyzer. The total methane emission rate from a source is obtained by simulating the source with a sulfur hexafluoride (SF_6) tracer gas release and by measuring methane and tracer concentrations along downwind sampling paths using mobile, real-time analyzers. Combustion sources of methane are distinguished from noncombustion sources by concurrent ambient carbon dioxide measurements. Three variations on the tracer ratio method are described for application to (1) small underground vaults, (2) aboveground natural gas facilities, and (3) diffuse methane emissions from an entire town. Results from controlled releases and from replicate tests demonstrate that the tracer ratio approach can yield total emission rates to within approximately ±15%. The estimated accuracy of emission estimates for urban areas with a variety of diffuse emissions is ±50%.

Introduction

Methane (CH_4) has been a contributor to the increasing burden of greenhouse gases in the earth's atmosphere for more than a century (*1*). Faced with significant risks identified in scenarios of increasing greenhouse gas concentrations, many countries are developing plans to reduce emissions. However, uncertainties in specific source emission rates for CH_4 and other non-CO_2 greenhouse gases currently limit the quantitative risk–benefit analysis needed to answer key policy questions related to the socioeconomic impacts of large-scale mitigation actions (*2*, *3*).

Initial attempts to estimate CH_4 losses to the atmosphere from natural gas production and use assumed that emissions could be approximated by industry reports of "unaccounted for" gas (e.g., ref 4). Unaccounted for gas, defined as the difference between the amount of natural gas metered into a system and the amount of gas metered out of a system, does not account for gas losses from wells to the processing plant, gas used as fuel in facilities, theft of gas, meter inaccuracies, and differences in accounting procedures between companies (*4*, *5*). Thus, the unaccounted for gas estimates cannot unambiguously be considered an upper or lower bound on emissions (*5*). Extrapolation of engineering estimates or data obtained from component by component sniffing methods also leads to large uncertainties in estimated emissions. In the United Kingdom, the British Gas Company estimates CH_4 emissions from gas distribution system components to be less than 1% of throughput, while others estimate losses as high as 11% of gas throughput (*6*). A recent estimate of CH_4 leakage from the natural gas system in the former Soviet Union, which was characterized as "tentative and highly conditional" suggested a range of total losses from 3.3% to 7% of gas production (*7*).

The U.S. Environmental Protection Agency (EPA) and the Gas Research Institute (GRI) have recently sponsored an integrated field measurement and analysis program to better define methane emissions from the U.S. natural gas system. Drawing on initial measurements using some of the techniques reported here as well as engineering estimates, GRI has developed a preliminary estimate of methane emissions from the gas industry that equals approximately 1.5 ± 0.5% of annual throughput (*8*).

In the case of CH_4 emissions due to the use of natural gas, there is an added motivation for correctly prescribing the methane source strength. Since natural gas typically produces 32–45% less CO_2 per unit of thermal output compared to coal and 30% less compared to fuel oil, switching from coal and fuel oil to natural gas has the potential to reduce carbon dioxide emissions and reduce global warming (*5*). However, CH_4 is a more potent greenhouse gas than CO_2 on a molecule for molecule basis (*9–11*). As a result, increasing the usage of natural gas may

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not yield the expected benefits with respect to climate change unless methane emissions from natural gas systems are minimized.

The purpose of this paper is to describe the development of a new integrated methodology designed to yield the total methane emission rate from a natural gas facility. This new tracer ratio approach is unique compared to typical emission measurement techniques in several ways. First, the method was designed from the outset to employ mobile, real-time instrumentation, which allows real-time identification of the source plume and any potential interfering sources, and it allows emission measurements to be made for a number of different sources in a very short period of time. Second, the method yields total methane emissions from a source and does not require the type of component by component sniffing and bagging tests that are commonly used in the gas industry. Third, the same set of instrumentation can be used to test sources ranging in scale from a few meters (underground vaults) to a few kilometers (small city distribution systems). Finally, the tracer ratio method provides built-in confirmation of the correctness of the tracer simulation for a specific source. This paper describes the details of three variations on the tracer ratio method and provides an example of how it can be applied to small gas facilities, to a moderately large gas production plant, and to a small city. The results from these demonstration tests are presented to show the flexibility of the method and to provide a basis for discussing the uncertainties associated with the techniques. Results from application of these methods will be presented in a separate paper.

Experimental Procedures

Isolated Source Tracer Ratio Method. The tracer ratio method applied to an isolated facility involves simulating the methane source with a tracer gas release, measuring the ratio of methane and tracer concentrations downwind of the source, and calculating the methane emission rate (Q_m) directly from

$$Q_m = Q_t \frac{C_m}{C_t} \quad (1)$$

where Q_t is the measured tracer release rate, C_m is the measured methane concentration above background, and C_t is the measured tracer concentration. The tracer ratio method has the advantages that no meteorological measurements are required and no dispersion modeling is invoked. The tracer ratio approach has been used previously to measure isoprene fluxes from an oak grove (*12*) and to measure hydrocarbon emissions from an oil refinery wastewater basin (*13*). These earlier studies employed whole air sample collection followed by laboratory gas chromatography analysis.

The current methodology is greatly improved because of the capability to monitor both the methane and tracer plumes in real time with mobile analyzer systems. This provides a way to establish that the methane and tracer plumes are collocated, and it allows sampling systems to be positioned directly in the plumes. The real-time methane analyzer also provides an excellent way to ensure that no interfering sources are present upwind of the test area and to determine the magnitude and variability in background concentrations. The method requires that the methane signal downwind of a source is sufficiently elevated above background (typically greater than 50 ppb difference), and the source distribution of methane, including any vertical plume rise due to momentum or thermal buoyancy, can be adequately simulated with one or more tracer releases. As will be demonstrated, making measurements of the average methane/tracer ratio at several locations downwind of a source using a combination of fixed samplers and the mobile analyzers provides a way to confirm that the tracer release is an accurate simulation of the methane source and that methane and tracer undergo the same transport and diffusion in the atmosphere. This is a powerful aspect of the technique because it provides a built-in quality control check on each individual experiment. If the methane/tracer ratios among the individual measurements during a test show good agreement, then it can be assumed that the tracer release was an accurate simulation of the source and that no interfering sources were present. In addition, since the canister samplers are analyzed independently of the calibration of the real-time methane and tracer analyzers, agreement between canister results and analyzer results provides a second check on the overall accuracy of the measurement. An error analysis of the tracer ratio approach, described in Appendix A, yields an overall uncertainty estimate of less than ±15% under typical experimental conditions.

Enclosed Source Tracer Ratio Method. In the course of this work, it became apparent that in many urban areas, pressure regulating or metering systems housed in underground vaults were an important component of natural gas distributions. To obtain emission rate measurements from these very small vaults, the isolated source technique was modified. This involved using a mechanical blower to ventilate the vault, introducing a dilute mixture of tracer (0.1% in air) into the vault through the blower, and measuring methane and tracer concentrations at the vault exhaust port and/or at locations a few meters downwind of the vault. The methane emission rate was then obtained directly using eq 1.

Area Source Tracer Ratio Method. For diffuse source areas, it is very difficult to deploy a distributed tracer release system capable of simulation of all of the methane sources. To circumvent this problem, Ludwig et al. (*14*) developed an area source tracer ratio method. To measure emissions from an industrial complex, Ludwig et al. deployed a line source of tracer along the upwind edge of the source, and fixed point measurements of concentration were combined with a Gaussian description of diffusion to estimate the area source emissions. For our purposes, this method was inverted so that a point source of tracer located within an urban area is used with crosswind integrated tracer concentrations (CWI_t) and the average crosswind concentration of methane (C_m) to calculate the methane flux (F_m) from the urban area:

$$F_m = Q_t \left(\frac{C_m}{CWI_t} \right) B \quad (2)$$

where the coefficient B accounts for the differences in vertical plume diffusion due to differences in travel distances between the methane (released from X_u to X_d) and tracer (released from a central point source at distance x_t upwind of the receptor):

$$B = \frac{(1-b)}{x_t^b (X_d^{1-b} - X_u^{1-b})} \quad (3)$$

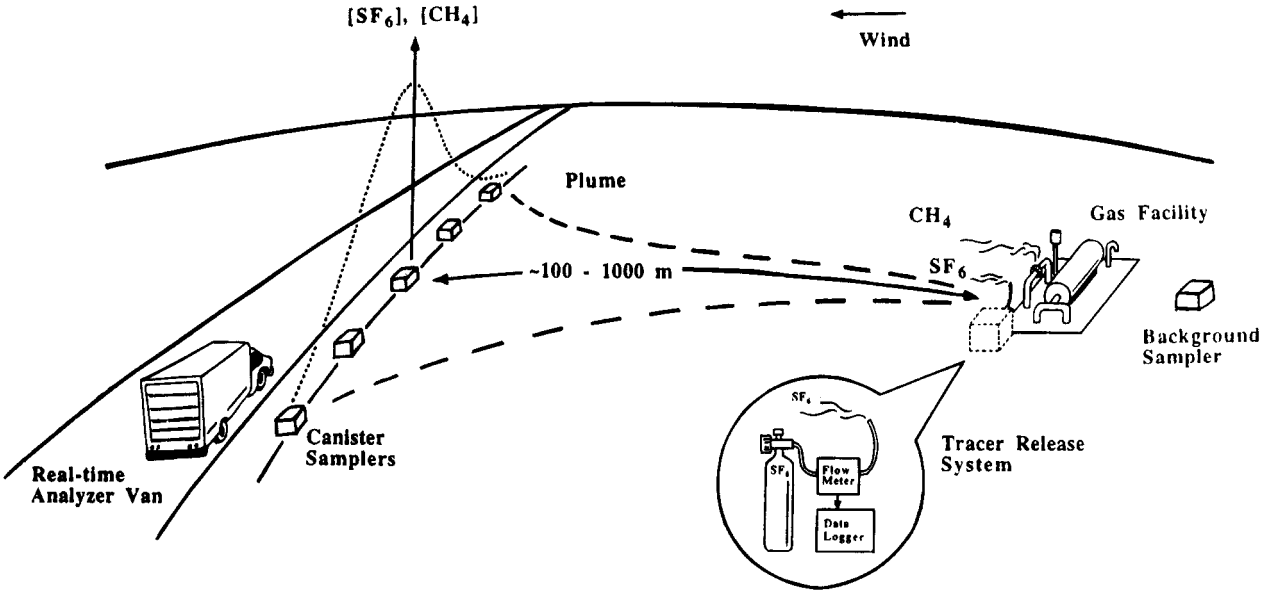

FIGURE 1. Schematic of the tracer ratio emission measurement method showing the tracer release at the source of interest, the use of the mobile analyzers to locate and sample the methane/tracer plumes, and the deployment of canister samplers for upwind and downwind measurements.

For a diffuse source, the area source tracer ratio method requires measurement of the wind speed, determination of the area source boundaries, and estimation of the vertical diffusion exponent b where $\sigma_z = ax^b$ and σ_z is the vertical plume diffusion parameter. Since the tracer release rate is measured directly, and the crosswind average methane concentration and the crosswind integrated tracer concentration are measured using the mobile analyzer system, the value of b can be obtained from the tracer measurements via mass balance or it can be taken from diffusion data in the literature. Depending upon the uncertainty associated with the value of b, the overall uncertainty estimated from a propagation of errors analysis (see Appendix A) ranges from approximately 50% to 60%. This level of uncertainty is primarily due to the variability in the measured methane and crosswind integrated concentrations and the uncertainty in the vertical diffusion coefficient.

Instrumentation. The overall approach developed in this work is illustrated in Figure 1. An ultrasensitive methane analyzer mounted in a van was used to identify and map methane concentrations in cities and in the vicinity of gas system facilities. After a source was identified, a tracer release system, mounted in a second van, was located at the source, and the tracer was released continuously at a steady, measured rate. After the release was established, the methane analyzer and a continuous tracer analyzer were used in the mobile system to measure crosswind concentration profiles downwind of the source. Whole air canister samplers were deployed at locations upwind of the source and downwind in the methane/tracer plumes to collect 30-min average air samples. The mobile system was used to measure methane/tracer concentrations along crosswind traverses or while parked in the plume. Integrated methane and tracer concentrations from both the fixed and mobile sampling systems were used in eq 1 to calculate the methane emission rate from the source.

ARI Methane Analyzer. The Aerodyne Research, Inc. (ARI) mobile methane monitor employed in this work is a unique, high-accuracy real-time instrument (*15–19*). The instrument is based on the absorption of infrared radiation (3.39 μm wavelength) produced by a precisely controlled HeNe laser. The laser is rapidly tuned on and off a methane absorption line at 2947.91 cm^{-1}, which gives a high-sensitivity differential absorption measurement.

The instrument is sensitive to changes in ambient concentration of about 0.3% or 5 ppb methane (RMS at 1 s averaging). The response time of 6 s is due to the gas flow time through the sampling cell. The instrument is shock-mounted and can operate in a van moving at normal roadway speeds. The instrument is calibrated on an hourly basis in the field using methane/air mixtures referenced to a NIST standard.

WSU Tracer Gas Analyzer. The continuous tracer analyzer, based upon the original design by Simmonds et al. (*20*), was developed as a fast response instrument for routine field operation at Washington State University (WSU) (*21*). The instrument is configured for turbulent fluctuation measurements with a response time of 0.4 s and a detection limit of less than 10 ppt. The instrument is calibrated approximately every hour during each sampling period using SF_6/air standards over the range 25 ppt to 10 ppb (±5% certified accuracy, Scott-Marrin, Inc.).

Carbon Dioxide Instrument. A LiCor infrared CO_2/H_2O analyzer (LI-6262) is used for the measurement of ambient atmospheric carbon dioxide concentrations. Frequent instrument calibrations are performed using zero gas and a CO_2 standard (NIST).

Global Positioning System (GPS). For purposes of mapping the location of sources, the geographic location of the instrumented van is determined using a two-receiver global positioning system (Trimble, Inc.). The GPS portable receiver is mounted in the van, while a base station is located at a known, fixed location—usually a hotel room. Post-processing of the data provided van position with an accuracy of approximately 2–5 m. The van is also equipped with a drive shaft counter, which yields driving distances accurate to ±1 m.

Data from the methane, tracer, and carbon dioxide analyzer along with the count from the drive shaft counter are recorded at 1 Hz with a laptop computer. The data system allows input of numbered event codes that are manually recorded and identified in terms of location and

time to aid in reconstruction of the sampling path and procedures. The data system time is synchronized with the GPS system time so that the data file and GPS files can be merged during data reduction.

Whole Air Canister Samplers. Whole air samples are collected for methane and tracer measurements using portable samplers. Air is drawn into a clean 6-L stainless steel electropolished canister using a small battery-powered pump fitted with a Teflon–aluminum head. During a 30-min sampling period, the canisters are pressurized to approximately 20 psia at a steady rate by pumping against a stainless steel capillary flow restrictor. Approximately four to eight samples are collected using the portable samplers during a tracer ratio test.

The samples are analyzed for methane using flame ionization gas chromatography (HP5880) with a fixed gas sampling loop. The instrument is calibrated with a commercial standard traceable to NIST standards. Each air sample is analyzed at least four times to obtain precision levels of approximately ±10 ppb or less. Air samples are analyzed for sulfur hexafluoride using electron capture gas chromatography (HP5880) calibrated periodically with commercial standards. The precision level of the tracer analyses is typically less than ±5%.

Tracer Release System. The tracer release system consists of a calibrated mass flowmeter housed in a portable case along with a microprocessor data acquisition system. Readings from the mass flowmeter are recorded at 1 Hz and stored as 1-min averages with standard deviations. The tracer is released from gas cylinders through a regulator to the mass flowmeter and then through a calibrated dry gas meter. Dry gas meter readings are recorded manually throughout each release period. Typically, the differences between average flow rates measured with the mass flowmeter and the dry gas meter are less than ±10%. Variability in the release rate is less than ±2%.

NCAR Balloon-Borne Sampling Sonde. During the city-wide tracer demonstration test, vertical profiles of methane along with wind speed, direction, and temperature were obtained using a tethersonde and tethered balloon. Methane concentrations were obtained via Teflon tubing hoisted aloft with the balloon. At each sampling level, the balloon was held steady, and air was drawn down the sampling line into electropolished canisters. The averaging time was approximately 5 min, and canisters were collected at heights ranging from the surface up to 100 m.

NCAR Mobile Methane Analyzer. Total hydrocarbon concentrations were measured through the balloon sampling lines and also during the gas plant demonstration tests using a flame ionization detector (Baseline Instruments, Inc.) operated as a continuous real-time instrument installed in a van. When non-methane hydrocarbon concentrations were in the few parts per billion range, the real-time FID essentially responded as a real-time methane analyzer.

Presentation of Results

Controlled Methane Release Tests. As a preliminary test of the method, small-scale tests were conducted using a controlled release of methane and tracer. Tracer and methane were released at a steady, measured rate into a small blower and length of duct which served as a mixing volume. In the first set of tests, measurements were made at a fixed position approximately 50 m from the release. In the second series of tests, measurements were made by traversing through the plume approximately 100 m downwind of the source. During a portion of these tests, the tracer and methane releases were separated by approximately 30 m to test the effects of not having the tracer and methane exactly collocated. Results from periodic traverses through the plumes are shown in Figure 2a for collocated releases and in Figure 2b for separated releases. In both cases, the close correlation of the methane and tracer plumes is clearly evident. The tracer signal tends to exhibit more structure due to the faster response time of the instrument. When the measured ratio of methane/tracer averaged concentrations is compared to the measured ratio of the methane/tracer release rates, the agreement is within 14%, which is within the experimental uncertainty associated with the tracer release rate and the measured methane and tracer concentrations. In this case, there was no apparent difference between the collocated and separated release tests.

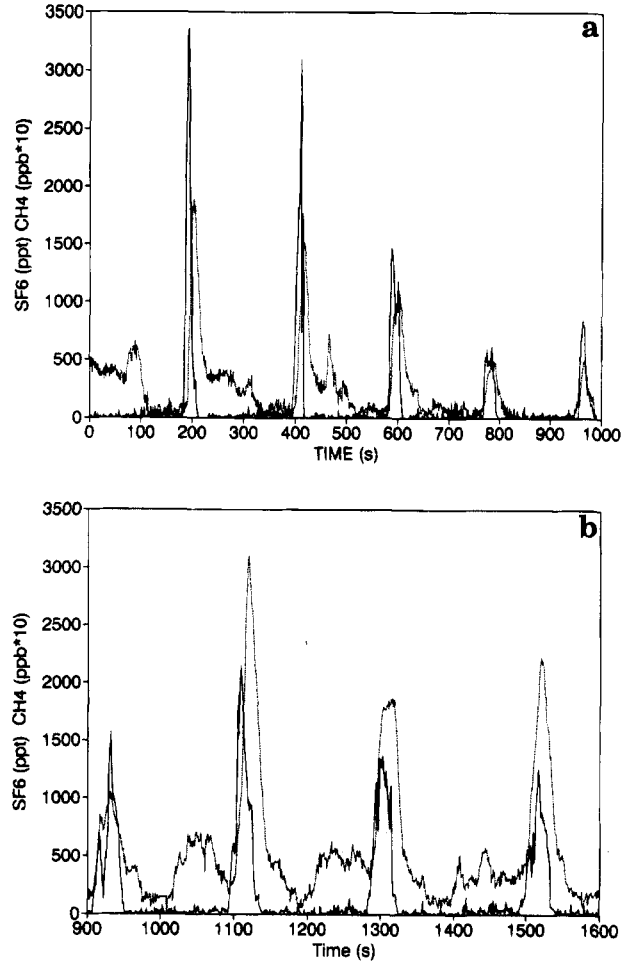

FIGURE 2. Illustration of real-time methane (dashed) and tracer (solid) concentration profiles collected along traverses approximately 100 m downwind of a controlled methane/tracer release: (a) collocated methane/tracer release; (b) methane and tracer release points separated by 30 m.

Methane Emissions from Gas Production Facilities. During the fall 1991, surveys of methane concentrations and isolated source tracer ratio measurements were conducted at a gas production area in the south-central United States. The purpose of these measurements was to demonstrate the feasibility of applying the survey and tracer methods to production facilities.

Initial methane surveys at the first site showed that significant hotspot emissions occurred from the gas pro-

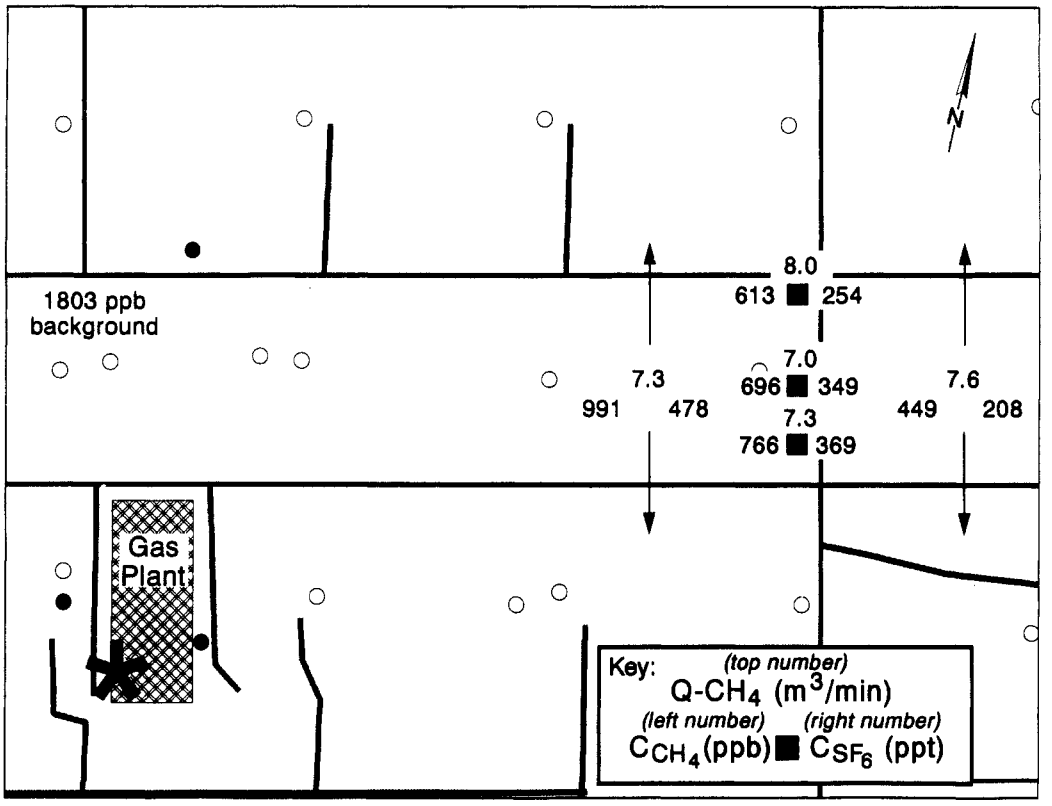

FIGURE 3. Methane emission rates, methane concentrations, and tracer concentrations obtained from canister and mobile sampling during a tracer ratio test at a gas production plant.

cessing plant and from three central gathering stations, while the general area exhibited elevated methane levels of approximately 100 ppb above background. The hotspot sources were readily identified by the fact that distinct methane plumes as high as 2–5 ppm above background could be measured at distances of 0.5 km or more downwind of the source.

Because the gas production plant produced a readily identified methane plume at 1–2 km downwind, the isolated source technique was used in four separate experiments to measure the total methane emissions from the gas plant. In three of the tests, the tracer was released from inside the main compressor building, which had a long roof ridge vent so that the tracer was mixed with building air and exhausted over a length of approximately 60 m. In the remaining test, the tracer was released directly into the flue gas at the top of a compressor exhaust stack located on the upwind side of the main compressor building. Walking traverses using a hand-held total hydrocarbon sniffer inside the plant indicated that the compressor building and the gathering lines immediately next to the building were the most significant source area within the plant.

Results from one of the gas plant tracer tests are shown in Figure 3. Methane concentrations measured approximately 1.5 km downwind were as high as 990 ppb above background, and the variability in the methane/tracer ratio was less than ±10% among three fixed points and two mobile integrated samples. This indicates that the tracer release was an accurate simulation of the source and that methane and tracer underwent the same transport and diffusion in the atmosphere. Results from the mobile analyzers also showed that a single broad methane plume existed and the tracer plume was well-correlated with the methane plume. As a result, the tracer ratio approach provided a built-in confirmation that the single tracer release provided an accurate simulation of the methane emissions from the gas plant.

TABLE 1

Methane Emissions from Gas Production Plant and Compressors

tracer test	release location	Q CH_4 (m^3/min)	SD (%)	sample type
1	compressor building	9.91	19	
2	compressor building	7.88	5.1	
3	compressor exhaust stack	7.55 8.54	6.8	canisters mobile
4	compressor building	8.31 7.46	1.6	canisters mobile
	mean SD	8.26 0.90 (11%)		

As shown in Table 1, the results for the four downwind tracer experiments were extremely reproducible with a mean emission and standard deviation of 8.26 ± 0.90 m^3/min (±11%). This high level of reproducibility for tests conducted on two different days with two different wind directions and downwind distances is an excellent indication that the tracer release accurately simulated the emissions of methane from the plant. This is also true for the case where tracer was released into the flue gas at the top of a compressor exhaust stack outside the building. The fact that there is no discernible difference among these tests indicates that the compressor exhaust underwent sufficient plume downwash to be well mixed with the remainder of the emissions. Given the short stack (less than the building height) and strong winds, this degree of downwash and mixing is not surprising. The good agree-

TABLE 2

Isolated Source Emission Rate Measurements in the Demonstration City

source	Q CH_4 (L/min)	SD (%)
primary regulating station	229	14
secondary regulating station	13.3	8
underground leak	179	22

ment from one day to the next also indicates that the methane emissions from the gas plant were quite steady. It should be emphasized that each of these four independent measurements of emissions from a moderate sized gas plant (capacity of 74×10^5 m^3/day) were obtained from a test that required less than 2 h setup and operation. In the overall GRI/EPA inventory program, the use of the tracer data from gas production facilities served as a quality assurance tool. This was extremely valuable because the tracer results highlighted potential uncertainties in the use of component sniffing and bagging methods, which were the basis for a portion of the inventory calculations.

Methane Emissions from Gas Transmission, Storage, and Distribution Facilities. The advantage of the tracer ratio method is its applicability to isolated sources where total methane emissions can be obtained quickly and accurately. As a result, tracer ratio tests were conducted at a variety of gas facilities associated with urban supply systems.

For the individual gas facilities, the approach was quite similar to that described for the gas plant. After identification of a facility, the methane signal was determined using the mobile analyzer. The tracer release van was parked at the facility, and a release line was secured into the source area. In many cases, this was accomplished by parking the van on the upwind side and securing the release tubing to the perimeter fence. In this way, access into the facility was not required. After the release was established, the mobile analyzer was used to locate the plume, fixed samplers were deployed, and mobile traverses were conducted. In practice, two to three tests could be conducted during each nighttime test period. As an example, during a demonstration study of the diffuse source urban technique (described below), emissions from three different isolated methane sources were tested during two nights, and each test required approximately 1 h. The sources included the primary city pressure-regulating station, a smaller pressure-regulating station, and an apparent underground leak identified from mapping surveys of the city with the mobile methane instrument. As shown in Table 2, methane emission rates from these urban hotspots ranged from approximately 10 L/min to more than 200 L/min. Table 2 also shows the reproducibility—from 8% to 22%—among the mobile system and a number of samplers in each test. This good reproducibility among samples from a single test helps to confirm the absence of interfering sources and the correct application of the method for these sources.

In addition to obtaining reproducible results among samples from a single test, it is also important to examine the replication of experiments at a given facility. As indicated in Table 3, replicate tests were conducted at a number of pressure-regulating and/or metering facilities. In the case of a primary city metering station located on the edge of an urban area, an initial test was conducted during a screening visit in 1990, and two additional tests

TABLE 3

Summary of Replicate Tracer Ratio Tests Conducted at Gas Distribution Facilities

U.S. location	date	Q (L/m)	Q (mean)	SD (%)
midwest 1	10/23/90	195		
	9/22/91	221		
	9/27/91	258	225	12
southplains 2	10/20/91	0.179		
	10/21/91	0.454	0.317	43
southcentral 1	1/22/92	15.4		
	1/24/92	9.8	12.6	22
southcentral 2	1/28/92	7.5		
	1/30/92	15.9	11.7	36
northeast 1	11/3/92	152		
	11/7/92	240	196	23
northeast 2	11/9/92	176		
	11/20/92	209	91	8.6
northeast 3	11/13/92	0.0093		
	11/13/92	0.0024	0.0048	51
northeast 4	1/17/93	46		
	1/20/93	19	33	42

were performed 1 year later. At this source, which had a mean emission rate of 225 L/min, the variability among these three tests was ±12%. This is an excellent example of the overall reproducibility of the method for an isolated source with a significant level of methane emissions. In other tests, where emissions were much smaller or there were potential interfering sources nearby, the level of reproducibility could be much less as indicated in Table 3. It is also possible in some cases that the change in emissions could be attributed to actual changes in emission rate due to changes in the source operating conditions.

To illustrate the wide range of applicability of the tracer ratio methods, the largest emission rate was measured at an LNG facility (4940 L/min) while very small emissions were measured from in-city regulators (<0.1 L/min). Generally there was a trend toward larger emissions at larger facilities and higher operating pressures. Emission rates as high as 900 L/min were measured at central facilities located at gas storage facilities and as high as 440 L/min at injection wells. The maximum observed emission rate at a town border station was 500 L/min, and the maximum observed emission rate at a transmission tie point was 142 L/min. In contrast, the maximum measured emission rate at a city regulating station was 13.8 L/min.

Because there are a relatively large number of distribution facilities housed in underground vaults, the enclosed source method described previously was developed and tested at more than 40 locations. This method was quite successful in demonstrating that gas facilities in below-ground vaults typically have very low emission rates. The range of vault emission rates was from 0.4 L/min to less than 0.01 L/min.

In summary, the tracer ratio approach has proven to be a very simple but powerful approach for surveying and measuring methane emissions from a wide range of above-ground pressure-regulating stations, metering stations, and storage facilities associated with gas transmission and distribution facilities. A simple modification of the method also provided a way to measure the relatively low emissions from pressure-regulating/metering systems located in below-ground vaults. The method has the advantage that the *total* emissions from a facility are obtained in less than

a few hours, and several facilities can be tested during each day. Uncertainties caused by aggregation of individual component measurements are avoided.

Tracer Tests for City-Wide Emissions. The tracer ratio was demonstrated to be a powerful technique for treating isolated sources over a range of sizes. However, urban gas distribution systems are an important component of the overall gas industry, but emissions from these urban-wide systems cannot be treated with the simple tracer ratio approach. The area source tracer method described above was developed as a way to obtain an independent estimate of urban methane emissions. To test the method, city-wide tracer tests were conducted at a small city using three measurement methods: (1) the single point tracer release based upon eq 2, (2) an along wind line source tracer release technique, and (3) a mass balance based upon vertical plane sampling. In the line source release approach, releasing tracer along the mean wind direction across the city was used to account for the distribution of methane sources upwind of a receptor traverse. Emissions were calculated using the crosswind integrated tracer concentration and the average methane concentration along traverses near the downwind edge of the city:

$$Q_m = \frac{Q_t C_m W}{CWI_t} \tag{4}$$

where W is the crosswind width of the methane source area and Q_t is the total tracer release rate along the line.

In the mass balance approach, the emission rate was obtained from measurements of the vertical profiles of wind speed, $u(z)$, and methane concentration, $C_m(z)$, taken at a point within the city plume near the downwind edge of the city:

$$Q_m = W\int_0^\infty u(z)C(z)\,dz \tag{5}$$

Using these three different methods on different nights to measure methane emissions from the city provided a way to determine the degree of uncertainty in the methane emission measurements.

The midwestern city used for the methane emission studies has a population of 35 000 and an urban area of approximately 23 km^2. There are 12829 gas customers with a total gas usage (1989) of approximately 25 million therm (annual average rate = 135 m^3/min). The distribution system included 16 km of cast iron pipe, 138 km of steel pipe, and 290 km of plastic pipe. There are 16 different pressurization systems within the urban area that operate at pressures ranging from 125 psig to 11 in. water (862−37 kPa). Other methane sources included a sewage treatment facility located on the west edge of the city and several industrial operations. These other sources were not measured directly. During the tests described below, the wind directions were such that the sewage treatment plant was not included in the measurements.

A representative example of urban methane emission patterns is illustrated in the methane map shown in Figure 4. The figure shows a general city-wide elevation of methane above the rural background level, and it also shows the presence of two significant hotspot sources of methane within the city distribution system. One of these was the main pressure-regulating station supplying gas to the city distribution system, while the second was apparently a leak associated with some roadway excavation activities.

The results of four city-wide tracer tests are given in Table 4. These four experiments were conducted under different wind conditions, with wind directions from east, southwest, north, and south. Also shown are results from a city-wide experiment conducted in 1990 during a screening visit to the same city. The screening test in 1990 and three of the 1991 city-wide tests (tests 1, 3, and 4 in Table 4) employed the single point tracer release approach. In test 6, an along wind line source tracer release was used. Results from tethered balloon flights using the vertical mass balance calculations were also obtained during test 1.

The results shown in Table 4 are based upon multiple traverses across the city during each test. During test 1, five traverses were conducted, while in test 3, 12 traverses were completed. For each experiment, the tracer crosswind integrated concentrations (CWI_t) and the average methane concentrations (C_m) show variations on the order of 20%−50% from traverse to traverse. This variability is due to the random nature of atmospheric turbulence and diffusion. The variability in the ratio of the methane concentration to the tracer crosswind integrated concentration is equal to or larger than the variability in the measured concentrations. For example, in test 3 (1991), the tracer and methane levels had percent standard deviations of approximately 42% and 30%, while the ratio (C_m/CWI_t) had a percent standard deviation of 57%. However, the calculated flux, which depends upon the ratio as well as the source-receptor geometry (see eqs 2 and 3), had a variability of only 32%. The fact that the final flux estimate has a variability comparable to the variations in concentrations and less than the ratio of concentrations suggests that the single tracer release model correctly accounts for the methane and tracer source-receptor geometry and for the vertical diffusion rates of both gases. This is an encouraging indication that the tracer method can be applied to estimate methane emissions from a large diffuse source.

The emission fluxes from the different tests are summarized in Table 5. An overall average value of 1.8 ± 0.8 μg m^{-2} s^{-1} is obtained for all of the tests, including the 1990 experiment. The total standard deviation, calculated as the square root of the sum of squares of the average individual standard deviations and the standard deviation of the average, is approximately 50%, which is comparable to the overall uncertainty estimated for the area source tracer technique.

To estimate a whole city emission rate, it is assumed that the flux is uniform over a 4.8 × 4.8 km square (23 km^2 area). This includes all of the residential area and the central portion of the city, and it is consistent with elevated methane concentrations measured during the various cross-city traverses on different nights. The average whole city methane emission rate was approximately 3.8 ± 1.8 m^3/min. This emission estimate is within the range estimated from the single mass balance calculation based upon the vertical balloon soundings that is also shown in Table 5. Together, the results from the 1990 and 1991 single release point tests, the mobile line source test, and the mass balance calculation show a very good level of agreement. As a result, this intercomparison of emission estimates based upon different experimental approaches provides confidence in the overall emission estimate.

A comparison of CO_2 and CH_4 levels yields information about the identity of leakage and combustion-related methane sources found in urban areas. Results from traverses immediately downwind of a gas regulator station

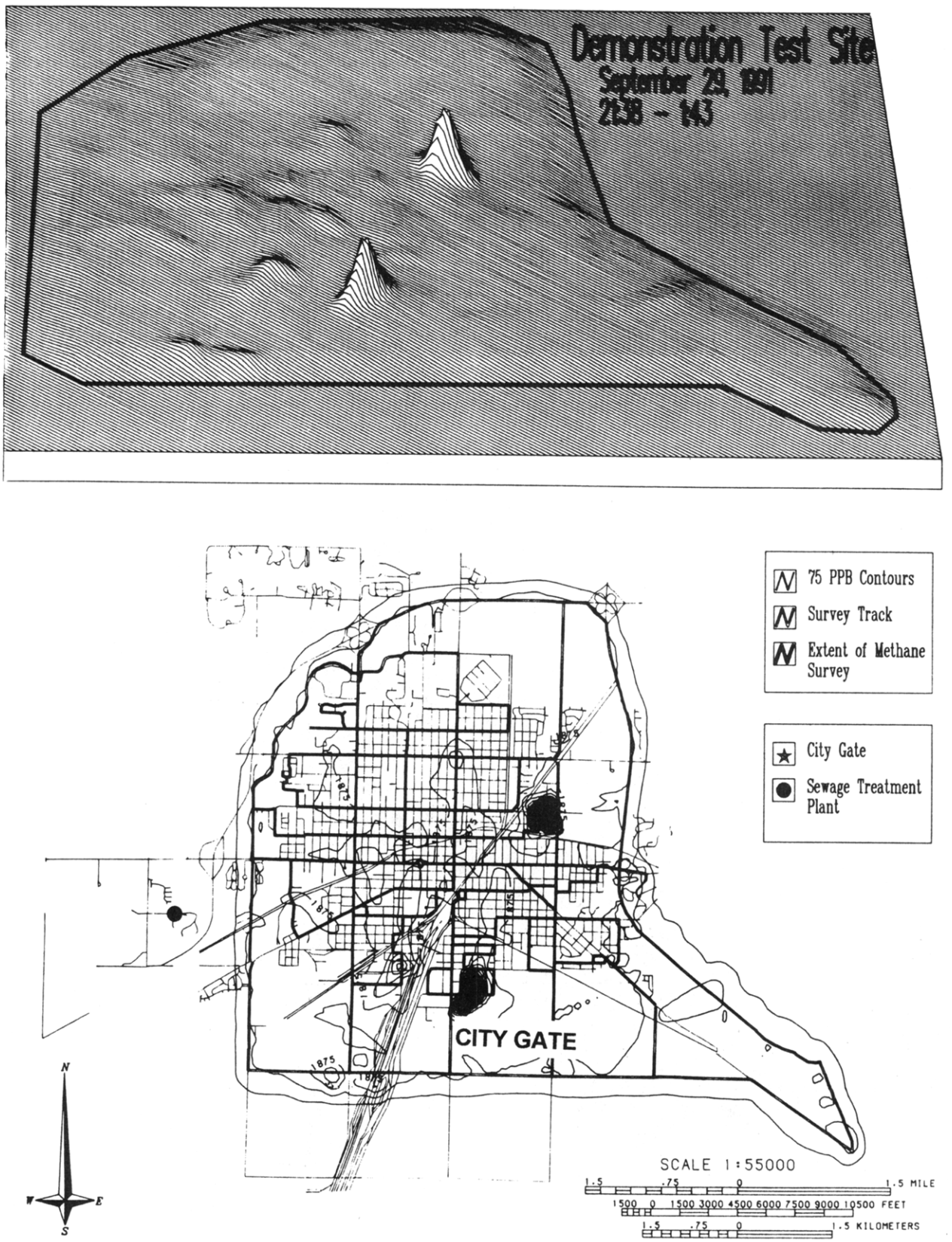

FIGURE 4. Methane ambient concentration contours in the demonstration city obtained from survey traverses conducted with the mobile methane analyzer during early morning stable atmospheric conditions.

show a characteristic "L" pattern (Figure 5a) where high levels of methane are associated with low carbon dioxide concentrations, and a range of carbon dioxide concentrations are associated with low methane concentrations. In Figure 5b, CH_4 and CO_2 data from mapping traverses on September 23, 1991, in the Midwest city are compared. In general, elevations in CH_4 corresponded to little or no CO_2 elevation, which suggests a natural gas source. The larger CO_2 elevation with only a small elevation in CH_4 is characteristic of combustion, probably from automobile exhaust. There were no landfills in the town and only one sewage treatment plant, located on the far outskirts of the

TABLE 4

Summary of Traverse Results for City-Wide Tracer Experiments

	time	distance from release (m)	CWI_t (ppb m)	av CH_4 (ppb)	CH_4/CWI_t	CH_4 flux ($\mu g\ m^{-2}\ s^{-1}$)	$Q(CH_4)$ (m^3/min)
			Screening Test October 26, 1990				
single release point							
		550	120	14	0.117	2.5	5.4
		1100	95	12	0.126	1.55	3.35
		550	105	18	0.172	3.69	7.97
		1100	76	12	0.159	2.02	4.36
		1100	75	17	0.226	2.86	6.18
		1100	144	16	0.111	1.43	3.09
		1100	135	21	0.156	2.03	4.38
		1100	136	18	0.133	1.67	3.61
		1100	141	22	0.156	1.99	4.3
		mean	114	17	0.151	2.19	4.74
		SD (%)	23	20	22	31	31
			Test 1a September 23–24, 1991				
single release point							
	2335	3546	173	9	0.052	0.13	0.28
	2339	1418	439	41	0.094	0.66	1.43
	2352	1418	245	53	0.217	1.53	3.31
	0002	1418	437	52	0.119	0.84	1.81
	0020	745	593	48	0.081	0.99	2.15
		mean	428	49	0.128	1.01	2.17
		SD (%)	29	10	42	32	32
			Test 3 September 26–27, 1991				
single release point							
	2328	2234	247	199	0.804	2.44	5.27
	2344	2234	449	238	0.531	1.61	3.48
	2355	2234	561	138	0.246	0.75	1.61
	0038	2234	921	158	0.172	0.52	1.13
	0102	2234	164	167	1.02	3.09	6.68
	0115	2234	416	259	0.622	1.89	4.07
	0016	3227	328	135	0.413	3.03	6.55
	0139	3227	510	130	0.254	1.86	4.03
	0146	3227	377	118	0.314	2.3	4.97
	0152	3227	355	125	0.352	2.58	5.57
	0159	3227	464	109	0.235	1.73	3.73
	0207	3227	400	112	0.28	2.05	4.44
		mean	433	157	0.437	1.99	4.29
		SD (%)	42	30	57	38	38
			Test 4 September 27, 1991				
single release point							
	0349	3316	327	134	0.409	3.81	8.23
	0405	3316	1034	130	0.126	1.17	2.53
	0413	3316	487	74	0.151	1.41	3.05
	0419	3316	413	71	0.171	1.59	3.44
	0428	3316	275	92	0.336	3.14	6.77
		mean	507	100	0.238	2.22	4.8
		SD (%)	54	27	47	47	47
			Test 6 October 2, 1991				
line source release							
	0126	1613	304	67	0.22	1.17	2.53
	0151	2003	243	97	0.399	2.12	4.58
	0240	2003	335	48	0.143	1.05	2.26
	0254	2003	449	69	0.153	1.12	2.41
	0311	3227	202	54	0.268	1.96	4.23
	0323	2411	354	66	0.185	1.35	2.92
	0337	3227	221	44	0.199	1.46	3.14
	0337	2411	428	60	0.14	1.02	2.21
	0359	3227	247	72	0.292	2.14	4.62
	0427	1613	536	49	0.091	0.67	1.44
	0433	2411	267	58	0.217	1.59	3.43
		mean	326	62	0.21	1.42	3.07
		SD (%)	31	23	39	33	33

town. Both of these types of sites typically emit significant amounts of methane and carbon dioxide as illustrated in Figure 5c for traverses downwind of a sewage treatment plant. The CH_4 and CO_2 traces recorded during cross-city traverses indicate that the dominant source of CH_4 in the whole town plumes was the natural gas system.

During the emissions study, whole air samples were collected for isotopic analysis. Samples were obtained

TABLE 5

Summary of City-Wide Methane Emission Rates

release type	date		CH_4 flux ($\mu g\ m^{-2}\ s^{-1}$)	total emission rate (m^3/min)
screening test	10/26/90	mean	1.79	3.87
		SD (%)	38	38
test 1a	9/26/91	mean	1.01	2.17
single release		SD (%)	32	32
test 1b	9/26/91	mass balance from balloon profiles		3.0–4.2
test 3	9/27/91	mean	1.99	4.29
single release		SD (%)	38	38
test 4	9/27/91	mean	2.22	4.80
single release		SD (%)	47	47
test 6	10/2/91	mean	1.42	3.07
		SD (%)	33	33
overall		mean	1.75	3.79
		SD (%)	26	26
total		SD (%)	47	47

downwind of the city center away from the sewage treatment plant and immediately downwind of the main regulating station near the south edge of the city. These samples were returned to NCAR for isotopic analysis of the $^{13}C/^{12}C$ ratio. The sources within the city had a $\delta^{13}C$ excess of −42.80‰, which is very similar to the value obtained immediately downwind of the city gate, −42.83‰. A sample was also taken upwind of the city, and the $\delta^{13}C$ excess was between −65.14 and −60.14‰, which is representative of biogenic methane (marsh gases, termites, cattle). Since only one sample was taken at each location, care must be exercised in interpreting the results. However, these isotopic analyses are in agreement with the CO_2/CH_4 results, which suggest that the gas system is the dominant source of nighttime methane within the city.

SUMMARY AND CONCLUSIONS

The tracer ratio approach has proven to be a very simple but powerful approach for surveying and measuring methane emissions from a wide range of above-ground pressure-regulating stations, metering stations, and storage facilities associated with gas transmission and distribution facilities. A simple modification of the method also provided a way to measure the relatively low emissions from pressure-regulating/metering systems located in below-ground vaults. The tracer method allows determination of the *total* emissions from a facility in the time frame of a few hours. Consequently, several facilities can be tested during each day. Uncertainties caused by extrapolation from individual component measurements are avoided. The results from controlled tests and from replicate measurements indicate that the total source emissions can be obtained with an accuracy of ±15%.

Within one midwestern city, the use of the area source tracer ratio technique was compared to a multi-point tracer release method and to a vertical plane mass balance. The results showed agreement to within the level of the overall uncertainty in the measurements which is approximately ±50%. While this is a relatively large uncertainty, the difficulty of determining total urban emissions of any pollutant are considerable. Further development of this approach has the potential to provide a quality control test of the typical summation of individual sources used in urban emission inventories.

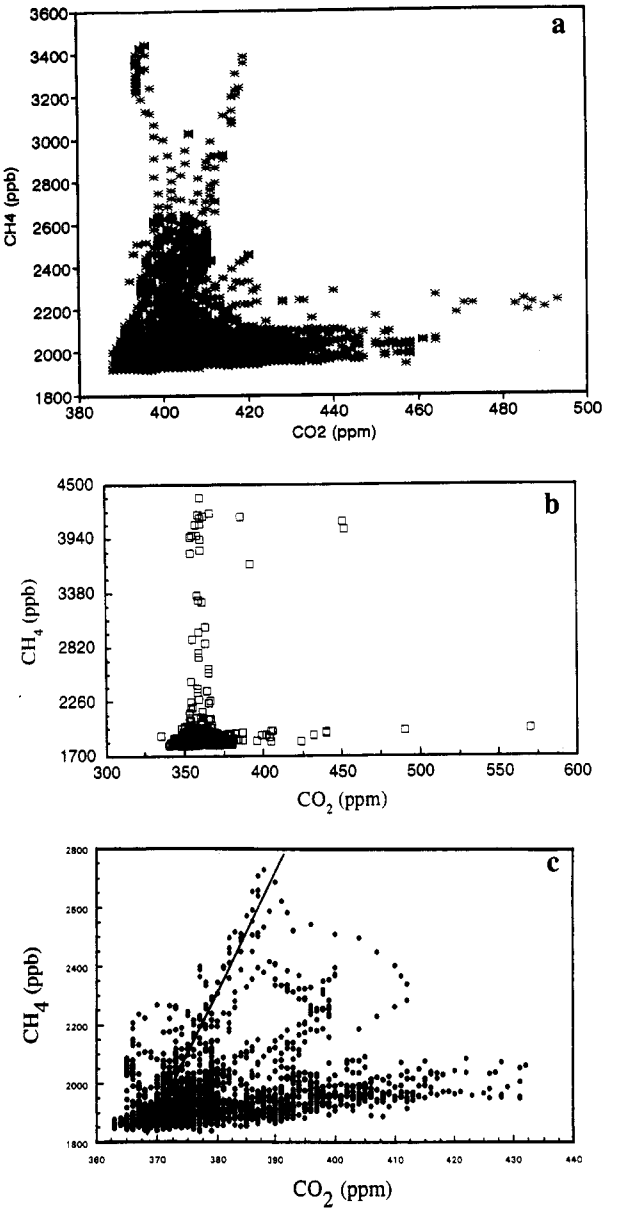

FIGURE 5. Methane concentrations versus carbon dioxide concentrations obtained from mobile sampling downwind of a natural gas facility (a), during survey traverses across the demonstration city (b), and downwind of a wastewater treatment plant (c).

The development and demonstration of these methods for methane has provided a basis for obtaining a broad data base of methane emissions from a variety of natural gas sources. Beyond that, however, the tracer ratio approach has widespread applicability to a range of pollutant emission problems including methane emissions from landfills, hydrocarbon emissions from urban areas, and air toxic emissions from industrial facilities.

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Appendix A: Tracer Ratio Methods Error Analysis

Isolated and Enclosed Source Tracer Ratio Measurement Reproducibility and Accuracy. Each step in the experimental program has been accompanied by careful quality control and assurance tests. This has included routine comparison of results obtained from the mobile system with those measured independently using the portable canister samplers and repeated tests at the same facility on different nights to test for reproducibility in methods and to investigate steadiness of the source. Results from intercomparison of round-robin analyses of methane standards among the collaborators using GC methods yielded levels of agreement to within 30 ppb.

The errors involved in the measurements of hotspot emissions can be estimated in a straightforward manner. The tracer release rate is measured with both a dry gas meter and a mass flowmeter. Typically differences in these two measurements are less than approximately 10−15%, and the reproducibility in measurements with either method is as low as ±2%. Measured methane concentrations have a precision as low as ±10 ppb so that the uncertainty in the difference between downwind and upwind concentrations is approximately ±14 ppb (calculated as the square root of the sum of squares of the uncertainty). Typical methane elevations above background range from 100 ppb to more than 1000 ppb, so the uncertainty ranges from ±14% to less than ±1.4%. The uncertainty in the tracer concentration depends upon the accuracy of the instrument calibration, which is based upon standards certified to ±5% accuracy and upon the precision of the measurements which is typically within ±5% for the concentrations used in these tests. The combination of these different uncertainties leads to an overall uncertainty in the approach of less than approximately ±15%.

This analysis assumes that the tracer release accurately simulates the methane source and that there are no other interfering sources. As a test of these two assumptions, the variability in calculated emission rate among individual canister samples is always calculated and listed with the results. Variabilities of less than ±5% in the methane/tracer concentration ratios among canisters have been observed in some cases. In other instances where methane elevations are low or the source is spatially distributed, differences can be as large as ±50%.

Area Source Tracer Ratio Method Error Analysis. In the application of the area source tracer method, errors can arise from both the measured quantities as well as from the assumptions and modeling steps invoked in the method. The most obvious source of uncertainty is the ability to correctly measure the elevated average methane concentration above rural background concentrations. In most cases, this elevation is of the order of 100 ppb; however, it is sometimes difficult to differentiate between the elevated city levels and variability in the rural background concentration. Typical measurements yield elevated levels which vary by approximately ±30% during a several hour test period. A similar level of uncertainty exists for the crosswind integrated tracer concentration. Much smaller errors are associated with the measurement of the tracer release rate (±10%).

There can be considerable uncertainty in specifying the diffusion parameter B. These uncertainties are related to the assumed value of the diffusion coefficient b and to assumptions regarding the size of the area where methane is being emitted (methane boundaries). There are also uncertainties related to the use of a power law to describe the vertical diffusion coefficient ($\sigma_z = ax^b$). The tracer data can be used to estimate b directly for a given experimental situation. In cases where this was possible, using the experimental value of b (typically ranging from 0.6 to 0.8) in place of the assumed value of 0.62 for stable conditions changes the estimated emissions by approximately 20%.

The upwind and downwind edges of the source area have to be estimated from a combination of city maps, gas distribution maps, and mapped methane concentrations. This is a somewhat subjective exercise, and it is not easy to assign an uncertainty to the upwind/downwind limits used in the calculation. However, it can be generally assumed that these boundaries can be selected to within approximately 500 m in comparison to typical city sizes of 3 km × 3 km.

Other errors involved in the final estimate arise from the need to convert the calculated methane flux (F_m in $\mu g\ m^{-2}\ s^{-1}$) to a whole city emission rate and from the possibility that hotspot sources of methane violate the general assumption that the area source is uniform. The conversion from a flux to an emission rate involves assumptions about the source area size in a manner essentially the same as indicated above in the specification of the B variable. However, the final result is probably less sensitive to errors in B than it is to errors involved in converting the flux to a whole city emission rate. For a 500-m error in each of the four edges of the boundary, given a 3 km by 3 km city size, the combined error equals 33% in the calculated whole city emission rate. In this case, a 33% error in source size results in a 33% error in the whole city emission rate even if the flux is accurately estimated.

The effects of hotspots on the estimated emission rate would lead to an overestimate of the methane emission rate since the average crosswind methane concentration might be unduly affected by a narrow, high concentration methane plume from a hotspot. For example, given an average methane elevation of 100 ppb over a 5-km traverse path and then adding a hotspot plume of approximately 500 ppb over 0.5 km of the path, the contribution of the hotspot to the overall crosswind average would be 40 ppb or 40%. However, this does not necessarily imply that the hotspot contributes 40% of the total methane emissions from the town. The concentration from the hotspot measured along the traverse will be strongly dependent upon how far upwind the hotspot is located. If the source is very near the traverse path, then a relatively small hotspot could have a big effect upon the estimated methane flux for the area source.

Another aspect of the uncertainty associated with the distribution of methane sources within the urban area is that diffuse emissions may be higher near the city center than near the edges. This could occur because the city center is typically the oldest part of a city and could be served with an older pipeline system compared to outlying, newer residential developments.

Results from a combination of an analytical and numerical analysis of the combined propagation of errors for the tracer ratio method applied to a city are summarized

TABLE 6

Error Analysis of Area Source Tracer Ratio Method for Estimating Urban Area Source Fluxes and Whole City Emission Rates

variable	base case	uncertainty	uncertainty in flux
Q_t	4 L/min	10%	10%
C_m	100 ppb	30%	33%
CWI_t	500 ppb m	30%	33%
b	0.62	13% ($b = 0.7$)	19% (moderate b)
b	0.62	29% ($b = 0.8$)	44% (large b)
Y_o	3000 m	500 m	1.8%
X_t	1000 m	0 m	0%
Q_h	200 L/min	15%	1.7%
X_h	1500 m	500 m	3.7%
		overall flux	52% (moderate b)[b]
		overall flux	65% (large b)[c]

[a] For whole city emissions, assuming the city area is 3 km × 3 km with an uncertainty of 500 m in each boundary yields an uncertainty of 33%. [b] Overall city emissions uncertainty, 62% (moderate b). [c] Overall city emissions uncertainty, 73% (large b).

in Table 6. This analysis is based upon selection of a typical city as a base case for the calculations. It is assumed that the methane elevation is 100 ppb, the crosswind tracer integral equals 500 ppb m, the tracer release rate is 4 L/min, and hotspot emissions of the order 200 L/min exist in the city. The tracer is released at $x = 1000$ m, approximately one-third of the distance across the city. In the base case, it is assumed that the diffuse emissions are uniformly distributed throughout the source area.

For the base case, the calculated error in the flux equals 52%, and the error in the whole city emission rate equals 61%. For the case where a larger range in b is used, the overall error in the flux increases to 65%, and the overall error in the whole city emission rate equals 73%. These error estimates imply that city emissions cannot be determined to an accuracy greater than approximately a factor of 2.

The effects of higher diffuse emissions near the city center versus the base case uniform distribution were investigated by comparing Gaussian plume diffusion calculations for the two cases. For a Gaussian distribution of emissions with average flux equal to the base case flux, the effect upon the methane concentration profile along the mean wind direction, and hence upon the calculated methane emission flux, is relatively small. A related aspect to the details of the calculation procedure is our assumption of sources and receptors located at the surface ($H = z = 0$ in eqs 3–5). For the case with $z = 0$, the modeling calculation yields a discontinuity at the edges of the source, but if the receptor height is set at a reasonable height ($z =$ 2 m), the discontinuity is avoided, and the differences between the uniform and Gaussian source distributions are smaller and not as sensitive to the location of the downwind edge receptor.

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