

## USING LIDAR TO MEASURE PERFLUOROCARBON TRACERS FOR THE VERIFICATION AND MONITORING OF CAP AND COVER SYSTEMS

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**Abstract.** Waste site cover systems used to prevent rainfall from reaching the waste need to remain intact throughout the lifetime of the waste site. Monitoring of these covers is needed to ascertain the performance and to determine if any degradation has occurred. Researchers at Brookhaven National Laboratory have used gaseous perfluorocarbon tracers (PFTs) to monitor the integrity of caps and covers for waste disposal sites. Detection of the PFTs currently uses gas chromatography techniques developed at BNL. This paper presents a potential approach to this wide-area screening problem by replacing conventional gas chromatography analysis with laser-based, lidar (Light Detection and Ranging) detection of the PFTs. Lidar can be used to scan the surface of the cover system, looking for fugitive PFTs. If successful this would enable the departure from soil gas analysis and instead look for PFTs in the air just above the soil surface. The advantages of using a lidar platform are multi-fold and include the elimination of soil monitoring ports.

Benchtop and pilot-scale indoor experiments using an a continuous wave, line-tunable infrared CO<sub>2</sub> laser were used to detect PMCH (perfluoromethylcyclohexane, one of a group of PFTs used at BNL). Laboratory measurements of the absorption cross-section were the same order of magnitude compared to literature values for similar perfluorocarbon compounds. Initial benchtop, fixed cell length experiments were successful in detecting PMCH to levels of 10 ppb-m. To improve the lower limit of detection, a HgCdTe detector was purchased that was more specific to the lasing region of interest and hence had a higher sensitivity at this spectral region. Using a pilot-scale lidar system in a 40 m indoor hallway air concentrations of PMCH were then measured down to 1 ppb-m. These results are very promising and show great potential for monitoring the integrity of cover systems using lidar and PFTs.

**Keywords:** caps, covers, landfill, lidar, perfluorocarbon tracer, verification, waste site

### Introduction and Background

Throughout the world, caps and cover systems (covers) are used to protect hazardous and/or radioactive waste sites from rainfall infiltration and subsequent mobilization of contaminants. Verification and long-term monitoring of covers is becoming of great interest, particularly to the US Department of Energy (DOE), which has committed itself to an accelerated cleanup of its national facilities. With the increased focus on accelerated clean up, there has been considerable concern about long-term stewardship issues in general, and verification and long-term monitoring of covers,

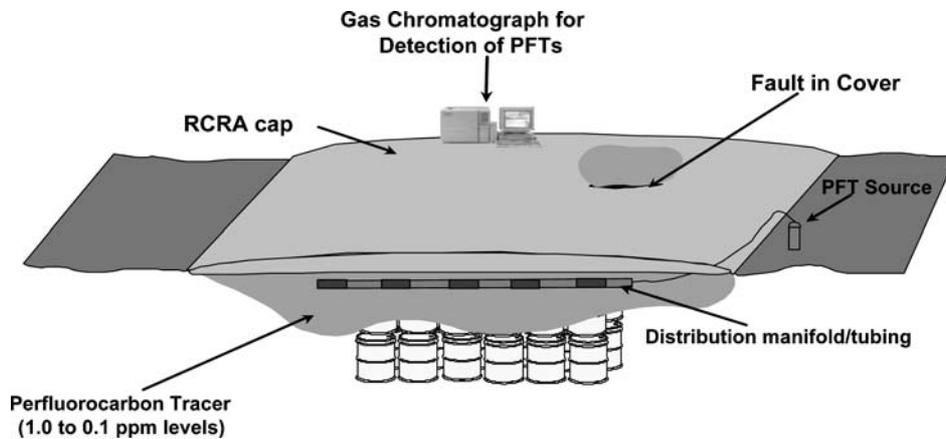


Figure 1. Perfluorocarbon tracer technology to verify and monitor cover system performance.

in particular. Covers are vital remedial options that will be extensively used in meeting the cleanup goals. Every buried waste site within the DOE complex will require some form of cover system. These covers are expected to last from 100 to 1000 years or more. The stakeholders can be expected to focus on system durability and sustained performance.

With funding from DOE, the Environmental Research and Technology Division (ERTD) at Brookhaven National Laboratory (BNL) developed a novel methodology for verifying and monitoring covers (Heiser and Sullivan, 2001; Heiser *et al.*, 2002). The technology uses gaseous perfluorocarbon tracers (PFTs) to determine the flaws (e.g., holes or cracks) and high permeability areas in a system. Gaseous tracers are injected below the cover and searched for in the soil gases above the cover (see Figure 1). The sampling grid, concentration and time of arrival of the tracer(s) are used to determine the size and location of flaws and to determine relative permeability of the cover. In addition, there are multiple tracers available, which allow different tracers to be injected in different quadrants or layers of the cover. This yields additional information on the transport pathways within the cover system and is particularly useful in multi layer covers where tortuous horizontal pathways are likely.

Traditionally, detection of the PFTs has been done using gas chromatography techniques developed at BNL. While this analytical method is very sensitive and allows detection of part per quadrillion (ppq) levels, it also requires gas sampling ports placed on 1.5 to 3 meter spacing throughout the barrier and air sampling equipment to draw the samples either into storage bags or directly into a field gas chromatograph (GC). Installation of the ports is time consuming and requires penetrations into the ground. Any penetrations into the ground, even if they do not penetrate the cover itself, introduce additional potential failure points. It may be as simple as causing water or wind erosion points (due to turbulent flow around

the stand pipe) or water ingress pathways. Sampling a typical one-acre site with 1.5 m spacing would require ~800 sampling ports. GC analysis of this many ports is therefore quite time consuming and can be very expensive (currently ~\$150 per sample or \$120 K for our one-acre example). The GCs used for PFTs are also prone to failure if used in a typical long-term monitoring application. The GC would be expected to operate one to four times each year and remain “dormant” the rest of the time. Experience shows that GCs are not best utilized in such a manner and heavy-duty cycle GCs typically require full-time operation.

One potential approach to this wide-area screening problem is to evaluate whether the GC analysis could be replaced by lidar (Light Detection and Ranging, *vide infra*) detection of the PFTs. If successful this would enable the departure from soil gas analysis and instead look for PFTs in the air just above the soil surface. Lidar can be used to scan the air space above the surface of the cover system for fugitive tracer gases that have been released beneath the cover. Currently lidar cannot compete with GC methodology in terms of sensitivity. However, in cover and subsurface barrier verification (Sullivan *et al.*, 1996; Heiser and Sullivan, 2002), typical tracer concentrations below the cover are 1 ppm and for a 2.5 cm hole in a cover, experience dictates a concentration on the order of 0.1 to 10 ppb in the soil gas above the cover in vicinity of the hole. Given the soil ranges at our test sites and those expected to be encountered, diffusion through 1 to 2 m of soil (standard cover thicknesses) yields concentrations after 1 to 3 days of 0.1 to 0.8 of the starting concentration. We have found that measuring lower concentrations does not yield better clarification of the barrier integrity. The “noise” or heterogeneity within the subsurface blurs to the point that it is no longer meaningful. Still, we have been able to find 1 cm diameter holes in a 6 m × 6 m barrier with reasonable clarity. What we need is not low detection limits, but rather fast, convenient detection that is fairly robust and can be operated for short periods while remaining dormant for longer periods without adverse behavior. Lidar may not be as sensitive as gas chromatography but it should be sensitive enough to meet the needs of environmental verification, monitoring and stewardship.

The above mentioned tracer concentrations are soil gas concentrations and air concentrations above the cover will be at least three orders of magnitude less than this. Reported absorption cross-sections for similar perfluorocarbon compounds suggested that detection limits (in air) as low as 0.1 ppb-m should be achievable with a lidar platform, depending upon range increment, receiver aperture and integration time. To further address some of the issues of detection sensitivity, it is envisioned that the use of lidar for this application would be restricted to moderate distances (i.e., 100s of meters) than is typical for lidar systems (km) through the  $1/\text{range}^2$ -dependence of the signal. Even with 0.1 ppb-m detection limit, this would require an increase in the below cover tracer concentrations of 100 or even to 1000 ppm, either of which is easily achievable.

The advantages of using a lidar platform are multi-fold. First, a lidar platform would allow interrogation of the air space immediately above the surface of the

cover and completely eliminate the need for soil gas monitoring ports. Second, lidar provides data in near real-time (i.e., min). Third, the lidar system is capable of scanning the entire field without having to relocate the sensor unit. Finally, a range-resolved lidar system provides location-specific concentrations of PFTs in the air above the cover. It is fully expected that the information gleaned using a lidar platform would be translated to assess the performance of covers in a manner similar to using conventional GC analysis.

### Lidar (Light Detection and Ranging)

At its most fundamental, lidar is simply the optical analog of radar (Measures, 1992). Just as in radar, there is a transmitter, a receiver and data processing subunit. In the specific case of lidar, the transmitter is typically a pulsed laser system operating in the IR (e.g., CO<sub>2</sub> laser), visible (dye lasers, OPO/OPA) or near-UV/UV (Nd:YAG, Nd:YAG-pumped dye lasers, Excimer lasers, OPO/OPA) spectral regions. Figure 2 shows a schematic of our mini-Raman Lidar System (MRLS) platform (Ray *et al.*, 2000) which, while specific to Raman lidar, contains the basic elements of lidar outlined above. The optical receiver telescope is typically either of a Cassegrainian or Newtonian design though other designs have been used. The collected return signal can then be sent to a variety of detection subsystems depending upon the desired information.

The phenomena that lidar platforms can exploit fall into two general categories, elastic scattering (for absorption measurements and aerosol density profiles) and inelastic scattering (fluorescence and Raman spectroscopy). For chemical species detection and monitoring, the phenomenon of choice in the atmospheric community is primarily absorption by specific target molecules due to the availability of large absorption cross-sections in readily accessible laser wavelengths. Leveraging these advantages translates to high-detection sensitivities on the order of low parts-per-million (ppm) (Milton *et al.*, 1992; Rothe *et al.*, 1974; Oh *et al.*, 1999)

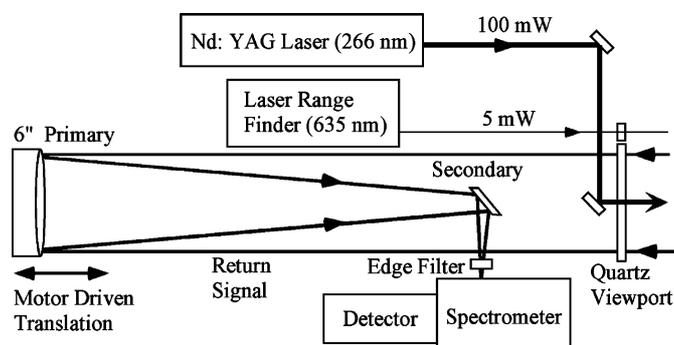


Figure 2. Schematic diagram of the Mini-Raman Lidar System (MRLS).

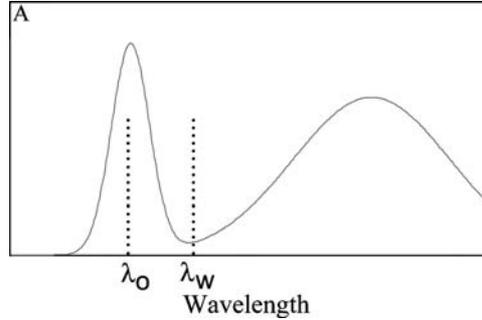


Figure 3. A schematic of the DIAL technique.

to low parts-per-billion (ppb) levels (Edner, 1995; Edner *et al.*, 1989). This type of absorption measurement is accomplished by using the differential absorption approach commonly referred to as DIAL (Differential Absorption Lidar) (Chyba *et al.*, 1999; Sunesson *et al.*, 1993; Papayannis *et al.*, 1989). As the name suggests, the implementation of DIAL involves using two laser frequencies that are directed to the area of interest and their respective elastic return signals monitored:  $\lambda_1$  located at a highly-absorbing wavelength for the chemical species-of-interest and  $\lambda_2$  in a non-absorbing spectral region, as shown in Figure 3. Elastic return of each outgoing laser line ( $\lambda_1$  and  $\lambda_2$ ) is provided through either a combination of Rayleigh scattering off air molecules and Mie scattering from the aerosols/particulates or, if range-resolved mapping is not important, hard-body return from a retro reflector [e.g., corner cube or a sand-blasted aluminum back-drop]. The lidar platform used in this present study is DIAL.

It can be shown that the ratio of the respective return signals for the “on” and “off” wavelengths can, to first order, be expressed as . . .

$$\bar{N}(R) = \frac{1}{2\sigma\Delta R} \left[ \ln \left( \frac{P_r(\lambda_1, R)}{P_r(\lambda_1, R + \Delta R)} \right) - \ln \left( \frac{P_r(\lambda_2, R)}{P_r(\lambda_2, R + \Delta R)} \right) + B' + T' \right]$$

where

$$\begin{aligned} T' &= -2[\bar{\alpha}_{\text{aero}}(\lambda_1, R) - \bar{\alpha}_{\text{aero}}(\lambda_2, R)]\Delta R, \\ B' &= \ln[\beta(\lambda_1, R + \Delta R)/\beta(\lambda_1, R)] - \ln[\beta(\lambda_2, R + \Delta R)/\beta(\lambda_2, R)], \\ \sigma &= \sigma_{\text{gas}}(\lambda_1) - \sigma_{\text{gas}}(\lambda_2), \end{aligned}$$

where the bar over the symbol indicates that the quantity is averaged over the range,  $\sigma_{\text{gas}}$  and  $\sigma_{\text{aero}}$  are the differential absorption cross-sections for the gas and aerosol, respectively;  $R$  is the range and  $\beta$  is the volume backscatter coefficient (Measures, 1992; Schotland, 1974). In the limit of negligible wavelength dependence of aerosol attenuation and if the measurement can be made nearly simultaneous (to avoid temporal changes in  $\beta$ ), then  $T'$  and  $B'$  can be ignored.

### Bench Top Studies

In order to more completely assess the detection sensitivity, the absorption cross-section of PMCH was measured. A continuous wave, line-tunable CO<sub>2</sub> laser was used because all of the PFTs of interest have significant absorption cross-sections in the mid-infrared spectral region (11–9 μm). A liquid nitrogen-cooled InSb detector was used to detect the mid-infrared signals. Optics and a one-meter gas cell were positioned on the laser table such that a simple two-pass (out and back) lidar configuration was obtained. The system schematic is depicted in Figure 4 along with a photo of the actual laboratory set-up.

The PFT used in this study was Perfluoromethylcyclohexane (PMCH), [C<sub>7</sub>F<sub>14</sub>]. The gas cell was filled with air containing a starting concentration level of nominally

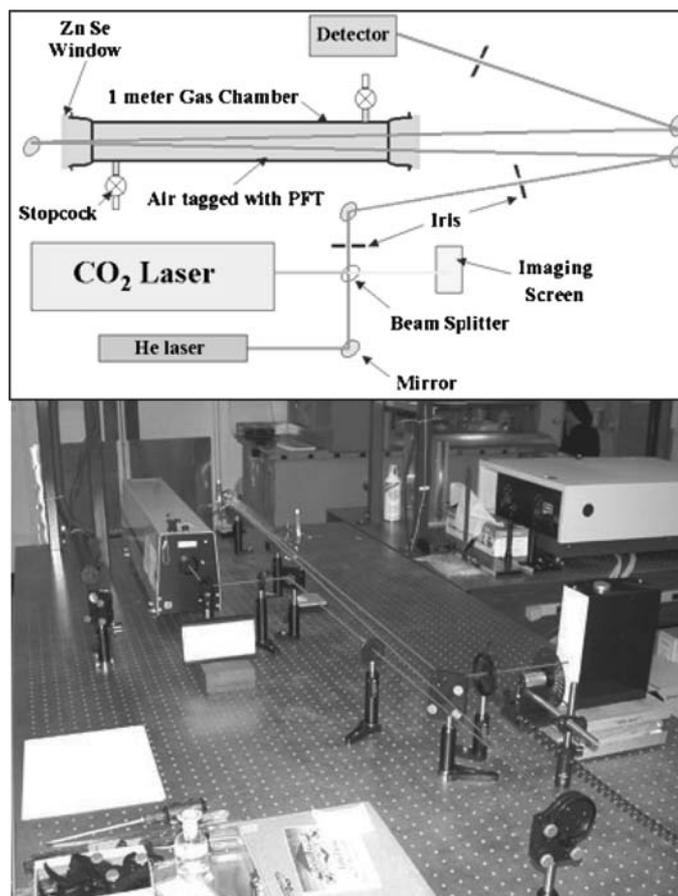


Figure 4. Schematic of laboratory test set-up for PFTs along with a Photograph of laboratory set-up (with laser path overlaid in red).

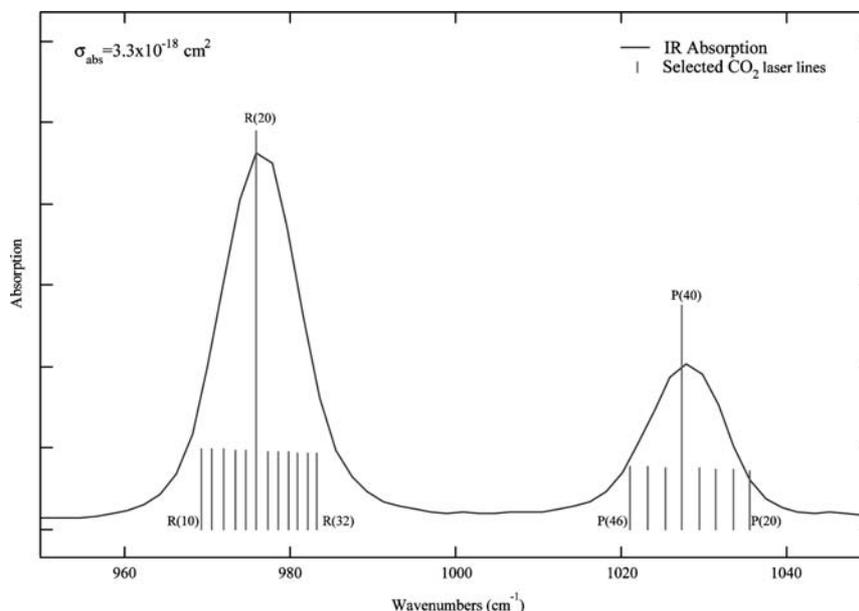


Figure 5. FTIR for the trace Perfluoromethylcyclohexane along with the various CO<sub>2</sub> laser lines that overlap the absorption features.

350 ppm. The laser was directed through the cell and the absorption measured. After each measurement the output wavelength of the laser was changed. This was done until the peak absorption was found. All later experiments were completed using the peak wavelength.

FTIR spectra for PMCH were measured to confirm the peak. Figure 5 depicts the FTIR spectra from 950 to 1050 wavenumbers. The R(20) is significantly higher than the P(40) laser lines and corresponds to the peak absorption found earlier.

With the laser system optimized, absorption versus concentration curves were then generated. The beam was chopped as it entered the detector to provide a differential output curve. The gas cell was filled with tracer-spiked air and the peak height was measured (average of 250 samples). After each measurement the cell contents were sampled into gas-sample bags and sent to an on-site laboratory for analysis of the PMCH concentration. The tracer concentration in the cell was then changed and the procedure repeated.

Figure 6 gives a series of raw signals for a series of PMCH concentrations. The peak height was plotted versus concentration to obtain the absorption cross-section for PMCH (see Figure 7). The value obtained,  $3 \times 10^{-18} \text{ cm}^2$  (base e), was the same order of magnitude compared to literature values for similar perfluorocarbon compounds.

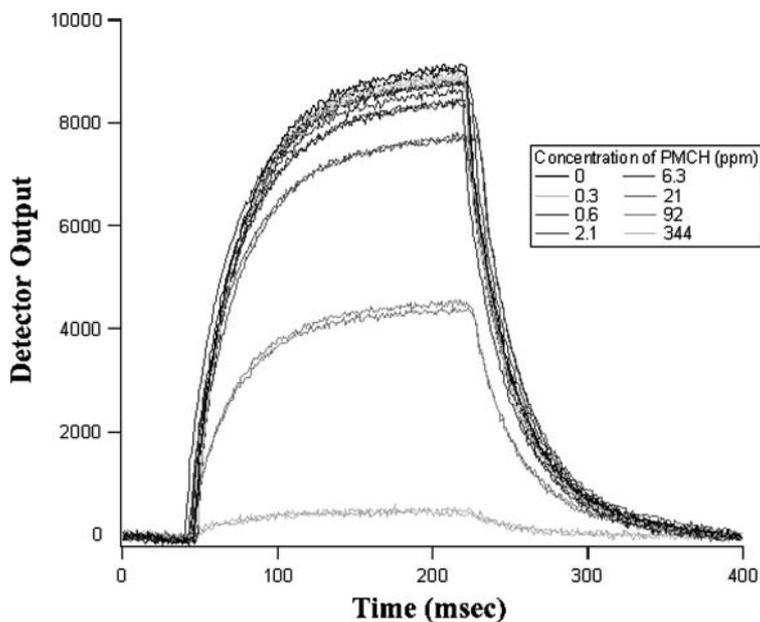


Figure 6. Absorption curves for perfluoromethylcyclohexane.

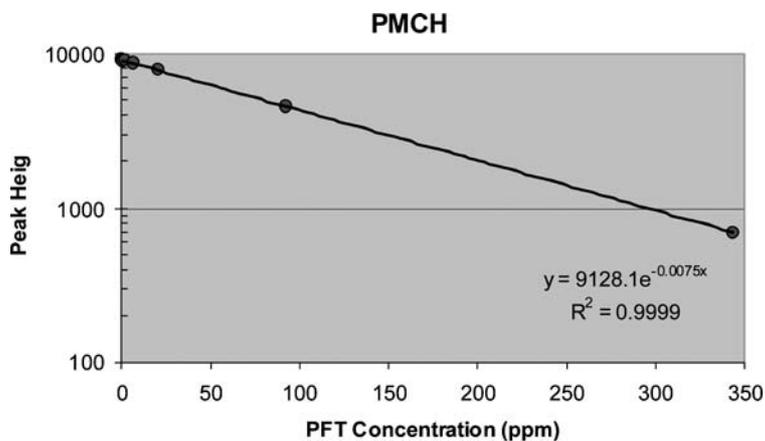


Figure 7. Peak height versus Perfluoromethylcyclohexane concentration.

The first round of experiments achieved a concentration resolution of approximately 30 ppb-m. The laser output was then more carefully stabilized using a feedback loop to the high voltage. This resulted in a resolution increase and detection down to 10 ppb-m was accomplished.

### Field Deployable Lidar

For the more demanding experiments involving the lidar platform, a HgCdTe detector (Judson Series J15D) was purchased that was more specific to the lasing region of interest and hence had a higher sensitivity at this spectral region. It was believed the 10 ppb-m detection limits would be improved using the new detector.

The lidar was reconfigured from a laboratory (sealed cell) fixed path length system to a field deployable variable path length system. These initial experiments were performed indoors to allow simple control of the PFT concentration in the air. Outdoor turbulence would result in extreme mixing and non-uniform tracer concentrations. This in turn would require large numbers of air samples to be taken and analyzed to obtain the concentration profile for the tracer. A narrow hallway approximately 40 m in length was chosen for the measurements. The CO<sub>2</sub> laser was positioned such that the laser light was directed into the hallway. A 10:1 ZnSe (99.2% transmission @ 10.6  $\mu\text{m}$ ) beam expander and collimating telescope was used to minimize beam divergence and enlarge the spot size to approximately 25 mm. A mirror and reflector were used to direct the beam down the 40-m hallway and back to the detector.

With the new detector, the baseline output proved to be two orders of magnitude greater than the first detector. A preliminary check of the lidar was completed by releasing PMCH into the hallway from a cylinder. As expected, the signal from the lidar decreased with time as the tracer concentrations in the hallway rose. Figure 8 shows the detector voltage versus time (chopped signal) for lidar measurements made during the tracer release (solid lines) and subsequent decay after the cylinder was closed (dashed lines). The baseline (no tracer) is represented by the top two curves. While the tracer concentration was not measured, this test was a quick check of the lidar's response to PFTs in the air and was very promising.

The next step was to tag the hallway air with a known or measurable amount of PMCH. The lidar returned to the zero tracer state rapidly in the first test and suggested a high air exchange rate in the hallway. We would need to know the exchange rate to determine the release rate of PMCH in order to tag the hallway to a known concentration. The exchange rate was measured by releasing Perfluoromethylcyclopentane (PMCP) into the hallway at a known rate. We chose to use permeation sources for the PMCP release. A permeation source consists of a container of liquid tracer capped with a silicone rubber seal (e.g., stopper or septum). The tracer permeates through the rubber seal at a constant rate (dependent on temperature). The source is very carefully constructed so that the rubber thickness is carefully measured and controlled and the weight of liquid is precisely known. The source is calibrated by keeping it in a constant temperature chamber and periodically weighing it to determine the tracer loss and hence release rate.

PMCP was chosen as it has a high nominal release rate and the hallway had an apparent high exchange rate. BNL has various diffusion source configurations that have different release rates for a given tracer. In this case, megasources were used,

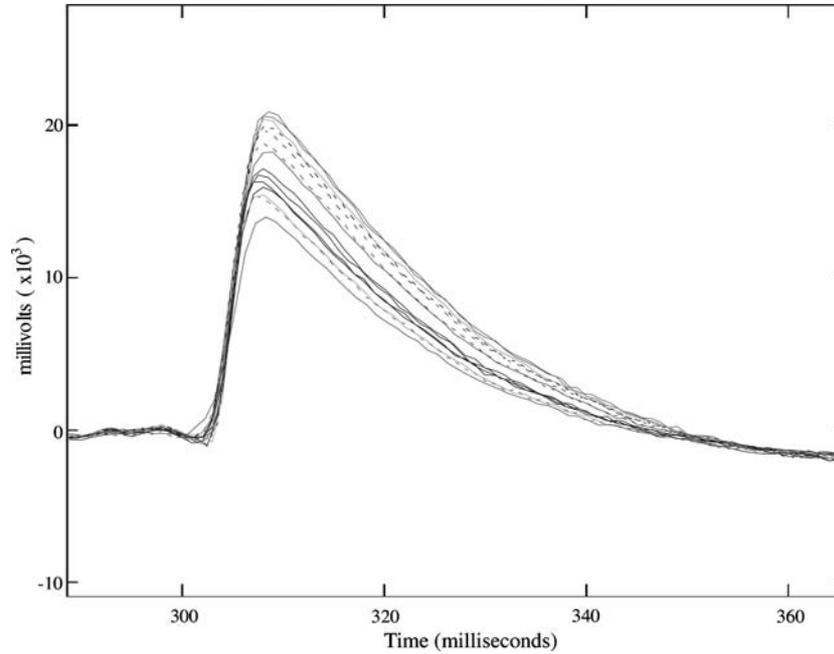


Figure 8. Preliminary (uncalibrated) adsorption curves for PMCH in air.

which are the highest release rate sources currently in production. For PMCP, at 21.5 °C, the rate is nominally 2100 nL/h.

Five PMCP megasources were evenly spaced along the 50 m hallway and allowed to equilibrate over night. The following morning, twelve capillary adsorption tube samplers (CATS) were evenly placed down both sides of the hallway. The CATS were positioned so that they were at the same height as the lidar beam would be. The CATS were used to collect the tracer for later analysis. One end of the sampler was capped and one end open to the air. This allowed the CATS to sample passively via diffusion. The sampling rate, for PMCP, is 0.216 L/day. The CATS were left in place for 24 h and the PMCP content was analyzed using gas chromatography with an electron capture detector. Knowing the release rate and measuring the equilibrium concentration allows the infiltration rate and exchange rate to be calculated from;

$$S = S_{(21.5^{\circ}\text{C})} \times n \times e^{\{-3400 \times [1/(273.2+t^{\circ}\text{C})-1/294.7]\}} \quad (1)$$

where  $S$  is the tracer release rate in nL/h;  $n$  the number of sources used and  $S_{(21.5^{\circ}\text{C})}$  the actual individual source rate in nL/h.

$$C = v / [\text{CATS rate} \times \text{time (days)}] \quad (2)$$

where  $C$  is the concentration of tracer in  $\text{pL/L} \equiv \text{nL/m}^3$ ,  $v$  the volume of tracer in  $\text{pL}$ , CATS rate the sampling rate for the CATS in  $\text{L/day}$ .

$$R = S/C \tag{3}$$

where  $R$  is the infiltration rate in  $\text{m}^3/\text{h}$

$$ACH = R/V \tag{4}$$

where ACH is the exchange rate (per hour) and  $V$  is the volume of the hallway in  $\text{m}^3$ .

The hallway volume was  $\sim 215 \text{ m}^3$  and the average PMCP concentration was  $3 \text{ pL/L}$  resulting in an exchange of 16 times per hour or a tracer half-life of 3.7 min. Since the laboratory experiments ended with a detection limit of  $10 \text{ ppb-m}$ , the initial hallway concentration was set to match this value. Using three PMCH permeation megasources with nominal release rates of  $1400 \text{ nL/h}$  each would result in a hallway concentration of  $240 \text{ ppt}$  ( $40 \text{ m} \times 240 \text{ ppt} = 10 \text{ ppb-m}$ ). The sources were evenly spaced along the hallway at the same height as the PMCP sources had been placed and allowed to equilibrate over night.

The following morning, the lidar was turned on and measurements taken. The lidar was left on and the PMCH sources were removed from the hallway. This allowed the PMCH concentration in the hallway to begin to decay away. Since the hallway air exchange rate was known, the decay rate was also known. This allowed us to calculate the hallway concentration at any given time. Data (average of 250 scans) from the lidar was taken every two minutes as the tracer depleted from the hallway atmosphere. Figure 9 gives the decay curve for the PMCH tracer in the

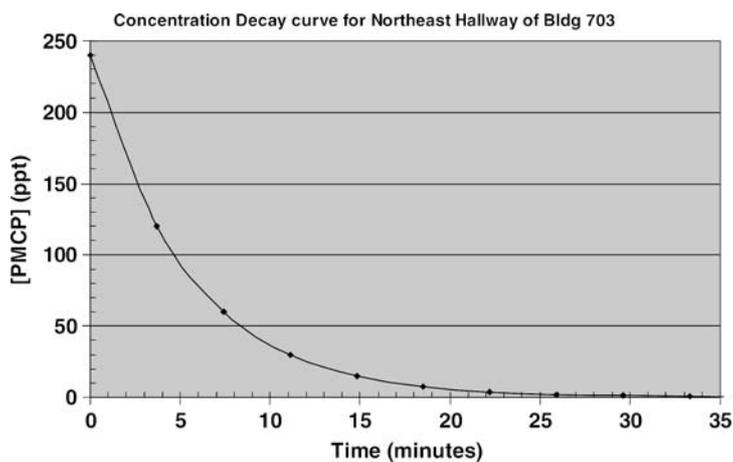


Figure 9. Tracer depletion curve for hallway LIDAR measurements.

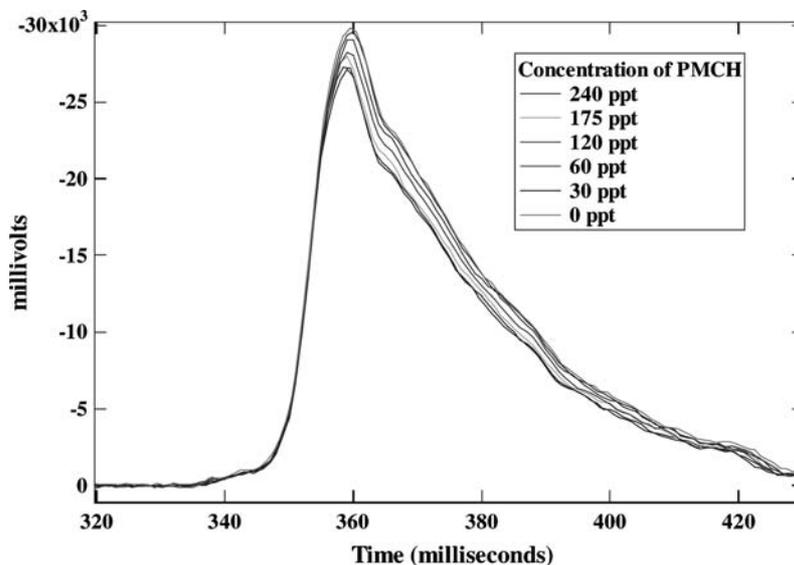


Figure 10. Adsorption curves for PMCH in air using lidar over 40 m.

hallway once the sources were removed. Figure 10 shows the adsorption traces taken from PMCH = 240 ppt until a stable unchanging baseline occurred (PMCH below detection levels). We were able to detect PMCH in the air at levels as low as 30 ppt. This corresponds to 1 ppb-m and is a ten-fold increase in sensitivity versus earlier benchtop results.

### Conclusions

Measurement of perfluorocarbon tracers is possible using an infrared CO<sub>2</sub> laser. Laboratory measurements of the absorption cross-section for perfluoromethylcyclohexane (PMCH) were the same order of magnitude compared to literature values for similar perfluorocarbon compounds. Air concentrations of PMCH were measured down to 1 ppb-m. This system would replace conventional subsurface air sampling (requiring many well locations) and subsequent gas-chromatographic analysis for PFTs.

While results are very promising, more work needs to be completed prior to field deployment of a cover monitoring system. Optimization of the laser system utilizing the newer compact CO<sub>2</sub> lasers and a more sophisticated detection system should increase the sensitivity another order of magnitude. Field studies to measure air concentrations as a function of subsurface (injected tracer) concentrations are needed to determine the working concentrations of PFTs needed to be detectable via the above surface laser.

The detection of PFTs with lidar may also have benefits in other tracer-based research areas such as atmospheric plume dispersion, pollution monitoring and building ventilation measurements. In particular, definition of the source area for dispersion studies would be beneficial. Laser detection could provide three dimensional data on tracer concentrations in the very near field (less than 100 meters from the source release point).

### References

- Chyba, T. H., Zenker, J. T., McCray, C. L., Lee, H. R., Elivert, R., Thomas, B., Toppin, C., Larson, D., Higdon, N. S. and Ritcher, D. A.: 1999, *SPIE Proceedings* **3757**, 80.
- Edner, H., Faris, G. W., Sunesson, A. and Svanberg, S.: 1989, *Appl. Opt.* **28**, 921.
- Edner, H.: 1995, *Review of Laser Engineering* **23**, 142.
- Heiser, J. and Sullivan, T. M.: 2001, 'Using Perfluorocarbon Tracers for Verification of Cap and Cover Systems Performance', Brookhaven National Laboratory, Upton, New York, BNL-52647.
- Heiser, J., Sullivan, T. and Serrato, M.: 2002, 'Proof-of-Concept Test of a Unique Gaseous Perfluorocarbon Tracer System for Verification and Long-Term Monitoring of Caps and Cover Systems Conducted at the Savannah River Site Bentonite Mat Test Facility', Proceedings of Waste Management 2002, Tucson, AZ.
- Heiser, J. H. and Sullivan, T. M.: The Brookhaven National Laboratory Perfluorocarbon Tracer Technology: A Proven And Cost-Effective Method To Verify Integrity And Monitor Long-Term Performance of Walls, Floors, Caps, and Cover Systems, Brookhaven National Laboratory, March 2002, Upton, New York, BNL-52657.
- Measures, R. M.: 1992, *Laser Remote Sensing: Fundamentals and Applications*, Krieger Publishing Co., Malabar FL.
- Milton, M. J. T., Woods, P. T., Jolliffe, B. W., Swann, N. R. W. and McIlveen, T. J.: 1992, *Appl. Phys. B* **55**, 41.
- Oh, C., Prasad, C. R., Fromzel, V., Hwang, I. H., Reagan, J. A., Fang, H. and Rubio, M.: 1999, *Proceedings of the SPIE Conference on Laser Radar Technology* **3707**, 17186.
- Papayannis, A., Ancellet, G., Pelon, J. and Megie, G.: 1989, *Appl. Opt.* **29**, 467.
- Ray, M. D., Sedlacek, A. J. and Wu, M.: 2000, *Rev. Sci. Instr.* **71**, 3485.
- Rothe, K. W., Brinkmann, U. and Walther, H.: 1974, *Appl. Opt.* **4**, 181.
- Schotland, R. M.: 1974, *J. Appl. Metero* **13**, 71.
- Sullivan, T. M., Heiser, J., Gard, A. and Senum, G.: 1996, *Monitoring Subsurface Barrier Integrity Using Perfluorocarbon Tracers*, ASCE Special Publication.
- Sunesson, J. A., Apituley, A. and Swart, D. P. J.: 1993, *Appl. Opt.* **33**, 7045.