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ATMOSPHERIC METHANE: SOURCES, SINKS AND ROLE IN GLOBAL CHANGE

GUEST EDITORS

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ESTIMATION OF METHANE EMISSIONS FROM A SURFACE COAL MINE USING OPEN-PATH FTIR SPECTROSCOPY AND MODELING TECHNIQUES

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ABSTRACT

A new measurements methodology has been developed which allows the rapid and efficient measurement of methane (CH₄) emissions from surface coal mines. An initial field trial of this methodology has been completed, and results from the field trial revealed that emissions from one surface coal mine in the U.S. are estimated to be 1,735,000 m³/year. The results provide some evidence that CH₄ concentrations determined by the FTIR may be low by 20 to 75 percent but the overall effect of this potential bias on the mine emissions estimate cannot be adequately quantified. The initial trial demonstrated that the methodology is an applicable and feasible approach for measuring CH₄ emissions from very large surface coal mines. It also highlighted several uncertainties and methodology questions which if resolved could further improve the performance and reliability of the methodology.

1. INTRODUCTION

Recent global methane (CH₄) emission estimates indicate that coal mining operations may contribute as low as 25 or as high as 64 teragrams (Tg) of CH₄ per year (Cicerone and Oremland, 1988; Boyer et al., 1990). Thus, coal mines may account for 7 to 18 percent of the total global anthropogenic emissions burden. For underground coal mines, CH₄ emissions measurements data are readily available, thus facilitating the development of global emissions estimates for this important source. For surface coal mines, emissions measurements data are not available, and measurements techniques have not been developed and tested.

A measurements methodology has been developed and tested by the authors which involves the use of an open-path Fourier Transform Infrared (FTIR) spectrometer and Gaussian based plume dispersion modeling

techniques (Piccot et al., 1991). The open-path FTIR spectrometer used here is a remote sensing device which directs a collimated beam of infrared radiation through the ambient air along a path of several hundred meters. The beam is reflected back to the FTIR with mirrors and a spectral analysis is performed to determine the infrared absorbance of individual compounds passing through the beam. Use of more conventional methods, such as emission isolation flux chambers, was considered for directly measuring the flux of CH_4 from small sections (about 0.5 m^2) of exposed coal surfaces (Klenbusch, 1986). However, it was concluded that these in-situ devices could not be safely or effectively used in a surface mine environment. In addition, because of the heterogeneity of the emissions patterns observed, a prohibitively large and expensive number of measurements would be needed to obtain a statistically representative set of flux measurements for a large mine. The use of conventional ambient point sampling techniques to determine mine plume CH_4 concentrations was also considered and dismissed for a similar reason. The plumes from surface coal mines can be over 1000 meters across requiring that a substantial number of point sampling systems be used. In addition, ambient measurements collected remotely do not contain potential errors which can result from sample line leaks and the loss or production of compounds in sampling containers.

Initial site surveys were conducted at surface mine sites in the U.S. to identify an initial mine site suitable for conducting full scale measurements. Six sites were visited, three in the Powder River region of Wyoming and Montana and three in the Illinois coal basin. Preliminary ambient measurements data were collected during these visits using a portable flame ionization detector (Foxboro OVA). Although these measurements provide only rough approximations, they indicate that surface mines are a very heterogeneous source of CH_4 emissions (ambient CH_4 concentrations ranged from 3 to over 1000 parts per million) and that disturbed coal areas, such as the coal rubble produced from blasting operations, may be the most potentially significant CH_4 source at the mines. As part of these initial site surveys, wind flow patterns within the mine area were studied to examine plume behavior and to assess the viability of measuring plume concentrations using remote sensing techniques. Several smoke releases were initiated, observed, and filmed at several mines. In most cases, these films revealed that wind flow patterns within the mine pits can be complex (i.e., air sometimes swirled in a helical pattern down the mine pit at 90° angles to the direction of the prevailing wind) but that the overall plume had Gaussian dispersion properties and dispersed in the direction of the prevailing wind once it reached the top of the pit. The Caballo mine, located in the Powder River region of Wyoming, was selected for conducting full scale measurements because the site has a straightforward rectangular configuration, the plume demonstrated consistent Gaussian dispersion characteristics under the meteorological conditions observed at the site, and the concentrations of CH_4 measured were moderate.

2. DESCRIPTION OF THE SAMPLING AND ANALYSIS APPROACH

2.1 Introduction and Mathematical Basis

A fundamental goal of the sampling methodology is to obtain an emission rate for total CH_4 emissions from a surface mine. The heterogeneity and size of the source called for a creative measurement approach. Since

smoke releases show that emissions from surface mines diffuse out of the pit in the direction of the prevailing winds, a near-ground-level concentration measurement downwind from the mine is used to estimate a total CH_4 emission rate for the mine. A CH_4 measurement of the cross-wind-integrated concentration of the plume at near-ground level is made using an open-path FTIR sensor. Using this near-ground-level concentration measurement and a measured background or natural ambient CH_4 concentration, the total mine release is estimated using an appropriate plume dispersion model. If site-specific plume dispersion characteristics can be determined, they can be used in the model to more accurately represent the behavioral characteristics of the plume at a given site. Using a tracer gas, these site-specific plume characteristics can be estimated as described below.

A tracer gas release can be assumed to be a continuously emitting point source. Based on this assumption and on the results of the smoke release studies conducted at the Caballo and Rawhide mines, standard Gaussian dispersion equations can be applied. When the standard Gaussian equation is integrated across the y direction (y is assumed to be in the direction normal to the wind direction) from $-\infty$ to $+\infty$, the following relationship can be developed (Turner, 1970):

$$C_{\text{cwi}} = \frac{2Q}{(2\pi)^{1/2} u \sigma_z} \exp \left[-\frac{1}{2} \left(\frac{H}{\sigma_z} \right)^2 \right] \quad (1)$$

where,

C_{cwi}	= ground-level cross-wind-integrated concentration (g/m^2)
Q	= emission rate (g/s)
u	= average wind speed (m/s)
σ_z	= vertical dispersion coefficient (m)
H	= effective emission height of plume centerline above ground level (m)

For a ground-level source such as a tracer release at a surface coal mine, H is effectively equal to zero so the exponent of the expression is equal to 1. Thus, Equation (1) can be simplified to:

$$C_{\text{cwi}} = \frac{2Q}{(2\pi)^{1/2} u \sigma_z} \quad (2)$$

Equation (2) can be used to obtain site-specific σ_z values for a mine if the values of the remaining unknowns can be determined. Specifically, σ_z can be determined for the plume given (1) a measured tracer gas concentration (C_{cwi}) from an FTIR sensor; (2) a measured value of u from a meteorological station located near the FTIR path; and (3) a known release rate Q from a tracer gas source, such as a metered gas cylinder located at the mine. To use this technique to estimate total mine emissions, a number of σ_z values must be determined based on tracer gas releases conducted at several different distances upwind from the monitoring path. These resulting values are used to construct a relationship of σ_z versus distance from the path for the area source. All tracer gas releases used to determine this σ_z relationship should be conducted as close in time as possible because atmospheric stability may change, thus changing the σ_z relationship.

A similar and somewhat simpler technique can also be used to assess plume dispersion characteristics using fewer tracer gas measurements. Given measured values for the tracer gas release rate Q , tracer release location, wind speed u , and wind direction, an appropriate area source plume dispersion model can be used to predict C_{CWT} for the tracer gas plume. The model is run to predict concentrations of the tracer gas at various points along the FTIR monitoring path. These predicted concentrations are integrated using the trapezoidal rule to calculate a path-integrated concentration or C_{CWT} for the FTIR monitoring path. The model is run seven times, once for each of the seven Pasquill-Gifford (P-G) atmospheric stability classes (Turner, 1970). These varying P-G assumptions, which incorporate the influence of σ_z , simulate increasing atmospheric stability and its effect on the dispersion of the tracer gas plume. Since several model results are produced, a range of C_{CWT} values are predicted under varying degrees of atmospheric stability. The predicted C_{CWT} value which most closely matches the C_{CWT} measured by the FTIR is used to define the P-G atmospheric stability class which occurred during the tracer gas monitoring event. If simultaneous CH_4 measurements are also collected during this monitoring event, this stability assumption is applied to the CH_4 plume. The model is then run assuming a unity emission rate for CH_4 (i.e., a homogeneous release rate of 1 g/m²-sec) and the P-G stability determined as described above. The model is run to predict concentrations of CH_4 at various points along the FTIR monitoring path. By again applying the trapezoidal rule to these predicted point concentrations, a path-integrated concentration or C_{CWT} for the assumed homogeneous release is predicted along the FTIR monitoring path. Of course the FTIR is actually measuring a path-integrated concentration due to a heterogeneous emission release pattern from the coal seam. However, this measured value is comparable to the concentration determined from the model for an assumed homogeneous release because the FTIR measurements integrated or 'averaged out' the variable concentrations which exist in the plume from the mine.

The actual CH_4 release rate for the mine is then calculated using the simple relationship shown below where $Q_{(predicted)}$ is the unity emission rate for CH_4 .

$$\frac{Q_{(actual)}}{Q_{(predicted)}} = \frac{\text{Concentration}_{(measured)}}{\text{Concentration}_{(predicted)}} \quad (3)$$

This technique is used to estimate CH_4 release rates in this study. The Point Area and Line (PAL) source model is used to predict point concentrations along the measurements path as described above (Petersen and Rumsey, 1987). A non-reactive gas, sulfur hexafluoride (SF_6), is the tracer gas used. Use of a synthetic trace gas such as SF_6 is important to the determination of plume dispersion characteristics because it is non-reactive, does not naturally occur, and there is no background concentration to cause potential interferences.

2.2 Experimental Setup and Caballo Mine Site Description

Sampling was conducted using an FTIR sensor to measure concentrations of CH_4 and SF_6 in the plume along a path located 1 meter above the ground. The FTIR sensor, shown in Figure 1, was assembled by MDA Scientific, Inc. of Norcross, Georgia. In general, the FTIR is a unistatic open-path device which contains a Bomem interferometer and a liquid nitrogen cooled mercury-cadmium-telluride detector. A modulated beam of

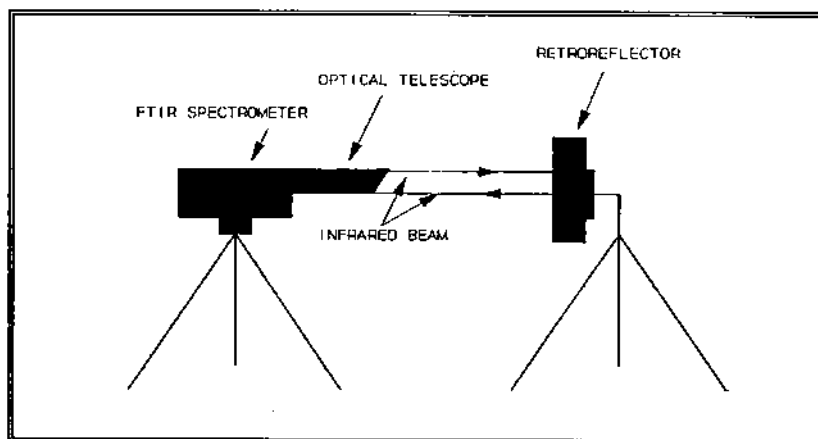


FIGURE 1. Simplified illustration of the FTIR sensor system.

infrared radiation is generated by a glowbar within the FTIR system and is directed into the atmosphere through an optical telescope which has a 30.5 cm (12 inch) primary mirror. Triangular apodization is used. The beam passes through the atmosphere and is reflected back to the detector via a corner cube retroreflector where it is subjected to absorption analysis to identify and quantify the gases present along the path of the beam. The divergence of the beam over the path is 2.2 milli-radians. Based on the absorption analysis, a path-integrated concentration is determined for the gases of interest. The analysis is carried out on a portable personal computer (PC). In addition to the analytical functions, the PC is used to operate the instrument and is an integral part of the FTIR sensor. The spectral resolution of the FTIR is 1 wave number at standard atmospheric conditions. Pressure broadening is 1/10 to 2/10 of a wave number for each atmosphere above atmospheric pressure. At the spectral resolution associated with this instrument, pressure broadening effects are not significant.

The absorbance of CH_4 was determined by performing a spectral analysis of the CH_4 peak located at 2915.8 cm^{-1} . The absorbance of SF_6 was determined by performing a spectral analysis of the SF_6 peak located at 948.7 cm^{-1} . Both peaks absorb in a region where interferences due to water vapor are minimized. Discrete measurements were collected by taking 32 scans over a 2.5 minute interval. Path-integrated concentrations for both gases were determined by comparing and analyzing the collected spectra against a "reference" spectra determined for both gases using known concentrations at standard atmospheric conditions.

The Caballo mine is owned by Exxon Corporation and operated by The Carter Mining Company. It is located in Campbell County, Wyoming, approximately 15 kilometers southeast of the town of Gillette. It is in an area of the northwestern Wyoming Powder River region which has been recognized for containing coalbed CH_4 resources (Rightmire et al., 1984). This mine is about 12 years old and has been operating since the fourth quarter of 1978. The annual coal production in 1989 was about 14.3 million metric tons of high moisture sub-bituminous coal. The mine operates primarily on the Smith coal seam and has one active pit that operates 24 hours a day, 7 days a week.

No coal bed CH_4 content measurements data have been collected at the Caballo mine. Only one sample is available for the Smith seam in Campbell County and it shows that CH_4 contents are low: less than 0.0013 $\text{cm}^3/\text{metric ton}$ of coal. Despite this low value, at least one mine in this area may have contributed to a sustained release of significant quantities of CH_4 in a nearby residential subdivision. This subdivision has since been abandoned by most of the residents due to CH_4 hazards.

Figure 2 shows a top view of the Caballo mine. The shaded area shows exposed coal surface areas at the mine. The series of five areas to the north and west of the coal seam are referred to as overburden benches. These benches are where strata overlying the coal seam are placed after removal from the working area just north of the coal seam. Structurally, they are constructed like plateaus and increase in elevation from bench 1 north to bench 5. The lowest point on the pit floor is 1,338 meters above mean sea level on the west end of the pit. The coal seam is in a line which runs along the southern edge of the pit. The coal seam, on average, rises 21.3 meters above the floor of the pit. The overburden on top of the coal rises an additional 20 to 25 meters above the pit floor (overall it is about 45 meters from ground level just north of the coal seam to the pit floor).

The initial site survey indicated that the coal seam itself was a primary source of emissions. With winds from the north the plume from the coal seam was sampled on the southern edge of the mine parallel to the southern edge of the coal seam. With winds from the south sampling was conducted north of the seam on overburden bench 1. Because the width of the mine plume is greater than the maximum path length the FTIR sensor can measure (i.e., the maximum path length claimed in the manufacturer's literature is 650 meters), the plume was divided into east and west segments.

Figures 3 and 4 show the sampling configuration on the east and west plume segments when the wind is out of the north. Examination of data collected by the OVA revealed that on the west side of the mine the primary source of emissions was a slow seepage of gas from all exposed coal surfaces while on the east side of the mine the primary source was the rapid seepage of gas from the blast area and surrounding coal surfaces that were fractured by the blasting operations. FTIR path lengths for the east and west segments ranged from about 375 to 525 meters. The segments were measured in close succession. That is, a series of several 2.5 minute measurements, or interferograms, were obtained on the east segment followed by a series of several 2.5 minute interferograms on the west segment. Background or ambient CH_4 concentrations were determined using shorter path lengths at various locations upwind from the mine. Site-specific wind speed, wind direction, and other data needed to estimate the total emissions from the mine were collected from a meteorological station erected 3 meters off the ground on bench 5 as shown in Figures 3 and 4. Two monitoring paths were used for the east plume in this configuration as Figure 4 shows. The reasons for using two paths are discussed later in the results section.

Calibration cell measurements were conducted at the site in an effort to assess FTIR drift and performance. This was done by passing the FTIR infrared beam in a closed-path configuration through a 15 centimeter calibration cell containing a CH_4 calibration gas certified to be 19,500 ppm (about 2 percent CH_4). This approximates the total optical density anticipated to occur in the long path measurements taken at the site. For these calibration measurements, the calculated CH_4 concentration from the FTIR sensor was compared with the expected 19,500 ppm.

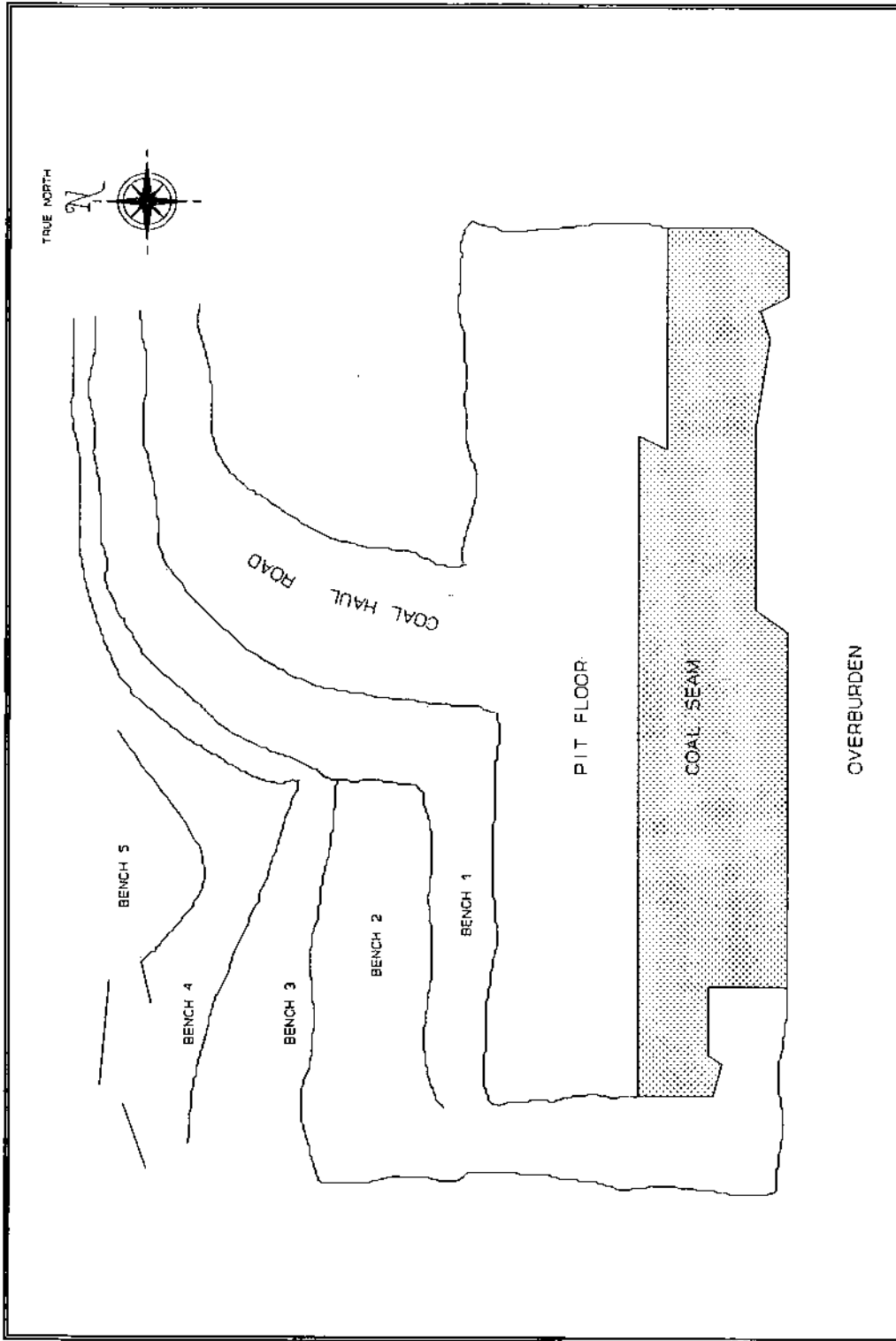


FIGURE 2. Top view of the Caballo mine.

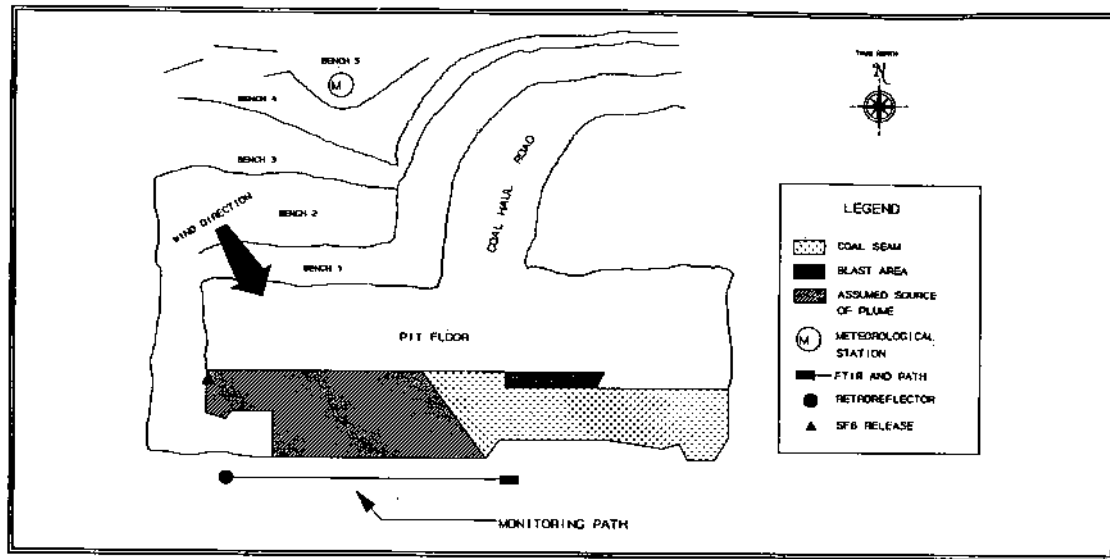


FIGURE 3. Sampling configuration for the west plume segment with a north wind.

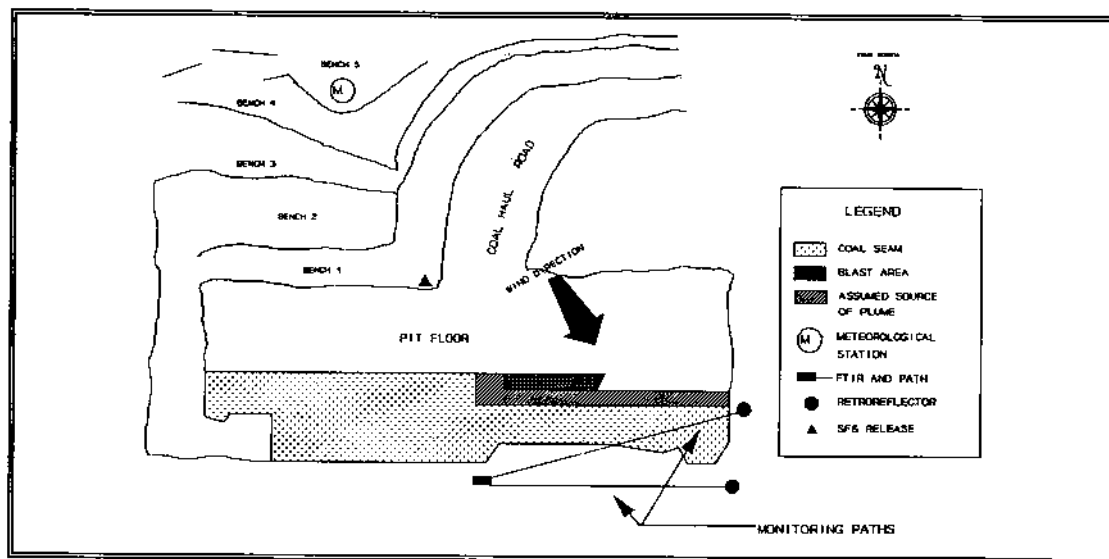


FIGURE 4. Sampling configuration for the east plume segment with a north wind.

On several days, a series of equally spaced point measurements were taken with the OVA along the FTIR path. The OVA was calibrated using certified calibration gases at two concentrations: 5 and 10 ppm. The accuracy of the OVA cited by the manufacturer at full range (1 to 1000 ppm) is ± 20 percent. The point measurements were collected to develop a second data set for comparison with the FTIR data. Another purpose

of the OVA measurements was to obtain a series of point samples that could be used to identify and examine the CH_4 concentration profile along the path of the plume.

3. RESULTS FROM THE FIELD TRIAL

3.1 Overview

Measurements activities at the mine began on December 10 and concluded on December 15, 1990. Severe weather conditions (i.e., heavy snow and high winds) suspended sampling activities on December 14. The extremely cold temperatures and consistently high winds at the mine complicated measurements activities.

Table 1 presents an overview of the number and types of measurements data collected at the Caballo mine. As the table shows, several types of data were collected, including 48 mine plume CH_4 measurements, 44 mine plume SF_6 measurements, 16 background or ambient CH_4 measurements, and 7 CH_4 calibration measurements. Nine CH_4 and five SF_6 measurements were eliminated from the data set as a result of FTIR operational problems or because the FTIR signal was too weak to perform a credible analysis.

TABLE 1. TYPES OF MEASUREMENTS DATA COLLECTED AT THE CABALLO MINE

Type of Measurement	Number of Measurements
FTIR CH_4 Measurements	
Mine Plume Concentration	48
Ambient Background Concentration	16
Calibration Concentration	7
FTIR SF_6 Measurements	
Plume Concentration	44
Meteorological Measurements	
Wind Speed	measured daily ^a
Wind Direction	measured daily ^a
Standard Deviation of the Wind Direction	measured daily ^a
Organic Vapor Analyzer Measurements	
Mine Plume Concentration Profiles	2 ^b

^aSampled continuously and recorded 5-minute average values.

^bA series of 10 to 20 point measurements were made for each profile.

After the sampling trip was completed a preliminary review of the mine plume concentration measurements revealed that most were unrealistically low. The FTIR vendor (MDA Scientific) proposed that, for the instrument used at the mine, interferences from light scattering within the instrument itself were significant due to the long paths and accompanying weak return signals experienced. For example, scattered light accounted for about 50

counts of the total 175 counts typically associated with the longest open-path measurements made at the Caballo mine. A correction factor formula was developed based on the premise that the internal scattering was diluting the overall signal and, thus, the detection of ambient CH_4 and SF_6 concentrations in the path. This formula was used to estimate a concentration correction factor which, when multiplied by the measured concentration from the FTIR sensor, provided an adjusted CH_4 or SF_6 concentration. The correction factor equation used for CH_4 was:

$$\text{Correction Factor} = \frac{A}{A'} \quad (4)$$

where

A = corrected absorbance of CH_4 at the 2915.8 cm^{-1} peak

A' = measured absorbance of CH_4 at the 2915.8 cm^{-1} peak associated with the collected sample

The corrected absorbance (A) is estimated based on a CO_2 spectrum observed by the detector. With an ideal measurement (i.e., the instrument is completely purged with nitrogen), no CO_2 spectrum will be observed. However, with very long path measurements such as those taken at the Caballo mine, an absorbance associated with the residual CO_2 within the instrument can be detected. The residual CO_2 absorbance observed in the spectra collected is assumed to be directly proportional to the loss of signal associated with the CH_4 peak at 2915.8 cm^{-1} .

The following describes the plume concentration measurements data collected at the Caballo mine. Following this, emissions estimates are presented and discussed.

3.2 Summary and Analysis of CH_4 Concentration Measurements

The results associated with the four types of CH_4 measurements collected (FTIR ambient or background measurements, FTIR mine plume measurements, FTIR calibration measurements, and OVA mine plume measurements) are discussed below.

FTIR Background or Ambient CH_4 Concentration Measurements. Sixteen background or ambient measurements were taken. Three are not considered valid because inspection of the meteorological data after the field program indicated that emissions from the mine may have entered the FTIR path while these samples were being taken. This may explain why the concentrations associated with these samples are generally higher than the other background samples collected.

Figure 5 shows the background concentrations associated with the 13 valid samples collected. The average concentration from these samples is 1.64 ppm, slightly lower than the global average of about 1.7 ppm. As the figure shows, ambient concentration measurements appear to be within the same range with the exception of the measurements taken on day 6. Measurements taken on days 2, 3, and 4 range from about 1.8 to 2.3 ppm, while measurements taken on day 6 are consistently below 1.6 ppm. On day 6, the measurements were taken in the afternoon, when winds were much stronger and more variable than at any other time when background measurements were collected. In addition, by the time these measurements were collected some etching of the instrument's main hygroscopic optical window had occurred due to moisture condensation. The effect of this

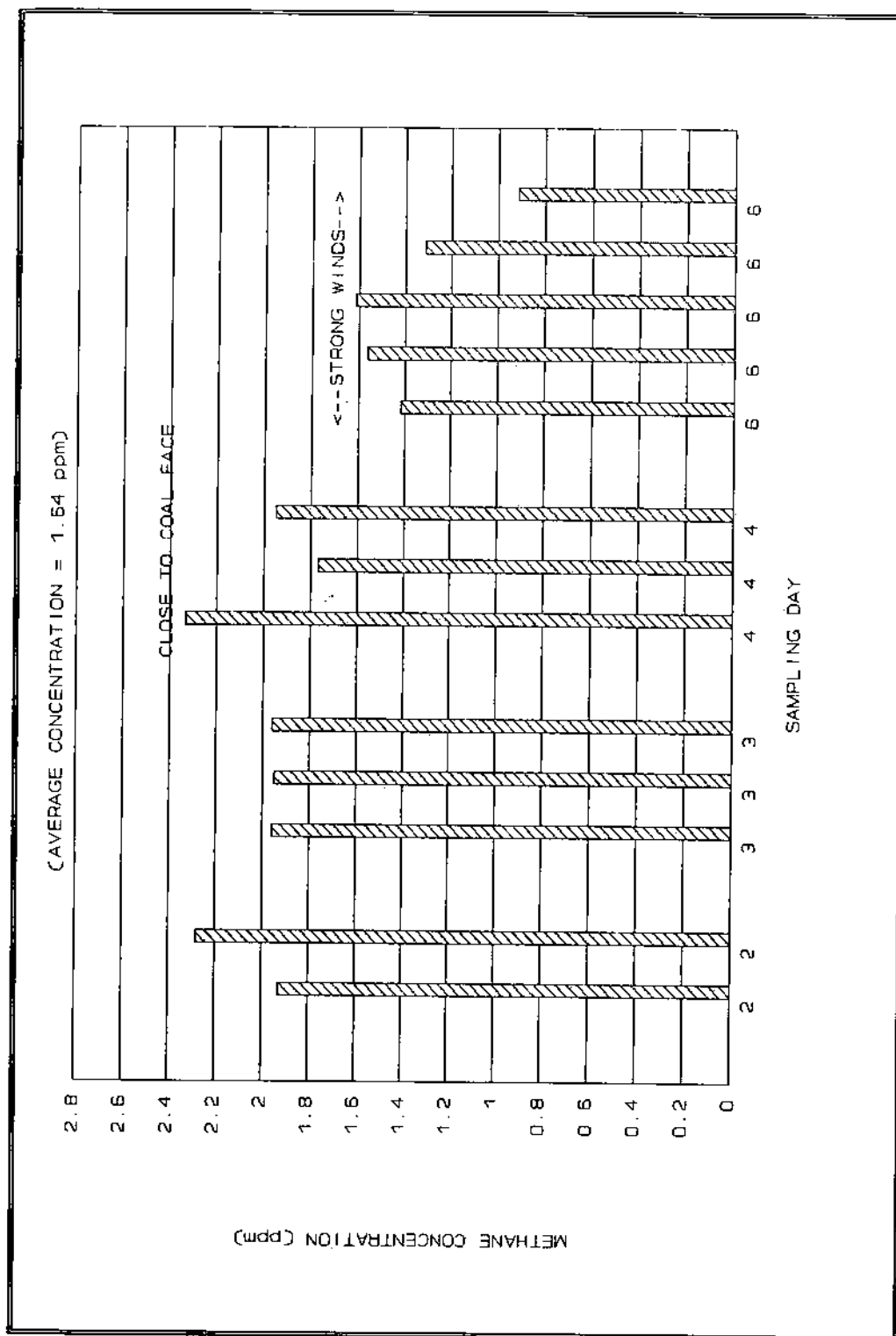


FIGURE 5. Summary of background or ambient CH₄ measurements collected.

etching on the measurements is not known but it likely reduced the incoming and outgoing signals.

Fluctuations in the background measurements can be significant. Although concentrations on day 3 are very consistent, the maximum variation in the concentrations for days 2 and 4 is on the order of 0.5 ppm. This variation may have occurred because measurements were taken close to the coal seam on day 4 (i.e., mine emissions could have potentially entered the path on occasion). Even so, variations seen in the ambient concentrations are almost as great as the apparent CH_4 contribution from the mine for at least some of the measurements. Because the emission flux from the mine is estimated by subtracting ambient CH_4 from the concentrations measured in the mine plume, it is mandatory that a representative ambient value be used to reduce uncertainty in the emissions estimates.

FTIR Mine Plume CH_4 Concentration Measurements. Figure 6 shows the CH_4 plume concentrations measured on December 12, 1990, while Figure 7 presents the data collected on December 15, 1990. For these two days, FTIR monitoring path lengths (i.e., the distance between the FTIR sensor and the retroreflector) ranged from 375 to 525 meters.

As Figure 7 shows, only one east leg measurement is reported for December 15. This is because there were difficulties in analyzing the spectral data collected for the east leg. For most east leg measurements, signal strengths were low, and the interferograms exhibited low signal-to-noise ratios. This is likely a result of the long path length associated with the east leg measurements (about 460 meters) and high wind velocities vibrating the retroreflector and FTIR on December 15. All west leg measurements were collected on December 15 with a path length of 375 meters and none contained unacceptably low signal-to-noise ratios. In addition, the west leg retroreflector was more sheltered from the strong winds than the east leg retroreflector.

The data in Figure 6 show that on December 12 measured path-integrated concentrations in the plume varied from a low of just under 2.0 ppm to a high of about 4.3 ppm. Figure 7 shows that on December 15 concentrations varied from a low of 1.6 ppm to a high of about 2.8 ppm. Three general trends have been observed in the December 12 and 15 data as outlined below.

- **Overall Mine Plume.** Ground-level CH_4 concentrations may increase by 20 to 50 percent as ambient air passes over the Caballo mine. Mine emission rate calculations discussed in the next section provide a more representative measure of the emissions contribution from the mine.
- **Effects of Measurements Configuration.** Figure 6 shows that measured concentrations significantly increased when the east path retroreflector was relocated in an effort to more fully encompass the plume (see the sampling configuration in Figure 4). When the retroreflector was moved, the path-integrated concentrations increased dramatically by a factor of 1.8 on average.
- **Effects of Coal Blasting.** Concentrations in the plume from the east side of the mine were higher than from the west side. The east side of the mine contained the blast area which, based on initial OVA measurements, was identified as a significant source of emissions at the mine.

FTIR Calibration Measurements. Although the FTIR cannot be "tuned" in the field based on the results of a calibration measurement, these measurements can be used to examine instrument performance and drift relative to a known standard. The results show that the percent difference between the measured concentration of the

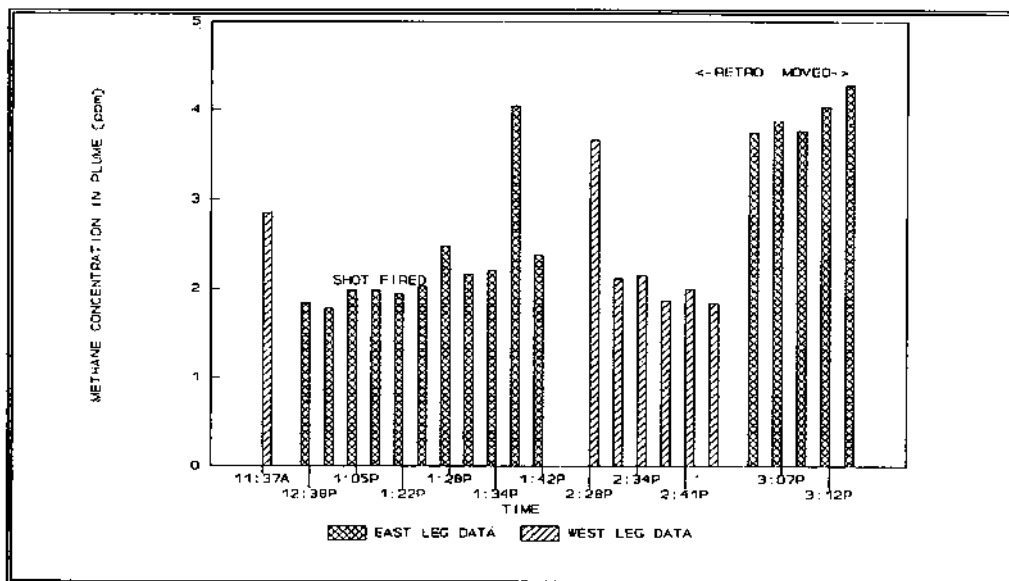


FIGURE 6. Summary of mine plume CH₄ measurements collected on 12/12/90.

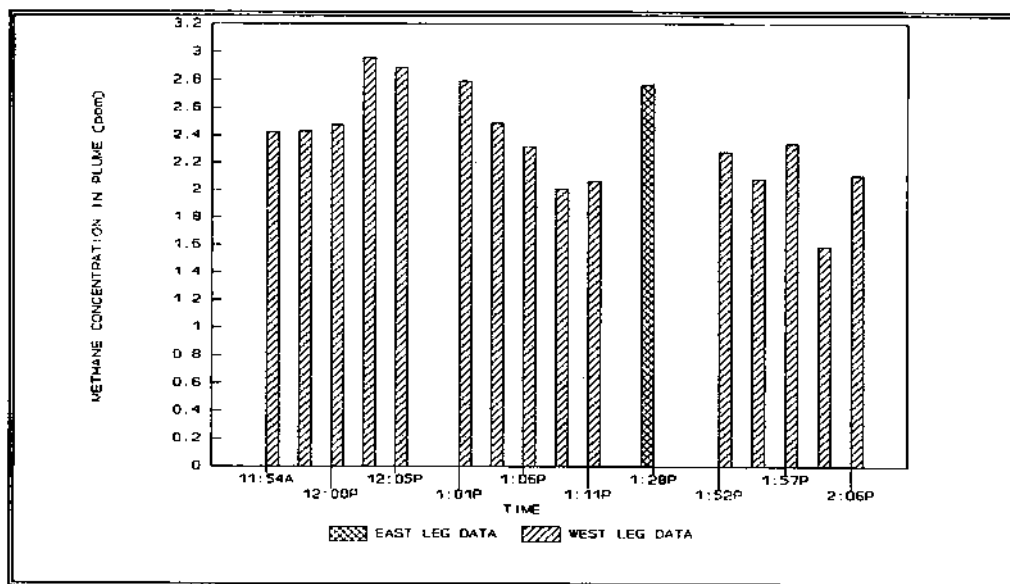


FIGURE 7. Summary of mine plume CH₄ measurements collected on 12/15/90.

calibration gas in the calibration cell and the known concentration generally ranges between -5 and -25 percent. In addition, this percent difference appeared to progressively increase between the first and final sampling day. On average, the FTIR measurements appear to consistently underestimate actual CH_4 calibration concentrations by about -20 percent. This suggests that some systematic error in the instrument's performance was occurring. As with the OVA measurements described below, these results provide strong evidence that concentrations determined from the particular FTIR used at the Caballo mine may be low.

OVA Point Measurements. Point samples were collected with an OVA on several different days after calibrating the OVA as described earlier. On December 12, a series of point samples was collected at 30-meter (100-foot) intervals along the FTIR path. These measurements were conducted simultaneously with a series of five FTIR measurements collected during the period from 3:10 to 3:40 pm. As expected, the point samples collected show that plume concentrations significantly increase at locations immediately downwind from the coal blast area. Concentrations outside the blast area plume ranged from 3.0 to 7.0 ppm while concentrations within the blast plume were generally between 10 and 20 ppm. On occasion, the concentration within the blast plume was as high as 30 to 50 ppm.

The OVA data collected between 3:10 and 3:40 pm were used to simulate a path-integrated measurement for the east leg plume. The trapezoidal rule was applied to the point measurements to determine a path-integrated concentration. The value estimated was 7.0 ppm. This is higher than the average of the east leg FTIR path-integrated measurements taken during the same time: 4.0 ppm. This finding is generally consistent with the earlier finding that the FTIR underestimated calibration gas concentrations. However, it should be noted that the OVA measures total hydrocarbons and it is possible that some emissions from a diesel truck operating near the coal loading area contributed somewhat to the OVA measurement. The degree of the potential contribution from a diesel truck has not been quantified but it is doubtful that, if truck emissions did cause an interference, their contribution accounts for all of the discrepancy seen between the OVA and FTIR measurements. An evaluation was conducted to identify other potential sources of interference (e.g., natural background hydrocarbon emissions); none were found to be significant.

3.3 Summary and Analysis of CH_4 Emission Rate Estimates

Tracer Gas Results and Atmospheric Stability Determination. As discussed earlier, CH_4 emission rates are estimated based on the plume dispersion characteristics determined from the SF_6 plume measurements. Specifically, the SF_6 measurements are used to identify the Pasquill-Gifford atmospheric stability class which most likely occurred during a specific tracer gas monitoring event. If simultaneous CH_4 measurements are also collected during this tracer gas monitoring event, the same stability class assumption is applied to the CH_4 plume. For several of the CH_4 concentration measurements collected, a simultaneous or near simultaneous¹ SF_6 measurement was not available. In many of these cases, SF_6 was released during the monitoring event but the resulting measurement could not be used because either low signal-to-noise ratios corrupted the measurement,

¹ Near simultaneous is defined as an SF_6 measurement having occurred within 4 to 6 minutes of a CH_4 measurement.

or an inadequate portion of the SF_6 plume was captured in the monitoring path (i.e., less than 70 percent was captured). The data developed in this study suggest that atmospheric stability at the mine could change significantly over a period of several hours. For this reason, CH_4 concentration measurements where simultaneous or near simultaneous SF_6 measurements were unavailable for determining stability were not used to estimate CH_4 emission rates.

Table 2 presents measured path-integrated SF_6 concentrations for the 10 SF_6 monitoring events which were not adversely affected by low signal-to-noise ratios or partial plume capture. It also presents a series of path-integrated concentrations predicted by the PAL model under different assumptions for the Pasquill-Gifford atmospheric stability class. The percent difference between the measured concentration and the predicted concentration is shown. Percent difference was calculated as shown below.

$$\text{Percent difference} = 100 * [(\text{measured} - \text{predicted}) / \text{predicted}] \quad (5)$$

The predicted concentration which most closely matches the measured concentration is used to define the atmospheric stability for each monitoring event in Table 2. In some cases, the measured value is about half way between two predicted values. In these cases it is assumed that a stability which is half way between the predicted values actually occurred (see measurements WCOAL 20 and WCOAL 24). Otherwise, the closest stability is used.

Prior to conducting field measurements at the mine it was anticipated that atmospheric stability class C or D would be encountered during the cool months in Wyoming. This was determined using conventional techniques to select a stability class based on such factors as the time of year, the solar angle, the anticipated cloud cover, and the anticipated wind speed (Turner, 1970). The data in Table 2 show that for 6 of the 10 SF_6 measurements stability A or B is indicated. For the remaining measurements stability C is the most prevalent. These results indicate that the atmospheric layer containing the mine plume was more unstable than expected (i.e., plume dispersion occurred more rapidly than anticipated). Although this was not an expected outcome of the study, it is possible that the dispersion properties of the near-ground atmospheric layer are greater than those of the overall atmosphere. Surface features at ground level can introduce turbulence and mixing in the air stream which do not occur in the overall atmosphere (i.e., overburden high walls, coal high walls, and dirt piles were located between the source and the FTIR sensor). In addition, if the surface temperature is significantly higher than the ambient air temperature, some convective mixing may occur near ground level. Since most of the surface over which the plume passed was black coal (an efficient absorber of solar radiation) it is conceivable that some thermal mixing occurred.

The SF_6 results also suggest that atmospheric stability changed throughout the day over a wide range. Because of this potential for significant variation, the use of monitoring event-specific stability classes for estimating CH_4 emissions from the mine appears to be warranted.

TABLE 2. COMPARISON OF PREDICTED AND MEASURED SF₆ CONCENTRATIONS

Assumed Stability	Predicted Path-average Concentration (ppm)	Measured Path-average Concentration (ppm)	Percent Difference
ECOAL15		0.0036	
Stability A	0.0046		-22
Stability B	0.0096		-63
Stability C	0.0151		-76
Stability D	0.0261		-86
ECOAL17		0.0042	
Stability A	0.0035		20
Stability B	0.0080		-48
Stability C	0.0138		-70
Stability D	0.0254		-83
WCOAL20		0.0181	
Stability A	0.0069		162
Stability B	0.0103		76
Stability C	0.0149		21
Stability D	0.0241		-25
WCOAL21		0.0157	
Stability A	0.0064		145
Stability B	0.0096		64
Stability C	0.0138		14
Stability D	0.0223		-30
WCOAL22		0.0103	
Stability A	0.0061		69
Stability B	0.0096		7
Stability C	0.0140		-26
Stability D	0.0229		-55
WCOAL23		0.0100	
Stability A	0.0061		64
Stability B	0.0096		4
Stability C	0.0140		-29
Stability D	0.0228		-56

(Continued)

TABLE 2. COMPARISON OF PREDICTED AND MEASURED SF₆ CONCENTRATIONS
(Continued)

Assumed Stability	Predicted Path-average Concentration (ppm)	Measured Path-average Concentration (ppm)	Percent Difference
WCOAL24		0.0076	
Stability A	0.0064		19
Stability B	0.0096		-21
Stability C	0.0143		-47
Stability D	0.0232		-67
WCOAL25		0.0085	
Stability A	0.0067		27
Stability B	0.0104		-18
Stability C	0.0152		-44
Stability D	0.0247		-66
ECOAL26		0.0106	
Stability A	0.0037		186
Stability B	0.0053		100
Stability C	0.0079		34
Stability D	0.0131		-19
ECOAL30		0.0073	
Stability A	0.0037		97
Stability B	0.0052		40
Stability C	0.0079		-8
Stability D	0.0131		-44

Methane Results and Mine Emission Estimates. As stated in the previous section, CH₄ concentration measurements where simultaneous or near simultaneous SF₆ measurements were not available are not used to estimate CH₄ emission rates. In addition, CH₄ concentration measurements which were collected on December 15 were not used because the background CH₄ measured on that day was suspect (see earlier CH₄ concentration results discussion). Without a representative background CH₄ concentration, it is not possible to distinguish between the contribution from background CH₄ and the mine's contribution to the plume. Finally, five CH₄ measurements were not included because low signal-to-noise ratios corrupted the measurement.

The data in Table 2 were used to estimate CH₄ emission rates for the mine as discussed earlier. The results are shown in Table 3. Monitoring event-specific stability classes determined from Table 2 were used to assign a stability class to the following CH₄ measurements: ECOAL15, ECOAL17, ECOAL26, ECOAL30, and WCOAL20 through WCOAL25. For ECOAL16, stability A was assumed because measurements taken immediately before (ECOAL15) and after (ECOAL17) indicated stability A was likely occurring. For ECOAL18 and ECOAL19, stability B was used because measurements taken immediately before (ECOAL15 and ECOAL17) and soon after (WCOAL20 and WCOAL21) indicated the atmospheric stability was changing from A to C. A similar approach was used to select stability C for ECOAL27 to ECOAL29.

Estimated emission rates for the mine range from 0.70 to 6.31 m³/min for the east side, and 0.77 to 6.24 m³/min for the west side. As expected, emissions from the east side are somewhat higher than those from the west side because the coal blast area was producing emissions on the east side of the mine at the time these measurements were taken. The average east side emission rate was 1.85 m³/min and the average west side emission rate was 1.45 m³/min.

Based on these two average values the total annual emissions from the Caballo mine were estimated to be about 1,735,000 m³/year (61.3 million ft³/yr). This emission rate is greater than the emission rates associated with 62 percent of the underground mines in the United States (Grau, 1987). However, it is lower than the emission rates associated with the most significant emitting underground mines. In addition, the specific emissions (emissions per ton of coal mined) are about a factor of 10 lower than many underground mines due to the low relative methane contents associated with surface minable coals. Great caution should be exercised in making these types of comparisons. Measurements at only one surface mine have been collected, and there is a great potential for significant variation to occur between individual mines (as is the case with underground coal mines).

4.0 SUMMARY AND CONCLUSIONS

The results presented here suggest that potentially significant quantities of CH₄ are emitted from the Caballo mine, and that the coal blasting operation is a significant contributor to total mine emissions. Based on the SF₆ and CH₄ concentration measurements collected, it is estimated that the mine emits about 1,735,000 m³ of CH₄ per year. The results also provide evidence that CH₄ concentrations determined by the FTIR are low (particularly those associated with the long-path mine plume measurements). Although the exact magnitude of this bias is not

**TABLE 3. ESTIMATED METHANE EMISSIONS FOR SPECIFIC SAMPLING EVENTS
AT THE CABALLO MINE**

Measurement	Emissions (g/sec)	Emissions (m ³ /min)	Stability Class
ECOAL15	18.98	1.59	A
ECOAL16	7.60	0.64	A
ECOAL17	11.82	0.99	A
ECOAL18	68.09	5.72	B
ECOAL19	11.85	1.00	B
ECOAL26	12.59	1.06	D
ECOAL27	20.90	1.76	C
ECOAL28	20.72	1.74	C
ECOAL29	21.89	1.84	C
ECOAL30	26.35	2.21	C
Average Values	22.08	1.85	-
WCOAL20	67.36	5.66	C-D
WCOAL21	8.32	0.70	C
WCOAL22	22.32	1.88	B
WCOAL23	0.00	0.00	B
WCOAL24	5.87	0.49	A-B
WCOAL25	0.00	0.00	B
Average Values	17.31	1.45	-

known, it could be as low as -20 percent (based on the calibration tube measurements) or as high as -75 percent (based on the OVA measurements). Unfortunately, these data cannot be used alone to assess the accuracy of the overall mine emissions estimate. This is because the accuracy associated with the SF₆ measurements made by the FTIR is not known so the overall effect on the estimation of stability classes cannot be determined.

Key objectives of this field trial were to: (1) demonstrate that the methodology developed here can be applied at large scale surface coal mines, (2) identify and assess uncertainties in the methodology, (3) identify methodology validation needs, and (4) develop necessary methodology modifications. The results of this field trial revealed that the methodology is an applicable and feasible approach for measuring CH₄ emissions from very large surface coal mines. It also highlighted several uncertainties, methodology questions, and areas where improvements could be made. These are outlined below.

- How accurately does the FTIR spectrometer measure path-integrated CH₄ and SF₆ concentrations and what is the effect of monitoring path length on the accuracy of the measured concentrations? Field validation studies are needed to determine detection limits and to identify the maximum FTIR path length which can be used and still produce acceptable results.
- What is the effect of meteorological station location and data averaging times on estimated CH₄ emissions rates. It may be more appropriate to locate the meteorological station at the FTIR path and to use averaging periods which are much shorter (e.g., 1 minute) than those used here.
- What is the reliability of the measurements methodology under partial plume capture conditions and under source conditions where the emissions release is strongly heterogeneous?
- Variability in the background or ambient CH₄ concentration can be on the same order as the CH₄ contribution from the mine. In future field investigations, more background measurements are needed to reduce this uncertainty. Alternatively, simultaneous mine plume and background sampling could be conducted.
- Changes in the wind direction occurred throughout the day which complicated measurements activities and which invalidated some of the measurements taken (i.e., only a small portion of the plume passed through the path on occasion). Several procedural changes would significantly reduce the number of invalid samples occurring as a result of meteorological variation. These include improved FTIR and retroreflector mobility, on-site/real time plume mapping, and the meteorological modifications described above.

The reader is cautioned not to use the data presented here as being representative of all surface mining operations. Since these measurements were completed, initial site surveys were conducted at other mines located in the vicinity of the Caballo mine (i.e., within 3 to 8 kilometers). Methane concentrations measured with the OVA at one small mine were an order of magnitude below the concentrations measured during the initial survey conducted at Caballo. Conversely, a large surface mine which also operates near Caballo has been recognized as likely producing a sustained release of significant quantities of CH₄. Interviews with former employees of this mine suggest that CH₄ liberations from within the site are significantly greater than those produced at Caballo.

These initial site surveys and interviews indicate that mines within the same general vicinity may have dramatically different emission rates. This phenomenon is consistent with the known emission characteristics of underground mines (Grau, 1987). As a result, it has been concluded that additional measurements will be needed before a representative set of surface mine emission factors can be developed.

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