CASE STUDY: ENVIRONMENTAL MONITORING USING REMOTE OPTICAL SENSING [OP-FTIR] TECHNOLOGY AT AN INDUSTRIAL WASTEWATER TREATMENT PLANT

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ABSTRACT

During production and maintenance operations at Tinker Air Force Base in Oklahoma City, Oklahoma, industrial wastewater streams are generated which contain organic and heavy metal compounds. These waste streams result from chemical depainting operations, chemical cleaning processes, and electroplating operations. Processes discharging wastewater are treated at the on-site industrial wastewater treatment facility [IWTF]. Regulatory reporting mandates require identifying volatile organic compound emission sources, estimating emissions from the IWTF, quantifying ambient air concentrations surrounding the facility via air dispersion modeling, and evaluating computer-generated numerical concentration estimates with respect to discontinuous field data and an open-path optical remote monitoring system. The objective of this paper is to compare three strategies for meeting air quality management requirements: (1) use of a coupled model [air emission model and air dispersion model]; (2) use of air quality monitoring data collected via discontinuous air sampling and analysis [*i.e.*, periodic canister monitoring]; and (3) use of air quality data generated by open-path optical remote monitoring using Fourier Transform InfraRed Spectroscopy [OP-FTIR]. Validation of the predictive accuracy of the three strategies will be made based on (a) comparisons and statistical testing of receptor location predictions with air quality data from periodic canister monitoring, (b) comparisons and statistical testing of predictions along the open path optical remote monitoring boundary line with measured concentrations based on OP-FTIR; and (c) comparisons and statistical testing of pertinent field canister monitoring data with open-path monitoring results.

INTRODUCTION

In production and maintenance operations at the Oklahoma City Air Logistics Center [OC-ALC], industrial wastewater streams are generated which contain organic compounds [*i.e.*, primarily phenol and methylene chloride]. These organic-containing wastewater streams result from both direct and indirect contact with organic compounds via chemical depainting operations, chemical cleaning processes, and electroplating operations. The organic materials in the wastewater are treated at the industrial wastewater treatment facility in open surface impoundments and collection systems. Some of these collection and treatment steps result in the release of volatile organic compounds [VOC] and semi-volatile organic compounds [SVOC] from the wastewater to the ambient air. Because emitted VOC / SVOCs can create potential health problems for treatment facility workers and the general public in surrounding areas, assessment of VOC / SVOC emissions to the atmosphere is necessary for decision makers who must determine the appropriateness of the inputs to and the design and operation of the IWTF. The objective of this effort is to identify potential VOC / SVOC emission sources, estimate emissions from the

IWTF, quantify atmospheric air dispersion concentrations surrounding the wastewater treatment facility, and evaluate computer-generated numerical concentration estimates with respect to field data.

In this effort, computer-generated coupled model predictions will be compared to open-path monitoring data. Coupled model output [geographically based profiles of the ground level concentrations] will be compared to concentrations obtained by an open-path monitoring system using Fourier Transform InfraRed spectroscopy. The open path FTIR monitoring system will measure atmospheric emissions by directing modulated infrared optical energy to retroreflectors [mirrors] along a physical path that crosses downwind of potential emission source plumes from the site. This paper will discuss comparison of the coupled model predictions to open-path monitoring FTIR data and field canister data.

The open path monitoring system measures atmospheric emissions by directing modulated infrared optical energy to retroreflectors [mirrors] along a physical path that crosses downwind of potential emission source plumes from the site [1,2,3]. The OP-FTIR sensor receives the reflected signal, which has twice crossed the plume path. Pollutants in the plumes crossing this path modify the spectral signal in a quantitative way so that the quantities of different species in the path can be determined by analyzing the changes in this signal. The retroreflector returns the beam on the same path with the flat mirror. An important advantage of this system is that the instrumentation allows information to be gathered over a wide area without requiring multiple sensors. Many paths can be sequentially observed with the use of the multidirectional telescope scanner configured with the basic system. An automated approach will be used to measure the effect of the effluent plumes from the multiple open processes in the IWTF under different weather conditions. The FTIR measures a signal associated with the pollutant concentration over the pathlength [plume width]. The multi-directional scanner automatically changes the lines of sight in response to changes in wind direction to attempt to intersect with the plumes.

Initially, remote optical open-path monitoring systems were developed for open-air use. These applications included battlefield detection of nerve agents by the military and environmental monitoring of ambient air by regulatory agencies [4]. Current uses include process monitoring, process control, and stationary source monitoring. Optical sensing is a valuable tool for determining the origin, identity, and amounts of fugitive emissions in an industrial environment. Optical sensing allows for real-time monitoring of gaseous emissions over a large region of space and therefore, is capable of providing a cost-effective means to meet certain ambient air monitoring objectives. Some of the key requirements for an advanced air monitoring system in an industrial facility is for the proposed technology to be cost-effective, reliable and simple, sensitive and accurate, operate continuously, large sensing volume, capable of detecting multiple analytes, and monitor a large dynamic range. Optical remote sensing offers promise as a cost-effective supplement to point monitoring systems [4]. Open-path Fourier Transform InfraRed systems offer versatility and commercial availability capable of monitoring long distances [typically greater than 100 meters]. The OP-FTIR has a larger dynamic range than the point monitor and does not require a recovery time before sensing is resumed. Automation is available which allows the determination of up to 40 compounds simultaneously on a continuous basis [4].

Optical monitoring systems are very powerful because of their ability to see many compounds simultaneously as well as their ability to report results in real time [5]. Optical remote sensing is rapidly being accepted as a viable means of performing industrial monitoring of all types. The U.S. EPA, as well as many state agencies, have now accepted FTIR for many monitoring applications [5]. OP-FTIR technology is going to clearly play a significant role in future environmental and industrial monitoring. FTIR systems are *spectral* meaning that they generate a full infrared spectrum of the sample. Any compound having infrared absorption will leave its characteristic signature [fingerprint] in this spectrum. The challenge is to detect the signature, to identify it, and to quantify it. The absorption signature arises from vibration / rotation transitions in the molecule [5,6]. Because these transitions are dependent on the molecular structure of the absorbing molecule, each compound will have a unique signature. This uniqueness allows the spectral systems to differentiate between various compounds even in complex mixtures. In addition, the intensity of this signature is also proportional to the concentration of the compound so identification and quantification is possible. To detect a given compound in the infrared, the system must locate the absorption band of the molecule that is distinct and as free as possible of interferences from other compounds that will or could be present in the measurement environment. Typical spectral instruments [FTIR] store a library of references and use these to identify and quantitate unknown spectra. OP-FTIR systems are used for accurate, automated, and unmanned operation to monitor ambient air, detect accidental releases, and monitor industrial processes [4,5,6].

Most spectroscopic air-quality measurements are made either in the infrared or the ultraviolet regions of the spectrum [1]. The analytical techniques for these two regions are almost identical where interferometers [FTIR] are typically used in conjunction with IR systems. The FTIR system used for air quality measurements are configured either as extractive systems [with flow-through cells] or as open-path systems, which measure the pollutants in the atmosphere. The open-path system has additional advantages: measurements are performed in situ and therefore maintain the sample integrity, they can provide extensive spatial coverage at much less cost than point sampling methods, open-path systems are remote sensors that can probe inaccessible or difficult to sample regions, systems are well suited for continuous emission monitoring and detection of leaks, and can determine emission rates and downwind receptor concentrations [1,2]. The OP-FTIR is basically a spectrometer with special configurations. The system emits infrared radiation used to probe the sample. The system contains a dispersing element designed to convert broadband radiation into a spectrum where spectrum is defined as a plot of the light intensity versus the optical frequency. In open-path systems, the region where the chemical gases are measured is the open path of the light beam through the atmosphere [1,2]. In open-path systems, the interaction region is the open path through the atmosphere. The transfer optics to and from the atmosphere are referred to as the transmitter and receiver. In order to maintain a collimated beam with small divergence and to increase the collection efficiency of the receiver, the transmitter and receivers are usually telescopes, most often of Cassegrain or Newtonian design [1,2].

Open-path FTIR sensors are configured as either bistatic or monostatic systems. In the bistatic configuration, the transmitter and receiver are placed on opposite ends of the atmospheric path of the light beam. In the monostatic configuration, the transmitter and receiver are essentially in the same location and a reflector is placed on the opposite side of the parcel of air to be measured. There are two types of monostatic systems, the coaxial single-telescope configuration and the two-telescope configuration [1,2]. In the single-telescope configuration, the light first passes through the interferometer and then through a second beam-splitter to the telescope. The telescope transmits the light as an enlarged collimated beam, which passes through the atmosphere to a corner-cube retroreflector array. The retroreflector returns the light beam to the receiver and the detector beam-splitter reflects the light to the IR detector. Combining the transmitter and receiver into a single telescope also lowers costs and improves the alignment stability of the system [1,3].

At OC-ALC [10], the air emission monitoring system utilized in this effort is an open-path Fourier Transform InfraRed spectrophotometer operated in a monostatic configuration with a single telescope, which functions both as a transmitter and a receiver. The infrared light from a silicon carbide glower is modulated by a Michelson interferometer and then transmitted by a single transmitter / receiver telescope, through the atmosphere being measured, to a retroreflector. The retroreflector returns the beam to the transmitter / receiver telescope and a beamsplitter directs the beam to a cryogenically-cooled, mercury cadmium telluride [MCT] detector. The FTIR Sensor system was designed to measure air emissions along five physical paths using a unistatic optical system coupled with a field-hardened MDA FTIR spectrometer system. The retroreflector placed at the end of each path is made up of an array of corner cubes that have sides aligned at 90 degrees. These three sides form a single corner-cube reflector. The optical properties of the corner cube are such that it always reflects back in the direction of the received beam, displaced only by some fraction of the cube width. The scanner output mirror is an elliptically shaped flat mirror. This optical component directs the modulated infrared beam toward a retroreflector or mirror along a path that traverses potential source plumes. The scanner output mirror also receives the reflected beam, which has returned across the plume path. The molecular species in the plume path absorbs infrared radiation at characteristic frequencies [wavelengths]. Three of the paths [P_1, P_2, and P_3] are directed along the northeast perimeter of the IWTF while two of the paths [P_4 and P_5] are directed within the perimeter. The five pathways are illustrated in Figure 1 and will be presented in the next section of this paper. The system was installed in 1995 and has operated off and on for the last five years. During the five years, data have been collected over only three months [December 1995, January 1996, and February 1996] since installation [10]. It is interesting to note that of the data collected for the targeted chemicals [phenol and methylene chloride] during the three months of operation, only 64 percent of the gathered information was of value. The remaining 36 percent of the data were considered invalid because either the concentrations were negative or the position of the concentration maxima was at the FTIR instrument.

The literature describes an automated OP-FTIR system that has been installed at Tinker Air Force Base to continuously monitor volatile organic hydrocarbon emissions [methylene chloride, phenol, trichloroethane, tetrachloroethylene, etc.] from the industrial wastewater treatment plant [10]. The IWTF occupies an area 200 by 250 meters. Using mirrors and retroreflectors on elevated platforms near ground level, five optical paths were established for open monitoring over path lengths ranging from 60 to 200 meters. The scanner is programmed to automatically cycle through the different optical paths and record infrared absorption spectra. Spectral libraries and control software are available with the remote sensing system, so that spectra can be identified and quantified. The system is designed with 99 receptors or calculated point concentrations. To determine the concentration profiles along the optical paths, separate calculations are made with all 99 point receptors distributed along each optical path. A calculation routine is available to determine the maximum concentrations of a species and its coordinates at the fenceline. The comprehensive studies involved simultaneous open path measurements with tracer gas release and collection of gas samples. Smoke releases were also conducted to allow visualization of plumes. The author concluded that the OP-FTIR system was operational, but neglects to include how the FTIR concentration predictions compare to gas sample concentrations [10].

A distinctive element of this effort is the comparative studies where the computer-generated coupled model predictions are compared to open-path FTIR monitoring data along two perimeters [three optical paths]. Most of the literature evaluates a single, downwind optical path. Another distinctive element is that there are multiple retroreflectors that bend the optical path, whereas the literature is typically limited to one retroreflector designed to make a single pass along the downwind path [monostatic design]. Another feature unique to this effort is that chemical depainting agents [phenol and methylene chloride] are analyzed by the OP-FTIR, whereas much of the literature is limited to primary criteria pollutants or tracer gases [sulfur hexafluoride and carbon tetrafluoride]. Most of the FTIR literature is compared to limited, short-term tracer gas releases without comparisons to air dispersion model predictions. Much of the OP-FTIR literature pertains to the monitoring of other industrial sources [industrial complexes, incinerators, petrochemical facilities, landfills, municipal waste sites, etc.] and not directed toward environmental monitoring of IWTF fencelines [facility perimeter].

TINKER AFB APPLICATION OF THE OPEN-PATH MONITORING SYSTEM

The open-path monitoring system utilized in this effort is the open path Fourier Transform InfraRed [OP-FTIR] spectrophotometer operated in a monostatic configuration. The FTIR sensor system will measure air emissions along several distinct physical paths by using a unistatic optical system coupled with a field-hardened MDA FTIR spectrometer system. The molecular species in the plume path absorbs infrared radiation at characteristic frequencies [wavelengths]. Figure 1 illustrates the series of paths over which this air monitoring system will be directed at the IWTF. The paths are labeled P_1 to P_5 and extend out from the IWTF control facility on which the FTIR is stationed [10]. The advantage of this location is that the system has direct optical access to most of the major pollution sources [see paths P_4 and P_5 in Figure 1] as well as having access to the paths along the fenceline [P_1, P_2, and P_3]. The paths over the sources will be coupled with the measurements made at the fenceline to validate the necessary pollution dispersion modeling. Usefulness of the paths for sample analysis along the fencelines is limited to the times when the wind is blowing plumes in the directions over those paths. Since the wind is from the south-southwest to south-southeast about 40 percent of the time, the northern paths will be used at least this much of the time. The eastern path [P_3] can be used as a background run during a southerly or northerly wind direction, and as a sample path during westerly winds. Optical paths P_4 and P_5 will not be considered because of the lack of comparison data [periodic canister monitoring data].

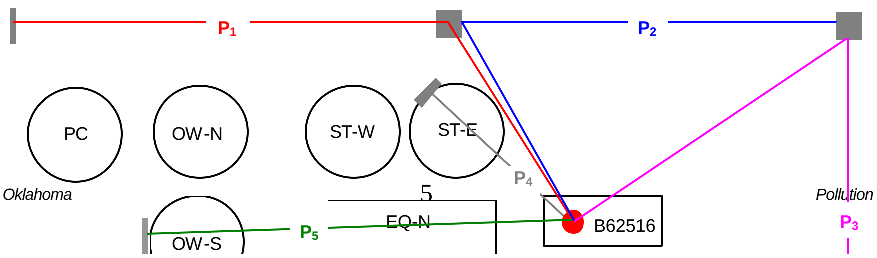

Figure 1. Top view of the IWTF remote optical monitoring paths

COMPARISON OF MODEL PREDICTIONS TO OPEN PATH MONITORING DATA

This part of the project involves comparing the computer-generated phenol and methylene chloride concentrations with open-path monitoring data and field canister data. The Open Path Monitoring [OPM] system, a Fourier Transform InfraRed remote sensing system, is one such system designed to monitor species emission levels in real time, along paths where plumes are expected. The paths of the OPM, set for operation at the IWTF, allow concentration information to be determined along the fenceline of the facility. The FTIR measures the average concentration along the beam path on this fenceline directly, and with modeling can verify that the defined MAAC is not exceeded on a path average. Measurements of 5 to 11 compounds were made on each run. The FTIR sensor observes changes in the beams intensity in the specified wavelength regions, due to optical absorption by the pollutants present in the plume. The spectral wavelength patterns of the sets of spectral regions monitored are compound dependent. The size of the changes in these concentration patterns is directly related to the size of the observed spectral absorbance patterns. The calculated values are average values attained during a measurement, which usually lasts ten minutes. Assuming steady wind directions, this can be extrapolated directly for comparison to the annual-average chemical concentrations. Concentration data show maxima on the path where the concentration-pathlength has been measured. The coordinates give the positions of the maxima. These are obtained by modeling 99 receptor points equally spaced on the path. By knowing the location of the concentration maxima along the path, the chemical concentrations predicted by the OP-FTIR can be plotted as a function of distance along the optical path. These OP-FTIR concentration predictions can be compared to concentrations predicted by the coupled model and field canister sample data. The field data are composed of three studies: RCRA facility investigation, Battelle Study, and OC-ALC Bioenvironmental data.

Figure 2 illustrates the methylene chloride concentration along optical Path P_1. This is a path running west-to-east along the fenceline north of the IWTF. The solid squares indicate the coupled model predictions positioned every ten meters. The black circle, diamond, and triangles represent the field data [RCRA facility investigation, Battelle study, and OC-ALC

Bioenvironmental data, respectively]. The OP-FTIR predictions are represented with the open blocks. It is important to note that the concentrations predicted by the FTIR are clearly several orders of magnitude larger than both the coupled model predictions and field canister data. It is also important to notice that there are no obvious trends as observed with the coupled model predictions [higher concentrations in the middle and decreasing concentrations approaching the outer limits of the facility perimeter]. The OP-FTIR data appears to be a scattered clump of data orders of magnitude greater than what is predicted by the coupled model and periodic field canister data.

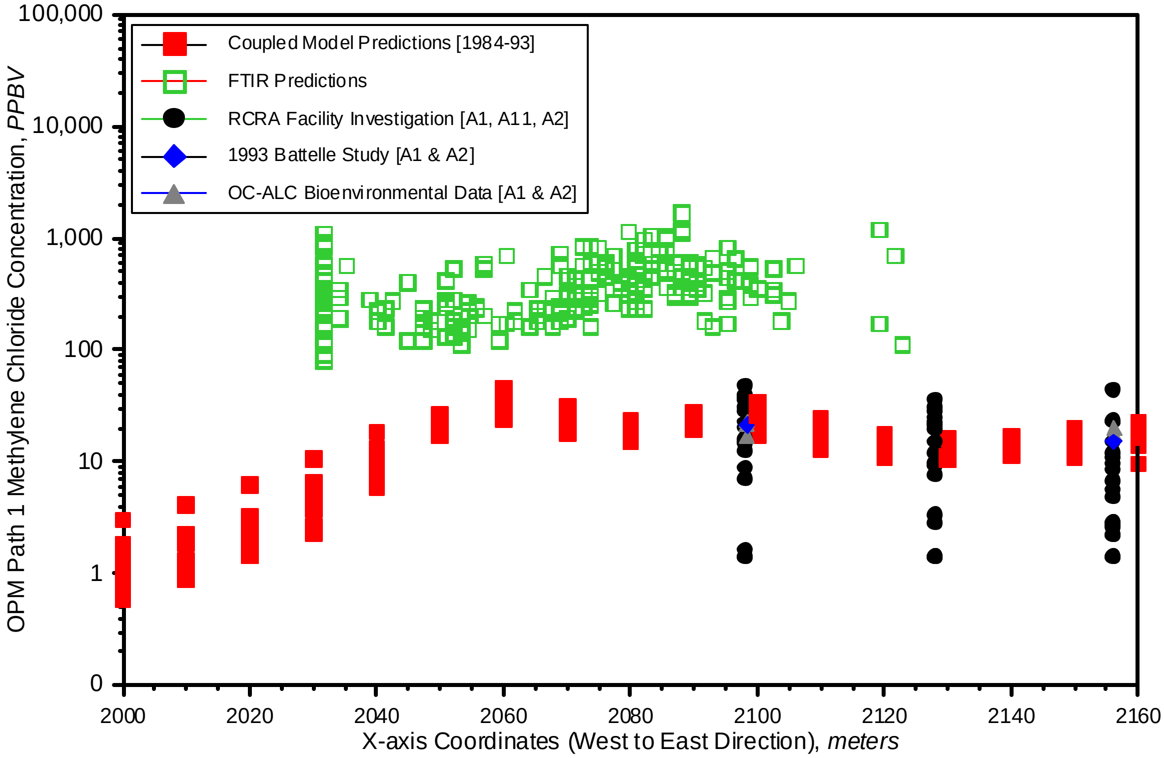

Figure 2. OPM Path P_1 concentration predictions for methylene chloride [PPB]

Figure 3 illustrates the methylene chloride concentration along optical Path P_2. This is a path running west-to-east along the fenceline north of the IWTF. The solid squares indicate the coupled model predictions positioned every ten meters while the black circle, diamond, and triangles represent the field data. The OP-FTIR predictions are represented with the open blocks. It is important to note that the concentrations predicted by the FTIR are clearly several orders of magnitude larger than both the coupled model predictions and field canister data. It is also important to notice that there are no obvious trends as observed with the coupled model predictions [higher concentrations in the middle and decreasing concentrations as you approach the outer limits of the facility perimeter]. The OP-FTIR data appears to be a scattered clump of data orders of magnitude greater than what is predicted by the coupled model and canister data. Another point that supports questioning the FTIR data is the fact that Path P_2 at *x*-axis coordinate 2152 in Figure 3 shows a large collection of FTIR data. This collection of data does not appear at *x*-axis coordinate 2152 in Figure 1 along Path P_1. The FTIR is able to detect the chemical concentration plume along one path [P_2], but miss it completely along an adjacent path [P_1] at the same coordinate location.

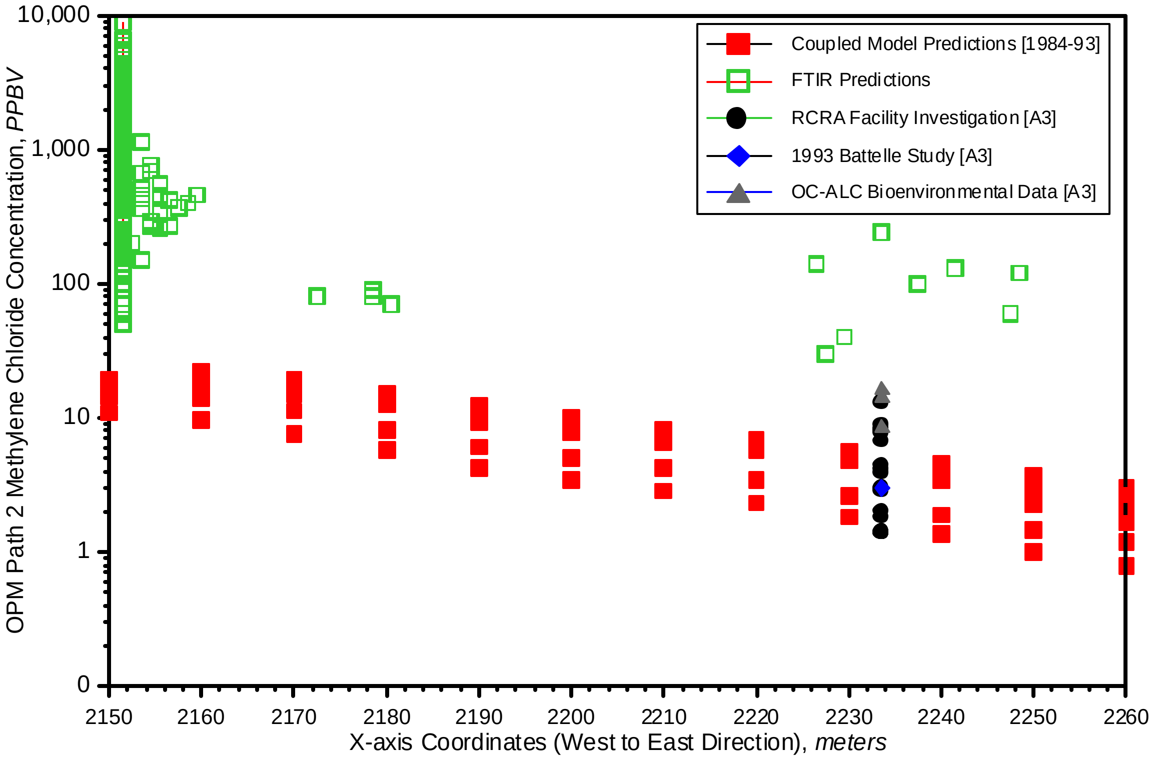

Figure 3. OPM Path P_2 concentration predictions for methylene chloride [PPB]

Figure 4 illustrates the methylene chloride concentration along optical Path P_3. Unlike P_1 and P_2, Optical Path P_3 extends south-to-north along the east perimeter fenceline of the IWTF. The solid squares indicate the coupled model predictions positioned every 10 meters while the black points represent the RCRA field data. Note that there are no Battelle or OC-ALC Bioenvironmental data for these sites [A4 and A5]. The OP-FTIR predictions are represented with the open blocks. As with the previous two optical paths, concentrations predicted by the FTIR are several orders of magnitude greater than both the coupled model predictions and RCRA field canister data.

Figures 5, 6, and 7 illustrate the phenol concentrations along the same optical paths P_1, P_2, and P_3, respectively. These paths extend west-to-east along the fenceline north of the IWTF, and north-to-south along the eastern perimeter. The solid squares indicate the coupled model predictions positioned every ten meters. The black circle, diamond, and triangles represent the field canister data [RCRA investigation, Battelle study, and OC-ALC Bioenvironmental data, respectively]. The OP-FTIR predictions are represented with the open blocks. In each case, it is important to note that the phenol concentrations predicted by the FTIR are clearly several orders of magnitude larger than both the coupled model predictions and field canister monitoring data. It is also of interest to note that there are no obvious trends as observed with the coupled model predictions [as observed with the coupled model predictions and periodic field canister data]. The OP-FTIR data appears to be a scattered clump of data orders of magnitude greater than what is predicted by the coupled model and field canister data.

SUMMARY

The following discussion will objectively answer which of the methods are more accurate: the coupled model predictions or OP-FTIR data. In reviewing the figures, the coupled model predictions clearly appear to duplicate the field canister data for both the methylene chloride and phenol in every figure, whereas the OP-FTIR over-predicts the field canister data by one-to-three orders of magnitude for both constituents in every figure [along three different optical paths]. The coupled model predictions produced numerical values that were in very good agreement with the field canister data. For both chemicals, 92 percent of the coupled model predictions were within a 99 percent level of confidence and 100 percent of the coupled model predictions were within a 98 percent confidence level. The field canister data consisted of over 270 data points from three independent sources [RCRA facility investigation, Battelle study, and OC-ALC Bioenvironmental study] collected over six weeks. There were 130 coupled model predictions made at 13 different receptor locations using ten years of meteorological data [1984 through 1993]. The coupled model predictions were compared using both a *z*-test and Student's-*t* test with both statistical tests indicating a high degree of correlation with the field canister data.

The FTIR was tested for a longer period of time [12 months], along multiple [three] optical paths, and down two facility perimeters [east-west and north-south] for both chemicals. The OP-FTIR was unable to predict the chemical concentrations for either chemical that was within one order of magnitude for either methylene chloride or phenol. Most OP-FTIR predictions were between two and three orders of magnitude difference with the field data.

Another indication that the OP-FTIR values are in question is the missing FTIR data along Optical Path P_1 at *x*-axis coordinate 2152 in Figure 2. This collection of data does not appear at *x*-axis coordinate 2152 in Figure 2 along Path P_1, but does detect the methylene chloride plume at the same location on the *x*-axis along Path P_2 in Figure 3. The FTIR is able to detect the chemical concentration plume along one path [P_2], but miss it completely along an adjacent path [P_1] at the same coordinate location. This fact not only brings into question the large collection of data in Figure 3 [*x*-axis coordinate 2152], but all of the methylene chloride concentrations along all three optical paths.

In reviewing the trends, there were no observed trends with the OP-FTIR predictions. Common sense dictates that the closer [shorter distance] that the measurement or predictive tool is to the emission source, the greater will be the dispersion plume concentration. For the coupled model predictions and field canister data, the receptors closest [within 100 meters] to the major emission sources [A1, A11, A2, and A3] showed a greater chemical concentration while the receptors farther away [over 100 meters] from the major emissions sources [A6, A7, A8, etc.] had lower chemical concentrations. The OP-FTIR data appears to be a scattered cluster of data without any similar trend and orders of magnitude greater than what was measured by the periodic canister monitoring data.

Critical to the investigation is the reliability and reproducibility of the existing data. The OP-FTIR installed at Tinker AFB provided a reliability-of-operation of less than three months over five years of operation [10]. Of that three-months of data, more than 36 percent of the collected information is considered unusable because of technically unsound data [negative concentrations, etc.].

Independent of this effort, the OP-FTIR has been shown to misidentify and produce predictions for chemical concentrations that are orders of magnitude greater than measured at the IWTF [20]. In a 1998 odor investigation of the industrial wastewater treatment facility, the OP-FTIR misidentified and misrepresented the chemical concentration of several pollutant plumes discharged from the IWTF. This study supports the information and conclusions provided in this effort [20].

There are a number of reasons for the OP-FTIR to over-predict the field canister data. Some of the potential reasons include interferences from stray light spectra, water vapor concentration, background or reference spectra, inappropriate location of the remote optical paths, routine noise interferences, calibration standards outside the range of interest, to name a few. Stray light inside the instrument can be caused by strong sources of IR energy that are in the field of view of the instrument [21]. For example, it is possible to have the sun in the instruments field of view during sunrise and sunset. This will probably give rise to an unwanted signal that actually comes from reflections inside the instrument. The stray light actually causes an error in the determination of the gas concentration and must be subtracted from the data spectra before processing [21]. Thus, the stray light component must be recorded at every monitoring session. Another potential concern is the impact the water vapor concentration has on the performance of the instrument. The return-beam intensity is a function of not only the path length, but also of the water vapor concentration in the atmosphere [21]. It is critical that the water vapor spectra be measured along each path at every monitoring session. The change in water vapor concentration must be considered the biggest potential source of error in the background measurement [21]. An accurate record of the partial pressure of water vapor should be maintained. These data should be taken continuously, or at least every two hours during quiet days or every half hour during times when weather fronts are passing [21].

Reference or background spectra can have a significant impact on the performance of the instrument. Ideally, the background spectrum is collected under the same experimental conditions as those for the sample spectrum, but without the target gas or gases present [21]. Errors are introduced into the measurements if background spectra are not obtained with every monitoring session. Acquisition of the reference spectrum represents one of the more difficult tasks in open-path FTIR monitoring [21]. Currently, there is not a universal method for obtaining a satisfactory background spectrum. The method chosen to obtain the reference spectrum must be determined on a site-by-site basis. General advice about the background spectra are that the spectra cannot contain any absorption features due to the target gases and the spectrum are only valid for the time period over which it was used [21].

Location of the remote optical paths is another consideration that can impact the accuracy of the instrument. According to the literature guidelines, 90 percent of the path must be at least 20 meters from the drip lines of trees [21]. This recommendation is violated along the north perimeter where 75 percent of Optical Paths P_1 and P_2 are well within the drip lines of the trees along the north perimeter.

Another consideration critical to the performance is the use of calibration standards for defining the concentration range for specific chemical constituents. The calibration standards should include the expected concentration within the range of standards to ensure correct identification and quantification of the target gases.

In addition, routine noise measurements [instrument electronic noise and random baseline noise] should be taken during every monitoring session. The noise measurements should be taken daily and recorded on a control chart to alert the operator of any gross changes or trends in the deterioration of the baseline noises [21].

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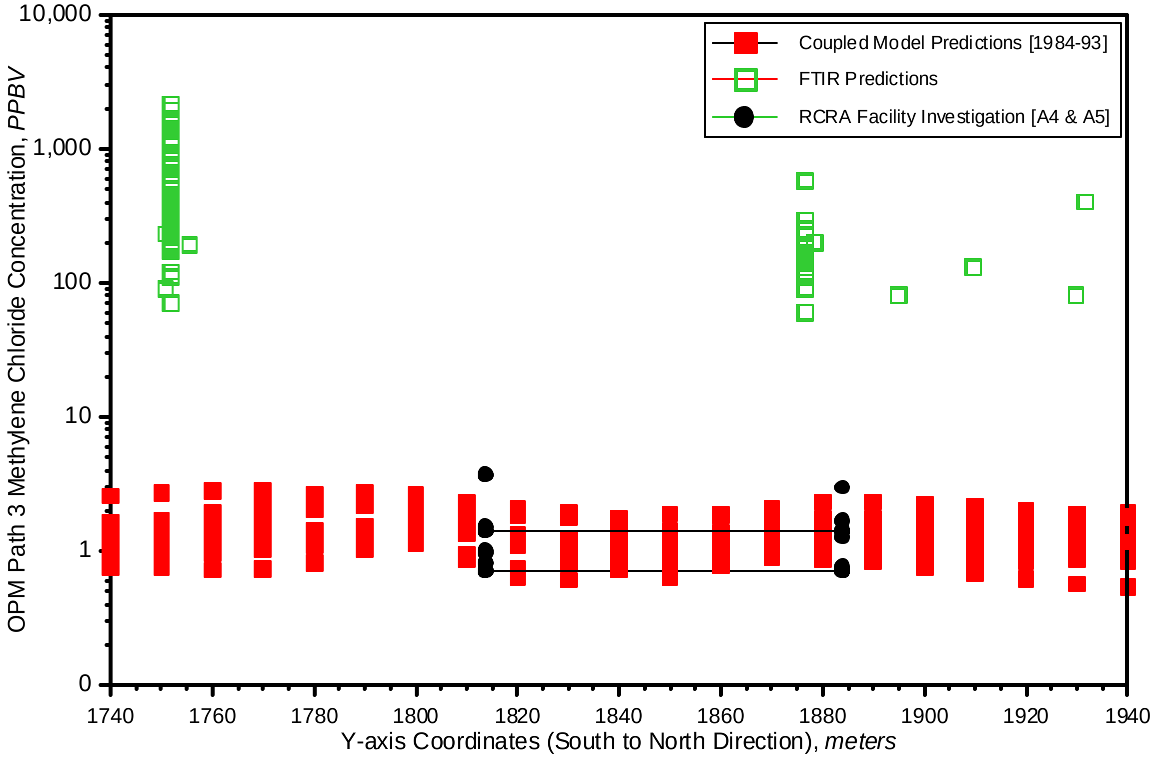

Figure 4. OPM Path P_3 concentration predictions for methylene chloride [PPB]

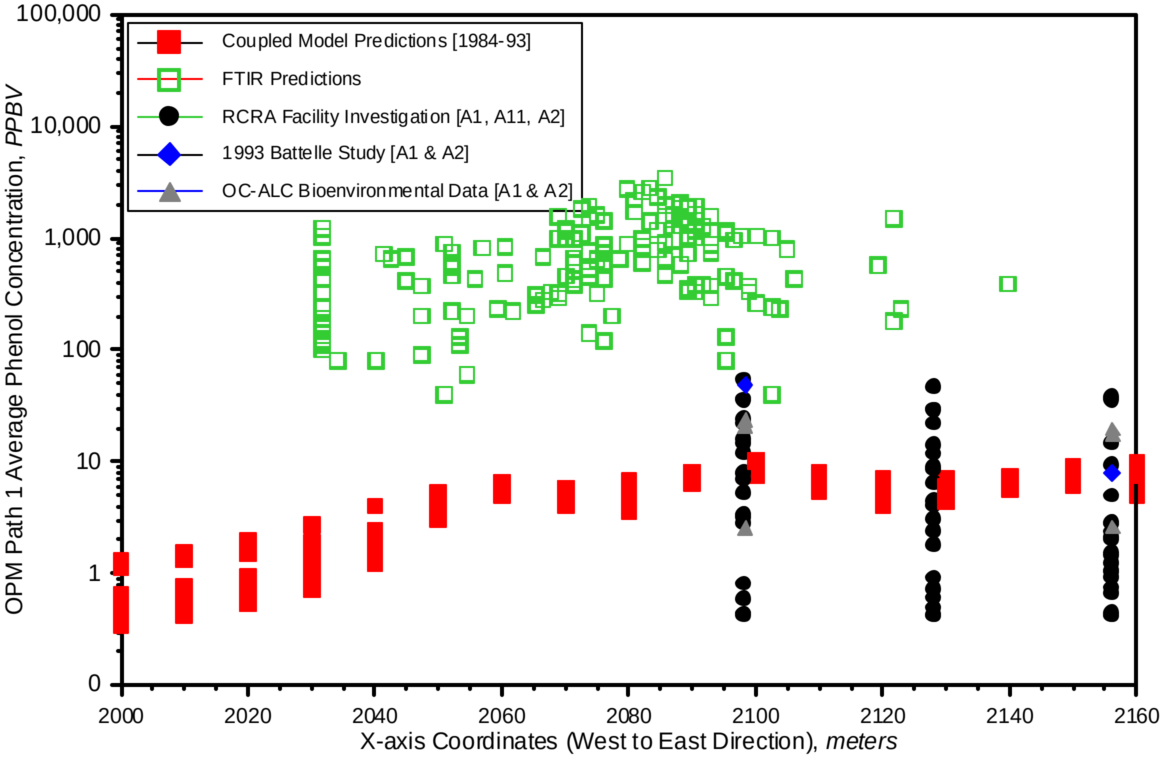

Figure 5. OPM Path P_1 concentration predictions for phenol [PPB]

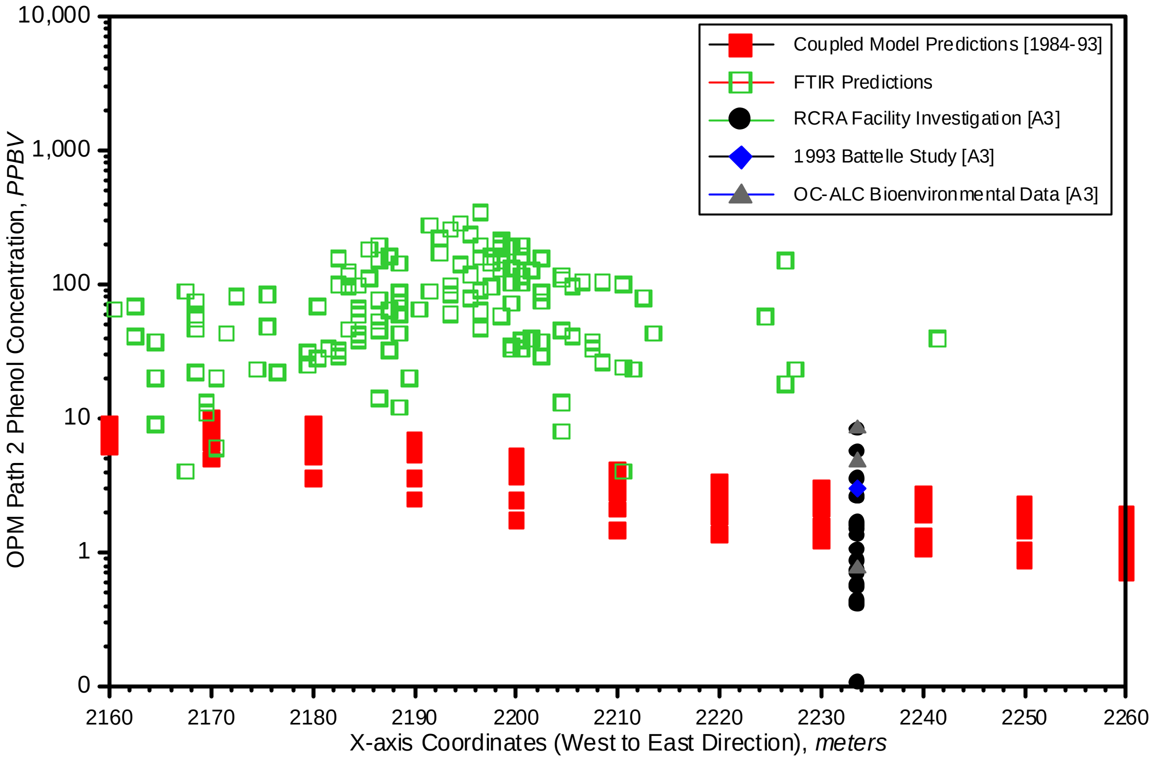

Figure 6. OPM Path P_2 concentration predictions for phenol [PPB]

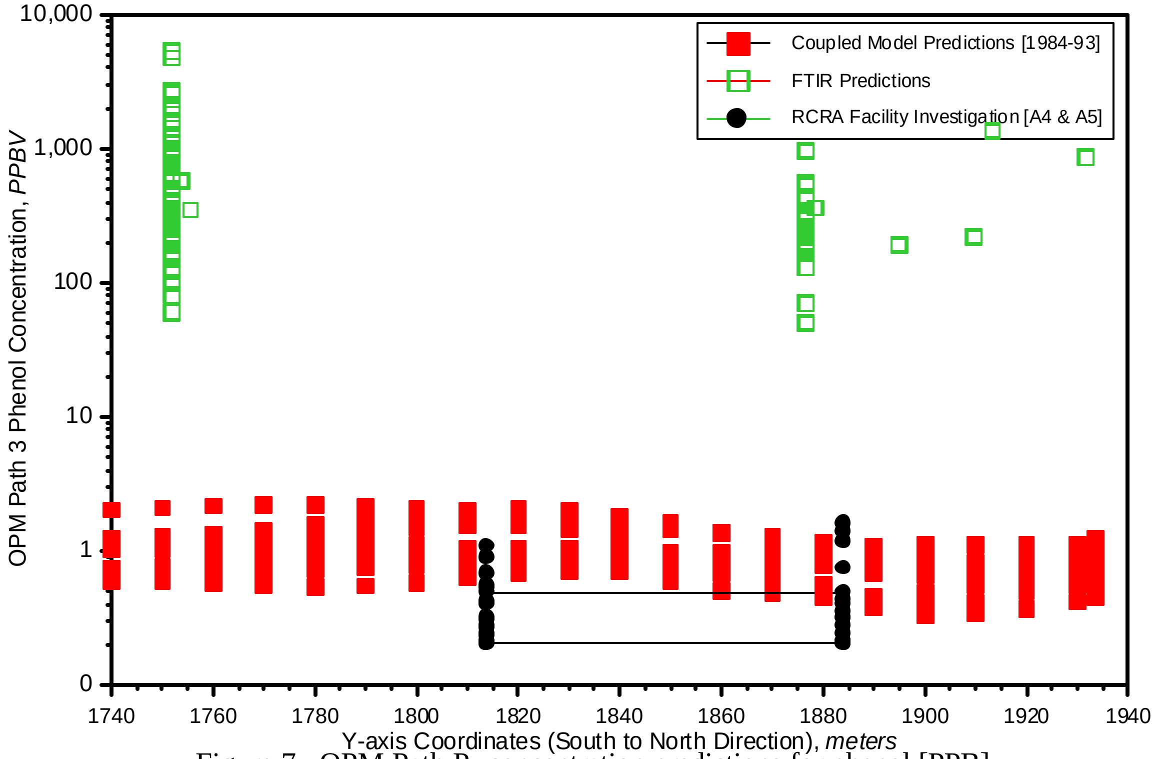

Figure 7. OPM Path P_3 concentration predictions for phenol [PPB]