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PERFLUOCARBON GAS TRACER STUDIES TO SUPPORT RISK ASSESSMENT MODELING OF CRITICAL INFRASTRUCTURE SUBJECTED TO TERRORIST ATTACKS

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Perfluorocarbon Gas Tracer Studies to Support Risk Assessment Modeling of Critical Infrastructure Subjected to Terrorist Attacks

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Abstract: Development of real-time predictive modeling to identify the dispersion and/or source(s) of airborne weapons of mass destruction including chemical, biological, radiological, and nuclear material in urban environments is needed to improve response to potential releases of these materials via either terrorist or accidental means. These models will also prove useful in defining airborne pollution dispersion in urban environments for pollution management/abatement programs. Predicting gas flow in an urban setting on a scale of less than a few kilometers is a complicated and challenging task due to the irregular flow paths that occur along streets and alleys and around buildings of different sizes and shapes, i.e., "urban canyons". In addition, air exchange between the outside and buildings and subway areas further complicate the situation. Transport models that are used to predict dispersion of WMD/CBRN materials or to back track the source of the release require high-density data and need defensible parameterizations of urban processes. Errors in the data or any of the parameter inputs or assumptions will lead to misidentification of the airborne spread or source release location(s). The need for these models to provide output in a real-time fashion if they are to be useful for emergency response provides another challenge. To improve the ability of New York City's (NYC's) emergency management teams and first response personnel to protect the public during releases of hazardous materials, the New York City Urban Dispersion Program (UDP) has been initiated. This is a four year research program being conducted from 2004 through 2007. This paper will discuss ground level and subway Perfluorocarbon tracer (PFT) release studies conducted in New York City. The studies released multiple tracers to study ground level and vertical transport of contaminants. This paper will discuss the results from these tests and how these results can be used for improving transport models needed for risk assessment.

1. Introduction

Street level wind flow patterns in cities are influenced by topography, the presence of different sizes and shapes of buildings forming urban canyons, and localized phenomena (e.g., traffic patterns, air intake/exhaust vents for subways and buildings). Development of real-time predictive modeling to identify the dispersion and/or source(s), of airborne contaminants through urban environments is needed to improve response to potential releases of weapons of mass destruction (WMD) or chemical, biological, or radioactive materials through either terrorist or accidental activities. These models will also prove useful in defining airborne pollution dispersion in urban environments for pollution management/abatement programs. Predicting air flow in an urban setting on a scale of less than a few kilometers is a complicated and challenging task due to the irregular flow paths that occur along streets and alleys and around buildings of different sizes and shapes. Transport models that are used to predict contaminant dispersion or back track the source require high-density data and effective parameterization of the physical processes governing dispersion. Errors in the data or any of the parameter inputs or assumptions will lead to misidentification of the airborne spread or source location(s). Complicating this further is the need for these models to provide output in a real-time fashion for use in emergency response situations.

The New York City Urban Dispersion Program (UDP) is a four-year research program being conducted from 2004 through 2007. The research conducted under this program will improve the ability of NYC's emergency management teams and first response personnel to protect the public during releases of hazardous materials. The program will:

Improve the permanent network of wind stations in and around New York City (NYC) to provide the data
necessary to accurately predict how released hazardous materials will be transported,

- Conduct field studies in NYC to advance knowledge about the movement of contaminants in and around NYC, into buildings, and within building interiors,
- Improve and validate computer models that simulate the atmospheric movement of contaminants in urban areas using data collected in the field studies, and
- Transfer the improved capabilities to NYC emergency management agencies.

The research program is being conducted by several U.S. Department of Energy national laboratories (Pacific Northwest National Laboratory (PNNL), Brookhaven National Laboratory (BNL), Lawrence Berkley National Laboratory (LBNL), Los Alamos National Laboratory (LANL), Argonne National Laboratory (ANL) and Lawrence Livermore National Laboratory (LLNL)), federal agencies (Environmental Protection Agency (EPA), and the National Oceanographic and Atmospheric Administration (NOAA)), and numerous academic institutions. It is supported by the U.S. Department of Homeland Security (DHS), with additional support from the U.S. Department of Defense – Defense Threat Reduction Agency (DTRA), the U.S. Department of Energy (DOE), and the U.S. Environmental Protection Agency (EPA). An overview of UDP is available at http://urbandispersion.pnl.gov/, and details about BNL's role in the program can be found at: www.bnl.gov/des/ERTD/TraceTechnologies/UDP.asp.

Two UDP field studies have been conducted to date in New York City's Midtown Manhattan. The first of these studies was conducted in the late winter of 2005 in the area around Madison Square Garden (MSG) and is designated as MSG05. Two Intensive Observation Periods (IOPs) were conducted during the MSG05 study, where IOPs are days when tracer were released and detailed measurement of meteorological conditions and tracer concentrations are made. The second more extensive study, MID05, was conducted during August 2005 consisting of six IOPs.

2. Field Study Approach

MSG05 consisted of two IOPs conducted on March 10 and March 14, 2005. The Brookhaven Tracer Technology Center released five perfluorocarbon tracers at the four corners of the block occupied by MSG (two tracers at one location for quality control), and one tracer at the northeast side of the One Penn Plaza building (Figure 1). MSG is a circular building surrounded by several much taller buildings. This configuration leads to street level winds that are variable and not always aligned with the prevailing winds. On both days there were two one-hour releases. The first release occurred from 9:00 to 10:00 Eastern Standard Time (EST) and the second release from 11:30 to 12:30 EST. Tracer sampling began at 9:00 and concluded at 14:00 EST resulting in 10 half-hour-average samples covering both releases. Air samples were collected at 17 street level locations at distances approximately 200 and 400 meters from the center of MSG (Figure 1), on the tops of roofs at various levels of four buildings, and with a quasi-real time mobile analyzer sampling at various locations around and downwind of the release area. In addition, people were equipped with Personal Air Samplers and given prescribed routes to walk in the study area to investigate personal exposures.

The Brookhaven Tracer Technology Group has a Quality Assurance Plan (BNL, 2003) that specifies practices and procedures for BNL tracer programs. This plan covers the preparation and acceptance of PFT release mixtures, preparation and testing of samplers and sampling media, analytical operations and data reporting. The planning, preparation, and execution of the field and laboratory activities of UDP were carried out in accordance with the practices and procedures outlined in this plan. Field plans were developed for both studies and were approved by appropriate NYC agencies.

Winds and other meteorological quantities (e.g., temperature, humidity) were measured using 18 meteorological systems at 15 locations in the vicinity of MSG and around the Midtown Manhattan area during MSG05. This included two sodar systems, seven rooftop and nine portable meteorological stations placed at street level during each IOP. The vertical profile of winds up to 500 m above-the-ground were also remotely measured using an acoustic sodar located on the west side of the Hudson River (about two miles from MSG) at the campus of the Stevens Institute of Technology at Castle Point, Hoboken, NJ.



Figure 1. Aerial view of the MSG05 study area, and the tracer release and sampling locations around Madison Square Garden.

The second UDP tracer and meteorological field study (MID05) had the following elements. A twenty-one day study period from August 6 – 26, 2005 was selected. During this time, six IOPs were conducted. Each IOP lasted for six hours where up to seven inert gas tracers were released (six PFTs and sulfur hexafluoride, SF₆) and collected at up to 180 sample locations. Meteorological measurements were made continuously at several locations throughout the study region during the twenty-one day period with additional meteorological measurements during the IOPs. Tests included three IOPs that released three PFTs within a building. During these tests, SF_6 released outside the building was measured inside the building and three additional PFTs were released at outdoor locations. One IOP had personal exposure measurements using PFT tracers made by more than a dozen individuals traveling prescribed paths in the study area. In the last three IOPs, one PFT tracer was released in the New York City Subway system and five PFTs above ground. Measurements were made of all PFT concentrations in the subway system for all PFTs. This permits following the ingress and egress of tracers from the subway system. The eight potential SF6 and PFT release locations are shown in black while the street sample locations are shown in red in Figure 2. During the first three IOPs, four tracers (three PFTs and SF6) were released from three of the eight locations (one PFT and SF6 from the same location). During the last three IOPs, PFTs were released from five of the eight locations. The choice of which locations was based on the prevailing wind direction expected during the 6-h study period. Figure 3 shows the release location and sampling stations in the subway.

Four acoustic sodars were deployed during the 21-day study period of MID05 continuously measuring vertical wind profiles to approximately 150 m above the instrument elevation. The sodars were deployed on tops of buildings spread throughout the study area. A radar wind profiler and radiosonde balloon launch system were located at Stevens Institute of Technology (SIT) across the Hudson River in Hoboken, New Jersey. The radar wind profiler continuously measured wind profiles up to two kilometers above the instrument elevation during the 21-day study period. Weather balloons were released four times during each IOP measuring temperature, pressure and humidity through several kilometers of the lower atmosphere. In addition, during each IOP fifteen portable tripod mounted weatherstations were deployed at street-level. The portable stations were deployed during the morning before the start of the IOP and taken down after completion of the IOP. The remainder of this paper will focus on PFT data.



Figure 2. MID05 street-level tracer release and sampling locations around Midtown Manhattan.



Figure 3. MID05 subway tracer release and sampling locations in Midtown Manhattan.

2.1. Perfluorocarbon Tracers

Perfluorocarbon tracers are colorless, odorless compounds that consist of a carbon and fluorine atoms joined by covalent single bonds. The tracers used in MSG05 and MID05 are molecules consisting of five (pentane) or six (hexane) member rings with one (methyl), two (di-methyl, ethyl) or three (propyl) additional carbon atom structures. These compounds are chemically inert, non-flammable, have no biological effects and are very safe. Perfluorocarbon background levels are in the parts per 10^{15} and have remained roughly constant at this low level over the past 4 decades (Dietz, 1987: Simmonds et al, 2002). The total amount of these tracers released in MSG05 was 31.6 grams.

The six perfluorocarbon tracers released in MSG05 and MID05 are listed in Table 1 along with their chemical name, molecular formula, and background concentrations measured in 1986 and 2002. Concentrations are given in mixing ratio and are in parts per quadrillion by volume (ppqv) or number of molecules of tracer per 10¹⁵ molecules of air.

2.1.1. Tracer release

In MSG05 the perfluorocarbon tracers were released from gas cylinders containing PFT mixed with N_2 at approximately 200 PSI. In MID05, a syringe pump was used to release liquid PFTs which rapidly evaporated into the atmosphere.

Table 1: Perfluorocarbon tracers used in MSG05 and MID05 and some of their background concentrations in 1986 and 2001.

Acronym	Chemical Name	Formula	Background 1986 ¹ (ppqv)	Background 2001 ² (ppqv)
PMCP	Perfluoromethylcyclopentane	$C_{6}F_{12}$	3.22 ± 0.03	6.29 ± 0.22
РМСН	Perfluoromethylcyclohexane	$C_{7}F_{14}$	4.6 ± 0.05	5.49 ± 0.23
oc-PDCH	Perfluoro-1,2-dimethylcyclohexane	$C_8 F_{16}$	0.30 ± 0.1	0.73 ± 0.09
PECH	Perfluoroethylcyclohexane	$C_8 F_{16}$	NA	NA
i-PPCH	Perfluoro-isopropylcyclohexane	C_9F_{18}	NA	NA
РТСН	Perfluorotrimethylcyclohexane	C_9F_{18}	0.07	NA

1. Dietz, 1987

2. Simmonds et al, 2002

2.2. Sampling

Three types of air samplers were used in the UDP field programs. All sampling media were cleaned and analyzed to check for residual tracer or other contamination before the field programs. The detailed description that follows applies for MSG05. Similar procedures, but with more data locations were followed in MID05.

The Brookhaven Airborne Tracer Sampler (BATS) was deployed at 17 ground locations and six locations on the roofs of buildings in MSG05. The BATS consists of a base unit containing a pump, timer, and control electronics, and a lid containing 22, 1/8 inch o.d. stainless steel tubes packed with Ambersorb[®] (Rhom and Hass, Philadelphia, PA). The lid also contains a multi-port valve that places the active sampling tube in the sample stream. The nominal pumping rate was 50 ml min⁻¹. Samples were collected for 30 minutes resulting in approximately 1.5 liters of air collected in each tube. On each test day samples were collected from 9:00 to 14:00 EST for a total of 10 samples. Samples from both IOPs were collected on a single lid. The first 10 tubes were used during the first IOP,

the 11th tube was skipped and the sampling began with the 12th tube during the second IOP. The ground level BATS samplers were deployed about two meters above street level in baskets attached to light poles. Students from City University of New York (CUNY) affiliated schools were stationed at each sampler for security. A similar procedure was used in MID05. Seven BATS were deployed on the roofs of One Penn and Two Penn Plaza, the Post Office, and the New Yorker Hotel.

Nine Sequential Air Samplers (SAS) were deployed during both IOPs in MSG05. The SAS units collect samples on 20, ¹/₄ inch diameter glass tubes containing Ambersorb[®]. These tubes are known as CATS tubes (Capillary Adsorption Tubes). The flow rates for these samplers are a nominal 500 ml min⁻¹. These units collected one sample every six minutes. Sampling began at 9:00 and ended at 11:00 EST. These samples were deployed on the roofs of One Penn and Two Penn Plaza, and the Post office to provide vertical data with a high degree of time resolution. During the first IOP, two SAS units collected samples in the indoor levels below Madison Square Garden and one inside the New Yorker Hotel conference room. These units were deployed on the roofs of One Penn and Two Penn Plaza, and the roof of the New Yorker during the second IOP.

Personal Air Samplers (PAS) were also used to collect samples during one IOP during MSG05 and during one IOP of MID05. People were given prescribe routes to walk during the course of the day. These units consisted of a small battery powered pump with a fitting for a CATS Tube. The people changed the CATS tubes at prescribed times depending on their location and proximity to a source.

3. Results and Discussion

The analysis of all 1300 PFT samples from MSG05 was completed in 2005. Analyses of the PFT samples from MID05 have been completed and are undergoing quality assurance checks. Therefore, results from MID05 are preliminary. This paper will present the results from MSG05 for the street level concentration contours and will give preliminary results for the subway studies in MID05.

3.1. MSG05 PFT concentration contours

Concentration contours for the five tracers and the average wind direction and speed at the street and rooftop levels are presented in Figure 4. During the first IOP (March 10, 2005) the above-building-top winds approaching Manhattan were approximately from the west-northwest, lining up reasonably well with Manhattan "streets," which are perpendicular to Manhattan "avenues." The winds approaching Manhattan during the second IOP (March 14, 2005) shifted to being from the north-northwest and were no longer aligned with the streets. The street-level winds were markedly different from the roof-top winds. The wind direction varied with location sometimes pointing south, other times north, but never aligning with the prevailing winds. Along the western side of MSG on 8th Avenue, the winds were aligned with the avenue, pointing approximately north-northeast on the north side of MSG and south-southwest on the south side. Roof-top winds were typically faster than street-level winds. The fastest street-level winds occurred at the northeast corner of MSG on both days and were directed northerly. In general, street-level winds were stronger on the first day, March 10th, than on March 14th.

Examining Figure 4 shows that the predominant direction of the plume is generally in the direction of the rooftop prevailing winds. However, street-level winds did impact the flow locally as evidenced by the movement of the tracer plume to the north-northeast along 8th Avenue of the tracer released from the north and west sides of MSG. On both experimental days, there was substantial spreading of the plume of much greater magnitude than would be expected over open terrain. In fact, the width of the plumes at 400 meters downwind from the source can be greater than 400 meters.

During MSG05, two tracers, iPPCH and PMCH, were released simultaneously, at the same nominal flow rates, from the release location on the east side of MSG. The ratio of the concentrations of the gas mixtures iPPCH to PMCH was 0.037. A correlation plot using 788 data points of the two tracers at all sampling locations showed reasonable agreement between the two. The correlation was C(iPPCH) = 0.038*C(PMCH) + 4.2, $R^2 = 0.89$, where C is the measured concentration at the sampling location. Duplicate samples taken at the same location generally were within 10% for the BATS measurement system.



Day 2: 2-Hour-Ave Plume by Source



Figure 4. Wind and tracer dispersion patterns from the two MSG05 IOPs conducted around Madison Square Garden on March 10 and March 14, 2005.

3.2. MID05 Subway Tracer Data

Subways provide an interesting challenge in understanding the flow dynamics along the subway paths. Many parameters will impact the conditions including the release location (e.g., within a subway car, on a track between stations, on a platform, in a stairway, at street level above an intake grate), type of release (e.g., instantaneous vs. continuous), weather conditions (temperature, humidity) and the number of passengers present. The movement of subways can pull or push contaminants along the tunnels for great distances. Many of New York's subway lines are interconnected and release of contaminants in one line can spread to others in relatively short times. New York City subways are very shallow and are well-connected with the atmosphere above ground through entrances and grates. All of these factors working simultaneously make understanding transport extremely complex.

In MID05, tracer samplers were located in the subway during all six IOPs as shown in Figure 3, and during the last three IOPs, in addition to the above-ground PFT releases, one PFT was released at 50th Street on the 1-2-3-9 line. The PFT sampling locations were at the 23rd, 34th, 42nd, 59th, and 72nd street stations along this line. At 42nd street, the N-R-Q-W line and the B-D-F-V line both come into this station. All three lines are connected through large open walkways. Each line has a separate air handling system. PFT air samples were collected at 42nd street station on the N-R-Q-W line and at Grand Central Station (less than one mile away) on the B-D-F-V line.

Figure 5 shows the 12:00 to 12:30 EDT average PFT concentrations in the subway and above-ground of the PFT released above-ground from 11:00 to 11:30 EDT near the intersection of 49th Street and Sixth Avenue on August 8, 2005. The winds are approximately from the south-southwest (along the Manhattan avenues) transporting the tracer plume approximately to the north-northeast from near the 49th Street and Sixth Avenue release location. The data shows that the tracer released above ground diminishes to low above-ground levels ¹/₂-hour after the release stopped, and the concentrations in the subway remain relatively high after the release stops. Additionally, the concentrations in the subway line are shown to extend over a mile south ("upwind") of the release location.



Figure 5. Approximately south-north transect of subway and above-ground $\frac{1}{2}$ -hour-average PFT concentrations of an above-ground PFT release near 49th Street and Sixth Avenue (mile 0.50). The concentrations are $\frac{1}{2}$ -hour after the release stopped.

Strong evidence for the infiltration of tracers released above ground into the subway is shown in Figure 6. Figure 6 shows the time history of PFT concentrations measured in the subway of five PFTs released above ground and one PFT released in the subway. The subway tracer is labeled in black with the oversized triangle. All other time histories are for tracers released above ground and measured in the subway system. At the 42nd Street Station on the 1-2-3-9 line the signal for the subway tracer is obvious. There were two release periods for the subway tracer as evidenced by the large peaks around 8 AM and 11:30 AM EDT. While not as large in magnitude, the evidence for five above-ground tracers in the subway is also obvious from the three peaks corresponding to the three release

times of these tracers. On the N-Q-R-W line at 42^{nd} Street, the signal from the above-ground tracers is clear and once again shows the three peaks corresponding to the release times. In general, the above-ground tracers were higher in the N-Q-R-W line than in the 1-2-3-9 line. This may be due to many different factors including different air handling systems, different subway characteristics at the station, or different distances from the source location to the different lines. At the N-Q-R-W line at 42^{nd} Street the tracer released in the subway showed a minor increase after the first subway release, but no measurable response to the second release. The high values at the 1-2-3-9 line at 42^{nd} street of this tracer, suggest that communication between the two platforms at this station is weak in the direction from 1-2-3-9 to the N-Q-R-W line. No inference about the transport of tracers from the N-Q-R-W line can be made from the data. The concentrations from above ground tracers at the 1-2-3-4-9 platforms at 42^{nd} street may be from the N-Q-R-W line or they may have entered the line at other points (grates, stations).



Figure 6. Subway PFT concentrations of five PFTs released above ground (colored lines) and one PFT released in the subway (lines with black triangular markers).

3.3. Link to Risk Assessment

The data and analyses that will be performed will provide important information to support risk management decisions in case of a terrorist attack. The first set of risk management decisions involve deciding on the region to evacuate and whether it is better to shelter in place for a period or evacuate immediately. Gas concentrations released from a source will diminish in time. Benefits include:

- a) Improved understanding of outdoor dispersion in urban settings. This will help in deciding evacuation zones.
- b) Improved modeling of dispersion in urban settings. The data generated in the eight IOPs will be used to refine and enhance numerical modeling. The data collected under a variety of wind conditions will help in understanding the range of behavior that can occur. This will help in role playing for emergency preparedness. The data will also help in understanding the time required to return to background conditions.
- c) Improved understanding of movement of gas into and out of buildings. The data will provide information on how long concentrations remain elevated when released inside a building and this can help with determining whether it is best to shelter in place or evacuate.
- d) Improved understanding of gas movement into and out of the subway system. The results above showed higher concentrations of tracers released above ground in one line of adjacent subway lines at 42nd Street. The data also showed little transfer of the tracer between the 1-2-3-9 line which had the tracer release and the N-Q-R-W line which did not, at the 42nd Street station.

4. Conclusions

Two field studies, MSG05 and MID05, were conducted in New York City during 2005 as part of the DHS Urban Dispersion Program. The data from these studies will be used to develop a better understanding of atmospheric dispersion in urban areas for providing guidance to first responders, and improving and validating atmospheric dispersion models. Preliminary results from the studies indicate the following:

- Street-level and roof-top winds were different in magnitude and direction. Transport is in the general direction of the prevailing (roof top) winds with minor perturbations from the street level winds under the study conditions of MSG05.
- The spread of the plume is extensive in the near field. Four hundred meters from the source, measurable concentrations were observed at widths in excess of four hundred meters. This has implications for responding to emergency events.
- Subway studies showed that there was exchange of tracers between the subway and above ground. Subway concentrations of tracers released above ground were found as far as a mile south ("upwind") of the release location.
- Subway studies also showed that there was strong infiltration of tracers released above ground into the subway. High concentrations were measured in subways from tracers released above ground and in some cases, hundreds of meters from the subway line.
- Subway concentrations diminish much less rapidly over distance than above ground released due to the restricted volume for mixing.
- Communication between the 1-2-3-9 line in which the tracer was released and the N-Q-R-W line at the 42^{nd} street station was weak as evidenced by the low concentration of the subway tracer in that line.

These preliminary results will be followed up by more detailed analysis of all of the data. Investigations will include:

- detailed mapping and interpretation of the concentration contours over time for the six IOPs in MID05,
- modeling of vertical mixing from data obtained in MSG05 and MID05,
- further analysis of the subway data from all six IOPs,
- analysis of data for the PFTs released inside a building in terms of interior and exterior levels (including subway) of these PFTs,
- modeling of concentration profiles from all IOPs at street level and as a function of elevation, and
- evaluation of the data in terms of emergency response protocols.

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