

THE NEW YORK CITY URBAN DISPERSION PROGRAM
MARCH 2005 FIELD STUDY:
TRACER METHODS AND RESULTS

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Cover Photo: Empire State building seen from the top of the PENN 1 building. Richard Wilke

Table of Contents

Table of Contents	ii
Abstract	1
Introduction	3
UDP Program	3
Field Programs	3
Experimental	3
Perfluorocarbon Tracers	5
Tracer Release	6
Application of a Simple Gaussian Plume Model to Estimate Expected Downwind Tracer Concentrations	8
Sampling	9
BATS	10
SAS	11
PAS	12
Data Recovery Rate	12
Continuous Dual Trap Analyzer	14
CDTA Performance Statistics	17
Analytical	18
Gas Chromatography	18
Data Processing	18
Calibration Standards	19
Calibration Method	19
Background Levels and Method Level of Detection and Quantitation	20
Simultaneous Tracer Release Results	20
Duplicate samples	21
Results from Collocated BATS and SAS Units	22
Confidence Limits In the Measurements	26
Flow Calibrations	26
Dataset Description	27
References	28
Appendix 1. Data Format	29
Appendix 2. Sampler Pump Rates	30
Appendix 3. CDTA	31
Appendix 4: Conversion of mixing ratio to mass per unit volume	38
Appendix 5. GC Control Charts	39

Abstract

The Urban Dispersion Program March 2005 Field Study tracer releases, sampling, and analytical methods are described in detail. There were two days where tracer releases and sampling were conducted. A total of 16.0 g of six tracers were released during the first test day or Intensive Observation Period (IOP) 1 and 15.7 g during IOP 2. Three types of sampling instruments were used in this study. Sequential air samplers, or SAS, collected six-minute samples, while Brookhaven atmospheric tracer samplers (BATS) and personal air samplers (PAS) collected thirty-minute samples. There were a total of 1300 samples resulting from the two IOPs. Confidence limits in the sampling and analysis method were 20% as determined from 100 duplicate samples. The sample recovery rate was 84%. The integrally averaged 6-minute samples were compared to the 30-minute samples. The agreement was found to be good in most cases. The validity of using a background tracer to calculate sample volumes was examined and also found to have a confidence level of 20%. Methods for improving sampling and analysis are discussed. The data described in this report are available as Excel files. An additional Excel file of quality assured tracer data for use in model validation efforts is also available. The file consists of extensively quality assured BATS tracer data with background concentrations subtracted.

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- Julia Flaherty (PNNL) provided review and comments on the report.

Introduction

UDP Program

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. national laboratories [Pacific Northwest National Laboratory (PNNL), Brookhaven National Laboratory (BNL), Lawrence Berkeley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL), and Argonne National Laboratory (ANL)], federal agencies [National Oceanographic and Atmospheric Administration (NOAA) and the U.S. Environmental Protection Agency (EPA)], and numerous academic institutions (Harvard School of Public Health, Stony Brook University, Stevens Institute of Technology, and San Jose State University). 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 EPA. Additional information about the UDP can be found at: <http://urbandispersion.pnl.gov/index.stm>.

Field Programs

Three UDP field studies, conducted in late winter (2005), summer (2005), and planned for spring (2007) will address seasonal differences in transport regimes. The first of these studies was conducted in March 2005 in the area around Madison Square Garden (MSG) and has been designated as MSG05. It was limited to two Intensive Observation Periods (IOPs). Subsequent field studies will be larger in scope.

Experimental

MSG05 consisted of 2 intensive observation periods conducted on March 10 and March 14, 2005. The BNL tracer team released five perfluorocarbon tracers (PFTs) at the corners of the block occupied by MSG and one tracer on the north-east side of the Penn 1 building (Figure 1).

On both days there were two one-hour releases. The first release occurred from 9:00 to 10:00 and the second release from 11:30 to 12:30. Sampling began at 9:00 and included 10 half-hour sample periods encompassing both releases. Sampling ended at 14:00. Air samples were collected at 19 street level locations on a 360° arc at distances approximately 200 and 400 meters from the center of MSG (Figure 1), on the tops of roofs at various levels of 4 buildings, and with a near-real-time mobile analyzer sampling at various locations around and downwind of the release area. The verified coordinates of the tracer release and sampling locations are given in Allwine et al. (2006).

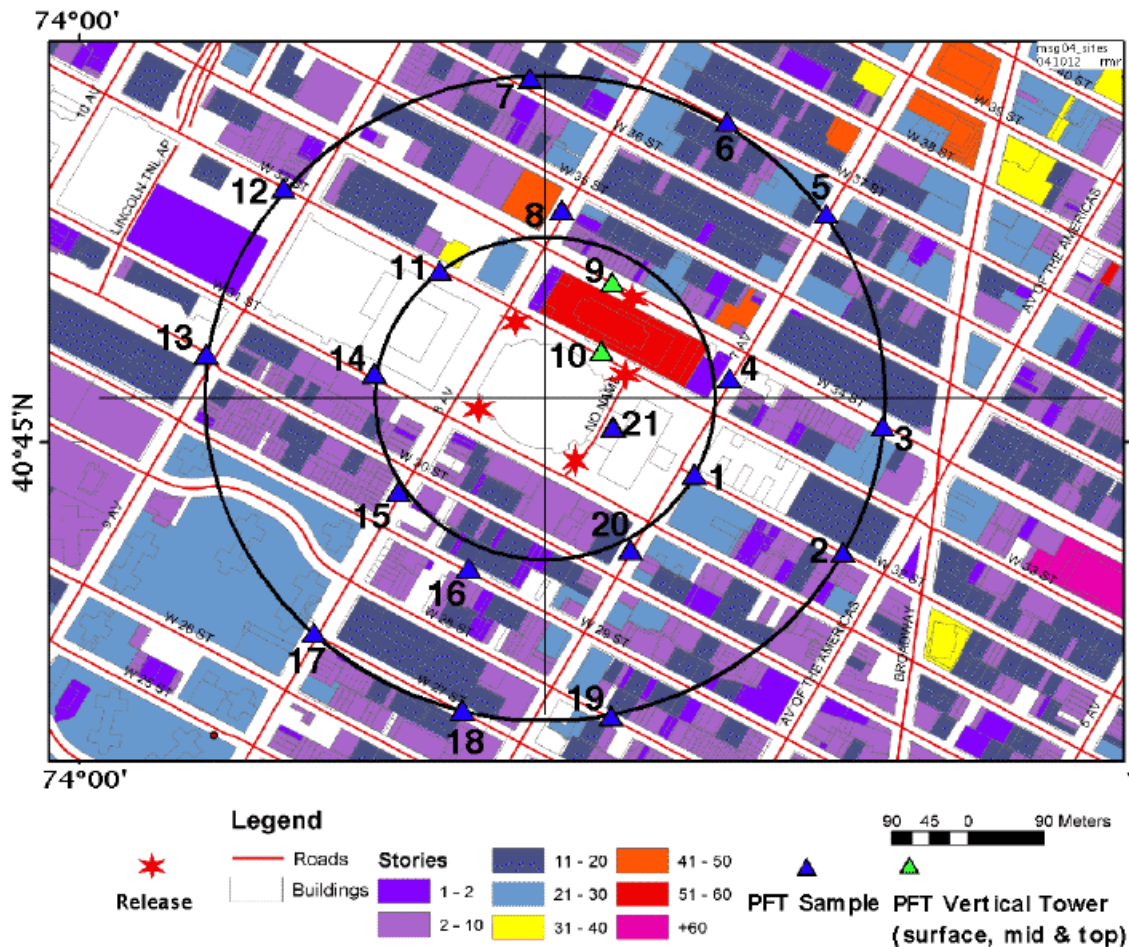


Figure 1. Release and Sampling Locations.

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 MSG05 were carried out in accordance with the practices and procedures outlined in this plan.

Table 1. Release Location Designations.

ID	Location
A	MSG - 8 th and 33 rd - north corner of MSG
B	MSG - 33 rd midway between 7 th and 8 th -E corner of MSG
C	MSG – 31 st midway between 7 th and 8 th - S corner of MSG
D	MSG – 8 th and 31 st - W corner of MSG
E	South side of 34 th between 7 th and 8 th - middle of Penn One

Perfluorocarbon Tracers

Perfluorocarbon tracers are colorless, odorless compounds that consist of carbon and fluorine atoms joined by covalent single bonds. The tracers used in MSG05 are molecules consisting of five (pentane) or six (hexane) member rings with 1 (methyl), 2 (di-methyl or ethyl) or three (propyl) additional carbon atom structures. These compounds are chemically inert, non-flammable, and have no biological effects. The safety of perfluorocarbon tracers and relevant Material Safety Data Sheets are presented in Allwine (2005). Perfluorocarbon background levels are in the parts per quadrillion (10^{15}) and have remained relatively 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 31.7 grams.

The six perfluorocarbon tracers released in MSG05 are listed in Table 2 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 10^{15} molecules of air. Formulae for conversion from mixing ratio to mass per unit volume at STP are given in Appendix 4.

Table 2. Perfluorocarbon Tracers Used in MSG05 and some of their Background Concentrations in 1986 and 2001.

Acronym	Chemical Name	Formula	Background 1986 ¹ (ppqv)	Background 2001 ² (ppqv)	Molecular weight (g mol ⁻¹)
PMCP	Perfluoromethylcyclopentane	C ₆ F ₁₂	3.22 ± 0.03	6.29 ± 0.22	300
PMCH	Perfluoromethylcyclohexane	C ₇ F ₁₄	4.6 ± 0.05	5.49 ± 0.23	350
oc-PDCH	Perfluoro-1,2-dimethylcyclohexane	C ₈ F ₁₆	0.30 ± 0.1	0.73 ± 0.09	400
PECH	Perfluoroethylcyclohexane	C ₈ F ₁₆	NA*	NA	400
i-PPCH	Perfluoro-isopropylcyclohexane	C ₉ F ₁₈	NA	NA	450
PTCH	Perfluorotrimethylcyclohexane	C ₉ F ₁₈	0.07	NA	450

¹ Dietz, 1987

² Simmonds et al., 2002

*Not Available

Tracer Release

The perfluorocarbon tracers were released from gas cylinders containing PFT mixed with N₂ at approximately 200 PSI. These mixtures were prepared by Scott Specialty Gasses (South Plainfield, NJ). Target concentration for preparation of the release gasses was determined using the integrated form of the Clausius-Clapeyron Equation:

$$p = p^* \exp\left\{\frac{-\Delta H_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right\}$$

Where:

T \equiv Temperature

T^* \equiv target temperature T

p \equiv vapor pressure at temperature T

p^* \equiv vapor pressure at temperature T^* reference temperature T^*

ΔH_{vap} \equiv enthalpy of vaporization

R \equiv molar gas constant

(Atkins, 1978, p. 187)

This equation was used to calculate the saturation vapor pressure of the tracer-Nitrogen mixtures. The concentration of the release mixtures was selected so the tracer would remain in the gas phase in the cylinders at -5°C. The final concentrations of the release mixtures were determined by gas chromatography using a Carbon Layer Open Tubular (CLOT) capillary column and a thermal conductivity detector. The concentrations of the release mixtures are given in Table 3 and 4.

The release rate of each PFT was controlled by a calibrated pressure regulator/ filter/ flow-restrictor combination (Figure 2). The PFT, location designation, start time, release rate, and PFT mass released during each test are also presented in Tables 3 and 4. Note that on March 14, the compounds released at positions A and D were reversed from their positions on March 10. Release rates were measured at the beginning and end of each release period using a digital flow meter (ADM 2000, J&W Scientific, Folsom, CA). The digital flow meter was calibrated with a DryCal[®] Primary Flow Meter (BIOS International Corp. Butler, NJ).



Figure 2. The Regulator/Flow Restrictor Combination Used to Control the Tracer Release and Close-Up of the Restrictor and Filter.

The first release began at 09:00. The second release began at 11:30. Both releases lasted one hour. Release gas concentration error limits are the 95% confidence interval, twice the standard deviation of multiple measurements. The release rate 95% level confidence limit is 0.01L based on the calibration of the flow meter.

Table 3. Tracer Release Data for MSG05, March 10, 2005

3/10/2005 9:00	Tracer Station	Start Time	Release Gas Conc. (ppmv)	Release Rate ¹ (L min ⁻¹)	Release Mass (g)
ocPDCH	A	9:00	321 ± 4	0.92	0.3
PMCP	B	9:05	6750 ± 100	0.93	5.0
PMCH	C1	9:00	1995 ± 20	0.93	1.7
iPPCH	C2	9:00	73.5 ± 2	0.93	0.1
PECH	D	9:02	650 ± 4	0.88	0.6
1PTCH	E	9:16	101 ± 2	1.01	0.1
					Total: 7.8
3/10/2005 11:30	Tracer Station	Start Time	Release Gas Conc. (ppmv)	Release Rate ¹ (L min ⁻¹)	Release Mass (g)
ocPDCH	A	11:30	321 ± 4	0.93	0.3
PMCP	B	11:30	6750 ± 100	0.97	5.3
PMCH	C1	11:30	1995 ± 20	0.95	1.8
iPPCH	C2	11:30	73.5 ± 2	0.95	0.1
PECH	D	11:30	650 ± 4	0.92	0.6
1PTCH	E	11:30	101 ± 2	1.01	0.1
					Total: 8.2

¹ 95% Confidence limit (2σ) is ± 0.01 L

Table 4. Tracer Release Data for MSG05, March 14, 2005

3/14/2005 9:00	Tracer Station	Start Time	Release Gas Conc. (ppmv)	Release Rate ¹ (L min ⁻¹)	Release Mass (g)
PECH	A	9:06	650 ± 4	0.91	0.6
PMCP	B	9:07	6750 ± 100	0.92	5.0
PMCH	C1	9:00	1995 ± 20	0.79	1.5
iPPCH	C2	9:00	73.5 ± 2	0.77	0.1
ocPDCH	D	9:06	321 ± 4	0.87	0.3
1PTCH	E	9:00	101 ± 2	0.95	0.1
					Total: 7.6

3/14/2005 11:30	Tracer Station	Start Time	Release Gas Conc. (ppmv)	Release Rate ¹ (L min ⁻¹)	Release Mass (g)
PECH	A	11:30	650 ± 4	0.96	0.7
PMCP	B	11:30	6750 ± 100	0.93	5.0
PMCH	C1	11:30	1995 ± 20	1.01	1.9
iPPCH	C2	11:30	73.5 ± 2	1.01	0.1
ocPDCH	D	11:30	321 ± 4	0.93	0.3
1PTCH	E	11:30	101 ± 2	0.99	0.1
					Total: 8.1

¹ 95% Confidence limit (2σ) is ± 0.01 L

Application of a Simple Gaussian Plume Model to Estimate Expected Downwind Tracer Concentrations

The tracer must be released at a rate that will result in atmospheric concentrations that will be sufficient to provide the desired dispersion information and that will not be so high that they overwhelm the analytical instrument. A simple Gaussian plume model (Smith, 1968) was used to estimate plume centerline concentration of all 6 PFTs at 5, 200, and 400 meters from MSG based on a one liter per minute release rate. The purpose of this calculation was to ensure that the release rate was sufficient to provide detectable concentrations of tracer at the margins of the plume. To be 2 times above background at a plume width of 4σ , the concentration at the maximum must be 20 times background. Near-surface concentration at a distance x downwind and y from the plume centerline is given by:

$$X_{(x,y,0)} = \frac{Q}{\pi\sigma(x)_y\sigma(x)_z u} \exp\left(\frac{-(y-y_0)^2}{2\sigma(x)_y^2}\right)$$

where:

X \equiv concentration of PFT
 Q \equiv PFT release rate
 π \equiv a constant, 3.141592
 x \equiv downwind distance
 y \equiv crosswind distance
 \bar{u} \equiv mean wind speed
 $\sigma(x)_y$ \equiv crosswind plume standard deviation
 $\sigma(x)_z$ \equiv vertical plume standard deviation

A wind speed of 5 ms⁻¹ was used for making the estimates and the very unstable classification was used to account for the mixing caused by the urban environment. The formulae for calculating crosswind and vertical plume standard deviation are given in Table 5. Results are given in Table 6 and show that for all tracers where data is available, the release rate of 1 liter per minute provides sufficient concentration at a distance of 400 m to detect the plume margins.

Table 5: Formulae for Open-Country σ_y or σ_z Under Various Atmospheric Conditions. (Smith, 1968)

Atmospheric turbulence classification	σ_y or σ_z
Very Unstable	$(0.40) x^{0.91}$
Unstable	$(0.36) x^{0.86}$
Neutral	$(0.32) x^{0.78}$
Stable	$(0.31) x^{0.71}$

Table 6: Results of Gaussian Plume Calculations and Comparison with 20x Background Levels of the PFTs. All Concentrations are Given in Units of ppqv.

PFT	conc @ 5m	conc @ 200m	conc @ 400 m	20 x bkgd
PMCP	2.4 E+06	2.9 E+03	8.2 E+02	12.6
PMCH	7.1 E+05	8.6 E+02	2.4 E+02	11
ocPDCH	1.1 E+05	1.4 E+02	3.9 E+01	1.5
PECH	2.3 E+05	2.8E+02	7.9 E+01	NA
iPPCH	2.6 E+04	3.2 E+01	9.0 E+00	NA
1PTCH	3.6 E+04	4.3 E+01	1.2 E+01	NA

Sampling

Three types of air samplers were used in the MSG05 field program. All sampling media were cleaned and analyzed to check for residual tracer or other contamination before the field program. The total number of samplers of each type and the total number of samples are given in Table 7.

BATS

The Brookhaven Atmospheric Tracer Sampler (BATS) was deployed at 19 ground locations and seven locations on the roofs of buildings. The BATS consists of a base unit containing a pump, timer, and control electronics, and a lid containing 22 or 23 1/8 inch outer diameter (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 (Figure 3). 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 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 3 meters above street level in baskets attached to light poles (Figure 4). Students from City University of New York (CUNY) affiliated schools were stationed at each sampler for security. Duplicate samples were taken at Locations 2 and 15. Seven BATS were deployed on the roofs of Penn 1 and 2, the Post Office, and the roof of the New Yorker Hotel. There were four sampler failures during the first IOP. The sampler at location V4 collected 8 samples before stopping. The samplers at location 5 and 20, and the duplicate at location 15 failed. During the second IOP, the samplers at location 16 and 20 failed and the sampler at location V5 has suspect data.

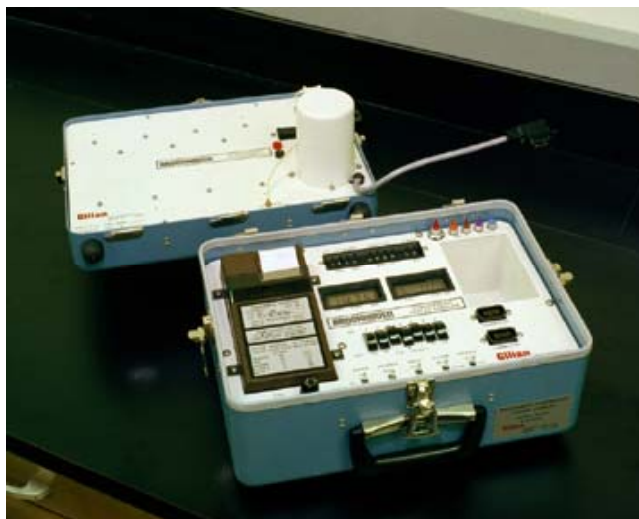


Figure 3. BATS and Lid.



Figure 4. BATS Installed on a Light Pole.

SAS

Nine Sequential Air Samplers (SAS) were deployed during both IOPs. The SAS units collect samples on 20, 1/4-inch o.d. glass tubes containing Amborsorb[®], known as Capillary Absorption Samplers (CATS). The flow rates for these samplers are a nominal 500 ml min^{-1} (Figure 5). These units collected one sample every six minutes. Sampling began at 9:00 and ended at 11:00. These samples were deployed on the roofs of Penn 1 and 2 and the Post office to provide vertical data with a greater time resolution. During the First IOP, two SAS units collected samples in the indoor levels below Madison Square Garden at the Amtrak and Long Island Railroad terminals in Penn Station as part of a related indoor exposure experiment. During IOP 1, one SAS collected samples inside the New Yorker Hotel conference room. These units were deployed on the roofs of Penn 1 and 2 and the roof of the New Yorker during the second IOP.



Figure 5. SAS Showing Tubes.

PAS

21 Personal Air Samplers (PAS) were also used to collect samples during both IOPs. These units consisted of a small battery-powered pump with a fitting for a capillary adsorption tube samplers (CATS) (Figure 6). The CUNY students changed the CATS tubes every half hour to duplicate the BATS samples collected at the same location. These samples were used for quality assurance and in the case of BATS sampler failure.



Figure 6. PAS and CATS Tube.

Data Recovery Rate

There were 1300 samples taken in MSG05. The data from 202 of these samples was not useable because of sampler failures, analytical problems, and computer errors. [Because of various mechanical or process difficulties a total of 202 samples were lost or are suspect.] The resulting data recovery rate is 84%. Sampler locations are shown in Figure 1 and described in Table 8 and Table 9. Verified coordinates for each of the sampler locations are available in Allwine et al (2006).

Table 7. Number of Each Type of Sampler and Number of Samples.

Sampler	Samplers	Samples Per Test	# of Tests	Total Samples
BATS	28	10	2	560
SAS	9	20	2	360
PAS	19	10	2	380
			Total	1300

Table 8. Identification Number and Location Description for All Ground Sampler Locations (see Figure 1.)

ID	Location
#1	7 th & 32 nd ; In front of the Hotel Pennsylvania – North side of street
#2	6 th & 32 nd ; In front of the Blarney Stone Bar - South side
#3	34 th & Broadway; South side - In front of Footlocker
#4	Midway between 34 th & 33 rd ; East side of 7 th - In front of McDonald's
#5	Between 36 th & 37 th ; In front of Bates Worldwide - West side of 7 th
#6	232 W. 37 th south side; In front of West Tandori Club - Midway 7 th & 8 th
#7	Midway 8 th & 9 th on south side 36 th ; In front of 320 Goldie Restaurant
#8	In front of McDonald's; Midway 34 th & 35 th - East side of 8 th
#10	One Penn Plaza - Middle of building ; North side of 33 rd
#11	In front of the Post Office; South side of 33 rd - Between 8 th & 9 th
#12	Across from St. Michael's Church; South side of 33 rd - Between 9 th & 10 th
#13	9 th and 30 th ; 370 W. 30 th - South side of 30 th close to 9 th
#14	South side of 31 st ; midway 8 th & 9 th - Across from bay 16 of the Post Office
#15	West side of 8 th #393; Midway between 30 th & 29 th - In front of 8 th Avenue Garden
#16	In front of the 29 th Street Marketplace ; North side of 29 th - Between 7 th & 8 th
#17	8 th & 27 th ; Middle of T-bone intersection - West side 8 th
#18	In front of Nagler Hall; South side of 27 th - Between 7 th & 8 th
#19	North side of 28 th ; In front of Center Floral Design - Between 6 th & 7 th
#20	In front of Seven Penn Plaza; Between 30 th & 31 st - West side of 7 th

Table 9: Locations of Vertical Samplers. Elevation is the approximate height above street level.

Sampler ID	Location	Elevation (m)
V1	12th story Penn One 33rd St side	48
V2	12th story Penn One 34th St side	48
V3	Top of Penn One 33rd St side	229
V4	Top of Penn One 34th St side	229
V5	Top of Penn Two	117
V6	Top of Post office 8th and 33rd	37
V7	Top of New Yorker Hotel	150

Continuous Dual Trap Analyzer

The Brookhaven Continuous Dual Trap Analyzer (CDTA) was used to take continuous samples during both IOPs of the MSG05 field study. The concept of the dual trap analyzer was described in D'Ottavio and Dietz (1986) and will be described briefly here. The current generation instrument incorporates several new features including the use of capillary columns instead of packed columns. The system consists of two absorbent traps that alternately collect air samples and desorb them into a dual column gas chromatograph with an electron capture detector (GC/ECD). Samples are collected for one minute at 1.5 L min^{-1} flow rate. While one trap is collecting a sample, the other trap is desorbed onto a Florisil[®] trap and then to a precut column. Each trap has its own precut column. Both pre-cut and main columns are capillary Carbon Layer Open Tubular columns. The system is tuned to detect the four early eluting PFTs: PDCB, PMCP, PMCH, and ocPDCH. PDCB was not released during MSG05. These compounds are separated on the precut column and directed onto the main Florisil trap as they elute. This trap is desorbed onto an injection Florisil trap that is maintained at the pressure of the main column. This trap buffers the detector from pressure changes associated with the heating caused by desorption and maintains a stable detector baseline. The carrier gas is 1% H_2 in N_2 . The flow rate in the main column is 5 cc min^{-1} . The chromatograph is controlled with Varian Star 6.20 software. This software controls the valve switching, firing of the traps, and records the chromatograms.

The four PFTs have elution times that range from approximately 1.3 to 5.5 minutes after injection. This causes a delay between the time when the sample is taken and when the results appear. Since samples are collected and desorbed at one-minute intervals it also means that some consecutive peaks on the chromatograms are from different injections. This is illustrated in two examples of chromatograms seen in Figures 7 and 8. Figure 7 is the result of a single injection and desorption of a calibration standard. It shows the elution timing of the four PFTs from a single collection and desorption cycle. Table 10 gives the retention times for the PFTs shown in Figure 7. Figure 8 shows a chromatogram taken during IOP 2. It is the result of multiple one minute collection and desorption cycles. It shows the data as it is seen by an operator in the field. Table 11 gives the retention times for the highlighted PFTs shown in Figure 8.

Because of the delay time and the fact that chromatograms from different injections overlap, it is necessary to record time and the location of the CDTA frequently on a strip chart. This record is then used to process the data and develop concentration versus time and concentration versus location views of the data.

The CDTA was used to accomplish three tasks during MSG05.

1. to establish a background baseline before the tracer release began;
2. to find the center of the plume at two downwind distances during the initial stages of each release; and
3. to measure the temporal variability of the tracer at a location near the plume centerline.

The van made a complete circuit of the test area using 6th Avenue, 37th Street, 9th Avenue, and 28th Street before the tracer release began to establish background concentrations. On both test

days the wind was from the western quadrant so the van made down wind traverses along 5th and 6th Avenues (Figure 9) to detect the plume.

The CDTA had a persistent ocPDCH peak during IOP 1 that was traced to a contaminated flow meter in the van. This problem did not occur in IOP 2. IOP 1 CDTA tracer data are limited to PMCP and PMCH. IOP 2 CDTA tracer data include ocPDCH. Time series of PFT concentrations, along with maps showing the locations of the CDTA measurements may be found in Appendix 3.

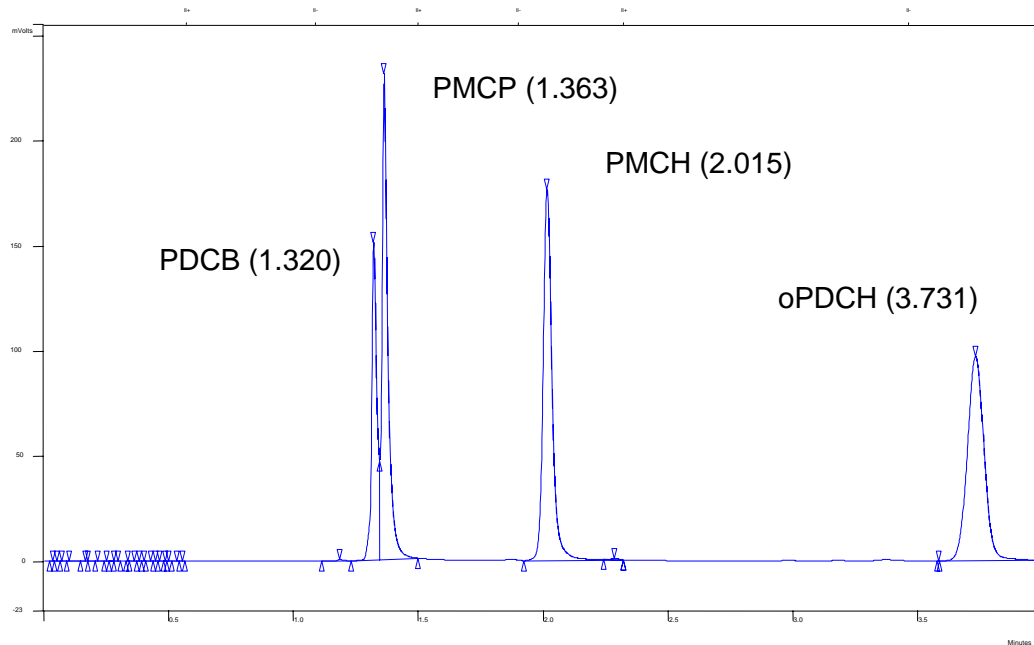


Figure 7. CDTA Chromatogram of Calibration Standard Injected and Desorbed from One of the Two Traps Showing PFT Peaks and Retention Times.

Table 10. Relative Retention Times of the 4 CDTA PFTs Shown in Figure 7.

Tracer	Retention Time (min)	Retention Time Relative to PDCB (min)
PDCB	1.302	0
PMCP	1.363	0.061
PMCH	2.015	0.713
ocPDCH	3.731	2.411

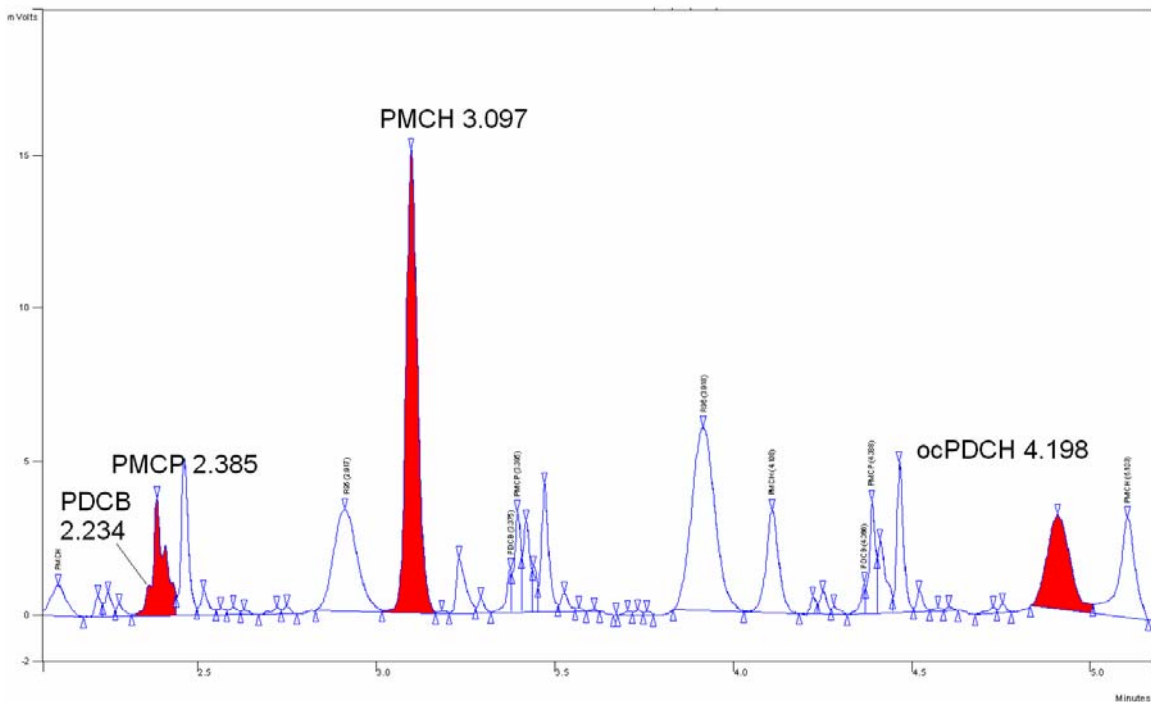


Figure 8. CDTA Chromatogram from IOP 2. Peaks resulting from one collection-desorption cycle are shown in red. PDCB is the small side lobe on the PMCP peak. The peaks that are not shaded are from both previous and subsequent injections.

Table 11. CDTA Relative Retention Times of the 4 PFTs Shown in Figure 8.

Tracer	Retention Time	Retention Time Relative to PDCB
PDCB	2.234	0
PMCP	2.385	0.061
PMCH	3.907	1.673
ocPDCH	4.918	2.684

Table 12. CDTA Performance Statistics. PFT level, peak areas, and concentrations during both IOPs.

	N	Mean (area)	Stdev (area)	Background Conc. (ppqv)	Noise (ppqv)	LOD (ppqv)	LOQ (ppqv)
3/10/2005							
PMCP	36	16620	5085	39	12	35	118
PMCH	118	32471	12828	66	26	78	261
3/14/2005							
PMCP	36	5131	1110	12	3	8	26
PMCH	118	4907	1356	10	3	8	28
ocPDCH	102	3018	1240	3	1	3	11

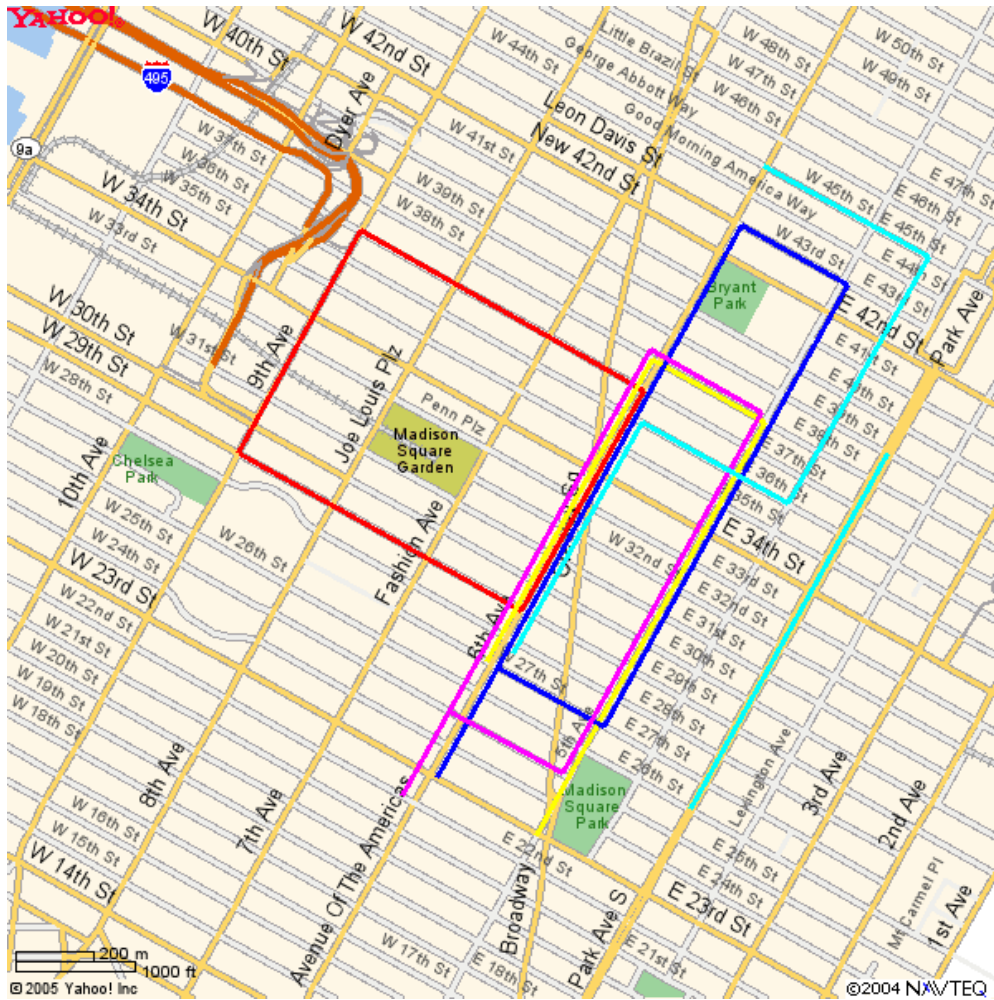


Figure 9. CDTA routes during the second IOP on March 14, 2005. They are representative of the CDTA routes during both IOPs. Shown are the initial traverse of the test area (red) and the passes downwind of the release sites.

CDTA Performance Statistics

The background mean and standard deviation are determined from uncorrected peak areas. The quantity of tracer is determined from the area and the calibration curve for the particular PFT. This is corrected by the sample volume to give fL/L or ppqv. Noise is determined from the standard deviation of the area counts multiplied by the calibration factor determined from the calibration curve for each PFT. The Limit of Detection (LOD) is three times noise. The Limit of Quantitation (LOQ) is 10 times noise. The confidence limits at the limit of quantitation are $\pm 30\%$ (Taylor, 1987).

The limits of detection and quantitation for both test days are given in Table 11. These values were determined from the ambient background seen by the CDTA before each release period. Levels are higher for March 10 because the contamination problem increased the background noise levels. Concentrations are determined using the calibration curve and a sample volume of 1.5L.

Analytical

Gas Chromatography

Analysis of the BATS Lids and CATS tubes was performed using gas chromatography with an electron capture detector. Details of this system are given in Draxler et al. (1991). A brief outline of the analysis method will be presented here.

The physical characteristics of PFTs make them ideal for analysis with an ECD. However, in ambient air samples, there are many other compounds, present in higher quantities than the PFTs, that can potentially interfere with their detection. Such compounds include SF₆, nitrogen oxides, and chlorofluorocarbons (CFCs) such as Freon[®]. The process of sample collection concentrates the PFT on the adsorbent. The quantity of PFT available for analysis is determined by the volume of air that is sampled. The ECD has the sensitivity to quantify background levels of PFT if the material in 1.5 liters of ambient air is collected.

The PFTs are separated from these compounds by several processes during sampling and analysis. The process of sampling helps eliminate SF₆ and similar substances with vapor pressures that are higher than those of the PFTs because these compounds are not efficiently collected on Ambersorb[®]. The analytical method has several steps that eliminate other interfering compounds that are collected with the PFTs.

The first step in the analytical process is desorption of the sample from the collection tube. Sample tubes are ballistically heated to 400°C driving the concentrated PFTs along with other compounds from the adsorbent into a 5% hydrogen in nitrogen carrier gas stream. The sample then undergoes chromatographic separation on a 1/8 in o.d., 18 in. long precut column packed with 0.1% SP-100 on 80-100 mesh Carbopack-C (Supelco, Inc., Bellefonte, PA). Flow from this column can be directed through a vent to the atmosphere or through a heated palladium (Pd) reducing catalyst onto a trap packed with Florisil[®] (Supelco, Inc., Bellefonte, PA). By switching the sample stream between the path to the vent and the path to the trap, windows when the perfluorocarbon compounds are eluting can be selected and directed onto the trap while interfering compounds are directed out the vent. The Pd catalyst combined with the 5% H₂ in the carrier gas reduces the compounds that co-elute with the PFTs to forms that are not detected by the ECD. After the PFTs have been collected on the trap, the precut column is back-flushed sweeping any higher molecular weight compounds still on the column out the vent and preparing it for the next desorption cycle. The sample on the trap is desorbed through a second Pd catalyst and dryer, completing the cleanup, and onto the 3 ft. main column. The main column is the same composition as the precut column. The PFTs are separated on the main column and delivered to the detector. The ECD signal is recorded using data acquisition software (PE Nelson, Cupertino, CA) that integrates peaks and records the raw and processed data. It takes approximately 15 minutes to analyze each sample.

Data Processing

Calibration Standards

Calibration of the GC was accomplished using standards prepared by the BNL Tracer Technology Group. These standards are compared to PFT permeation sources that are calibrated gravimetrically on balances and provide an absolute standard (Dietz, 1986; BNL, 2003). The standard designated ei8 was used for calibration during the analysis of samples from MSG05. The standards were prepared by loading the sample tubes in a BATS lid or CATS tubes with volumes of ei8 injected into a stream of pure N₂ flowing through the tube at 30 ml min⁻¹. The quantities of the standards were measured using volumetric syringes. Volumes and the corresponding tracer quantities are given in Table 13.

Calibration Method

A total of 146 calibration standards for each PFT were run during the course of analysis of the MSG05 samples. The instrument response was consistent for analysis of some initial PAS samples, all the BATS lids, and 6 days of the SAS samples. At that point the instrument response deteriorated. This can be seen in the control charts for all calibration standards at all concentration levels. Examples of the 10 and 50 μL standard volumes are given Appendix 5. A large part of this change was traced to one of two auto-sampler racks used to analyze CATS tubes. Examination of the calibration standards run in this rack showed erratic responses. We found a crack in the tube that carries sample from this rack to the GC that could explain the change in response as well as the erratic nature of the change. No clear way to quantify the change could be identified. Therefore, samples from rack one analyzed during this

Table 13. Syringe Volumes, Number of Runs, and Quantity of PFT Used as Standards. The units are pico liters (pL) or 10⁻¹² liters.

μL ei8	N	PMCP	PMCH	ocPDCH	PECH	ptPDCH	iPPCH	PTCH
10	32	0.08	0.09	0.05	0.03	0.06	0.06	0.050
25	18	0.20	0.20	0.13	0.07	0.14	0.14	0.125
50	32	0.406	0.45	0.25	0.14	0.28	0.28	0.25
100	25	0.812	0.90	0.51	0.28	0.56	0.56	0.50
250	14	2.0	2.2	1.27	0.70	1.40	1.4	1.25
500	13	4.1	4.5	2.5	1.4	2.80	2.8	2.50
1000	6	8.1	9.0	5.1	2.8	5.60	5.6	5.0
2500	6	20.3	22.5	12.8	7.0	13.97	14.0	12.5

period are suspect and are not included in the final data. This resulted in the loss of the data from seven of the SAS units or 140 samples. We plan to avoid this problem in the future by keeping daily control charts so any changes in instrument response can be spotted immediately.

The calibration data were fit with a quadratic equation of the form:

$$y = ax^2 + bx.$$

The y intercept forced through zero. Fit parameters and statistics are given in Appendix 6.

Background Levels and Method Level of Detection and Quantitation

Background level PFT concentrations were determined from BATS samples taken in the northwest quadrant of the test area. The sampler locations were 7, 11-14, 16, 17, 19, and the top of the New Yorker Hotel. Details of the background level studies are given in Table 13.

These numbers show background levels significantly higher than previously reported levels. This can be partially explained because the measurements are all close to the LOQ (see “CDTA Performance Statistics” p13 for definitions of LOD and LOQ). At levels near background, there is a significant uncertainty in assigning a value to this area. Notice that the relative standard deviation of the background areas range from 7 to 300% and the percentages of LOD to background concentration range from 19 to 900%.

Table 14. Background Levels and Statistics for PFT Samples in the Northwest Quadrant of the Study Area. Area is the PFT peak area from the chromatogram. Concentration is determined using these areas and the calibration curve determined from the standards.

PFT	N	Mean (area)	Stdev (area)	Concentration (ppqv)	Literature value ¹ (ppqv)	Noise (ppqv)	LOD (ppqv)	LOQ (ppqv)
PMCP	183	4800	380	18	6.29	1.4	4	14
PMCH	182	3600	250	16	4.6	1.1	3	11
ocPDCH	179	1250	270	3	0.3	0.6	2	6
PECH	93	6700	3300	1	NA	3	9	30
ptPDCH	187	4350	330	5	4.5	1.0	3	10
iPPCH	189	1940	330	5	NA	0.9	3	9
1PTCH	126	1000	500	2	0.07	1.2	4	12

¹ Dietz, 1987, Simmonds et al., 2002, Draxler et al., 1991.

Simultaneous Tracer Release Results

We released the gas mixtures containing the tracers iPPCH and PMCH simultaneously, at the same nominal flow rates, from release location C (Tables 3 and 4). The ratio of the concentrations of the gas mixtures iPPCH to PMCH was 0.037. A correlation plot of the two tracers at all sampling locations is given in Figure 10. One extremely high concentration point at (17960, 532) has been eliminated from this plot because it is an isolated point at high concentration. When this point is included, the fit changes to $y=0.030x + 4.7$, $r^2 = 0.93$.

iPPCH vs PMCH

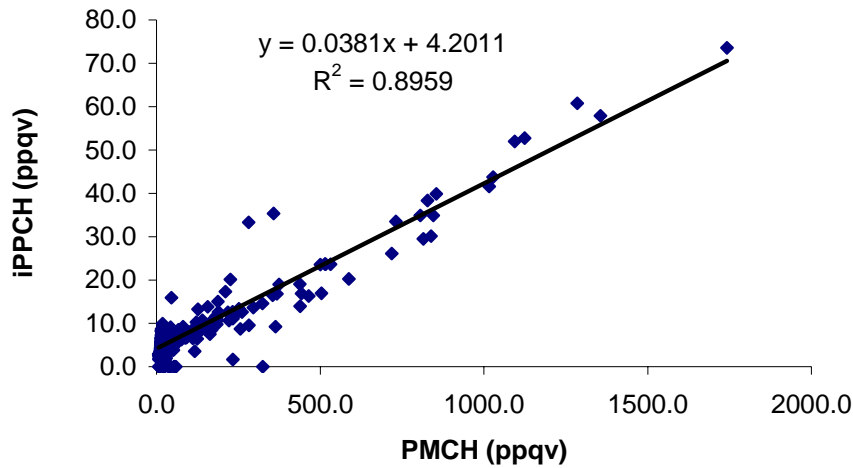


Figure 10. Correlation Plot of Tracers Simultaneously Released at the Same Location. The ratio of the tracer concentrations at the point of release was 0.037. Number of points is 788. Data is from all BATS and SAS samplers. One extreme point is excluded.

Duplicate samples

There were two sets of duplicate BATS samplers deployed during the experiment. One of the two BATS units at location 15 failed during both IOPs, leaving only one pair of duplicate BATS at street level. Data from these units are presented in Figure 11. The data are in excellent agreement with a slope of 0.97 and a correlation coefficient (r^2) of 0.997. The average relative difference between the two samplers is 20%. Since the majority of samples were not taken in the plume, this is in agreement with the uncertainties in the background levels (Table 14).

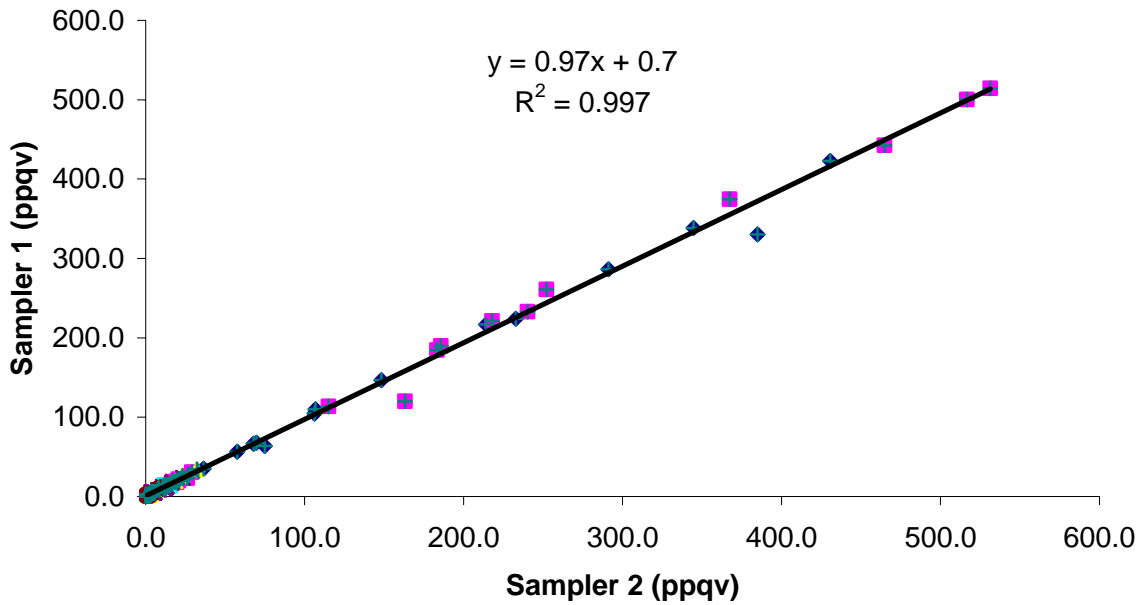


Figure 11. Duplicate BATS Data from Location 2. Data is for 5 PFTs. The number of points is 100.

Results from Collocated BATS and SAS Units

BATS and SAS samplers were collocated at the seven rooftop sampling locations. Out of 14 sets of samples collected, seven are unusable because of the problems in analysis of the SAS samples described in the Calibration Method section. The deployment of the rooftop samplers on the Post Office was delayed during IOP 1. The SAS and BATS units were in the Post Office garage until 10:45. The BATS unit was then placed on the roof. The SAS unit was left in the garage. The BATS-SAS pair located on top of Penn 2 (V5) were deployed after the first release began during both IOPs. During transport to the roof, they passed close to the release sites while sampling. Only samples taken after 10:00 are useable. The delay timer on SAS unit 80, at location V2, malfunctioned during both tests. No samples are useable from this unit. The first sample of the BAT located at V6 taken during IOP 2 was contaminated and was not used.

There are some discrepancies in the useable data between the SAS and BATS units. These discrepancies can be seen in the time series and in the comparison of the BATS data to the integral average of five, six-minute SAS samples.

Since the SAS units took six-minute samples and the BATS 30 minute samples, the SAS data must be integrally averaged over five samples before it can be compared with the BATS data.

The discrete form of the integral average is given by:

$$\frac{1}{30} \sum_{i=1}^5 \left(c_i 6 + \frac{1}{2} (c_{i+1} - c_i) 6 \right)$$

where :

c_i \equiv concentration of the i^{th} sample

6 minutes is the SAS sampling time

30 minutes is the BATs sampling time

A time series comparison of the BATS and SAS at the Penn 1 roof, 33rd Street side during IOP and 2 are given in Figures 12 and 13.

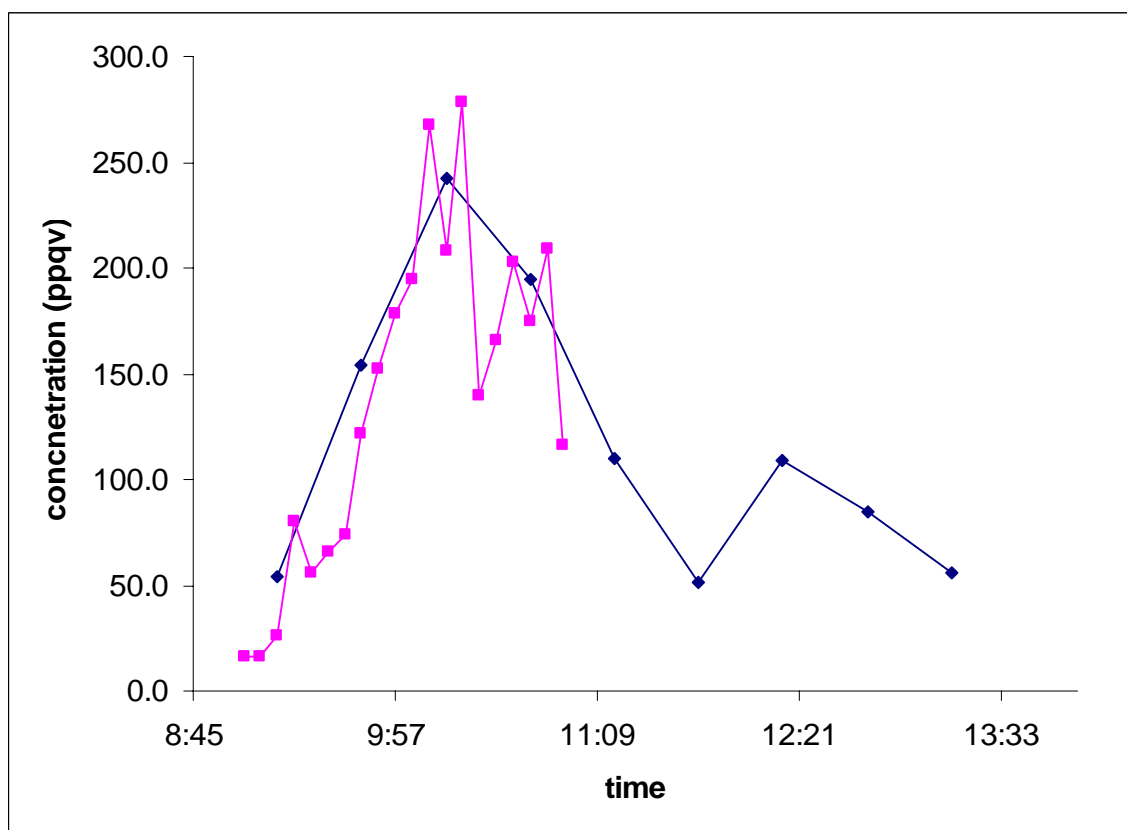


Figure 12. Time Series of the Collocated SAS and BATS on the Top of Penn 1, 33rd Street Side, IOP 1. SAS data are in pink. BATS data are blue.

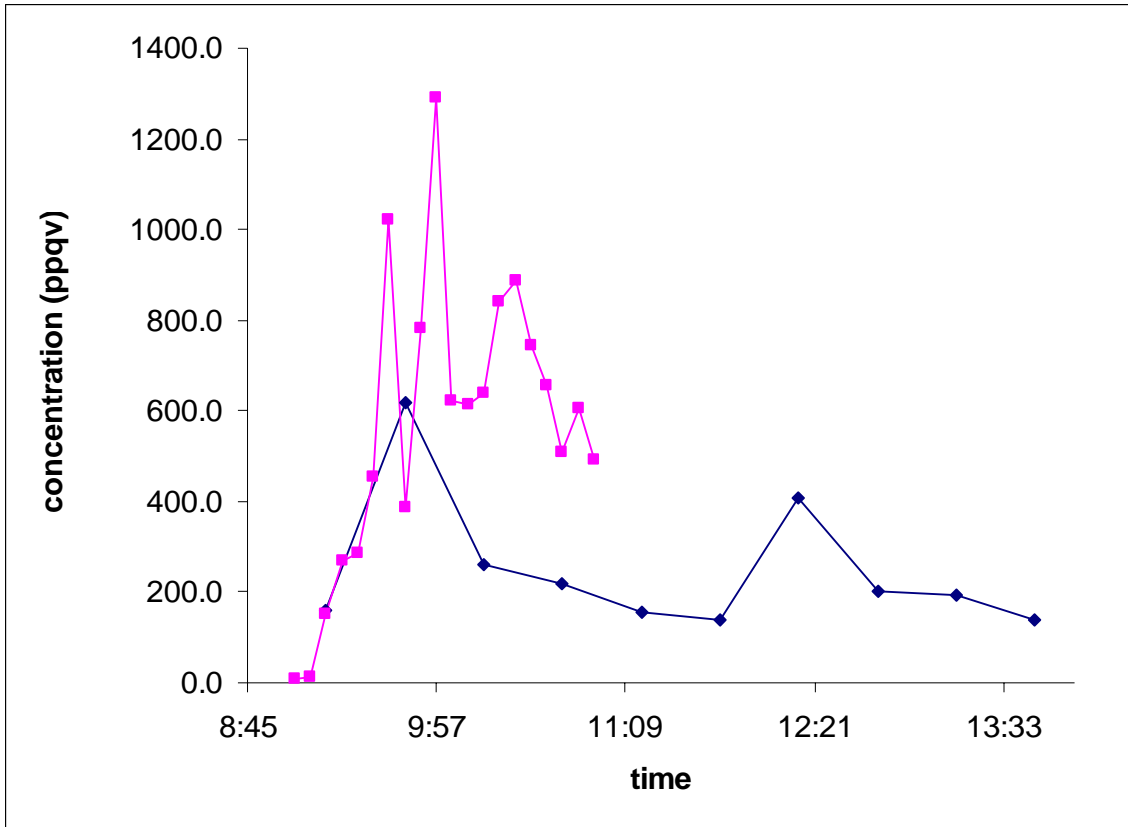


Figure 13. Time Series of the Collocated SAS and BATS on the Top of Penn 1, 33rd Street Side, IOP 2. SAS data are in pink. BATS data are blue.

The agreement for IOP 1 and the first half of IOP 2 are excellent. The reason for the divergence in the second half of IOP 2 is unknown. It is not an artifact of the analysis process.

Correlation plots for BATS vs. integrally averaged SAS are presented in Figures 14 and 15. Figure 14 presents all useable data. The agreement is poor. The slope is 0.55 with a correlation coefficient of 0.81. Figure 15 presents the same data without the points from V3, IOP 2. The agreement of these data is excellent with a slope of 1.05 and a correlation coefficient of 0.93. We do not know the reason for this discrepancy.

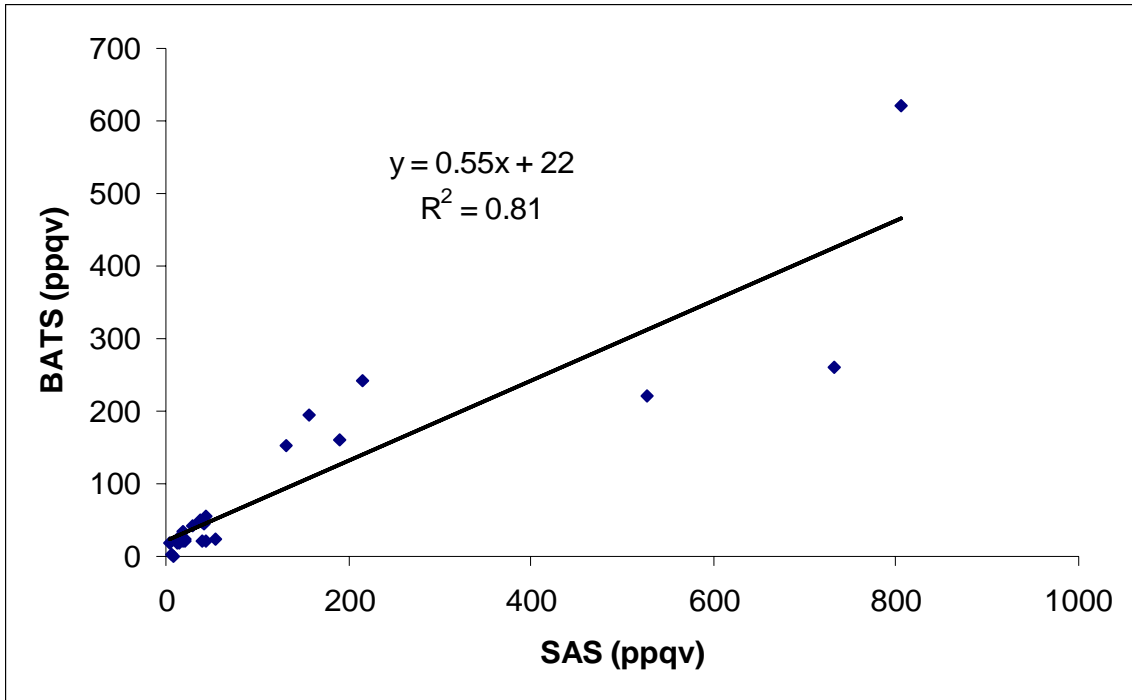


Figure 14. Correlation Plot of SAS Data vs. BATs Data. All reliable data are plotted.

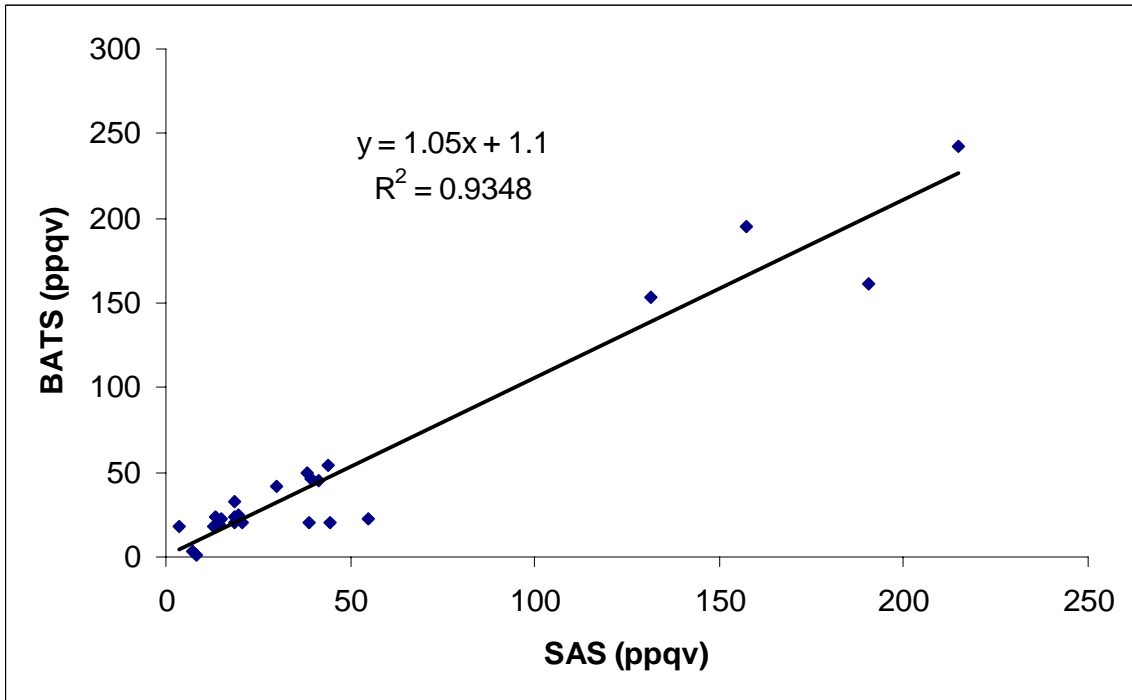


Figure 15. Correlation Plot of SAS Data vs. BATs Data. The data from the second V3, IOP 2 are not plotted.

Confidence Limits In the Measurements

The relative confidence limit in the tracer measurements is 20%, calculated from the average relative difference in the duplicate BATS measurements. A larger number of duplicate measurements are necessary to firmly establish this value. More duplicate samples will be collected in future UDP field studies.

Flow Calibrations

Method of calibration of BATS flows

The flow rate of all BATS SAS and PAS were measured before and after the experiment with a Dry Test Meter (Bios International, Butler New Jersey) and are presented in Appendix 2.

Comparison with ambient PFT ratio method

The Brookhaven Tracer Group often uses the PFT ptPDCH as a reference to calibrate sampler volumes (Draxler et al., 1991). Since this compound is not released as a tracer and the background level can be measured, the amount of ptPDCH in a sample provides a convenient method to check the calibrated flow rate of the sampler. We calculated the ptPDCH per liter of sample from the background samples (Table 13) and measured flow rates for those samplers. The mean value was 14 fL of pt PDCH per liter of air sample with a standard deviation of 1.3 fL/L. We then used this factor and the quantity of pt PDCH measured in each sample to calculate the sample volume for each sample. The mean of this calculated volume for each base, the measured flow rate and sample volume calculated from this rate, and the difference between these two values is presented for each sampler in Table 15. The difference between the volume determined with the calibrated flow rate and that determined with the quantity of the tracer are plotted in Figure 14. The agreement is within 20% in all but three locations. These locations were very close to the release point. Location 10 was less than 50 m from location B where PMCP was released. V1 and V2 were on the 12th floor roof of Penn 1. V6 was on the roof of the post office. These locations showed large concentrations of PMCP that correspond with the elevated ptPDCH values. There are two possibilities for the unusually high ptPDCH concentrations in these locations. Either there is a local unidentified source of PFT or a substance that interferes with the reference tracer, or there is contamination of our release mixture. We are in the process of analyzing our release mixtures to determine if they are the source of the ptPDCH observed at these locations. We also plan to do extensive background measurements in advance of the August field program to determine if there is a local source close to MSG and in other locations in the test area.

Table 15: Results of Comparison of Sample Volumes. Volume 1 (V1) is determined from the measured flow rate and the sampling time of 6 or 30 minutes. Volume 2 (V2) is the sample volume calculated from the measured quantity of ptPDCH. V1-V2 is the difference between these two quantities. The relative difference is the ratio between V1-V2 and V1.

Location	Measured Flow Rate (ml min ⁻¹)	Vol 1 (L)	Vol 2 (L)	V1-V2 (L)	Rel Difference
1	56.0	1.7	1.8	0.1	0.07
2	45.2	1.4	1.3	0.1	0.05
3	54.7	1.6	1.7	0.1	0.04

4	43.7	1.3	1.6	0.3	0.21
5	50.2	1.5	1.4	0.1	0.08
6	48.2	1.4	1.3	0.1	0.08
7	46.5	1.4	1.4	0.0	0.01
8	51.1	1.5	1.4	0.1	0.07
10	52.4	1.6	9.3	7.7	1.42
11	54.0	1.6	1.6	0.0	0.03
11	46.7	1.4	1.4	0.0	0.01
12	47.2	1.4	1.5	0.1	0.09
13	52.7	1.6	1.6	0.0	0.02
14	46.9	1.4	1.5	0.1	0.10
15	55.4	1.7	1.4	0.3	0.17
15	46.7	1.4	1.4	0.0	0.01
16	57.1	1.7	1.4	0.3	0.20
17	46.5	1.4	1.6	0.2	0.12
19	47.8	1.4	1.5	0.0	0.02
V1	43.7	1.3	2.5	1.2	0.63
V1	504.4	3.0	2.7	0.3	0.12
V2	46.1	1.4	2.4	1.0	0.53
V2	512.0	3.1	2.4	0.7	0.24
V3	50.2	1.5	1.4	0.1	0.06
V3	506.0	3.0	2.9	0.1	0.04
V3	506.0	3.0	2.6	0.5	0.16
V3	514.2	3.1	2.9	0.2	0.08
V4	51.1	1.5	1.8	0.3	0.18
V5	50.3	1.5	1.4	0.1	0.06
V5	507.7	3.0	2.4	0.6	0.23
V5	513.0	3.1	2.5	0.6	0.21
V6	45.6	1.4	2.4	1.1	0.57
V6	517.5	3.1	2.8	0.3	0.10
V7	52.7	1.6	1.5	0.1	0.07
V7	510.9	3.1	2.0	1.1	0.41

Dataset Description

The processed data for the BATS, SAS, CDTA, and some PAS (??) described in this report are available as Excel spreadsheets in the format described in Appendix 1. In addition to this dataset, the BATS tracer data has been examined critically to develop a quality assured dataset that is ready for model validation efforts. Background concentrations were subtracted from the BATS data so that only the measurements that are attributable to the tracer released during the study are reported. This quality assured BATS dataset for model validation efforts is also available as an Excel file. Details about the quality assurance procedures applied to this verified dataset can be found on the “Info” tab of the Excel workbook that contains these data.

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Appendix 1. Data Format

Data are in an Excel spreadsheet. The spreadsheet has one worksheet for BATS, SAS, and CDTA data for each test day. BATS and SAS data are identified by location number keyed to Tables 7 and 8. The zero values occur when the PFT concentration was below the detection limit. The value -999 occurs when there are problems with the data.

CDTA locations are identified by the street intersections closest to point where the data were taken. For example:

9 36

is the intersection of 9th Avenue and 36th street.

All concentrations are expressed in parts per quadrillion by volume (ppqv) or parts in 10^{15} .

Appendix 2. Sampler Pump Rates

Table A2: Sampler pump rates measured in the laboratory before and after the field experiment. Values are an average of two measurements. The 95% confidence interval is 2mL min^{-1} .

Location	Sampler serial number	Rate
1	3	61
2	2	49
3	15	59
4	1057	47
5	16	55
6	19	52
7	21	50
8	28	55
10	29	57
11	36	59
12	1004	51
13	1024	57
14	1032	51
15	1046	60
16	1047	62
17	1049	50
18	1050	50
19	1056	52
20	4	44
V1	1058	52
V2	1060	50
V3	1061	55
V4	1063	55
V5	2006	55
V6	1067	49
V7	2088	57
V1	SAS 90	548
V2	SAS 80	557
V3	SAS 20	550
V4	SAS 60	550
V5	SAS 70	552
V6	SAS 100	562
V7	SAS 50	555.3

Appendix 3. CDTA

CDTA PMCP fL/L vs. time 3/10/05

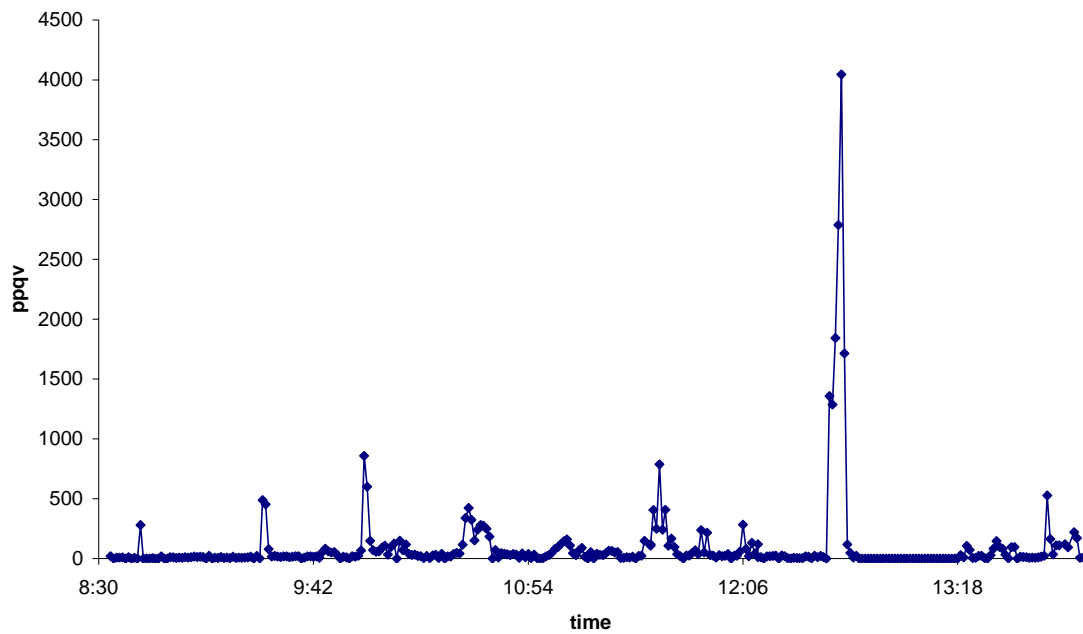


Figure 3A. CDTA PMCP Time Series 3/10/05.



Figure 3B. CDTA Locations and Times of PMCP Detected Above LOQ, 3/10/05. A 12:35 – 12:40, 13:31, B 8:44, C 11:06, 07:33, 36-40, 42, 52, 54, 12:16, D 10:09 – 10:11, E 10:00 – 10:02, F 9:25 – 9:26, G 13:48 – 13:49

CDTA PMCH fL/L vs time 3/10/05

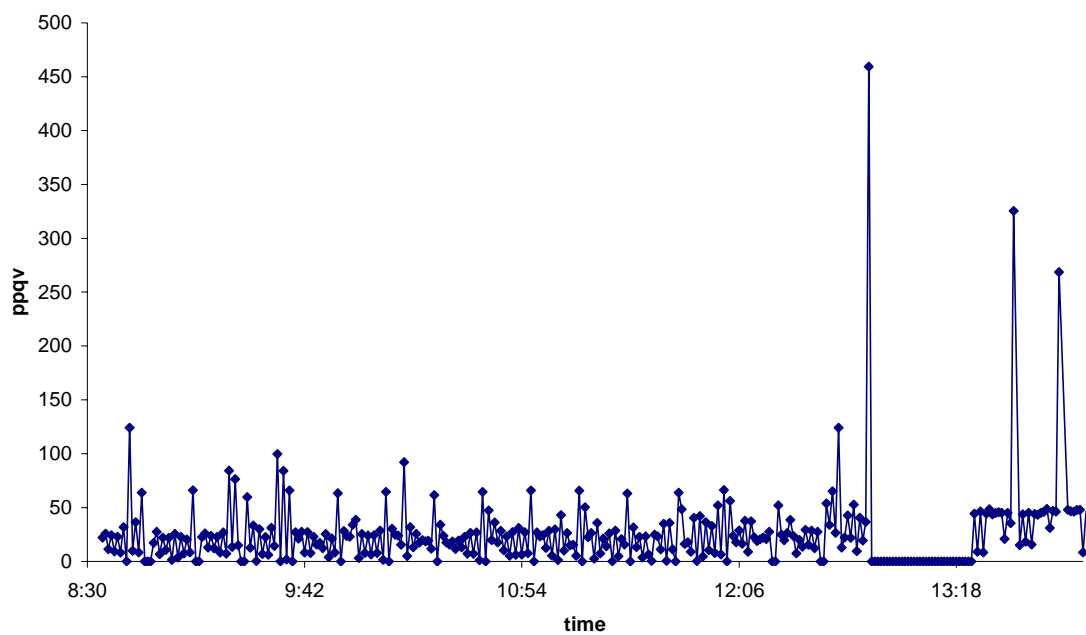


Figure 3C. CDTA PMCH Time Series 3/10/05.

PMCH above LOQ on March 10th

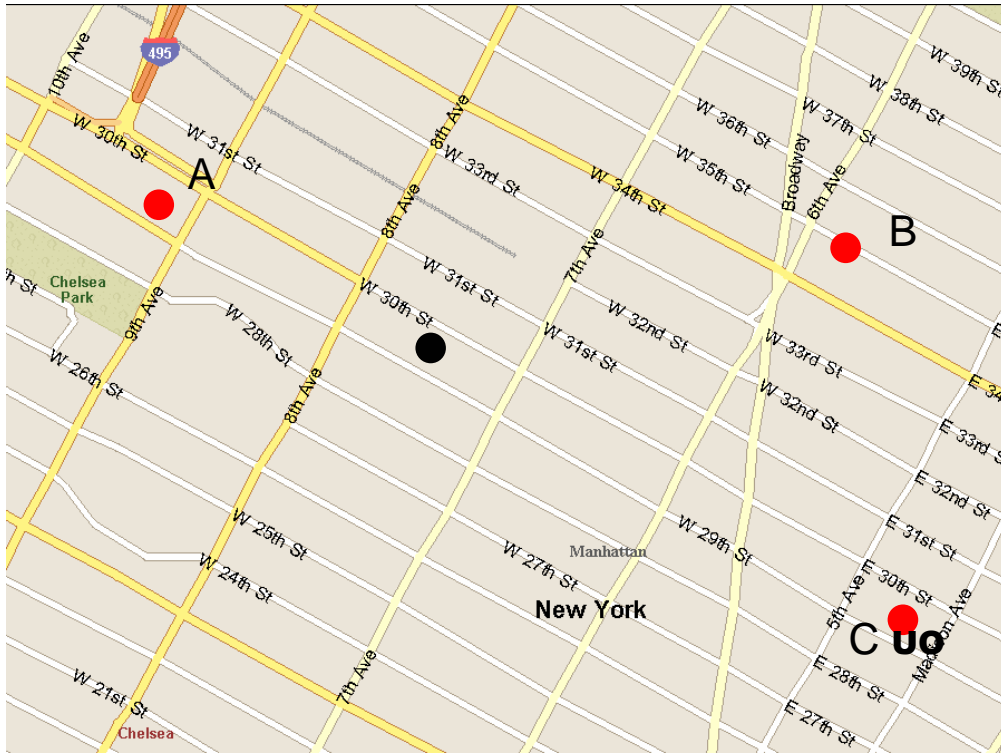


Figure 3D. CDTA Locations and Times of PMCP Detected Above LOQ, 3/10/05. A 12:49, B 13:39, C 13:52.

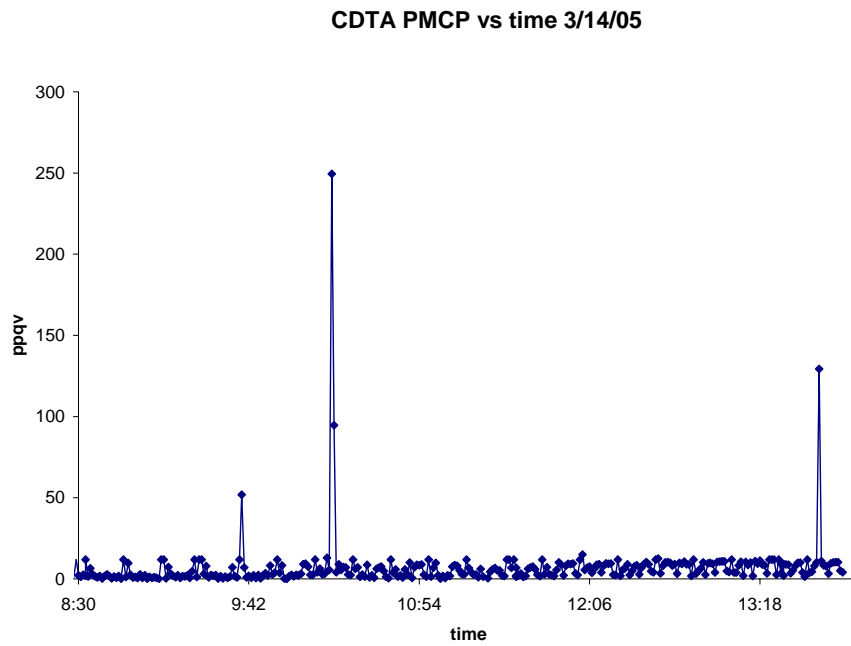


Figure 3E. CDTA PMCP Time Series 3/14/05.

Error!

PMCP above LOQ March 14th



Figure 3F. CDTA Locations and Times of PMCP Detected Above LOQ, 3/14/05. A 9:40, B 13:44, C 10:18 – 10:19

CDTA PMCH vs time 3/14/05

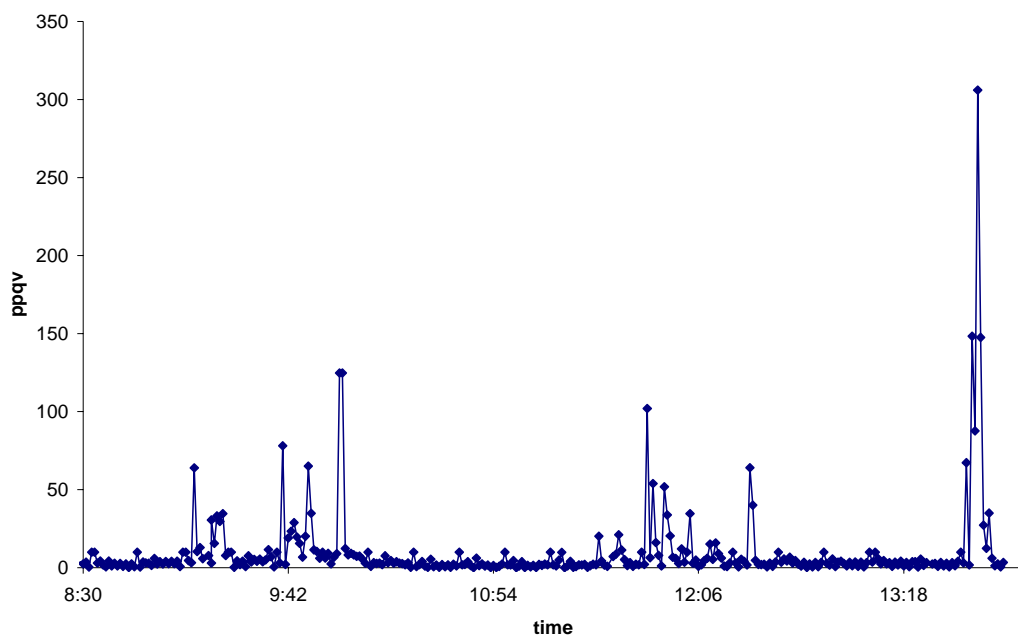


Figure 3G. CDTA PMCH Time Series 3/14/05.

PMCH above LOQ on March 14th



Figure 3H. CDTA Locations and Times of PMCH Detected Above LOQ, 3/14/05. A: 11:50 - 9:44, B: 12:03, C: 11:48, D: 9:09, E: 9:40, F: 11:54 - 11:55, G: 12:24 - 12:25, H: 9:49 - 9:50, I: 10:00 - 10:01, J: 9:15 - 9:19, 13:40, 42-45, 48

CDTA ocPDCH vs time 3/14/05

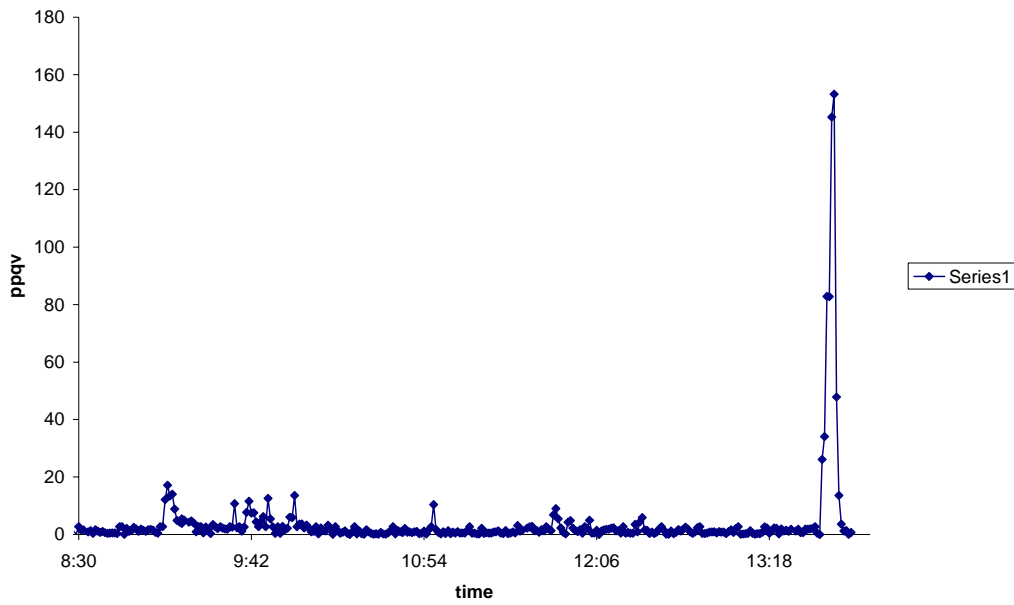


Figure 3I. CDTA PMCH Time Series 3/14/05.

ocPDCH above LOQ on March 14th



Figure 3J. CDTA Locations and Times of ocPDCH Detected Above LOQ, 3/14/05.
 A: 9:06 – 9:09, B : 9:49, C: 9:41, 13:40 – 13:47, D: 10:00

Appendix 4: Conversion of mixing ratio to mass per unit volume

The conversion of mixing ratio to units of mass per unit volume is accomplished using the ideal gas law and the molecular weight of the perfluorocarbon tracer.

The ideal gas law is given by the equation :

$$pV = nkT$$

where

p \equiv pressure

V \equiv Volume

n \equiv number of molecules

k \equiv the Boltzman constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$)

T \equiv the temperature in Kelvin

This can be rearranged to give number of molecules per unit volume.

$$\frac{n}{V} = \frac{p}{kT}$$

The number of molecules of air in a cubic meter is 2.68×10^{25} , assuming a pressure of 1 atmosphere or $1.01 \times 10^5 \text{ Pa}$, and a temperature of 0° C or 273 K . Multiplying this by the mixing ratio of the PFT gives the number of molecules of PFT per cubic meter. Remember that the mixing ratio is the ppq value multiplied by 10^{-15} . Divide this quantity by Avagadro's number to get the number of mols of PFT and multiply by the molecular weight to determine the mass in units of grams per cubic meter. This value divided by 10^{-6} is the mass per unit volume in micro grams per cubic meter (μgm^{-3}).

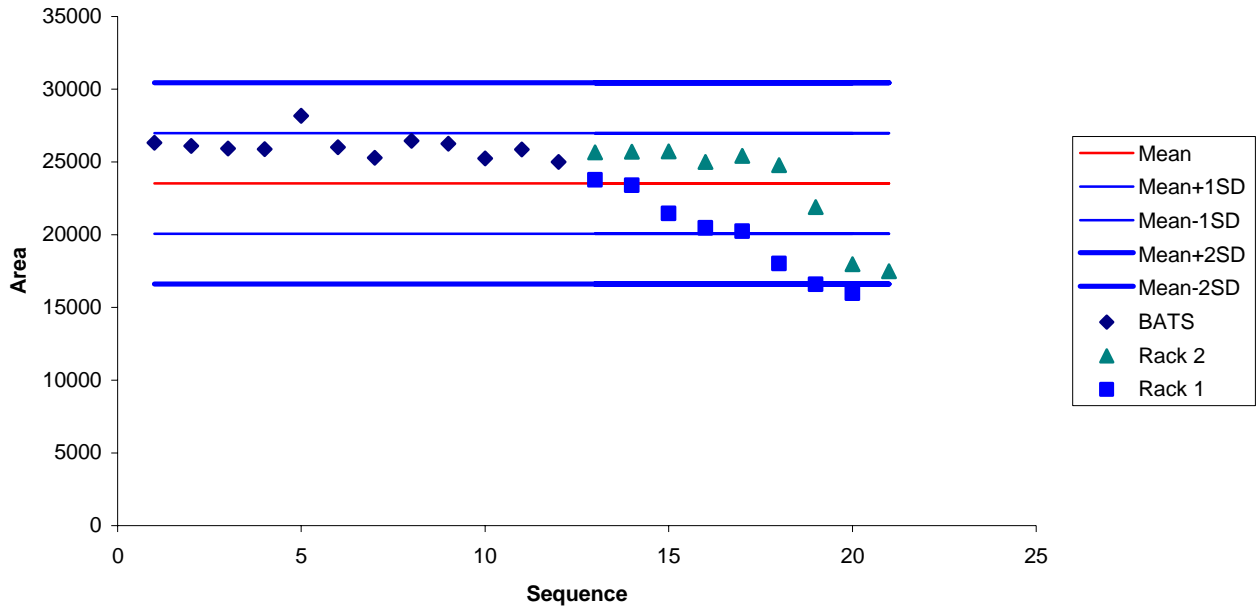
Therefore:

$$\frac{\text{mass PFT}}{\text{m}^3} = (\text{mixing ratio of PFT}(\text{ppq} \times 10^{-15})) \frac{(2.68 \times 10^{25} \text{ molecules m}^{-3})}{(6.02 \times 10^{23} \text{ molecules mol}^{-1})} \frac{(\text{molecular weight PFT gmol}^{-1})}{\left(10^{-6} \frac{\text{g}}{\mu\text{g}}\right)}$$

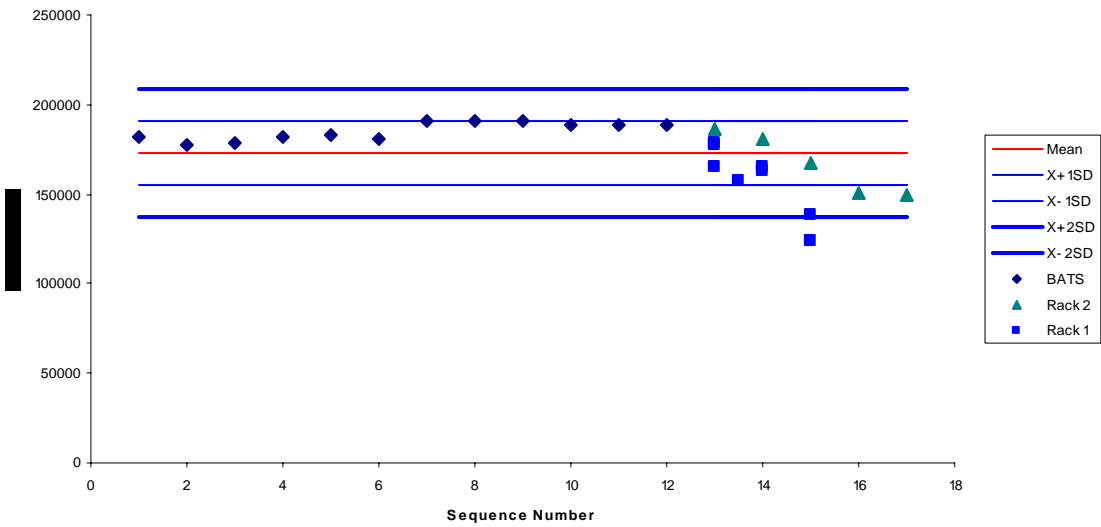
$$\frac{\text{mass PFT}}{\text{m}^3} = (4.45 \times 10^7)(\text{mixing ratio of PFT})(\text{molecular weight PFT})$$

Appendix 5. GC Control Charts

10uL E18 Standard - PMCP



100uL PMCP Data



Appendix 6: GC Calibration Data

The calibration data was fit with a quadratic equation of the form . The y intercept was forced through zero.

PFT	PMCP	PMCH	ocPDCH	PECH	ptPDCH	iPPCH	PTCH
a	6.30E-13	1.01E-12	4.87E-13	7.79E-11	1.33E-12	1.25E-12	8.38E-13
σ_a	4.61E-14	6.5E-14	3.9E-14	5.7 E-12	1.13E-13	1.13E-13	1.04E-13
b	5.60E-06	6.57E-06	3.10E-06	9.4E-4	4.66E-06	4.17E-06	3.74E-06
σ_b	1.12E-07	1.41E-07	9.55E-08	1.9E-5	1.87E-07	2.00E-07	1.98E-07
r2	0.996	0.996	0.9912	0.997	0.9866	0.9822	0.9748