

Using Tunable Diode Lasers to Measure Emissions from Animal Housing and Waste Lagoons

D. Bruce Harris, Richard C Shores and Eben D. Thoma
National Risk Management Research Laboratory
Office of Research and Development
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

ABSTRACT

Open-path optical spectroscopy has been applied to several fugitive sources by scientists at the EPA National Risk Management Research Laboratory (NRMRL) for more than a decade. Open-path Fourier transform infrared (OPFTIR) was used during the initial research phase because of the ability to detect multiple compounds simultaneously. Recent improvements in solid state, near infrared (NIR), tunable diode lasers (TDL) has led to their development as a spectroscopic measurement system when only a single pollutant is of interest. Emissions from agricultural husbandry facilities have become of interest both as a particulate precursor (ammonia) and a greenhouse gas (methane) source. The OP-FTIR was used initially to monitor both gases and the TDL has been deployed lately to focus on ammonia. The TDL has developed into a reliable instrument for collecting long-term data at animal husbandry facilities and is a major component of testing by the agricultural industry to develop sector-specific emission factors.

BACKGROUND

Fugitive emissions have long been an EPA interest. In the early years of the national effort to reduce emissions, NRMRL's predecessors developed several measurement methods for these nonducted emissions.^{1,2,3} These methods used point samplers to develop an array of concentration zones that could be integrated into a flux in a manner similar to manual stack sampling methods which collected samples from points at the centroid of equal areas within the stack.

MEASUREMENT METHOD

The measurement of gaseous compounds can be made using optical absorption spectroscopy. This relies on the unique characteristic of each compound to absorb light at specific wavelengths which allows their identification. If the amount of light sent through the sample is known, then the concentration can be determined by measuring the reduction of light received by the detector after passing through the sample (known as Beer's Law). The first instruments using this technique were laboratory-based units for analyzing samples contained in a small chamber attached to the unit. For the measurement of fugitive emissions, the sample cell has been enlarged by directing the source light across an open space (such as beside a waste water lagoon) to the detector in the analytical section of the instrument. The source and detector can be mounted within one unit which requires a retroreflector to define the measurement path by returning the light back to the unit and, effectively, doubling the measurement path. (Figure 1) This configuration is called open-path

spectroscopy which has several advantages. The measurement is the path-average concentration of each compound within the defined path. It would take many samples along that path for a traditional point sampling method to provide the same data. No collection or handling of the sample is required which has been a source of error when using laboratory analysis methods. Additionally, a calibration cell may be inserted directly into the path to assure the performance of the instrument as it collects data.

Initial environmental applications of this technology used instruments with infrared light sources because hundreds of compounds have unique absorption patterns in these wavelengths. These early efforts targeted highways and Superfund sites for volatile organic chemicals.^{4,5} NRMRL's first application of the OP-FTIR was to measure methane emissions from large surface coal mines.^{6,7} In 1992, EPA's Office of Air Quality Planning and Standards (OAQPS) convened a workshop to bring these early users together to chart the needs of this new technology.⁸ Among the steps cited was the need for further validation studies. Tracer gas releases during the test period are the normal method for relating a single measurement path near the ground to the total plume emission.^{9,10}

NRMRL has developed a multi-beam method (Figure 2) that measures the vertical concentration variation in the plume and therefore, is closer to a true concentration measurement than a single, ground path measurement with a model derived result.¹¹ Further work^{12,13,14,15} has been conducted over the last decade that has resulted in the inclusion of this technology in the EPA's Other Test Methods (OTM) list as OTM-10.¹⁶ These methods are peer reviewed and then placed before the public for use and comment.

As mentioned earlier, OP-FTIR has the ability to measure many compounds at once, but this ability comes at a high cost and a large footprint. NRMRL teamed with Aerodyne Research to investigate solid-state tunable diode lasers to monitor nitrogen oxide emissions from roadways.¹⁷ These lasers were among the first available, and therefore expensive but the technology was successfully demonstrated. The recent development of near infrared (NIR) TDL sources for fiber-optic communications has allowed compact and reasonably priced open-path units to be developed for a limited set of compounds. These lasers emit light at a very narrow bandwidth, so usually only a single compound can be detected. The first accepted application of this technology was for long roof vents in aluminum production facilities to monitor hydrogen fluoride emissions. Using a one-meter calibration cell inserted into the open-path, Thoma et al.¹⁸ compared the measurement of OP-FTIR and OP-TDL for ammonia and methane and found good agreement.

MEASUREMENT OF EMISSIONS FROM ANIMAL WASTE

Analysis of ambient air particle samples is usually dominated by secondary particles formed by the reaction of ammonia with sulfur dioxide and nitrogen oxides from combustion sources. Much has been done to reduce emissions from combustion sources. Interest has now turned to reducing the ammonia contribution to this reaction. Animal wastes are a major source of ammonia. A second significant gaseous emission from animal waste is methane which is a significant greenhouse gas and contributor to global climate change. Thus, initial measurement activities of gaseous emissions from waste water lagoons at animal husbandry facilities used the OP-FTIR to simultaneously measure both gases. Childers has reported single beam concentrations at various sites around a swine facility in eastern North Carolina and the improved analytical procedures developed during

the study.^{19,20} The comparison of calculated emission fluxes using these results with other data available at that time showed those flux rates to be slightly lower than the emission factor being used by EPA, but higher than the USDA value.²¹

It was apparent that a better method was needed to measure the flux rates from barns and lagoons at swine operations. The multi-beam measurement method described above was similar to work reported by Hashmonay et al.¹⁴, who had developed an improved data analysis algorithm. A controlled release validation study confirmed the merger of these efforts for stable wind conditions that allow good plume flow through the measurement plane.²² This method has been called vertical radial plume mapping (VRPM) and was applied by Shores et al.²³ (Figure 3) to evaluate the long term performance of an experimental cover on a swine waste lagoon. The data (Table 1) shows significant reduction of ammonia, but none for methane. The biofilm on the cover utilized the ammonia for food, but could not use the methane.

The OP-FTIR VRPM has been used to separate the emissions from a waste lagoon from those escaping swine housing units. Two systems were set up such that one established a measurement plane between the lagoon and barns and the other downwind of both. These planes met perpendicularly to form a “T”. (Figure 4) The downwind system had additional retroreflectors on the ground beam to define the separate source plumes. The wind was varying about the plane between the two sources such that it was measuring either the lagoon or barn plume and, when combined with the downwind section adjacent to that source, the flux could be calculated. This configuration and wind conditions provided the ideal situation to measure the two sources at the same time.

USING TDL FOR ANIMAL WASTE AIR EMISSIONS

Animal waste generated in animal housing collects between cleaning events. The interval between most cleaning cycles is several days to several months. The waste generates air emissions during this period, with methane and ammonia the most common gases. Natural and mechanical ventilation systems are used in the houses to provide a thermally and environmentally stable facility for the well being of the animals and the farm personnel. The TDL has been used to monitor the exhaust from these facilities. Mechanically ventilated buildings have been measured by locating the TDL beam through the centerline of the exhaust fans to obtain the average concentration and multiplying it by the fan flow volume to yield the emission rate. (Figure 5) Data reported for layers and broiler chickens show emission rates of 1.3-1.6 g/bird-day.²⁴

Little data had been collected from the spray application of lagoon liquid to agricultural fields. Thoma et al¹⁸ used a TDL system in a VRPM configuration (Figure 6) to measure the flux from a traveling gun sprayer applying swine lagoon liquid to the farm field. The detail with which the method located the emission plume allowed the position of the gun to be determined within 1 meter of the surveyed position as it moved across the field (Figure 7). This finding is a valuable output of the VRPM method. Fugitive sources within a complex facility can be found using the plume location in the measurement plane and the wind vector through that plane at the moment of the measurement. As the center of the plume varies across the plane, drawing a vector back from those points toward the source will locate that source near the intersection of the vectors. The flux

data confirmed the industry accepted rule-of-thumb that 50% of the ammonia is lost before the liquid reaches the ground.

As part of an environmental consent decree²⁵, many sectors of the agricultural animal husbandry industry are conducting a two-year study to develop emission factors for each of the participating sectors. The TDL-VRPM method is being used to conduct measurements of ammonia from waste water lagoons. The "T" deployment discussed above has been modified to provide a system to surround the lagoon with measurement planes. Scanning TDLs are placed on opposite corners of the lagoon with vertical towers at the other corners holding the vertical arrays of three retroreflectors aimed at those TDLs. The TDLs conduct a VRPM scan on one side and then rotate 90 degrees to the adjacent side to conduct a VRPM there. Thus, the emissions plumes from the lagoon are measured regardless of the wind direction. The sides of the lagoon that are on the upwind provide the background flux while the others monitor the lagoon flux. When completed, this long-term study will provide a valuable evaluation of the measurement technology.

CONCLUSIONS

Open-path optical absorption spectroscopy has been established as a useful technique to measure air concentrations of pollutants from fugitive sources such as agricultural waste disposal facilities. A vertical radial plume mapping procedure has used this technique to measure emission fluxes from these and other sources. When only a single gas is of interest, a tunable diode laser system offers cost effective choice compared to OP-FTIR. The OP-TDL has been demonstrated to gather ammonia fluxes from waste lagoons and waste spraying applications. A long-term study is underway using TDL systems to monitor ammonia emissions from waste lagoons of several types of agricultural husbandry sources.

REFERENCES

1. Kolnsberg, H. J. *Technical Manual for the Measurement of Fugitive Emissions: Upwind/Downwind Sampling Method for Industrial Fugitive Emissions*; EPA-600/2-76-089a; U. S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC, 1976.
2. Kenson, R. E. and Bartlett, P. T. *Technical Manual for the Measurement of Fugitive Emissions: Roof Monitor Sampling Method for Industrial Fugitive Emissions*; EPA-600/2-76-089b; U. S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC, 1976.
3. Kolnsberg, H. J.; Kalika, P. W.; Kenson, R. E. and Marrow, W. A. *Technical Manual for the Measurement of Fugitive Emissions: Quasi-Stack Sampling Method for Industrial Fugitive Emissions*; EPA-600/2-76-089c; U. S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC, 1976.
4. McLaren, S. E.; Hannigan, J. W.; New, D. L. and Stedman, D. H. Direct Measurement of Freeway Emissions using Long-Path Spectroscopy. In *Proceedings of the 1991 U. S.*

EPA/AWMA International Symposium (Air and Waste Management Association, Pittsburgh, PA); **VIP-21**: 741-746, 1991.

5. Herget, W. F. and Brasher, J. D. Remote Fourier Transform Infrared Air Pollution Studies. *Opt. Eng.* **19**: 508, 1980.
6. Piccot, S. D.; Chadha, W.; Kirchgessner, D. A. Kagann, A.; Czerniawski, M. J. and Minnich T. Measurement of Methane Emissions in the Plume of a Large Surface Coal Mine Using Open-Path FTIR Spectroscopy. In *Proceeding of the Air and Waste Management Association 84th Annual Meeting and Exposition*, Vancouver, BC, June 16-21, 1991.
7. Kirchgessner, D. A.; Piccot, S. D. and Chadha, A. Estimation of Methane Emissions from a Surface Coal Mine Using Open-Path FTIR Spectroscopy and Modeling. *Chemosphere* **26**: 23-44, 1993.
8. Eklund, B. and LaCosse, J. *Open-Path Monitoring Workshop Summary Document*; EMB Report 92-OPM-01, Contract No. 68-D9-0054, U. S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1992.
9. Scotto, R. L.; Minnich; T. R. and Leo, M. R. A Method for Estimating VOC Emission Rates from Area Sources Using Remote Optical Sensing. In *Proceedings of the 1991 U. S. EPA/AWMA International Symposium* (Air and Waste Management Association, Pittsburgh, PA); VIP-21. pp. 698-703, 1991.
10. Piccot, S. D.; Masemore, S. S.; Ringler, E. S.; Srinivasan, S.; Kirchgessner, D. S. and Herget, W. F. Validation of a Method for Estimating Pollution Emission Rates from Area Sources Using Open-Path Spectroscopy and Dispersion Modeling Techniques. *J. Air & Waste Manage. Assoc.* **44**: 271-279, 1994.
11. Piccot, S. D.; Masemore, S. S.; Lewis-Bevan, W.; Ringler, E. S. and Harris, D. B. Field Assessment of a New Method for Estimating Emission Rates from Volume Sources Using Open-Path FTIR Spectroscopy. *J. Air & Waste Manage. Assoc.* **46**: 159-171, 1996.
12. Hashmonay, R. A.; Yost, M. G. Innovative Approach for Estimating Gaseous Fugitive Fluxes Using Computed Tomography and Remote Optical Sensing Techniques. *J. Air Waste Manage. Assoc.*, **49**, 966-972, 1999.
13. Hashmonay, R. A., Yost, M. G., Localizing gaseous fugitive emission sources by combining real- time optical remote sensing and wind data. *J. Air & Waste Manage Assoc* **49**(11), 1374-1379, 1999.
14. Hashmonay, R. A., Yost, M. G., Mamane, Y., Benayahu, Y. Emission rate apportionment from fugitive sources using open- path FTIR and mathematical inversion. *Atmos. Environ.* **33**(5), 735-743, 1999.

15. Hashmonay, R. A., Yost, M. G., Wu, C. F. Computed tomography of air pollutants using radial scanning path-integrated optical remote sensing. *Atmos. Environ.* 33(2), 267-274, 1999.
16. <http://www.epa.gov/ttn/emc/tmethods.html> (accessed May 2007).
17. Jimenez, J. L.; McRae, G. J.; Nelson, D. D.; Zahniser, M. S. And Kolb, C. E. Remote Sensing of NO and NO₂ Emissions from Heavy-Duty Diesel Trucks Using Tunable Diode Lasers. *ES&T* 34 (12) 2380-2387, 2000.
18. Thoma, E. D.; Shores, R. C.; Thompson Jr, E. L.; Harris, D. B.; Thorneloe, S. A.; Varma, R. M.; Hashmonay, R. A.; Modrak, M. T.; Natschke, D. F. and Gamble, H. A. Open-Path Tunable Diode Laser Absorption Spectroscopy for Acquisition of Fugitive Emission Flux Data. *J. Air & Waste Manage. Assoc.* 55: 658-668, 2005.
19. Childers, J. W.; Thompson Jr, E. L.; Harris D. B.; Kirchgessner, D. A.; Clayton, M.; Natschke, D. F. and Phillips, W. J. Multi-pollutant Concentration Measurements around a Concentrated Swine Production Facility using Open-Path FTIR Spectrometry. *Atmos. Environ.* 35: 1923-1936, 2001.
20. Childers, J. W.; Phillips, W. J.; Thompson Jr, E. L.; Harris D. B.; Kirchgessner, D. A.; Natschke, D. F. and Clayton, M. Comparison of an Innovative Nonlinear Algorithm to Classical Least-Squares for Analyzing Open-Path Fourier Transform Infrared Spectra Collected at a Concentrated Swine Production Facility. *App. Spec.* 56(3), 325-336, 2002.
21. Harris, D. B.; Shores, R. C. and Jones, L. G. Ammonia Emission Factors from Swine Finishing Operations. *International Emissions Inventory Conference*, "One Atmosphere, One Inventory, Many Challenges.", Denver, CO, 2001.
www.epa.gov/ttn/chief/conference/ei10/index.html#ses-1.
22. Hashmonay, R. A.; Natschke, D. F.; Wagoner, K.; Harris, D. B.; Thompson Jr, E. L. and Yost, M. G. Field Evaluation of a Method for Estimating Gaseous Fluxes from Area Sources Using Open-Path Fourier Transform Infrared. *Environ. Sci. Technol.* 35: 2309-2313, 2001.
23. Shores, R. C.; Harris, D. B.; Thompson Jr, E. L.; Vogel, C. A.; Natschke, D.; Hashmonay, R. A.; Wagoner, K. R. and Modrak, M. Plane-Integrated Open-Path Fourier Transform Infrared Spectrometry Methodology for Anaerobic Swine Lagoon Emission Measurements. *App. Eng. Ag.* 21(21): 487-492, 2005.
24. Thoma, E. D.; Shores, R. C.; Harris, D. B.; Natschke, D. F.; Hashmonay, R. A.; Casey, K. D. and Gates, R. S. Measurement of Ammonia Emissions from Mechanically Ventilated Poultry Houses using Multi-path Tunable Diode Laser Spectroscopy. In *Proceedings of the 98th Annual Conference of the Air & Waste Management Association*, Minneapolis, MN June 21-24, 2005.
25. Environmental Protection Agency. Animal Feeding Operations Consent Agreement and Final Order: Notice, Part IV, Environmental Protection Agency, Federal Register 70(19):4958-4877, 2005 .

Dates	Biocover Installed (days)	Ammonia Flux (g/s)	s. d. ^[a] for Ammonia ± (g/s)	Ammonia Flux (kg-NH ₃ ha ⁻¹ d ⁻¹)	Ammonia Emission Reduction (%) ^[b]	Methane Flux (g/s)	s. d. ^[a] for Methane ± (g/s)	Methane Flux (kg-CH ₄ ha ⁻¹ d ⁻¹)	Methane Emission Reduction (%) ^[b]
11 July 2000	0	0.50	0.0250	144.54	Baseline	0.78	0.0461	223.90	Baseline
16 August 2000	36	0.13	0.0116	36.63	75	1.55	0.1501	447.31	-100
27 February 2001	231	0.043	0.0035	12.24	91	0.73	0.2652	209.23	7
16 August 2001	401	0.029	Insufficient data to calculate	8.35	94	0.41	Insufficient data to calculate	118.08	47
24 July 2002	743	0.06	0.0038	18.58	87	2.02	0.1707	580.75	-159

^[a] s. d. = standard deviation. Standard deviation values represent the mean of the data sets.

^[b] Percent change, positive percent change indicates a reduction in emissions after the permeable cover was installed.

Table 1. Summary of two years of measurement data collected at the eastern North Carolina swine waste lagoon both before and after the installation of a permeable cover.

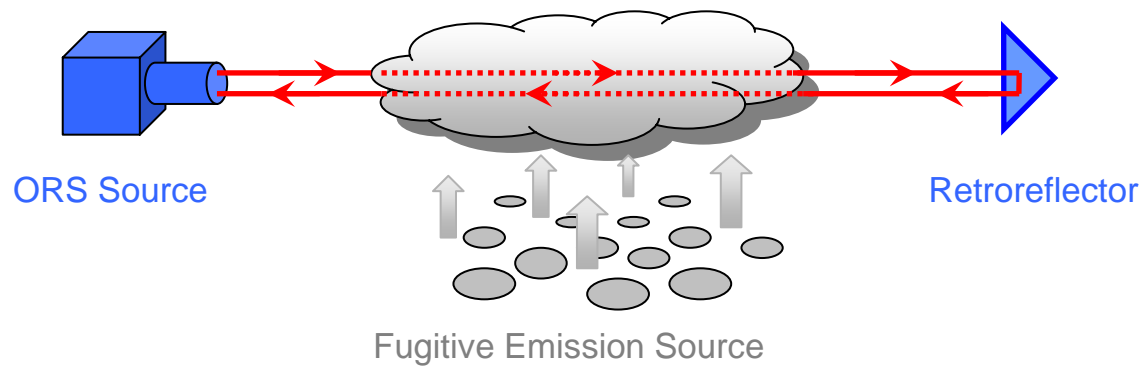


Figure 1. Optical absorption spectroscopy for fugitive emission measurement.

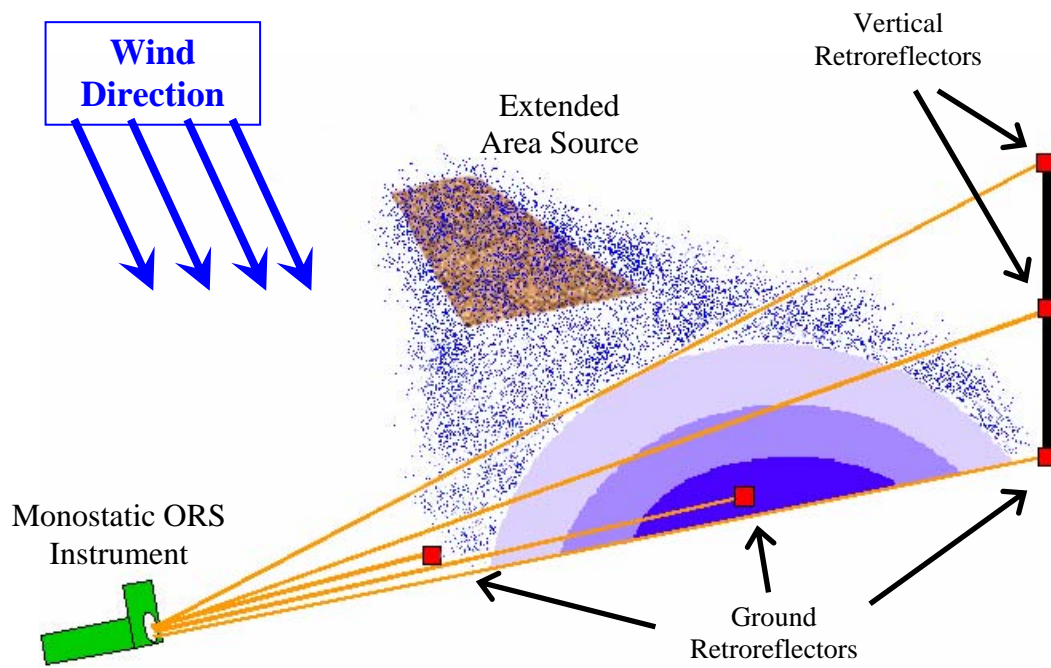


Figure 2. Vertical radial plume mapping (VRPM) schematic.

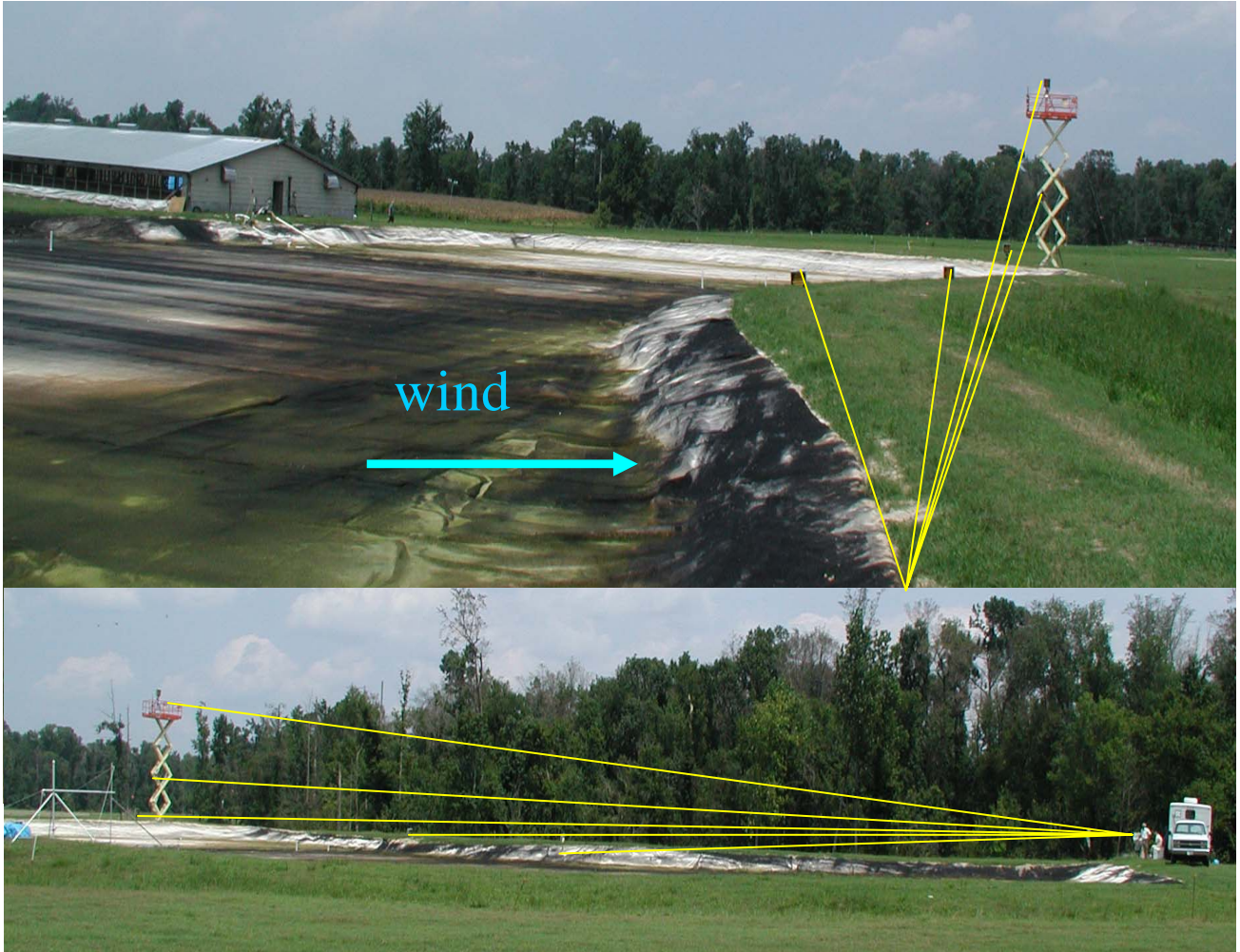


Figure 3. VRPM applied to covered swine lagoon

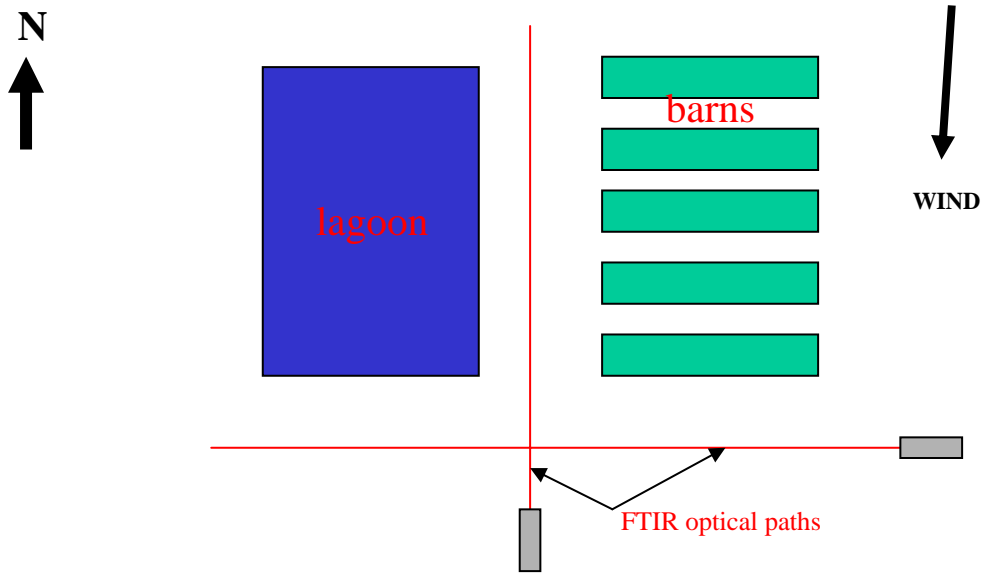


Figure 4. Dual VRPM paths used to isolate emissions from 2 sources.

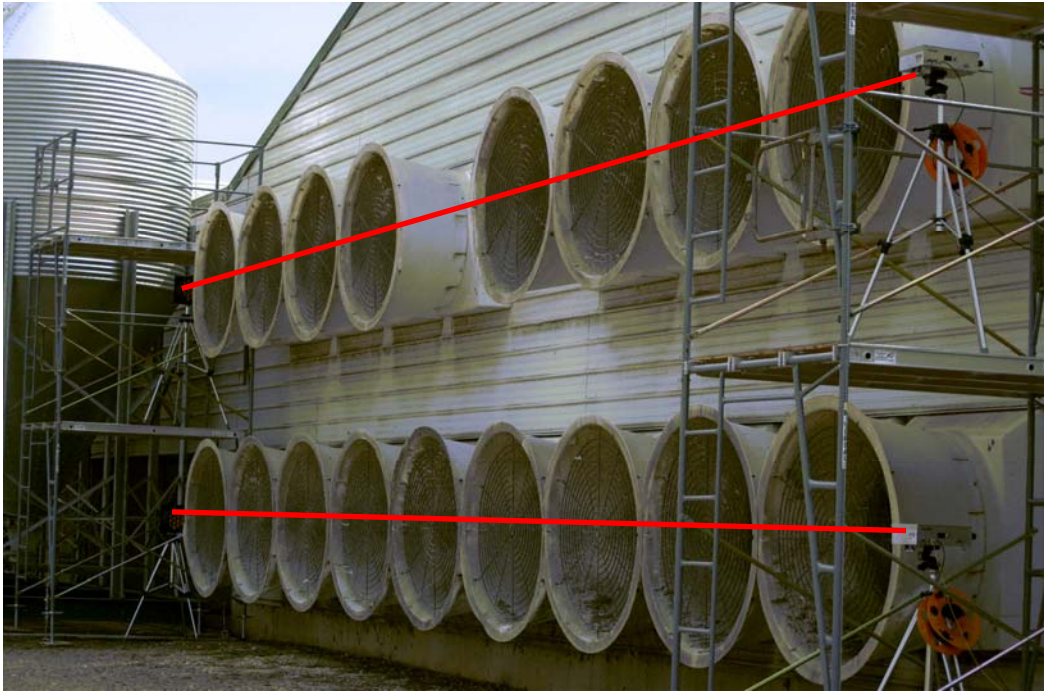


Figure 5. Using TDLs to measure emissions from high rise layer house.

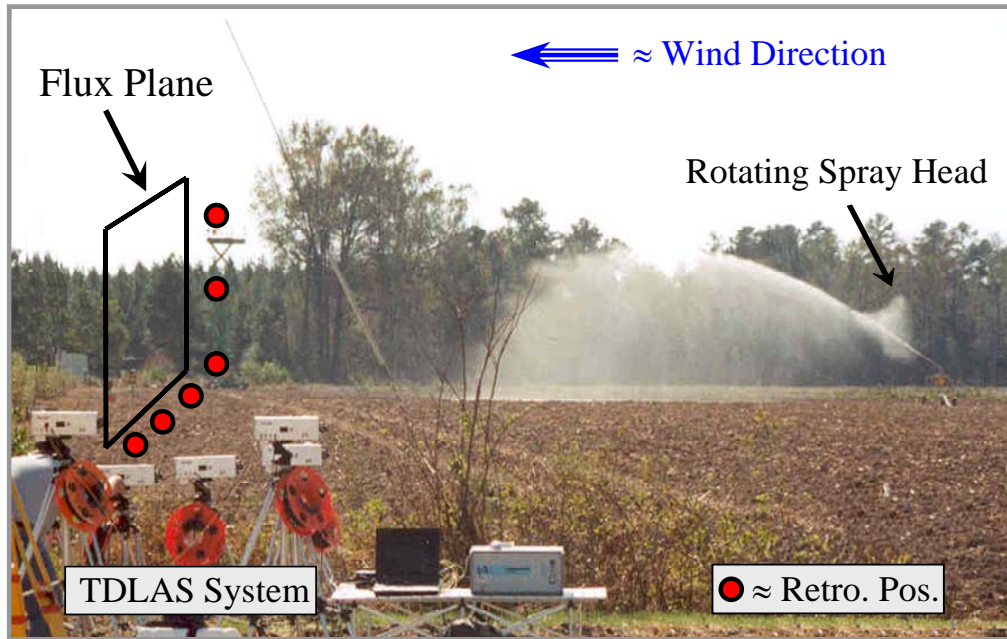


Figure 6. Measuring emissions from field application of lagoon effluent.

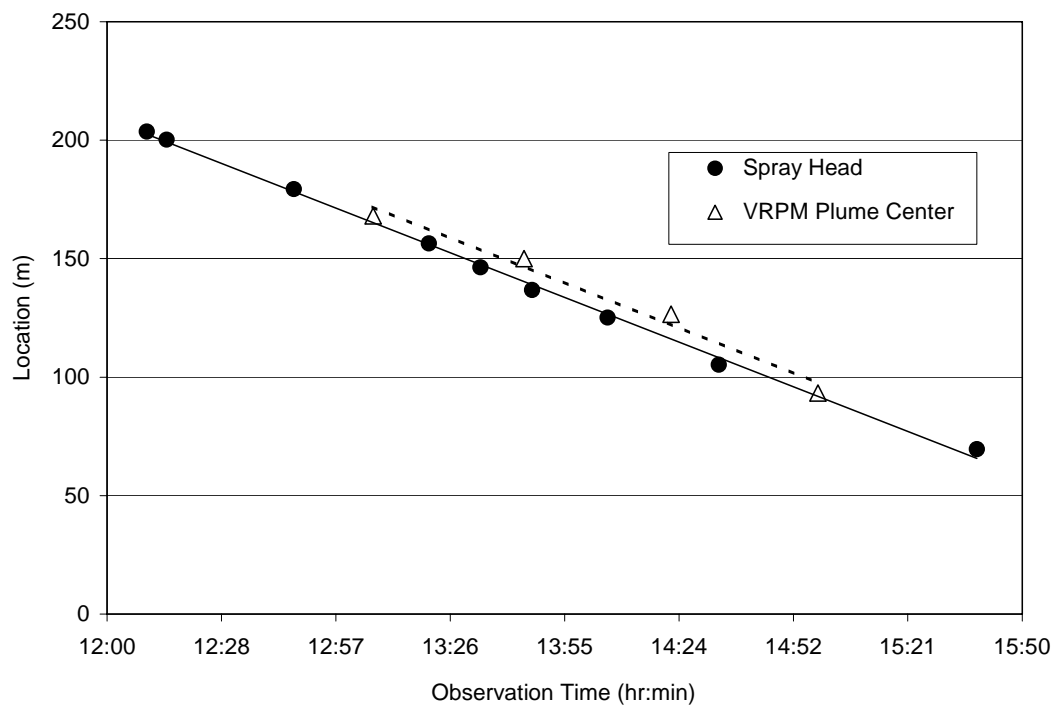


Figure 7. Comparison of actual spray head location with VRPM derived location.

