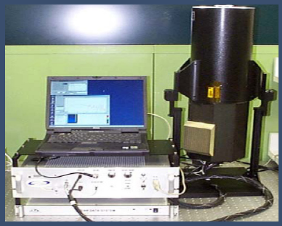
2nd International Workshop on

REMOTE SENSING OF EMISSIONS:

New Technologies and Recent Work

2008



Office of Air Quality Planning and Standards
Research Triangle Park

Office of Research and Development
Research Triangle Park

Office of Solid Waste and Emergency Response
Washington, DC

Notice

Preface

As a result of studies done in Canada and Europe that showed a surprising quantity of hitherto unsuspected quantities of volatile organic chemicals (VOCs) are lost (emitted) nationally by the processing, distribution, and consumption of petroleum and petroleum byproducts, the First International Workshop on VOC Fugitive Losses: New Monitors, Emission Losses, and Potential Policy Gaps was held in 2006. The studies utilized open-path spectroscopy techniques and infrared (IR) video cameras to detect the releases, and they indicate that high levels of fugitive VOC losses may be emitted on a routine basis from storage tanks, pumps, pipes, cooling towers and wastewater separators among other operations. One study suggests that actual VOC emissions could be more than fifteen times the amounts previously estimated. These emissions are extremely important for two reasons: (1) many are end-products of the refining process, which means they are both volatile and toxic and (2) they occur throughout the national energy network, ranging from well-head to refining to distribution to storage and retailing.

This workshop was held to discuss developments that have occurred since the 2006 meeting. Presentations were given on DIAL and SOF surveys done in the Houston, Texas area, monitoring for pipeline gas leaks with an aircraft mounted DIAL system, the results of an ongoing two-year continuous fenceline FTIR activity at a petrochemical plant, the use of VRPM to measure landfill fugitive gas emissions and mercury emissions from a chlor-alkali plant, a fully automated VRPM TDLAS system for continuous monitoring of lagoons at consolidated animal feeding operations, the use of FTIR fenceline monitoring MGP cleanups, and a research update on equipment being developed to detect in the mid to far IR spectrum that does not require cryogenic cooling. Also discussed were the implications for facility monitoring as these cutting edge tools become more common place and how to promote their use to reduce overall emissions. The workshop resulted in suggestions and recommendations for future actions to be taken by the various entities represented at the meeting.

Acknowledgment

We wish to publicly acknowledge and give special thanks to a few key individuals and organizations who made especially significant contributions to the success of this Workshop:

Dr. Eben Thoma from EPA's Office of Research and Development and Dr. Ram Hashmonay from ARCADIS for providing the scientific leadership and oversight for the Workshop.

Dan Powell and Michael Adam from EPA's Office of Solid Waste and Emergency Response (OSWER) for their Workshop co-sponsorship and scientific leadership in solid waste and remediation discussions. Also we greatly appreciate the service of their contractor, Environmental Management Support, Inc. in providing Workshop administrative support and the compilation of these Proceedings.

Russ Nettles from the Texas Commission on Environmental Quality (TCEQ) who presented detailed findings of his recent refinery study. His work provided a solid foundation for other scientists, speakers, and panelists to build upon in planning our future optical remote sensing (ORS) projects.

And last but not least, many thanks to all our presenters, panelists, and exhibitors at the Workshop from EPA, State/local regulatory agencies, international organizations, Universities, manufacturers, consultants, and trade associations. All contributed to make it a great success.

Thanks again,

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Acronyms and Abbreviations

API	American Petroleum Institute
BTEX	benzene, toluene, ethylbenzene, xylenes
CAFO	consolidated animal feeding operation
DIAL	differential absorption light detection and ranging
EPA	United States Environmental Protection Agency
FLIR	forward-looking infrared
FTIR	Fourier transform infrared spectroscopy
GC/MS	gas chromatography/mass spectrometry
H_2S	hydrogen sulfide
hr	hour
kg	kilogram
LDAR	leak detection and repair
LIDAR	light detection and ranging
NEIC	National Enforcement Investigations Center
NIST	National Institute of Standards and Technology
NPL	National Physical Laboratory
OP-FTIR	Open Path Fourier transform infrared spectroscopy
OP-TDL	open path tunable diode laser
ORS	optical remote sensing
OTM-10	Other Test Method 10
ppb	parts per billion
ppm	parts per million
PPT	PowerPoint™
QA	quality assurance
QC	quality control
SOF	solar occultation flux method
RPM	radial plume mapping
TDL	tunable diode laser
UK	United Kingdom
VOC	volatile organic compound
VRPM	vertical radial plume mapping
UV-DOAS	ultraviolet differential optical absorption spectroscopy

Executive Summary

The Second International Workshop on Remote Sensing of Emissions: New Technologies and Recent Work was held April 1-3, 2008. The workshop was sponsored by the U.S. Environmental Protection Agency's (EPA) Office of Air Quality Planning and Standards at Research Triangle Park (RTP), Office of Research and Development (RTP), and Office of Solid Waste and Emergency Response (HQ). At the workshop, studies involving the use of differential absorption light detection and ranging systems (DIAL), solar occultation flux (SOF), and Fourier transform infrared spectroscopy (FTIR) techniques at petroleum related facilities in the Houston, TX area and open path techniques for use at other types of facilities were discussed. The sponsors organized this second International workshop for the purpose of (1) summarizing the capabilities of open path technologies and relating them to estimation methods now in use, (2) exploring current applications of open path technologies, and (3) evaluating the ways and means for expanding the use of these technologies in evaluating and reducing fugitive emissions.

Attendees included state and local representatives of air quality agencies; EPA regional, headquarters, and laboratory personnel; Canadian and European air quality experts; and equipment vendors and contractors.

Technology Descriptions

The specific technologies discussed at the workshop were DIAL; radial plume mapping (RPM) and vertical radial plume mapping (VRPM) methods using open path Fourier transform infrared (OP-FTIR) systems, differential optical absorption spectroscopy (DOAS), and tunable diode lasers (TDL); SOF; infrared sensing video cameras; and advances in quantum cascade lasers and how they might affect equipment using laser technology.

The ground-based DIAL technique has been used extensively in Europe and more recently in Canada and the United States. As currently configured, it uses both ultraviolet (UV) and infrared (IR) lasers to measure criteria pollutants (NOx, SO_2, and O_3) and light aromatic compounds (benzene, toulene, ethylbenzene, and xylene) in the UV, and methane and total hydrocarbon plumes in the IR. DIAL is capable of providing a 2-dimensional contour of concentrations across a scanning plane. By combining this concentration contour with separately obtained wind speeds, a contaminant flux can be calculated. The DIAL system has been validated in European studies for hydrocarbon emissions. Estimated fluxes obtained by the DIAL system are generally assumed to be conservative.

Airborne DIAL systems have been deployed to detect leaks in natural gas transmission lines. The laser is mounted in a helicopter or small airplane and is tuned to methane. The aircraft flies along a pipeline right-of-way where it can detect gas seeps from leaks in the pipeline. It is capable of quantitating the gas concentration and providing

concentration contours, but it has not been used to estimate the emissions rate. With a different laser tuning it can be used to look for leaks at petroleum and chemical facilities.

The RPM method is primarily applicable for VOC losses when using OP-FTIR systems. It can also utilize any path integrated optical remote sensing technique such as UV-DOAS, open path tunable diode laser absorption spectroscopy (OP-TDLAS), and path-integrated DIAL (diffusely reflected from hard targets). In the OP-FTIR technique a beam of collimated infrared light is sent across the area to be measured, and in the monostatic configuration the light is reflected back to a receiving unit by a mirror (retroreflector). OP-FTIR systems provide an average concentration of chemicals over the distance measured. The advantage of the FTIR is that it speciates as well as quantifies the chemicals in the plume. If the objective of the survey is to locate hotspots a number of retroreflectors are needed at different distances and heights from the sending unit in various RPM configurations. Traditionally FTIR has been used to measure fenceline concentrations at a set height off the ground. This alone (without RPM) may be very useful for detailed speciation when deploying a DIAL system at a site.

EPA speakers talked about the use of RPM and VRPM with:

- FTIR to map emission fluxes from closed landfills.
- UV-DOAS instruments to measure mercury emissions at a chlor-alkali plant.
- TDL to continuously monitor ammonia emissions from consolidated animal feeding operations (CAFO) lagoons. The TDL system is automated and the data are accessed by Purdue University using telemetry.

The SOF method is a passive FTIR that relies on an external energy source, the sun. It provides the infrared signatures to speciate and quantitate the chemicals in a vertical column. The Swedish government has approved the SOF system (method) for whole plant emissions measurements. This system is less accurate than the DIAL and is subject to climatic constraints (high sun and steady winds). However, experience has generally shown the same emission levels as the DIAL at comparable measurement points. The SOF system was used in a recent emissions study in the Houston, TX area.

Infrared sensing video cameras record the differences in absorption of specific infrared wavelengths in their field of vision. This produces the appearance of a cloud where chemicals are present that absorb at the specified wavelengths. The camera has been very effective in locating large hydrocarbon releases from hard to access places. It does not detect all chemicals, nor does it speciate or quantify them. Releases under 500 ppm are generally not detectable. The camera can be combined with a passive FTIR system that together provides a visual of where the release originated as well as its chemical composition and concentrations.

Researchers at Princeton and Rice universities have developed a new external cavity-quantum cascade laser (EC-QCL) system. The lasers are thermoelectrically cooled, operate in continuous wave, and are widely tunable (up to 15 percent of the center wavelength). The mode-hop free wavelength tuning enables high resolution (<0.001 cm^{-1})

and it has good optical power output (up to 50 mW). The value in the EC-QCL system to environmental open path monitoring is that it does not require cryogenic cooling (generally liquid nitrogen), operates in the mid-to far-infrared range where absorption lines are strongest, and has excellent detection limits. Most lasers that operate without cryogenic cooling are in the near-infrared range and have much higher detection limits.

Recommendations

Recommendations were developed by small workgroups for three specific areas. These recommendations included:

- Develop more data on the comparability of measurements made with an ORS system versus traditional methods.
- Develop and/or compile standard protocols, including data quality, for the use of various technologies.
- Develop a technology matrix document that provides a way to evaluate the instruments. The matrix would include information such as the different means of conducting ORS studies with a discussion of what exactly they produce, what they can be used for, the maturity of the technology for the given application, where the technology works well and where it does not, cost ranges, setup time, and operator experience requirements. The matrix would allow a project manager to screen the technologies before spending time evaluating the most promising ones.
- Build a webpage devoted to project profiles for promoting the use of these technologies.
- Develop a series of Internet seminars to present the theory of operation and application of the technologies and to answer questions.
- Promote remote sensing as a means to adjust emission estimates and reduce emissions.
- Find ways to provide incentives for identifying and correcting emissions that are not specifically regulated. We need to think in a broader way to promote and/or allow remote sensing.
- Promulgate remote sensing methods that are accepted by the regulatory community. Until these standards are in place, it is unlikely that remote sensing will be widely adopted. Note that it was mentioned during the discussions that EPA can adopt consensus standards like ASTM and ISO by reference so this does not necessarily mean a large effort on the part of EPA.
- Explore conducting a specific ORS webcast using the OSWER facilities and the presentations given during this workshop.
- Complete the proceedings of this workshop and post them on the OAQPS webpage.
- Construct and complete the ORS technologies matrix for posting on a webpage. Also identify any useful documents that might be posted on the same webpage.
- Mr. Bosch will work with Ralph Marquez and others on ways to influence the acceptance of technologies by federal, state, and local management.

Findings

Several ORS applications were presented, and there are findings related to each.

<u>Active Petroleum Related and Chemical Facilities</u>

The Texas Commission on Environmental Quality 2006 DIAL study looked at a bulk storage tank facility and a refinery. Tentative conclusions from evaluating the data produced by this study include:

- Low flow from routine processes sent to a large steam assisted emergency/process flare may not have an effective 98 percent destruction/removal efficiency (DRE).
- VOC and benzene emissions from the coker at this refinery were reasonably low.
- DIAL measurements were validated in a field setting.
- Night time tank measurements did not appear to be substantially different than day time measurements.
- DIAL gasoline tanks measurements were fairly close to calculated emissions using the TANKS program.
- DIAL crude oil tanks measurements were 5–10 times greater than calculated emissions using the TANKS program.
    - Crude oil default parameter data in TANKS, including vapor pressure, need to be investigated.
    - Refined gasoline has pipeline specifications and better known and expected vapor pressure values for estimating tank emissions.
- Chemical parameter default data for crude oil and mid-refined products in TANKS may need improvements.

With support from the Houston Advanced Research Center, a SOF study was also conducted in areas around Houston and in the Houston Ship Channel. That study found:

- For the Houston Ship Channel, there were 5–50 times greater VOC emissions than reported in the 2004 TCEQ inventory. For NO_2 and SO_2 values, the discrepancy is less, a factor of 1.5 and 1.9, respectively. Similar discrepancies were observed for the other sites.
- The discrepancies between measurements and conventional estimates are consistent with differences observed elsewhere, e.g. Sweden.

FTIR VRPM was used to examine emissions at a refinery and chemical plant located in Israel. The instrument successfully identified hotspot releases at the plants with a fuel distribution center (tanker filling) contributing a significant amount of the fugitive emissions. Results from FTIR VRPM should be used with care at these types of facilities since part of the plume may be missed because of the inability to place a retroreflector sufficiently high to capture all of the plume.

An identified problem with emission factor calculations is that they assume all equipment is operating as designed; they do not include some major release areas, and the leak detection and repair (LDAR) programs typically do not measure tanks and difficult to access plant areas. Whole plant measurements can identify problem areas that are not being monitored and allow them to be addressed. Direct measurement of plant emissions is a way to identify areas for improvement. They are not necessarily a replacement for emission factor estimations. The issue should not be framed in an either/or fashion.

Consolidated Animal Feeding Operations

EPA is involved in a national study of ammonia emissions from CAFOs. The study has demonstrated that waste lagoons can be monitored remotely by using automated TDLs in a VRPM configuration that are queried by telemetry. This setup can provide a continuous stream of data for long-term emissions monitoring purposes.

Fenceline Monitoring for Safety

FTIR RPM was used to make continuous fenceline measurements over a two-year period at a petrochemical facility. The results indicate the following:

- The equipment was able to identify changes in emission flux in near real time.
- Most emission flux changes were transient and due to process changes and procedures.
- The RPM data (chemical concentration, position, time, and wind direction) generally could be used to identify what was going on at the plant when the emission occurred. This knowledge allowed the facility operators to fix problems quickly. RPM is an excellent tool for lowering emission levels and alerting plant personnel that an increase in emissions has occurred before emissions reach adjacent neighborhoods.

While remediating MGP plants there is a danger that the exposed excavation area may emit VOCs (especially benzene). An FTIR RPM system that was set up on the down-wind side of the excavation measured the integrated average concentration of chemicals passing through the beam. Site personnel were notified when a preset concentration was exceeded so that mitigation actions could be taken.

As is demonstrated at the petrochemical plant and the MGP remediation sites, the RPM method can be a useful safety tool in detecting downwind emissions that may occur in offsite inhabitants' breathing zone. The real time measurements allow for corrective actions to be taken before the emissions can become a health risk. The RPM method provides more certainty in detecting excursions than point samplers.

ORS can also be used within a facility to monitor especially hazardous processes such as alkylation units at refineries where a malfunction might lead to the release of hydrogen fluoride gas. Point samplers may not be as effective because they do not cover the entire area.

Redevelopment of Old Landfills

An older active landfill was often out of sight and out of mind. Today, the same landfill is likely to be a potentially valuable piece of property on a grassy hill surrounded by development. One of the most likely redevelopment scenarios for such a landfill is some kind of recreational use—but is it safe for that use?

EPA has undertaken several FTIR VRPM studies at closed municipal landfills to determine if the landfills were safe to redevelop or if they would require further gas controls before being redeveloped. Despite some challenges from uneven topography, the method was successful in locating hotspots and/or general emissions, or demonstrating that no emissions were occurring. Because it provides an average flux across all segments of a site, the method lowers the uncertainty of not detecting a dangerous release and hence is a cost-effective means of determining the safety of the land for redevelopment.

Use of Aircraft and DIAL for Emissions Detection

DIAL systems can be mounted in aircraft. When combined with a video camera and a high resolution mapping camera, these systems can provide fairly precise location and concentration contour data on fugitive emissions. To date they do not have the capability of estimating flux. Aircraft equipped with a DIAL system provide very cost effective fugitive emissions monitoring for spatially large areas such as natural gas pipelines.

IR Camera

The IR camera is gaining acceptance in some industrial sectors as an excellent tool for find-and-fix programs. Promulgation of the SMART LDAR rule, which addresses the camera, is expected to lead to even more use. The cameras are also finding use at refineries for safety purposes. The cameras can identify potentially explosive pockets of gas before startup.

Other Issues Identified at the Workshop

- Regulatory liability issues were identified as an impediment to voluntary adoption of ORS technology by industry. If a facility does not know it has an unmonitored emission they are not liable for it; however, if they use a tool such as the IR camera and discover a previously unknown emission that puts them over their permit level, they could be liable to an enforcement action.
- Another impediment to the adoption of ORS technology is the absence of standardized protocols. Without an approved protocol, there is a risk the data will not be accepted by the regulatory community or the general public.
- The 2007 TCEQ study identified potential problems with flares that need further evaluation.

- Pipeline surveys have revealed that natural gas compressor stations consistently show fugitive emissions.

The existence and capabilities of ORS systems do not appear to be known to policy makers at all levels of government. This lack of knowledge has the effect of hindering the adoption of the systems for environmental use.

Introduction

In 2006 EPA sponsored an emissions workshop to discuss remote sensing studies that had been performed in Europe and Canada that indicated that emissions from refinery and natural gas operations may be 10 to 20 times greater than the amount estimated using current standard emission factors. Since that time considerable work with remote sensing has been done in the US including a DIAL and SOF study in the Houston, TX area. As a result, the U.S. Environmental Protection Agency's Office of Air Quality Planning and Standards, Office of Research and Development, and Office of Solid Waste and Emergency Response sponsored a second workshop on April 1-3 2008 to discuss the findings of these studies and other applications for remote sensing technologies. Representatives from Environment Canada, Sweden, United Kingdom (UK), EPA, state and local agencies, equipment vendors, consultants, and industry attended the workshop. Appendix B contains a list of the attendees.

The technologies discussed at the workshop were DIAL; radial plume mapping (RPM) and vertical radial plume mapping (VRPM) methods using open path Fourier transform infrared (OP-FTIR) systems, differential optical absorption spectroscopy (DOAS), and tunable diode lasers (TDL); infrared sensing video cameras; SOF; and advances in quantum cascade lasers and how they might affect equipment using laser technology.

Organization

This workshop summary is organized into five main sections. The first section summarizes 14 technical presentations made by invited speakers. Appendix C contains the speakers Powerpoint™ presentations.

The panel discussion section contains three panel discussions with a question and answer session following each panel.

The small groups section summarizes the findings of three breakout groups. Each group was given a topic of concern and asked to relate it to information presented during the course of the workshop. They were asked to report on any barriers to conveying the information or implementing programs, suggest ways of overcoming these barriers, and draw up a set of recommendations for each topic of concern.

The recommendations summary section consolidates and summarizes recommendations made by the breakout groups.

Technical Presentations

The speakers described the science behind optical remote sensing, and used case studies to illustrate how the techniques can be used. The case studies also illustrated some of the issues that arise when whole site emissions are monitored. They also provided a basis for later discussions in the workshop.

Welcome
John Bosch (EPA/OAQPS)

Mr. Bosch welcomed attendees and laid out the structure and purpose of the workshop. He asked attendees to introduce themselves and urged all participants to join one of the three breakout groups:

- How to employ optical remote sensing results to inventory emission estimates
- What studies need to be conducted in the future to advance the state of the art of emissions monitoring
- How optical remote sensing can be applied to remedial actions and solid waste management issues

ORS Technical Sessions Introduction
Dr. Ram Hashmonay (ARCADIS)

Optical remote sensing has been in use for the past 20 years, since improvements of personal computers allowed for their deployment in the field. Dr. Hashmonay displayed the front page of an article written in 1992 for the Journal of the Air and Waste Management Association entitled Optical Remote Measurement of Toxic Gases. This overview article, which discusses many of the same instruments on display at this workshop, gives fundamental information that has not changed much since then. The vendors of the instruments on display were available to discuss their wares with workshop attendees.

The technical presentations of the workshop cover three areas. The first session contains two presentations on DIAL, including some results from the DIAL project in Texas City, TX; a presentation on an alternative to DIAL—Solar Occultation Flux and mobile DOAS methods; and a talk on industry emission inventory calculations and their relation to short-term studies. The second session presents studies on the use of open path UV-DOAS and FT-IR in long term OTM10 configurations. The last session discusses cleanup and hazardous/solid waste monitoring using open path technologies, and it includes a presentation on the state of the art of quantum cascade lasers and how improvements in laser technology may affect the operational capabilities of open path instrumentation.

Reflections on 20 years of DIAL VOC Measurements in the Oil and Gas Industries
Jan Moncrieff (Spectrasyne, Ltd. UK)

Ms. Moncrieff began with a brief explanation of how DIAL works. The instrument sends out two pulses of laser light at different wavelengths. One wavelength is chosen to be absorbed by specific bonds in the target species while the other is intended to be less absorbed by the target species. The light is backscattered by atmospheric aerosol etc in its path to a receiving system in the DIAL vehicle. The ratio of the backscattered intensities from the wavelength prone to absorption and th lesser absorbing wavelength can be used to derive the concentration of the target species. The receiving system timegates the return signals and by relating these return times to the speed of light, this allows it to provide a changing concentration profile along the laser light's path. By measuring along multiple scan lines perpendicular to plume movement (driven by the wind) two-dimensional contours of target species concentrations can be developed. When combined with the appropriate wind velocity vectors, this can be used to derive a mass emission of the target species through the laser scan area.

The Spectrasyne DIAL technique uses two laser systems, one operating in the ultraviolet and the other in the infrared. This allows simultaneous profiling of both aromatic or some inorganic gas compounds (NO, NO_2, SO_2, O_3) and aliphatic hydrocarbons or groups/cocktails of hydrocarbons or HCl, N_2O among others. When measuring cocktails of species speciation is achieved by taking static measurements within the plume, in or close to the laser scan line, with canisters or sorbant tubes and later analyzing them using a speciating instrument such as GC/MS. While the profiles are being taken, meteorological stations, placed as close to the measured vertical plane as possible, record wind speeds and directions in the plume. The perpendicular wind speed multiplied across the concentration contour provides a mass emission flux for the plume at the time of measurement. Since the DIAL truck is mobile, it can easily be moved around a facility to investigate different processes, tankage areas, flares, etc. It also can be moved quickly if the wind direction changes. The sending and receiving equipment is located on the back of the DIAL truck and it’s steering mirrors can be rotated to provide hemispherical coverage. Processing of the Spectrasyne DIAL data is always carried out on site and in close to “real” time to ensure that any unusual emissions detected can be reported to site staff immediately and if possible related to changes in the process under study and where possible rectified and remeasured.

Development of the DIAL technology began around 1978. By 1988 a commercial version was ready for final validation. Validation studies took place at a military base in the UK. About 10 percent methane in a nitrogen mixture was released into the open air from a pipe where the concentrations and flow rates were measured to determine the mass efflux. About 500 meters downwind, the DIAL system measured concentration and wind profilesacross the methane plume to derive the mass emission downwind. The agreement factor between the in-pipe measurements and the DIAL measurements was within 10 percent. A further validation exercise was carried out with CONCAWE, where the DIAL measurement of cocktails of species were correlated with “accepted” techniques. A river barge loading gasoline, having previously held gasoline was used as the source and losses of gasoline were measured. CONCAWE measured the concentrations of gasoline in the barge's single vent. This vent allowed the contaminated air in the tank to escape while being displaced with the liquid gasoline. The concentrations in the vent coupled with the loading rate allowed for a determination of emission flux. The DIAL measurements were performed downwind. While the total mass emissions measured by each technique were within 12% of each other, the DIAL estimate was always less than the measurement at the vent. Ms. Moncrieff attributed this lower result, in the main, to the plume dispersion as it moves downwind and the inability of the DIAL to measure the very low concentrations (below it's detection limit) at the plume boundaries. Validation exercises over the years have shown DIAL agreement to be within 15 percent or less of other measuring techniques.

Spectrasyne has done 145 DIAL surveys since 1990. The studies performed at refineries have shown that emissions, as a percentage of throughput, have ranged from well under 0.1 percent to over 0.7 percent. Sweden has made considerable progress in cutting emissions at its refineries through a targeted DIAL and more recently SOF survey effort. The surveys have identified trouble spots that have been addressed through maintenance, changes in procedures, and redesign and refitting.

Ms. Moncrieff presented data on how emissions are distributed in different refinery configurations (e.g., simple refinery, complex refinery with crackers and cokers, etc.). Specific numbers can be found in her slide presentation. Tankage (crude and product) storage areas are generally major contributors to air emissions, and when cokers are present at a facility, they too can contribute large amounts to fugitive emission fluxes. At one site, where measurements were done on different cycles from the same coker during the same campaign, the emissions were seen to be significantly different from cycle to cycle. Ultimately, this was attributed to different shifts operating the the cokers differently. Undisturbed coke storage on site has not been seen to give rise to large emissions, but as soon as the coke is disturbed and new surfaces are exposed, emissions rise.

Question: The Gothenburg Refinery Emissions slide shows a dramatic decline in emissions from a high in July 1988 to a low in February 1992. How much of this decline is related to facility changes and how much is due to temperature differences?
Answer: We believe the difference is primarily related to changes in refinery operations and tank seals. Solar radiation may have some affect on emissions from tankage when the refinery is located in a southerly area where the summer sun is overhead and solar heating can occur in the surface layers of the product just under the tank roof. In Sweden, where, even in the summer the sun angle is very oblique it is not thought that the solar radiation factor is likely to be very important. Wind is more likely to be an important climatic factor for floating roof tankage emissions in Sweden or anywhere for that matter.

Texas Commission on Environmental Quality (TCEQ) Differential Absorption Lidar (DIAL) Project Summer 2007 Texas City, TX
Russell Nettles (TCEQ, US)

Studies performed by TCEQ in the Houston, TX, area have shown that VOC concentrations in the air are higher than the emissions inventory would indicate. Flyovers of facilities using an IR camera have revealed potential fugitive emission sources that are not part of the traditional emission factors and calculation techniques. The objective of the Texas City project was to compare actual DIAL measurements of emission flux with those arrived at by these traditional methods on sources that are difficult to measure such as flares and cooling tower. The project was not an enforcement effort nor was it set up to compare DIAL numbers with emissions reported by the facility.

The project concentrated on a variety of storage tanks, a delayed coker unit, various kinds of flares, a wastewater treatment area, and a sulfur recovery unit. A draft DIAL field data report has been released and TCEQ expects the final report to be finished in the fall of 2008.

Bulk Terminal
The bulk terminal is a commercial bulk storage facility that temporarily stores liquids for customers. Any given tank may store various types of liquids during the course of a year. The site had two new tanks that used floating roofs hung from overhead cables. This cable arrangement had a minimum number of holes and allowed for easy maintenance. The IR camera detected a strong plume at one of the tanks. It was not apparent why the one tank was emitting gases while the other was not since they both contained the same product. Subsequent investigation revealed that the operators were conducting a mixing operation in the tank with the plume. This type of tank operation is not accounted for in EPA TANKs program. The DIAL survey isolated an emission coming from the largest tank on site—Naphtha tank 22. The tank was well maintained, had an additional wiper seal, and the gauge pole openings were wrapped to avoid vapor loss. The plume was only barely visible to the IR camera when the wind was blowing. The apparent reason for the release was wind action blowing vapors between the tank seals even though the tank was full. The DIAL measurements estimated the release at this tank to be one to seven pounds per hour while the TANKS program expected emissions are less than one pound per hour.

Refinery
The refinery was operating at 50 percent capacity due to hurricane damage and turnaround projects. The IR camera detected significant amounts of emissions from the crude tanks and there was a noticeable VOC odor on the top of the tanks. The DIAL estimates ranged from under two pounds per hour for one tank to 23-39 pounds per hour for another. The TANKS program expected emissions are under one pound per hour. The large discrepancy in DIAL measurements and predicted TANKs estimates from the crude tanks may be due to improper vapor pressure of crude oil being used in TANKs program. No VOC odors were detected by the IR camera team when they were

on top of the finished gasoline tanks, but small amounts of vapor were picked up by the camera. The DIAL measurements for the gasoline tank emissions were impacted by the presence of a ground flare; however, estimates for the group of gasoline tanks with DIAL were in the two to 18 pounds per hour range. The TANKS program expected emissions are between two and 20 pounds per hour—comparable numbers. A limited DIAL survey was performed on heated oil tanks. The DIAL estimated release rate was six to nine pounds per hour while the TANKS program estimated less than one pound per hour. Mr. Nettles thought one potential reason for the difference in values between the two measuring systems for heated tanks is that the TANKS program has a 100 degree upper limit for heat and some of the heated tanks can reach 400 degrees.

The coker design at this refinery is set up for four cuts with overhead vapor sent to a vapor recovery unit or into the refinery fuel gas system. The coker is capable of processing any grade crude. DIAL measurements were taken during all phases of the coking process with releases estimated to be 10 to 32 pounds per hour of VOC emissions. The DIAL measurements of benzene were generally below detection limits for most of the process; however, 1.5 to 2.1 pounds per hour of emissions were estimated for the decoking process (drilling the coke out).

Two flares were examined at the refinery. The steam assisted temporary flare was burning a high volume of 80 percent hydrogen waste gas and achieved a 99.7 percent destruction/removal efficiency (DRE) according to DIAL measurements and monitored flow to the flare. The steam-assisted ultra cracker flare did not perform well. During one measurement survey, the DIAL estimated that its emissions rate was 88 to 326 pounds per hour with its highest efficiency being less than 85 percent DRE. Mr. Nettles believes that this problem may be caused by low flow from routine processes being sent to a large steam-assisted emergency/process flare. DIAL measurements taken downwind of the wastewater secondary and tertiary treatment areas estimated emissions of 30 pounds per hour. The IR camera did not pick up any plume from the separator unit and estimated releases were similar to those reported for other facilities.

Some tentative conclusions from the study include:

- Low flow from routine processes sent to a large steam assisted emergency/process flare may not have an effective 98% DRE
- VOC and benzene emissions from the coker at this refinery were reasonably low
- DIAL measurements validated in field setting
- Night time tank measurements did not appear to be substantially different than day time measurements
- DIAL gasoline tanks measurements were fairly close to calculated emissions using the TANKS program
- DIAL crude oil tanks measurements were 5 –10 times greater than calculated emissions using TANKS program
    - Crude oil default parameter data in TANKS, including vapor pressure, needs to be investigated
    - Refined gasoline has pipeline specifications and better known and expected vapor pressure values for estimating tank emissions

- Chemical parameter default data for crude oil and mid-refined products in TANKS may need to be improved

Mr. Nettles slide presentation identifies a bulleted set of areas for further investigation.

Question: Did you take a sample of the crude before doing the DIAL survey?
Answer: No and in retrospect they should have as it appears crude vapor pressure may be an issue in the TANKS program calculation.

Question: At any time did the coker depressurize to atmospheric pressure?
Answer: Does not know.

Industrial Emission Measurements Using Solar Occultation Flux and Mobile DOAS Methods
Dr. Johan Mellqvist (Chalmers University of Technology, Sweden)

Dr. Mellqvist's experience has shown that the standard approach for estimating VOC emissions at refineries and other plants is associated with significant uncertainties, and a number of plant processes and activities occur that are not part of the emission inventory calculations. These include difficult to measure areas where malfunctioning equipment can contribute to a considerable fraction of total emissions. Dr. Mellqvist and his colleagues use three techniques for studying fugitive emissions: solar occulation flux, time correlation tracer, and IR camera.

Solar Occulation Flux
The FTIR unit is mounted in a truck with a solar tracker (optical device that tracks the sun and keeps the instrument pointed to it). Measurements of key species are made as the truck moves. The movement of the truck brings the instrument's line of sight through any plume, allowing for the construction of a two-dimensional map of average concentrations with distance. The flux is obtained by multiplying the mass times the wind speed. The unit typically measures alkanes, olefins, CO, NH_3, formaldehyde, NO_2, and SO_2. The technique only works in the day time under clear skies. The uncertainty of the results is generally between 20 and 50 percent depending upon the object of study. Specific measurements and examples of the sampling technique can be found in the presentation.

Time Correlation Tracer
This method was developed for methane releases from landfills and VOC emissions from industry. A tracer gas of N_2O is released at a known concentration and rate from the suspected source area. Fifty to 300 m downwind the air is sampled using an FTIR with a White Cell. The tracer gas provides the dispersion and the VOC/N_2O concentration ratio integrated across the plume yields the emission in kilograms per hour. This technique is used for more detailed studies such as emissions over tank refilling cycles, ship loading, and truck loading. The measurements can be done at night and they have a 15 to 40 percent uncertainty.

IR Camera
The IR camera is used to identify specific equipment leaks. It does not quantify leak rate and has a relatively high detection limit.

Currently Dr. Mellqvist's group runs the KORUS monitoring program, which is used to identify and quantify emissions at three refineries and the Göteborg oil harbor. A SOF-TCT survey is performed each year and a mid-infrared camera (forward looking infrared (FLIR) GasFindIR) is used to find large emitting leaks identified by the SOF-TCT. Following repairs by the facility, another SOF-TCT survey is done to ensure that the leaks were corrected.

With support from the Houston Advanced Research Center, Dr. Mellqvist participated in the TexAQS 2006 campaign in the Houston area. They found that SOF-measured emissions in the Houston Ship Channel were 5 to 50 times as high as those in the reported inventories. The discrepancies between the measurements and conventional estimates were consistent with differences observed in Sweden. The presentation provides measurement locations and concentrations plus some comment on methodology.

Question: The technique of driving back and forth (box method) between potential sources at a refinery definitely allows for the determination and subtraction of background from upwind sources. However, in Houston, the area being measured was a large circuit. How do you handle mobile source background?
Answer: Mobile source emissions are usually a very small part of total emissions, so we generally ignore them.

Question: Would background mobile source emissions of compounds like NO_2 be minimal or might they play a larger role?
Answer: For NO_2 they might be significant.
Comment: Mobile source emissions for this campaign were a very minor contributor.

Question: Have you ever tried to use FTIR for measuring benzene and other aromatics?
Answer: For aromatics, they usually rely on canister samples and measure the ratio of the different canister tanks. It might be possible to do some aromatics but benzene has a strong CO_2 interference. UV-DOAS is usually better suited.

Emission Factor Uncertainty & the Role of Remote Sensing
Randy Kissell (The TGB Partnership)

Using storage tanks as an example, Mr. Kissell illustrated that the variability in underlying parameters that define emissions impacts the accuracy of any estimation protocol. While not questioning the accuracy of point-in-time measurements such as DIAL, he does not believe that the emission rates calculated from these measurements can be applied as a means of estimating annual emissions. For example, a refinery that handles a wide range of crude oils may have different emission rates from the same tanks depending upon the volatility of the specific crude.

There can be large uncertainty in using fixed value emission factors. For example, if one says that a refinery looses 0.05 percent of its throughput without taking into account the products it is handling, temperatures, wind speeds, etc. there will be large uncertainties. Actual values may range over a couple of orders of magnitude and the fixed value (emission factor) used to estimate the emission lies at some random point in this range. A similar problem lies with point-in-time measurements that measure a transient condition. As with a fixed-value emission factor, a snap-shot measurement represents only one point in a range of actual emissions and cannot be used to characterize the average.

The API 19.1 and 19.2 for estimating emissions specifically state that they are for use with annual average emission rates and are not to be used for short-term measurements. For storage tanks the emission factor values jointly developed by API and EPA are based on tests conducted over a 20 year period to measure emission rates with varying parameters (vapor pressure, temperature, wind speed, type and number of fittings, etc.). Mr. Kissell discussed in his presentation the storage tank emission factors and provided an example of how a snap-shot measurement might readily differ from the average by more than a factor of two considering just one parameter.

Mr. Kissell cites a CONCAWE side-by-side test of the DIAL system with the API emission factor calculations for five tanks and for a barge loading event. The difference between the two methods for the tanks was 10 percent and for the barges where actual emissions were measured at the barge vent, the DIAL system was within 10 percent and the API calculation was within three percent. This does not demonstrate that emissions are never underreported but rather that under or over reporting of emissions is a separate issue from using API emission factors for routine conditions.

Mr. Kissell believes that remote sensing has a role in identifying underreported emissions such as unaccounted for operations at known sources (e.g., floating roof landing losses), previously overlooked sources (e.g., leaking heat exchangers), and poorly maintained sources (e.g., failed rim seals on floating roofs). A list of his summary points can be found in the presentation.

Question: You are saying that DIAL measurements cannot be used to estimate emissions over time. We have been to a refinery nine times over 16 years at different times during the year and the results are very similar. This consistency should count for something.
Answer: The DIAL system is good for finding sources—especially sources that are not currently recognized as such; however, API calculations, which are averages taken over time to give a yearly estimation, should not be compared to a measured emission rate taken over a short time and then extrapolated to an annual total.
Comment: Including roof landing emissions in the Houston ship channel area increased the emission estimate from about 13,000 tons to 20,000 tons from one source.
Comment: This is a good point; emissions will definitely be underestimated if roof landings are not included in the calculations.

Long-Term Application of OTM-10 Using DOAS in Industrial Settings
Dr. Eben Thoma (US EPA/ORD/NRMRL)

There are many types of area emission sources such as CAFOs, landfills, and industrial emissions. They share several characteristics in that they are generally large in area, spatially complex, and temporally variable. In general, we don't know much about the temporal variability of area source emissions since our field campaigns are usually short in duration. Long-term fixed deployments of EPA method OTM 10 can help provide information on temporal variability of area source emissions.

EPA test method OTM 10 ("Optical remote sensing for emission characterization from non-point sources") describes direct measurement of pollutant mass emission flux from area sources using ground-based optical remote sensing (ORS). The technique utilizes open-path spectroscopic instrumentation to obtain path-integrated pollutant concentration information along multiple plane-configured optical paths set up downwind from the source. The multi-path pollutant concentration data along with wind vector information are processed with a plane-integrating computer algorithm to yield a mass emission flux for the source.

EPA OTM-10 can help investigate temporal variability of area sources by providing long-term observation of the source. Once this system is deployed it has several advantages over systems like DIAL or SOF. It can provide 24/7 remote operation at low cost (after installation) for extended periods of time. On the other hand it has a fixed observation area and depends on a fairly constant wind direction. In some cases, multiple OTM setups can be defined, which makes continual measurement less dependant on wind direction.

Case Study of Mercury Cell Chlor-Alkali Facility
Chlor-alkali facilities produce H_2, Cl_2, KOH, and NaOH by electrolysis of brine solutions using liquid mercury as the cathode. Significant mercury fugitive emissions can occur through leaks in equipment, maintenance events, and process upsets.

Most previous studies of chlor-alkali plants have been done in Europe using a DIAL system. These studies have tended to be short term. In this study a fixed OTM-10 deployment using three UV-DOAS units in a bistatic configuration was used. The light sources were mounted at three different heights on a nearby water tower to provide about a 220-meter path. The study lasted eight weeks with the equipment running 24 hours per day seven days a week with one minute base time-resolution. The system was automated and required very little operator attention. The monitored facility included a cell room building with large fans pulling air from the outside at both ends of the building, and a roof venting area with induced flow fans directing the air out of the building. Facility operators monitored the venting with a multi-point UV monitoring system. The objective of the study was to estimate total emissions from the facility and compare the results with EPA historical estimates, which are on the order of 1,300 grams per day. In addition to the UV-DOAS system, the project used a Lumex point analyzer with three sampling points for ground-level measurements.

The extrapolated 24-hour mercury emissions from the facility were found to be about 400 grams per day mean value. The OTM-10 readings were similar in distribution to those of the facility's instrumentation in the cell room but slightly higher. Analysis of the distribution of flux values showed a number of high outliers in the OTM-10 data as compared with the cell room data. Dr. Thoma believes these are caused by emission events occurring outside of the cell room. The outlier fluxes were detected in all three of the UV DOAS instruments and hence are high in confidence.

During monitoring, the ORS data were provided in near real time to the facility operators. Through several examples, Dr. Thoma illustrated the use of the near real time data to provide feedback to the facility to help increase knowledge of their process and emissions. This point helped illustrate one of the values of operating a long-term fixed monitoring system at a facility. It can alert facility operators that a non-routine event may be occurring.

In summary, many forms of ORS with different capabilities exist. There are satellites and airborne platforms that have a very large spatial scale, modest detection/speciation capability, and limited long-term monitoring uses. The DIAL and SOF systems have a large spatial scale since they can move about, have good detection/speciation capabilities, and limited long-term monitoring due to deployment costs. The fixed deployment ORS using UV-DOAS and FTIR have a smaller spatial scale but very good detection/speciation capabilities and they have proven long-term monitoring uses that can provide plume flux estimates when using multiple instruments or multiple retroreflectors.

Question: With the chlor-alkali plant, the emissions data can be checked against a mercury mass balance within the plant (i.e., they start with X pounds of mercury and every so often they add y pounds of makeup). How does this correlate with the measured flux?
Answer: That would be a valuable comparison but I don't have access to the mass balance data for this facility. This study was undertaken as part of a rulemaking effort to provide flux data from an actual plant.
Comment: The comparison has been made in other studies.

Long-Term, Continuous, Fence-line Monitoring of VOC in TX Using OTM-10
Dr. Robert Spellicy (IMACC, US)

Sometimes it is difficult to extrapolate long-term or annual emissions from short-term measurements. Dr. Spellicy discussed the operation of two permanent installations that monitor 24/7 at a petrochemical plant fenceline. The installation was part of a consent agreement between Texas Petrochemicals and the State of Texas. The objectives included isolating process and procedure-related emissions with the ultimate goal of reaching one part per billion (ppb) emission levels at the fenceline.

FTIR can be operated in an active or passive transmission mode. In the active mode the light source is part of the instrument and is passed through media to be tested and recovered by a receiving instrument. Retroreflectors are commonly used to return light back through the media to the receiving unit. This type of setup is useful in gas-phase monitoring at fencelines, stacks, and process equipment releases. They also have been using active FTIR using cell technology to measure vapor concentrations in the parts per trillion range in cooling tower vapors, condensate stream vapors, and waste water stream vapor.

In the passive mode the instrument uses outside energy to collect spectra. For example radiation emitted by hot gases (>120° C) can be collected and used for speciation and quantification of constituents. This technique is useful for looking at flare efficiency and stack emissions. The spectra emitted by hot gases are identical to those absorbed by active methods. The main difference is that the quantification of the constituents using emission spectra is dependent on the temperature of the gas as well as concentration so it is necessary to measure it when the spectra are collected.

Dr. Spellicy discussed the spectra in terms of the kind of information various parts of the infrared spectra contain. Detection limits in the infrared vary by compound because they are dependent upon the compound's dipole moment. For example hydrogen chloride has a large dipole moment with a detection limit of 2 ppb, while hydrogen sulfide (H_2S) has a low dipole moment with a detection limit of 300 ppb. Some of the common compounds that can be detected by FTIR and their approximate detection limits are provided in a table in his presentation.

Portable FTIR System

This system was built by ARCADIS for the State of North Carolina for use in emergency response actions. It has a small corner cube retroreflector that can be deployed quickly for screening 130 chemicals at say a train derailment. If a second retroreflector is used, they may be able to determine flux.

Fixed Fenceline Monitoring at Texas Petrochemicals

The monitoring equipment is housed in two small shelters with a window to allow the instrument to send and receive light. The detector requires liquid nitrogen cooling so there are tanks for the nitrogen, which is automatically added as needed. A computer controlled tracking system allows querying of each retroreflector placed along the fenceline. The retroreflectors are corner cube arrays. The most important feature of these arrays is that they eliminate the need for precision aiming of the light. Any light that is picked up from the FTIR instrument is returned along the exact same pathway that it entered—so minor shifting of the array does not affect its ability to return the light to the sending/receiving instrument. One set of instrumentation measures the upwind fenceline while another measures the downwind fenceline.

In the simplest case of FTIR fenceline monitoring with one beam and one set of mirrors the average concentrations are measured as a function of time. With wind correlation, the source of the emission might be determined and the distance to the plume (close versus far) might be estimated by how compact the plume is (e.g., with a small wind change, plume concentrations can disappear, implying that the plume has not had sufficient time to disperse and the source is close).

At Texas Petrochemicals, retroreflectors occur at 100, 200, 300, and 400 meters. They dwell on the 400 meter retroreflector doing continuous measurements every three minutes until they detect an exceedance of 15 ppb at which point they begin scanning the other retroreflectors. Continuous scanning allows for a determination of the 100-meter interval where the exceedance is occurring and for how long. When the 400-meter reading drops below 15 ppb they go back to their dwell mode.

As an initial demonstration that the system functions and can accurately measure gases in the air, a sewer pipe (24 inch diameter by 30 meters long) was placed in the light path. The pipe was capped with transparent plastic that would not produce spectral interferences, and it was filled with a known amount of gas. The instrument detected the gas and provided an accurate estimate of concentration. For quality control, the instrument contains a calibration cell filled with a known amount of calibration gases. This cell moves into the light path once a day and provides evidence that the system is functioning and accurate.

Information about dominant species, approximate location along the fenceline, time, and wind direction at the time of detection can be used by the facility to determine the location and cause of the release.

Passive Mode Flare Example

The spectra from a passive instrument include an emission spectra and are entirely different from the absorption spectra of the active system. When measuring flares, the FTIR signal has four components: background radiance, flare radiance, atmospheric path radiance, and transmission radiance. Generally atmospheric radiance is negligible. For the mathematical expression of an example spectra, see the presentation. The peak of the emission spectra is temperature dependent. For example, the heat emitted by a person's body will produce a weak spectra in the far infrared because it is low in energy. As the temperature increases the peak grows and moves towards shorter wavelengths. Since background radiance has to be subtracted out of the calculations, it is necessary to point the instrument to the side of the flare to obtain background measurements. The temperature of the plume is needed to quantitate the compounds in the spectra. Temperature estimates can be obtained from the CO_2 spectra. The flare efficiency is given by total CO_2 divided by the sum of CO, CO_2, total hydrocarbons (THC), and soot. CO, CO_2, and methane are easy to obtain. If desired, the spectra for hydrocarbons with <C5 and above threshold concentrations can also be obtained. Other hydrocarbons fall under the THC concentration, which is obtained by using the C-H stretch region and calibrated against a specific heavy organic compound or a mixture of organic gases. For the results of a flare test at John Zink, see the presentation.

Generally, when flares are operated carefully, they can obtain 89-99 percent efficiency; however, this efficiency can drop precipitously (into the 80s or lower) when the flare is assisted with steam or air. Wind fields also diminish efficiency and the facility does not have much control over them.

Comment: From a design standpoint someone has said that the flares are often designed specifically to avoid smoke and noise not to minimize emissions. What is your opinion?
Answer: This may be true with assisted efforts where the idea is to produce a lot of ambient air mixing to get more complete combustion. This works up to a point, after which it becomes counter productive because the assisted air/steam cools the flame.

International Applications of OTM-10 in Chemical and Petroleum Industries
Dr. Ram Hashmonay (ARCADIS)

Dr. Hashmonay used FTIR to measure fugitive emission fluxes at chemical and petrochemical facilities in Israel. The technique employed vertical radial plume mapping (VRPM), the protocol for which can be found in OTM-10 (http://www.epa.gov/ttn/emc/tmethods.html). VRPM deploys several retroreflectors along a line of sight at various distances, much like the setup described by Dr. Spellicy at Texas Petrochemicals; however, the technique also uses retroreflectors that are deployed vertically, thereby allowing for the development of a vertical concentration plane. By multiplying the concentration plane by the wind speed crossing the plane, the emission flux can be estimated. VRPM has been used at several locations, some long term (e.g., the two-year study of CAFOs presented later).

A 2.5-day VRPM study was conducted at a refinery in Israel to estimate emission fluxes from tanks and some process areas. One area with very high emissions occurred where trucks were filled without vapor recovery systems for product distribution. The FTIR and UV-DOAS detected alkenes, alkanes, some aromatics, nitrous oxide, MTBE, and methanol (list). Open path FTIR and UV-DOAS can be used in conjunction with a DIAL system (not used at this site) to provide an estimate of the distribution of carbon compounds in a plume. This estimate allows refinement of the DIAL measurements to obtain a better estimate of the mass present and to identify emissions such as MTBE that are not directly related to crude compounds.

In another example of FTIR use for determining component mix, Dr. Hashmonay presented two spectra of n-butane and n-octane from measurements taken in opposite directions at the refinery. In one, the distribution center plays a role and the spectrum is dominated by n-butane showing releases of lighter compounds. In the other, where finished products are not expected to be present, the heavier n-octane spectrum dominates. The spectrum at the distribution center also reflects truck traffic with higher emissions being associated with more trucks being filled. A comparison of the VRPM study with the DIAL study done in Alberta shows good agreement for the process and storage areas for C2+ hydrocarbon emissions; however benzene emissions are approximately an order of magnitude higher at the VRPM site than in Alberta. Dr. Hashmonay attributed the difference to the presence of the product distribution center in the VRPM study.

The second study involved a fenceline VRPM, conducted at a site with several chemical facilities. A number of halogenated compounds were detected as well as aromatics, alcohols, and ketones among others. Because different facilities were involved, a change in wind direction would generally yield a change in compounds detected.

VRPM surveys occur on a smaller scale than DIAL systems, and they may not measure the whole plume because of the need for a structure on which to mount the vertical retroreflectors. Accessible plant or fenceline structures are rarely higher than 25 to 30 meters. The choice between DIAL and VRPM depends on the application. VRPM is usually favored when more long-term monitoring is desired. VRPM can be used to provide a good estimate of the annual emissions of a facility.

Question: It is difficult to get good background measurements with the SOF at a plant. How are background levels determined with the VRPM?
Answer: With the single beam, the spectra intensities can be compared and an appropriate one chosen for background.

Hazardous Liquids Airborne Lidar Observation Study (DOT-HALOS)
Dr. Steven Stearns and Mr. Daniel Brake (ITT Corporation, US)

Dr. Stearns described ITT's airborne natural gas emission lidar (ANGEL) system. The system uses a light plane that contains a mid-IR DIAL instrument, digital video camera, and a high resolution mapping camera. The DIAL is tuned to methane when used for natural gas detection. The digital camera images can be overlain with DIAL results and GIS locations so that a client can "play" the overflight on their computers. The plane can fly the right of way much quicker than a ground based survey and it eliminates property access issues.

The mapping imagery can provide one foot ground resolution which gives the client a view not only of their pipeline but also the surrounding area. The surrounding area view is an added advantage in that it allows the pipeline owner to identify any activities such as construction that may endanger the pipeline integrity. The survey is placed on a CD to provide a permanent record of the aerial patrol, pipeline easement conditions, potential encroachment, and leaks, if any.

Dr. Stearns presented the results of a study done in Geneseo, NY, during April 2007. The study measured the release of methane into the air at different flow rates and mapped the resulting plumes in terms of concentration contours. While flying over the site at about 120 miles per hour (175 feet per second), the instrument took 1,000 measurements per second. The intent was not to cover just the pipeline but also the areas on either side in the event that leaking gas was migrating underground before surfacing. Dr. Stearns provided several pipeline leak examples including one where the DIAL was able to differentiate between gas escaping from the right of way, gas escaping from a nearby compressor facility, and gas leaking from a stuck valve in an overhead pipeline.

The DIAL system can be used in all seasons (rain and snow interfere) and light conditions. While the ANGEL system is geared to methane, in the mid-infrared spectrum, almost any hydrocarbon can be detected by retuning the laser. There are four types of products transported in underground pipelines: natural gas (methane), liquefied petroleum gas (propane and butane mixture), refined products (gasoline, diesel), and crude. DIAL can be used to detect any of them.

The next challenge for this system is to develop a way to quantify the leak rate (flux). Experiments are currently underway using a straight-line (as opposed to scan) overflight measurement in conjunction with a met station on the ground to provide wind speed data. One test for validating this method is to fly a number of measurement lines spaced at different distances from a known source. The plume should increase in size due to dispersion but the flux should remain the same. Another application of this concept would be to fly measurement lines downwind of a facility to determine high flux areas. If high fluxes are found, then scanning could be performed over the facility to identify specific sources.

Question: Using the conical scanning approach, is there a way you can fly at a higher altitude to increase the ground covered per pass?
Answer: We fly between 500 and 1,000 feet. The 1,000 foot upper limit is due to the power requirements of the laser. The higher you fly the more laser power is needed to maintain the signal. The lower you fly, the more sensitivity you have.

Overview: New Technologies to Meet Waste Program Needs
Dan Powell (EPA/OSRTI)

Mr. Powell represents the Office of Superfund Remediation and Technology Innovation's Technology Innovation and Field Services Division (TIFSD) which has been an advocate for developing and using innovative technologies for cleanup, site characterization and monitoring, and data management. TIFSD is not a grant making organization. It does not routinely fund research or demonstration projects but rather, it works to ensure that practitioners are aware of the latest capabilities and innovations in their field. Innovative tools and technologies find common applications across all of the waste programs (Superfund, RCRA, UST, and brownfields).

<u>Waste Programs Mission Needs</u>
Many Superfund sites have reached construction complete status and are now in the long-term monitoring post-construction phase. Thus, Superfund is emphasizing remediation performance monitoring, which involves determining whether the remedy functions as designed and is protective. Such monitoring takes into account emissions and capture issues.

Health and safety issues associated with characterization and remediation activities require monitoring (e.g., fence-line monitoring) to ensure that potential air emissions do not impact the public off-site. For this purpose, open path technologies that can run continuously and detect chemicals crossing long path lines can provide more information over the large areas and thus address sampling uncertainty (e.g, when, where, how much) issues that may be present in strategies solely using point-in-space equipment such as canisters. A collaborative approach that addresses the sampling uncertainty reduces the likelihood of “missing something” based on the the location of the sample collection or the timing of the collection period. Open-path tools can help provide better “collaborative” information on site conditions than traditional approaches alone. Mr. Powell said the focus of one technical section of the workshop would be the applicability of the open path tools outside of the air program.

Breaches in landfill covers can act as point-source hotspots for escaping gases. Thus, TIFSD has worked with EPA’s Office of Research and Development to demonstrate the usefulness of radial plume mapping to identify breach areas on landfills. Information on the demonstration projects related to this issue area can be found at http://cluin.org/21m2.

Another potential need area for more options and alternative for monitoring involves soil vapor intrusion. Can open path tools prove useful for addressing soil vapor intrusion? Soil vapor intrusion into overlying buildings from underlying soil gas or groundwater plumes has become a large issue during the past few years, and it is expected to continue to be an issue as old contaminated land is cleaned up and redeveloped.

TIFSD is now examining the carbon footprint of remediation activities to make them as "green" as possible. Open path tools are part of this evaluation to identify and measure potential greenhouse emissions from clean-up operations. This will be important for both establishing emissions baselines for our cleanup efforts and for monitoring performance and documenting savings.

Understanding the Market

EPA’s waste programs set cleanup requirements and oversee site characterization and cleanup activities. They are not technology buyers. In fact, 75 percent of the sites in the Superfund program are remediated by responsible parties. The regional laboratories, while not a large market, do purchase analytical equipment. Much of the work funded directly by EPA is conducted through the Corps of Engineers and implemented by clean-up contractors. The Superfund program's primary focus involves purchasing services, generally through contractors. The remedial action contractors, whether working directly for the government or responsible parties, develop and execute characterization and remedial action activities. It is these contractors who need to be convinced of the value of a technology before it can be used effectively.

Understanding the Issues

While standard methods for analytical laboratories exist (RCRA SW 846 and Superfund Contract Laboratory Program), they are no longer required. Contractors are free to propose different methods as long as the method meets the data quality objectives of the intended use of the data. For field work, not all decisions require the same level of quality. For instance, inexpensive sampling techniques that give yes/no or high/low results may be better for some purposes than one expensive method that provides an exact value. The latter may be necessary for a risk assessment decision but may not be necessary for monitoring a fence line to determine if volatile organics from a soil cleanup are escaping the site. Arguments have been made that many field technology measurements will not hold up to legal challenge; however, the courts generally side with the technology when it is shown that the precision, accuracy, and detection limits of the technology are appropriate for the purpose. In fact, when less expensive screening technologies are used to augment more definitive measurements, the uncertainty involved in ensuring that the decision being made is based on a truly representative value is vastly decreased. Because EPA's technology research and demonstration funding has been declining over the past few years, EPA now looks to partnerships with the Department of Defense and Department of Energy to obtain the maximum benefit from technology development.

<u>What We Hope to Achieve</u>
Mr. Powell and his staff member Mr. Adam are attending this workshop to learn about the latest developments in open path technologies in order to keep EPA regional project managers and response personnel abreast of open path technology developments. Mr. Powell anticipates marketing open path technologies to the air program and promoting their use in the waste programs. He intends to produce a better information database on the uses of technologies that includes their cost, application, and performance and team with the air program and ORD to develop training seminars.

Knowing the limitations and correct application of a technology, especially a new one, is very important. If a technology is tried and fails in an inappropriate application, word of the failure may give the wrong impression that it does not work for any application. Workshops like this are important because they allow participants to share experiences and obtain a better understanding of what works and where.

Quantum Cascade Lasers-Recent Advances and Future Directions
Dr. Gerard Wysocki (Princeton University, US)

Trace gas sensing applications are not limited to environmental and industrial emissions monitoring. They have also found uses in life sciences (breath analysis), law enforcement, and national security.

Several well established laser spectroscopic techniques for trace gas detection exist. They include multi-pass cells which can be stationary or mounted in a conveyance; cavity ring down spectroscopy that uses ultra-high finesse optical cavities to extract very low absorption signals; photoaccoustic spectroscopy; and open path remote sensing. Improvement of the existing techniques as well as development of new sensing methods strongly relies on availability of new laser sources.

Gaseous chemicals (especially those with five or fewer atoms) generally have strong absorption fundamentals (rotation-vibration) in the mid- to far- infrared spectrum. The absorption of light by these fundamentals provides a means for detecting and quantifying chemicals down to very low concentrations. The near-infrared light also can be used for identifying and quantifying chemicals; however, absorption in this region is due to overtone or combination bands with strengths that are typically two orders of magnitude weaker than the mid-infrared (mid-IR) fundamentals and hence, have much higher detection limits.

Many lasers are available for molecular sensing. Dr. Wysocki showed the absorption spectrum of carbon dioxide (CO_2) to demonstrate that the absorption intensity in one of the fundamental bands (4.2 µm) is several orders of magnitude higher than absorption wavelengths for CO_2 at shorter wavelengths (e.g. in the so-called telecommunication bands at 1.3-1.6 µm). Not many sources can emit into the fundamental band areas. Also, if the application is atmospheric remote sensing, then wavelength windows must be chosen in which the atmosphere is transparent. These atmospheric windows are found at the 3-5 µm and 8-12 µm wavelength ranges.

The mid-IR source requirements for laser spectroscopy are:

- Sensitivity (% to parts per trillion [ppt]): the laser must have an appropriate wavelength and power may be an issue especially in open path application where long distances and low returning powers are involved.
- Selectivity (Spectral Resolution): the laser should operate single mode with a narrow line width.
- Multi-Gas Components, Multiple Absorption Lines, and Broadband Absorbers: laser should be broadly tunable.
- Directionality or Cavity Mode Matching: the light source should produce good beam quality (well collimated with little divergence over distance).
- Rapid Data Acquisition: the laser should have fast time response.
- Field Deployable: equipment should be compact, robust and should not require any consumables.

<u>Laser Sources in mid-IR</u>

Many frequency-conversion based sources exist but they are complex and not easy to use in the field. Gas lasers such as CO and CO_2 lasers tend to be bulky and tuning of their emission wavelength is difficult. Lead salt lasers have the potential for field sensing but require liquid nitrogen for cooling and hence need more attention during operation.

Quantum cascade lasers (QCLs) cover the entire mid-IR wavelength range (3 to 24 µm). They have high power with greater than a five-watt peak when pulsed. QCLs are also becoming available for shorter wavelengths. These however, require materials with high energy band offset. The best material for QCL in the 3 µm region (C-H stretch) is InAs/AlSb. Pulsed operation using a InAs/AlSb QCL at room temperature has been demonstrated in this spectral region.

Single mode QCLs with embedded distributed feedback (DFB) gratings show thermal tuning ranges up to about 10 cm^{-1}; however, their typical yield is low (approximately >10 percent) and they are currently very expensive to purchase. When a QCL is configured in an external cavity (EC) system, the tuning range can be greater than 200 cm^{-1}. Dr. Wysocki and his colleagues have built an EC QCL system with high resolution mode-hop free wavelength tuning that is accomplished using piezoelectric transducers to control EC length and grating angle and QCL current control.

In summary, QCLs have high reliability, are compact, and have the advantage of room temperature operation in many, but not all, spectral regions. This however is relatively new (first QCL demonstrated in 1994) and dynamically developing technology and substantial progress in device performance is being observed every year.

Dr. Wysocki provided examples of spectral coverage when using a widely tunable EC-QCL laser at 5.3 μm and at 8.4 μm. The 5.3 μm EC-QCL produced a tuning range of 155 cm^{-1} and the 8.4 μm produced a tuning range of 182 cm^{-1}. Wide tunability enables excellent molecular selectivity for broad band absorbers (e.g. large hydrocarbons or volatile organic compounds VOCs). If a limited wavelength region is of interest it may be possible to replace FTIR with the EC-QCL based spectrometers to get better sensitivity and selectivity as well as faster measurement capabilities.

As an example a EC-QCL based quartz-enhanced photoacoustic gas sensor has been presented. The instruments exhibit high sensitivity and an excellent dynamic range. They are not configured in an open path mode but rather serve as point samplers. A small sample volume is required for their measurement cell. Several measurements of molecules both with broadband absorption bands as well as small molecules with well resolved ro-vibrational structure were presented.

In summary, Dr. Wysocki discussed a new EC-QCL laser system that he and his colleagues have developed. The lasers are thermoelectrically cooled, operate in continuous wave, and are widely tunable (up to 15 percent of the center wavelength). The mode-hop free wavelength tuning enables high resolution (<0.001 cm^{-1}) and it has good optical power output (up to 50 mW). EC-QCLs should provide new capabilities to current laser remote sensing technologies.

Question: What are the driving forces for lowering the costs of the technologies you have discussed?
Answer: Costs will come down if the researchers can trigger interest of large manufacturers to mass produce the instruments. The open path capabilities of these instruments have a number of different applications so they would not be restricted to environmental applications only. One of the most promising technologies that has potential to open new markets for volume production of QCLs are distributed wireless spectroscopic sensor networks.

Question: What do they cost now?
Answer: The laser with electronics would cost $40,000 to $50,000.

Perimeter Air Monitoring during Manufactured Gas Plant Cleanups
Dr. Steve Takach (Gas Technology Institute [GTI])

From the mid-1880s until about 1950, manufactured gas plants (MGP) generated combustible gas from coal and oil. Large volumes of coal tar that were created as a by-product from these processes were often disposed of onsite. Although there are many risk drivers for cleanup (volatile organic compounds [VOCs] and polycyclic aromatic hydrocarbons [PAHs]) of MGP sites, the main contaminants of concern from a community exposure perspective are benzene and naphthalene fugitive emissions when subsurface soil is disturbed.

About 3,000 to 5,000 MGP sites exist in the country and while they may have been at the periphery of a town or city when they were constructed, they are now found well within the city limits. Since cleanup and hence potential exposure times are brief, the risk associated with remediation is typically low; however, public perception of odors coming from a site are generally negative and may lead to lawsuits alleging health effects. It is therefore in the interest of a company to install fenceline monitoring that shows what levels of contaminants, if any, are escaping from the site during cleanup. Typically these data are collected at downwind points along the fenceline and an argument can be made that they are not spatially representative of the emissions crossing the fenceline.

In 2004, Atmos Energy Corporation initiated a MGP cleanup in Bristol, TN. The site was within 30 meters of the Sullivan County Court House and the Bristol Police Department. The company chose to monitor for fugitive emissions with an open path FTIR system. Ten minute averaged action levels were established to ensure timely mitigation in the event of an exceedance. The project was very successful.

In 2005, the Operations Technology Development Group, a consortium of utility companies, agreed to fund a 26-month effort to develop optical remote sensing (ORS) methods for perimeter air monitoring during MGP site cleanups. The project objectives were to compare ORS-based and traditional point-monitoring approaches, enhance existing ORS data management and reporting software, and create a methods guidance document. Two sites were chosen to conduct the research—Pitney Court in Chicago, IL, and Coney Island in Brooklyn, NY.

The approach adopted for the FTIR was a modified cross-sector averaging technique. This technique employs a three step process:

- Make a 10-minute averaged FTIR measurement immediately downwind of the source (usually excavation area).
- Divide the path intergrated concentration by the plume width to yield a representative point concentration (RPC).
- Based on the onsite meterology, apply a dilution factor (dispersion) to the RPC to assess compliance with a 10-minute averaged action level at the nearest community receptor.

They have developed a decision rule for taking mitigative action. Continuous monitoring is conducted during site work. When an action level exceedance is detected, it is reported to the designated site personnel, and monitoring continues. One exceedance does not trigger mitigation; however multiple exceedances result in suspended site activities and initiation of whatever predetermined measures are necessary to reduce the emission. Site activities can resume after two successive monitoring events with no exceedances. This strategy is consistent with the EPA Triad approach—that advocates systematic planning with real time decision making based on onsite measurements.

Dr. Takach provided an example of the data management reporting software screen that shows input and output data. The Methods Guidance Document is now under development, but a draft of its table of contents is in the presentation.

Identified Benefits:

- The modified cross-sector averaging (MCSA) technique is substantially less expensive (at least 25 percent) than fixed-station, point-monitoring systems typically employed during MGP site cleanups.
- Regarding community acceptance and litigation avoidance, the high-tech nature of open path FTIR spectroscopy can allay public fear of the remediation.
- The permanent electronic retention of the records evidencing insignificant community exposure, together with the raw FTIR measurement spectra themselves, provide a compelling defense against legal claims.

Question: Do the companies that have access to this technology plan to market it to industries other than MGP?
Answer: We anticipate that the success of this project will make it easier to convince other entities that need fenceline monitoring for health and safety purposes to use it.
Comment: GTI should consider collaborating with Mr. Powell of EPA to offer a web cast to make more people aware of this technology's existence and capabilities.

Question: Did you compare what you were estimating to be the concentration at the receptor to an actual measurement?
Answer: No, but by comparing a 10-minute average with a 24-hour ambient air acceptable concentration and conservative plume width estimates, among other things, the applied dilution factor is very conservative. Since this technique is used as a screening tool, as long as fenceline levels remain below the action levels, you are assured that downwind exposure poses no problems.

Question: Are you aware of any lawsuits that have been dismissed because of this technology?
Answer: No.

Question: What happens when the wind direction changes radically?
Answer: You can establish an acceptance window and work within it, or you can use extra retroreflectors to cover other legs of the site. You could use multiple FTIR instruments to generate multiple beams. If only working with a single setup, you can use

an auto-positioner that responds to significant changes in the wind direction, or you may have to reposition your open path instrumentation. In such a case, the open path system can usually resume operation within about 20 minutes. What scheme to employ depends on the needs of the site.

Landfill Applications of ORS
Susan Thorneloe (EPA/ORD)

Although the amount of greenhouse gases (GHG) emitted from landfills generally is not known, landfills are the largest source of methane in the United States. The typical municipal landfill gas (LFG), which is generated by the decomposition of biodegradable waste, contains 10-60 percent methane, 40-60 percent CO_2, and trace constituents of VOCs, hazardous air pollutants (HAPs), and persistent bioaccumulative toxics. The EPA Urban Air Toxic Strategy has identified landfills for residual risk evaluation. More than 30 HAPs have been identified in LFG and new data suggest that there is an increasing occurrence of hydrogen sulfide (H_2S) concentrations.

The adoption of wet/bioreactor landfill operations where porous materials are used as covers to increase infiltration may increase LFG emissions, but by how much is not known. ORS might provide a way to measure these emission changes. The redevelopment of landfills for recreational use can result in damage to their covers and increased water infiltration due to increased irrigation to maintain turf grasses. Ms. Thorneloe provided an example of a site in Colorado Springs, CO, where the local community wanted to turn a landfill that was closed in the 1980s into a park with a view of Pike's Peak. An ORS survey found a substantial amount of gas emissions coming from the landfill. Thus, if a park were located on the landfill, the landfill cover and a well field would have to be maintained.

ORS can be used to identify sites with few emissions and to determine how well current controls are working. The traditional way of measuring LFG emissions at landfills is through flux boxes embedded in the cover; however, flux boxes do not capture leaks and they may not represent emissions from the entire cover. ORS provides a means for measuring flux across the entire landfill and can be used to build a better GHG inventory for these sources.

Recent developments in landfill emissions research has been possible through cooperation between EPA's ORD and EPA's Office of Superfund Remediation and Technology Innovation's Technology Integration and Information Branch (contact: Mr. Powell). The branch maintains an ORS technology webpage at http://www.cluin.org/programs/21m2/openpath and the air office has protocols for conducting the measurements at http://www.epa.gov/ttn/emc/tmethods.html.

The technologies employed in the ORS landfill research are scanning boreal turnable diode laser (TDL) and open path FTIR. Ms. Thornloe believes that the TDL may be more appropriate for landfill applications because it is easy to setup and costs less than FTIR. On the other hand, if the objective is to identify a wide range of pollutants, FTIR is the better choice. The results of the collaboration between Ms. Thornloe and Mr. Powell are summarized in Evaluation of Fugitive Emissions Using Ground-Based Optical Remote Sensing Technology.

This document reflects the initial work to evaluate performance and identify the challenges in landfill emissions measurement. One of the challenges involved how to ensure total plume capture—especially with an uneven topography. Also during the initial work, ARCADIS developed software (radial plume mapping) that allows for near real time analysis of the data. The software gives vertical and horizontal two-dimensional planes of contaminant concentrations.

Ms. Thornloe briefly discussed ORD's efforts to measure various landfill emissions and provided links to them on the ORD website. There is one more report on uncontrolled air emissions from two landfill sites in Florida that are using leachate recirculation to accelerate waste decomposition. Samples of header pipe gas were collected to determine gas composition. They will use the ratios of gas concentrations from the header pipes to extrapolate to total emissions from the TDL measurements of methane. Release of this report is anticipated in the fall of 2008.

EPA has a cooperative research and development agreement with Waste Management to advance OTM-10 applications to landfills. They are conducting ORS RPM studies at 12 U.S. landfills. These studies are using tracer releases and different test configurations to evaluate the capture of total emissions including side slopes and difficult topographies. The results of these studies will be used to add landfill-specific guidance to OTM-10 information.

The standard OTM-10 application assumes a relatively small source area, the topography is flat with good wind sweep, and there is temporal stability. Landfills on the other hand are large, can have very uneven topography, can have general or multiple source releases, and may be surrounded by other nearby sources making open path measurement challenging.

One of the techniques they have tried is to install retroreflector towers at opposite corners of the landfill and place an instrument at the remaining two corners so they can rapidly adjust for wind changes. In the tracer studies, investigators calculated an RPM flux rate for acetylene gas released from tanks at a known rate to determine if the tower design was capturing the entire plume.

Question: Do you think that the IR camera could be used as a screening tool at landfills?
Answer: The air program requires some survey with tip instruments to determine leaks but neither they nor the camera will give flux for risk assessment.
Comment: The camera probably has too high a detection limit for use at landfills where there is low release over very large areas.

Question: How long do you spend at each landfill to get a flux?
Answer: At the two Florida sites they were there for three to four days at a time. Ideally it would be better to stay longer and of course the complexity of the site plays a role.
Comment: Waste Management surveys take four to five days on average.

Question: You have said that RPM is the preferred method of measurement but how do you ensure that you are capturing the plume at complex sites with slopes. Are the towers high enough?
Answer: Many validation and tracer studies show they are capturing the whole plume but improvements are needed.
Comment: The Waste Management studies use the four corners approach (two towers) mentioned above combined with tracers to test what is captured from various parts of the site (e.g., top, bottom, slope, middle, edge).

ORS at Consolidated Animal Feeding Operations
Dr. Richard Grant (Purdue University, US, and Mr. Richard Shores, EPA/ORD)

Mr. Shores discussed the history of ORS at Consolidated Animal Feeding Operations (CAFOs). Fugitive emissions measurements with FTIR began in 1995. Since that time, emissions measurements have continued and the techniques have been refined. A consent agreement, signed in 2007 with farming organizations, provides for extensive study of CAFO emissions funded by the farming organizations. Several links to more information on the consent agreement are available.

Mr. Shores gave as an example, the monitoring of a poultry house operation using a Unisearch TDL. A poultry house can be large (e.g., 600 ft long by 50 ft wide). The one that was monitored contained 100,000 laying hens that lived on the top level of the building. Their manure fell to the bottom level. Seventeen fans were placed at each end of the building to draw emissions off the manure out of the building. Large inlet areas on the other two sides of the building allowed fresh air to enter. Investigators set up their equipment to measure fan-driven air exiting both the top and bottom levels at both ends of the building and to measure the ammonia concentration entering the building at the inlet area—there really is no "clean air" at the farm.

Each building, or the farm itself, can be considered a point source. This particular farm had over one million hens and manure lagoons to hold the refuse. The farm practiced spray application of manure to fertilize their crops. The ammonia concentrations taken from the building were nine to 14 ppm off the manure level, three to five ppm for the animal layer, and between zero and two ppm for the inlet air. The measurements were taken at 120-second intervals and were reasonably consistent.

Mr. Shores briefly discussed monitoring a naturally ventilated swine barn with TDL. These barns have a curtain along their entire length. As the temperature rises the curtain falls and as the temperature falls the curtain rises until there are few emissions. The setup has to account for different heights of the curtain—including measuring at the base, which is the point of highest emissions.

At a lagoon in Jacksonville, NC, a FTIR VRPM system was deployed to evaluate the effectiveness of a biomass cover to control ammonia emissions. The theory is that the microbes in the biomass consume the ammonia gas before it reaches open air. The VRPM, with three retroreflectors (highest set at 10 meters), was set up to measure downwind emissions.

Manure lagoon levels are frequently drawn down by spray irrigation, and Mr. Shores used TDLs and VRPM to develop a flux plane to evaluate ammonia air emissions from this operation. The regulatory control at this type of operation is governed by the water program, which is concerned about potential surface water contamination from the runoff of nitrates and the percolation of nitrates to groundwater. The farmer evaluates total nitrogen in the effluent to determine when spraying is allowed. The air program is not involved. Mr. Shores found that about half the total nitrogen was lost to the air, while the other half went into the soil.

The CAFO study shows that the combination of farming techniques, different regions of the country (frost belts versus non-frost belts), different feeds, different animals, and farming size all affect emissions.

ORS at Consolidated Animal Feeding Operations National Air Emissions Measurement Study (Continued)
Dr. Richard Grant (Purdue University)

This study is funded by industry and consists of two major components: barns and lagoons. Ten swine and dairy farms from around the country were selected to collect data on lagoons with different operations and climatic conditions. Over a two-year period, two teams are rotating among eight farms to collect data once each quarter for an average of 14 to 21 days per event. Continuous measurements are being conducted at two farms for a complete year each. The continuous measurements will be compared to annual emissions extrapolated from selected quarterly data to determine if extrapolation is an appropriate technique to obtain annual averages.

Setting up the instruments, which are monitored from Purdue University, takes about three days. The project does not have the funding to fully staff the instruments at the sites, so the instruments are operated remotely. They monitor for ammonia with TDL instruments attached to scanner bases that automatically align them with the retroreflectors. The retroreflectors (cubes), which are mounted on tripods and towers, are heated to avoid condensation and pressure vented to avoid seal damage and water entry. Path lengths varied from 30 to 750 meters and they used the four corners setup with towers in opposing corners and instruments in the remaining corners.

The swine barns were generally close to the lagoons, so they chose farms where the building exhaust fans were not blowing across the lagoons. Swine farms as opposed to dairy farms tend be designed the same. In all, six swine farm lagoons were monitored.

The equipment included Boreal Laser GasFinder2.0s measuring ammonia absorption at 1512 nm. This system is operated by remote telemetry from Purdue. System failures are detected but not fixed remotely. The most frequent problems were shutter failure due to heat and signal return interferences due to heavy fog or rain, water films on the retroreflectors, and dust films. The scanners were Directed Perception PTU D-300s (step motor type system). Keeping the scanner aligned with the retroreflectors posed problems, and they had to install uninterrupted power supply units on site because a power loss caused the instrument to lose its sense of direction and hence its ability to locate the retroreflectors. While summertime heat affected shutter performance winter time cold caused stiffness due to cold lubricants.

The sampling protocol called for about a 15-second dwell time for each retroreflector with eight to ten measurements depending on the measurement quality. The scanner can take up to five seconds to move from one retroreflector to another. At every measurement the light level is measured, and at the beginning and end of a measurement period, single-point calibration verification (50 ppm-m) occurred. They allow up to ten minutes for light optimization before moving to the next retroreflector. Optimization reflected an attempt to find a light level that was above background but below the maximum acceptable limit. Typically the alignments were not aimed directly at the retroreflector which would produce too strong a return signal. With the TDLs, an r^2 or correlation coefficient was generated with each measurement. The r^2 was the correlation between the sampled absorption and an internal reference spectrum. It is usually a function of concentration—the higher the concentration the higher the r^2.

The cell windows of the calibration cell posed problems. The window causes polarization of the laser and since each laser is unique this can cause problems. Rotating the window gave different concentrations of the known calibration gas, so they could not get a true verification calibration. Typically, they strived for a bias of ten percent and precision of five percent with the cells. The method detection limit varied by laser from a little over 1 ppm-m to a little under 3 ppm-m.

At a site in Oklahoma they found significant ammonia fluxes coming off the lagoon with mean path integrated values up to 174 ppm-m (tower reading) over a 13-day period.

Panel Discussions

Mapping, Ranges, and Complementary Aspects of Different Open Path Technologies
Hamish Adam (Boreal Laser), Alex Cuclis (Houston Advanced Research Center), Lennart Frisch (Agenda Enviro AB, Sweden), Ken Garing (EPA/NEIC), Bob Spellicy (IMACC Instruments)

Ken Garing. About ten years ago Mr. Garing, his colleagues, and industry (e.g., American Petroleum Institute), began looking for a better way to find fugitive emissions. Initially they were interested in an active laser system and had Sandia National Laboratory evaluating options, when a prototype passive IR camera that cost a fifth of the active camera cost surfaced. The success of the video camera has spurred a change in the concentration-based emission-measurement rule to the proposed alternative work practice that estimates mass. Previously, a leak measured by a total vapor analyzer type instrument was defined as a specific concentration e.g., 500 ppm to 10,000 ppm. However, the proposed SMART LDAR rule, would allow a mass number in lieu of a concentration number. [This rule was still Draft at the time of this writing.] Some facilities are reluctant to use the IR camera, opting instead for the established system, because of regulatory uncertainty: they still have to perform the LDAR measurments until alternative methods are approved (because the camera does not have low enough detection limits for the current paradigm), and additionally the camera may find emissions in areas not currently in the monitoring program.

The cameras are finding other uses as well. They are used in safety surveys to identify major leaks before start up and in aerial surveys to identify pipeline leaks. They also are finding their way into the hands of advocacy groups, causing some facilities to step up their vigilance to detect leaks and prevent any potential negative publicity that could result if a chemical plume is identified by such groups. Mr. Garing has used an IR camera as a screening tool for Method 21. If the camera sees a leak, a total vapor analyzer will show very high readings at the release point.

Lennart Frisch (slides). Mr. Frisch discussed a proposal of the basic provisions for a *Protocol on Measurement Strategies* for the purpose of both reducing emissions and to keeping them low. The protocol involves identifying the types of facilities that may require emission flux measurements, the VOC-substance(s) requiring measurement for each type of facility, and the areas likely to have emissions.

The measurement campaign should be designed to achieve specific objectives. It should determine beforehand the data management, and reporting requirements, as well as funding sources. A site reconnaissance should be conducted to assist the decision on which measurement strategy to use, appropriate time needed on site for the measurements and where to locate the measurement devices to be used. Once the measuring begins, it is important to maintain a continuous dialogue with plant personnel who can identify transient events as they occur.

A preliminary report should be presented to the facility and fluxes and VOC distributions discussed. Authorities should, if they are involved in the study, also as much as possible take part in the discussions.

A final report should be released within two months in order to keep its immediate interest high. The report forms the basis for deciding if more measurements are needed and if so, their frequency and if focus should be put on certain hot spots of the premises. It also may be used to improve the LDAR design. Combining traditional LDAR methods with the newer equipment such as mobile cameras could also mean better coverage of non-easily accessible potential leaking points.

As issues of high VOC-emissions can be expected to gather substantial public interest it is recommended to elaborate at least a brief community relations plan, especially if the open path method shows a much higher total emission level than the one calculated for the facility. The latter situation is expected to be the case in most situations, especially as a result of a “first-measurement” campaign.

Flux measurements based on a sufficient number of relevant scans for each of the functional parts of the facility in most cases can be generalized in describing annual average levels and they provide a way to determine where measures to reduce emissions primarily should be undertaken, whether more or less maintenance may be required and also how maintenance relates to equipment age and use.

It is important that the monitoring equipment be reliable and capable of detecting all the relevant volatile species at useful detection limits. In order to achieve this the basic measurement device has to be used in combination with tools being able to specifically cover the meteorological conditions such as the wind speed, direction and variability in height as well as the the VOC-species specification. More than one instrument may be needed to do this. Considerations have to be given to the mobility of the equipment and its ability to adapt to such ambient factors as wind speed and direction, clear or cloudy skies, and the impact of high humidity which can affect some equipment. The staff using the equipment has to be experienced and well acquainted with the type of industry or other type of installation at which the measurements are to be undertaken.

A report on fugitive VOC-emissions at refineries and oil harbors, which he authored, is available in English at http://www.o.lst.se/o/Publikationer/Rapporter/2003/2003_56.htm

Bob Spellicy (slides). When open path technologies began to blossom in the early 1990s, Mr. Spellicy and his colleagues expected these technologies to excel but they have not. He attributed their lack of growth to the absence of protocols for their use. Industry does not adopt new monitoring technology unless it is mandated to do so or it believes that doing so will give advantageous results that are cost effective. In contrast, the IR camera has been accepted. It is easy to use and not too expensive, but it does have a high detection limit. He hopes that the next step will take a 2-D RPM approach in which mirrors are placed either permanently or temporarily throughout the plant. Different process areas can be scanned separately for the appropriate compounds or species. Lower detection limits will allow smaller leaks to be detected and an increase in mirror density can locate those areas that are leaking. After a leak is detected, the camera or a TIP instrument can then be brought in to locate the exact valve or flange.

Often, available technologies are compared for the purpose of choosing one that satisfies the most needs. This approach misses the opportunity to combine technologies that are synergistic and provide a better result than either technology could alone. While current optical monitoring technologies offer powerful capabilities, each has its own strengths and weaknesses. Combining technologies can play to their strengths. For example Lidar with its capability of mapping plume species can be combined with FTIR/DOAS measurements to give both plume distribution and composition. More attention needs to be given to combining technologies.

Hamish Adam (slides). Open path monitoring is a relatively new technology, particularly in North America. As a manufacturer of these technologies, Boreal Laser tends to get invited to work on applications for which nothing else works. It is really important in open path environmental work to maintain strong lines of communication with the manufacturer to improve the operation and capability of the technology.

Currently FTIR open path technologies that operate at room temperature operate in the near infrared (NIR) spectrum. NIR has weak absorption bands and hence can only measure small molecules; however, as was mentioned earlier, research with diode technologies hold the promise of extending this capability into the mid-infrared range and beyond where strong fundamental absorption bands exist. Mr. Adam demonstrated this with a spectrum of methane in the near and mid-infrared range that showed that while both are well resolved, the mid-infrared is much stronger.

The focus of this workshop has been on environmental monitoring; however most of Boreal Laser's work with these technologies is for health and safety purposes. In these applications, the objective is to produce a clear and unambiguous alarm when specific toxic gases are detected. An example would be continuous monitoring for hydrogen fluoride at refinery alkylation units. In this application, multiple paths are set up around the perimeter of the unit to provide an immediate warning in the event of a leak. The spectrometer units provide full path coverage that is lacking with point sensors. Another application is to monitor sour gas wells for hydrogen sulfide leaks.

Alex Cuclis (slides). Mr. Cuclis has been studying the results of DIAL and SOF campaigns and comparing them to studies performed in Houston. About 35 refinery studies (primarily in Europe) over the past 20 years show that at the best refineries, about 30 barrels of emissions are lost for every 100,000 barrels of throughput. The worst refinery was losing more than 200 barrels for every 100,000 barrels of throughput. These studies span all seasons, including winter in Sweden where the average temperature is well below freezing, and still there are substantial emissions. When the reported emission estimates are compared to the open path measurements they are about an order of magnitude lower.

A $20 million field study, conducted in Texas in 2000, measured the amount of NOx and VOCs in the air. The NOx numbers matched relatively well with what was expected using projected inventory numbers. The VOCs, on the other hand, were about 1000 percent higher than what was expected given projected inventory numbers. Shortly after the 2000 study the IR cameras became available and facilities started using them to identify releases. In 2006, the TexAQS study found that NOx values were getting even better while VOCs had improved but were still not good (10 to 50 times higher than expected given inventory projections).

Houston has many point source monitoring stations that provide some data on concentrations but cannot provide data on mass flux or the source of the plume. Open path techniques help fill these gaps.

Question: There is an obvious disconnect between the inventories and the integrated source measurements. How do you take the next step to identify the problem sources from an inventory perspective and from a control perspective?
Answer: Industry is beginning to use the IR camera to identify source areas that should be monitored as part of the inventory and to help find leaks and/or practices that can be fixed or modified.
Comment: We have been doing fenceline monitoring on a continuous basis and most of the emissions are very transient. At Texas Petrochemicals, emissions have come down quite a bit. Using fenceline monitoring, wind direction, and time of occurrence data, the plant managers can estimate where the emission came from and what was happening at that time. Typically, the emission was not a leak but a process change or procedure—both of which can be adjusted.
Comment: Every site must be treated individually. The experience in Sweden showed that the initial DIAL/SOF measurement was worth while in that it resulted in the facility modifying or fixing equipment/procedures that led to an economic pay off for them.

Question: When will the SMART LDAR rule on the IR camera be out? The point was made earlier that adoption of technologies by industry generally does not happen without a protocol.
Answer. The proposed rule for SMART LDAR was issued and the time for comments was extended. To date all the comments have been addressed and the rule is awaiting final approval.

Question: For the SMART LDAR rule, were any other technologies considered other than the cameras?
Answer: No.

Lessons Learned from Previous Studies and How to Learn from Them Through Standard Test Practices
Jan Moncrieff (Spectrasyne, Ltd, UK), Russ Nettles (Texas Commission on Environmental Quality), Rod Robinson (NPL, UK), Steve Stearns (ITT Corp, Space Systems Division), Eben Thoma (EPA/ORD)

Russ Nettles. The most important take home message is this: design studies that not only identify general problems (e.g., discrepancy between VOC levels in the air and inventory) but also provide information on how to fix problems if found. The 2000 study showed a problem, but it did not tell TCEQ where the problem was, other than suggest that it probably was not in the LDAR monitored areas. The IR camera helped identify problem tanks and practices such as allowing tank roofs to land.

The 2007 DIAL campaign identified potential problems with flares that need further investigation. Process upsets are very visible in flares but routine burning assumes high efficiency which is not necessarily true. The issues identified in the 2007 DIAL study such as flare efficiency and not using lot-specific crude vapor pressures to calculate emissions are industry wide problems, not facility-specific issues.

Steve Stearns. The technologies discussed at this workshop are barely mature (except DIAL which has been in use in Europe since 1980s) with the airborne technologies being even less advanced. One area that appears to present an opportunity for improvement but needs more research is how to best use the technologies to complement each other. For example, land-based technologies to monitor a facility several miles square might benefit from periodic overflights to identify areas within the plant that need closer scrutiny with land-based technologies. In the case of landfills where methane may be an issue, an overflight survey can be done quickly and can show whether further investigation of the landfill is needed. Although overflights have a low probability of picking up transient events, they can be very valuable in identifying chronic issues. Pipeline surveys have revealed that natural gas compressor stations consistently show emissions, an issue that has not received much attention. The current technology does not quantify the amount of an emission; however, it does allow a visual interpretation of size (small, medium, and large).

The capability of mapping large areas has opened two very new types of investigations. The first involves mapping about 50 square miles of thawing Alaska tundra for methane releases. The second involves overflying an area containing coal beds that are scheduled for methane mining to locate preexisting seeps. The client in the methane mining project does not want to be blamed for causing the seeps.

Jan Moncrieff (slides). In Europe it is quite common to combine technologies to give a fuller picture of emissions. For example, when conducting long-term monitoring with FTIR/VRPM, the DIAL system can be brought on site to determine optimum positioning for the retroreflectors under various wind conditions to allow maximum plume capture. The FTIR can also be used during a DIAL campaign to help speciate mixed hydrocarbon plumes. In Canada, the IR Camera has been used very successfully in conjunction with DIAL to help pinpoint leak sources seen on DIAL scan lines even when these have been in awkward positions e.g. out of reach from a ladder or platform on a piece of the plant. DIAL quantifies, IR Camera pinpoints. Since the early 1990s, in Europe, more traditional “sniffing” methods have been used with DIAL for this purpose, but the IR camera is much more flexible.

Ms. Moncrieff discussed the components of a DIAL survey with specific emphasis on the protocols. Spectrasyne is participating in the Remote Optical Sensing Evaluation (ROSE) project sponsored by the European Union (EU). This three-year project will determine the QA/QC parameters defining the performance of remote optical measurement techniques in support of future EU standardization.

Rod Robinson. (slides). Optical open path instruments have several configurations. The DIAL system, which uses both infrared and UV/visible light, can achieve ppb detection limits. Any statement about detection limits should include the path-interval that was used. Examples of the maximum range of the instrument vary from 500 meters for methanol to 3 kilometers for sulfur dioxide. Atmospheric water vapor can be a strong interferent for some compounds. The vertical scans enable DIAL to map the plume and calculate emission flux. Also the DIAL vehicle allows the measurement to be made away from the source where the wind patterns may be less complex.

All protocols have similar sections that address the specific measurement technology. These include system operation (source power, wavelength, and calibration), measurement configuration, and wind field. For a more complete listing, click here. Also remember that DIAL uses path-integral measurements with lots of paths.

There are some published standards available. These include:

- CEN WG 18 open path methods for OP-FTIR and DOAS (The National Physical Laboratory may initiate a DIAL standard)
- VDI standard 4210:Blatt 1 for LIDAR remote sensing
- OTM 10 for long path integral tomography

Eben Thoma (slides). Open Path QC protocols are extremely important. As a first step, data quality indicator tests should be developed to periodically verify that the system is operating correctly. These indicator tests for FTIR include signal return, single beam ratio, and signal-to-noise ratio. Signal return, fit deviation, and function testing are indicator tests for UV DOAS and TDL. If appropriate, infield calibration cells should be used to test the unit's precision and accuracy.

Side-by-side measurements using different types of instruments can be useful. For example FTIR and TDLAS instrument beams are directed through an open ended tube to a retroreflector and back. The tube has a known amount of gas blowing into it. The two instruments should give similar results. Dr. Thoma showed the measurement results of two TDL instruments made by different manufacturers. There were large differences in the achieved precision between them. Knowing the capabilities and characteristics of the chosen instrument is important to interpreting the data it produces. Finally a TDLAS and an FTIR instrument operating at different wavelengths to measure methane at a landfill were compared. Their measured concentrations over time were in very good agreement and provided solid evidence that the calculated concentrations are real.

Question and comment: Do you need information about the wind conditions at a site for overflight measurements and have you considered doppler lidar? Advances in doppler lidar are making them smaller, lighter, and cheaper. A doppler system that provides exact wind conditions at the point measured instead of relying on a met station could be integrated into the DIAL system.
Answer: Wind is an issue during pipeline inspections. The wind speed has to be less than 12-14 mph or there will not be a methane plume to detect. Portable met stations give wind speeds about every 15 seconds, which is good enough for plume mapping. Since quantification has just started to become important, precise wind speed measurements are not needed. If advancements reach the point where they can calculate a flux, they will need better wind measurements, and doppler might be the technology of choice.
Answer: For DIAL, anemometers can provide sufficiently accurate wind speed data for flux calculations provided they are placed “in” or close to the DIAL scan plane. They did look into integrating doppler with their equipment; however doppler gives information along its path when what is needed is the crosswind speed, so the doppler and the DIAL would have to be deployed in different locations.

Question: Why is it that the overflight lidar system can be deployed in a light plane while the ground-based system requires a much bigger area?
Answer: One reason is that the overflight lidar is a very new instrument and advances in lidar technology over the past few years have been tremendous. If they had decided to do this work five years ago they would have needed a much larger aircraft.
Answer: The DIAL system requires a steering system, measures more than one species, and is time gated/range resolved (measures change in concentration along the path using the atmosphere as a back scattering medium); whereas, the aircraft lidar is not time gated, uses the ground as a reflecting tool, and measures only the total integrated signal between the plane and the ground. The DIAL vehicle is set up to allow multiple workstations for staff. Over 20 years of operation the physical size of the DIAL vehicle has never been an issue in achieving the required measurements.
Comment: All that aside, it may be possible to build a system that is smaller, less costly and hence more commercially available; however, a more compact system would necessarily be less flexible.

Question: Mr. Nettles said in his presentation that flares should be given more attention in the next measuring exercise. Could DIAL be used for this or would some other ORS instrument such as passive FTIR be better?
Answer: Texas is planning flare investigations in the near future and is looking at all available technologies to determine which would be best.
Comment: Another approach might be to determine if the flare type used in Texas is also used in Europe. There could already be data on the flares's efficiency under different operating circumstances. Spectrasyne alone has performed over 20 DIAL flare surveys in Europe and Canada.

Thoughts on Future Applications and New Opportunities

Ralph Marquez (Environmental Strategies and Planning), Roy McArthur (Environment Canada), Felix Mestey (Naval Facilities Engineering Command, Washington DC), Dan Powell (EPA/OSRTI), Brenda Shine (EPA/OAQPS)

Ralph Marquez. Scientific advances in technologies in this country are occurring at a rapid pace. But in order for these advances to benefit the environment, they must be commercialized and their application proven. Mr. Marquez believes that good technologies also must be accompanied by good policy making. New technologies may not survive under old policies.

Some of the tools discussed here are the best thing that has happened to air pollution control in the last 25 years but key policy level people do not know about them. When he was at a meeting with EPA policy makers last year, he discovered that no one, including about a dozen directors of state agencies, had heard about the IR camera. After policy makers find out about a good technology, five years of rulemaking followed by three years for industry to adjust to the rules takes place. Meanwhile emissions have continued for those eight years. When Texas first saw the IR camera they immediately bought one, overflew their refineries in a helicopter, made videos of what they saw, and mailed the videos to the refinery managers with a letter that said you have 45 days to tell us what you are going to do about these problems. For the most part the responses were positive and problems were fixed. They did not take enforcement action unless the facility balked at fixing the problems. This demonstrates that when government takes the lead with a new technology, problems get fixed sooner rather than later.

Roy McArthur (slides). There has been a shift towards direct measurement of emissions. Environment Canada started using DIAL in 2003. In March 2006 the U.S. EPA's Inspector General released a report that found the use of emission factors results in a significant under reporting of emissions at refineries (among other industries) and recommended more direct monitoring. In October 2006 U.S. EPA released the proceedings of the first VOC emissions workshop. The proceedings report indicated that a large body of observations has found emissions were under reported by 10-20 times those of actual measurements. In September 2007 EPA proposed new rules, adding new requirements to the existing rule for certain storage vessels and wastewater treatment units as well as new work-practice standards for the detection and repair of leaks from cooling towers.

An aggressive ORS monitoring program at a refinery in Sweden reduced an emission rate of 1,500 kg/hr by 84 percent. This reduction shows the usefulness of employing direct measurement tools. Environment Canada funded or co-funded several demonstration projects at industrial facilities between 2003 and 2005. These demonstrations highlighted DIAL's unique ability to quantify and apportion sources of VOCs and other emissions at complex processing facilities.

The TCEQ conducted a DIAL study of a refinery in Texas City and representative petroleum facilities along the Houston Ship Channel. The City of Houston is planning a DIAL study of air toxics (e.g., butadiene, benzene, PAHs) from petrochemical and refining operations with a preliminary start date in 2008. A DIAL study is being planned for a steel mill in Canada (start 2008/09) that will concentrate on quantifying mercury, VOC, and PAH releases from coking operations. Another petroleum refinery may be included in this effort.

Quality assurance for ORS was established as an important development objective at the first workshop, and it remains an important part of the program. Mr. McArthur provided some thoughts on quality assurance topics in his slide presentation.

Felix Mestey. DoD installations can benefit from the technologies displayed at this workshop. Like the civilian sector, DoD has large fuel handling facilities and landfills. DoD in cooperation with EPA supports research to test technologies and help develop guidance on its use. In the context of daily operations, the question is how to get the technology to the base commanders and get them to use it. DoD has what are called class 1 mandatory compliance requirements that do not necessarily include applications that the new technologies can fill; hence, new technologies compete for resources. Also as was pointed out earlier with the regulatory agencies, it usually takes DoD about seven years to put a new requirement into the field. One area that needs further exploring is how to provide incentives for identifying and correcting emissions that are not specifically regulated—both in the civilian and military sectors.

Brenda Shine. Ms. Shine works on refinery standards and was involved in the residual risk proposal. While imposing the additional standards, they took into account the uncertainty in the emission values from the ORS studies and the values submitted by industry. She stated that while the current emission factors and models are not necessarily bad, they need further calibration and refinement. Direct measurement by ORS is a great idea but may not be necessary at many facilities. Last summer they used open path data to calibrate an existing model and it was a useful exercise.

Dan Powell. Mr. Powell is looking for opportunities to advance practical technologies and opportunities for use in EPA's waste programs, which do not fund research. At EPA, the Office of Research and Development funds science projects. The work done at the MGP sites and the studies Ms. Thornloe has done at landfill sites provide practical experiences that are useful for advancing technologies. These types of projects can show that new technologies perform better than current practices. For example, flux measurements to estimate risk perform better at landfills than point sampling methods that may not be representative of releases for the entire landfill.

While advocating for the use of the Triad approach, which involves using new tools to measure contaminants in soil and groundwater, Mr. Powell's office (TIFSD) has met with a lot of resistance. Technology decisions in the waste programs are driven by site-specific objectives rather than by regulations typical of the air program. Hence the waste programs are not hindered by regulatory barriers that may forestall the use of new technologies.

At first, TIFSD took a technology transfer approach to promoting technologies, providing information on how new technologies work and their advantages over existing technologies. This effort had limited success. With the Triad approach, TIFSD is focusing on the use of technologies that allow better and cheaper results. They also emphasize the concept of uncertainty when promoting technologies. Uncertainty related questions take into account, for instance, how representative the results from analyzing a 5-gram subsample of soil pulled from a 50-foot grid spacing are to the site and what confidence level can be placed on a decision that is based on such a sample result. The value of many of the new technologies is that their use can reduce the sampling and spatial uncertainties that occur in environmental matrices. The people who own environmental problems look for ways to solve them as cheaply as possible. They need assurance that the technology will work, is comparable in price or costs less than traditional methods, provides greater certainty, and has experienced vendor(s) that can provide the data needed to make decisions.

Survey cost data need to be more readily available for new technologies. For instance, how much does it cost to monitor a two-month MGP excavation? The more that is known about cost and availability (not a science project), the more likely the technology will come to the minds of site managers as they weigh alternatives.

Opportunities for using technologies can be extensive in the waste programs. For example, there are thousands of MGP sites around the country and they are often valuable properties, if cleaned up. There also are thousands of closed landfills across the country and many communities are looking to reuse them. Fugitive emission issues often arise during dry cleaner and gas station cleanups when excavation is one of the cleanup technologies. Another growing field is homeland security and emergency response.

EPA is now looking at the carbon footprint of characterization and cleanup activities and how it can be reduced. There may be opportunities to show that these technologies cause less of a footprint than traditional monitoring methods.

There are a lot of electronic resources that TISFD has developed to provide information on soil and groundwater technologies. These resources can easily incorporate new technologies, such as the ORS technologies. TISFD's Internet seminar program offers live two-hour training courses that typically draw several hundred people from around the country and transfers information with no travel cost. The Interstate Technology and Regulatory Council regularly publishes guidance documents on various sampling, analysis, and cleanup technologies for state regulators. ORS would probably be of interest to them.

Comment: At the last VOC Emissions Workshop Mr. Chambers discussed the DIAL work that was done in Alberta. He said that they had not done actual measurements at the tanks and other processes for comparison with their DIAL measurements but relied instead on what the facility reported. They calculated an hourly emission rate by manipulating the facility's annual data. More attention may need to be paid to the completeness of the facility data in terms of when the measurements were taken, vapor pressure of the materials in the tanks, wind speed, etc.

Question: It was mentioned that a number of innovative technologies developed to characterize soil and groundwater contamination were met with resistance in the waste programs. Are there any lessons to be learned for the air program?
Answer: In many cases the technology was tried in its infancy and did not work well or was misapplied; hence, potential users considered it a failure and did not reconsider it later. Vendors might want to develop their own case histories or success stories for their Web sites rather than provide only a list of clients for their technologies. Developers should focus on reducing the uncertainties associated with using their technologies. The instruments should provide benefits such as real to near real time results over a spatially complete area. Not having readily available and understandable contract language with vendors is also a barrier to the use of new technologies.

Question: One of the things we see preventing the spread of the technology is the idea that knowledge is a liability. How can government convey the concept that if you find contamination and fix it, you will not be penalized?
Answer: When we went out with the IR camera, our goal was to reduce emissions, the faster the better. This approach has worked well for some companies but others are reluctant. The lawyers for a number of reluctant companies, some very large, are saying, do not use the camera because of the liability that may be incurred. Last year the Texas legislature passed a bill that says if you use a new technology and discover emissions that would otherwise not have been found without the technology and you report that to the state and submit a plan to deal with it, the state cannot take enforcement action against you. However, the law says that the facility can only use U.S. EPA approved technologies—so the reluctant companies are waiting for the SMART LDAR to be promulgated.
Comment: Another opportunity might be to approach the corporate lawyers to see if some of their concerns can be alleviated.

Small Group Discussions

Mr. Bosch charged attendees, who joined one of three breakout groups, to develop conclusions and recommendations on the topics discussed at this workshop. He asked them to give special attention to gaps in research, policy, and procedures.

Applications of ORS to EPA Waste Programs
Dan Powell (spokesperson)
Because community acceptance is important, effective communication methods are needed to convey the message that the technology is protective of communities.

More documentation is needed to show that although different instruments used at waste sites may yield different results, the results can still be accurate. More information is needed on the comparability of measurements made with an ORS versus traditional methods.

Protocols, including data quality, for the use of various technologies need to be developed and compiled. For example, do data quality objectives for process monitoring differ from those for fugitive emission monitoring during cleanup?

As touched upon earlier, many opportunities to apply ORS exist in the waste programs. They can be used during the cleanup of MGP sites, closed refineries, closed wood treating plants, and dry cleaners; emergency response actions; homeland security incidents; gas pipelines; and landfills.

A technology matrix document should be developed to evaluate the instruments. The matrix would include information such as where the technology works well and where it does not, cost ranges, setup time, and operator experience requirements. The matrix would allow a project manager to screen the technologies before spending time evaluating the most promising ones.

A webpage devoted to project profiles would be useful for promoting the use of these technologies in the waste programs. Project profiles would give project managers information on how a technology of interest performed on other sites. Example websites are the Federal Remediation Technologies Roundtable website (http://costperformance.org/search.cfm), which provides cost and performance information, and the State Coalition of Drycleaners website (http://www.drycleancoalition.org/profiles/).

To familiarize waste program managers with new technologies, Mr. Powell proposed developing a series of Internet seminars to present the theory of operation and application of the technologies and to answer questions.

An effort should be made to involve the Interstate Technology and Regulatory Council (ITRC) in guidance development. ITRC is a state-led coalition working together with industry and stakeholders to achieve regulatory acceptance of environmental technologies. The ITRC workgroup involved with the development of any given technology guidance, can include representatives of states, industry, U.S. EPA, DOE/DoD, private consulting firms, and others.

Remote Sensing of Emissions and Emission Inventories

Randy Kissell (spokesperson)

Mr. Kissell reported that this breakout group concentrated on two major areas: obstacles to using remote sensing to estimate emissions and opportunities for using remote sensing to estimate emissions.

Obstacles to Using Remote Sensing

- There is a lack of approved protocols for most remote sensing devices.
- Currently costs (real or perceived) are relatively high for using most remote sensing instruments compared with other options. These costs may fall if the technology gains more use and production prices come down.
- If unreported emissions are detected using remote sensing, the operator of the plant may have a serious regulatory problem. Whether the operator was aware of these emissions or not, they may provide evidence that the plant is exceeding its permit.
- Currently it is difficult to extrapolate short-term measurements to long-term emission rates.

Opportunities to Use Remote Sensing

- Remote sensing is excellent for detecting process upsets or equipment malfunctions (e.g., a defective seal that is difficult to access). If remote sensing enables a facility to find and fix leaks and other upsets, actual emissions may come closer to estimated ones.
- Remote sensing can provide additional data to inform the determination of emission factors and address the variability of emission factors. Many of the AP 42 emission factors are single numbers and probably vary for different parameters for different industries and for different times. This means there must be some variability that has not been traditionally addressed.

Emission Factors

- Emission factors will continue to be needed in the future. For example, when it is not possible to measure emission output at a plant that is slated for construction, a way is needed to predict its likely contribution to the emission inventory.
- Traditionally EPA has not addressed long-term versus short-term emission rates. The RS studies tend to be short term which does not mean that they can't become long term, but we need to recognize that there can be differences between short and long term rates.

Fenceline Measurements

- Fenceline measurements using automated equipment are suitable for long-term monitoring. They can detect temporal and spatial variations and ground-truth large scale inventories. The detected variations can be used to identify practices and procedures that can be changed to cut emissions.

Conclusions

- Remote sensing data can be used to adjust emission estimates and reduce emissions.
- Remote sensing also can be used to measure ambient concentrations at the fenceline.
- We need to think in a broader way to promote and/or allow remote sensing.

Recommendations

- A remote sensing technology comparison matrix for the regulated community is needed that shows among other things cost and applications.
- There is a need to promulgate remote sensing methods that are accepted by the regulatory community. Until these standards are in place, it is unlikely that remote sensing will be widely adopted.

Comment: Another opportunity to use remote sensing might be to document a reduction in emissions for use in potential future banking/offset programs. With regard to promulgating remote sensing methods, it might be easier and quicker for ASTM or ISO to produce technology-specific standards that EPA can incorporate by reference. Also the experts on the cost and capabilities of commercially available equipment are not necessarily in EPA. It might be useful for those in the audience who do this work to get together to produce a matrix of costs, applications, and limitations.

Blueprint for Future ORS Field Studies

Roy McArthur

The breakout group decided to continue beyond the workshop as a standing body and solicit professional associations for representation on the workgroup. The group identified three future products that it believes can be developed through email and conference calls.

Matrix Comparing ORS technologies. The first step will be to develop a matrix structure and ask provider experts to review it. They envision the matrix containing such items as the different means of conducting ORS studies with a discussion of what exactly they produce, what they can be used for, the maturity of the technology for the given application, and cost if available. The group identified a number of information sources and Eben Thoma will take the lead.

A recommendation was made to develop a website to house the matrix and other pertinent information such as reports and references. The workgroup will collaborate with Mr. Powell to determine how this can be done.

Projects/technologies generally require a project-specific quality assurance plan. The workgroup recommended gathering existing protocols in one place for review. This effort may identify guidance that can be recommended by the group. The issues to be covered would include meteorology, facility characteristics, validation/verification, and representativeness. Dennis Mikel will take the lead. Rod Robinson and Jan Moncrieff will expand their list of protocols and disseminate them to the group. To help provide a model, Walter Gray will assemble existing approved quality assurance plans.

Comment: The matrix should cover all methods and not concentrate on just one or two.

Future Information Exchange Activities

Michael Adam
Mr. Adam explained that his branch (EPA's Technology Information and Integration Branch) provides platforms for information dissemination and outreach. They do this through Web meetings, Internet Web seminars, and other online tools. An example of a Web meeting tool is the Environmental Science Connector developed by ORD. At the push of a button you can start an online Web collaboration. Had EPA wanted, it could have opened this workshop to people online—giving them complete screen sharing and a conference call number for audio.

His office sponsors two-hour Internet seminars through its CLU-IN Studio. As speakers present their PowerPoint slides, attendees view them on their computer screens while listening through their computer sound system or conference call line. The studio has approximately 60 conference call lines and 135 simulcast lines. The seminars usually include a question and answer session during which questions can be sent by email to the presenters or called in if the person is on a call line. Seminars are archived.

EPA also makes provisions under certain circumstances for venders to make seminar type presentations on their technology to EPA personnel. The ground rules for this are at http://www.cluin.org/vendor/e-briefings/. These seminars should be to educate an internal government audience about innovative technologies and innovative strategies for using technologies. The government does not guarantee an audience but does inform potentially interested personnel of the event.

For ORS information dissemination, Mr. Adam's office maintains an open path webpage (http://www.cluin.org/programs/21m2/openpath/) that has summary descriptions of FTIR, UV-DOAS, TDL, LIDAR, and Raman technologies, examples of where they have been used, and some advantages and limitations.

Question: Did you say that you can archive these seminars?
Answer: Yes we have several years worth and anyone wanting to view/listen to them can go to our pod caster and download them.

Comment: Mr. Cuclis has been making presentations from Europe to his facility in Houston. He is planning another presentation in May and invites suggestions on topics.

Recommendations Summary

Below are the recommendations that were developed by the workshop for future activities.

- Develop more data on the comparability of measurements made with an ORS system versus traditional methods.
- Develop and/or compile standard protocols, including data quality, for the use of various technologies.
- Develop a technology matrix document that provides a way to evaluate the instruments. The matrix would include information such as the different means of conducting ORS studies with a discussion of what exactly they produce, what they can be used for, the maturity of the technology for the given application where the technology works well and where it does not, cost ranges, setup time, and operator experience requirements. The matrix would allow a project manager to screen the technologies before spending time evaluating the most promising ones.
- Build a webpage devoted to project profiles for promoting the use of these technologies.
- Develop a series of Internet seminars to present the theory of operation and application of the technologies and to answer questions.
- Promote remote sensing as a means to adjust emission estimates and reduce emissions.
- Find ways to provide incentives for identifying and correcting emissions that are not specifically regulated. We need to think in a broader way to promote and/or allow remote sensing.
- Promulgate remote sensing methods that are accepted by the regulatory community. Until these standards are in place, it is unlikely that remote sensing will be widely adopted.
- Explore conducting a specific ORS webcast using the OSWER facilities and the presentations given during this workshop.
- Complete the proceedings of this workshop and post them on the OAQPS webpage.
- Construct and complete the ORS technologies matrix for posting on a webpage. Also identify any useful documents that might be posted on the same webpage.
- Mr. Bosch will work with Ralph Marquez and others on ways to influence the acceptance of technologies by federal, state, and local management.