Use of Open-Path FTIR Monitoring For Emission Rate Assessment Of Industrial Area Sources During Winter Conditions

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ABSTRACT

Open-path Fourier transform-infrared (OP-FTIR) was used to collect emission data for a number of chemical compounds for several area sources at the FMC- Pocatello facility. The data collected was used in conjunction with meteorological measurements to assess the emission rate of several of the compounds from these area sources. The release of a tracer gas at a known emission rate and its subsequent measurement with the OP-FTIR allowed for correction of emission rates to account for local effects on the site specific vertical dispersion co-efficients used for emission assessments. The methodology for emission rate assessment is presented, and the implications of correcting for site specific vertical dispersion are discussed. Four area source case studies are included for the study. Most of this data was collected during cold temperature conditions, and some of the data collected during the night time hours, this represents one of the first studies of site specific vertical dispersion under these conditions. Possible impacts of these conditions on emission rate determinations will be presented. The effectiveness of OP-FTIR as a tool for area source emission rate assessment will be evaluated.

OP-FTIR was employed for data collection because of its ability to detect the compounds of interest accurately and with reasonable levels of detectability. Emission rate determinations were done for ponds 16S, and the Phase IV group ponds (11, 12, 13, & 14). Fence-line concentration measurements were also made north of pond 16S. The on-site study was conducted from 11/10/97 through 11/26/97. The data collected indicated that moderate to significant levels of two target compounds were being emitted by pond 16S and the phase 4 pond group. Emission rates were estimated using text book dispersion co-efficients and found to overestimate actual emission rates based on tracer gas release significantly. One target compound's emission rate was found to also be related to wind speed.

Keywords: open-path FTIR, emission rates, sigma z, vertical dispersion, meteorological conditions, tracer gas release, area sources

1. Introduction

FMC required information on the potential air quality impacts of inorganic species emissions from a number of surface impoundments located within the property of the Pocatello Phosphorus Manufacturing Facility. FMC decided to carry out a study of the emissions from the storage impounds, and to assess fence-line concentrations downwind of the most active of these impounds. OP-FTIR was employed for data collection because of its ability to detect the compounds of interest accurately and with reasonable levels of detectability. Because OP-FTIR has the ability to collect data over long, open-air paths it was ideally suited for a) collection of data that could be used for emission rate determination, and b) measurement of actual fence-line concentrations arising from the ponds along a representative section of facility fence-line. A data collection program was carried out over the course of about a two week period from November 12 through November 26, 1997. Emission rates were determined for two surface impoundments, defined as ponds 16S, and Phase 4 (a group of adjacent ponds designated ponds 14S,13S,12S, and 11S).

A number of previous studies had been conducted in the past which involved the refinement of text book sigma z values thru use of measurement of tracer gas release to determine site-specific sigma z effects on area source emissions.[1-3] These studies had generally been conducted during reasonably worse case meteorological conditions for producing highest source emission rates. For these cases text book sigma z values computed for specific Pascal -Gifford stability classes tended to overestimate vertical dispersion and under predict the actual source emissions rates. The present study was conducted under quite different meteorological conditions than typical of past studies as the main project purpose was to get some immediate information on the magnitude of emissions for several of the target compounds. The study results were used to evaluate sigma z effects and also to study the relationship between wind speed and emission rate for several of the target compounds.

2. Experimental

2.1 Equipment Description

The open path FTIR data was collected with a Unisearch Associates open-path FTIR system. This system consisted of a Nicolet Magna FTIR with custom transfer optics, a pair of 11- inch Newtonian transmitter and receiver telescopes, and a liquid nitrogen cooled mercury cadmium telluride detector. Resolution of 0.5 cm-1 was selected for data collection. A large displacing corner cube retro reflector was supplied to receive the transmitted IR signal, displace it, and return it to the receiver telescope sitting adjacent to the transmitter telescope. A Pentium based PC was supplied to control the FTIR bench, perform all sample collection, and process/store data. This software once initialized for the data collection task to be carried out operated automatically to acquire spectral data and archive analyses results. The PC was equipped with customized Unisearch software that performed all a) sample acquisition control, b) data analysis functions, c) reporting of gas concentrations and associated analysis error bars in real time, d) acquisition and display of meteorological parameters, e) display real time system diagnostic parameters, and f) archival of each sample with a unique date/ time identifier.
The FTIR and computer hardware were equipped with a UPS module which could provide about 5 minutes of power should there be momentary power interruptions. The meteorological system provided data on wind direction, wind speed, and air temperature. A mast was supplied to allow for data collection at about 30 feet above base elevation. At each monitoring area the meteorological system was deployed and aligned to true north using a compass and the known magnetic north deviation from true north which was 17.5 degrees to the east for this location. A 5 minute averaging interval was chosen for the data. This represents a good signal averaging time for the FTIR and an adequate averaging time for meteorological data. Sulfur hexafluoride (SF6) was chosen as the tracer gas because of its strong infrared absorption characteristics, non-interference with the target compounds of interest, and inert or non-toxic nature. It is known from other OP-FTIR studies that SF6 is dispersed in the same manner as less dense gases within 5 meters of its release point. The tracer gas release system used for this program consisted of an A cylinder of SF6 (technical grade @ about 99 %) and a two-stage regulator and rotameter that delivered 0 to 2 sch. of air. The equivalent SF6 release rate was 0 to 0.807 sch.. Connections between the regulator and the rotameter were Swagelock, and about 50 feet of 0.25 inch OD Tygon tubing was connected to the rotameter outlet to allow flexibility in final set-up of the tracer outlet point. During use the rotameter was used to adjust the SF6 emission rate. It was found that, once set, the flow was very stable. In only in one data collection sequence were actual SF6 emission rates adjusted because of an observed rotameter variation.

2.2 Preparation For Data Collection

Prior to data collection a preliminary site visit was conducted to define the project work scope and to review site logistics required for data collection. The pond areas of interest were inspected. Information on site area wind patterns, compounds of interest and potential interferant compounds, and plant engineering drawings accurately showing the areas to be monitored were obtained during this visit. A site specific analysis method was developed based on potential target compounds and known atmospheric interferant compounds. This method was tested prior to deployment to the site. Table 1 provides the target and interferant compounds for the project. A FMC supplied meteorologist provided weather forecast information over the course of the data collection period.

Based on the expected wind flow, the OP-FTIR configuration was determined and the FTIR and retro reflector positioned. The tracer gas release position with alternates based on observed wind direction was chosen and the tracer release equipment set-up at the selected location. Measurements were made from facility blue print bench marks to locate FTIR, retro reflector, and tracer release point precisely for use in emission rate modeling. The meteorological system was assembled and aligned to North. The OP-FTIR system components were aligned optically, and signal-to-noise data collected. A location-specific synthetic background spectrum was prepared from an initial spectrum collected along the measurement path with no apparent emissions present. The automated collection software was finalized for the location and data collection prepared for. Stability class was determined based on current USEPA procedures for daytime estimation which include wind speed and solar insolation. Given the latitude and time of year the maximum instability would be B under clear skies and light winds. Variable cloudy to cloudy skies would yield D stability. At night because of no delta temperature data being available, stability was assigned primarily based on wind speed.

2.3 Data Collection

2.3.1 Pond 16S

The measurement system was relocated to pond 16S on 11/15. Wind forecasts predicted SW to WSW winds, so the OP-FTIR beam path was located to the east of the basin. The measurement path extended north of the basin perimeter by about 70 meters to accommodate the expected winds. The retro reflector was positioned on scaffolding about 25 feet above base elevation to allow for a relatively level beam path. Alignment was completed at about 20:30. Winds were S to SSW at this time so data collection was held until 11/17 at 11:00. Data was then collected from about 11:00 hrs on 11/17 to 10:00 hrs on 11/18. During this period, winds were predominately S to W with wind speeds from 10 m/s to calm. Moderate snow showers on 11/17 from 11:15 hrs to 14:00 hrs caused reduction in signal and some of valid data. Stability class for data collection was predominantly D. SF6 tracer gas was released at a flow meter setting of 2 SCH. air which corresponds to 0.0389 g/s SF6. The FTIR signal-to-noise ratio was acceptable for this data set. The round trip beam path was 484.8 meters and the pond surface area was 41,508 square meters.

2.3.2 Phase 4 Ponds

The OP-FTIR system was relocated to the east side of pond 11S for emission rate monitoring. The beam-path location had the FTIR located just east of pond 8E and the retro reflector on a line parallel to the west edge of 8E about 50 feet north of the north edge of pond 11S. Tracer gas release was set up on the west side of pond 14S anticipating a SSW to SW wind. The release rate was set at 2.0 SCFH air which corresponds to 0.0389 g/s for SF6. This flow was stable at 22:30 hrs on 11/25 but had decreased to 1.75 SCFH air on 11/26 at 05:40 hrs possibly due to ambient temperature variation. Data collection was carried out from about 15:30 hrs on 11/25 to about 05:40 hrs on 11/26. A new synthetic background was made and installed in the automated data collection software at about 22:25 on 11/25. Wind direction was S to W during data collection period, with variable wind speeds and some calm periods. Stability class was primarily D. The FTIR signal-to-noise ratio was good throughout the measurements. The round trip beam path in this case was 369 meters. The Phase IV group combined pond area was 44,000 square meters.

2.4 Emission Rate Determination

Emission rates for the ponds were deduced based on:

1) Target compound path integrated concentrations (ppm-m) measured by the OP-FTIR.
2) SF6 tracer path-integrated concentrations (ppm-m) measured by the OP-FTIR.
3) Actual SF6 emission rate(s) (g/s) provided by a calibrated rotameter.
4) Wind speed and wind direction provided from the meteorological tower.

5) Stability classes provided from onsite observations and meteorological data.

The SF6 tracer calculated emission rate, Q, was obtained by entering its path-integrated concentration into the following equation:

$$\text{Eq.1} \qquad Q = 0.5(pi^*2)^{0.5} * C(x) * s\,z * u$$

where: C(x)= OP-FTIR path-integrated measurement for SF6 converted to mg/m2 using mg/m2 = [ppm-m* Mol.Wt./ 24.45]* 10-3 = ppm-m * 0.005974
s z = textbook vertical dispersion coefficient for given stability class at a the downwind distance of the measurement path (meters)
u = wind speed (m/s) provided by meteorological tower

A ratio was then calculated (E/CE) where E is the actual SF6 emission rate provided by the rotameter and CE the calculated emission rate, Q. This ratio corresponds to the ratio of the site-specific s z to the text book s z at the tracer release upwind distance. This can be used to adjust the modeled area source emission rates for the actual s z. The area sources are modeled using the actual s z values appropriate for the upwind distance from the receptor for each portion of the source. The use of the E/CE ratio corrects the average s z employed to reflect the actual vertical dispersion profile over the pond.

The Screen3 model was then utilized by entering the site-specific parameters. The area source algorithm in Screen3 is based on a numerical integration approach, and allows the area source to be approximated by a rectangular area.

The downwind distance of the FTIR beam to the center of the area source was calculated from site maps and the known FTIR beam position. The stability class was provided from on-site observations. The concentration, at a given distance downwind from a rectangular area, is dependent on the orientation of the area relative to the wind direction. As a result, the Screen3 model allows for user specified wind direction to account for orientation. Receptor distances were represented by 10 meter increments along the FTIR beam-path.

In summary, the main steps in using the Screen3 model for OP-FTIR calculations are:

1. Input correct area source orientation and wind direction to the Screen3 model
2. Use the model to predict point concentrations along the OP-FTIR measurement path based on a unity emission rate (1 g/m2/s) and actual wind direction and speed.
3. Use an appropriate numerical technique to integrate the function, (parabolic approximation) in this case Simpsons Rule. Simpsons rule approximates the integral of the point concentrations along the measurement path by a summation function of the individual predicted point concentrations.
4. Scale unity modeling results to converge on an appropriate emission factor.

For the unitary modeling, emission rates were entered as 1 g/s*m2. For the source release height a value of zero meters was chosen. Receptor height above ground was entered as 1 m. A rural setting was entered for this site location.

Each model iteration which yielded a concentration with respect to the 10 m increments within the OP-FTIR beam

path was then summed using Simpsons rule to yield a path integrated concentration (C modeled g/m2). The calculated emission rate (Q(g/s*m2) was determined from by multuplying the unity emission rate by the ratio of measured path integrated concentration to the modeled path integrated concentration. Finally Q (g/s*m2) was multiplied by the area of the corresponding source to yield (Q) in units of g/s. Using the results of the SF6 tracer gas release concentration measurement via the OP-FTIR, the upwind location of the tracer release point and its emission rate from flow measurements, the actual tracer emission rate and predicted tracer emission rate were compared. The ratio of the actual tracer emission rate to the calculated tracer emission rate was used to correct the calculated target compound emission rates during the same timeframe. This is equivalent to adjusting the sigma z function across each pond based on Screen3 text book sigma z value to the measured sigma z value at one fixed point upwind of the measurement point. The emission rate for each contaminant generated in this manner is referred to as Corrected ER.

3.0 Results

The following subsections present a summary of the results of the measurement program. Data acceptability was limited primarily by meteorological conditions at the site location.

The data set collected for each pond was reviewed using Unisearch viewing software to determine the periods of time when the data was acceptable for use in emission rate determinations. Three criteria were used in the initial screening of data collected to select candidates for use in emission rate determinations. The first was availability of adequate IR signal-to-noise for optimum OP-FTIR data use. The second criterion was acceptable wind direction for capture of a majority of area source emissions. The third was the detection of one or more target compounds and adequate SF6 concentrations in the individual data points.

Individual data points consisted of spectra that were co-added over a 5 minute interval and meteorological data that was averaged over the same 5 minute period. All data used showed constant tracer release rates, except for Phase 4 data, for which emission rates of SF6 were linearly decreased with time over the period from hour 23 on 11/25 through hour 6 on 11/26.

Application of the screening criteria produced a data set for each pond location that provided suitable parameters that could be used for emission rate determinations. These data sets ranged from 10 five minute averages to 30 five minute averages. These data sets were further refined by carefully reviewing the wind speed and direction information. Data points with wind speeds less than 0.5 m/s were eliminated. The data sets were optimized by selecting data points with wind directions as close as possible to the optimum direction which would yield maximum tracer gas plume capture for each site. The optimum wind directions were: pond 16S - 235 degrees, and Phase 4 pond group - 245 degrees. The data points that survived this screening were used for model input to produce emission rates. If a large set of points were usable, which would produce computationally intensive emission rate calculations, some of the points close in time were averaged prior to inputting to the model.

The include tables present the study data. Emission rates were calculated as described in section 2.4. The known tracer gas emission rate was compared to the calculated emission rate applying equation 1 at the tracer release distance (between 250 and 300 meters) from the OP-FTIR beampath. The ratio of the actual SF6 emission rate to the calculated SF6 emission rate was determined as E/CE. This ratio is equivalent to the ratio of the site specific sigma z to the text book sigma z at this distance and was uniformly applied to all sigma z values used in the area source emission algorithm to yield a corrected area source emission rate for the compounds of interest.

Table 2 provides the emission rate determinations for pond 16S for Phosphine. As shown there were consistent detections of PH3 with the average corrected emission rate for all measurement events being 0.349 grams PH3 per second. There were a considerable number of usable data points at this site and some were averaged prior to applying the emission rate modeling.

Table 3 provides the emission rate determinations for pond 16S for hydrogen cyanide. There were significant

detections of HCN throughout the measurement events and the averagecorected emission rate for all measurement events was 1.685 grams HCN per second. Again, as there were a considerable amount of useable data points and some were averaged prior to applying the emission rate modeling.

Table 4 provides the emission rate results for the Phase 4 pond group for Phosphine. PH3 concentrations for measurement events on 11/26 were considerably higher than those observed on 11/25. This is most likely the result of the lower wind speeds on 11/26. The determined average PH3 corrected emission rate for all events was 0.111 grams PH3 per second.

Table 5 provides the emission rate results for the Phase 4 pond group for hydrogen cyanide. HCN concentrations were fairly uniform for most of the measurement events but the corresponding emission rates were lower for the 11/26 measurement points consistent with the lower wind speeds on 11/26 (for a given concentration, higher wind speeds produce higher emission rates per equation 1). The observed average HCN corrected emission rate was 0.905 grams HCN per second.

The results of all data sets show that ratio of E/CE was less than 1 for all measurement events and typically in the 0.2 to 0.4 range. This suggests that the site specific sigma z values are considerably smaller than text book values. This is different than previous studies which showed site specific sigma z values larger than text book sigma z values. These studies were typically carried out in summer conditions during day time hours. The results of this study are consistent with a very stable atmosphere, typical of winter and night conditions. The Phase4 ponds data set showed more variability than did the 16S pond data set in this ratio. This may be due potential more non-homogenity in emission rates of the four ponds involved. It is expected that two of these ponds would be more "active " than the others at times.

Table 6 provides a summary of pond 16S and Phase 4 pond group measurement events grouped by wind speed and then averaged. The uncorrected emission rates were used to remove any influence of wind speed on sigma z . HCN emissions are clearly a function of wind speed as illustrated in the similarity of the values of emission rate divided by wind speed (ER/WS). However PH3 does not appear to follow this type of relationship. If the corected emission rates are substituted the HCN and wind speed relationship becomes more evident as the CE/ WS ratios become more uniform and PH3 data shows no difference in behavior. The significantly higher PH3 emission rates under low wind speed conditions observed for the Phase 4 pond group could suggest that ponds 11S and 12S may be much more significant sources of PH3 than ponds 13S and 14S. This is the case, because with low transport speeds and vertical diffusion, the FTIR beam path would be exposed to more emissions from those ponds closer to the beam path than those from farther ponds.

4.0 Quality Assurance and Data Validation

OP-FTIR quality assurance generally followed the guidelines provided in USEPA compendium method TO-16.

Precision was not directly determined for the target compounds using calibration gases. However data for N2O, which is present at nearly constant values in non-urban environments, could be used to estimate the precision. Reviewing data collected on site indicated that that system precision was at acceptable levels throughout the measurement program. Accuracy was not directly measured using calibration gases for this program. However, a good measure of estimate of accuracy can be determined from the ratio of measured concentration to analysis error. This ratio indicated concentration inaccuracies of about 10% to 33% for data collected in the program for PH3 and HCN. In general it was observed that the higher concentration values had the lower associated inaccuracies.

The wind speed, wind direction, and temperature equipment was re-calibrated in accordance with manufacturers requirements. The alignment to true north was checked a minimum of two times at each measurement location. Parameter readings were checked with actual conditions several times per day when OP-FTIR data was being collected as a reality check. The tracer release rate was checked by observing the rotameter setting several times per day at each release location. The rotameter calibration was verified by measuring the air flow with a dry gas

meter after completion of project data collection. Agreement with the nominal flows was within 1%.

Data validation was carried out by manually recreating the absorbance spectrum from a single beam spectrum using location-specific background spectra. This absorbance spectrum was then reanalyzed using the same analysis method employed by the automated software and the results compared to those outputted by the OP-FTIR system on site. The spectrum was also manually reviewed and target compound peaks specifically identified (if present in sufficient concentrations for visual ID). The quantitation was checked for by evaluating concentrations manually through comparison of sample absorbance strength to reference spectra absorbance strength. This procedure was carried out for a minimum of two spectra in the data sets from each location. All results showed that the data reported by the automated software were within acceptable levels of the validation check and all compounds were correctly identified as present or absent. The input parameters for all Screen3 model applications and all support calculations were double checked or done twice done. If a there was a disagreement in a value, then a third check or computation was used to verify the data.

5.0 Conclusions

Concentrations of PH3 and HCN were measured downwind of pond sites at the FMC Pocatello facility during this program. PH3 and HCN were the only target compounds detected above normal background levels. Actual emission rates were determined for these compounds for pond 16S and the Phase 4 pond group, with moderate to significant levels being emitted of both these compounds. The emission rates produced by the ponds were significantly underestimated using text box vertical dispersion parameters. The emission rate of HCN appears to be directly related to wind speed across the pond surface, while the emission rate for PH3 does not clearly show such a relationship. This may be the result of a fraction of the PH3 emissions originating from exposed embankment surfaces and exposed surface areas within the ponds or due to low transport speeds combined with very non-homogenous emissions from the four ponds which comprise the Phase 4 group. For emission rate determinations the overall error in the values obtained(which include errors introduced by meteorological measurements, errors in OP-FTIR measurements, errors in tracer gas release rate, and errors inherent in dispersion model application) range from about +/- 70 to 100 %. The largest error component by far is that associated with the model even with inclusion of the site specific sigma-z correction. The emissions reported here are those appropriate for winter conditions. Since emission rates for most ponds increase with air and water temperature, it may be appropriate to check emissions from these ponds under warmer conditions. A further refinement of site specific sigma z values might be achieved by incorporating a second tracer gas , released fairly close to the beampath allowing for a " mapping of sigma Z over the entire pond upwind surface.

6.0 References

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3.

Table 1 Target And Interferant Compounds For The FMC Program

Target Compounds:
Hydrogen Cyanide (HCN)
Phosphine (PH3)
Arsine (AsH3)
Sulfur Dioxide (SO2)