Title: Simulating Real-World Exposures during Emergency Events: Studying Effects of Indoor and Outdoor Releases in the Urban Dispersion Project in Upper Manhattan, NY

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## ABSTRACT

A prospective personal exposure study, focusing on indoor and outdoor releases, was conducted in upper Midtown Manhattan in New York City as part of the Urban Dispersion Program (UDP) focusing on atmospheric dispersion of chemicals in complex urban settings. The UDP experiments involved releases of very low levels of perfluorocarbon tracers (PFT) in Midtown Manhattan at separate locations, during two seasons in 2005. The study presented here focuses on both outdoor and indoor releases of the tracers, as well as including realistic scripted activities for characterizing near-source and neighborhood scale exposures using 1-minute and 10-minute duration samples, respectively. Results showed that distributions of individual tracers and exposures to them within the study area were significantly influenced by surface winds, urban terrain, and movements of people and vehicles typical of urban centers. While in general, PFT levels returned quickly to zero in general after cessation of the emissions, in some cases, the concentrations stayed at higher levels after the releases stopped. This is likely due to accumulation of the PFTs in some buildings, which then serve as "secondary sources" when outside levels are lower than indoor levels. Measurements of neighborhood scale PFT concentrations (up to distances of several blocks away from the release points) provided information needed to establish a baseline for determining how different types of releases could affect exposures both to the general public and to emergency responders. These data highlight the factors impacting the toxic threat levels following releases of hazardous chemicals and provide supporting information for evaluating and refining protocols for emergency event response.

## INTRODUCTION

Assessment of potential human exposures resulting from contaminant releases within urban areas typically requires detailed information on flow velocities, turbulence, and concentration distributions. This is critical in cases when contaminant releases are sudden and large, such as those associated with transportation-related accidents and acts of terrorism involving chemical or biological agents. Urban systems are characterized by vertical venting behind large/tall buildings, channeling down street canyons, and both horizontal and vertical re-circulations associated with individual structures and groups of tall and closely located buildings. Emergency response and planning efforts in general require detailed characterization of these aspects to assess contaminant accumulation in commercial hubs within urban centers and other locations vulnerable to releases of biological, chemical, and radiological agents with potential serious acute health effects.

Various field campaigns, wind tunnel experiments, and modeling experiments have been conducted in the recent past in order to characterize the impact of various structural, meteorological, and release characteristics on dispersion of chemicals in urban environments. These include the Urban Dispersion experiments in Salt Lake City in 2000 (Allwine et al., 2002), in Oklahoma City in 2003 (Allwine et al., 2004), and in New York City in 2005 (Allwine and Flaherty, 2007), as well as the DAPPLE (Dispersion of Air Pollutants and their Penetration into the Local Environment) field studies in London in 2003 and 2004 (Martin et al., 2010a; Martin et al., 2010b). Data from these field studies have been used in identifying major factors associated with dispersion of chemicals in urban areas (Flaherty et al., 2007a; Hanna et al., 2007; Lioy et

al., 2007; Richmond-Bryant et al., 2011), and evaluation of atmospheric dispersion models (Flaherty et al., 2007b; Hanna and Baja, 2009; Hanna et al., 2011; Hendricks et al., 2007; Tewari et al., 2010; Urban et al., 2011). However, to date, no major urban field campaigns have focused on indoor releases of agents and the impact on exposures to general populations.

The Urban Dispersion Program (UDP) (Allwine and Flaherty, 2007; Lioy et al., 2007; Watson et al., 2006) was jointly funded by the U.S. Departments of Homeland Security, Energy, Commerce, and Defense, and the U.S. Environmental Protection Agency (EPA), and implemented by multiple national laboratories and local universities. The UDP focused on obtaining baseline information for use in predicting potential personal exposures in complex urban settings. These data can be used for improving the mathematical models for predicting potential acute human exposures from accidental or deliberate releases of harmful gases (Hanna and Baja, 2009), for establishing more effective guidelines for emergency response entrance and exit strategies, and for estimating the location of potential victims.

The personal exposure studies embedded within the overall UDP in New York City focused on (1) how gas transport in the atmosphere of a complex urban setting affects one's exposure to the gas, and (2) how one's movements and activities immediately following a release may affect the magnitude of their short-term exposures (Lioy et al., 2007). The specific scientific objectives were (i) to carry out tracer experiments with concurrent detailed meteorology measurements to aid in understanding exposures, and (ii) to obtain a high quality field measurement data set that can be used by the general scientific community for evaluating dispersion models for urban areas (Hanna and Baja, 2009). The study conducted in August 2005 and presented here expanded upon

the first study conducted in Manhattan near Madison Square Garden during March 2005 (Lioy et al., 2007). The area in Midtown Manhattan surrounding Rockefeller Center (RC) (Figure 1) experiences large densities and numbers of motor vehicles, tourists and workers. It also includes multiple office buildings, shopping areas, and tourist spots.

The personal exposure study involved specific scripted paths that aimed to capture (a) different types of populations at risk following releases of contaminants (e.g. emergency workers, workers in nearby offices, local shoppers, pedestrian traffic, and tourists spending time near landmark areas), and realistic activity patterns of people (e.g. people evacuating, exiting or approaching a point of release, and emergency workers remaining near the release). The overall area covered by the paths was roughly symmetric around the points of release. One of the novel aspects of this study included releases from multiple indoor locations.

The exposure monitoring was feasible because the PFT personal samplers available from Brookhaven National Laboratory (BNL) were very sensitive and could be worn by individuals completing a set of scripted tasks along specific near source and neighborhood routes. A very low limit of quantification in the parts per quadrillion by volume (ppqv) allowed for analyzing PFT personal samples collected for 10 min durations away from the source, while relying only on very small amounts of inert tracers at very low levels (Watson et al., 2006).

### METHODS

On August 12, 2005, prospective, personal exposure samples were collected from individuals in the Rockefeller Center area (RC; Figure 1). The RC area is located in the center of Midtown Manhattan. Pedestrian movement and vehicular traffic are high and quite variable each day. Therefore, outdoor releases of the PFTs were timed to start in the early morning before the peak of the morning rush and when meteorological conditions were stationary.

To characterize the potential exposures that would be experienced by different types of people (emergency workers, employees of local businesses, visitors, etc.), personal exposure scripts were developed that required trained personnel wearing very sensitive PFT personal samplers and walking along a pre-defined route during the study period. The exposure scripts were developed using trial runs involving walking along the streets and timing exactly how a person might move through the city in the morning and early afternoon. The paths used in the RC study were selected to reflect the most likely areas of high concentrations under various major meteorological conditions. The scripts were refined based on information on pedestrian and vehicular traffic patterns around the RC area, prior experience of the emergency response members on the UDP team, major points of interest and activities around the RC area, and types of activities that might lead to high exposures. Each route of the script accounted for (a) the time of release, (b) foot traffic and motor traffic in the personal sampling areas, (c) potential wind directions (by capturing paths in all directions around the release locations), and (d) nature of buildings surrounding the release locations. One set of scripted paths focused on the tourist area outside of Rockefeller Square, where tourists spend a significant amount of time, and where office workers in the area participate in lunchtime activities. The scripted movements consisted

of personnel taking samples representing 1 minute exposures (near source) or 10 min exposures (away from release), that could occur downwind, upwind, and crosswind of the four PFT release points. Personal activity scripts for the volunteers, including short walks near the sources (source-scale exposures) and walking and standing, were developed for this study in a manner similar to that for the Madison Square Garden study (Lioy et al., 2007). All scripted activities were completed in the field by trained EPA emergency response personnel.

#### **Exposure Scripts and Routes**

Figure 1 presents a summary overview of the location of releases and the exposure routes employed in this study, while Table 1 presents additional details on the release locations and characteristics. At any given time, one person was walking along each of the source level and community level paths. In case of the CE1 through CE4 paths, one volunteer started walking along the path at the start of the sampling time period (starting at 09:00, 10:00, and 11:00), and up on reaching the intermediate point, replaced the sampling canister with a new one, thus collecting approximately 10 min average concentrations at different periods and different segments of the path. These intermediate points are shown in Figure 1 by the labels 10 min, 20 min, and 30 min, along each of the paths. The total time period for each of the scripted paths of CE1 through CE4 were 30 min each.

#### **Release Locations**

The multiple PFTs were released at specific points, from indoors and outdoors, around the Rockefeller Center area, as shown in Table 1. The source characteristics differed substantially from those of the earlier UDP exposure study, and thus to very different exposure scenarios for

the persons following the predefined routes. In the Madison Square Garden study, all releases were outdoors and above ground at about the same height. The present study included both aboveground and underground releases, as well as outdoor and indoor releases. Four outdoor releases, spaced at locations separated by large buildings. These were complemented by three indoor releases (IND1, IND2, and IND3) released from different floors of one building, which allowed for a vertical release profile which included underground (building basement) and two above ground releases (10<sup>th</sup> floor and 22<sup>nd</sup> floor).

The release day had two "on" periods separated by a suitable ventilation time and the day was selected to achieve optimal and consistent meteorological conditions (clear days with NW winds). In general, each release period was for 30 min, followed by a 30 min period of no release. The PMCP release spanned longer periods with a lower release rate during the intended "off periods" (hence, Table 1 shows a periods of release that span the entire period from 06:00 -- 11:30). The scripted movement activities of the personnel were repeated to examine the changes in exposure over both space and time. This was selected for preliminary characterization of the variability that can be expected under specific exposure scenarios. There were variations in the release rates (within a factor of 2) to ensure security against straight-forward reconstruction of release patterns; while these data are not cleared for publication for homeland security reasons, they are available to the emergency planning agencies.

## Source Scale Personal Exposure Monitoring

The source scale scripted personal monitoring tasks were completed by four different individuals in locations near one of the four outdoor release locations (S1 through S4). Each personal monitor was capable of simultaneously collecting all six PFTs. Each 1 min integrated exposure task consisted of one individual walking back and forth along the side walk up to a distance of 10 ft (3 m) from the source (the arrows around the points S1 through S4 are not to scale). The four individuals collected 1 min samples along these paths every 15 min (four samples per hour).

## Community Scale Personal Exposure Monitoring

Each of the four community scale personal monitoring routes (10 min samples) was designed to cover an approximately rectangular region in Midtown Manhattan covering the Rockefeller Center area. Each route was coupled loosely to one or more PFT source locations (See Figure 1). The goal was to include directions of motion that cover two to three specific walking activities that would lead to 10 min integrated exposure.

For the first path (CE1), the starting point was at the intersection of 51<sup>st</sup> Street and Broadway, moving south along Broadway, and stopping at the intersection of 43<sup>rd</sup> Street. The second segment of CE1 involved movement away from the source location, on 43<sup>rd</sup> Street and 8<sup>th</sup> Avenue. The third segment involved movement towards the source locations, along 8<sup>th</sup> Avenue and 52<sup>nd</sup> Street. For the second path (CE2), the starting point was the intersection of 51<sup>st</sup> Street and 6<sup>th</sup> Avenue, moving towards the S3 source along 6<sup>th</sup> Avenue. The second segment involved movement away from the source locations along 51<sup>st</sup> Street. For the third segment involved movement away from the source along 57<sup>th</sup> Street and 8<sup>th</sup> Avenue, while the third segment involved movement towards the source locations along 51<sup>st</sup> Street. For the third path (CE3), the starting point was at the intersection of 47<sup>th</sup> Street and 6<sup>th</sup> Avenue, moving away from S2 along 7<sup>th</sup> Avenue towards S3. The second segment was along 55<sup>th</sup> Street and then along 5<sup>th</sup> Avenue going "around" S3, ending up at Rockefeller Plaza. The third segment involved movement along

5<sup>th</sup> Avenue and then along 48<sup>th</sup> Street towards S2. For the fourth path (CE4), the starting point was at the intersection of 47<sup>th</sup> Street and 5<sup>th</sup> Avenue, moving along 5<sup>th</sup> avenue away from S4. The second segment involved movement along 43<sup>rd</sup> Street and then along 7<sup>th</sup> Avenue towards S1. The third segment involved movement towards S4, crossing S1 along the way. Together, the minor overlaps among different routes coupled with the different walking directions capture the multitude of exposure-related activities that are expected to occur during a week day in Midtown Manhattan.

## Additional Personal Exposure Monitoring to Capture Tourist Activity

To capture exposures to groups of people spending significant time away from a release location (e.g. tourists or office workers spending time near Rockefeller Plaza, unaware of an emergency event), additional routes were used. These involved clockwise loops in the two walk ways (skating rink and walking area) outside of Rockefeller Plaza. The paths are shown in CE5 (Figure 1), with the left loop representing the skating rink area, and the right loop representing the walking area outside the nearby cafeteria. Both the loops were walked by one volunteer, two times within each sampling period. For example, during the 09:00 -- 09:30 period, the volunteer walked along left loop of CE5 from 09:00 to 09:02, replaced the canister, and then walked along the right loop of CE5 from 09:05 to 09:06. This pattern was repeated again at 09:15, resulting in two samples for each of the CE5 loops within a sampling period.

#### **PFT Sampling Technology**

PFTs have been used worldwide as tracers and in many other applications for decades by both government and private organizations. The compounds are fully fluorinated (saturated with

fluorine), contain only carbon and fluorine, and have only saturated bonds. For these reasons, these compounds are extremely stable, chemically and physically. In the pure state, PFTs are clear, slightly viscous liquids, boiling between 450 °C and 1300 °C, with a density about 1.75 times that of water. Being extremely stable chemically indicates that relatively small amounts of PFTs can be inhaled and ingested without resulting in adverse effects. The BNL Tracer Technology Center PFTs are in the generic class of perfluoroalkylcycloalkanes, have regulatory acceptance, and are used for leak detection, atmospheric tracing, and building ventilation (NOAA, 2011).

The main advantages of PFTs are that they have the ability to be measured at very low concentrations; have negligible background concentrations in relation to even very small releases of chemicals; are non-toxic, non-reactive, and non-flammable; and are commercially available (Dietz, 1987; Simmonds et al., 2002; Watson et al., 2006). PFTs are the most sensitive of all non-radioactive tracer technologies and samples can routinely be detected at concentrations in the range of 10 ppqv of air; six to eight different PFTs can be released from the same location with different sequences, or from different locations; and individual PFTs can be detected in the same gas sample. The release equipment used in the present study consisted of one gas cylinder for each release similar in size to a 1A cylinder. The release of the PFT by BNL was conducted in coordination with the New York City Office of Emergency Management (OEM).

PFT personal samplers from Brookhaven National Laboratory (BNL) provided PFT concentration levels in the ppqv range (Watson et al., 2007). This allowed for the release of PFT at small enough levels to avoid any environmental health concerns in the immediate vicinity of

the release as well as in the larger airshed. The high sensitivity of the samplers also allowed for measurements at high temporal resolution of 1 and 10 minutes in duration, since small amounts of air sampled was sufficient to characterize the analyte concentrations during each portion of an exposure script. The study focused on measurement and characterization of integrated personal exposure to the PFTs in and around the Rockefeller Center area, as shown in Figure 1. Since PFT behavior is similar to that of an ideal gas, their measured concentrations provide a baseline estimate for the atmospheric dispersion of other chemical agents.

The specific PFTs released were: PMCP (perfluoromethylcyclopentane), oc-PDCH (perfluoro-1,2-dimethylcyclohexane), PMCH (perfluoromethylcyclohexane), PECH (perfluoroethylcyclohexane), i-PPCH (perfluoro-iso-propylcyclohexane), and PTCH (perfluoro-1,3,5-trimethylcyclohexane). Additional details are shown in Table 1.

The PFTs were analyzed using a gas chromatograph with an electron capture detector (ECD). Calibration was achieved using standards prepared by the BNL Tracer Technology Group. A total of 146 calibration standards were run for each PFT during the experiment (Watson et al., 2006). The PFT detection limits for all the PFTs were 1 ppqv per 1.5 liters of volume collected, and the results reflect corrections for detected background and detection limit. Details on the measurement methods are presented in Watson et al. (2006).

The PFT samples were collected using BNL personal air samplers (PAS) that were carried on the upper body (i.e., in the shirt pocket) by the field personnel walking in the area surrounding the vicinity of Rockefeller Center (Figure 1). The PAS measures 2.5 cm wide  $\times$  2.0 cm thick  $\times$  10

cm long and holds a capillary adsorbent tracer sampler (CATS) tube for passively sampling the tracer. The CATS tube is a 0.6 cm diameter  $\times$  5.1 cm long glass tube filled with granulated activated carbon to trap the PFTs. With a limit of quantification in the ppqv range (Watson et al., 2006), the PFT personal samples could be collected for 1 and 10 minutes in duration, and with time-integrated concentrations linked with specific activity patterns and the distance from the release point.

The PFT releases were more diverse and extensive than those used in the March 2005 study in the Madison Square Garden area (Lioy et al., 2007). The present study included releases from inside of a building below and above-ground, as well as from outdoor, above-ground locations, as shown in Figure 2 and Table 1. In addition, the landscape (i.e. building profile and density, transportation system and micrometeorology) differs considerably from previous studies. For example, the Rockefeller Center study area has more street canyons than the area around Madison Square Garden, has no arena cylindrical edifice, and has a very different underground construction layout. Additionally, the release locations themselves were spaced much wider than in the Madison Square Garden study.

#### Analytical Methods

Details of the analytical methods are presented elsewhere (Watson et al., 2006). Briefly, the PFTs were analyzed using a gas chromatograph with an electron capture detector (ECD). The samples were desorbed from the collection tube by heating it to 400°C into a 5% hydrogen, and nitrogen carrier gas stream. The air stream was separated on a 1/8 inch o.d., 18 inch precut column packed with a 0.1% SPF100 mesh Carbopack-C (Superloo Inc. Bellefonte, PA, USA).

The flow was directed to the atmosphere or through a heated palladium (Pd) reducing catalyst on to a Florisil (Superloo Inc. Bellefonte, PA, USA) packed trap. The air stream was switched between the vent to the atmosphere and the trap windows. The perfluorocarbons were separated and the eluting interfering compounds were directed out of the vent. The Pd catalyst combined with the 5% hydrogen also reduced co-eluting gases to a form that was detected by the ECD (Watson et al., 2006). After the PFTs were trapped, the column was back-flushed to remove any remaining high molecular weight compounds. The sample was then desorbed through a second Pd catalyst trap and dryer. This completed the cleanup, and the sample was passed to the main column. The PFTs were then separated and passed to the ECD detector for quantification. Calibration was achieved using standards prepared by the BNL Tracer Technology Group. A total of 146 calibration standards were run for each PFT during the experiment (Watson et al., 2006).

## RESULTS

The dispersion of the PFTs following their release was affected by multiple factors, including the buildings near the points of release, prevailing winds, and street configuration.

## Source Scale Personal Exposures

Time series plots corresponding to the source scale personal exposure measurements are shown in Figure 3. Data from the S3 path are not presented here due to sample contamination problems. As expected, for the paths S1, S2, and S4, the highest concentrations measured corresponded to the specific PFTs released closest to the measurement location. Likewise, concentrations of the PFTs released at other locations were about 10-100 times lower than those for the PFTs released nearby. However, the drops in concentrations were not uniform throughout, thus indicating that the local meteorological and building conditions had a significant effect on the distribution of each tracer, and consequently the exposure received by each individual. The prevailing winds during this time, based on data from the meteorological station in Central Park, NY, showed low wind speeds for most of the sampling time period, and low speed during the remaining time period, with variable wind direction. Additionally, since the local wind patterns fluctuate substantially due to street canyon effects, correlations of local levels with prevailing winds are not expected to be strong.

## Community Scale Personal Exposures

Figure 4 shows maps of integrated 10 min exposure measurements for the different community scale exposure paths for contaminants released outdoors (PCMP, iPPCH, and PTCH) during three distinct time periods: On (9:00 - 9:30 am), Off (10:00 - 10:30 am), except for a leak of

PMCP), and again On (11:00 – 11:30 am). The "On" and "Off" periods were generally consistent, except for the case of PMCP, which had a slow leak during the entire period of 9:30 to 11:00, in addition to the release during the planned released period In addition, there was a leak of PMCP during the time period of 07:30 to 09:00, thus influencing the concentration levels during the first sampling period. It must be noted that the actual release amounts were slightly different across different tracers (but within a factor of 1.5 across the numbers). The actual release rates have not been reported here because of security implications, but the emergency planning agencies have access to the exact rates.

Within each panel of the figure, locations corresponding to the endpoint of each sampling segment are shown for paths CE1 through CE4 in the format (x,y), with x representing the path (1 through 4) and y indicating the 10 minute interval corresponding to the segment within the path. For example, a value of (1,2) represents the end point for Segment 2 (end of the second 20 minute portion) of Path CE1. Additionally, on each concentration line plot, the cross-bars represent logical breaks for an easy comparison of multiple concentration plots. The top panel shows the exposures during the initial "On" period, the middle panel shows the corresponding exposures during the "Off" period, while the bottom panel shows the exposures for the subsequent "On" period. No vertical bars are shown for cases where the concentration levels were below 0.1 ppqv.

The middle panel shows an anomaly because of continued release of PMCP during the "Off" period (as shown in Table 1), which impacted the resulting exposures. The other two tracers dropped off significantly during the "Off period", as expected. The top and bottom panels show

elevated concentrations at locations north-east of the release points, and show very low levels to west of release locations, indicating that the overall regional flow has the major effect.

Figure 5 shows the corresponding personal exposure concentration plots for tracers released indoors (PDCB, PMCH, and ocPDCH). The notation used in this plot for path and segment information is the same as in Figure 4. Specifically, integrated 10 min exposure measurements are shown for the different community scale exposure paths for contaminants released indoors during the three release-related time periods described above. The levels of traces during the "Off" time (10:00 to 10:30 am; middle panel) were expected to be significantly lower in general, but showed no significant reduction due to the "capacitor effect", i.e. the building where these releases have occurred functions as a storage for some amount of the contaminants released, and subsequently functions as a source when the releases are stopped.

Figure 6 shows a summary of the personal exposure measurements for Paths CE1 and CE4 in a tabular manner. The columns correspond to different time periods of measurement, and rows correspond to different chemicals. The size and color of the circles inside the table cells represent the tracer concentration.

Maps of integrated exposure measurements for contaminants released outdoors (PCMP, iPPCH, and PTCH) are shown in Figure 7 for the additional community scale exposure paths in the Rockefeller Plaza (reflecting exposures to tourists and office workers staying outside). As with the case shown in Figure 5, there is an anomaly because of continued release of PMCP during the "Off" period (as shown in Table 1), which impacted the resulting exposures. The other two

tracers dropped off significantly during the "Off period", as expected. Furthermore, only concentrations of PMCH (released at the 10<sup>th</sup> floor) show significant concentrations, with the only exception being ocPDCH (released at the 22<sup>nd</sup> floor) in the second "On" period. This indicates that releases occurring at the basement level have a limited impact for above ground populations, though they may impact exposures for people in underground structures such as subway stations with entrances close to the underground release points. On the other hand, releases that occur at much higher elevations follow the pattern of those released at lower locations with a "time delay" effect, reflecting the additional time-of-travel distance of the plume. The negligible difference in the two areas within Rockefeller Plaza, is as expected.

## DISCUSSION

This study examined the local horizontal and vertical dispersion of perfluorocarbon (PFT) tracers released at strategic points outdoors and indoors in the Rockefeller Center area. As was found in the Madison Square Garden study. PFTs were detected in locations and at concentrations not anticipated from analysis conducted prior to the study. The methods and data developed in the study provide New York City officials with data useful in studying the dispersion of contaminants in a complex urban terrain under variable wind conditions. The exposure data along with ambient concentration measurement data can also provide a reference concentration data set for evaluating complex dispersion models. Most dispersion modeling applies fixed data locations; however, prospective exposure data, like those gathered in this study, capture the movement of people and, in turn, better represent real-world exposures (either typical day-to-day movement of general public or movement of emergency responders). Even though these data present an average of concentration profiles over space and time, they also provide a evaluation data sets that are complementary to the commonly used fixed point measurements. The study also provides state and local officials in New York City with tracer gas exposure data collected at specific points outdoors; these data points can be utilized to scale up and evaluate their current emergency exit and re-entry strategies that help in reducing potential human exposure in the event that a chemical agent is released and distributed through the areas of study as well as other locations.

The exposure encountered by each individual depends on many local variables, such as meteorology, traffic, and building geometries along the route. In contrast to typical urban air pollutant exposure measurement studies, this study focused on specific paths associated with the movement of volunteers and specific activity patterns (e.g. people evacuating, exiting or approaching the point of release, and emergency workers remaining near the release). Each path was tailored to types of activities that could provide both source and neighborhood scale information about contact with each PFT. Large variabilities and sharp changes in meteorological factors within urban settings are possible (e.g. due to street canyons, buildings, and traffic), and the release of a chemical may result in different exposures across different paths. The present study area consisted almost entirely of street canyons, with confined open spaces, and lacked anomalous structures reported in the earlier UDP study (Lioy et al., 2007). This study also included finer resolution of personal exposure measurements away from the release location, with predefined, looping paths near Rockefeller Center. These data allow for a better understanding of the effect of slight differences in possible evacuations on personal exposures, especially when it involves tourists or visitors not familiar with the city landscape and hence may decide to stay longer at their current location.

Surface winds, the complexity of the urban terrain, and the activities that typically occur in an urban center have effects on personal exposures. Baffling effects of buildings, sorption and interferences, such as materials in flooring, walls and ceilings, and heating, ventilation and other air handling equipment can influence releases and may ultimately affect exposures. Such factors were not sufficiently characterized in this study and need to be addressed in future studies.

It must be noted that the primary utility of data collected on urban dispersion is in establishin specific correlations between prevailing winds, temperature, and the local geography. The variable patterns of prevailing winds imposed a substantial limitation on the amount of straightforward analysis that can be performed to establish correlations between the prevailing winds and local exposure levels. The main utility of these data would be in conjunction with other data sets on urban scale contaminant dispersion; pooling of multiple data sets will allow for a better understanding of dispersion of contaminants in a complex urban terrain under variable wind conditions. The study, however, presents data that can be used to quantify the degree of variability in the expected levels, and can be used in conjunction with computational fluid dynamics models of urban dispersion in order to evaluate the model performance under variable wind profiles.

Arguably, the most important finding of this study was that associated with a release from within a building. An indoor release led to a protraction of measurable concentrations of the tracers compared to those associated with an outdoor release. This "capacitor effect" of a building has strong implications on the planning of emergency response and evacuations, both within and from buildings. It also can prolong the time before an "all clear" can be given.

Another important finding was that distance between source and receptor is certainly not the only factor in potential exposure. The complexity of the New York City landscape led to varying measurements of each of the tracers at various locations along the scripted routes. One important emerging tool available to first responders to help explain these complexities is the application of computational fluid dynamics (CFD) techniques, which are based on the first principles of physics, starting with Navier-Stokes equations. In the recent past, CFD models and complex dispersion models have been applied for studying contaminant transport in urban areas (Flaherty et al., 2007a; Hanna et al., 2006; Hanna et al., 2009; Huber et al., 2004; Long et al., 2009; Zheng

et al., 2010). However, several limitations exist with respect to the amount and representativeness of available evaluation data. Intensive field studies such as those reported here are essential to provide realistic field data on exposures to contaminants released in complex urban settings.

Since each route was personalized to the types of activities that could provide both source and neighborhood scale information about contact with each PFT, these results can be used in evaluating models that simulate contacts with actual chemical, physical or biological agents, so that human exposure to environmental agents, including highly toxic agents within urban street canyons, can be predicted. Of course, atmospheric chemistry is complicated by reactions and other chemodynamic factors, so a relatively inert gas will not reflect these conditions, i.e. the concentration estimates are based on a conservative, low-reactivity scenario, which will need to be adjusted for reactive gases and for aerosols (Vallero, 2008).

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## References

- Allwine, K., Shinn, J., Streit, G., Clawson, K. and Brown, M. Overview of URBAN 2000. *B Am Meteorol Soc*, 2002; 83(4): 521-536.
- Allwine, K.J. and Flaherty, J.E. Urban dispersion program overview and MID05 field study summary, Pacific Northwest National Laboratory (PNNL), Richland, WA (US), 2007.
- Allwine, K.J., Leach, M., Stockham, L., Shinn, J., Hosker, R., Bowers, J. and Pace, J. Overview of joint urban 2003—An atmospheric dispersion study in Oklahoma City, 2004.
- Dietz, R.N. Perfluorocarbon tracer technology. In: S. Sandroni (Editor), *Regional and Long-Range Transport of Air Pollution*. Elsevier, Amsterdam, 1987; 215-247.
- Flaherty, J.E., Lamb, B., Allwine, K.J. and Allwine, E. Vertical tracer concentration profiles measured during the Joint Urban 2003 dispersion study. *J Appl Meteorol Clim*, 2007a; 46(12): 2019-2037.
- Flaherty, J.E., Stock, D. and Lamb, B. Computational fluid dynamic simulations of plume dispersion in urban Oklahoma City. *J Appl Meteorol Clim*, 2007b; 46(12): 2110-2126.
- Hanna, S. and Baja, E. A simple urban dispersion model tested with tracer data from Oklahoma City and Manhattan. *Atmos Environ*, 2009; 43(4): 778-786.
- Hanna, S., White, J., Trolier, J., Vernot, R., Brown, M., Gowardhan, A., Kaplan, H., Alexander, Y., Moussafir, J., Wang, Y.S., Williamson, C., Hannan, J. and Hendrick, E. Comparisons of JU2003 observations with four diagnostic urban wind flow and Lagrangian particle dispersion models. *Atmos Environ*, 2011; 45(24): 4073-4081.
- Hanna, S., White, J. and Zhou, Y. Observed winds, turbulence, and dispersion in built-up downtown areas of Oklahoma City and Manhattan. *Bound-Lay Meteorol*, 2007; 125(3): 441-468.
- Hanna, S.R., Brown, M.J., Camell, F.E., Chan, S.T., Coirier, W.J., Hansen, O.R., Huber, A.H., Kim, S. and Reynolds, R.M. Detailed simulations of atmospheric flow and dispersion in downtown Manhattan: An application of five computational fluid dynamics models. *B Am Meteorol Soc*, 2006; 87(12): 1713-1726.
- Hanna, S.R., Hansen, O.R., Ichard, M. and Strimaitis, D. CFD model simulation of dispersion from chlorine railcar releases in industrial and urban areas. *Atmos Environ*, 2009; 43(2): 262-270.
- Hendricks, E.A., Diehl, S.R., Burrows, D.A. and Keith, R. Evaluation of a fast-running urban dispersion modeling system using Joint Urban 2003 field data. *J Appl Meteorol Clim*, 2007; 46(12): 2165-2179.

- Huber, A., Georgopoulos, P., Gilliam, R., Stenchikov, G., Wang, S.-W., Kelly, B. and Feingersh, H. Modeling Air Pollution from the Collapse of the World Trade Center and Assessing the Potential Impacts on Human Exposures. *Environmental Manager*, 2004; February 2004: 35-40.
- Lioy, P.J., Vallero, D., Foley, G., Georgopoulos, P., Heiser, J., Watson, T., Reynolds, M., Daloia, J., Tong, S. and Isukapalli, S. A personal exposure study employing scripted activities and paths in conjunction with atmospheric releases of perfluorocarbon tracers in Manhattan, New York. *Journal of Exposure Science and Environmental Epidemiology*, 2007; 17(5): 409-425.
- Long, K.J., Zajaczkowski, F.J., Haupt, S.E. and Peltier, L.J. Modeling a Hypothetical Chlorine Release on a College Campus. *Journal of Computers*, 2009; 4(9): 881-890.
- Martin, D., Nickless, G., Price, C.S., Britter, R.E., Neophytou, M.K., Cheng, H., Robins, A.G., Dobre, A., Belcher, S.E., Barlow, J.F., Tomlin, A.S., Smalley, R.J., Tate, J.E., Colvile, R.N., Arnold, S.J. and Shallcross, D.E. Urban tracer dispersion experiment in London (DAPPLE) 2003: field study and comparison with empirical prediction. *Atmos Sci Lett*, 2010a; 11(4): 241-248.
- Martin, D., Price, C.S., White, I.R., Nickless, G., Petersson, K.F., Britter, R.E., Robins, A.G., Belcher, S.E., Barlow, J.F., Neophytou, M., Arnold, S.J., Tomlin, A.S., Smalley, R.J. and Shallcross, D.E. Urban tracer dispersion experiments during the second DAPPLE field campaign in London 2004. *Atmos Environ*, 2010b; 44(25): 3043-3052.
- NOAA. Air Resources Laboratory. Atmospheric tracer safety. National Oceanic and Atmospheric Administration (NOAA), 2011. <u>http://www.noaa.inel.gov/capabilities/tracers/tracersafety.htm</u>
- Richmond-Bryant, J., Isukapalli, S.S. and Vallero, D.A. Air pollutant retention within a complex of urban street canyons. *Atmos Environ*, 2011; 45(40): 7612-7618.
- Simmonds, P.G., Greally, B.R., Olivier, S., Nickless, G., Cooke, K.M. and Dietz, R.N. The background atmospheric concentrations of cyclic perfluorocarbon tracers determined by negative ion-chemical ionization mass spectrometry. *Atmos Environ*, 2002; 36(13): 2147-2156.
- Tewari, M., Kusaka, H., Chen, F., Coirier, W.J., Kim, S., Wyszogrodzki, A.A. and Warner, T.T. Impact of coupling a microscale computational fluid dynamics model with a mesoscale model on urban scale contaminant transport and dispersion. *Atmos Res*, 2010; 96(4): 656-664.
- Urban, J.T., Warner, S., Platt, N. and Heagy, J.F. Assessment of HPAC urban modelling capabilities using data from the Joint Urban 2003 field experiment. *Int J Environ Pollut*, 2011; 44(1-4): 24-31.

- Vallero, D. Air Pollution Chemodynamics. In: D. Vallero (Editor), *Fundamentals of Air Pollution: Fourth Edition*. Elsevier Academic Press, Amsterdam, 2008.
- Watson, T.B., Heiser, J., Kalb, P., Dietz, R.N., Wilke, R., Weiser, R. and Vignato, G. The New York City Urban Dispersion Program March 2005 Field Study: Tracer Methods and Results (Report). BNL-75552-2006, Brookhaven National Laboratory, 2006.
- Watson, T.B., Wilke, R., Dietz, R.N., Heiser, J. and Kalb, P. The Atmospheric Background of Perfluorocarbon Compounds Used as Tracers. *Environmental Science & Technology*, 2007; 41(20): 6909-6913.
- Zheng, M., Guo, Y., Ai, X., Qin, T., Wang, Q. and Xu, J. Coupling GIS with CFD modeling to simulate urban pollutant dispersion. IEEE, 2010; 1785-1788.