Remote Sensing Feasibility Study of Refinery Fenceline Emissions

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
API PUBLICATION NUMBER 4587
APRIL 1994

STEP
Strategies for Today's Environmental Partnership

American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005

Remote Sensing Feasibility Study of Refinery Fenceline Emissions

Health and Environmental Sciences Department

PUBLICATION NUMBER 4587

PREPARED UNDER CONTRACT BY:

WILLIAM M. VAUGHAN, PH.D.
JUDITH O. ZWICKER, PH.D.
ROBERT H. DUNAWAY

REMOTE SENSING AIR, INC.
ST. LOUIS, MISSOURI

APRIL 1994

American
Petroleum
Institute

FOREWORD

API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

API IS NOT UNDERTAKING TO MEET THE DUTIES OF EMPLOYERS, MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.

NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.

ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

API STAFF CONTACT(s)

Paul Martino, Health and Environmental Sciences Department

MEMBERS OF THE REMOTE SENSING PROJECT GROUP

Lee Gilmer, Texaco Research
George Lauer, ARCO
Dan Van Der Zanden, Chevron Research and Technology Company
Kathryn Kelly, Shell Oil Company
Miriam Lev-On, ARCO Products Company

Remote Sensing ≡ Air, Inc. (RS≡A) would also like to thank its team members who contributed to this effort including:

John Lague and John Deuble (Ogden Environmental and Energy Services)
Donald Stedman and Scott McLaren, University of Denver
Robert Kagann, MDA Scientific
Mark Witkowski, Kansas State University
Peter Woods, National Physical Laboratory
Konradin Weber, Verein Deutscher Ingenieure

ABSTRACT

This report reviews the state of the art of optical remote sensing (ORS) technology and examines the potential use of ORS systems combined with ancillary measurements such as meteorological and tracer gas release data to determine fugitive emission rates. With the need to track the effectiveness of controls of fugitive emission sources and to conduct downwind health risk assessments for refineries, ORS technology appears to be an attractive tool for characterizing an entire facility's emissions. The American Petroleum Institute (API) sponsored this technical review effort as part of its planning for a refinery emissions field study in which ORS methods might be used. The report concludes that under some special conditions, ORS systems can document the fugitive emissions and that no prior studies preclude the need for API to carry out an evaluation of the general concept. The report highlights some issues to consider in planning such a study and clarifies the attendant tradeoffs for issues such as: selection of appropriate ORS systems, consideration of detection limits and beam placement, choice of dispersion models, use of tracer gas releases, time scale and timing of field studies and the requisite meteorological measurements. Finally, the report emphasizes that the uses of ORS instrumentation for the determination of aromatic emissions is perhaps the most difficult and challenging of the possible use of the ORS at refineries. When compared to the current point sampling methods, however, the current ORS systems have the potential for integrating the multiple small sources that comprise the overall fugitive emission plume.

TABLE OF CONTENTS

Section Page

LIST OF APPENDICES

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

Under Title III of the Clean Air Act amendments of 1990, the U.S. Environmental Protection Agency (EPA) is required to promulgate Maximum Achievable Control Technology (MACT) regulations for emissions of hazardous air pollutants (air toxics) from various industrial sources including refineries. Once the control technology is in place, EPA must develop information on the residual risks associated with exposure to low-level air toxics downwind of major industrial sources. It is anticipated that the EPA will require industry to use actual emission measurements or emission estimates derived from emission factors and dispersion modeling to estimate the risks. Recent studies, however, have shown that EPA dispersion models may significantly overestimate ambient concentrations of low-level air toxics for areas less than one kilometer from the source (near field). In addition, at the time this study was initiated, EPA and several state agencies were considering requiring industry to use open-path optical remote sensing (ORS) technology to establish concentrations of low level air toxics downwind of industrial sources.

For these reasons, the American Petroleum Institute (API) considered conducting a comprehensive field study at a refinery to assess whether upwind and downwind ORS measurements, combined with ancillary measurements such as meteorological and tracer gas release data, could be used to calculate emission rates of air toxics from a refinery. A secondary objective was to develop better information on the near-field dispersion of air toxic emissions from refineries for the purposes of improving existing dispersion models.

Before embarking on a costly field study, API sponsored this study to review the state of the art of optical remote sensing technology and to provide answers to several questions which arose concerning the feasibility of achieving the field study objectives.

STUDY APPROACH

The feasibility study was conducted by performing two major tasks. The first task was to conduct a comprehensive review of studies related to the use of optical remote sensing for the measurement of emissions of refinery-related compounds both in refinery settings and non-refinery settings. In addition, conventional sampling studies for emission rate estimates were reviewed. In the second task, the reviewed information was synthesized and key technical issues such as detection limits, light beam placement, dispersion modeling, tracer gas releases, and time interval for measurements were summarized. Based on the review, the questions posed by API were answered and technical considerations for design of a refinery emissions study using ORS were developed.

SUMMARY OF FINDINGS

The findings of this study can best be summarized in the context of the answers to the feasibility questions posed by API and the design considerations that were developed.

Is the amount of information collected from other, recent studies of a similar nature sufficient to accomplish the objectives of the proposed field study thereby negating the necessity for the field study?

None of the reported studies addressed detection limits and transport parameters in sufficient detail to provide technically defensible emission rate data, especially for the benzene, toluene, ethylbenzene, xylenes (BTEX) compounds and, specifically, benzene. There are indications that progress has been made in the past four to five years in obtaining emission rates for these compounds but more work is still needed. Hence, there is not sufficient data at present to rule out the need for a field study.

Most of the experience in using ORS for fugitive emissions estimates at refineries has been gained from two studies at Swedish refineries in the late 1980s. The reports (mainly internal and not peer-reviewed) from these studies were reviewed for the apparent successes and problems with this application. No specific studies have been completed with a focus on benzene. The Swedish studies involved total non-methane hydrocarbon estimates as well as toluene and p-xylene. Several suggestions regarding use of vertically-scanning laser-based systems and the time scale for measurements emerged from these programs. There seem to be no hard numbers evaluating the emissions determinations from these studies.

The refinery experience in the United States has been predominantly a series of measurement demonstrations with no published attempts to estimate fugitive emissions. While many successful measurement efforts are reported using both infrared and ultraviolet systems, none have been carried out with sufficient meteorological support data and measurement strategy to allow computation of emission rates.

Several ORS studies have looked at downward concentrations of benzene, toluene, ethylbenzene, and the xylenes emitted from refinery process areas such as land farms and impoundments, but not from entire facilities. For the simpler geometry of these area sources having surface releases, emission rate estimates have been made and compared to tracer releases and modeling predictions with some success.

Will it be possible to separate a refinery's contribution from the background contribution for low-level concentrations measured along the fenceline and further downwind from a refinery?

Adequate detection limits are important to be able to separate a refinery's contribution from background contributions of air toxics downwind of a refinery. The ultraviolet (UV) ORS systems have lower detection limits for the aromatic compounds of most concern to the petroleum industry; however, the one commercially available system had not been tested reliably in fenceline studies as of the end of 1992. The versatility of the open-path Fourier Transform Infrared (OP-FTIR) ORS systems in being able to detect a large number of organic and inorganic vapors is offset by their relatively poor sensitivity for aromatic compounds caused by water vapor interference in the regions of strong absorption. A number of factors affect the actual detection limits attained at a particular site, at a particular time. These include the presence of interfering compounds, the path length, meteorological conditions, the time interval of sampling, and the detector in the particular instrument being used. These factors need to be considered in the design of a field study.

For refineries in isolated locations, it should be possible to separate the contributions due to the refinery from the background provided that a UV-based ORS system is used for the BTEX compounds. Of course, if the refinery emits low concentrations of air toxics even those isolated downwind levels may be below currently achievable minimum detection limits (MDLs). No information on the actual contribution from the refinery would be gained if both the upwind and downwind concentrations are below the MDLs.

For non-BTEX air toxics unique to refineries, it should also be possible to the separate the contribution due to the refinery from the background by either a UV or FTIR system even in a more complex industrial setting, again with certain MDL caveats.

For BTEX compounds at refineries in an urban or industrial setting, it will probably not be possible to separate the contribution due to the refinery from the background with the currently available systems due in part to the complex source pattern and present MDLs for these compounds. This qualification recognizes that the presence of BTEX, especially benzene, in the ambient air comes from the cars and trucks in parking lots as well as the nearby highways (Stevens and Vossler, 1991) and other nearby industrial sources and, thus, must be compensated for. The concentrations from these non-refinery sources may be significantly higher than those from the refinery itself. For such complex settings, monitoring close to the various process areas at the refinery may make it possible to determine emissions rates for each process area since the ambient concentrations due to the process area will be significantly higher near the process area (source) than at the fenceline, thus, reducing the importance of the upwind concentrations.

Is the state of the technology of optical remote sensing (and required ancillary measurements) sufficiently refined to provide technically defensible data for the calculation of air toxics emission rates due to a refinery complex located in either an isolated setting or in a complex industrial area?

To address the issue of the technical defensibility of the calculated refinery specific emission rates, one must address not only the defensibility of the path-integrated concentration measurements but also the defensibility of the contribution due to the refinery determined from these measurements and the defensibility of the models and/or tracer data which combine the meteorological data with the concentration data to produce emission rates.

With respect to ORS path-integrated or path-average concentrations, ORS instrumentation and field techniques have been improving rapidly in recent years and have compared well with conventional sampling methods in several field intercomparison studies. In addition two draft guidance documents have been prepared by the EPA to provide guidance on quality assurance and quality control measures to ensure that path-average concentrations determined with the FTIR are technically defensible. Thus, the ORS systems are sufficiently refined to provide technically defensible **path-integrated or path-average concentrations**. These technically defensible data may consist of statements that the concentrations are below the MDL.

To determine the contribution due to the refinery, the technical defensibility depends on having sufficiently low MDLs and, thus, sufficient sensitivity to determine the difference between the upwind and downwind concentrations as discussed in the answer to the second question. While the individual upwind and downwind path-integrated concentrations may be technically defensible, if these path-integrated concentrations are similar to each other or both are below the MDL, it may not be possible to determine the refinery's contribution to the downwind concentration field outside the overall uncertainties of the measurements. When more sensitive instruments are available to provide lower detection limits and reduced uncertainties in the path-averaged concentrations, the separation of a refinery's contribution will be possible for refineries in complex settings.

To determine the refinery specific emission rates, the technical defensibility depends on the defensibility of the modeling, meteorological data and possible tracer data in addition to the path-average concentration and refinery specific contribution discussed above. In order to determine the emission rate, the upwind and downwind path-average concentrations or MDLs must be used to determine the refinery's contribution which then must be combined with either tracer gas release data or a dispersion model. Although there have been wind tunnel studies with models of refineries with different surface roughness, very litle field verification data similar to the ORS intercomparison studies exist to technically defend the modeling of turbulent transport conditions in a physically complex setting or the use of tracer gas releases for the determination of emission rates from such complex settings. Thus, it would be very useful to combine a dispersion model and tracer gas release evaluation program with an ORS field study/evaluation.

In summary, the state of the technology of ORS systems is sufficiently refined to provide technically defensible path-average concentrations which could be used for the calculation of emission rates. There is somewhat less certainty about determining the contribution due to the refinery at the fenceline or about the technical defensibility of the emission rates calculated from these path-average concentrations using dispersion models and/or tracer gas releases with meteorological data.

DESIGN CONSIDERATIONS

With refinements and incorporation of a broader understanding of the issues as discussed in this report, a field study can be designed that meets both of the objectives stated by API. The fact that a refinery has elevated releases and buoyant plumes in addition to near-surface releases requires consideration of what ORS observation path(s) are adequate and in what settings. Thus, the vertical and downwind placement of the ORS beams need to be considered along with the air dispersion modeling implications for interpreting the data. The physical and meteorological complexity of a refinery setting must be considered, not only in gathering an adequate data set during a field study, but also in using the appropriate models for interpreting the ORS and supporting measurements.

Section 1
INTRODUCTION

Under Title III of the Clean Air Act amendments of 1990, the U.S. Environmental Protection Agency (EPA) is required to promulgate Maximum Achievable Control Technology (MACT) regulations for emissions of hazardous air pollutants (air toxics) from various industrial sources including refineries. Once the control technology is in place, EPA must develop information on the residual risks associated with exposure to low-level air toxics downwind of major industrial sources. It is anticipated that the EPA will require industry to use actual emission measurements or emission estimates derived from emission factors and dispersion modeling to estimate the risks. Recent studies, however, have shown that EPA dispersion models may significantly overestimate ambient concentrations of low-level air toxics for areas less than one kilometer from the source (near field). In addition, at the time this study was initiated, EPA and several state agencies were considering requiring industry to use open-path optical remote sensing (ORS) technology to establish concentrations of low level air toxics downwind of industrial sources.

For these reasons, the American Petroleum Institute (API) considered conducting a comprehensive field study at a refinery to assess whether upwind and downwind ORS measurements, combined with ancillary measurements such as meteorological and tracer gas release data, could be used to calculate emission rates of air toxics from a refinery. A secondary objective was to develop better information on the near-field dispersion of air toxic emissions from refineries for the purposes of improving existing dispersion models.

Before embarking on a costly field study, API sponsored this study to provide answers to the following questions which arose concerning the feasibility of achieving the field study objectives:

1. Is the amount of information collected from other, recent studies of a similar nature sufficient to accomplish the objectives of the proposed field study thereby negating the necessity for the field study?

2. Will it be possible to separate a refinery's contribution from the background contribution for low-level concentrations measured along the fenceline and further downwind from a refinery?

3. Is the state of the technology of optical remote sensing (and required ancillary measurements) sufficiently refined to provide technically defensible data for the calculation of air toxics emission rates from a refinery complex located in either an isolated setting or in a complex industrial area?

API proposed using two versions of ORS technology, infrared (IR) and ultraviolet (UV) absorption, to measure the path-integrated or path-average concentrations of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes--also designated as BTEX) along the fenceline of a petroleum refinery. For comparative purposes, point sampling of aromatic hydrocarbons would also be conducted along the fenceline using wind-directional whole air canisters. Additionally, a non-toxic, non-reactive tracer gas (e.g., sulfur hexafluoride) would be released from a large source of emissions within the refinery and traced to and beyond the downwind fenceline using a tracer monitoring system. On-site meteorological data would be collected to calculate more accurately the emission rates from the refinery.

At this point it should be noted that there is an important distinction between measurements of concentration of air toxics along a fenceline and determinations of emission rates for the same air toxics from a facility. Concentrations of air toxics can be measured by a number of presently available point samplers/monitors at discrete points and by ORS systems along the path of the beam. Determination of emission rates requires knowledge of concentrations upwind of the facility and at the fenceline as well as dispersion information gained from ancillary data such as simultaneous meteorological measurements, simultaneous tracer gas release data and/or dispersion modeling. The problems and uncertainties related to determining emission rates using such ancillary data are similar whether concentrations are measured by point samplers/monitors or by open-path ORS systems. Hence, emission rate determinations are more complicated than concentration measurements.

The primary focus of the proposed field study was directed at BTEX compounds, with special focus on benzene. The monitoring of other air toxics was also of interest. Since ORS systems can monitor multiple species simultaneously, there is the possibility that the concentrations of benzene as well as other gases might be measured using a single measurement system. Thus, attention was given to the experienced minimum detection limits (MDLs) for the refinery emissions of interest but with an emphasis on the BTEX compounds.

This report presents a review of previously conducted ORS field studies and a review of traditional methods of determining emissions rates. The feasibility of the proposed field study is presented along with design considerations for conducting such a study. Technical advancements are occurring rapidly in ORS technology; thus, it must be kept in mind that the perspective of the present report is limited to the general state of the technology at the end of 1992.

This feasibility study was conducted by a technical team organized by **R**emote **S**ensing≡**A**ir, Inc. (**RS≡A**). The team was managed and coordinated by **RS≡A** with Dr. William M. Vaughan as Project Manager. Formal input came from the University of Denver group under Dr. Donald H. Stedman, the Kansas State University group under Dr. William G. Fateley, MDA Scientific, Inc., and Ogden Environmental and Energy Services, Inc. Informal input was received from Dr. Peter T. Woods of the National Physical Laboratory in the United Kingdom and Dr. Konradin Weber, formerly of the VDI (Din Deutsches Institut für Normung e.v. Verein Deutscher Ingenieure) in Germany (See Figure 1-1).

The team examined existing ORS studies of emissions at petroleum refineries and petrochemical plants. Non-petroleum industry ORS monitoring programs conducted at facilities where BTEX compounds were measured and emission calculations carried out were also reviewed.

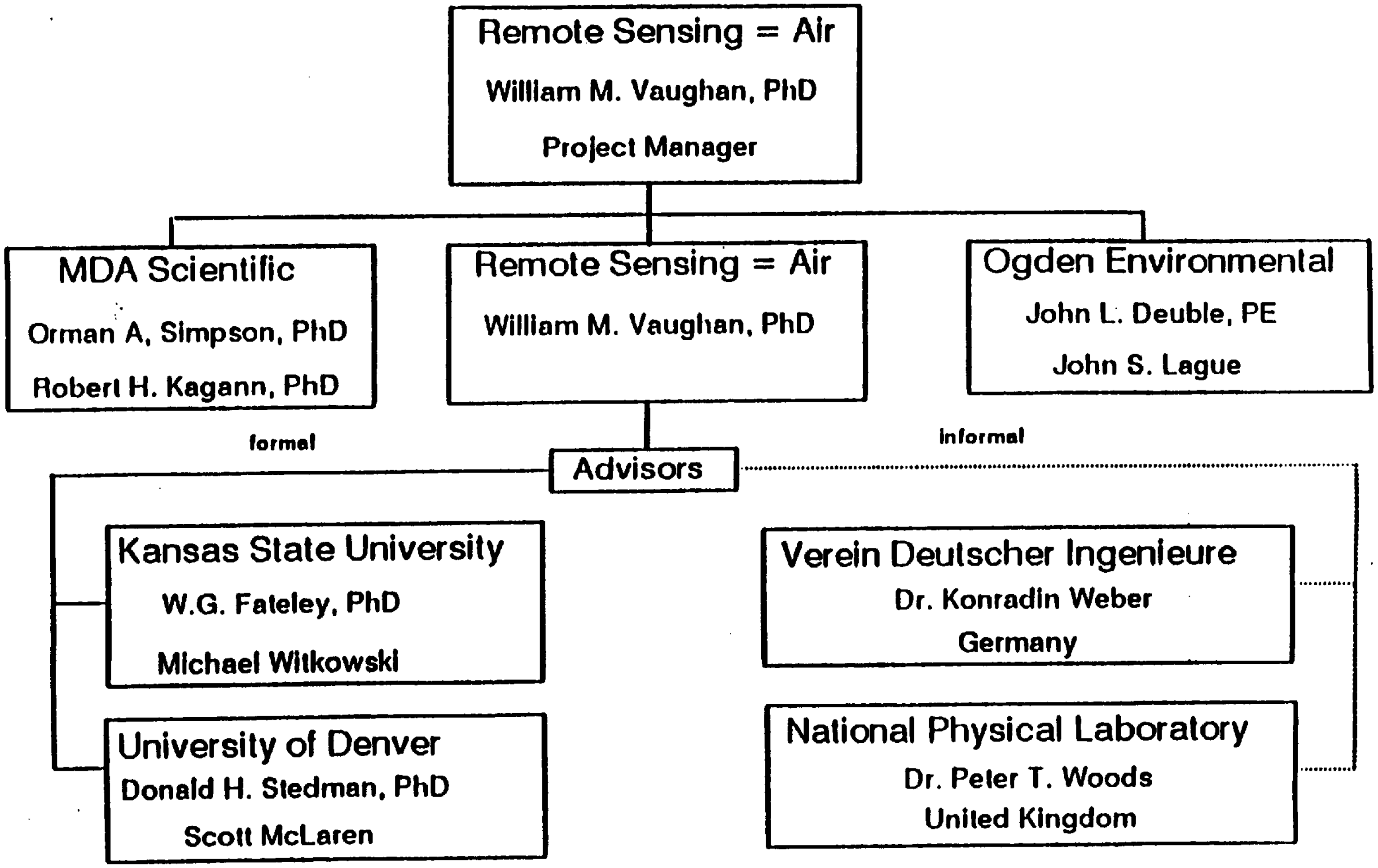

Figure 1-1. Project Organization Chart.

Traditional emissions estimates were reviewed also to provide insights on process areas where ORS techniques might be tested. These traditional methods of determining fugitive emissions include (1) using EPA's stationary source emission factors (AP-42) for specific operations; (2) making an inventory of any leaking equipment components such as valves, fittings, or seals using EPA Method 21 and applying emission factors to those components; and (3) releasing tracer gases at known flow rates while conducting grab and time-averaged sampling of both tracer gas and chemical compounds to establish approximate emission rates of chemical compounds by ratio techniques.

The project team provided design and research recommendations to enhance the proposed field study. Appendix A is a glossary of the acronyms and terminology used throughout this report. Appendix B is a copy of "Remote Sensing Terminology" (Vaughan, 1991) that will assist the reader in understanding specific remote sensing terminology.

Section 2

STATE-OF-TECHNOLOGY OF OPTICAL REMOTE SENSING

The several optical remote sensing (ORS) systems used in the studies discussed in this report are summarized below. There is no attempt to discuss in detail the theory behind ORS systems as this is provided in several recent review articles (Grant, *et al.*, 1992; Skippon, 1992b; Weber, 1992). Each of these ORS systems determines the total molecular content per unit of beam area and the results are generally reported as the product of concentration times the path length for a beam of electromagnetic radiation (UV or IR) between a source and a detector.

The **Fourier Transform Infrared** (FTIR) systems discussed in this study are open-path systems. Extractive instruments are also referred to as FTIR since they use the same basic instrumentation and principles for analysis of the spectra. The FTIR uses an IR source, an interferometer, and a detector to produce an interferogram for a range of wavelengths. The interferogram is transformed into an absorption spectrum using computer algorithms, and the resulting spectrum is compared to the library of available spectra to provide path-integrated concentration data. At present there are about 130 compounds available in the spectral libraries of the commercially available systems. The system is capable of determining unknown compounds and compensating for known interferences. There are several open-path systems in use which are sometimes termed long-path IR (LPIR) or open-path FTIR (OP-FTIR). FTIR open-path systems have been used at refinery and petrochemical sites as well as industrial, urban and Superfund sites in the United States. The Kansas Intercomparison study (Carter *et al.*, 1992) indicated that the two commercial instruments and one research instrument studied were comparable; thus, the study does not refer to the manufacturers of the open-path FTIR systems. FTIR will be used as the general term for the open-path technique.

The **Differential Absorption Lidar** (DIAL) system manufactured by the National Physical Laboratory of the United Kingdom (NPL) was used in the studies reviewed. A DIAL instrument uses a pulsed laser whose selected wavelengths (IR, visible or UV) are backscattered by the atmosphere and collected by the detector (IR, visible or UV). One wavelength is selected from a region of the spectrum which is expected to absorb radiation due to the compound being measured while the other is selected from a region where no absorption is expected from the compound of interest or interfering compounds. The laser is tuned to evaluate one pair of wavelengths at a time and, thus, can determine the concentration of only one compound or class of compounds (e.g., total hydrocarbons using the C-H stretch spectral region) at a time. If, in addition to the specific wavelength radiation, a short duration pulse is transmitted, the backscattered radiation can be measured as a function of time to provide the range resolved profile of a plume directly. This system has been used in refinery settings in Europe in both its IR and UV modes as well as in Superfund studies in the United States.

The **Differential Optical Absorption Spectrometer** (DOAS) manufactured by Opsis in Sweden, uses broad band visible and ultraviolet (UV) light, usually from a high pressure lamp housed at one end of the path. The spectral pattern received at the detector at the other end of the path is compared with stored spectra of a gas-specific spectral band. At present there are about 30 compounds available in the spectral library. The spectra obtained are compared to library spectra for determining the path-averaged concentrations. Path lengths for this system range from 1 meter to 2,000 meters. This system has been used in studies at refinery settings in Europe and the United States as well as other industrial and urban settings.

The **long path UV** (LPUV) refers to the system from the University of Denver which is more properly known as an open-path UV (OPUV) to indicate that the path is open to the free flow of air rather than an enclosed cell in which the beam is folded by multiple reflections to achieve a long path measurement. OPUV systems use a high pressure lamp but incorporate the lamp into the main instrument to transmit a beam of UV light along the measurement path to a retroreflector. The resulting beam is projected onto an array of photodetectors (or diodes) so that a spectrum is built up from many individual detectors, each representing a small wavelength window. Like the other UV systems, the OPUV system can detect some compounds that FTIR cannot, as well as detect some compounds with greater sensitivity;

however, its spectral library is not nearly so large as that of the FTIR. To date, path lengths have ranged up to 500 meters. This system has been used in refinery and Superfund sites in the United States but is not commercially available at the time of this writing.

This report focuses on the feasibility of using ORS systems to provide accurate data on refinery air toxics concentrations at the fenceline with emphasis on the use of the ORS data in the calculation of emission rates. To determine emission rates, the path-averaged concentration data supplied by the ORS system needs to be coordinated with meteorological data as well as dispersion modeling and/or tracer gas releases at known rates. This section presents a summary of ORS measurement experience as of the end of 1992 along with the issues and tradeoffs for improving detection limits and the representativeness of ORS measurements.

SUMMARY OF ORS MEASUREMENT EXPERIENCE

A number of studies that have used ORS systems were reviewed in depth to prepare this report and are summarized below. A detailed presentation can be found in Appendix C.

Since the late 1980s, a number of studies using ORS systems to determine petroleum-related compound emissions have been conducted at refinery and petrochemical facilities as well as at other sites both in Europe and the United States. A summary of the ORS systems used at refineries or petrochemical facilities is presented in Table 2-1. The two most ambitious studies were performed in the Hisingen district of Sweden in 1988 and 1989 (Indic, 1988; Woods, 1992a). The results of these studies are available only as un-reviewed reports and do not clearly state minimum detection limits (MDLs) or comparisons between the conventional and ORS methods for determining the concentration of the same compounds. The goal of each study was to determine the hydrocarbon emission rates.

Table 2-1. ORS Systems Used in Studies in Refinery or Petrochemical Settings

STUDY	DATE OF STUDY	ORS SYSTEM(S)	EMISSIONS CALCULATIONS
Hisingen (Indic, 1988)	1988	DOAS	Yes
Gothenburg (Woods, 1992a)	1988, 1989	IR-DIAL	Yes
Wastewater Impoundments (Indaco,Inc.,1990)	1989	FTIR and OPUV	Yes
Land Farm (Lupo, *et al.*, 1991)	1991	FTIR and OPUV	No
Tank Truck Loading Area (Milton, *et al.*, 1992)	1991	UV-DIAL	No
Exxon Chemical Americas (Spellicy, *et al.*, 1992)	1991	FTIR and DOAS	No
Shell Deer Park (Thomas, *et al.*, 1992)	1992	FTIR	No

Indic and Opsis (Indic, 1988) attempted to determine emission rates of hydrocarbons from both the Shell and British Petroleum (BP) refineries using the DOAS system and various methods of calculating the emissions rates, but were successful in calculating emission rates for only toluene (using DOAS data) and p-xylene (using conventional sorbent tube concentration data) at the Shell refinery. Indic's limited 1988 efforts do not seem to have been duplicated in more recent published reports although Indic has indicated plans for the implementation of an upgraded approach for a new refinery in Chile (Gidhagen, 1992a). The NPL study at the BP refinery (Woods, 1992a) was successful in determining plume profiles as well as non-methane hydrocarbon and toluene emission rates from discrete process areas at the refinery using the IR-DIAL. The system had problems measuring toluene (used as a surrogate to determine aromatics). Later refinery studies with this instrument are not reported; however, a 1991 study (Milton, *et al.*, 1992) indicates that the UV-DIAL system is preferable to the IR-DIAL for determining toluene concentrations. The 1991 study presents measurements of toluene concentration profiles using a UV-DIAL system and calculation of the total flux by combining the concentration data with simultaneous wind speed data.

To date, the most ambitious U.S. study of refinery-related emissions using ORS systems reported was conducted by the University of Denver and Indaco. BTEX emission rates from a refinery's wastewater impoundment were determined (Indaco, Inc. 1990; McLaren and Stedman, 1990). This study was more complete than the NPL (Woods, 1992a) and Indic (Indic, 1988) studies in that tracer releases were used to simulate emissions and provide a methodological cross-check. In addition, Indaco and the University of Denver were able to evaluate the performance of the EPA CHEMDAT7 air emissions model against these field data. The study indicated that the OPUV system can measure concentrations of benezene at low levels which are comparable to SUMMA® canister results and that the variations in the OPUV signals could be correlated with site sources. The report also suggests that more work is needed to improve air emission models for use in refinery settings.

A study at a land farm to monitor concentrations of BTEX and hexane using OPUV, FTIR and conventional sorbent tube sampling (Lupo, *et al.*, 1991) suggested two advantages of the ORS systems over the conventional sampling. These advantages were the ability of the ORS samplers to determine temporal variations in the concentrations which could be linked to site activities and the fact that the ORS data were less costly and less labor intensive to gather.

The study at Exxon Chemical Americas (Radian, 1991b; Spellicy, *et al.*, 1992) demonstrated that the DOAS and FTIR systems could operate in a stand-alone mode for extended periods and that correlations could be made between temporal variations in the measured concentrations and meteorological and plant conditions. As expected, the reported MDL for benzene with the DOAS was lower (0.76 ppm-m) than that reported for the FTIR (12.5-15 ppm-m).

The Shell Deer Park study (Thomas, *et al.*, 1992) again demonstrated the ability of the FTIR to determine concentrations of compounds of interest and the ability to correlate temporal variations with plant operations. It also confirmed the difficulty of using the FTIR to determine benzene at very low concentrations.

Several emission rate studies using ORS have been performed at Superfund sites for surface emission releases where conditions are simpler than at refineries or petrochemical plants, making evaluation less complicated. Usually these emission rate estimates have been determined using simultaneous tracer releases with known emission rates so they are related to empirical values rather than engineering estimates (Kricks, *et al.*, 1991; Scotto, *et al.*, 1992).

In discussing the ORS programs in Appendix C, some of the individual system limitations are presented such as stability of alignment, the inability to identify unknown compounds with the UV systems, the limited frequencies for the older DIAL systems, and the difficulty in attaining sufficiently low MDLs for benzene. Most of these "limitations" are related to the earlier stages of rapidly developing technologies. Some, such as attaining sufficiently low MDLs, are less an issue than they were 3 to 4 years ago due to recent improvements in system equipment design and processing software. For FTIR systems the ever-present issue of water vapor interference is being addressed by new measurement and data processing procedures.

In summary, most, if not all, of the measurement components required for determination of emissions rates from a refinery or process area have been conducted at one or more locations. Many recognized problems have been addressed to some extent, but not necessarily solved. Yet, no studies reported, to date, adequately answer the question, "Has the state-of-technology of ORS advanced far enough to provide technically defensible data of incremental air toxic emissions from an isolated or chemically complex refinery setting?" These studies, however, have raised several issues that would need to be addressed in planning a definitive refinery field study.

ISSUES AND TRADEOFFS

In considering the implementation of an emissions measurement program using ORS techniques with possible combinations of meteorological and tracer gas measurements and modeling, one must acknowledge that each site is different both physically and meteorologically. Specific measurement needs, such as configurations of light beams, timing of measurements and the presence of possible interfering compounds, may not be ascertainable until the site itself is known and observed. Some of the technical issues that are part of the planning and evaluation of an overall measurement strategy include: detection limits, light beam placement, dispersion modeling, tracer gas release, time intervals for measurements, and meteorological measurements.

Detection Limits

Detection limits for ORS systems are dependent on the type of compound being identified, the system to be used, the path length, and conditions that affect the signal-to-noise ratio such as the number of spectra coadded, the stability of the placement of the system, and the type of electrical generator being used. The lowest realistic MDLs are preferred for determining risks of exposure and for tracking of control emissions. The most desirable detection limit for a compound like benzene would be one near its "one-in-a-million" 70-year cancer risk level, ≈0.035 ppb [this concentration was calculated, assuming standard temperature and pressure, from the value of 0.12 $\mu g/m^3$ reported in the IRIS Database which cited a 1985 Interim Quantitation from the Office of Health and Environmental Affairs (USEPA, 1985).] Measurements with such a low detection limit would support the validity of exposure assessments. However, at present no air monitoring system is able to meet these limits. Thus, assumptions must be made regarding whether the levels should be conservatively estimated at or below the actual detection limits. Of course, if an exposure assessment is based on a detection limit which is well above the actual level at which the compound is present, unnecessarily large projected exposures and risks will be predicted. Further complications arise when trying to show that combined cancer risks for all species of toxics are below the "one-in-a-million" level. Unless one species really dominates, actual MDLs must be even lower than the "one-in-a-million" risk level to preclude overpredicting exposures based on poor MDLs. Progress in emissions control cannot be tracked by an analytical method if levels determined before controls were imposed were already below the detection limits of the systems. Therefore, it is important to attempt to attain the lowest detection limits possible but also to realize the real limitations of the present technology when setting requirements for detection limits.

Both laboratory-determined and field-determined detection limits for the BTEX compounds are presented in Tables 2-2a (as path-averaged concentrations in ppb units) and 2-2b (as path-integrated concentrations in ppm-m units) for the ORS systems described in this report. As can be seen, in most cases, the UV systems (OPUV, DOAS and UV-DIAL) have the lowest detection limits for these compounds. The FTIR limits are 2 to 100 times higher than the UV values. However, even the FTIR detection limits are well below the NIOSH and OSHA time weighted average (TWA) exposure limits of 100 ppm (100,000 ppb) for toluene, ethylbenzene and the xylenes and the OSHA 1 ppm (1,000 ppb) for benzene (NIOSH, 1990). The NIOSH TWA for benzene is 0.1 ppm (100 ppb) which is below some of the FTIR MDLs.

In the following paragraphs, some of the factors that affect the MDLs obtained with a specific system at a specific site are discussed. These factors include the absorbance bands used to determine the specific compounds of interest, the type of detector, the strength of the source, the size and focus of the optics, the time interval of the data collection, the meteorology, the path length, and the background/upwind spectra corrections.

Absorbance Bands. The ORS systems discussed in this report use light sources and detectors that operate in either the UV or IR regions of the electromagnetic radiation spectrum. Because aromatic compounds, which are the focus of this report, absorb most strongly in the UV region, their MDLs are lower for the UV systems than for the FTIR systems. It has been noted (Milton, *et al.*, 1992; Axelsson, *et al.*, 1991) that atmospheric oxygen and ozone absorb in the same uv regions as the aromatics in much the same way as water and carbon dioxide absorb in the infrared regions. However, careful background correction can be used to reduce their interference and allow the MDLs shown in Tables 2-2a and 2-2b even under field conditions.

Table 2-2a. Summary of BTEX Path-Averaged Detection Limits for ORS Systems

ORS Method (Path length, m)	Path-average Concentrations (ppb)				Source/ Reference
	Benzene	Toluene	Ethylbenzene	Xylenes	
FTIR (200)[a]	310	690	600	310, 640, 400	Kagann, 1992a
FTIR (200)[b]	34	34	34	1.5, 2.7, 1.4	Kagann, 1992b
FTIR (500)[c]	25-30	50	NR	20	Spellicy, *et al.*, 1992
FTIR (400)[d]	NR	~100	NR	NR	Carter, *et al.*, 1992
FTIR (300)[e]	177	291	54	49	Scotto, *et al.*, 1992
FTIR (200)[f]	10	30	NR	30	Thomas, *et al.*, 1992
OPUV (200)[g]	NR	NR	NR	<30	McLaren, *et al.*,1992
OPUV (102)[h]	29	29	196	20-294	Indaco, Inc., 1990
DOAS (500)[i]	1.6	1.6	NR	1.6	Spellicy, *et al.*, 1992
DOAS (600)[j]	2.9	2.4	NR	NR	Lofgren & Ramnas, 1991
DOAS (1000+)[k]	<2.1	<3.4	NR	<0.9	Stevens and Vossler, 1991
DOAS (2000+)[k]	<2.4	<4.9	NR	<1.1	Stevens and Vossler, 1991
UV-DIAL (unknown)[j]	NR	10	NR	NR	Milton, *et al.*, 1992
UV-DIAL (500)[j]	1.5	2-20	NR	1-10	Woods, 1992b

NR No MDL reported for this compound.

Note: FTIR path lengths are twice the distance from the instrument to the retroreflector.

a Determined by R. Kagann using the "visual estimation method"; xylenes are listed as meta, ortho, and para.
b Optimized detection limits achieved with careful data acquisition and manipulation; xylene are listed as meta, ortho and para.
c Using 0.5 cm^{-1} resolution. Xylene is the meta isomer. MDL determined from spectra and long term time series plots.
d Estimated from the fact that the FTIR systems could not detect the 30 ppb test but some could detect the 100 ppb test.
e Average of daily MDLs calculated by Scotto; the ppm-m values have been converted to ppb using twice the background path length of 150 m, The MDLs were determined as twice the observed noise in the spectral region.
f Using 20 inch optics. No method of MDL determination stated.
g Based on the ability of the OPUV to determine the ~30 ppb release with good correlation with the conventional method.
h Determined by adding the spectrum of each BTEX compound to the measured spectrum until peaks were observed above the noise. This concentration for each was termed the detection limit.
i Detections observed and limits from time series plots are consistent with Opsis MDLs.
j Method of MDL determination not stated.
k Actual concentration determined in $\mu g/m^3$; MDL assumed to be less than these values and calculated as ppb from $\mu g/m^3$ MDLs assuming standard temperature and pressure during the measurement.

Table 2-2b. Summary of BTEX Path-Integrated Detection Limits for ORS Systems

ORS Method (Path length, m)	Path-integrated Concentrations (ppm-m)				Source/ Reference
	Benzene	Toluene	Ethylbenzene	Xylenes	
FTIR (200)[a]	62	138	120	62, 128, 80	Kagann, 1992a
FTIR (200)[b]	6.8	6.8	6.8	0.30,0.52,0.28	Kagann, 1992b
FTIR (500)[c]	12.5-15	25	NR	10	Spellicy, *et al.*, 1992
FTIR (400)[d]	NR	~40	NR	NR	Carter, *et al.*, 1992
FTIR (300)[e]	53	87	16	15	Scotto, *et al.*, 1992
FTIR (200)[f]	2	6	NR	6	Thomas, *et al.*, 1992
OPUV (200)[g]	NR	NR	NR	<6	McLaren, *et al.*,1992
OPUV (102)[h]	3	3	20	2-30	Indaco, Inc., 1990
DOAS (500)[i]	0.8	0.8	NR	0.8	Spellicy, *et al.*, 1992
DOAS (600)[j]	1.7	1.4	NR	NR	Lofgren & Ramnas, 1991
DOAS (1000+)[k]	<2.1	<3.4	NR	<0.9	Stevens and Vossler, 1991
DOAS (2000+)[k]	<4.8	<9.8	NR	<2.2	Stevens and Vossler, 1991
UV-DIAL (unknown)[j]	NR	unk	NR	NR	Milton, *et al.*, 1992
UV-DIAL (500)[j]	0.75	1-10	NR	0.5-5	Woods, 1992b

NR No MDL reported for this compound.

a Determined by R. Kagann using the "visual estimation method"; xylenes are listed as meta, ortho, and para.
b Optimized detection limits achieved with careful data acquisition and manipulation; xylene are listed as meta, ortho and para.
c Using 0.5 cm^{-1} resolution. Xylene is the meta isomer. MDL determined from spectra and long term time series plots.
d Estimated from the fact that the FTIR systems could not detect the 30 ppb test but some could detect the 100 ppb test.
e Average of daily MDLs calculated by Scotto. The MDLs were determined as twice the observed noise in the spectral region.
f Using 20 inch optics. No method of MDL determination stated.
g Based on the ability of the OPUV to determine the ~30 ppb release with good correlation with the conventional method.
h Determined by adding the spectrum of each BTEX compound to the measured spectrum until peaks were observed above the noise. This concentration for each was termed the detection limit.
i Detections observed and limits from time series plots are consistent with Opsis MDLs.
j Method of MDL determination not stated.
k Actual concentration determined in $\mu g/m^3$; MDL assumed to be less than these values and calculated as ppm-m from $\mu g/m^3$ MDLs using the path length and assuming standard temperature and pressure during the measurement.

Chlorinated and fluorinated hydrocarbons exhibit strong infrared absorption bands in the 1400 to 650 cm^{-1} (wavenumber) region of the mid-infrared spectrum. Because of this strong infrared absorption, the ORS detection limits for these types of compounds using FTIR systems are low (≈5 to 20 ppb average concentration along a total beam of 100 m). While aromatic hydrocarbons like benzene and toluene are strong infrared absorbers, their strongest absorbance bands occur in the regions of the mid-infrared which include interferences from ubiquitous carbon dioxide and water vapor. The available alternative for obtaining lower MDLs for aromatic compounds using FTIR systems is to use the weaker absorbance bands for these compounds which are affected less by the carbon dioxide and water vapor bands. For example, the strongest absorption band for benzene is at 671 cm^{-1} (in the same region where carbon dioxide and water vapor absorb); however, benzene also has a much weaker band at 1038 cm^{-1} (≈ 1/50th the absorbance of that at 671 cm^{-1}) in a region relatively free of the interferences. If one could use the more intense 671 cm^{-1} region, an MDL of about 1 ppb over a 100 m path could be achieved for benzene; however, carbon dioxide will absorb nearly all the energy at 671 cm^{-1} leaving no signal for benzene to absorb. For the 1038 cm^{-1} region that is used to avoid the carbon dioxide interferences, the MDL is a couple orders of magnitude higher (or ≈310 ppb over 100 m for commercial units). If the analytical software can compensate for water vapor interferences in this region this MDL can be moved downward to about 70 to 100 ppb over 100 m and, with careful manual subtraction, an MDL of 34 ppb over 100 m has been obtained.

Detectors. There is the possibility that the FTIR MDL for benzene might be lowered if the detector were modified. The common commercial detector is a mercury cadmium telluride (MCT) crystal that can be "customized" (by altering the ratio of M, C and T) for different spectral ranges - wide, medium and narrow. Since the narrow band detector has somewhat greater response in the 900 to 1100 cm^{-1} region than the wide band detector, it might be more useful for detecting benzene. However, with its sharp cutoff at 800 cm^{-1}, the strong absorption bands for chlorinated compounds, such as 1,1,1-trichloroethane at 725 cm^{-1}, would not be available. Similarly one would lose the ability to observe the sharp 730 to 800 cm^{-1} bands of the xylene isomers. These tradeoffs might not be acceptable if the facility being studied had the probability of emitting these species or if a more versatile ORS system were needed.

Time Interval of Sampling. For ORS systems for which detection limits can be affected by the data collection time, the more spectra that are gathered and processed, the better the detection limit. The signal-to-noise ratio of a single-beam spectrum improves as the square root of the number of spectral scans that are co-added to produce the final spectrum. However, there is loss in time resolution as these extra spectral scans are accumulated. If there is a fairly uniform release rate of vapors and steady meteorological conditions, as opposed to rapid and unpredictable emission swings from a process or unstable meteorological conditions, the poorer temporal resolution would be acceptable in light of improved MDLs. The time required for collection of spectra with a high spectral resolution IR instrument with 0.1 to 0.5 cm^{-1} resolution, compared to one with 1 to 2 cm^{-1} resolution, is appreciably longer and time resolution is further compromised. More detailed spectra to assist in the identification and quantification of some species is obtained but at the loss of time resolution.

Path Length. Because ORS systems are path-integrating devices, a longer path length offers the possibility that more molecules of interest can be encompassed in the light beam, thus giving a stronger signal and lowering the apparent MDL for path-averaged concentration. Theoretical MDLs are based on laboratory determinations of the absorbance of a compound in a given spectral region using a closed cell with a uniform gas distribution. This presents two problems. First, if the plume of interest is narrow and already enclosed in the shorter distance, lengthening the observing path will not bring in more molecules of interest and the change in theoretical MDL will not make any difference. Second, the longer paths may cause the loss of light beam intensity due to divergence of the light beam, scattering losses in the atmosphere, or the chance that mechanical vibrations will disrupt optimal alignment. Uni-static ORS systems with retroreflectors effectively double their path length and achieve a lower MDL compared to a bi-static system with a light source at one end and the detector at the other end of the path (see Appendix A). Doubling the path in this way (i.e., by reflection) does not result in adding more path which might not contain molecules of interest. The range of path-lengths used, to date, for the BTEX compounds seems to be up to 3,600 meters (single path) (Stevens and Vossler, 1991) for the Opsis DOAS and 2,000+ meters (total folded path) at one FTIR installation. Optimum path length ultimately involves consideration of source strength and optics of the ORS unit, the ability to capture a sufficient amount of the diverging light beam for detection, the dimensions and uniformity of the emissions plume being monitored and the facility dimensions and spatial array.

Background/Upwind Correction. To achieve facility-specific emission information, the ideal method would involve simultaneous measurements with a second similar ORS system on the upwind side of a facility. Then the analysis would involve computer ratioing of the simultaneous upwind spectra against the downwind spectra. Such ratioing might help compensate for the changing interference levels from non-facility sources during the course of measurements. Since the use of two systems doubles the cost, the next best alternative is to determine upwind concentrations frequently by relocating one unit for short time periods to compensate for meteorological changes and interferences from nearby sources. For long-term monitoring, two systems may be more cost effective than the labor costs related to moving and realigning the system to obtain intermediate upwind readings.

Light Beam Placement

The actual path along which the light beam travels is important for data interpretation. Consideration of light beam height, distance downwind, and whether multi-height (e.g., DIAL or Special Plane-integration arrangement) scanning will occur depends on many factors. These factors include the site geometry, site activities, nature of the sources (hot or ambient, natural or forced draft, etc.) and the dispersion and emission models that might be used to interpret the data gathered.

Most of the above discussions have dealt with uni-static and bi-static IR and UV systems, and most U.S. familiarity is with non-DIAL ORS systems. Hence, the basic assumption in most applications is that the ORS light beam will be horizontal. This assumption is valid if low altitude or surface releases are being monitored, such as at Superfund sites, lagoons, or land farms. The object of any measurement is to capture a typical and representative portion of the emissions of interest in the light beam. This goal can usually be achieved for these simpler sources with a horizontal light beam placed a few meters above the ground surface. Emissions from elevated sources or sources from a variety of elevations cannot be monitored with such a simple installation unless meteorologically well-mixed conditions exist.

Site-specific questions must be answered in considering light beam placement. How high do measurements have to be made to capture a representative portion of the plume? Will an important heated plume loft over a chosen light beam height? Will some emissions pass under the light beam if the instrument path is placed too high? Where might atmospheric turbulence bring the facility's plume to the ground? Are there nearby facilities whose emissions might be contributing to the measured concentrations? These questions regarding light beam placement will be addressed below.

Light Beam Height. Refinery emissions can enter the atmosphere from thousands of points and at a number of heights ranging up to 70 meters and more above the ground. The list of sources includes stacks, flares, storage and process tanks, as well as leaking valves, flanges, and seals. For low sources, a light beam height of a couple of meters would be sufficient unless nearby cooling fans loft surface emissions to levels above 50 m. During DIAL measurements at a Swedish refinery, it was observed that one mechanically lofted plume was returned to the surface some 300 m downwind during a refinery study (Woods, 1992b). For storage tanks, light beam heights near the tank top of ≈20 m might be preferable to capture that plume if it is necessary to monitor close to the tanks.

It seems clear that fenceline concentrations at multiple heights would be needed to have any chance of characterizing plant-wide emissions of these air toxics. Yet there has been little, if any, information published on light beam height considerations. There is one evaluation of light beam height being planned by Kansas State University. Controlled solvent releases, similar to those used for EPA Region VII's 1991 Kansas Inter-comparison Study (Carter, *et* *al.*, 1992) will be used. Up to three simultaneous FTIR beams will operate at different heights. The usual Gaussian dispersion models will then be used to predict initial light beam placement and then to evaluate the representativeness of plume capture at each height to see how consistently those light beams can be used to determine the releases.

The University of Denver (Indaco, Inc., 1990; McLaren and Stedman, 1990) made measurements at a single light beam height during a surface impoundment study for the API. The focus of these measurements was to compare emission flux estimates using tracer gas (SF_6) releases with simultaneous determinations of BTEX and SF_6 concentrations downwind of the source with the CHEMDAT7 receptor model. The BTEX and SF_6 concentrations were determined by SUMMA® canister point samples as well as ORS path-averaged concentrations of BTEX using the OPUV and of SF_6 using the FTIR. The results indicated that the emission rates calculated using the tracer data from both point sampling and ORS compared well with each other while the CHEMDAT7 model overpredicted the emissions by a factor of three to seventeen. It is possible that the use of one light beam height (the same as the canister height) may have biased the tracer study data if the tracer and hydrocarbon plume were not well mixed.

The use of an "optical fence" to carry out a plane-integrated calculation of total plume flux has been suggested by Minnich, *et al.* (Minnich, 1992). A modified version of this approach was used by Whitcraft and Wood (Whitcraft and Wood, 1990) in field measurements downwind of a lagoon where methanol and methylene chloride were measured (see Figure 2-1).

While the concept of an optical fence is at first simple and attractive, the engineering and design for a stable enough pair of towers or a manageable zig-zag beam array could add considerable expense. Use of inexpensive, rental hoists or scissor-lift equipment may allow a short term program to evaluate the feasibility of this concept.

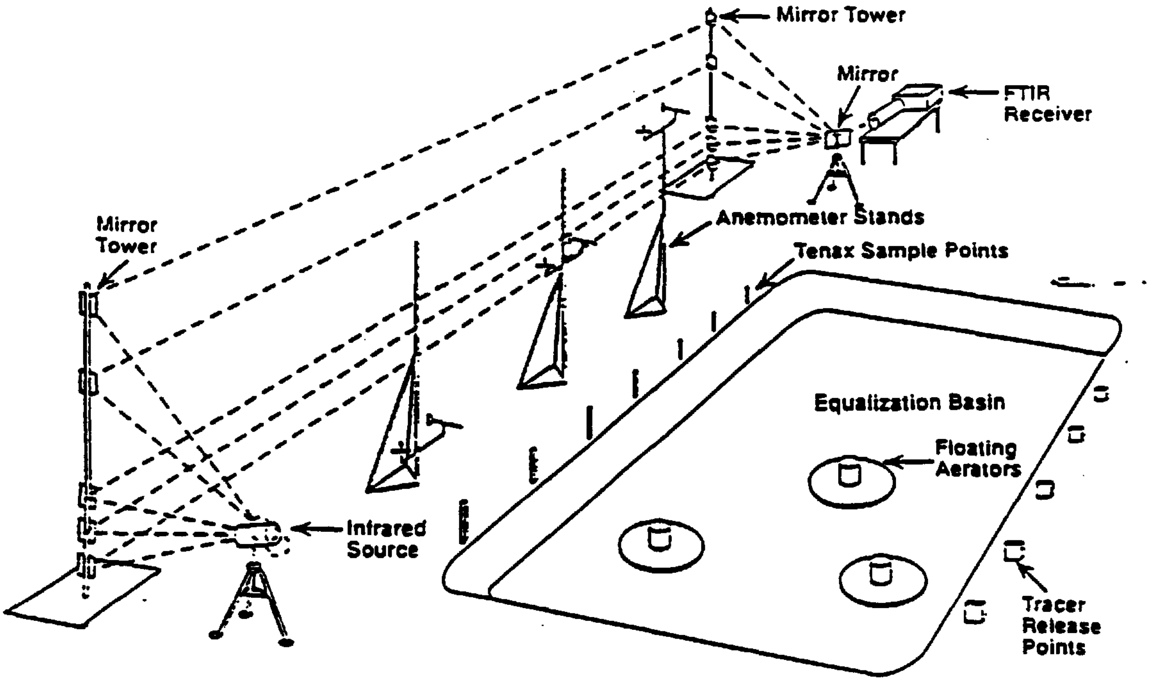

Figure 2-1. Arrangement of Equipment for Optical Fence Measurements

Light Beam Downwind Distance. The horizontal spread of a plume is an initial consideration for downwind placement of ORS systems. One can use the simple Gaussian dispersion equation with some site specific (or tabular) values of the vertical dispersion coefficient, σ_z, to calculate plume capture with various combinations of path-length, beam height and downwind location of the beam. Basically, the length of the light beam should be adequate to encompass the projected plume width with sufficient allowance for shifting wind directions and plume meandering. Obviously, light beams completely encompassing a facility or process unit would be needed to accommodate all wind directions--an impractical consideration at this time unless the risk from a given emission warranted the expense of documenting its release.

The further downwind the beam is located to capture the plume, the more both the positive and negative effects of longer path length on detection limits, has to be considered. However, the further downwind a measurement is made, the better the chance there is that higher altitude plumes from a refinery would be mixed to the ground for a low light beam to monitor it. There is, of course, the tradeoff that, unless the refinery is geographically-isolated, the chances increase that other sources will have an impact on measurements made further downwind from the refinery. There is also the possibility that the ideal downwind site for a particular plant is inaccessible.

P.T. Woods of NPL (Woods, 1992b), whose DIAL system can monitor the vertical distribution of the plumes, prefers an empirical approach to selecting his downwind distances. He combines preliminary surveillance measurements with interviews with plant operators before selecting his final downwind scanning locations. Site-specific and time-specific meteorological conditions need to be considered for downwind placement.

Vertical Scanning DIAL. DIAL systems can achieve plume capture and monitor the vertical distribution of a plume. While identification of unknown chemical species present in a given emissions plume is currently not available from DIAL systems, the information on vertical plume distribution that is available is often a valuable tradeoff. The species information aloft is approximated from ratios of vapors found in grab samples in the "surface plume" to those species that are identified aloft. However, the accuracy achievable with this process is not reported in the reviewed literature and is subject to differences in vapor densities, reactivities, and adsorption for the species determined at the "surface plume" and aloft.

Dispersion Modeling

No matter which technique is used to measure fenceline concentrations (conventional or ORS), some form of air quality dispersion modeling will be needed to link emission transport conditions as well as time-varying processes and releases to estimates of community exposure. Dispersion models or simultaneous tracer gas releases at known rates are needed to convert conventional or ORS concentration measurements to estimates of emission rates from a process unit or facility. Because of the topological and operational complexity of refineries and petrochemical facilities, the choice of an appropriate model is not straightforward. The following discussion is not intended to present a detailed discussion of dispersion modeling which would require at least a book to cover (for example, Seinfeld, 1986 or Zannetti, 1990).

The discussion presents some data, problems and questions related to choosing the appropriate model to use with concentration measurements that might be made at a complex refinery.

In Phase I of a study conducted for API and the Chemical Manufacturers Association (CMA) (Ogden Environmental and Energy Services Co., Inc. (1992b), candidate area source and volume source dispersion models were evaluated for their "physical reasonableness (in representing) relevant physical processes," primarily fugitive emissions. These models were evaluated because the many possible sources of hydrocarbon fugitive emissions at refinery and chemical facilities (e.g., valves, flanges, pump seals, roof vents, and building windows) are not readily represented by single or multiple point source algorithms. Table 2-3, from the report provides an overview of the sources considered for the review and the potential representation of each. It is evident from this summary that non-point source models are important for describing typical refinery emissions. In the Phase I portion of the study, groups of models were compared by the general trends in their output data. Two area source models, Point Area Line-Source (PAL) and Fugitive Dust Model (FDM), emerged as being the most reasonable in the trends and patterns of their predictions. PAL has been used frequently to estimate emission strengths as well as fenceline and downwind impact using ORS measurements at Superfund cleanup sites (Kricks, *et al.*, 1991; Scotto, *et al.*, 1991); however, Superfund sites are relatively simple area sources with mostly ground-level releases having relatively few complicating issues.

Phase II of the API/CMA study (Ogden Environmental and Energy Services, 1992c) evaluated model performance versus limited tracer study results at various locations including several refinery units. Overall, the results were encouraging in terms of agreement between predicted and measured concentrations, at least for the simple area sources such as waste treatment ponds. Except for short distances downwind, there was surprisingly little difference in the performance of the various models.

Certainly, a refinery facility is a complex combination of sources at varying heights with the impact of additional complications of building downwash effects and non-homogeneous

Table 2-3. Potential Dispersion Modeling Representations for Various Petroleum and Chemical Industry Operations and Equipment.

Facility	Operation	Equipment	Emission Characteristics	Potential Representation
Petroleum refinery	Coking unit	Furnace Coke drums Fractionators	Combustion chamber/stack Vessel/tank, fugitives 50-ft columns/fugitives	Point source Point or area source Volume source
	Catalytic cracking unit	Process heaters CO boilers Fractionators Catalyst bed reactor Regenerator	Combustion/stack Combustion/stack 50-ft columns/fugitives Large vessels/fugitives Large vessels/fugitives	Point source Point source Volume source Volume source Volume source
	Catalytic reforming	Process heaters Reactors Stabilizers	Combustion/stack Vessels/fugitives Tall columns/fugitives	Point source Volume source Volume source
	Hydrotreating	Process heaters Reactors Hydrogen separators Stabilizers	Vessel/fugitives Enclosed vessel/fugitives Tall columns/fugitives	Point source Volume source Volume source Volume source
	Sulfur recovery	Tail gas incinerator Sour water stripping	Combustion/stack Tall columns/fugitives	Point source Volume source
	Product storage	Storage tanks	Large vessels	Elevated area sources
	Wastewater treatment	Oil/water separators Open sumps/ponds	Tanks, ponds/fugitives Surface impoundments	Area source Area source
	Asphalt plant	Flasher and blower	Stack	Point source
	Product loading	Loading racks	Displaced fugitive vapors, leaks	Area or volume source
	Refinery gas plant	Compressors Separators, absorption towers	Shaft leaks/fugitives Fugitives, tall columns	Volume source Volume source
	Alkylation	Chiller Reactors Acid separator Caustic wash Distilling column	Shaft leaks/fugitives Vessels/fugitives Vessels/fugitives Column/fugitives Column/fugitives	Volume source Volume source Volume source Volume source Volume source
	Auxiliary facilities	Boilers and heaters Gas turbines Flare Piping, connections	Fuel combustion/stack Fuel combustion/stack Combustion/stack Fugitives	Point source Point source Point source Area, volume sources
Wastewater treatment plant	Primary, secondary treatment	Basins, ponds, storage vessels	Fugitive vapors from liquids exposed to atmosphere	Area source at surface
	Tertiary treatment	Pressure vessels, piping	Fugitives from vessels, components	Area, volume source

Source: Ogden Environmental and Energy Services, 1992b surfaces. Besides the physical complexity of a refinery, there are problems for model applications arising from the basic assumptions of the current generation of EPA-accepted air quality models, especially the area and volume models. Most of these models are based on the Gaussian dispersion model assumptions of continuous emissions, a steady-state concentration, as well as homogenous and steady-state meteorological conditions in the area of calculation. In addition, Gaussian dispersion models assume that the plume dispersion is Gaussian in both the vertical and horizontal directions and, thus, tend to predict maximum centerline concentrations that rapidly fall off to the edges of the plume. However, the reality of area and volume souces leads to far more homogeneity across the plume. At present dispersion coefficients, σ_y and σ_z, are usually selected from a table and fixed regardless of wind direction, as long as stability class does not change. However, because of the different physical profiles which the facility presents to the wind, a refinery may have a changing σ_y and σ_z with changing wind directions. Such considerations limit the physical "reality" of the predictions of concentration from the prevailing models. A few of the above-referenced applications (Kricks, *et al.* , 1991; Scotto, *et al.*, 1991) of the PAL model to Superfund sites used site-specific σ_z values determined from atmospheric tracer releases to improve their predictive capabilities.

To calculate emissions rates, it is necessary to link the integrated, cross-plume measurements of the cloud of gases in the remote sensing beam with the dispersion process, either through dispersion models or tracer gas releases. If the remote sensor measurements can be limited to the emissions from a process area that has a simple configuration and is easy to model, field verification of the models could be facilitated.

Now that we have a means of determining vertical wind profiles and "instantaneous" measurements of path-integrated concentrations, there is the strong possibility that improved models such as the Langrangian Monte-Carlo particle models may be able to deal with the temporal and spatial issues associated with refinery emission sources in a more satisfactory manner than the Gaussian models (Zannetti, 1992). While the Gaussian-based models may be limited, some of the particle models can deal with time scales comparable with the "instantaneous" optical measurements. Yet, particle models can perfectly replicate Gaussian model results when applied in simplified, homogeneous conditions. It should be remembered that the Gaussian models were developed at a time when very limited meteorological and air quality data were available. The Gaussian models may well be inadequate for many applications, especially advanced applications envisioned for refinery fugitive emissions computations. However, at this point, Gaussian models cannot be dismissed since they are required by EPA for regulatory issues.

Tracer Gas Releases

A refinery presents a complex physical profile to the incoming wind, and the refinery structures affect the speed, direction and turbulence level of the airflow traversing the facility. In addition, the high temperatures that characterize many refinery processes combined with the heat radiation characteristics of paved areas and man-made structures give rise to thermal effects that can alter the height and enhance the initial dispersion of emitted contaminant plumes. In general, the combined effects of these phenomena are too complex to be incorporated into currently available dispersion models as discussed above. This complexity suggests that the use of atmospheric tracer gas releases and their downwind measurement at the fenceline (or beyond) offer the best hope of confirming the performance of ORS systems at actual sites.

On the positive side, the current tracer technology uses substances for which background levels and ORS detection limits are extremely low and, thus, can help evaluate the adequacy of MDLs for various air toxics. On the negative side it may not be feasible to set up a tracer experiment that addresses refinery-wide emissions of, say, benzene, because the experiments would probably need to focus on simulating point, area and volume sources simultaneously (Table 2-3).

In addition to being used to confirm the performance of ORS systems at actual sites, the use of the tracer gas along with monitoring at downwind distances can be used to test modeling results. For example, tracer releases and monitoring could be used to test the physical modeling of Peterson and Ratcliff (1989) who observed dilutions of 10^4 for downwind receptors at the equivalent of 80 to 200 m.

Averaging Time For Measurements

Determination of an appropriate averaging time for atmospheric tracer and air toxic substance sampling is not trivial. Source strengths, wind speed, wind direction, and turbulence are subject to varying degrees of fluctuation such that short term grab sampling is not appropriate. API has done extensive wind tunnel studies related to surface roughness at a typical refinery as well as the effects of wind speed, wind direction and turbulence which could help in determining the appropriate time scales (Peterson and Ratcliff, 1989). It should also be possible to use information such as Pasquill's plots (Pasquill, 1962) relating the contributions of various eddy length and time scales to overall turbulent energy along with refinery surface roughness and heat effects to determine minimum acceptable sampling durations for different weather conditions. To our knowledge, this approach has not been tried before.

P.T. Woods (Woods, 1992b) has indicated that the sampling interval, or integration time, used during his DIAL-based flux measurements at refineries was 15-30 minutes. The choice of sampling time, however, needs to include the consideration of a number of factors to ensure that the sampling interval chosen is compatible with a given refinery's operations and characteristics. These factors could include:

- Variable emissions from tanks - Most storage tank emissions will depend on diurnal variations of environmental conditions such as product vapor pressure and surface temperature (higher evaporation from warmer top layers just under floating roofs during mid-day and afternoons), variations in pressure ("breathing" in and out due to ambient pressure changes), and variations in wind speed (puff releases from the cavity above partially filled floating roof tanks or emissions approximately proportional to the square of the wind speed). In general, uncontrolled tank emissions increase during loading operations regardless of environmental conditions.
- Releases involved with material handling that are dependent on materials handled, duration and pressure of operation.

- Irregular process and waste treatment operations in terms of occurrence and duration.

Meteorological Measurements

Meteorological conditions can affect the ability to make meaningful ambient air measurements for any sampling system and are even more significant for ORS systems. Even with an optimized detector and a strong absorption band, meteorological conditions can affect emissions measurements from a given source. High wind speeds and/or turbulence can result in emissions flux calculations that are biased low. Such low emissions flux values would result from path-averaged concentrations in the beam under these conditions being near or below the MDL, even though the flux (wind speed times true concentration) might be significant. With greater uncertainty in measurements near the MDL due to these conditions and greater cross beam transport velocities, extreme fluctuations can be expected in emissions calculations even for a steady release rate. While not a short-coming of the instrument itself, meteorological conditions will nonetheless alter the ability to make valid measurements.

For individual measurements of gases of interest and tracer gases to be useful, the transporting meteorology during the measurement must be documented. Prior ORS flux studies (Woods, 1992b) have used multiple anemometers arrayed to document horizontal variations and intermittent vertical wind profiling with air borne sensors along with continuous measurements with mini-sodars (acoustic sounders). According to Woods, the goal should be to accurately characterize the meteorological transport over the vertical range of 15 to 150 m to support the ORS measurements. Somewhat lower measurements would be needed to support ORS measurements at lower beam heights.

Section 3

TECHNICAL CONSIDERATIONS FOR DESIGNING A REFINERY EMISSIONS FIELD STUDY

Based on the review of previously conducted ORS studies as well as the issues and tradeoffs discussed in Section 2, this section provides answers to the specific questions raised by API relating to the feasibility of using ORS measurements in a refinery emissions field study and provides design considerations for conducting such a study.

An important distinction exists between measurements of the concentration of air toxics along a fenceline and determinations of emission rates of the same air toxics from a facility. <u>Concentrations</u> of air toxics at discrete points can be measured by a number of presently available point samplers, which collect samples for later analysis, or point monitors, which measure near real time data at discrete points. Path-average concentrations can be measured by ORS systems in the near real time along the path of the beam. Determination of <u>emission rates</u> due to a facility requires not only the knowledge of average concentrations upwind of the facility and at the fenceline downwind but also dispersion and transport information gained from ancillary measurements such as simultaneous meteorological measurements, simultaneous tracer gas release data and/or dispersion modeling. Hence, emission rate determinations are more complicated than concentration measurements. The reader needs to bear this distinction in mind as the questions related to the feasibility of measuring concentrations versus the feasibility of calculating emission rates are discussed.

The adequacy of point samplers to determine average concentrations is limited by the ability to gather sufficient samples to average and not by the analytical detection limit that may be better than the ORS. An ORS system can accomplish the averaging easily but may have a less adequate detection limit. The problems and uncertainties related to determining emission rates using ancillary sources are similar whether the concentrations are measured by point samplers/monitors or by open-path ORS systems.

RESPONSE TO API QUESTIONS

The following responses reflect consideration of current (1992) ORS, meteorological, and tracer gas release technologies, as well as dispersion models.

Is the amount of information collected from other, recent studies of a similar nature sufficient to accomplish the objectives of the proposed field study thereby negating the necessity for the field study?

None of the reported studies addressed detection limits and transport parameters in sufficient detail to provide technically defensible emission rate data, especially for the BTEX compounds and, specifically, benzene. There are indications that progress has been made in the past four to five years in obtaining emission rates for these compounds but more work is still needed. At this time, there is not sufficient data to rule out the need for a field study.

Will it be possible to separate a refinery's contribution from the background contribution for low-level concentrations measured along the fenceline and further downwind from a refinery?

For refineries in isolated locations, it should be possible to separate the contributions due to the refinery from the background provided that a UV-based ORS system is used for the BTEX compounds. Of course, if the refinery emits low concentrations of air toxics even those isolated downwind levels may be below currently achievable MDLs. No information on the actual contribution from the refinery would be gained if both the upwind and downwind concentrations are below the MDLs.

For non-BTEX air toxics unique to refineries, it should also be possible to the separate the contribution due to the refinery from the background by either a UV or FTIR system even in a more complex industrial setting, again with certain MDL caveats.

For BTEX compounds at refineries in an urban or industrial setting, it will probably not be possible to separate the contribution due to the refinery from the background with the currently available systems due in part to the complex source pattern and present MDLs for these compounds. This qualification recognizes that the presence of BTEX, especially benzene, in the ambient air comes from the cars and trucks in parking lots as well as the nearby highways (Stevens and Vossler, 1991) and other nearby industrial sources and, thus, must be compensated for. The concentrations from these non-refinery sources may be significantly higher than those from the refinery itself. For such urban or industrial settings, monitoring close to the various process areas at the refinery may make it possible to determine emission rates for each process area since the ambient concentrations due to the process area will be significantly higher near the process area (source) than at the fenceline, thus, reducing the importance of the upwind concentrations.

Is the state of the technology of optical remote sensing (and required ancillary measurements) sufficiently refined to provide technically defensible data for the calculation of air toxics emission rates due to a refinery complex located in either an isolated setting or in a complex industrial area?

To address the issue of the technical defensibility of the calculated refinery specific emission rates, one must address not only the defensibility of the path-integrated concentration measurements but also the defensibility of the contribution due to the refinery determined from these and the defensibility of the models and/or tracer data which combine the meteorological data with the concentration data to produce emission rates.

With respect to ORS path-integrated or path-average concentrations, ORS instrumentation and field techniques have been improving rapidly in recent years and have compared well with conventional sampling methods in several field intercomparison studies (Indaco, Inc., 1990; Lupo, *et al.*, 1991; Spellicy, *et al.*, 1992; Carter, *et al.*, 1992). In addition two draft guidance documents have been prepared by the EPA (USEPA, 1992 and USEPA, 1993) to provide guidance on quality assurance and quality control measures to ensure that path-average concentrations determined with the FTIR are technically defensible. Thus, the ORS systems are sufficiently refined to provide technically defensible **path-integrated or path-average concentrations**. These technically defensible data may consist of statements that the concentrations are below the MDL.

To determine the contribution due to the refinery, the technical defensibility depends on having sufficiently low MDLs and, thus, sufficient sensitivity to determine the difference between the upwind and downwind concentrations as discussed in the answer to the second question. While the individual upwind and downwind path-integrated concentrations may be technically defensible, if these path-integrated concentrations are similar to each other or both are below the MDL, it may not be possible to determine the refinery's contribution to the downwind concentration field outside the overall uncertainties of the measurements. When more sensitive instruments are available to provide lower detection limits and reduced uncertainties in the path-averaged concentrations, the separation of a refinery's contribution will be possible for refineries in complex settings.

To determine the refinery specific emission rates, the technical defensibility depends on the defensibility of the modeling, meteorological data and possible tracer data in addition to the path-average concentration and refinery specific contribution discussed above. In order to determine the emission rate, the upwind and downwind path-average concentrations or MDLs must be used to determine the refinery's contribution which then must be combined with either tracer gas release data or a dispersion model. Although there have been wind tunnel studies with models of refineries with different surface roughness (e.g., Peterson and Ratcliff, 1989), very little field verification data similar to the ORS intercomparison studies exist to technically defend the modeling of turbulent transport conditions in a physically complex setting or the use of tracer gas releases for the determination of emission rates from such complex settings (Ogden Environmental and Energy Services, 1992b and 1992c). Thus, it would be very useful to combine a dispersion model and tracer gas release evaluation program with the proposed ORS field study/evaluation.

In summary, the state of the technology of ORS systems is sufficiently refined to provide technically defensible <u>path-average concentrations</u> which could be used for the calculation of emission rates. There is somewhat less certainty about determining the contribution due to the refinery at the fenceline or about the technical defensibility of the emission rates calculated from these path-average concentrations using dispersion models and/or tracer gas releases with meteorological data.

CONSIDERATIONS FOR THE DESIGN OF A REFINERY EMISSIONS FIELD STUDY

The considerations listed below are based on the detailed discussion of the issues and trade-offs in Section 2. The basic steps required to determine emission rates using concentration data collected either with point sampling/monitoring or ORS systems are the same:

- **Selection of Optimum Sampling Locations:** Set up monitoring systems upwind and downwind of the facility at optimized locations. For point samplers/monitors there must be a sufficient number of sampling points to obtain a representative average.
- **Tracer Gas Release:** Release tracer gas at known rates.
- **Concentration Determinations:** Determine the average upwind and downwind concentrations and take the difference to determine the concentration due to the facility for each compound of interest (C_i) as well as for the tracer gas (C_t).
- **Emission Rate from Tracer Gas Data:** Divide C_i for each compound of interest by C_t and multiply by the rate of release of the tracer gas (Q_t) to determine the emission rate for each compound of interest (Q_i).
- **Emission Rate from Dispersion Models:** Use dispersion models with the on-site meteorological data and C_i to determine emission rates for each compound of interest.
- **Comparison of Emission Rates:** Compare the results of the tracer gas emission rates and the various models.

These steps appear simple and straightforward for point sources and perhaps simple area sources; however, each step becomes significantly more complicated when evaluating a refinery made up of multiple sources emitting the same compounds at different rates and heights as proposed for the API field study. A detailed discussion of these steps follows, as well as additional design considerations such as the issues to be tested during the study, choice of an appropriate test refinery, the time frame of the study, the choice of sampling equipment for concentration determination, meteorological data requirements, tracer gas release design, and models to be tested.

Issues Which Could Be Tested During A Field Study

- Evaluation of the effect of ORS beam height on characterizing emissions from process areas and/or complexes using a combination of tracers and routine emissions data.
- Comparison of urban background levels of selected compounds to the actual industrial site fenceline levels of those compounds to see if the compound level increment from a facility is technically distinguishable.
- Evaluation of the impact of below MDL measurements on emission rate estimates from long-term ORS and meteorological measurements to determine if the use of MDL readings along with detected values provides more appropriate annual emission rates than using only data collected during those periods when compounds are actually detected. (There has been an indication that, if monitoring indicates compound levels are below the MDL, calculation of emission rates using the MDL as the compound level gives an emission estimate that is considerably smaller than the emission estimate from the short periods of actual detection.)
- Evaluation of the effect of using simultaneous upwind measurements, intermittent upwind measurements, or parallel wind measurements to gain background data.
- Determination of concentrations at different downwind distances in order to evaluate the near-field dispersion of low-level air toxics emissions.
- Evaluation of tracer releases in conjunction with model validation studies to determine emission rates of sources from single tracer and multi-tracer studies along with single beam and multi-beam ORS measurements.
- Evaluation of techniques for defining the wind field in the lower 20-100 meters of the atmosphere where most of the dispersion and transport of interest are taking place.

- Evaluation of the best combination of Gaussian and/or non-Gaussian modeling techniques combined with ORS measurements to give improved fugitive emission information.

- Evaluation of stochastical (e.g. Monte Carlo) modeling techniques for describing area and volume sources.

- Evaluation of the role of wind direction over a facility to alter the vertical dispersion coefficient, σ_z, as the surface roughness varies with the facility profile under different wind directions.

- Evaluation of the cost effectiveness of routine air toxics emissions determinations using point sampling, FTIR ORS and UV ORS systems.

Selection of Test Refinery

Site selection criteria must be developed for appropriate field testing of the objectives of the study.

- The refinery should emit compounds representative of an average refinery.

- The refinery should be sufficiently large and have sufficient emissions that path-average concentrations at the fenceline will be detectable with available systems.

- The refinery should be as isolated as possible from other sources (especially from BTEX sources such as urban air, vehicle emissions, and other industrial sources) to make it easier to determine the refinery contribution downwind of the refinery.

- Appropriate upwind and downwind monitoring locations must be accessible.

- The existence of supporting data from prior studies and a good fugitive emission database for comparison of field study results would be useful.

- The availability of current meteorological data for the area would be useful.

If an appropriate refinery cannot be found, it may be useful to start with monitoring near one or more process areas within a refinery in order to reduce the significance of upwind concentrations.

Time Considerations

Time issues must address the purpose of the study. If the study is aimed at obtaining an "annual average" emission rate, there must be sufficient duration of measurements to encounter as broad a range of refinery activities and meteorological conditions as possible. The experience of two of the research teams is helpful here. P. T. Woods (Woods, 1992b) found that DIAL measurements which focused on one process area and were made on four different days and nights with different meteorology were helpful in developing data consistent with repeated measurements in another season three months later. McLaren (McLaren, 1992) pointed out that duration of measurements is important to characterize the more significant, but less frequent, contributions to emissions over a year. During the wastewater impoundment study (Indaco, Inc., 1990; McLaren and Stedman, 1990), for example, toluene measurements were made with an OPUV system for a total of 507 minutes. For 330 minutes, the concentration was below the detection limit and the emission rate calculated to be less than 1.8 g/min. For the other 177 minutes, the concentrations were above the detection limits and the emission rate calculated to be 41 g/min. Thus, in this eight hours of measurements, 35% of the interval (when toluene was detected) accounted for 92% of the emissions even treating the non-detects at their full MDL level.

In light of these thoughts, a multi-month study, perhaps looking at a couple of seasons, is recommended.

The time frame for the collection of data is also important. Canister samples are usually collected over an 8-hour or 24-hour period to get time-averaged data because of the cost of analyzing a large number of samples. ORS data can be collected for periods as short as seconds; however, for the determination of the low-level concentrations expected, periods of 30 minutes to an hour would be preferable. Beyond the issue of improving detection limits by lengthening the averaging time there are the temporal issues of process cycles and meteorological representativeness that also need to be considered in planning the study.

The time frame of plant processes will affect emission cycles -

Continuous emissions:	Usually small amounts from leaking valves and tank evaporation, etc.
Regular but less frequent:	Larger amounts from process operations, tank/ship loading and unloading, etc.
Infrequent emissions:	Much larger amounts due to plant upsets, process startup or shutdown, shift changes, etc.

The time frame of ORS measurements to optimize the MDL for a given gas may be compatible with the "less frequent" activities, but still miss the smaller continuous emissions. P. T. Woods suggests a 15 to 30-minute time frame for averaging the air quality measurements. According to MDA personnel, single beam FTIR spectra can be saved in small time intervals (e.g. 5 minutes) and these spectra then co-added if necessary to gain better signal-to-noise ratios. This approach may allow data collection for shorter time intervals when concentrations are well above the MDLs for certain compounds and allow co-adding of spectra to increase the monitoring time intervals and, hence, lower the MDLs for compounds with concentrations near their MDLs. Whatever time frame is chosen for air quality measurements, it should then be used to select the averaging time for supporting meteorological measurements, perhaps twice to four times as frequently as the ORS data collection to reveal some of the micrometeorological variability. Any time frame chosen for measurements will eventually need to be compatible with required averaging times for dispersion models.

Selection of Optimum Sampling Locations

The choice of optimum upwind and downwind sampling locations will depend on physical accessibility as well as optimum beam height, path length, and position estimates based on dispersion modeling.

Sampling Height. Depending on the source elevation or the buoyancy of the plume being monitored, different light beam elevations need to be evaluated. Controlled-release studies such as those planned by Kansas State University (KSU) may be helpful here. Use of multiple ORS beams at different heights could be evaluated for consistency in determining emission rates if the upwind instrument is periodically moved downwind for specialized measurements. Use of scissor-lifts could allow determination of various heights with little movement of the instrument.

Upwind Placement. The choice of the optimum upwind placement of ORS and point samplers will depend on the numbers and types of upwind sources and/or how close they are to the facility of interest as well as the meteorology on the sampling day.

Downwind Distance. In an isolated setting, the advantage of measuring further downwind to sample a vertically well-mixed plume can be evaluated. Use of two ORS systems operated simultaneously at two different distances would provide an optimal data base to address this issue.

Path Length to Cover the Plume. The path length required will depend on the distance downwind, meteorological variation expected and the dispersion of the plume. With good meteorological data and dispersion models, good estimates can be made at the beginning of each sampling day. The upwind path length should be based on similar considerations in relation to the upwind sources and in relation to the downwind path length.

Selection of Sampling Equipment

A number of factors need to be considered in the selection of sampling and monitoring equipment for such a study: Will the detection limits for the BTEX compounds be low enough? Will the tracer gas concentrations be measurable? Will other compounds specific to specific processes or areas be detectable? What time resolution can be obtained? How soon can the data be obtained? What spatial resolution and coverage can be obtained? For the proposed study, it would be useful to compare different types of ORS systems to determine which is the most cost effective system or combination of systems for routine monitoring.

Detection Limits for BTEX. The point sampling with SUMMA® canisters combined with GC/FID or GC/MS analysis or field GC systems provide the lowest MDLs for the BTEX compounds at the present time with the UV ORS systems next lowest and the FTIR highest. If detection limits were the only limiting factor and the BTEX compounds the only compounds to be determined, there would be no point in considering the ORS systems. However, for the same path coverage and temporal resolution, the point sampling is far more costly and the canister sample data results are not received for days and, thus, cannot provide near real time information.

Tracer Gas Detectability. The FTIR ORS systems provide the best means of measuring low concentrations of the tracer gases which are likely to be used (SF_6 and carbon tetrafluoride [CF_4]). The FTIR can determine these concentrations with high temporal resolution in near real time reporting (Thomas, 1992). UV ORS systems cannot be used to determine these tracer gas concentrations. An on-site GC with an electron capture detector (ECD) or flame-photometric detector (FPD) as well as SUMMA® canister samplers also analyzed by GC/ECD or GC/FPD can be used to determine the tracer gas concentrations but with poorer spatial coverage and the requirement of different analyses for the BTEX and tracer gases. The SUMMA® canister sampler data will also have poorer time resolution and data availability.

Time Resolution. The ORS systems and the on-site GC systems can provide near real time resolution for determining the impact of variability in operations and meteorology. However, it is not cost effective to use on-site GC systems to obtain the same spatial fenceline coverage as is possible with the ORS systems.

Spatial Resolution. The ORS systems do not provide detailed spatial resolution along the beam path but can be moved relatively easily to obtain vertical resolution as well as resolution at varying downwind distances. Point samplers could provide spatial resolution of plume details along the path with a sufficient number of samplers; however, the greater resolution will come at greater cost.

Spatial Coverage. The ORS systems provide greater spatial coverage at less cost since they can be used over paths up to about 600 m for the FTIR system without special modifications and about 2,000 m for the UV systems. It would be extremely costly to have sufficient point samplers to cover these paths.

Deployment of Measurement/Sampling Equipment. There should be at least one FTIR system to use for tracer gas concentration determinations. The FTIR should be combined with point sampling data to determine the practicality of using the FTIR MDL for calculation of emission rates and predicting maximum downwind concentrations. There should be at least one UV ORS system to determine the cost effectiveness and practicality of using such a system for routine determinations of BTEX emissions and downwind concentrations in light of their lower MDLs relative to the FTIR. It is recommended that there be two FTIR units as well as two UV units to provide simultaneous upwind and downwind ORS measurements as well as to allow for simultaneous ORS measurements at more than one beam height or at different downwind distances. There should be sufficient canister samplers to provide data comparable to the ORS data along the measurement path both upwind and downwind. There should be about seven canisters for each 100 m of beam path. As an alternative, a single canister could be moved along the path, e.g. or a bicycle to obtain a path-averaged concentration. The total number of canisters needed for the program would probably be at least double those for each sampling site to allow for sampling while the canisters are being analyzed. It would be useful to have additional canisters for further downwind measurements since their sensitivity should allow determination of lower BTEX concentrations and, thus, the ability to obtain more data for comparison with the model predictions. It would be useful to have at least one on-site gas chromatograph (GC) for determining low-level concentrations of the BTEX compounds on a near real time basis for comparison with the ORS data. If the field GC were portable, it could be used on a point measurement basis to determine the plume width and possibly the horizontal and vertical centerline while the ORS system measured the path-integrated concentration at a given downwind distance. The field GC might also be used further downwind to check on the reliability of downwind concentration predictions using the calculated emission rates and models.

Meteorological Measurements

On-site meteorological measurements need to adequately define micrometeorological parameters near the process areas of interest. At a minimum, there should be several small towers (~3 meters) to define the low altitude transport, a couple of intermediate towers (~10 meters) for traditional transport considerations and at least one higher tower or tethered balloon system to help define conditions in the 50-100 meter height range. There may be adequate low altitude resolution from the current generation of acoustic sounders to allow tracing of detailed wind fields. The site-specific, temporal variation in σ_z should be determined. A meteorologist would need to be involved to set up a usable database for these spatially distributed measurements in such a way that transport and turbulence fields can be described and provide useful input to the modelers.

Tracer Gas Release

With the ability of FTIR ORS systems to readily detect tracer gases such as SF_6 and CF_4, it would be possible to design a tracer release program for multiple area and/or volume sources that would tag different process areas and allow ratios of emissions to be determined. J. Deuble (Deuble, 1992) of Ogden Environmental and Energy Services has prepared a draft experimental design for use in a VOC emissions project that may be a valuable starting point for this aspect of the proposed evaluation study. Multiple tracers should be included in any ORS evaluation study to provide some empirical release numbers to compare with ORS-based calculations. The prior experience in ranking refinery fugitive sources (e.g., Taback, 1992a; Radian, 1991a) and various Toxic Release Inventory information (i.e., Sara Title III) can indicate which source categories should be labelled for various aromatics and/or other air toxics.

Dispersion Models

As indicated above, the dispersion modeling aspect of these measurements is, perhaps, the weakest link. Until some of the issues of concern are addressed, this area will continue to pose a problem. Perhaps API's on-going model evaluation effort could be combined with an ORS effort to develop a sound data base for model improvement and ORS application.

It should be noted that whatever dispersion models are used for emission rate determinations they should be adapted so that emission rates are not reported when the meteorological conditions are too uncertain. These conditions include calms and high speed wind conditions. The use of proper innovative ORS/meteorological data processing software would report those conditions when emission rates cannot be accurately computed, thus, avoiding incorrect reporting of highly uncertain values.

RESEARCH RECOMMENDATIONS

Because of the unresolved issues identified in this feasibility study, the practical near-term routine use of ORS systems at refinery, petrochemical, and other air toxic-emitting facilities will be limited. To address and possibly resolve some of these issues, the following research topics should be considered for funding by the regulatory and industrial communities.

- Improve the operating sensitivity for aromatic compounds in the infrared, possibly by increasing the power source, better collimating the infrared beam, etc.
- Improve the UV systems to enhance their use as short term screening tools (similar to current FTIR systems) and enhance their sensitivity and field QA protocols.
- Improve the DIAL technique to achieve a more compact, less expensive and versatile system to address species-specific detection of air toxic vapors.
- Improve field/data processing techniques to identify and compensate for water vapor and carbon dioxide interferences for the FTIR systems.

REFERENCES

Amoco Corporation. 1992. *Executive Summary, Amoco/U.S.EPA Pollution Prevention Project.* Obtained from the American Petroleum Institute's Health and Environmental Affairs Department, (May, 1992).

Axelsson, H., H. Kloo, H. Ender, and P. Ragnarson. 1991. *Long Path DOAS Measurement of Light Aromatic Hydrocarbons.* Opsis, Inc. (1991).

Carter,Jr., R.E., M.J. Thomas, G.A. Marotz, D.D. Lane and J.L. Hudson. 1992. Compound Detection and Concentration Estimation by Open-Path Fourier Transform Infrared Spectroscopy, *Environmental Science and Technology*, Vol. 26, No. 11.

Deuble, J. 1992. "Experimental Design - Fugitive VOC Tracer Study," Personal communication (September 1992).

Gidhagen, L. 1992a. Personal communication - facsimile (30 September 1992).

Gidhagen, L. 1992b. Personal communication - facsimile (27 October 1992).

Grant, W. B., R. H. Kagann, W. A. McClenny. 1992. Optical Remote Measurement of Toxic Gases, *Journal of Air & Waste Management Association*, Vol. 42, No. 1.

Hallstadius, H. 1992. Personal communication (28 September 1992).

Hudson, J.L., M.J. Thomas, J. Arello, J.R. Helvig, B.J. Fairless, R.E. Carter, D.D. Lane, and G.A. Marotz. 1992. *An Overview Assessment of the Intercomparability and Performance of Multiple Open-Path FTIR Systems as Applied to the Measurement of Air Toxics.* Paper 92-73.08 presented at the 85th Annual Meeting of the Air and Waste Management Association, Kansas City, MO (1992).

Indaco, Inc. 1990. *Measurement of BTEX Emission Fluxes from Refinery Wastewater Impoundments Using Atmospheric Tracer Techniques.* API Publication No. 4518. American Petroleum Institute. Washington, D.C.

Indic. 1988. Indic AB Report no. 23, *Estimation of Hydrocarbon Emissions from the Refineries in Hisingen.* Opsis, Inc., (1988).

Kagann, R. 1992a. Personal communication (June).

Kagann, R. 1992b. Personal communication (September).

Kricks, R.J., T.R. Minnich, D.E. Pescatore, P.J. Solinski, D. Mickunas, L. Kaelin, O. Simpson, M.J. Czerniawski, and T.H. Prichett. 1991. *Perimeter Monitoring at Lipari Landfill Using Open-Path FTIR Spectroscopy: An Overview of Lessons Learned.* Paper 91-57.10 presented at the 84th Annual Meeting and Exhibition of the Air & Waste Management Association, Vancouver (1991).

Lague, J. 1992. Personal communication (October).

Lofgren, L., O. Ramnas. 1991. *Determination of Benzene and Toluene in Urban Air with Differential Optical Absorption Spectroscopy.* OPSIS, Inc.

Lupo, M. J., C. E. Magnuson, R. L. Shiver, F. K. Hamilton, R.L. Scotto, T. R. Minnich, D. E. Pescatore, R. H. Kagann, O. A. Simpson, S. E. McLaren, D. H. Stedman. 1991. *Air Pathway Monitoring for a Land Ban No-Migration Petition.* Paper No. 91- 57.4 presented at the 84th Annual Meeting of the Air & Waste Management Association, Vancouver, B.C. (June 1991).

Lute, R., *et al.* 1992. *Effects of Atmospheric Water Vapor on Open-path FTIR Spectroscopy Data.* Paper presented at the 1992 EPA/AWMA International Symposium on the Measurement of Toxic and Related Air Pollutants, Durham, North Carolina (May 1992).

McLaren, S.E., D.H. Stedman. 1990. *Flux Measurements using Simultaneous Long Path Ultraviolet and Infrared Spectroscopy.* Paper 90-86.6 presented at the 83rd Annual Meeting of the Air and Waste Management Association, Pittsburgh, Pennsylvania (June, 1990).

McLaren, S.E., D.H. Stedman, P.D. Greenlaw, R.J. Bath, and R. D. Speer. 1992. *Comparison of an Open Path UV and FTIR Spectrometer.* Paper 92-73.10 presented at 85th Annual American Waste & Management Association Meeting, Kansas City, MO (1992).

McLaren, S. 1992. Personal communication (Facsimile, 25 September 1992).

Milton, M.J.T., P.T. Woods, B.W. Jolliffe, N.R.W. Swann and T.J. McIlveen. 1992. Measurements of Toluene and Other Aromatic Hydrocarbons by Differential-Absorption LIDAR in the Near-Ultraviolet. *Applied Physics B, 54* (1992).

Minnich, T.R., R.L. Scotto, M.R. Leo, B.C. Sanders, S.H. Perry, and T.H. Pritchett. 1992. *A Practical Methodology using Open-Path FTIR Spectroscopy to Generate Gaseous Fugitive-Source Emission Factors at Industrial Facilities.* Paper presented at the International Symposium on the Measurement of Toxic and Related Air Pollutants," Durham, NC (May, 1992).

NIOSH. 1990. *Pocket Guide to Chemical Hazards*, U.S. Department of Health and Human Services (June, 1990).

Ogden Environmental and Energy Services. 1992a. *Evaluation of Area and Volume Source Dispersion Models for Petroleum and Chemical Industry Facilities: Phase I Final Report.* API Publication No. 4539. American Petroleum Institute. Washington, D.C.

Ogden Environmental and Energy Services. 1992b. *Area and Volume Source Air Quality Model Performance Evaluation: Phase II Final Report.* API Publication No. 4540. American Petroleum Institute. Washington, D.C.

Ogden Environmental and Energy Services. 1992c. *Design of Field Tracer Studies to Support Further Area/Volume Source Dispersion Model Performance Evaluation, Phase III Final Report.* API Publication No. Draft Report 4541. American Petroleum Institute. Washington, D.C.

Pasquill, F. 1962. *Atmospheric Diffusion*, D. Van Nostrand, Co., Ltd, London (1962).

Peterson, R. L. and M.A. Ratcliff. 1989. *Effects of Homogeneous and Heterogeneous Surface Roughness on Heavier-Than-Air Gas Dispersion.* API Publication No. 4491. American Petroleum Institute. Washington, D.C.

Radian. 1991a. *Measurements of Hydrocarbon Emissions and Ambient Air Concentrations at the Amoco Yorktown Refinery.* Draft prepared by Radian Corporation (30 September 1991).

Radian. 1991b. *Optical Remote Sensing - A Technology Demonstration Program.* Draft prepared by Radian Corporation (12 December 1991).

Russwurm, G. M. 1992. *Quality Assurance, Water Vapor, and Analysis of FTIR Data.* Paper No. 92-73.03. Paper presented at the 85th Annual Meeting of AWMA, Kansas City, Missouri (June, 1992).

Scotto, R.L., T.R. Minnich and M.R. Leo. 1991. *A Method for Estimating VOC Emission Rates from Area Sources Using Remote Optical Sensing.* Paper presented at the 1991 International Symposium on the Measurement of Toxic and Related Air Pollutants, Durham, NC (May, 1991).

Scotto, R.L., R.J. Kricks, D.E. Pescatore, P.J. Solinski, T.R. Minnich, T.H. Pritchett, D.B. Mickunas, M.A. Hansen, A.D. Schober, and B.M. Eklund. 1992. *VOC Emission Rate Determinations Using Open-Path FTIR Spectroscopy During Pilot- Scale Site Disturbances and Remediation Activities: A Case Study Using the Ratio Technique.* Paper 92-83.04 presented at the 85th Annual Meeting of the Air & Waste Management Association, Kansas City, MO (1992).

Seinfeld, John H. 1986. *Atmospheric Chemistry and Physics of Air Pollution.* Wiley, New York, 1986.

Skippon, S. 1992a. Personal Communication (October 1992).

Skippon, S. 1992b. Shell Oil Company Technical Report, Project #60423. *Optical Remote Sensing and its Applications in the Petrochemical Industry.*

Spellicy, R.L., J.A. Draves, W. Crow, W.F. Herget, and W. Buchholtz. *A Demonstration of Open-Path Fenceline and Extractive Workplace Monitoring with FTIR and UV-DOAS Systems.* Paper 92-73.05 presented at the 85th Annual Meeting of the Air and Waste Management Association, Kansas City, MO (1992).

Stevens, R.K., T.L. Vossler. 1991. DOAS Urban Pollution Measurements. *SPIE Proc., Ser., 1433,* 25.

Taback, H., 1992. *Analysis of Toxic-Hotspots (AB-2588) Data for Eleven California Refineries.* API Publication No. 308. American Petroleum Institute. Washington, D.C.

Thomas, M. J., M. Witkowski, C. Chaffin and T. Marshall. 1992. *Report for Open-Path FTIR Measurements at the Shell Deer Park Manufacturing Complex, Deer Park, Texas.* Environmental Services Division, EPA Region VII (June 1992).

U.S.EPA. 1985. *Research and Development: Interim Quantitative Cancer Unit Risk Estimates Due to Inhalation of Benzene.* Carcinogen Assessment Group, Office of Health and Environmental Assessment, Washington D.C. (June 1985).

U.S.EPA. 1992. *Field Standard Operating Procedure for the Use of Open-Path FTIR Spectroscopy at Hazardous Waste Sites, PRELIMINARY DRAFT.* (March 1992).

U.S.EPA. 1993. G.M. Russwurm and J.W. Childers. *FT-IR Open-Path Monitoring Guidance Document.* U.S.EPA contract number 68-DO-0106, March 1993.

Vaughan, W. M. 1991. Remote Sensing Terminology. *Air and Waste Management* **41**(11) (1991).

Weber, E.J. 1992. Continuous Emission Monitoring -- The Wave of the Future. *The Air Pollution Consultant 2*, p 2.10 (1992).

Western States Petroleum Association. 1992. *Refinery Fugitive Emissions Study.* Glendale, CA (June 1992).

Whitcraft & Wood, 1990 - Wilfred K. Whitcraft and Kenneth N. Wood. *Use of Remote Sensing To Measure Wastewater Treatment Plant Emissions*. Paper No. 90-86.4, presented at the 83rd Annual Meeting of the Air & Waste Management Association, Pittsburgh, PA (June 1990).

Williams, C. H. 1992. *Measurements of Hydrocarbon Emissions and Ambient Air Concentrations at the AMOCO Yorktown Refinery*. Volume 1 (30 September 1991).

Woods, P. T. 1992a. Personal communication on the 1989 Gothenburg study (received July 1992).

Woods, P.T. 1992b. Personal communication (facsimile, 18 August 1992).

Zannetti, P. 1990. *Air Pollution Modeling*. Van Nostrand Reinhold, New York, 1990.

Zannetti, P. 1992. Personal communication (facsimile 9 October 1992).

Appendix A

GLOSSARY

API	American Petroleum Institute
ATMYS	Air Toxics Multi-Year Study; A Workgroup of API
BP	British Petroleum
BTEX	Benzene, toluene, ethylbenzene, xylenes
BTX	Benzene, toluene, xylene
CAAA	Clean Air Act Amendments of 1990
CDHS	California Division of Health Services
CHEMDAT7	Air emissions model
CMA	Chemical Manufacturers Association
DIAL	Differential Absorption LIDAR
DOAS	Differential Optical Absorption Spectrometer
FDM	Fugitive Dust Model
FTIR	Fourier Transform Infrared
HAP	Hazardous Air Pollutant as listed in CAAA Title III
HRM	Houston Regional Monitoring Corporation
IVL	Swedish Environmental Research Institute
IR	Infrared
KSU	Kansas State University
LIDAR	Light Distance and Ranging
MDL	Minimum detection limit
NPL	National Physical Laboratory (U.K.)
OPUV	Open Path Ultraviolet
ORS	Optical remote sensing
PAL	Point area line model
RS≡A	Remote Sensing≡Air, Inc.
VDI	Verein Deutscher Ingenieure
WSPA	Western States Petroleum Association

Appendix B
REMOTE SENSING TERMINOLOGY

William M. Vaughan, Chair
Moving and Remote Monitoring
Technical Committee (EM-6)

This remote sensing terminology glossary was prepared by members of Technical Committee EM-6, Moving and Remote Monitoring, of the Air & Waste Management Association.

The members of EM-6 are aware that some of the terms, principles and applications of remote sensing systems can be confusing to those recently introduced to this field. Hence, we have compiled the following glossary and figures to assist in improved understanding of this field. Initially compiled for the A&WMA short course, "The Basics of Remote Sensing of Atmospheric Pollutants," this listing is to be the start of an on-going process of gathering and refining terms for a growing phase of measurement activity. The EM-6 committee hopes that a more consistent use and understanding of terms will result. (Questions and input from the A&WMA community are solicited to expand this initial list and improve its clarity.)

Remote Sensing Glossary

(Words appearing in all caps are found elsewhere in the Glossary)

Absorbance: Negative log (base 10) of fractional transmission of energy as a function of WAVE NUMBER. $A = -\log_{10} (I/I_0)$. [Note that most chemists generally use base 10 while most physicists and atmospheric scientists use base e.]

Active System: Any remote sensing system which includes a controlled source (i.e., electromagnetic energy source, light) as a necessary component of its operating such as a DIAL, DOAS, FTIR or OPUV system. See PASSIVE SYSTEM.

Analytical Software: The computer routines used to identify and quantify compounds in complex spectra from sensing system measurements.

Aperture: An adjustable iris (hole) on which the signal from the RECEIVER TELESCOPE is focused.

Average Concentration: The mean concentration in the beam of a remote sensing system obtained by dividing the PATH INTEGRATED CONCENTRATION (the engineering units of a remote sensing instrument) by the path length of the analyzing beam (or known width of a cloud of gas that is smaller than the distance from the reflector or source to the detector). Depending on the units of the measurement (ppm-m, ppb-m, $\mu g/m^2$ or molecules/cm^2) the results are in units of ppm, ppb, $\mu g/m^3$ or molecules/cm^3. See PATH AVERAGE CONCENTRATION.

Background Spectrum, I_0 (V): For a laboratory environment, I_0 (V) would be the spectrum obtained when no sample is present. In the open path mode, the I_0 (v) is a "clean air" spectrum (or an upwind spectrum in the case of a localized emission source.)

Band Pass Filter: An optical filter designed specifically to allow only a discrete range of wavelengths to pass through it. These filters are usually added to a BROAD BAND INSTRUMENT to narrow the working wavelength range in order to achieve improved detection specificity for different classes of compounds that are known to absorb preferentially in the wavelength region common to the filter.

Bandwidth: A term referring to either (1) instrument resolution or (2) peak width. (1) The effective resolution of the spectrometer used or its ability to separate peaks in the spectrum. A narrower bandwidth yields a "sharper" resolution so that adjacent narrow peaks can be seen separately rather than as one broad peak. This parameter is not always constant across a single spectrum. In grating spectrometers bandwidth is constant in wavelength units and is usually slit width dependent (i.e. narrow slits imply narrow band width). In FOURIER TRANSFORM INSTRUMENT'S bandwidth is usually constant in WAVE NUMBER (units of cm^{-1}). (2) A peak's horizontal size (width) measured at 1/2 peak height and expressed in microns or WAVE NUMBERS.

Beer's Law: The ABSORBANCE of a spectral line (or band) is proportional to the concentration times the pathlength. The law is valid as long as the instrument resolution is narrower than the width of the bands, under study. When there is weak absorption it is valid irrespective of resolution. It becomes less valid with increasing ABSORBANCE.

Bistatic System: A remote sensing system having active components at both ends of the analytical path (See Figure 1), usually a light source at one end and a receiver at the opposite end. See UNISTATIC, MONOSTATIC.

Broad Band Instrument: A devise that utilizes a source emitting a wide range of wave lengths, as differentiated from discrete wavelengths, for the detection of general absorption changes in the atmosphere.

Burden: An alternate term for PATH INTEGRATED CONCENTRATION, usually used for vertical remote sensor readings. The units are expressed as either ppm-m, $\mu g/m^2$ or atm cm^{-1}.

Closed Path: A path travelled by a beam of electromagnetic energy which is not open to the ambient air and does not allow the wind to move the air through the beam. Examples would be stack sampling systems based on the GASSPEC principle or FOLDED PATH, POINT MONITOR instruments that use a pump or fan to draw air through the beam.

Concentration Path Length: Another term for PATH INTEGRATED CONCENTRATION used more in the early days of this technology in environmental usage but still in use by optical scientists.

Cooler: The low temperature cooling device used to control the temperature of the photon detector particularly in IR instruments. Cryogenic systems using fluids like liquid nitrogen in a closed cycle or electrical systems using Peltier cooling are used by different manufacturers.

Reprinted with permission from *Journal of the Air & Waste Management Association*, Vol. 41, No. 11, November 1991

Corner Cube: See RETROREFLECTOR

COSPEC (Correlation Spectrometer): A remote sensing system that detects the presence of a gas by monitoring the differential energy passing through a series of slits aligned with absorption wavelengths of a gas compared with the energy passing through a second set of slits aligned with non-absorbing wavelengths in the same general spectral window. Its primary use has been in the detection of atmospheric SO_2 and NO_2 using the sky-light spectrum in the PASSIVE mode and pulsed Xenon lamps in the ACTIVE mode.

DIAL (Differential Absorption Laser) (Def. 1): A system where two different wavelength continuous wave (cw) laser beams are passed through a cloud of gas along the same path to a solid beam return target. If one wavelength is selected to be at the absorption maximum of the gas of interest (L_1) and the second is at a nonabsorbing wavelength (L_2) then the differential absorbtion between the two returned beams is proportional to the amount of absorbing gas in the beam. Species quantification is possible if there are no interfering gases.

DIAL (Differential Absorption Lidar) (Def. 2): A DIAL system with pulsed lasers that allow ranging to the pollutant cloud. (These two terms are often interchanged in conversation and publication. Ranging capabilities are the main difference between cw laser systems and LIDAR systems.)

DOAS (Differential Optical Absorption Spectroscopy): An active remote sensing technique using primarily visible and near UV light where absorption spectra are generated for a long viewing path and compared to library spectra for various known gases. Species identification and quantification are possible with such a device. (Note: for a DOAS system spectra are compared as opposed to use of a pre-selected pair of discrete absorbing and nonabsorbing wavelengths.)

Dual Beam System: A system using two wavelengths of light selected so that one will be absorbed by a gas of interest and the second will not be absorbed. The difference in intensity of the returned signals can be used to compute the amount of gas in the beam's path. See DIAL, DOAS.

Emission Flux: The mass transport of a contaminant through a plane. This quantity is obtained by multiplying the measured PATH INTEGRATED CONCENTRATION by the wind velocity perpendicular to the beam's orientation and by an estimate of the plume's vertical spread or height. The final units are mass per second across a plane, e.g., $\mu g/m^2 \times m/sec$ (wind) $\times$ m (beam cross section) $= \mu g/sec$. See PLANE INTEGRATED MEASUREMENT.

Fingerprint Region: The region of an absorbtion spectrum, where distinguishing differences in ABSORBANCE can often be found that can be used by the ANALYTICAL SOFTWARE to analyze for the presence of specific species.

Flat Mirror: A conventional front surface mirror consisting of one planar surface used primarily to change the direction of a beam of electromagnetic energy (i.e., light) in a remote sensing system.

Folded Path System: A system that uses multiple reflection inside a sample cell to extend the analytical beam's path through the air being analyzed, usually used in POINT MONITORS.

FTIR (Fourier Transform Infrared): An analytical technique utilizing an INTERFEROMETER with moving and stationary mirrors to "transform" the spectral distribution of wavelengths in the IR into a form that can be mathematically converted to a conventional infrared intensity spectrum. By using an INTERFEROMETER there are no spectral losses due to dispersion through a prism or to reflection off of gratings and greater sensitivity is achieved as a result of the greater throughput of energy (*no slits are needed*). An FTIR achieves species specificity by comparing either INTERFEROGRAMS or ABSORBANCE spectra obtained in the field to comparable data developed in the laboratory for known compounds.

GASSPEC: A device similar to the COSPEC where sealed cells containing different concentrations of the gas of interest (instead of slit patterns) alternate in the beam of light passing through the atmosphere to create the differential signal used to indicate the presence of that same gas. These devices are one of a subset of generic gas filter correlation spectrometers which, in the CLOSED PATH mode, are used for cross-stack sampling or ambient measurements for CO, for example.

Imaging System: A device that converts reflected "light" to a visual image on a video screen or, in today's terminology, a video camera for detecting chemical clouds in the atmosphere. Usually the "light" is IR, either broad band or narrow band. Passive IR emission (e.g., hot objects), a specific IR source or IR laser beams can provide the illumination. The absence of a returned signal implies the presence of an absorbing gas. If the imaging system sends out a beam and scans a field of view it is an ACTIVE SYSTEM.

Infrared Spectrum: A display of infrared signal strength (I) as a function of wavenumber (cm^{-1}), or wavelength. The signal strength is expressed in ABSORBANCE or TRANSMITTANCE. ABSORBANCE is proportional to the product of the concentration of the absorbing gas times the pathlength of the IR beam. See BEERS LAW, PATH INTEGRATED CONCENTRATION, CONCENTRATION PATH LENGTH.

Interferogram: The optical signal produced by an INTERFEROMETER. The inverse transform of the interferogram is an INFRARED intensity SPECTRUM.

Interferometer: An optical device that splits a light beam (IR in the case of FTIR remote sensors) into two components. Within the interferometer, each component travels over a different distance and then the beams are recombined. Because of the path difference of the two separate beams, when they are combined the phase of one will have shifted with respect to the other. This phase shift depends on the wavelength. The path difference is modulated by moving a mirror used for one of the separated beams. This manipulation results in an INTERFEROGRAM (a plot of the combined signals versus the path difference). The major components of the device are the moving mirror, a fixed mirror, and the beamsplitter. See FTIR.

IR (Infrared): Low frequency electromagnetic radiation usually having a wave number range of 400 to 4,000 cm^{-1} i.e., a wavelength range of 2.5 to 25 μ. (μ = micron = 1 millionth of a meter)

Laser: Hardware: Source of very coherent monochromatic light used as analytical beams in some ACTIVE remote sensing systems. Lasers are also used for alignment of reflectors or for control of INTERFEROMETER mirror movement.

Technical: Light Amplification by Stimulated Emission of Radiation.

Lidar (Light Detection And Ranging): A pulsed laser system used like a radar system where the time of return of reflected light is detected and used to determine distance to the cloud of reflecting material or solid reflecting target. These systems are used in the DIAL mode. (The terms "lidar" is often misused in place of "laser" where no distance resolution is possible from a continuous laser beam or fixed targets.)

Light: The generic term for electromagnetic energy which may or may not be visible but can be absorbed or otherwise changed by gases in the atmosphere to indicate their presence.

Long Path Monitoring: Long path monitoring involves use of reflective surfaces to create an extended path length by multiple passes of light energy across the volume sampled. Typically this lengthening is accomplished in a closed "white cell" chamber. Often such "folded path" systems, even if open to the atmo-

Reprinted with permission from *Journal of the Air & Waste Management Association*, Vol. 41, No. 11, November 1991

sphere, are designed to provide a point concentration value rather than an average concentration on a long viewing line. See OPEN-PATH MONITORING. (It should be noted that the instruments that achieve "long paths" in closed chambers by using reflecting surfaces to repeatedly bounce the light beam across the small volume of the chamber often require pumped air flow to draw air through the chamber and are actually CLOSED PATH systems used as sophisticated POINT MONITORS.)

LPUV (Long Path Ultra Violet): LPUV is another name for a subset of the more general OPUV spectrometer technique. One current LPUV design obtains species identification by dispersing the UV light across a fixed array of small photodiode detectors and comparing the observed absorption patterns to a library of REFERENCE SPECTRA.

LSFIT Program: The ANALYTICAL SOFTWARE that calculates species concentrations by performing a least-squares *fit* between the sample and selected REFERENCE SPECTRA while simultaneously fitting a linear baseline over the selected spectral region. Some programs assume BEER'S LAW is valid while others use more complex calibration curves. The spectral region for the analysis of a particular species is generally chosen to minimize effects from interfering species. The compound of interest and all interfering compounds are included in an analysis.

$\mu g/m^2$: Alternate units to express PATH INTEGRATED CONCENTRATION or BURDEN indicating the amount of gas in the beam. If the cross sectional area of the beam of light is known, these units can be readily multiplied by that area to yield the total mass of gas in the beam.

Monostatic System: A REMOTE SENSING system having the light source and receiver co-located and often using the same optical system. The optical signal is usually returned by use of a RETROREFLECTOR at the far end of the observation path. (See Figure 1.)

Open Ended System: A REMOTE SENSING System, usually PASSIVE, that utilizes a target of opportunity in its field of view (or skylight) for its light source and the receiver processes the spectral information from that available source.

Open-Path Monitoring: REMOTE SENSING that utilizes a configuration where the extended path that the beam(s) traverse is fully open to the atmosphere so that plumes and/or clouds of pollutants move across the path under the influence of wind or diffusion. Usually open path monitors are used to define pollutant conditions along a site perimeter rather than at a point.

Optical Remote Sensing: A term used to describe REMOTE SENSING devices that operate using light energy ranging from the IR through the visible to the UV as opposed to microwave or radar techniques. (The variation of "Remote Optical Sensing" has been used in the Superfund community but has the same meaning.)

OPUV (Open Path Ultra Violet) Spectrometer: A remote sensing system that utilizes ultraviolet energy to detect the presence of atmospheric gases in the path of a beam of UV Light. Species identification is achieved by comparing observed absorption patterns to previously stored patterns obtained for known compounds and mixtures in a computer library—REFERENCE SPECTRA. OPUV systems are especially effective for aromatic compounds. See DOAS and LPUV.

Passive System: Any REMOTE SENSING system which uses uncontrolled light sources already present to indicate the presence of a substance. Examples are the COSPEC which utilizes sky light, an IR IMAGING SYSTEM which utilizes ambient heat or those FTIR systems which utilize natural IR emission by species of interest.

Path Averaged Concentration: This concentration is obtained either from a remote sensor measurement or from a physical sampling along the path of the remote sensor. In the first definition, the path average concentration can be obtained by dividing the remote sensor's reading of PATH INTEGRATED CONCENTRATION by the total path length traveled by the analyzing beam (e.g., 2x distance from sensor to RETROREFLECTOR) to give the AVERAGE CONCENTRATION per meter of the viewing path or OPEN PATH. Typical units are $\mu g/m^3$, ppm or ppb. In the second definition, the concentration of a compound captured in a sampling container (such as a stainless steel canister) that has been moved back and forth along the open path while continuously sampling the air to provide confirmatory/comparative air quality data. Typical units are $\mu g/m^3$, ppm or ppb. If the meteorology can be assumed to be constant during this physical sampling, then multiplying these values by the "path length" can approximate a path-integrated concentration obtained from a remote sensor.

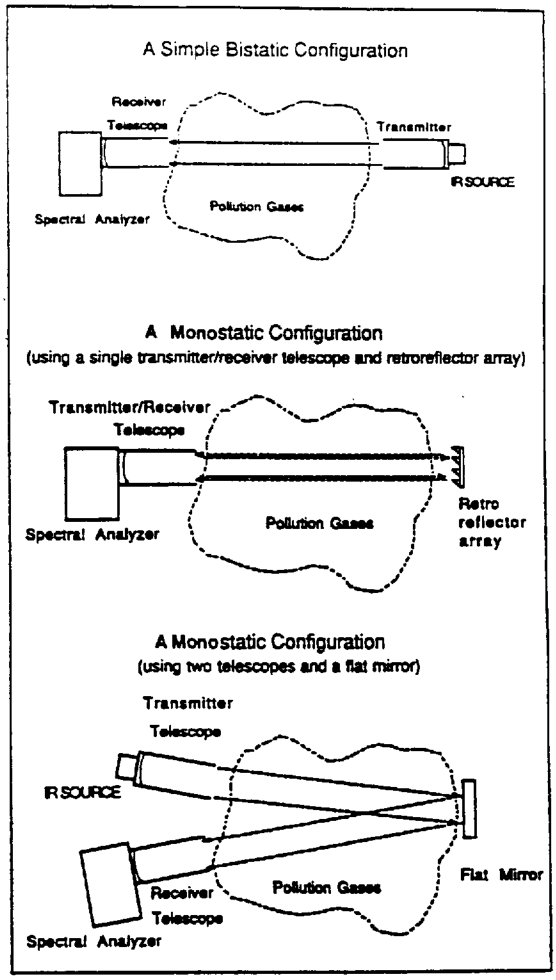

Figure 1. Example of single- and double-ended configuration of remote sensing systems. (Courtesy of Orman Simpson, MDA Scientific.)

Path Integrated Concentration (PIC): The product of a gaseous concentration and the length of the light path through the gas. This product is proportional to the total amount of gas within the beam and is not affected by the relative distribution of the gas (see Figures 2 and 3).

In BEER'S LAW the path integrated concentration corresponds to the product of the mass per unit volume concentration and the cell length terms. With air this Beer's Law product will always be in units of either $\mu g/m^2$, mg/m^2, or $moles/m^2$ although with information on temperature and pressure, these units can be converted to units of ppb-m and ppm-m. Also, when measurements are made directly in $\mu g/m^2$, source emission calculations are more straight forward (see EMISSION FLUX).

Note: ppm-m and ppb-m units are volumetric or mole ratios. Consequently, measurements in these concentrations units are not governed solely by Beer's Law. With open-path optical

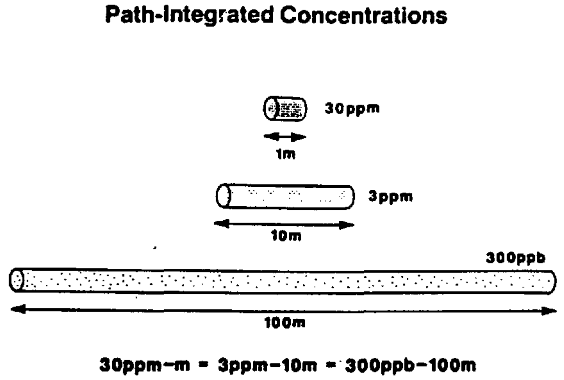

Figure 2. The same path integrated concentration would be measured for each of the distributions shown above. (Courtesy of Tim Minnich; Blasland, Bouck & Lee.)

measurements all conversions from $\mu g/m^2$ or mg/m^2, to ppb-m or ppm-m can be performed using the following conversion:

$$\text{ppm-m}_{\text{amb}} = \text{PIC}(\mu g/m^2) \times \frac{0.02445}{\text{MW of gas}} \times \frac{760\ (\text{mmHg})}{\text{P(mmHg)}} \times \frac{\text{T(°K)}}{298\ \text{°K}}$$

Where ppm-m_{amb} indicates the validity of the conversion to ambient conditions T and P different from 298°K and 760 mmHg during the actual measurement. See BURDEN, CONCENTRATION PATH LENGTH, and REFERENCE SPECTRA.

Plane Integrated Measurement: These measurements are made by characterizing the PIC at different viewing paths through a plume. The resulting information is directly proportional to the flux of pollutants through the measured plane and, when multiplied by the appropriate wind information, can yield the pollutant emission rate through that plane.

This measurement can be achieved using multiple REMOTE SENSING systems viewing either different heights in a horizontally moving plume or different horizontal cross sections of a vertically moving plume (e.g., roof exhausts). This measurement can also be achieved by using mirrors to direct the beam from a single remote sensing system to different viewing paths. (See Figure 4 for a schematic for a plane integrated measurement of a horizontally moving plume.)

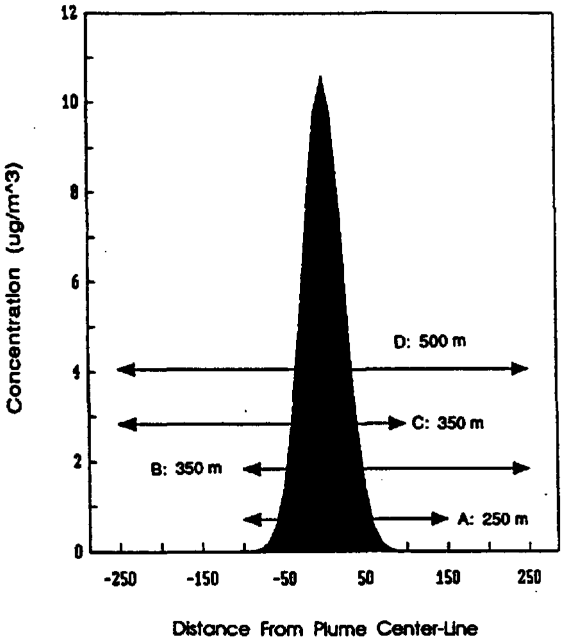

Figure 3. A given plume that is fully contained within the beam of a remote sensing system will produce the same path integrated concentration signal no matter what the length of the beam (A, B, C, or D) or relative position of the plume. That is, all four plotted beams (A through D) will produce the same measured output of 1.33 mg/m² for this example. (Courtesy of Tom Pritchett; EPA Environmental Response Team.)

Point Monitor: A monitoring instrument that provides information on gas concentration at one point in space—the instrument's inlet—as opposed to information integrated along a line in the ambient air. See REMOTE SENSING.

ppm-m (Parts Per Million-Meters): One of the units for the parameter measured by REMOTE SENSING SYSTEMS. See PATH INTEGRATED CONCENTRATION, BEER'S LAW, BURDEN.

Real Time Systems: An analytical device which gives timely readout of changing levels of a substance of interest as opposed to obtaining similar information (with no time resolution) after a sample has been gathered, transported to a laboratory and then analyzed.

Reference Spectra: A set of spectra of various compounds measured at known pathlength, temperature and pressure. These REFERENCE SPECTRA are measured at a central laboratory. The spectra are obtained using samples obtained from various chemical companies. The REFERENCE SPECTRA from a "spectral library" are stored as a data-base to be used in analyzing the field spectra from REMOTE SENSING SYSTEMS.

Remote Monitoring: A term used in conjunction with three different monitoring approaches. (1) Use of *true remote sensors* to monitor changing pollutant concentration. (2) Use of a network of individual analytical devices at *remote locations* and controlled by a central computer system to monitor changes in pollutant concentrations. (3) Use of a REMOTE SAMPLING network.

Remote Optical Sensing: See OPTICAL REMOTE SENSING.

Remote Sampling: Use of a network of sampling points remote from a central facility to gather gas samples and bring them to a central analyzer. If the sampling is done by long sample lines and vacuum pumps bringing the sample to a central analyzer, it is a quasi-real time system. If at the remote locations there are sampling canisters whose inlets are controlled by a central controller it is a remotely controlled integrated sampling network.

Remote Sensing: The measurement of the presence of gases, solids and liquid in-situ using the physical properties of the substance to cause attenuation in or reflection of beams of electromagnetic energy—without taking a sample into a chamber in a laboratory instrument. Since changes can be readily detected and measured, these systems are basically REAL TIME systems. See OPEN-PATH MONITORING.

Resolution: The minimum wavelength data intervals used by a given instrument for separating details from one another in absorption spectra. The narrower the resolution, the more spectral details can be evaluated. See BANDWIDTH.

Retroreflector: A special arrangement of front surfaced mirrors in three perpendicular planes that look like the inside corner of a cube and has the property that any beam of light entering it will be returned exactly along its incident path back to the source.

Search Program: A computer program that matches spectral line peak locations in a sample spectrum with peak locations stored in a library of REFERENCE SPECTRA for the purpose of compound identification. For an FTIR system one program operates

Reprinted with permission from *Journal of the Air & Waste Management Association,* Vol. 41, No. 11, November 1991

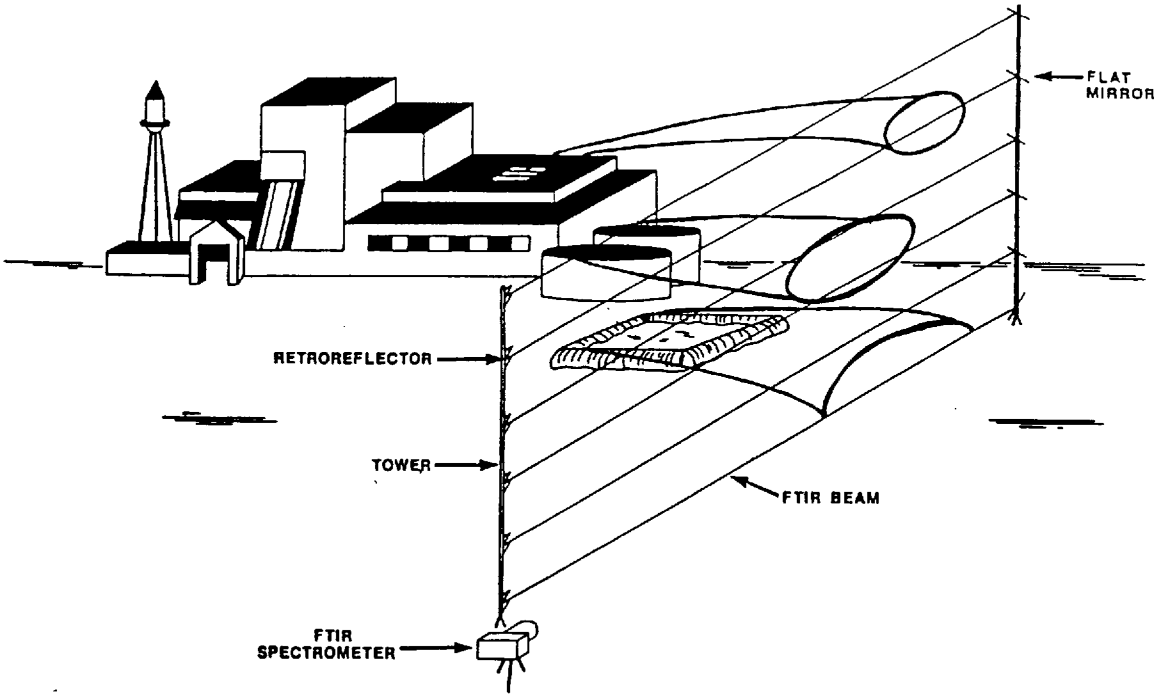

Figure 4. A possible set-up to achieve multiple viewing paths from a single remote sensing system to achieve a plane integrated measurement. (Courtesy of Tim Minnich; Blasland, Bouck & Lee.)

in the following manner: a cm^{-1} peak value from the sample spectrum is entered or transferred from the operating program, and the program immediately prints out all compound names that have a peak within a preset interval around the input cm^{-1}. Visual inspection by the operator of the sample and indicated references finalizes the identification. (Automated techniques are under development to iteratively identify absorbing components in a mixture.)

Spectral Subtraction: A manual technique to analyze complex mixtures of contaminants. First, an identified and quantified component has its spectrum subtracted from the mixture's spectrum. The residual spectrum can then be evaluated for other components whose spectra can be sequentially subtracted until, ideally, the residual spectrum shows no absorption pattern, indicating all components have been identified and quantified.

Source For FTIR: A black body light source providing infrared energy at a brightness temperature of about 1300 K, usually a simple restive glow bar gas igniter or Nerst glower.

Unistatic: A REMOTE SENSING system that has all its active, controlled components at one end of the viewing path as opposed to a BISTATIC SYSTEM. Same as MONOSTATIC. (See Figure 1.)

Water Interference: The limitations imposed on REMOTE SENSING techniques (primarily FTIR) operating in the OPEN-PATH mode due to the presence of water vapor in the atmosphere.

Wave Number: Inverse of wavelength expressed as the number of waves per unit length; wavenumber (cm^{-1}) = 10,000/wavelength (microns).

W.M. Vaughan is chair of the EM-6 committee and president of Environmental Solutions, Inc., PO Box 11323, St. Louis, MO 63105.

Reprinted with permission from *Journal of the Air & Waste Management Association*, Vol. 41, No. 11, November 1991

Appendix C

REVIEW OF OPTICAL REMOTE SENSING STUDIES
REFINERY-RELATED COMPOUNDS

Appendix C

REVIEW OF OPTICAL REMOTE SENSING STUDIES REFINERY-RELATED COMPOUNDS

Because of the potential advantages of ORS systems over conventional methods for detecting and measuring air quality parameters of interest to the petroleum industry, several remote sensor studies at refineries and petrochemical plants have been conducted recently. Some of these studies were designed to demonstrate the ability of remote sensors to detect the variety of fugitive vapors expected from these facilities. Others were aimed at estimating mass emission rates by combining meteorological measurements with remote sensing data and atmospheric tracer releases. The studies reviewed below touch on many of the issues crucial to the API feasibility study.

Additional remote sensing studies have been carried out to address compounds of interest to the petroleum industry but not necessarily in a refinery or petrochemical setting. Such remote sensor studies which primarily address monitoring of the BTEX compounds are discussed following the review of the refinery and petrochemical site studies.

STUDIES IN A REFINERY OR PETROCHEMICAL PLANT SETTING

Several studies were performed in a refinery or petrochemical setting between 1988 and 1992. Discussions of these studies follow in chronological order and are summarized in Table C-1.

Hisingen Study

The Gothenburg Environmental Project commissioned a study to estimate the total hydrocarbon emissions from the refineries in the Hisingen district of Gothenburg (Indic, 1988). The British Petroleum (BP) and the Shell refineries were monitored during the study (May to July 1988). Indic AB (Indic) served as the consulting firm for the modeling aspect of the study and Opsis manufactured the DOAS system used in the study.

Table C-1. ORS Systems Used in Studies in Refinery or Petrochemical Settings

STUDY	DATE OF STUDY	ORS SYSTEM(S)	EMISSIONS CALCULATIONS
Hisingen (Indic, 1988)	1988	DOAS	Yes
Gothenburg (Woods, 1992b)	1988, 1989	IR-DIAL	Yes
Wastewater Impoundments (Indaco, 1990)	1989	FTIR and OPUV	Yes
Land Farm (Lupo, *et al.*, 1991)	1991	FTIR and OPUV	No
Tank Truck Loading Area (Milton, *et al.*, 1992)	1991	UV-DIAL	No
Exxon Chemical Americas (Spellicy, *et al.*, 1992)	1991	FTIR and DOAS	No
Shell Deer Park (Thomas, *et al.*, 1992)	1992	FTIR	No

Source: **RS≡A**, 1993

The study plan was to determine the emission rates of the hydrocarbon and aromatic compounds using DOAS measurements and the tenax tube measurements along with the Indic methods. Target compounds for the DOAS system included the aromatic compounds toluene, benzene, and styrene as well as several non-aromatic compounds. Point sampling using tenax tubes was planned for benzene, toluene, xylene (BTX) as well as for styrene and other compounds.

To allow for calculation of emission rates, Indic developed two methods for estimating refinery emissions based on DOAS measurements and meteorological data (Gidhagen, 1992a). These methods, the *classification method* and the *relational method*, are described below:

> The *classification method* takes advantage of two DOAS viewing paths. From the archived meteorological data, the wind and

> DOAS measurements are "classified" into upwind and downwind sets. After correcting for "an exponential decay (Gaussian) between the refinery and the downwind measurement" beam, a subtraction approach yields refinery emission estimates.
>
> The *relational method* uses a computer simulation of the refinery source areas combined with the assumption that the "contribution from surrounding and/or distant sources yields a constant background concentration." Using an assumed 100 g/s emission rate, the impact of the emissions from the refinery on the DOAS beam is simulated by dispersion modeling. The measurement results are then scaled to match the simulated pattern with that scaling factor then used as a multiplier of the 100 g/s to obtain the emissions estimate.

Dispersion parameters were calculated based on "a previous tracer study at a nearby town." Meteorological data were taken from meteorological towers located at several locations around the Hisingen complex as well as from a meteorological tower located at the nearby town of Risholmen.

Although the study failed to acquire sufficient data to allow computation of total hydrocarbon emissions from either refinery, the authors did report emissions of two specific compounds from the Shell refinery: toluene and p-xylene. While emission rates for these compounds were reported, there was no indication of MDLs for any of the compounds measured by the DOAS system nor comparisons between the point concentrations of toluene and p-xylene determined by the sorbent tube measurements and the path averaged concentrations determined by the DOAS system.

Toluene emissions from the Shell refinery were calculated from DOAS measurements using the *relational method* only since the upwind toluene concentrations appeared to be impacted by a local source. The residual background was apparently ignored in the relational calculations since Indic could not prove the background was constant (Gidhagen, 1992b). The results were 12.5 g/s ± 3.1 g/s (32.4 tons/month ± 8.1 tons/month) for toluene.

Calculations using the *classification method* were made for the Shell facility using one viewing path across the northeast (NE) boundary and one across the southwest (SW) boundary of the facility. The data sets with winds generally from the NE were assumed to bring background air to the NE DOAS beam and refinery plus background air to the SW beam. Similarly, winds out of the SW were assumed to reverse the roles of the two observing beams and allow refinery-specific emissions estimates. Upwind toluene concentrations appeared to be impacted by a local source; thus, no emission rate determinations were made for toluene using this method. The p-xylene rates were calculated to be 4 g/s using the classification method and 5.5 g/s using the relational method. Both rate calculations had an unknown uncertainty due to questions about the p-xylene determinations. It is unclear whether the calculations were performed using p-xylene data from the sorbent tube data or the DOAS measurements.

The overall goal of the study, to estimate the total hydrocarbon emissions from the refineries in the Hisingen district, was not accomplished. Total hydrocarbon emission rates were not determined; however, the rates for the two compounds (toluene and p-xylene) were calculated for one of the two refineries. Some of the problems of this early study seem to have been overcome in later studies. Hans Hallstadius of Opsis, Inc. (Hallstadius, 1992) indicates that aromatic compounds can be readily measured by their DOAS unit as indicated in later urban studies (Lofgren and Ramnas, 1991; Stevens and Vossler, 1991; Axelsson, *et al.*, 1991) discussed below although no more recent refinery studies have been performed. In addition to possible improvements in the DOAS system, the urban results may result from the fact that the urban and vehicular emissions are often released at levels below those of the instrument path while, for the refinery setting, the plumes may have lofted over the beam resulting in levels that could not be detected.

Gothenburg Study

Another study was conducted during July 1989 at the BP refinery in the Hisingen district of Gothenburg, Sweden (Woods, 1992a). This 1989 work followed up a 1988 measurement effort with a less sophisticated DIAL system. The 1988 study appears to have been performed during the same time frame as the study of refineries in the Hisingen district commissioned by the Gothenburg Environmental Project, discussed above (Indic, 1988). In this 1989 study, a DIAL system, developed by the NPL, was operated to determine "fugitive hydrocarbon fluxes" for four areas within the refinery - the central process area, product tank farm, wastewater treatment area and crude tank farm. The DIAL measurements were supplemented by sorbent tube sampling that gathered time-averaged samples for analysis of C_3 - C_{10} hydrocarbons at regular intervals along the downwind side of an area and at one to two locations on the upwind side.

The DIAL system was operated in the infrared (IR) mode scanning several unstated wavelengths in a region used for general hydrocarbon detection. DIAL determinations of total non-methane hydrocarbon measurements established by tuning the instrument to regions of hydrocarbon absorption and separate toluene measurements were reported for this 1989 Gothenburg study. The study planned to use the sorbent tube values for the aromatic BTX compounds to determine a ratio of the individual BTX species and then ratio the DIAL toluene readings to calculate aromatic compound fluxes. Estimates of total aromatic emissions were then extrapolated from the DIAL toluene measurements and the ground level sorbent tube data.

The DIAL trailer was located at a variety of positions on the perimeter of the various areas to scan through the fugitive emissions plumes. To improve on the 1988 measurement program, NPL supplemented the data from its extendible meteorological tower mounted on the DIAL trailer by installing several smaller meteorological stations and a tethered balloon with wind speed and direction capability to document the wind conditions in more detail. Thus, the researchers could determine the transport conditions for each of their DIAL cross-plume measurement sets. Emission fluxes were calculated for each of the areas. For the floating roof storage tanks, the emissions fluxes were compared to API 2517 evaporative losses and found to be appreciably higher. The lower values calculated using API 2517 were thought to be due to underestimating the temperature of the stored product nearest the roof which would have been heated by the sun during the day (Woods, 1992a).

Total hydrocarbon fluxes were determined and plotted against time for each of the four areas studied. Discussions attempted correlations of operations with the temporal variation in these emission fluxes; however, correlations were not possible for all areas. The fluctuations from the crude tank farm were suggested to be associated with "thermal effects and wind swirl effects in floating roof tanks that are not full...(causing)...'gulps' of emissions."

Toluene fluxes were reported in only 40% of the cases where hydrocarbon fluxes could be determined. No explanation of the lack of toluene data was given except that toluene measurements were possible only on certain days. Sorbent tube aromatic data appeared to be available only for the same days as the toluene flux data (apparently from the DIAL system). No correlations between the DIAL and sorbent tube values for toluene were reported, and it was unclear what concentrations of other aromatic compounds or non-methane hydrocarbons were obtained using the sorbent tubes. Benzene was detected by sorbent tube sampling above the lower benzene detection limit of 5 ppb only downwind of the Water Treatment Area. Throughout this un-reviewed study there is no reporting of detection limits for the DIAL measurements and no detailed evaluation of the flux uncertainties. While total hydrocarbon fluxes are calculated, their uncertainties may be large and the compounds included as total hydrocarbons in this measurement is really undefined.

From the atmospheric backscatter signals, the DIAL system is able to indicate the height and contour of the general hydrocarbon plume in the optical path (see Figure C-1 for an example). Such information provides insights on plume lofting, dispersion, etc. and whether Gaussian plume assumptions hold. The 1989 measurements showed maximum plume heights of about 80 meters for the crude tank farm, 50 meters for the central process area, and 45 meters for the water treatment area. These results were expected. However, combined with the observation of the non-Gaussian shape of the plumes, they raise the question of the practical limits on interpretation of remote sensing data from a single beam height relatively close to the ground using Gaussian models for dispersion assumptions.

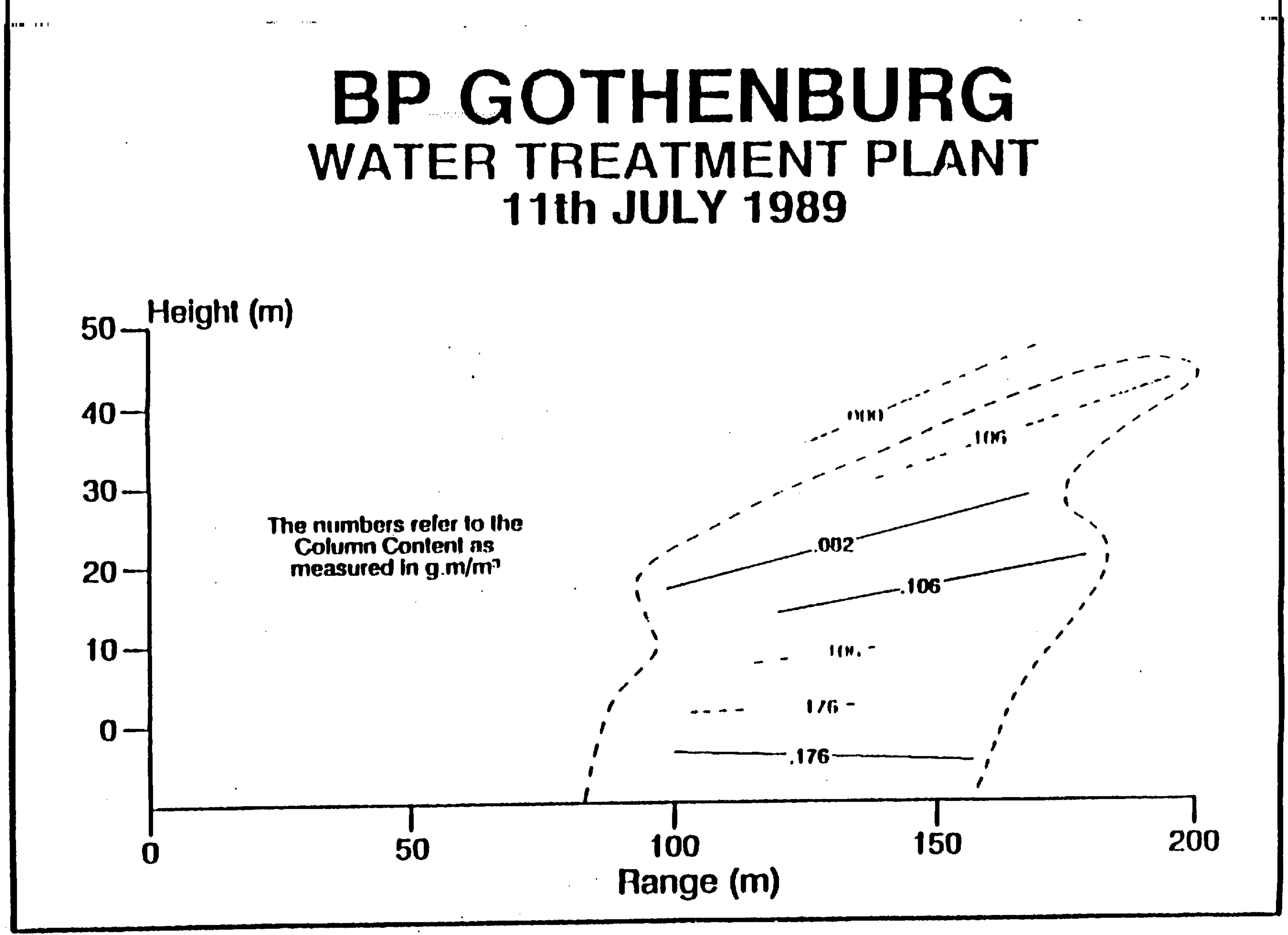

Figure C-1. Example of cross-plume scans from a DIAL system downwind of one process area. Note the non-Gaussian shape and ability of DIAL to document plume height, etc. (Note: Original had poor type quality for numbers.)

Wastewater Impoundments

The University of Denver and Indaco Air Quality Services carried out a study of BTEX emissions from refinery wastewater impoundments during 1989 (Indaco, 1990; McLaren and Stedman, 1990). This study involved a combination of sulfur hexafluoride (SF_6) tracer gas release, whole air canister sampling and simultaneous measurements of BTEX compounds by OPUV and SF_6 by FTIR. The FTIR measurements of the SF_6 were to be used in the determination of the emission rates. In the McLaren and Stedman paper (McLaren and Stedman, 1990) the systems are referred to as LPIR and LPUV but are equivalent to the open path FTIR and OPUV used in this report; both systems used are not commercially available at this time. The impoundment studied was a "phenolic equalization basin."

One set of data from the SUMMA® air sample canisters could be directly compared to the ORS data. That set showed good comparison of emission rates calculated from the canister data, 7.6 g/min of benzene and 26.4 g/min of toluene, compared to 5.5 g/min and 28.0 g/min respectively calculated from the OPUV data. The concentrations of ethylbenzene and o-xylene were typically below the detection limits of 20 ppm-m and 30 ppm-m respectively for the OPUV; so, no emission calculations could be based on detected levels.

In moving the OPUV so that the beam was upwind of the API separator, the University of Denver observed a marked decrease in the signal. They concluded "that during periods of high BTEX emissions, most of the emissions appeared to be coming from the 'API separator' adjacent to the holding pond."

The ORS data (OPUV and FTIR) were compared to the predictions of the CHEMDAT7 air emissions model. The study concluded that the model generally overpredicted the emissions by at least a factor of three and sometimes by more than an order of magnitude.

This Denver study indicates that the OPUV system can determine path-averaged concentrations of benzene and toluene at low levels that are comparable to the SUMMA® canister results and that variations in the signal can be correlated with site sources. The report also suggests that more work is needed to determine the proper models for refinery settings.

Land Farm Study

As part of a land ban evaluation for off-site migration of air toxics, optical remote sensors (OPUV and FTIR) were used with tenax sorbent tube sampling to document air quality at the perimeter of a land farm operation (Lupo, *et al.* 1991). The three methods provided a unique opportunity for intercomparison and confirmation. Because of the continuous nature of the ORS measurements, temporal variation in emissions could be linked to site activities such as unloading and tilling. While isolation flux chamber measurements were used periodically on-site, there was no discussion in this paper of those findings or their relation to the ORS emission determinations.

The FTIR system readily detected toluene and xylene during the study but was unable to detect the benzene and ethylbenzene. The levels of the latter compounds indicated by the OPUV sampling were below the MDLs for the FTIR. The point sampling using the tenax sorbent tubes at the plume centerline indicated levels barely above the FTIR MDLs at the point that maximum concentration was expected. Hence, the path-averaged concentrations for benzene and ethylbenzene over the 36-65 meter path length of the beam would have been below their respective MDLs for the FTIR (benzene: ~20 ppm-m; ethylbenzene: ~15 ppm-m).

The FTIR also measured hexane to be used as a surrogate to model aliphatic hydrocarbon levels and to determine relative BTEX levels when individual levels were below the FTIR MDLs. The hexane data was also used to show the dependence of the emissions on the soil temperature.

The OPUV detected the BTX compounds, but it did not detect ethylbenzene because of its poor UV absorption. The OPUV system MDL for benzene in this study was 3 ppm-m for the 36-65 meter optical paths, 20 ppm-m for ethylbenzene, 2 to 3 ppm-m for m- and p-xylene, and 30 ppm-m for o-xylene.

The xylenes (probably only m- and p-xylene since the o-xylene MDL is a factor of 10 higher) and toluene were the primary vapors detected in the plume at the edge of the landfill. This pattern is consistent with the composition of the waste being dumped. None of the less volatile compounds of the refinery waste, such as naphthalene, were detected in any of the spectra even though they were known to be present in the waste.

This land farm study was not set up to provide a rigorous inter-method comparison. However, it was able to show the relative merits of the ORS techniques when compared to tenax sorbent tube sampling. Because of the ability to provide temporal resolution of the data, the ORS systems were able to account for the effect of the nearby refinery on the upwind spectra. This ability demonstrated the need to either plan data collection to avoid that problem or take care in interpreting the data where background impact may vary as well. The primary advantage of the ORS techniques was their ability to examine the temporal variation in downwind measurements in relation to site activity and upwind measurements in relation to non-site sources. It was also noted that the ORS data were less costly and less labor intensive to gather than the point sampling using tenax tubes.

Tank Truck Loading Area Study

In 1991, NPL conducted a small measurement program with their UV-DIAL unit at a tank truck loading area (Milton, *et al.* 1992). The purpose of the program was to demonstrate the ability of NPL's UV-DIAL system to monitor the concentration profile of toluene leaving this loading facility. The UV-DIAL system used in this study is similar to the unit used for the Gothenburg study discussed earlier, except that this detector was a UV system rather than the IR used in the earlier study. The UV-DIAL system appears to achieve lower MDLs than the earlier IR version. The instrument was able to determine the toluene concentration profiles in the downwind plume with about 12 meter spatial resolution along each line of sight.

The detection limit for toluene along these lines of sight was reported at about 10 ppb with the primary compounds causing interference in the detection of toluene for their system being p-xylene and ozone. The study indicates that benzene can be measured with the NPL UV-

DIAL if care is taken to avoid the spectral lines where oxygen also absorbs; however, no data are reported for this compound. The Milton paper also refers to NPL's UV-DIAL measurements for toluene at a chemical plant which were used to calculate fugitive emission losses. This latter work is apparently unpublished but would be directly related to refinery fugitive emission determinations.

This study leaves open the question as to why benzene was not determined during the study. Was it because of its inability to avoid the spectral lines where oxygen also absorbs? The results from the study do indicate that toluene concentration profiles can be determined using the UV-DIAL. Such profiles can be used to determine emission fluxes including the unpublished emission fluxes determined by NPL at a chemical plant. These studies suggest that the UV-DIAL could be used to determine emission fluxes of toluene at refinery sites as well as to determine the plume shape and extent.

Exxon Chemical Americas Study

During the spring of 1991, Radian Corporation operated two open-path ORS systems along the fenceline of the Exxon Chemical Americas facility in Baytown, Texas (Radian, 1991b; Spellicy, *et al.*, 1992). This measurement program was termed a "technology demonstration program" and was designed to show the feasibility of ORS systems as "alternative measurement technologies" for meeting some of the requirements of the Clean Air Act Amendments (CAAA) of 1990. Radian used an FTIR unit and an DOAS unit in conjunction with measurements taken at one of the non-profit Houston Regional Monitoring Corporation (HRM) sites. As described in the report, "the demonstration was limited to evaluating the ability of these devices to measure constituents in the ambient air."

This demonstration program showed that the FTIR and DOAS systems were capable of making routine perimeter measurements at a petrochemical facility. The modified Nicolet FTIR system unit had 0.5 cm^{-1} (wavenumber) resolution and detected some 20 compounds. These included benzene and m-xylene, which are among the compounds of primary interest as fugitive emissions for this evaluation.

A DOAS system was set up in the bistatic mode to monitor air quality along two different light paths. While there are fewer compounds that can be detected by this DOAS system, it is optimal for detecting aromatic hydrocarbon compounds such as the BTX compounds. The DOAS system consistently detected the BTX compounds during the demonstration program. The detection limit for benzene for the DOAS system was reported at 0.76 ppm-m (which translates to a path-averaged concentration of 1.6 ppb for a 500 m total path length) compared to the FTIR detection limit of 12.5 to 15 ppm-m (which translates to a path-averaged concentration of 25 to 30 ppb for a 500 meter total path length).

This 1991 program demonstrated the capability of commercially available optical remote sensing instruments to operate in a stand-alone mode for extended periods. While there was no attempt to determine mass flux across these beams, such limited emissions determinations could well have been accomplished with available meteorological data.

Shell Deer Park Study

In January 1992, there was a joint study by EPA Regions VI and VII to determine if FTIR optical remote sensing equipment could detect volatile organic emissions (including aromatic and non-aromatic compounds) from the Shell Deer Park facility in Texas. There was no intention of determining emission rates. The remote sensing equipment was developed, provided and operated for EPA by staff from Kansas State University's (KSU's) Chemistry Department. A report of this measurement program was prepared by EPA Region VII (Thomas, *et al.* 1992).

The FTIR system used was equipped with a 20-inch diameter optical system. These optics are larger than most commercial systems, have a greater energy throughput, and can thus achieve lower detection limits. The study had a target list of eleven compounds (see Table C-2) but only xylene was detected from this list. The target list was determined by the plant's reported releases, rather than a prior set of grab samples. The FTIR ultimately identified several non-target compounds as well, all of which are listed in Table C-3.

In addition to occasional background measurements "upwind" of the facility, attempts were made to characterize the fugitive emissions from the following process areas:

Ship Transfer	Aromatic Units
Vinyl Chloride Unit	Wastewater Treatment Units
Olefin Unit	Hex/Glycol Formulation Unit

During the limited, weeklong measurement program, there were indications of vinyl acetate being transported from beyond the facility by the wind and widespread low concentrations of ethylene, a basic feedstock at the facility. Other non-target compounds found in the facility were related to specific processes. The cleaning solvent 1,1,1-trichloroethane was detected and eventually linked to maintenance activity within one of the hex/glycol units.

The only target compound detected was o-xylene downwind of the hex/glycol units. None of the target compounds were detected in the vicinity of the aromatic units.

This study indicates that FTIR systems can be used to determine fugitive emissions in a refinery setting. The system was able to determine compounds being transported to the facility as well as indicate compounds with widespread concentrations. Because there is no indication from Shell, EPA or KSU personnel that any point sampling was conducted during this measurement period that would corroborate or refute these ORS findings, there is no way to know whether target compounds that were not detected were actually present but at concentrations below the FTIR MDLs.

MEASUREMENTS OF REFINERY-RELATED COMPOUNDS BY ORS

Studies of refinery-related compounds have been made in non-refinery settings using the ORS systems discussed above. The following reviews are organized according to ORS system used in the study and then chronologically.

Table C-2. Target Compounds for the Shell Deer Park Study.

Compound	MDL (ppb)	Compound Was Detected
Benzene	10	No
1,3-Butadiene	~20	No
Carbon tetrachloride	1.7	No
Chloroform	4.3	No
Cumene	~50	No
1,2-Dichloroethane	4	No
Epichlorhydrin	~45	No
Hydrogen cyanide	4	No
Methyl methacrylate	~25	No
Toluene	30	No
Xylene	30	Yes

Note that path average detection limits in ppb are for a total optical path length of 100 meters.

Source: Thomas, *et al.*, 1992

Table C-3. Non-Target Compounds Detected During the Shell Deer Park Study.

Compound	MDL (ppb)	Compound Was Detected
Acetone	17.4	Yes
Ethylene	1.8	Yes
Methanol	5.0	Yes
Methyl ethyl ketone	24	Yes
Propylene	8.8	Yes
Tetrachloroethylene	5.8	Yes
1,1,1-Trichloroethane	2.8	Yes
Vinyl acetate	8.5	Yes

Note that path average detection limits in ppb are for a total optical path length of 100 meters.

Source: Thomas, *et al.*, 1992

DOAS Studies

Since 1989, several measurement programs have been carried out in Europe and one in the United States using the Opsis DOAS system to monitor ambient air in urban areas. Several of the compounds targeted were the aromatics of interest to this study.

Sweden/Switzerland Traffic Study. The Chalmers University of Technology's Department of Chemical Environmental Science in Sweden carried out measurements in Sweden and Switzerland to track urban ambient air levels of benzene and toluene. The compounds were measured with an Opsis DOAS system along path lengths from 200 to 600 meters. The lowest path average detection level for each compound was determined to be 10 $\mu g/m^3$ [2.4 to 2.8 ppb] with measurements ranging from 10 to 20 $\mu g/m^3$ ±3 $\mu g/m^3$ [2.8 to 5.7 ppb ± 0.9 ppb] for benzene and from 10 to 40 $\mu g/m^3$ ±5 $\mu g/m^3$ [2.4 to 9.7 ppb ± 1.2 ppb] for toluene. The concentrations in ppb have been calculated assuming that the measurements were done at standard temperature and pressure.

During these 1989 studies, benzene and toluene concentrations increased with increased vehicular traffic flow. Lofgren and Ramnas concluded that "the hydrocarbons determined originated mainly from traffic exhaust" (Lofgren and Ramnas, 1991). This conclusion suggests that fugitive emissions from automobiles on nearby parking lots and highways must be accounted for in determining refinery contributions to downwind concentrations.

Atlanta Study. In July and August of 1990, the EPA used a DOAS instrument to evaluate volatile organic compounds and ozone as part of a larger EPA study in Atlanta, Georgia (Stevens and Vossler, 1991). Monitored compounds included the BTX compounds.

This DOAS system was set up to measure three different path lengths simultaneously. Three pathlengths were used, 1,099 m, 1,824 m, and 143 m with three different light sources and receivers tied into one computer. The BTX compounds were measured over the two longer path lengths in the 240-310 nm wavelength range. In order to compare the DOAS data with conventional data a gas chromatograph (GC) point monitoring station was located at the common point of the three paths. The correlation between DOAS and GC data from this study are presented in Table C-4. The correlation coefficients for benzene and o-xylene are reasonably good and are consistent. The low correlation coefficients for toluene were explained as being due to a local source of toluene near the end of the sampling array where the GC point sampler was positioned. Because the GC data showed spikes of toluene at certain times, these data points were removed from the averaging to avoid biased results. However, it appears that the GC data for toluene is biased lower than the DOAS concentrations because the toluene plume could well be crossing the DOAS beams and influencing those readings while missing the point monitor.

Table C-4: Comparative Results from Atlanta Study

COMPOUND	PATH #	DOAS PATH-AVG (ug/m^3) [ppb]	POINT CONC. (ug/m^3) [ppb]	CORR COEF GC vs DOAS
Benzene	1	7.4 [2.1]	4.5 [1.3]	0.65
	2	8.3 [2.4]	3.7 [1.1]	0.68
Toluene	1	13.9 [3.4]	12.2 [3.0]	0.17
	2	20.1 [4.9]	12.2 [3.0]	0.12
o-Xylene	1	4.2 [0.9]	6.9 [1.5]	0.63
	2	5.0 [1.1]	5.2 [1.1]	0.68

Note that concentrations have been converted to ppb assuming standard temperature and pressure at the time of measurement.

Source: Stevens and Vossler, 1991

Path 2 went over a major highway, accounting for the increase in BTX compounds in the results; benzene levels were increased by an average of 1 μg/m^3 [0.3 ppb]. This observation again points up the necessity of accounting for nearby parking lots and highways when measuring BTX levels at a refinery site.

From this study, it was discovered that each DOAS instrument is very task/site specific. Each ambient air spectrum is divided by a pre-recorded system reference spectrum to eliminate wavelength dependency of the xenon lamp and other system optics. The reference spectrum must vary from instrument-to-instrument to account for various lamp and optics properties. Also, pre-recorded differential cross-section curves for interferences must be stored in the computer for interference classification. Since different sites will certainly have different interfering chemical species, all possible interfering species must be known before the system is ordered.

This study points up the ability of the DOAS system to determine BTX compounds at relatively low concentrations. The correlation with the GC data was reasonable for the benzene and o-xylene, although the benzene results for the DOAS were about twice those for the GC. The study reinforced the need for determining and compensating for vehicular contributions to BTX measurements.

Volvo - Gothenburg Study

In 1991, the Swedish Environmental Research Institute (IVL) conducted a study at the paint shop at the Volvo factory in Gothenburg, Sweden using a DOAS system (Axelsson, *et al.* 1991). The project objectives included the study of spectral interference between different aromatics, O_2, and O_3, and the study of the differential absorption characteristics of various aromatic hydrocarbons.

Target compounds included the entire BTEX group as well as several other benzene derivatives. Due to unspecified limitations in the DOAS system's software at the time, only six of the target compounds could be monitored. These included:

p-xylene
m-xylene
toluene
ethylbenzene
1,2,3-trimethylbenzene
1,2,4-trimethylbenzene.

Benzene was not one of the compounds that could be measured. Axelsson notes that the benzene UV absorption spectra is almost totally overlapped by O_2 interference, as are the spectra of many of the other aromatics. To help counter this, a "zero-spectrum" reference was taken at night while there was no activity at the paint shop. Since O_2 is constant, the "zero-spectrum" background was used to ratio each measurement spectrum. However, this approach has the drawback that, for each species present, there is a fixed negative offset that will affect later measurements. Also, variations in atmospheric pressure adversely affect the quality of the O_2 compensation in the background spectrum. This Volvo plant is just north of the BP Gothenburg refinery and northwest of the Shell Hisingen refinery discussed above. However, no mention is made of the interference from or observation of plumes from these facilities or their impact on the "zero-spectrum."

While MDLs were not reported for any of the compounds, Axelsson states that "the differential absorption cross sections for the studied aromatics are strong enough to allow measurements down to the 1 to 10 $\mu g/m^3$ range " (Axelsson, *et al.* 1991). These MDLs convert to 0.4 ppb to 6 ppb assuming standard temperature and pressure during measurement and using the molecular weights of xylene to obtain the low limit and benzene to obtain the high limit. However, these MDLs were based on the assumption that only one aromatic compound was present at the time. For mixtures or complex settings, the MDL will increase. These theoretical path average MDLs are consistent with comments made by Hans Hallstadius of Opsis (Hallstadius, 1992b) in a personal communication in which he indicated that the "standard detection limits for benzene, toluene and xylene" in urban ambient air are "of the order of 1 ppb with path lengths of 500 meters and a monitoring time of 5 minutes."

This study pointed up some of the problems in determining benzene especially in a plant setting where the plume may be diluted near the sampling height; and thus, the effects of interferences are more significant than in the lower and denser urban plumes. The study pointed up the difficulty of a UV system and the DOAS system in particular to distinguish between aromatic compounds because of their similar UV absorption features. This problem was particularly significant for toluene and ethylbenzene. However, path-averaged concentrations were determined for six aromatics and temporal plots correlated with meteorological variations and plant operations.

FTIR Studies

While FTIR may not be the most sensitive approach to monitoring aromatic hydrocarbons such as benzene and toluene in ambient air, these systems have been used during federal superfund and industrial studies measurements where these compounds as well as others were targeted. Other studies were directed at understanding the significance of water vapor interference in determining BTEX spectra with the goal of effectively dealing with the interference. These studies are discussed below.

Superfund Site: Lipari Landfill Study. In September and October 1990, Blasland, Bouck and Lee (BB&L), a consulting firm, conducted a study at the Lipari Landfill Superfund Site in New Jersey to monitor emissions at the fenceline during site cleanup (Kricks, *et al.* 1991). Many compounds were targeted, including the BTEX group.

Before the study began, a one-day tracer study was performed to calculate site-specific vertical dispersion coefficient (σ_z) values for emissions calculation. A portable 3-m meteorological tower determined wind speed, wind direction, temperature, relative humidity, and barometric pressure during the course of the study. During field measurements, each FTIR run consisted of 32 scans added together (co-added spectra) to gain better signal to noise ratios. Background spectra were taken several times during each day to account for changing meteorological conditions such as possible changes in upwind source mix.

None of the monitored compounds were detected, revealing that based on MDLs no project action levels were exceeded. The path-average MDLs quoted in the paper were significantly lower than the action limits, which were all at least 1,000 ppb. Quality assurance tests involving both known and unknown gas mixtures including the target compounds were performed before the start of actual measurements. The tests indicated an average error of ≈70% of audit standard for single unknown compounds and ≈57% for unknown mixtures.

The authors (Kricks, *et al.*, 1991) concluded that for these compounds while "the FTIR gave good qualitative performance, quantitative performance was only fair," attributing the sizeable error to water vapor interferences and problems with the system software package.

The study indicated problems that needed attention in the use of the FTIR system including the compensation for the interference of carbon dioxide and water vapor contributions and improvements in the software. Further modification of the 1990 software and development of field methodologies to deal with the interference problem were recommended (and have been partially completed as discussed below).

Superfund Site: Gulf Coast Vacuum Services Study. In August 1991, BB&L monitored emissions over a four-day period at the Louisiana Gulf Coast Vacuum Services Superfund Site with an FTIR spectrometer (Scotto, *et al.* 1992). Target compounds included all of the BTEX group.

N-octane, iso-octane, and methane were detected during this monitoring and used as "representative" indicator compounds to determine BTEX fluxes since none of the BTEX compounds were detected above MDLs during measurements. The maximum possible impact was computed by assuming the BTEX compounds to be present at their daily calculated path average MDLs (given in Table C-5). These MDLs were determined as a factor of the signal to noise ratio over the measurement path and, thus, reflect actual conditions. Emission rates were calculated based on ratios of indicator concentrations to tracer concentrations.

Kansas Intercomparison Study. In June 1991, EPA Region VII sponsored an FTIR intercomparison study in Kansas (Hudson, *et al.* 1992; Carter, *et al.* 1992). Three open-path FTIR systems were set up with parallel 200-m total (folded) path lengths. The three systems are referred to as "A", "B," and "C" to prevent bias in interpreting the data. Unknown volatile organic compound (VOC) concentrations and mixtures of known compounds were released upwind from the FTIRs over 12-minute intervals with the FTIRs operating concurrently with SUMMA® canister sampling. Validation of the release concentrations was performed in accordance with EPA Method TO-14 by using SUMMA® air sample canisters sampled every 10 meters along a path parallel to the FTIR beam paths. Meteorological data were taken both at the VOC release point and near the mid-point of the FTIR beams.

Table C-5. Variations in MDLs during the Gulf Coast Vacuum Services Site Study

COMPOUND	MDLs by Day (ppm-m)			
	DAY 1	DAY 2	DAY 3	DAY 4
Benzene	30.1	38.7	21.3	15.7
p-Xylene	13.6	9.0	10.5	7.0
o-Xylene	7.0	4.8	5.5	4.6
m-Xylene	9.4	7.5	12.7	6.5
Toluene	17.7	54.9	58.4	43.9
Ethylbenzene	7.1	9.5	9.5	6.3

Source: Scotto, *et al.* 1992

Compounds released (with aromatics highlighted) were:

- Dichloromethane
- Trichloroethylene
- Freon 113
- Iso-octane
- 1,1,1-Trichloroethane
- Tetrachloroethylene
- **Chlorobenzene**
- **Toluene**

EPA Region VII concluded that performance of the open-path FTIR systems was excellent for determining the path-average concentrations of the halogenated VOCs (i.e. those containing chlorine), but there were inconsistencies in measurements of the non-halogenated VOC compounds. Only system B was able to determine iso-octane (the only non-aromatic, unsubstituted hydrocarbon) because it did not use the optical filters used in systems A and C. System A was unable to determine toluene at any concentration, and systems B and C were able to determine path-average concentrations only for the approximately 100 ppb release. Quantitative performance was good in accuracy and precision (for the compounds detected) for all three systems (see Figures C-2 and C-3). The highest accuracy was with halogenated aliphatics (73-120% accuracy).

For the FTIR systems, the accuracy for the aromatics and one of the unsubstituted hydrocarbons was inconsistent. Accuracy was dependent on the specific ORS system and the chemical species present. Part of this behavior was attributed to differences in the reference spectral libraries used by each system.

EPA Region II also provided an OPUV system developed by the University of Denver. The OPUV was able to detect only the aromatics (toluene and chlorobenzene). The agreement of the OPUV data with the low concentration toluene (~30 ppb) was very good; however, the correlation decreased at higher concentrations (near 100 ppb) with the OPUV concentrations running high (McLaren, *et al.*, 1992).

Water Vapor Studies

Considering the potential presence of water vapor from cooling towers, surface impoundments, treatment lagoons, etc., at refineries, attention to the water vapor issue will be required to obtain reliable benzene values at the lower detection limits desired for fugitive emission measurements using the FTIR.

Several studies have been carried out to determine the impact of water vapor absorbance on the determination of BTEX compounds and the ability of the FTIR systems to obtain MDLs as low as possible for these compounds. One study of field spectra (Lute, 1992) concluded that a water vapor reference library should be developed. Then using the library, a "best matching water reference" could be subtracted from the field spectrum in order to improve detection of benzene. This approach improved the determination of benzene to within 10.9% of a 45 ppm-m standard with a 300 meter total path length through ambient air (equivalent to a path-averaged concentration of 150 ppb).

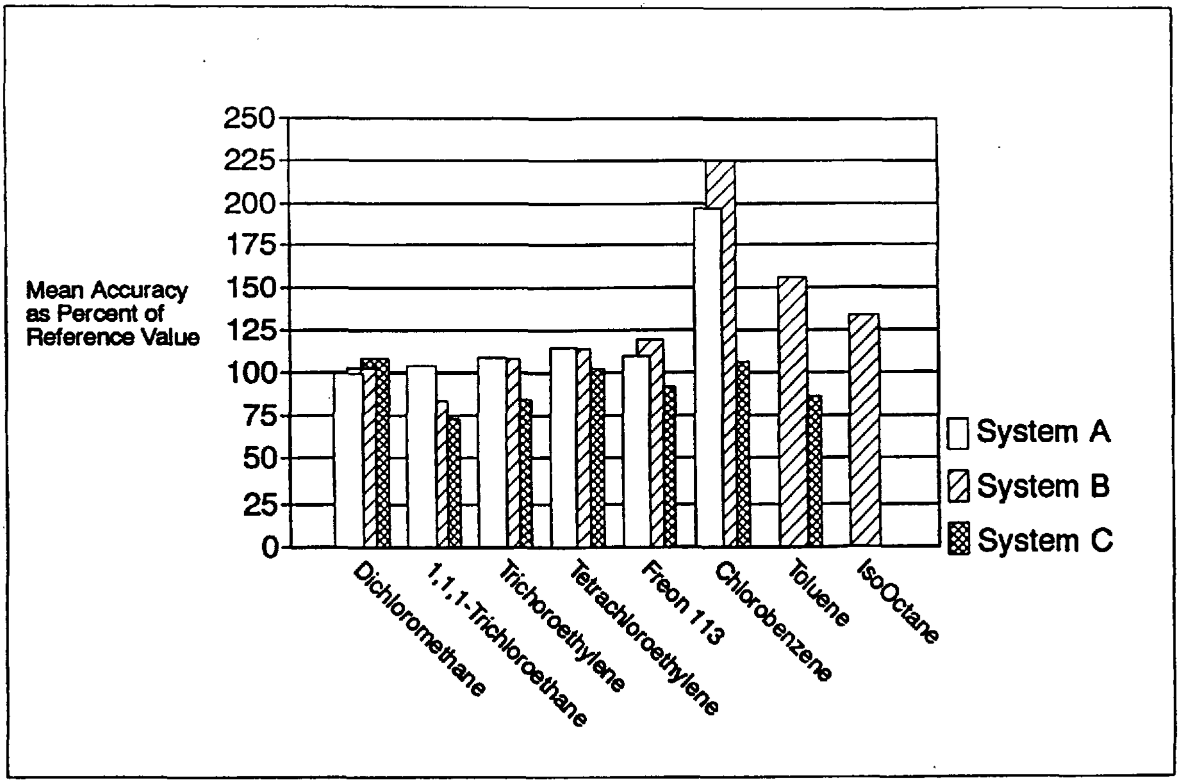

Figure C-2 OP-FTIR Quantitative Performance Summary for Accuracy from the EPA's Intercomparison Study. Reference is from canister data.

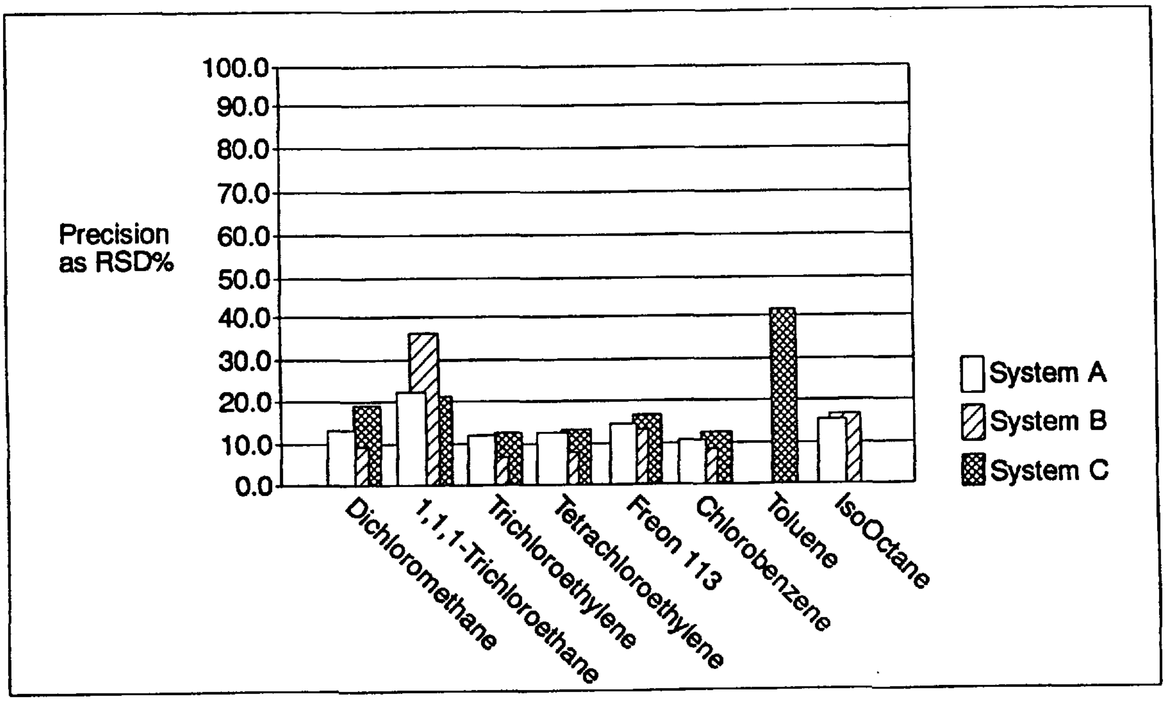

Figure C-3 OP-FTIR Quantitative Performance Summary for Precision from EPA's Intercomparison Study.

George Russwurm (Russwurm, 1992) has looked at the interference of water vapor with detection of toluene. His analyses attempted to determine toluene levels while retaining the water vapor signal in his spectra. His conclusion was that the FTIR detection limit "for toluene in the presence of 10.5 torr of water vapor (50% RH at 23°C) is about 1 ppm for a path length of 60-420 meters." While this level is too high to be useful for most meaningful fugitive emission studies, Russwurm indicates that the initial subtraction of the water vapor spectrum before analysis for toluene may improve this limit. He is investigating this approach.

With careful spectral analysis and under conditions where there is little water vapor interference, Robert Kagann of MDA Scientific indicates that the MDL for benzene and for toluene can each approach 3.4 ppm-m for a 100-meter path (Kagann, 1992). His optimum conditions involve very close matching of the upwind/downwind spectra for cancellation of water vapor. If the match is close enough, almost all of the water effects will be negated. After upwind/downwind spectra matching, Kagann indicates that water reference spectra for specific relative humidities and temperatures also help to counter water vapor interference problems. However, the method of using specific water spectra is still not fully developed and is currently only marginally beneficial in countering the water vapor interference.

Appendix D

REFINERY FUGITIVE EMISSIONS -- CONVENTIONAL POINT SAMPLING, TRACER STUDIES AND EMISSIONS ESTIMATES

Appendix D

REFINERY FUGITIVE EMISSIONS - CONVENTIONAL POINT SAMPLING, TRACER STUDIES AND EMISSIONS ESTIMATES

There have been some recent studies and evaluations of fugitive emissions from refineries using conventional point sampling, tracer studies and emissions estimates. The review of these studies presented below will provide some insights into the relative contributions of various process areas to fugitive emissions. It should be noted that the different studies do not necessarily result in the same relative ranking due to differences in compounds used in calculation as well as individual differences between refineries.

AMOCO YORKTOWN

In the fall of 1990, Radian Corporation, the EPA, and Amoco conducted an air emissions study at the Amoco refinery in Yorktown, Virginia (Williams, 1991; Radian, 1991a). Project objectives included: 1) development of an emissions "inventory" for the Yorktown plant, 2) association/characterization of these emissions with specific processes/areas within the site, and 3) a tracer gas study to aid in evaluation of emission paths and dispersion. No optical remote sensing techniques were used in this study. Instead, conventional point sampling methods (charcoal sorbent tubes, SUMMA® air sampling canisters, and emission flux chambers) were used to address project objectives (Amoco, 1992). Ambient air samples were collected using sorbent tubes and SUMMA® canisters for determination of BTEX and using SUMMA® canisters for VOCs. Surface to air sampling was done with flux chambers from which samples were collected using sorbent tubes and SUMMA® canisters for determination of BTEX and Teflon filters with XAD resin for determination of PNAs.

The study was successful in achieving its objectives, revealing new sources of benzene (e.g. marine loading operations) and showing that some sources that were thought to be high emitters were not (i.e. API separators). Emissions were determined directly for the wastewater sewer vents, the API separator, inactive landfarm and the coker unit's quenching and overflow ponds. Some emissions were estimated by EPA's AP-42 calculations (marine loading) and others determined by the tracer study (land farm). The resulting hydrocarbon emissions allowed each area to be ranked in order from highest emitters of hydrocarbons to lowest as follows:

Blowdown stacks;
Fugitives from pumps, valves, etc.;
Barge loading/marine operations;
Leaks from storage tanks;
Coker pond;
Sewer vents;
API Separator;
Land farm.

Figure D-1 shows the percentage breakdown of emissions from the refinery. Unfortunately, at the time of this writing the Phase II report had not yet been released, so further findings and field experience cannot be discussed.

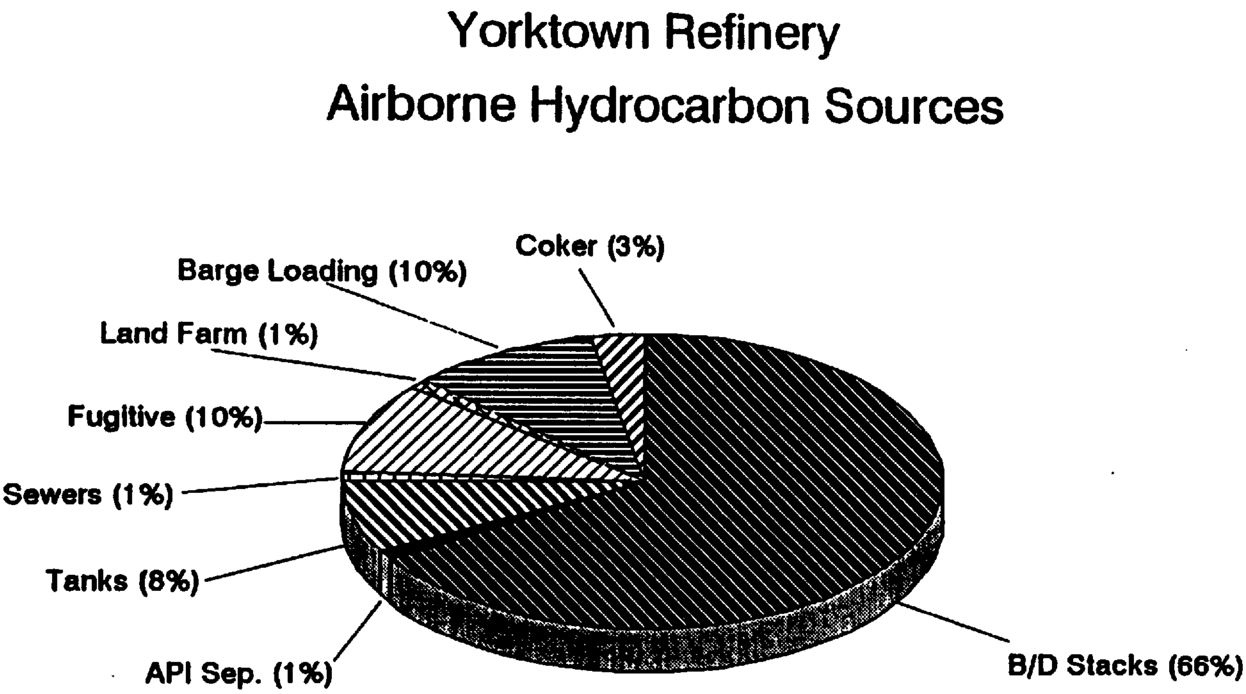

Figure D-1. Summary of Contributions to Airborne Hydrocarbons at the Yorktown Refinery.

CALIFORNIA REFINERIES HOTSPOTS REVIEW

A recent analysis of refinery hazardous air pollutant emission data (Taback, 1992) for eleven California refineries has provided a relative ranking of refinery processes contributing to fugitive BTX emissions. This ranking was based on the California Air Resources Board AB2588 reporting forms (with their attendant inconsistencies). The analysis was focused on the reported emissions of four hazardous air pollutants (HAPs): benzene, toluene, xylenes, and 1,3-butadiene. It was recommended based on the findings that the results of the study serve as a first-order indication of processes at which special monitoring attention may prove the most valuable. It was stressed in the recommendations that the report not be used to determine species-specific emission factors. The processes, with the exclusion of marine loading activities which were not considered, in descending order of total estimated releases for the collection of the eleven California refineries are:

Catalytic reforming (especially with BTX extractor);
Blending and treating catalytic cracking;
Crude distillation;
Full-range distillation;
Hydro cracking;
Thermal cracking.

It is not necessarily true that this pattern would hold for refineries in other locations due, in part, to different regulatory environments requiring different controls.

WESTERN STATES PETROLEUM ASSOCIATION FUGITIVE REPORT

WSPA commissioned a study to rank fugitive emission sources from various devices within a petroleum refinery. Using conventional fugitive estimating techniques such as engineering estimates, mass balance, and EPA Method 21, they obtained the relative ranking of devices within process units as summarized in Table D-1 (WSPA, 1992) where pressure relief devices are indicated as PRDs.

Table D-1. Representative Sources/Devices Fugitive Emissions - Petroleum Refinery

Process Unit	Fugitive Emissions, % of Total				
	Valves	Pumps	Converters	PRDs	Comprêssors
Crude distillation	3.6	0.9	4.2	3.3	0.4
Alkylation unit	14.1	11.1	8.4	17.0	0.1
Catalytic reforming	22.1	14.3	14.2	3.7	13.8
Hydrocracking unit	7.0	0.4	9.7	7.4	52.9
Hydrotreating/ hydrorefining	6.5	1.2	7.0	2.3	20.9
Catalytic cracking and CO boiler	7.7	17.4	4.7	1.3	0.3
Thermal cracking (vis-breaking)	0.3	---	0.1	0.3	---
Thermal cracking (coking)	4.5	15.5	7.1	0.3	---
Hydrogen plant	4.6	15.5	7.1	0.3	---
Asphalt plant	---	---	---	---	---
Product blending & treating	7.8	12.5	6.5	5.8	0.1
Sulfur plant	0.2	---	0.6	---	---
Vacuum distillation towers	---	---	---	---	---
Full-range distillation units	6.5	3.4	4.9	2.1	0.1
Isomerization unit	0.2	---	0.8	---	---
Polymerization unit	1.4	0.3	0.6	0.1	---
MEK dewaxing unit	---	---	---	---	---
Lube & specialties processing	---	---	---	---	---
Interunit pipeline system	12.7	22.0	14.6	54.5	9.0
Sour & other water strippers	0.3	0.2	0.4	---	---
MTBE unit	---	0.1	0.1	---	---
Other miscellaneous units	0.5	0.4	0.2	---	0.1
TOTALS:	100.0	100.0	100.0	100.0	100.0

Source: WSPA 1992

Order No. 841-45870

104PP

04941.5C1P

American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005