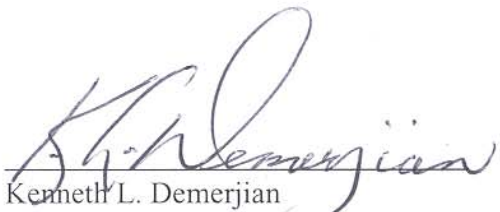


**QUALITY ASSURANCE PROJECT PLAN**  
**For the EPA Particulate Matter "Supersite": PM2.5 Technology Assessment**  
**and Characterization Study in New York (PMTACS-NY)**

**Version 1.1**  
**November 11, 2000**

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### DOCUMENT DISTRIBUTION LIST

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## **SUMMARY OF CHANGES BETWEEN EDITIONS**

This is a “living” document; it will be changed and updated from time to time. Minor changes will be issued as updates to the major revisions. Users should ensure that they have the current edition of this document. Major changes will be issued as new whole revision numbers as needed.

### **First Edition 1.0, June 15, 2000**

The original PMTACS-NY SS Quality Assurance Project Plan (QAPP) was released.

## **Quality Assurance Project Plan for EPA Particulate Matter "Supersite": PM2.5 Technology Assessment and Characterization Study in New York**

### **1 Project Planning and Organization**

#### **1.1 Introduction**

The Clean Air Act (CAA) requires the U.S. Environmental Protection Agency (EPA) to review the National Ambient Air Quality Standards (NAAQS) every five years. During the most recent review, the agency decided to develop an additional standard for particles with an aerometric diameter of 2.5 microns or less (PM2.5). These "fine" particles were shown to have increased adverse health effects upon certain segments of the American public, such as those most susceptible to respiratory ailments of children and the elderly. This program required the development of a new standard for daily and yearly PM2.5 concentration formats, a new Federal Reference Method program to ensure qualitative and quantitative sampling, and a Quality Control and Quality Assurance program to ensure that the collected data are valid and verifiable and meet the established quality objectives.

#### **1.2 Background**

The proposed revisions to the particulate matter NAAQS included two new primary PM2.5 standards. The annual standard for PM2.5 is  $15 \text{ } \Phi\text{g/m}^3$  and the daily, or 24-hour standard, is  $65 \text{ } \Phi\text{g/m}^3$ . EPA also proposed a new PM2.5 reference method and developed new requirements for designating reference and equivalent methods for PM2.5 and for ambient air quality surveillance for particulate matter in 40 Code of Federal Regulations (CFR) Parts 50, 53, and 58, respectively. EPA added these two NAAQSs to provide increased protection to the nation's public health, particularly with regard to respiratory and pulmonary illnesses identified in the community-based studies focusing on fine particles.

Because PM2.5, like tropospheric ozone, probably has a regional component, comprehensive measurements at both urban and regional representative sites are needed. Such measurements will require advanced instrumentation technologies and measurement strategies to support analyses that will elucidate our understanding of: 1) the chemical and physical processes that couple urban and regional air quality, 2) the role that anthropogenic and biogenic sources of VOC, NO<sub>x</sub>, SO<sub>2</sub> and primary particulate play in the production of the PM2.5/co-pollutant complex in time (diurnal, seasonal, and inter annual) and space (local to regional); and 3) the effectiveness of emission control technologies on air quality.

The long-term monitoring of the PM2.5/co-pollutant complex and its precursors at urban and regional representative sites provides the opportunity to track the impact of emission controls and their effectiveness on air quality. These data can be used to verify that implemented PM2.5 primary and secondary precursor (including ozone precursor) emission controls are performing

according to specifications and verify that PM<sub>2.5</sub> and ozone air quality has responded to the emission changes achieved as expected. Without adequate monitoring systems to track the progress and effectiveness of implemented control programs, the air quality management approach remains unaccountable.

The primary purpose of this investigation is to conduct comprehensive measurement of PM<sub>2.5</sub> mass, chemical speciation and gaseous precursors to be collected at five monitoring sites located in the New York City and at regional representative locations in upstate New York and to operate this network throughout most of the five year PMTACS-NY Supersite program. These sites include two regional research monitoring sites, Whiteface Mountain (Wilmington, NY) operational since 1973 and Pinnacle State Park (Addison, NY) operational since 1995 and three urban monitoring sites (NYS DEC SLAMS/PAMS sites); Marble Dean Bacon or alternate (Manhattan, NY), Middle School M.S. 52 (South Bronx, NY) and Queensborough Community College or alternate (Queens, NY). Standard routine measurements of criteria pollutants and the mandated PM<sub>2.5</sub> mass and chemical speciation measurements will be supplemented with advance instrumentation providing complimentary chemical and temporal specificity.

### **1.3 Project Scope and Work Objectives**

The primary objectives of the PM<sub>2.5</sub> Technology Assessment and Characterization Study in New York (PMTACS-NY), is to provide enhanced measurement data on chemical and physical composition PM and its associated precursors so as to 1) characterize the PM<sub>2.5</sub>/Co-pollutant complex and its related sources and sinks; 2) support health effects and exposure research; 3) evaluate new measurement technologies and establish their potential for routine monitoring; and establish and demonstrate the use of these data analyses to track mitigation progress and support an accountable air quality management process.

It is a highly leveraged measurement; technology development and evaluation program that will be operated as one of several EPA designated PM Air Quality Supersites to be established within the United States.

To achieve the stated objectives requires:

§ The measurement of the temporal and spatial distribution of the PM<sub>2.5</sub>/Co-Pollutant Complex including: SO<sub>2</sub>, CO, VOCs/air toxics, NO, NO<sub>2</sub>, O<sub>3</sub>, NO<sub>y</sub>, H<sub>2</sub>CO, HNO<sub>3</sub>, HONO, PM<sub>2.5</sub> (mass, SO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, OC, EC, trace elements), single particle aerosol composition, CN, OH and HO<sub>2</sub> to support regulatory requirements to develop cost effective mitigation strategies PM<sub>2.5</sub> and its co-pollutants. Although detection of trends in precursor substances is not an explicit goal of this five year program, the measurement network should nevertheless be conceived and implemented in such a way that trends can be deduced given data collection exceeds significantly the projected five year period.

§ The monitoring of the effectiveness of new emission control technologies [i.e. compressed natural gas (CNG), bus deployment, and continuously regenerating technology (CRT)] introduced in New York City and its impact on ambient air quality, thorough remote open path roadside, mobile platform, and fixed site measurements of CO<sub>2</sub>, CO, NO, H<sub>2</sub>CO, CN and aerosol chemical composition.

and

§ The execution of special intensive studies. Two special intensive field studies will be carried out, the first in the summer of 2001 and the second in the winter of 2003. Both studies will be deployed from a host site that will likely be one of the urban measurement sites. The 4-6 weeks intensive studies will engage several research groups performing research grade measurements using emerging measurement technologies. The measurements will provide detailed real-time chemical and physical characterization of the PM/co-pollutant complex to a) help elucidate the operative gas-to-particle transformation processes occurring in urban centers; b) enhance the chemical source signature data base in support of source attribution studies; and c) intercompare emerging technologies and evaluate their performance and in comparison with the operational routine measurement systems.

## **1.4 Project Description, Experimental Design and Project Schedule**

### **1.4.1 Core Sites**

Comprehensive measurement of PM<sub>2.5</sub> mass, chemical speciation and gaseous precursors will be collected at five monitoring sites located in the New York City metropolitan area and at regional representative locations in upstate NY. These sites shown in the map in Figure 1 include two research regional monitoring sites, Whiteface Mountain (Wilmington, NY) operational since 1973 and Pinnacle State Park (Addison, NY) operational since 1995 and three urban monitoring sites (see map in Figure 2), Mable Dean Bacon (Manhattan, NY or equivalent), Middle School M.S. 52 (South Bronx, NY) and Queensborough Community College (Queens, NY or equivalent).

These measurement sites constitute the backbone of the PM<sub>2.5</sub> “Supersites Network”. In addition to standard routine measurements of criteria pollutants and the mandated PM<sub>2.5</sub> mass and chemical speciation measurements, these sites will be operating advance instrumentation that will compliment and provide more chemical and temporal specificity of the air quality at these locations. Details regarding siting, measurement parameters, and techniques are discussed in the Site Selection section of this QA plan. The highly relevant measurements provide over the course of this program fill a substantial data need associated with the characterization of the chemical composition of PM<sub>2.5</sub> within New York City and the transport-impacted regional background of upstate NY.

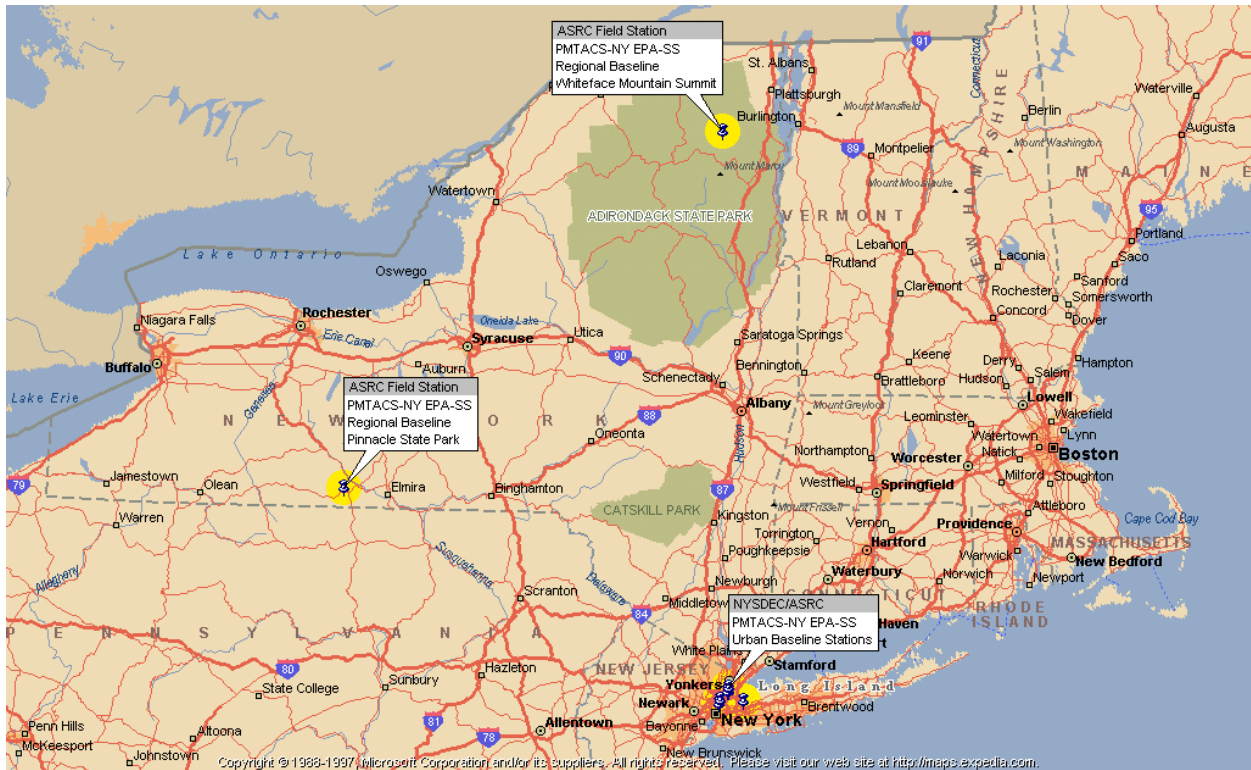


Figure 1. PMTACS-NY Supersite Network

### 1.4.2 Special Intensive Field Studies

In addition to the PMTACS, PM<sub>2.5</sub> Supersite measurement network, which will operate throughout most of the 5 year program period as described in Table 1, two special intensive field studies will also be carried out. The first study will occur in the summer of 2001 and the second in the winter of 2003. Both studies will be deployed from a host site that will likely be one of the backbone urban measurement sites shown in Figure 2. The intensive field studies will be 4-6 weeks in duration, involving several research groups performing research grade measurements using emerging measurement technologies. These measurements will provide detailed real-time chemical and physical characterization of the PM/co-pollutant complex to 1) help elucidate the operative gas-to-particle transformation processes occurring in urban centers; 2) enhance the chemical source signature data base in support of source attribution studies; and 3) intercompare emerging technologies and evaluate their performance and in comparison with the operational routine measurement systems. Participating research groups include: Aerodyne Research, Inc., Aerosol Dynamics, Inc., Brookhaven National Laboratories, Clarkson University, Penn State University, NYS Department of Environmental Conservation, NYS Department of Health, Rupprecht and Patashnick, Co., Inc., and the University at Albany/SUNY. The new measurement technologies to be deployed as part of the PMTACS special studies are summarized in Table 2.



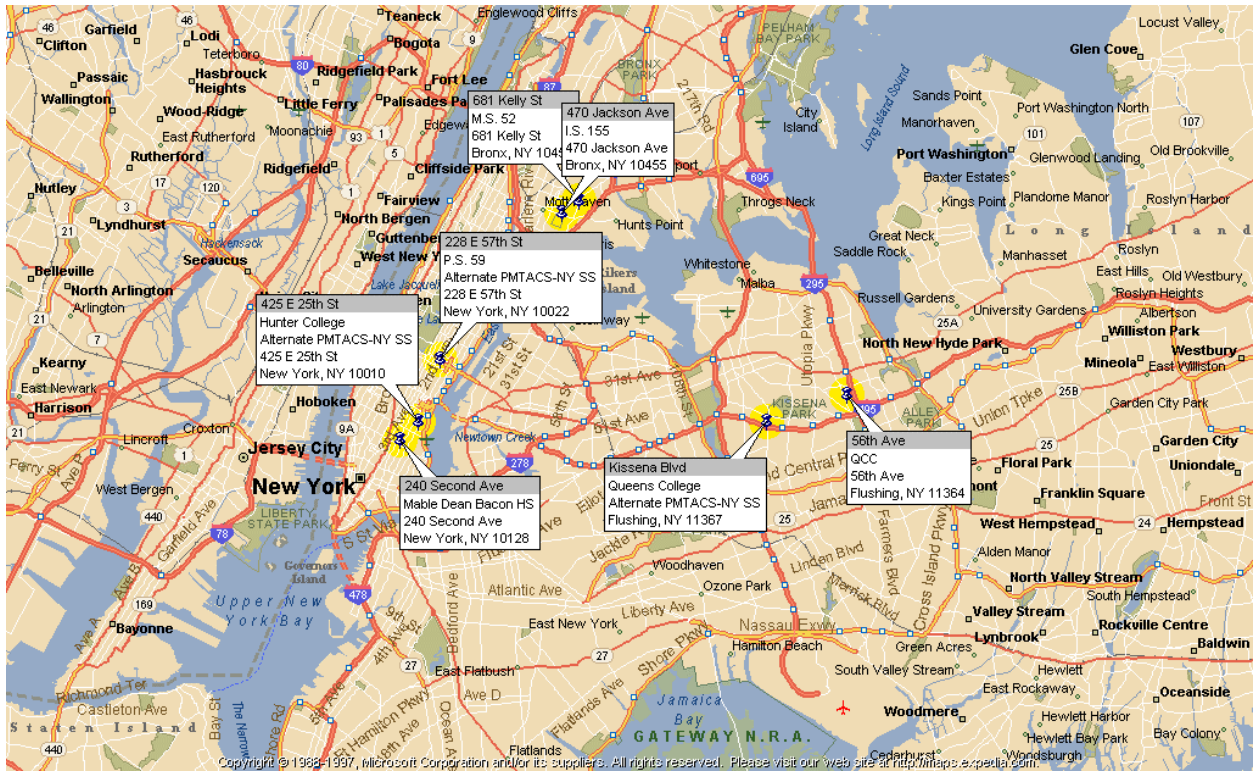


Figure 2. PMTACS-NY Urban Supersites

**Table 1. PMTACS-NY Sites, Measurement Parameters And Specifications**

PARAMETER/METHOD	Sites*	Operator**	Period	Averaging	Frequency
<b><i>PM Filter Mass and Chemistry</i></b>					
PM2.5 mass, sulfate, nitrate /Ion Chromatograph	WFML	DEC, ASRC	July 2000 - Oct. 2004	24-hr	daily
PM2.5 (Chemical Species Measurements, as outlined in EPA, 1999)	QCC	DEC (Analysis/RTI)	July 2000 – Oct. 2004	24-hr	3 <sup>rd</sup> day
PM10 mass, sulfate, nitrate /Ion Chrom	WFML, MDB, SB	DEC, ASRC	July 2000 – Oct. 2004	24-hr	6 <sup>th</sup> day
PM2.5 mass (FRM-R&P Partisol Sampler)	PSP, WFML, MDB, SB, QCC	DEC, ASRC	July 2000 – Oct. 2004	24-hr	daily
PM2.5 metals Mg, Al, K, Ca, V, Cr, Mn, Ni, Fe, Zn, As, Se, Cd, Sb, Hg, and Pb /ICP/AES, ICP/MS, & neutron activation	PSP, MDB, SB, QCC, NNJ	DEC, ASRC, DOH	July 2000 – June 2001	24-hr	daily
PM2.5 SO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> /Ion Chromatograph	PSP, MDB, SB, QCC, NNJ	DEC, ASRC, DOH	July 2000 – June 2001	24-hr	daily
PM2.5 metals Mg, Al, K, Ca, V, Cr, Mn, Ni, Fe, Zn, As, Se, Cd, Sb, Hg, and Pb/ XRF	PSP, MDB, SB, QCC, NNJ	DEC, ASRC	July 2001 – Dec. 2003	24-hr	6 <sup>th</sup> day
PM2.5 SO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> /Ion Chromatograph	PSP, MDB, SB, QCC, NNJ	DEC, ASRC	July 2001 – Dec. 2003	24-hr	6 <sup>th</sup> day
PM2.5 metals Mg, Al, K, Ca, V, Cr, Mn, Ni, Fe, Zn, As, Se, Cd, Sb, Hg, and Pb /ICP/AES, ICP/MS, & neutron activation	PSP, MDB, SB, QCC, NNJ	DEC, ASRC, NYSDOH	Intensive: 4 weeks ea. Summer 2001 Winter 2003	6-hr	daily
PM2.5 SO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> /Ion Chromatograph	PSP, MDB, SB, QCC, NNJ	DEC, ASRC, DOH	Intensive: 4 weeks ea. Summer 2001 Winter 2003	6-hr	daily
PM10/PM2.5 Particle Concentrator (R&P ChemTox Model 2400) <sup>1</sup>	PSP MDB or SB	DEC, ASRC	Seasonal year 2000 Seasonal 2001-2003	variable	variable

<sup>1</sup> Particle collection subject to health effects community interest and participation (i.e. sample storage/archival)

**Table 1. PMTACS-NY Sites, Measurement Parameters and Specifications (continued)**

<i>Continuous PM Mass and Chemistry</i>					
PM2.5 mass (heated R&P TEOM 1400AB)	PSP, WFML, MDB, SB, QCC	DEC,ASRC	July 2000 – Oct. 2004	10-min	daily
PM10 mass (heated R&P TEOM 1400AB)	MDB, SB	DEC,ASRC	July 2000 – Oct. 2004	10-min	daily
PM2.5 mass (T/RH modified R&P TEOM 1400AB)	PSP, WFML, MDB/SB	DEC,ASRC	June 2000 – May 2003	10-min	daily
PM2.5 mass (Differential ESP R&P TEOM )	PSP, MDB	ASRC	July 2001 – Oct. 2004	5-min	daily
PM2.5 nitrate and sulfate (R&P flash volatilization 8400NS) <sup>2</sup>	PSP, WFML, MDB, SB, QCC	DEC,ASRC	July 1, 2000 - Oct. 2004 June 1, 2001 – Oct. 2004	10-min	daily
PM2.5 Organic and elemental carbon (R&P 5400)	PSP, WFML, MDB, SB, QCC	DEC,ASRC	July 2001 – Oct. 2004	1-hr	daily
Single particle chemical speciation (Aerodyne, Inc Aerosol Mass Spectrometer [AMS])	MDB/QCC	ASRC	Intensive: 4 weeks ea. Summer 2001 Winter 2003	TBD	TBD
Single particle chemical speciation (BNL Single Particle Laser Ablation Time of Flight Mass Spectrometer [SPLAT-MS])	MDB/QCC	BNL	Intensive: 4 weeks ea. Summer 2001 Winter 2003	TBD	TBD
<i>Gases</i>					
NO - TECO 42	PSP, WFMS, MDB, SB, QCC	DEC,ASRC	July 2000 – Oct. 2004	5-min	daily
NO <sub>2</sub> -photolytic titration modified TECO 42	PSP, WFMS, MDB, SB, QCC	DEC,ASRC	July 2000 – Oct. 2004	5-min	daily
NO <sub>y</sub> Moly. Modified TECO 42	PSP, WFMS, MDB, SB, QCC	DEC,ASRC	July 2000 – Oct. 2004	5-min	daily
SO <sub>2</sub> TECO 43	PSP, WFMS, MDB, SB, QCC	DEC,ASRC	July 2000 – Oct. 2004	5-min	daily
O <sub>3</sub> TECO	PSP, WFML, MDB, SB, QCC	DEC,ASRC	July 2000 – Oct. 2004	5-min	daily

<sup>2</sup> July 2000 start date subject to availability of R&P 8400N instrument, June 2001 start date subject to availability of R&P 8400S instrument

**Table 1. PMTACS-NY Sites, Measurement Parameters and Specifications (continued)**

CO Modified TECO 48	PSP, WFMS, MDB, SB, QCC	DEC,ASRC	July 2000 – Oct. 2004	5-min	daily
NO/CO or H2CO/HONO open path TILDAS	MDB/QCC	DEC,ASRC, Aerodyne	Intensive: 4 weeks ea. Summer 2001 Winter 2003	5-min	daily
OH/HO2 LIF	WFM MDB/QCC	PSU	Intensives: 4 weeks ea. Summer 2000 – WFM Summer 2001 - MDB Winter 2003 - MDB	10-min	daily
HONO/HNO3 scrubbed derivatization HPLC	MDB/QCC	DOH	Intensive: 4 weeks ea. Summer 2001 Winter 2003	5-min	daily
Hydrocarbons C2-C10 Canisters GC/FID	WFMS, WFML	ASRC	May 15, 2000 – October 15, 2004	3-hr integrated	2 <sup>nd</sup> day in Summer; weekly in winter
Hydrocarbons C2-C10 PE Auto GC	PSP, QCC	ASRC, DEC	May 15 - October 15 2000-2004	40-min	daily summer
H2CO /AEROLaser 4001A and/or Alpha Omega	PSP, WFML, MDB/SB, QCC	DEC, ASRC	12 week Summer Intensives: 2000-04 6 week Winter Intensives: 2000-2003	5-min	daily
Air Toxics	MDB/QCC; SB	DEC	Seasonal 2000-04	24-hr	3 <sup>rd</sup> day

**Table 1. PMTACS-NY Sites, Measurement Parameters and Specifications (continued)**

<i>Particle Number, Size &amp; Optical Properties</i>					
Condensation Nuclei Counter/ TSI 3025A (0.003µm to 1 µm)	MDB, SB, QCC	DEC	July 2000 – Dec. 2004	5-min	daily
Condensation Nuclei Counter/ GE	PSP, WFML	ASRC	July 2000 – Dec. 2004	5-min	daily
Aerosol Size Distribution (0.003µm to 1 µm) / TSI 3934	PSP, MDB/SB	ASRC	4 week Summer Intensives: 2001-2003 4 week Winter Intensives: 2001-2003	5-min	daily
Aerodynamic Particle Sizer Spectrometer (0.37µm to 20 µm) / TSI 3320	PSP, MDB/SB	ASRC, DEC	4 week Summer Intensives: 2001-2003 4 week Winter Intensives: 2001-2003	5-min	daily
Aerosol optical depth MFRSR (multi-filter rotating shadowband radiometer)	PSP, MDB/SB	ASRC, DEC	Jan. 2001 – Dec. 2003	5-min	daily
Aerosol Light Scattering: 3-color integrating nephelometer /TSI 3563 or equivalent system	PSP, MDB/QCC	ASRC, DEC	Jan. 2001 – Dec. 2003	5-min	Daily
<b><i>Meteorological Measurements</i></b>					
Wind speed and direction, temperature, barometric pressure, relative humidity	PSP, WFMS, MDB, SB, QCC	DEC,ASRC	July 2000 – Oct. 2004	5-min	Daily

\*Sites -

Whiteface Mountain Summit and Lodge: WFMS, WFML  
 Pinnacle State Park: PSP  
 Mable Dean Bacon: MDB or comparable Manhattan site  
 I.S. 52 South Bronx: SB or comparable South Bronx site  
 Queensborough Community College: QCC or comparable  
 Queens site  
 Northern NJ site to be designated and contingent upon state  
 DEP and EPA cooperation and support

\*\* Operators –

Aerodyne Research, Inc: ARI  
 Atmospheric Sciences Research Center: ASRC  
 Brookhaven National Laboratories: BNL  
 NYS Department of Environmental Conservation: DEC  
 NYS Department of Health: DOH  
 Pennsylvania State University: PSU

**Table 2. PMTACS-NY - New Measurement Technology Deployment**

Measurement Technology/Description	Testing & Evaluation	Operational Status
<p><b>R&amp;P TEOM (modified Low T/dryer)</b>                      A continuous mass monitor based on the tapered element oscillating has been modified to operate at 30°C and sample a de-humidified ambient air stream passed through a Nafion dryer.</p>	<p>Laboratory &amp; Field Evaluation                      QA and SOPs available</p>	<p>To be deployed as part of the enhanced operational network in July 2000</p>
<p><b>R&amp;P Differential Dual ESP TEOM (DDET)</b>                      The instrument is based on the direct mass reading and real-time capability of the TEOM system. A matched pair of TEOM sensors (A and B) is run at ambient temperature. Downstream from a common size selective inlet and ahead of each TEOM sensor is an electrostatic precipitator (ESP). The ESP's are alternately switched on and off and out of phase with each other. Each ESP is on or off for a time period, Δt. Frequency data are collected for both TEOM sensors on a continuous basis. The effective mass is the mass that is calculated from the frequency of the TEOM sensor including all sources that affect the frequency during the given time period. The difference between the effective masses of the TEOM A and B sensors provides a direct measure of the non-volatile and volatile component of particle mass collected during the time interval.</p>	<p>Laboratory &amp; Field Evaluation                      QA and SOPs to be developed</p>	<p>To be deployed as part of the enhanced operational network in July 2001</p>
<p><b>R&amp;P 8400NS (PM2.5 Nitrate &amp; Sulfate Analyzer)</b>                      This automated monitor for semi-continuous measurement of nitrate and sulfate is based on the method of Stolzenburg and Hering (1998, 1999). Particles are collected by a humidified impaction process and analyzed in place by flash vaporization. The approach is based on the manual method that has been used for over twenty years to measure the size distribution of sulfate aerosols (Hering and Friedlander, 1982). In the new instrument design, particle collection and analysis have been combined into a single, integrated collection and vaporization cell, allowing the system to be automated. Particles are humidified prior to impaction to eliminate the rebound of particles from the collection surface without the use of grease (Winkler, 1974 and Stein et al 1994). Interference from vapors such as nitric acid is minimized by use of a denuder upstream of the humidifier. The flow system is configured such that there are no valves on the aerosol sampling line. Analysis is done by flash-vaporization with quantitative detection of the evolved gases. For sulfate the evolved gases are analyzed for SO<sub>2</sub>, as described by Roberts and Friedlander, (1974). For nitrate the evolved vapors are analyzed for nitrogen oxides (Yamamoto and Kosaka,1994).</p>	<p>Laboratory &amp; Field Evaluation                      QA and SOPs available (using liquid standards). Laboratory/field aerosol calibration system must be developed for generating known quantities (number/size) of nitrate/sulfate aerosols.</p>	<p>To be deployed as part of the enhanced operational network in July 2000 and 2001</p>

<p><b>Aerodyne Research, Inc. (AMS)</b>          Ambient aerosol particles in the size range 0.05 to 2 to 5 micrometers are focused into a high vacuum system. Particle velocity measurements determine particle aerodynamic diameter. Volatile and semivolatile chemical components are thermally vaporized and detected via electron impact ionization quadrupole mass spectrometry. Detection sensitivity for the base system corresponds to aerosol loading of 0.1 to 1 microgram/m<sup>3</sup>, depending on the molecular mass interferences and background levels.</p>	<p>Laboratory &amp; Field Evaluation/Intercomparison          Research Method: QA and SOPs under development.          Laboratory/field aerosol calibration system must be developed for generating known quantities (number/size) of aerosols of known chemical composition.</p>	<p>To be deployed as part of intensive study programs in summer of 2001 and winter 2003</p>
<p><b>BNL Single Particle Laser Ablation Time of Flight Mass Spectrometer (SPLAT-MS)</b>          Designed to be a universal tool for characterizing the size and composition of individual aerosols from ~10 nm up to tens of micrometers. It utilizes two continuously operative detection modes; VUV photoionization and more conventional light scattering for small and large particle detection respectively. These will be used to synchronize the ablation laser with the particle's arrival for all sizes. Ambient aerosols are focused by the aerodynamic lens system, and accelerated during supersonic expansion through a nozzle to velocities between 100 and 400 m/sec, depending on particle size. Two stages of optical detection are used to indicate the presence of particles larger than 100 nm and for velocity/size determination. To maximize the contrast between particle and gas, the signal is integrated for ~1 microsecond and a requirement for a coincidence between the two laser beams. A continuous VUV light source is used for nanoparticle charging by photoemission and electron detection allows detection and size characterization for particle smaller than 100 nm. An excimer laser is used to ablate particles and generate ions. Operating an excimer laser at 157 nm the system allows in-resonance particle ionization as opposed to off-resonance process for longer wavelengths. A Reflectron time of flight mass spectrometer is used for single particle composition analysis.</p>	<p>Field Evaluation/Intercomparison          Research Method: QA and SOPs under development.          Laboratory/field aerosol calibration system must be developed for generating known quantities (number/size) of aerosols of known chemical composition.</p>	<p>To be deployed as part of intensive study programs in summer of 2001 and winter 2003</p>

<p><b>Aerodyne Research, Inc. (TILDAS)</b>        The tunable diode laser system for cross-road vehicle measurements of motor vehicle exhaust gases uses infrared laser differential absorption spectroscopy to determine the absolute fractional absorption by the gaseous medium between the laser source and a remotely placed retro-reflector mirror system. Spectroscopic constants of the gases of interest are applied to the measured fractional absorption to calculate the pertinent absolute column densities. Multiple species concentrations are determined by spatially combining two laser beams from separate laser diodes. Ratios of gases, such as NO/CO<sub>2</sub>, may be used to directly determine the emission indices for individual motor vehicles at highway speeds. A 3σ detection limit of ~ 9 ppm with a measurement precision as small as 3 ppm for NO in the vehicle exhaust have been demonstrated. The system is capable of measuring small molecules including NO, NO<sub>2</sub>, N<sub>2</sub>O, HONO, NH<sub>3</sub>, CO, H<sub>2</sub>CO, and SO<sub>2</sub> using different laser diodes. The time resolution of 0.02 seconds is sufficient to resolve the plumes from individual automobiles. The range of greater than 100 meters is sufficient to make measurements across multiple lane highways without impeding traffic flow. Extended ranges up to 1 km may be used with longer time averaging to obtain integrated column measurements of urban pollutants using open-path infrared absorption. A more detailed description of the instrument may be found in (Nelson, et al., 1998); (Jiménez, et al., 1999); and (Nelson, et al., 1999).</p>	<p>Field Evaluation        QA and SOPs available</p>	<p>To be deployed as part of intensive study programs in summer of 2001 and winter 2003</p>
<p><b>Aerodyne Research, Inc. Mobile Laboratory</b>        The mobile laboratory has a series of sensitive, specific, real-time (~1 second response) sensors for aerosol and ozone precursor trace gases and fine particulates; a global positioning system (GPS); and a central data logging computer. Specifically, the sensors include: an ARI two-color tunable infrared laser differential absorption spectrometer (TILDAS), capable of measuring between 2 and 4 trace gases simultaneously, such as carbon monoxide (CO), nitrogen oxides (NO, NO<sub>2</sub>), nitrous acid (HONO), formaldehyde (CH<sub>2</sub>O), and sulfur dioxide (SO<sub>2</sub>); a Licor NDIR instrument to measure carbon dioxide (CO<sub>2</sub>); a aerosol mass spectrometer (AMS) to measure particulate number densities, size distributions (0.05 to ~2.5 μm), and volatile and semi-volatile chemical composition as a function of particle size. CN counter to measure particulate number densities (0.003 to 1). The real-time instruments have been described in detail previously [see Lamb et al. (1995), Nelson et al., (1996), Zahniser (1995), and Jayne et al., 1999]. Data from the individual instruments are logged on a central computer, enabling all data streams to be stored synchronously. A Trimble GPS system with real-time differential correction collects position information at 1 Hz.</p>	<p>Field Evaluation        QA and SOPs for individual instrument systems available or under development        QA field experiments (1-2 days) during which calibration/ intercomparisons performed with collocated systems measuring the same chemical parameter.</p>	<p>To be deployed in 2000 as part of the CEPEX and in the summer of 2001 intensive study program. Deployment in the winter 2003 intensive study will be optional and dependent on additional cost sharing resources</p>



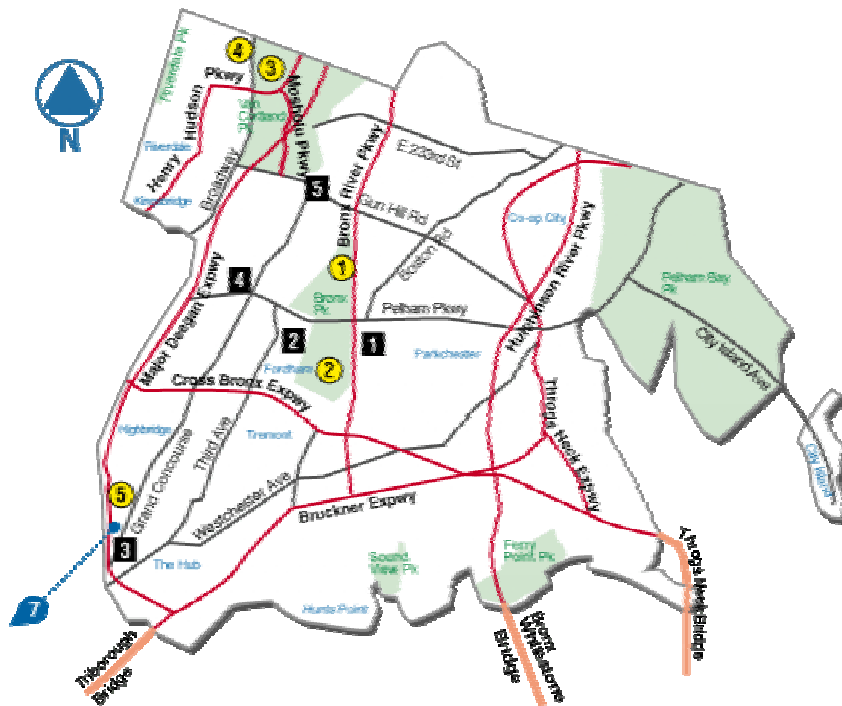
<p><b>AEROLaser 1401 &amp; Texas Tech H<sub>2</sub>CO Analyzers</b>        Gaseous formaldehyde is scrubbed from ambient air into solution with the reagents 2,4-pentanedione and ammonium acetate (Dasguta et al., 1988) to form stoichiometrically the product derivative 3,5-diacetyl 1,4-dihydrolutidine (DDL). DDL is detected via fluorescence using 254nm radiation from a Hg lamp. The fluorescence signal is calibrated against known concentrations of formaldehyde generated by an internal permeation source and may also be calibrated using external liquid standards.</p>	<p>Field Evaluation/Intercomparison        QA and SOPs available or under development</p>	<p>To be deployed as part of intensive study programs in summer of 2001 and winter 2003</p>
<p><b>NYS Department of Health HONO/HNO<sub>3</sub> Analyzer</b> - The gaseous analytes are sampled by two coil samplers. The scrubbed nitric acid in channel 2 is converted to nitrite using a Cd-reductor: <math>\text{NO}_3^- + \text{Cd}_{(s)} + 2\text{H}^+ \rightarrow \text{NO}_2^- + \text{Cd}^{2+} + \text{H}_2\text{O}</math>. The nitrite in the two channels is converted to a highly light-absorbing azo dye by a two step derivatization with sulfanilamide (SA) and N-(1-naphthyl)-ethylenediamine (NED), which proceeds in on-line derivatization coils with 5 min. The derivative azo dye is preconcentrated on two on-line C18 reversed-phase cartridges on a 10-port injection valve, and is separated with a reversed-phase C<sub>18</sub> HPLC column and detected with an absorbance detector at 540 nm. The auto-injection valve is controlled by a PC-based HPLC software and the valve position is switched every 5 min, resulting in a 10-min sampling cycle with a 5-min sampling integration time for both channels. The method detection limits are 3 ppt and 10 ppt for HONO and nitric acid, respectively.</p>	<p>Field Evaluation/Intercomparison        QA field experiments (1-2 days) during which calibration/ intercomparisons performed with collocated systems measuring the same chemical parameters.</p>	<p>To be deployed as part of intensive study programs in summer of 2001 and winter 2003</p>

<p><b>Penn State University GTHOS (Ground-based Tropospheric Hydrogen Oxides Sensor)</b>        GTHOS uses laser-induced fluorescence (LIF) to measure OH and HO<sub>2</sub> simultaneously (Mather et al., 1997). OH is both excited and detected with the A<sup>2</sup>Σ<sup>+</sup> (v'=0)→X<sup>2</sup>Π (v''=0) transition near 308 nm. HO<sub>2</sub> is first reacted with reagent NO to form OH and is then detected with LIF. The ambient air is pulled by a vacuum pump through a small upward facing inlet (1mm diameter), down a short, sampling tube, and into two low-pressure multipass White cell detection cells. The first cell is for OH and the second for HO<sub>2</sub>. Detection occurs in each detection cell at the intersection of the airflow, the laser beam, and the detector field-of-view. The pulsed laser has a 3 kHz repetition frequency, 28 ns long pulses, and produces about 10-20 mW of tunable UV near 308 nm. The laser is tuned on and off resonance with the OH transition in a 20-second cycle; the OH fluorescence is the difference between the signal on resonance and the signal off resonance. The detector is gated to detect the OH fluorescence after each laser pulse has cleared the detection cell. A reference cell containing OH indicates when the laser is on and off resonance with the OH transition. The absolute uncertainty, which is determined in the laboratory and maintained with power and signal monitors and weekly <i>in situ</i> calibrations is ±40%, although planned advances in the calibration technique over the next year should reduce this uncertainty to ±25%. The minimum detectable mixing ratio (S/N=2, 60 seconds) is 0.015 pptv (3.5x10<sup>5</sup> cm<sup>-3</sup>) for OH and 0.06 pptv for HO<sub>2</sub>. Because the signals obey Poisson statistics, the OH detection limit is about 10<sup>5</sup> cm<sup>-3</sup> in 10 minutes.</p>	<p>Field Evaluation</p> <p>Research Method: QA and SOPs are under development; no direct calibration standard exists.</p> <p>Previous field tests include: PROPHET summertime intensive in 1998 and Nashville, TN as part of the 1999 Southern Oxidant Study (SOS).</p>	<p>To be deployed as part of intensive study programs in summer of 2001 and winter 2003 and in the summer 2002 at Whiteface Mountain.</p>
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In the next several years, a major opportunity exists to evaluate the impact of two emission control strategies on the ambient air in New York City, resulting from the current phased conversion of the Metropolitan Transit Authority (MTA) bus fleet to compressed natural gas (CNG) and the prototype testing of new emission control technology, continuously regenerating technology (CRT), for heavy duty diesel.

The introduction of two emission reduction technologies in New York City (CNG fueled buses and clean diesel vehicle program through CRT) into the operational environment provides an outstanding target of opportunity to evaluate and assess the performance and impact of these control technologies while in use. The CEPEX studies proposed will be designed to monitor on-road vehicle emissions of the CNG/CRT modified buses and that of the traditional diesel-fueled buses to be replaced using open-path roadside remote sensing and a mobile measurement platform. In addition, enhanced fixed-site monitors, as part of the urban PMTACS baseline network, will be used to discern changes in ambient air quality as a result of the implementation of these emission control technologies.

The first prototype study will be carried out in the vicinity of the CNG bus depot deployment currently under discussion with the New York Metropolitan Transit Authority. A site identified and under consideration in Brooklyn (see Figure 3 below) will be studied using three distinct measurement components.



- § An open path tunable infrared laser differential absorption spectrometer (TILDAS) remote sensing system will be deployed across one or more roadways representative of the routes traveled by the MTA CNG bus fleet. The TILDAS system will be configured to monitor CO<sub>2</sub>, CO, NO under one set of experiments and CO<sub>2</sub>, H<sub>2</sub>CO and SO<sub>2</sub> under a second set of experiments.
- § A mobile measurement platform equipped to perform real time mobile measurements of multiple trace gases and particulate with stationary trace gaseous species, particulate and meteorological data collection in combination with a global positioning system. The instrumented mobile laboratory provides real time, fast response (1 sec), simultaneous measurement of multiple trace gases as well as particulate matter under normal driving conditions and can map background pollutant levels as well as characterize on-road emissions from selected mobile sources. Fast response measurements allow the detection of discrete changes in pollutant levels with location and the opportunity to react immediately to probe further into those changes. In this case the mobile measurement system will be used specifically to follow standard diesel buses and their compressed natural gas replacements along their operational bus routes and at stations sampling their exhaust emissions for CO, NO, H<sub>2</sub>CO and CO<sub>2</sub> and aerosol chemical species and ultrafine CN. The measured species will be normalized to fuel consumption (CO<sub>2</sub> output) allowing emissions to be determined as a function of time and by vehicle type; revealing as well, dependencies on operating and environmental parameters such as speed, grade, and ambient temperature. The experiments provide the opportunity to directly measure emission changes in CO, NO, H<sub>2</sub>CO, aerosol chemical composition and ultrafine CN for standard in-use vehicles and their new control technology counterparts.
- The mobile measurement system will also be deployed for concentration surveys to identify and map major emission sources in the metropolitan area. Concentration surveys include a coarse set of traverses in an area to identify major emission sources, while concentration maps are a fine set of traverses designed for more detailed identification of source location or trends in concentration with location. The concentration data are combined with the GPS position record to create a "map" of trace gas concentrations. The data of measurement parameters and instrumentation available in the mobile laboratory is summarized in Table 2.
- § Fixed site measurements of SO<sub>2</sub>, CO, NO, NO<sub>2</sub>, H<sub>2</sub>CO, PM<sub>2.5</sub>, SO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, C, ultrafine CN as part of the PMTACS-NY urban network will be evaluated to determine if emission perturbations are observable in the overall ambient urban air quality.

In addition, the NYS DEC Emissions Division is performing chassis dynamometer studies to measure source profile of in-use heavy-duty diesel vehicles in NYC. The studies are specifically interested in the characterization of the physical and chemical makeup of PM using advanced measurement techniques. These include: scanning electron microscopy; R&P Model 5100 carbon analyzer for PM characterization on individual vehicle/engine tests; Eco-Chem PAS Analyzer with 1,000-to-1 variable dilution system for detection of PM-bound poly-nuclear aromatic hydrocarbons; Dekati Ltd.-Electrical Low Pressure Impactor (ELPI) for PM aerodynamic size measurements from 30 nm-20 microns; Thermo-Systems Inc.-Scanning Mobility Particle Sizer (SMPS) for PM mobility size generation and measurement, and real-time particle size distributions from 5-1,000 nm; E-Flow total exhaust flow measurement instrument for application to ultra-low emission vehicle measurements using only raw exhaust without dilution Sensors Inc., Lambda Master for real-time vehicle combustion air/fuel analysis.

### **1.4.3 Project Schedule**

Scheduling of major tasks to be performed in the PMTACS-NY program are shown in Tables 3.A and 3.B which are broken out for years 2000-2001 and 2002-2004 respectively. The deployment schedule for the diverse measurement platforms and systems is presented in Table 4.

**Table 3.A PMTACS-NY Project Schedule 2000 – 2001**

Year	2000				2001			
	1 <sup>st</sup> Qrt	2 <sup>nd</sup> Qrt	3 <sup>rd</sup> Qrt	4 <sup>th</sup> Qrt	1 <sup>st</sup> Qrt	2 <sup>nd</sup> Qrt	3 <sup>rd</sup> Qrt	4 <sup>th</sup> Qrt
Task:	1 <sup>st</sup> Qrt	2 <sup>nd</sup> Qrt	3 <sup>rd</sup> Qrt	4 <sup>th</sup> Qrt	1 <sup>st</sup> Qrt	2 <sup>nd</sup> Qrt	3 <sup>rd</sup> Qrt	4 <sup>th</sup> Qrt
Planning And Coordination Meetings	→				→			
Preparation of QA Project Plan		→						
Order major permanent equipment for Supersite network	→							
Build NO <sub>2</sub> measurement system (Photolytic Titration)	→	→						
Initiate operation of urban monitoring sites for criteria pollutant measurements, (see Table 1 for deployment details)		→	→	→	→	→	→	→
Site renovations and power upgrades as needed	→	→	→					
Initiate enhanced measurement systems: (see Table 1 for deployment details)			→	→	→	→	→	→
CEPEX site selection/ preparation (TILDAS) and selection of deployment routes for mobile laboratory		→	→					
CEPEX-NYC intensive measurement studies			→				→	
QA experiments/intercomparison studies		→				→		
Special Intensive Field Studies							→	
Data quality assessment and management of site measurements			→			→		
Annual Data Summary Report					→			
Presentation and Publication of Scientific Findings and Results					→			

**Table 3.B PMTACS-NY Project Schedule 2002 - 2004**

Year	2002				2003				2004			
	1 <sup>st</sup> Qrt	2 <sup>nd</sup> Qrt	3 <sup>rd</sup> Qrt	4 <sup>th</sup> Qrt	1 <sup>st</sup> Qrt	2 <sup>nd</sup> Qrt	3 <sup>rd</sup> Qrt	4 <sup>th</sup> Qrt	1 <sup>st</sup> Qrt	2 <sup>nd</sup> Qrt	3 <sup>rd</sup> Qrt	4 <sup>th</sup> Qrt
Planning And Coordination Meetings	→				→	→			→			
Data Assessment and Analysis Workshop	→								→			
Continue operation of urban monitoring sites for criteria pollutant measurements: (see Table 1 for deployment details)	→											
Continue operation of enhanced measurement systems: (see Table 1 for deployment details)	→											
CEPEX-NYC Intensive Measurement Studies							→					
QA experiments/intercomparison studies		→				→						
Special Intensive Field Studies							→					
Data quality assessment and management of site measurements	→			→			→			→		
Annual Data Summary Report	→								→			→
Final Quality Assurance Report												→
Project Final Report												→
Presentation and Publication of Scientific Findings and Results					→				→			→





**Table 4. PMTACS-NY "Project at a Glance" (continued)**

<i>Project Sites</i>	<b>Major Activities by Year</b>				
	<b>2000</b>	<b>2001</b>	<b>2002</b>	<b>2003</b>	<b>2004</b>
<b>Upstate/Regional:</b>					
Whiteface Mountain	----- Deploy and operate research grade baseline measurements <sup>2</sup> ----->				
	----- Deploy and operate PM enhanced measurements <sup>4</sup> ----->				
	-OH/HO <sub>2</sub> <sup>3</sup> ->				
Special Studies:	-- R&P 8400NS Field Testing & Evaluation <sup>7</sup> ----->				
	--Low T/Dryer TEOM Field Testing & Evaluation <sup>8</sup> ----->				
	-- R&P DDET Field Testing & Evaluation <sup>9</sup> ----->				

<sup>a</sup> Special intensive studies will be performed at one of the three urban sites identified in NYC, final selection will be made early in 2000 in consultation with NYSDEC, EPA and special study collaborators.

<sup>1</sup> Measurements to be performed and specifications are summarized in Table 1.

<sup>2</sup> Enhanced measurements to be performed and specification are summarized in Table 1 and details of the new technologies are described in Table 2.

<sup>3</sup> PSU GTHOS OH/HO<sub>2</sub> intensive study measurement, details of the new technology are described in Table 2.

<sup>4</sup> Single particle aerosol chemical composition as a function of size, intensive study measurement, details of the new technologies are described in Table 2

<sup>5</sup> Aerosol size distribution intensive study measurements

<sup>6</sup> NYSDOH HONO/HNO<sub>3</sub> Analyzer intensive study measurement, details of the new technology are described in Table 2.

<sup>7</sup> PM2.5 nitrate and sulfate analyzer under commercial development by R&P, details of the new technology are described in Table 2, deployment beyond 2001 assumes acceptable performance based on 2000-2001 field testing and evaluation.

<sup>8</sup> PM2.5 T&RH modified R&P TEOM, details of the new technology are described in Table 2, deployment beyond 2001 assumes acceptable performance based on 2000-2001 field-testing and evaluation.

<sup>9</sup> PM2.5 Differential Dual EPS TEOM, under commercial development by R&P, details of the new technology are described in Table 2, deployment beyond 2001 assumes acceptable performance based on 2000-2001 field testing and evaluation.

<sup>10</sup> Photochemical Assessment Monitoring Station, measurements to be performed and specifications are summarized in Table 1.

<sup>11</sup> Aerodyne Research, Inc mobile laboratory intensive study measurements, details of the new technology are described in Table 2.

d remote measurements; details of the new technology are described in Table 2.

## **1.5 Personnel Qualification**

PMTACS-NY deploys a multitude of continuous and discontinuous measurement technologies ranging from standard instruments for measuring criteria pollutant to new and yet unproven measurement technologies operating in the research mode. A designated technician or scientist (depending on the complexity of the instrumentation) will be responsible for each instrument operating at a particular site or in the laboratory. The appropriate SOP will name the person responsible for this task.

## **1.6 Training Required**

The personnel involved in measuring ambient pollutants as envisioned in this project have gained extensive experience in past experiments and are familiar with and will follow all SOPs and RPs. Additional training programs are therefore not scheduled at this time.

## **2.0 Management Assessment**

### **2.1 Assessment Responsibilities and Types**

The scientific steering committee, made up of participating principal investigators, cost sharing sponsors and a select group of experts representing various stakeholders will meet once a year to review program progress, opportunities and options for mid-course corrections as needed.

Dr. Demerjian will chair the scientific steering committee. To help assure effective interactions and collaboration with the health effects community, directors of three EPA PM Health Effects Research Centers and the director of the NYS DOH asthma study have indicated a willingness to serve on a PMTACS-NY scientific steering committee. The final makeup of the Scientific Steering Committee will be decided upon further discussions with PM Health Center directors and in consultation with EPA. We anticipate that collaboration with the Health Centers will provide value added research opportunities and benefits to both our programs. A proposed scientific steering committee is identified below.

Dr. Demerjian and a designated DEC scientist and a rotating member of the steering committee will also serve as members of the EPA Supersite Liaison Team. This group under the terms of the cooperative agreement will meet twice a year with EPA to review research progress and develop plans to coordinate activities amongst the Supersite programs.

### **Proposed Scientific Steering Committee**

Kenneth L. Demerjian, Chair	University at Albany
William Brune	Penn State University
Phil Galvin	NYS DEC
Dick Gibbs	NYS DEC
Phil Hopke	Clarkson University
Liquat Husain	NYS Department of Health
Janet Joseph	NYSERDA (Cost Sharing Sponsor)
Chuck Kolb	Aerodyne Research Inc.
Petros Koutrakis	Harvard School of Public Health - (Health Effects Liaison)
Morton Lippman	New York University - (Health Effects Liaison)
Nancy Kim	NYS Department of Health - (Health Effects Liaison)
Volker Mohnen	University at Albany - (Program QA Officer)
Harvey Patashnick	Rupprecht and Patashnick Co.
John Zamurs	NYS Department of Transportation

### **2.2 Assessment Criteria**

The management of PMTACS-NY is committed to achieving and maintaining the highest level of quality possible throughout the performance of the program. The data generated by PMTACS-NY will be both technically sound, and, where appropriate, legally defensible. The former is an obvious requirement but is not, in and of itself, sufficient to defend the data against and adversarial inquiry. The latter will address, through documentation, the level of quality achieved. The quality of PMTACS-NY will be maintained not only through the use of data quality objectives (DQOs), which place numerical limits on the quality control indicators, but also through the use of subjective science quality objectives, which evaluate both the PMTACS-NY program and individual research activities. Where appropriate the quality assurance program for PMTACS-NY will adhere to the guidelines given in 40 CFR, Part 58 for a State and Local Air Monitoring Station (SLAMS).

Science quality objectives are used to provide a subjective evaluation of the quality of the research projects and goals of the PMTACS-NY study. Evaluation of all research activities by a peer review/scientific steering committee for the following will assure that the "science" provided by PMTACS-NY is of the highest quality possible:

1. The clarity and precision with which statements of hypotheses are formulated;
2. The logical methods of inference that are used in analysis and interpretation of data and evidence;

3. The rigor of proof that is used and the criteria by which judgements are formulated about cause-and-effect relationships;
4. The processes by which consensus judgements are developed from diverse pieces of data and evidence;
5. The quality of organizational arrangements and effectiveness in use of available human resources, financial resources, in kind resources, scientific resources, data processing resources, information transfer and display resources, and communication resources;
6. The precision and clarity with which statements of scientific findings are formulated and articulated in publications, in scientific meetings, and in public meetings; and
7. The timeliness and extent to which available data, evidence, inferences, and technical and scientific findings are understood by decision makers in industry, government, trade associations, public interest groups, and citizens in various sectors of society.

For assessing the data quality from measurement systems for which FRMs or EPA methods exist a set of formal Technical Systems Audits (TSAs) and Performance Evaluations (PE s) will be performed annually at all sites by the auditing group of the New York State Department of Environmental Conservation (DEC). The results of these formal audits will be forwarded to the Project QA Officer who will include them together with suggested corrective actions, if necessary in the annual QA report to the management.

New measurement technologies, for which no SOP's exist at this time, will be assessed and documented by the Project QA Officer on a case by case basis through specially designed QA experiments prior to the field experiments (including instrument intercomparison and challenges with calibration substances).

### **2.3 Assessment Documentation**

An annual quality assessment report will be prepared by the Project QA Officer detailing the results of these QA experiments and assessment activities and delivered to the PMTACS-NY PI on March 1 following each completed project study year. Key findings of the quality assessment report will be included in the respective EPA quarterly report to the EPA Project Officer.

### **3.0 Project Implementation**

#### **3.1 Project Responsibilities**

The PMTACS-NY program is directed by Dr. Kenneth L. Demerjian, Atmospheric Sciences Research Center, University at Albany in collaboration with scientists at the University at Albany (Drs. G. Lala, V. Mohnen, J. Schwab, U. Roychowdhury) and in the Department of Environmental Conservation (Drs. Phil Galvin, R. Gibbs, T. Lanni, and D. Felton) and with participating project team members (Aerodyne Research, Inc., C. Kolb; Aerosol Dynamics, Inc., S. Hering; Brookhaven National Laboratories, L. Newman; Clarkson University, P. Hopke; Penn State University, W. Brune; NYS Department of Health, Drs. Husain, Zhou and Kim; Rupprecht and Patashnick Co., H. Patashnick).

The ASRC/University at Albany and NYS DEC have had a long standing Memorandum of Understanding and a demonstrated record of collaboration in instrumentation development and field measurements. The ASRC currently has collaborative measurement programs with NYS DEC underway at Whiteface Mountain, Pinnacle State Park and an urban site in New York City.

In addition, the program offers many opportunities for research collaboration with EPA scientists. These will likely include collaboration: 1) in the deployment, testing and evaluation of new measurement technologies both in the laboratory and in the field (P. Solomon, W. McClenny, J. Homoya, and J. Rice); 2) in the data analysis and interpretation of the rich data sets to be collected under the subject program (S. Eberly, K. Schere and J. Ching); and/or 3) collaboration in research and development activities underway in our PM analytical and aerosol generation, characterization and calibration standards facilities (P. Solomon and J. Lewtas). During the first quarter of this program Dr. Demerjian will meet with the named scientists and others identified to explore these opportunities and/or others that are of mutual interest and benefit to the proposed research program.

Dr. Demerjian, has overall responsibility for managing the program and coordinating the activities of external PIs and University at Albany and participating DEC personnel. The Scientific Steering and the EPA Supersite Liaison committees will review research progress, identify new research opportunities and emerging measurement technologies and provide coordination with other Supersite activities.

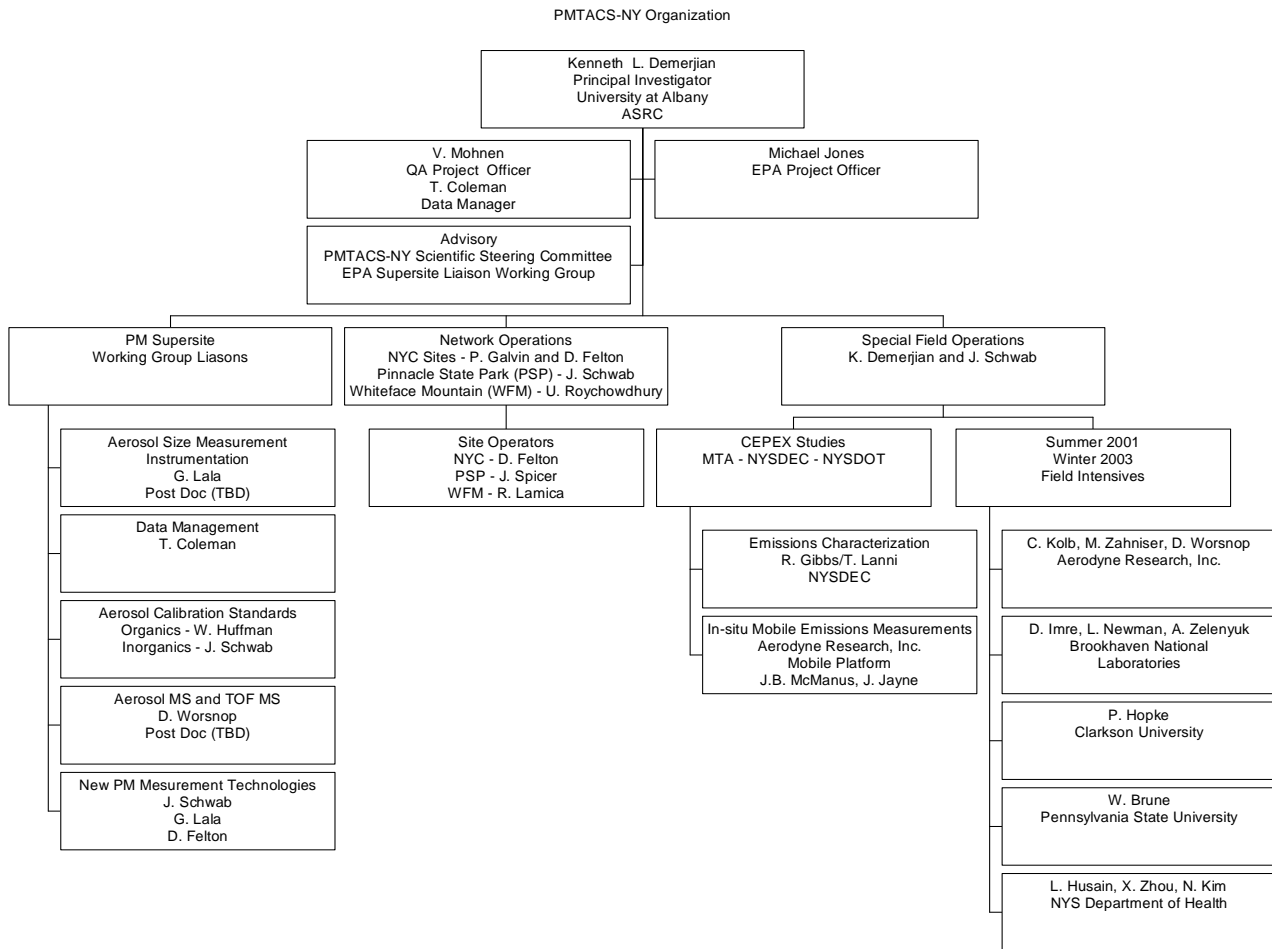
All QA/QC related matters are coordinated by the QA Project Officer (Prof. V.A. Mohnen), who reports directly to the Principal Project Director (Prof. K.L. Demerjian). The QA officer's duties include, but are not limited to:

- Assist Principal Investigators with development of Standard Operating Procedures and Reference Protocols, as needed. Upon completion, assess these documents and recommend to

the Project Director their acceptance as an official PMTACS-NY QA-document.

- Review the Annual Quality Assessment Reports detailing the quality management and assessment activities conducted during the previous calendar year and submitted to the Project Director by each Principal Investigator. In particular, review all data relating to the performance criteria. Based on this review and additional information requested by the QA-officer, if needed, prepare within one month an annual quality assessment report for the Project Director.
- Review all audit results as soon as available, notify the Project Director immediately of problems and recommend corrective actions if required.
- Perform additional QA related assessments at any time as requested by the Project Director to assure him that the PMTACS-NY QA-program is operational and effective.

Organization of project personnel and their responsibilities are identified in Figure 4 below.



## 3.2 Project Design Criteria

The PM2.5 Technology Assessment and Characterization Study in New York (PMTACS-NY) should be viewed as a "Supersite Network" consisting of five highly enhanced measurement operations. Two regional and three urban sites make up the network that will operate a series of advancement measurement technologies over the course of this five-year program. The two rural sites, Whiteface Mountain and Pinnacle State Park, are operational research measurement sites with a substantial historical data record for a variety of atmospheric trace gases. In 2000 these two sites will be enhanced to perform series of PM2.5 related measurement that are of direct benefit to the PMTACS goals and objectives. These rural sites are strategically located to monitor aged air masses impacted by major metropolitan areas and large industrial source regions with travel times of 2 to 4 days. The urban site selection process considered the historical data record, the representativeness of socioeconomic areas, existing or planned health related studies in the area and operational logistics associated with measurement enhancements. A brief description of the five sites is presented below with the measurement parameters, deployment schedules and operational specifications for sites provided in Table 1.

### 3.2.1 Regional Background Sites:

**Whiteface Mountain** (44.4°N, 73.9°W) is located in the Adirondack Mountains of northern New York at an elevation of 1500 m and is forested from the base to ~ 1400 m altitude. A conifer forest region from ~ 900 m to 1400 m is made up of balsam fir mixed with an increasing percentage of red spruce with increasing elevation. The summit is ~ 90 m above the tree line. Measurement facilities are maintained at the lodge facility at 600 m, situated in clearing with a deciduous forest canopy on the eastern shoulder of the mountain and the summit facility housed in a three-story observatory at the mountaintop. The nearest major urban centers are Montreal ~ 130 km to the north; Albany ~ 180 km to the south; Syracuse ~ 220 km to the southwest.

**Pinnacle State Park** (42.1°N, 72.2°W) in Addison, NY is located in a rural area in the New York/Pennsylvania Twin Tiers Region at an elevation of 515 m. The site is located in an open clearing on Orr Hill, which is ~ 12 m below and about 100 m east of the highest hill in the park. The closest trees are ~ 50 m away and the surrounding areas include a 50 acre pond, pastures, undeveloped state forest lands and a 9-hole golf course. The instrumentation is housed in a newly acquired Eco shelter, with a 10 m meteorological tower installed at the site. The village of Addison (pop. ~ 1,800) is 4 km to the northwest and the town of Corning (pop. ~ 12,000) is 15 km to the northeast.

### 3.2.2 Urban Core Sites

**Mable Dean Bacon High School** (40.7°N, 74.0°W) in Manhattan, NY is located at 240 Second Avenue (between 14<sup>th</sup> and 15<sup>th</sup> Streets). The gas monitoring systems are located on the sixth

floor roof top room. Gases are sampled from a 3" glass manifold that extends through the roof of the room above the highest physical obstruction on the roof. PM monitoring systems are placed outside on a tier platform above the main roof surface. Substantial space is available on the main roof for additional instrumentation, with good field of view and fetch. Shelter space and upgrades in power will be required to deploy additional instrumentation. Enhanced PM chemical species data are being collected at the site in 1999 as part of NYS DOH asthma study. [Note: this school site may undergo renovation in the summer of 2000; two alternate Manhattan sites (Hunter College and PS 59) have been identified should the Mable Dean Bacon HS monitor site be closed down].

**M.S. 52** (40.8°N, 73.9°W) in South Bronx, NY is located at 681 Kelly St. The gas monitoring systems are located in Room #342 on the third floor on the north side of the school. Gases are sampled from a 3" glass manifold that extends through a window and approximately one meter above roof level. PM monitoring systems are placed outside on the roof. Substantial space is available on the roof for additional instrumentation, with good field of view and fetch. Shelter space and upgrades in power will be required to deploy additional instrumentation. Enhanced PM chemical species data are being collected at the site in 1999 as part of NYS DOH asthma study [Note: this site was moved from an adjacent school location (IS 155 - 470 Jackson Ave) on July 14, 1999].

**Queensborough Community College** (40.7°N, 73.8°W) in Queens, NY is located at 56<sup>th</sup> Avenue and Springfield Blvd. PAMS gas monitoring systems are located in room 21 on the second floor on the north side of the Oakland Building. Gases are sampled from a 3" glass manifold that extends through a window and approximately 1 meter above the peak of the roof. PM monitoring systems are placed outside on an adjacent rooftop approximately 100 meters across from and approximately 50 meters below the PAMS inlet. Substantial space is available on the PM systems rooftop for additional instrumentation, with a good field of view and fetch. A brief description of each new measurement technology to be deployed under PMTACS-NY, planned testing and evaluation, their QA and expected operational status is summarized in Table 2. [Note: an alternate site is also being considered on the campus of Queens College, Queens, NY].

### **3.3 Data Quality Indicators (DQOs and MPC)**

It is the policy of the Supersite participants that all ambient air quality monitoring and research measurement data generated for internal and external use shall meet specific qualitative requirements, referred to as data quality objectives (DQOs). The DQO process is a systematic planning process to be performed by any project that receives EPA/governmental funding as stated in "EPA Quality Manual for Environmental Programs". The DQO process is detailed in US-EPA's "Guidance for the Data Quality Objectives Process, EPA QA/G-4. Measurement performance criteria (MPC) are the set of criteria for each measurement system that are used to achieve the DQO's. These vary from instrument to instrument. For some instruments, i.e., the



PM2.5 Federal Reference Method samplers and most gaseous instruments, the MPC are known due to the extensive testing that has been performed. However, there will be many instruments employed during the study where the MPC will not be known. It will be part of the principle investigators and the Quality Assurance Managers responsibility to attempt to determine through quality assurance experiments, the individual MPC.

It is the goal of EPA and the PMTACS-NY to minimize expenditures related to data collection by eliminating unnecessary, duplicative, or overly precise data. At the same time, the data collected should have sufficient quality and quantity to support defensible decision-making. The most efficient way to accomplish both of these goals is to establish criteria for defensible decision making before the study begins, and then develop a data collection design based on these criteria. By using the DQO Process to plan environmental data collection efforts, EPA and PMTACS-NY can improve the effectiveness, efficiency, and defensibility of decisions in a resource-effective manner.

The DQOs are then used to develop a scientific and resource-effective data collection design. It provides a systematic procedure for defining the criteria that a data collection design should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision errors for the study, and how many samples to collect. By using the DQO Process, the EPA and PMTACS-NY will assure that the type, quantity, and the quality of environmental data used in decision making will be appropriate for the intended application. In addition, the Agency will guard against committing resources to data collection efforts that do not support a defensible decision.

The DQO Process consists of seven steps as outlined in Mikel, 1999. The output from each step influences the choices that will be made later in the Process. During the first six steps of the DQO Process, the planning team developed the decision performance criteria that were used to develop the data collection design. The final step of the Process involves developing the data collection design based on the DQOs.

The seven steps of the DQO process are:

- 1) State the Problem
- 2) Identify the Decision
- 3) Identify the Inputs to the Decision
- 4) Define the Study Boundaries
- 5) Develop a Decision Rule
- 6) Specify Tolerable Limits on Decision Errors
- 7) Optimize the Design

Each of these steps has been performed to ensure a maximized project.

It is the policy of PMTACS-NY that all ambient air quality monitoring and research

measurement data generated by PMTACS-NY for internal and external use shall be complete, representative, accurate, precise, comparable, and be acceptable by EPA and State agencies for the determination of national air pollution control strategies. Where appropriate QA methods and procedures are lacking, the PMTACS-NY program is committed to the development of such methods and procedures.

The MPC indicators for the Northeast Supersite Experiment will be determined in the usual way for a research project. The typical MPC associated with data measurements are: Precision, Accuracy, Representativeness, Completeness, Estimation of Bias, Minimum Detection Limits (MDLs) and Comparability. These MPC can be measured on most of the instrument and the project as a whole. The MPC will be determined for each individual instrument/system. However, some of the experimental instruments perform analyses are not easily reproducible or cannot be compared against conventional analyzers. Therefore, the Supersite study provides an interesting scenario in terms expanding the relationship of quality assurance and data quality. It is also conceivable that some MPC will be developed during the course of the study. The typical MPC can be used as indicators of error or bias in a data set, however, there are a number of additional indicators that can be documented and can assess the data qualitatively. These are: Inference of Analysis, Intercomparison and Trend Analysis. By using all indicators, the following statements can be made about the quality of the data set:

- The error of data generated shall be quantified using tools and methodologies outlined in this and related documents. This shall be accomplished by performing performance audits against gas phase instruments, accuracy flow checks and Technical System Audits. The QA data collected will be used to document accuracy, precision and bias.
- Data generated shall be of sufficient quality to facilitate intercomparison with differing methodologies measuring the same parameters. The QAM and principle investigators will perform statistical evaluation of data. Intercomparisons will only be performed on ambient data generated in the field.
- All researchers shall strive to provide the maximum quantity of data possible for the duration study to allow for a robust intercomparison of data (data completeness).
- Communication will be encouraged throughout the study. Sharing of Level 0 data is encouraged but not required. Level 0 intercomparisons should help investigators identify instrumentation and operational problems.

Each of the MPC is discussed in detail below.

### ***Accuracy***

The accuracy of the continuous gas monitors will be determined from performance audits

of the individual gas phase instruments. The performance audit will challenge the instrument with standards, from an independent, NIST traceable source not used for calibration, encompassing the operational range of the instrument. A minimum of three data points, including zero will be used to conduct the performance audit. The following equation will be used to estimate the slope, intercept and correlation coefficient. The following equation is to be employed:

$$Y = mx + b \quad (1)$$

Where the audit standard concentration is the independent (x) variable, the instrument reading is the dependent (y) variable, m is the slope, and b is the y intercept, will be used to assess accuracy.

For gravimetric and speciated fine particle samplers, the accuracy will be defined as an accuracy flow check. The estimation of accuracy for this method is:

$$\% \text{ Accuracy} = [(Q_a - Q_m) / Q_a] \times 100 \quad (2)$$

where  $Q_a$  is the flow rate measured using a NIST traceable flow device,  $Q_m$  is the flow rate measured by investigator.

In the case of FRM's, accuracy (total measurement system bias) is determined by collocated audits performed by an independent EPA contractor. Each year 25% of NYSEDC's FRMs are selected to be audited in each calendar quarter by the PM2.5 Performance Evaluation Program. Sites to be audited will be selected by an EPA contractor with the caveat that all sites must be audited within four years. The Performance Evaluation Program Method Compendium is available on the AMTIC website. <http://www.epa.gov/ttn/amtic/pmqa.html>

The accuracy of laboratory measurements will be determined by analyzing an independently prepared reference sample in each batch and calculating the percent recovery relative to the target value. The percent recovery is expected to meet or exceed the acceptance criteria listed in Table 5. When possible, the references will be traceable to NIST standards or based on standards obtained directly from NIST.

### ***Bias***

Due to the unique research nature of many of the measurements to be conducted by Supersite, the situation may arise where primary standards are unavailable to determine bias. In addition, bias of the discrete methodologies can only be determined for the analytical instruments, and does include effects introduced by sample collection and transport. In these instances the determination of bias is the correct action. Bias will be calculated under three distinct situations:

- A primary standard does not exist to determine instrumental accuracy
- The comparison of two discrete methodologies using ambient data
- Comparison two discrete methodologies using ambient data, one of which is a Federal reference method.

When a primary standard method is not available, bias will be calculated using the equation:

$$Bias = 1/n \sum_{i=1}^n [(S - X_i)/S] \cdot 100 \quad (3)$$

where S is the standard value and X<sub>i</sub> is the instrument results of the ith measurement of the standard.

For comparison of two methodologies, neither of which is considered a reference standard or method, bias will be calculated by the equation:

$$Bias = 1/n \sum_{i=1}^n [(M1_i - M2_i)/((M1_i + M2_i)/2)] \cdot 100 \quad (4)$$

where M1<sub>i</sub> and M2<sub>i</sub> are the ith measurement of the two methodologies (M1 and M2) being subjected to comparison. The use of the average of the two methodologies in computing bias recognizes that a primary standard is not available.

If the results of a particular methodology are being compared to a reference method then the following equation:

$$Bias = 1/n \sum_{i=1}^n [(M1_i - M2_i)/M1_i] \cdot 100 \quad (5)$$

where the denominator has been replaced with the ith measurement of the reference method will be used to determine bias.

### ***Precision***

Precision of the continuous gas monitors will be determined from replicate analyses of calibration standards, instrument span check standard and/or precision check standard records. Precision for the GC/FID and GC/MS system will be determined using a multi-component PAMS standard supplied by EPA. A minimum of 5 data points should be used for the precision

to be calculated. Precision should be determined for data time periods between calibrations or other major maintenance periods that may effect the operation performance of the instrument. Precision for filter based instruments will be performed by comparing the percent difference between similar methods. Precision will be determined from the standard deviation using the following equations:

$$STANDARD\_DEVIATION(\sigma) = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}} \quad (6)$$

where  $x_i$  is the experimentally determined value for the  $i^{\text{th}}$  measurement,  $n$  is the number of measurements performed, and  $\bar{x}$  is the mean of the experimentally determined values.

The precision will be determined as percentage of the average concentration of the span check standard or precision check standard using the following equation:

$$\text{Precision} = (1.96 * \sigma / \{x\}_{\text{avg}}) * 100 \quad (7)$$

Where  $\{x\}_{\text{avg}}$  is the average of the span or precision measurements,  $\sigma$  is the standard deviation of the replicate span check standard or precision check standard data. The upper and lower 95% probability limits are set using this statistical test.

Analytical precision within sample batches is assessed by calculating the relative percent difference and percent recovery of coefficient of variation runs within the batch. Coefficients of variation are independently produced standards, that approximate the midpoint of the analytical range for an analyte and will be run after every tenth environmental sample. Precision within the batch will be also assessed by replicating 5 percent of the samples within a run. Replicated samples will be selected randomly.

The procedures outlined in the EPA Quality Assurance Guidance Document 2.12 (Monitoring PM 2.5 in Ambient Air Using Designated Reference Class I Equivalent Methods (Nov. 1998)) will be followed to the maximum extent possible and /or appropriate.

### ***Minimum Detection Limits***

The MDL is defined as a statistically determined value above which the reported concentration can be differentiated, at a specific probability, from a zero concentration. For determining the MDL, PMTACS will adhere to the maximum extent possible the Code of Federal Regulations, Title 40, Appendix B to Part 136, revision 1.11. Analytical procedures and sampling equipment impose specific constraints on the determination of detection limits. For the

gaseous parameters, MDLs are determined by challenging the instruments with purified zero air, followed by span and multiple calibration. This procedure will be repeated several times to calculate the appropriated statistical parameters. For non-gaseous semi-continuous PM carbon, nitrate and sulfate instruments, MDLs are determined by challenging the instruments with filtered particle free zero air. There currently are no aerosol calibration standards available to challenge these research methods to establish multi-point calibrations. Techniques for laboratory calibrations are under development in the PMTACS-NY aerosol calibration facility. No field deployable aerosol calibration systems exist at this time. It is recommended that for all other filter-based instruments, MDL determinations be performed as follows. Laboratory analyses include field and laboratory blanks and filter standards with known concentrations of select chemical species to establish multiple point calibrations for the respective analytical systems of choice. The success of these activities resides with the ability to produce NIST trace calibration standards. In the absent of which laboratories will resort to their now established procedure to consider field and laboratory blanks only. Field blanks are defined as a filter that travels with the filters that will be utilized in sample collection and should be treated in the same manner as any other filter with the exception that it does not collect sample.

It is a good field practice to take the field blank up to the sampler and leave it inside the instrument housing with the filter cover on. When the sample filters are removed after the sample run, the field blank is also removed and processed in the same manner as all filters. It should also travel in the same carry case as all filters. Storage and handling should be as identical to all processed filters. Laboratory (lab) blanks are filters that are pre-weighed and processed in the same manner as all filters. It is a good laboratory practice to randomly pick a filter and leave it in the weighing room. This filter is then post-weighed and handled in the same manner as all filters arriving from the field. It is recommended that 10% of all filters handled should be lab and field blanks. The following sections will illustrate how MDLs are quantified for filter and non-filter methods.

### *Continuous Measurements*

The configuration of the continuous gas monitors (in particular the ability to introduce standards at the sample inlet) allows for the determination of the MDL for each continuous analyte. The MDL includes all sampling and analytical procedures and therefore represents a detection limit that can be applied to ambient concentrations. The MDL concentration is determined in zero air and therefore will not address matrix interferences.

The MDL for each continuous gas monitor will be determined through statistical evaluation of the zero check standard, followed by span and multiple calibration. This procedure will be repeated several times to calculate the appropriated statistical parameters. The following equation:

$$\text{MDL} = t_{(n-1, 1-a = 0.99)} * \sigma \quad (8)$$

Where  $\sigma$  is the standard deviation of the replicate zero analyses,  $t$  is the student's  $t$  value appropriate to a 99% confidence level and a standard deviation estimate with  $n-1$  degrees of freedom, will be used to determine the method detection limit.

Specific methodologies used to determine MDL for unique research instruments will be provided in the SOP and approved by the QA officer. In developing MDLs for research instruments, the ISO 5724-1 through 5724-3 and the Code of Federal Regulations, Title 40 Part 136, Appendix B will be followed to the maximum extent applicable.

### ***Discrete Measurements***

The laboratory analytical protocol requires that samples be collected at a location away from analysis. Standards for the determination of detection limits for these laboratory instruments are prepared in the laboratory and therefore are not subjected to the same procedures and equipment as the ambient samples. This detection limit is referred to as the instrument detection limit (IDL) although the procedure for quantifying this limit is similar to the determination of MDLs. The IDL is indicative of the ability of the instrument to differentiate, at a specific probability (typically 99% level), between zero and at a specific concentration. The IDL standard does not experience the same handling procedures; collection on filter medium and denuders for HPLC analysis or canister collection for GC-FID/MS analysis; and therefore does not provide information relating to the detection limit at ambient. The IDL for each HPLC and GC/FID-MS analyte will be specified by the instrument manufacturer or experimentally determined through analysis of known analytes (NIST traceable, where appropriate) in addition to zero air. The final MDLs for ions, trace metals, and other components will be determined individually following the procedures defined in Part 136, Appendix B. Similarly, the MDLs based on ion chromatography, thermal optical reflectance, and XRF will be determined using specially prepared filters coated with NIST traceable chemicals/material. For XRF, where three laboratories are involved in analysis, an additional laboratory intercomparison will be conducted to harmonize the measurements.

### ***Completeness***

Completeness will be determined from the data generated using the following equation:

$$\text{Completeness} = (D_x - D_c)/D_c \times 100 \quad (9)$$

where  $D_x$  is the number of samples for which valid results are reported and  $D_c$  is the number of samples that are scheduled to be collected and analyzed during the year.

### ***Representativeness***

Generally, representativeness expresses how closely a sample reflects the characteristics of the surrounding environment. This is usually quantified in terms of monitoring scale. 40 CFR 58, Appendix D discusses monitoring scale in great detail. It is not the scope of this QAPP to discuss monitoring scale in detail, however, monitoring scale has been seriously considered for the selection of the PMTACS-NY sites. The major components of the Supersite are ozone, ozone precursors, fine and coarse particles.

### ***Comparability***

Comparability refers to how confidently one data set can be compared with another. Ideally, two instruments that measure the same parameter would be statistically comparable. One of the objectives of the Supersite is to test new state-of-the-science instruments to see if the values collected are comparable with instruments of well-known and documented accuracy and precision. For a research study that will be testing state-of-the-science instruments and methods, comparability becomes more difficult to estimate. The way to ascertain comparability can be estimated using the MPCs. The ISO Guide 13752 (“Assessment of uncertainty of a measurement under field conditions using a second method as reference.”) will be applied to assess the data sets from intercomparisons.

### ***Inference of Analysis***

At times, when instruments are used research projects, such as a Supersite, there may be one instrument that measures species that cannot be duplicated or compared against other methods. In this case, the only QA activity would be internal calibrations or maintenance checks. To enhance the QA for this instrument, it is recommended that an instrument of known quality be operated and inferences be made by the collection of the research instrument. As an example, if a new method for analyzing sulfates in vapor phase is developed, but there are no instruments to compare against, it would be recommended that data be used from a speciated particle sampler that captures sulfates. By using phase to particle models, the sulfate data can be compared against the sulfate vapor data and inferences about the quality of the sulfate data can be made. The QAM must be aware of these types of analyses and perform the final analysis in the QAFR.

### ***Intercomparisons***

A major goal of the quality assurance related data analysis is to assess comparability of different PM<sub>2.5</sub> measurement techniques. Our major emphasis will be placed on technologies that quantify PM<sub>2.5</sub> mass and chemical composition using: (1) filter-based integrated sampling, and (b) semi-continuous monitoring. Qualitative assessments will also be carried out on the data gathered from the more experimental single particle mass spectrometers. For the assessment of integrated samplers and semi-continuous monitors, the primary data of interest are: mass, sulfate, nitrate, ammonium, elemental carbon, and organic carbon. Trace elements virtually never



comprise a major fraction of PM<sub>2.5</sub> mass, but are extremely important for receptor modeling and will be quantified in the integrated measurements. For each of these data, a “standard” or control value and related uncertainty will be derived for the integrated samplers and (where appropriate) for the semi-continuous monitors from the mean and the standard deviation of the mean of all verified, validated, and fully assimilated quality assured measurements made during a given time interval by the integrated samplers and the semi-continuous monitors, respectively. Control values can be refined by eliminating outliers through standard statistical tests. Within each of the measurement categories, consistency between various instruments will be assessed by comparing individual data with the control values.

Additional quality assurance related data analysis will be made by assessing the ability of integrated samplers to account for PM<sub>2.5</sub> mass measured gravimetrically with that obtained by reconstructing the mass from chemical speciation. Since mass balance checks on data from individual samplers will be carried out by each of the principle investigators, the overall QA analysis will focus on the control values derived from the combined data set. The chemical speciation of the combined data set will be deemed to be statistically consistent with the PM<sub>2.5</sub> gravimetric mass measurements if the two values agree to within the combined uncertainties (or accuracies) of the component measurements. Control values for any time interval when the two mass-values differ by more than the combined uncertainties (or accuracies) of the component measurements will be flagged in the final archive. In addition to gravimetric analysis, there is a natural grouping of instruments that will be collecting data at the Northeast Supersites. Therefore, control values will be generated for each group of instruments and the data will be intercompared against the individual instruments of that particular group. For groups that do not have common parameters (i.e., Single Particle Mass Spectrometers and Semi-Continuous Speciation Samplers), this statistical analysis will not be applicable.

The PMTACS-NY has been designed to address a number of scientific objectives and technological issues. All of these scientific/technological objectives do not require the same level of measurement quality. Therefore, appropriate DQOs have been developed in conjunction with scientific/technological objectives. Tables 5-7 specify the DQOs (accuracy, precision and completeness) for the PMTACS-NY generated at the five fixed sites.

While accuracy, precision, comparability and completeness can be directly quantified by the data producer through procedures such as calibration, instrument intercomparison, adherence to standard operating procedures and data review, and independently verified during the quality assessment process through systems- and performance audits, it is difficult to assess the three-dimensional representativeness of a data set. Assuring the representativeness of the PMTACS-NY data will be accomplished by meeting the site selection and sampling procedures.

**Table 5: PM2.5 Physical and Chemical measurements**

<b>Parameter</b>	<b>Accuracy</b>	<b>Precision</b>	<b>Completeness</b>
PM2.5 Mass (Filter)	10% <sup>†</sup> or 3xMDL	10% <sup>†</sup> or 3xMDL	75% of possible data p.a.
PM2.5 chemical composition on filter	20% or 3xMDL	10% or 3xMDL	“
PM2.5 mass TEOM (continuous)	20% or 3xMDL	10% or 3xMDL	“
PM2.5 total sulfate	To be determined	To be determined	“
PM2.5 total nitrate	“	“	“
PM2.5 organic fraction (carbon)	“	“	75% of possible data
PM2.5 elemental carbon	“	“	75% of possible data
PM2.5 metals Mg, Al, K, Ca, V, Cr, Mn, Ni, Fe, Zn, As, Se, Cd, Sb, Hg, and Pb*	20% or 3xMDL	10% or 3xMDL	75% of possible data
PM2.5 SO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup>	20% or 3xMDL	10% or 3xMDL	75% of possible data

<sup>†</sup>Based on EPA flow audit

\* A variety of techniques will be employed including: ICP/MS, neutron activation and XRF. Performance stated will meet or exceed values reported in EPA Compendium methods for Inorganic Air Pollutants (IO-3.3,-3.5,-3.7 and IO-4.0) EPA/625/R-96/010a June, 1999.

**Table 6: Precursor or Co-Pollutant Chemical Measurements**

	<b>Accuracy</b>	<b>Precision</b>	<b>Completeness</b>
Surface ozone	10% or 2 ppb	5% or 1 ppb	> 80% of possible data
NO, NO <sub>2</sub> , NO <sub>x</sub>	20% or 0.5 ppb	10% or 0.2 ppb	“
NO <sub>y</sub>	20% or 2 ppb	10% or 1 ppb	“
CO	10% or 50 ppb	5% or 20 ppb	“
NMHC C <sub>2</sub> -C <sub>7</sub>	25% > 20 ppt C	15% > 10 ppt C	“
HCHO	25% or 0.5 ppb	15% or 0.3 ppb	75% of possible data
SO <sub>2</sub>	10% or 1 ppb	5% or 0.5 ppb	“
HNO <sub>3</sub> (gas)	25% or 1 ppb	15% or 0.5 ppb	“

Concurrent measurements of O<sub>3</sub> and NO<sub>2</sub> (to determine O<sub>x</sub>, which is an essential prerequisite for assessing the comparability of ozone measurements in lightly and heavily polluted areas) are required. No MQOs have been set for HO and HO<sub>2</sub>.

**Table 7: Ground based meteorological stations**

	<b>Accuracy</b>	<b>Precision</b>	<b>Completeness</b>
Temperature	0.3°C	0.2°C	> 90% of possible data
Relative humidity*	5%	2%	“
Wind speed	0.5 m/sec	0.5 m/sec	“
Wind direction	5°	5°	“
Pressure	0.5 Kpa	0.5 Kpa	“

\*Range 10-95% RH.

New QA requirements for sonic meteorological equipment are under development in collaboration with NYSDEC. These systems will be adopted within the year. The QA requirements for the previous mechanical systems included annual audits for direction, directional bearing, drag, speed zero, temperature and barometric pressure. The QA requirements for the new systems will include at a minimum Annual audits for direction, speed zero, temperature and barometric pressure. Additional requirements may be added depending on vendor recommendations.

### **3.4 Quality Control Protocols**

A description of the quality control protocols for the relevant instrumentation is provided in the SOPs. Each principle investigator will perform the needed quality control to keep their instruments within internal QC limits. All investigators will calibrate their instruments at the beginning, middle and end of the monitoring period or as specified in the appropriate SOP. The QAM will review all QC activities. Calibration records and operational procedures will be reviewed during the Technical Systems Audit and incorporated in the QAM report.

### **4.0 Data Acquisition**

Data acquisition for continuous gas sampling instrumentation, PM semi-continuous and continuous mass instrumentation is performed via a local Environmental Systems Corporation (ESC) Model 8816 data logger installed at each site. The data logger records the generated analog DC outputs from the respective instruments which are scaled from either 0 to 5 or 0 to 10 volts and correspond to the measurement range of the sampling instrument. Instrument output voltages are converted to engineering units and stored in engineering units in the datalogger's memory. The concentrations recorded by the data logger are only delayed from real-time by the measurement delay inherent to each specific instrument. The loggers register the value of each measurement channel and average these values each minute. The loggers are configured to save the five-minute data for selected instruments and hourly averages for all instruments. A NYSDEC computer in Albany automatically calls the data loggers several times a day to transfer the hourly data, site flags, and power outage information. Five-minute average data are polled (transferred) to a computer at the monitoring site every few hours. These five-minute data are manually copied off of the local computer via a zip disk and delivered to the data manager for processing.

#### **4.1 Data Recording and Identification**

All Measurements: Site operators are required to keep detailed site and/or instrument log books which detail operating conditions, calibrations, audits, maintenance, and any exceptions to normal operation of the site/instrument. In addition, daily and weekly check sheets, field data sheets, chain of custody forms, and audit forms are generated and stored on site when necessary. Log book recorded information is required to be at a level of detail sufficient to identify all periods of normal data collection; and all periods during which known problems exist for one or more instruments.

Core Continuous Measurements: Instruments producing continuous data will be connected directly to data loggers at the measurement site. The data logger will collect the data, average it to the appropriate averaging period, and store the value internally in memory until polled by the data collection computer. The data collection computer may reside at the site, or may reside at a central location and connect to the site data logger via modem. In either case, the data is

downloaded from data logger to data storage computer hourly or daily. Data is backed up from the data storage computer to removable magnetic media at least once a month. This data is transported to Albany for analysis and archival storage.

Core Semi-Continuous and Non-Continuous (Discrete) Measurements: These measurements at the core sites fall into two broad classes; the semi-continuous measurements analyzed on site, and the discrete measurements analyzed at an off site laboratory. Examples of semi-continuous measurements analyzed on site include the autosystem GC and the R&P 5400 Carbon Particulate Monitor. For this class of instrument, data is generated by the instrument (in some cases stored internally in the instrument for a period of time) and recorded (downloaded) to a storage computer at the site. As with continuous data, this data is backed up from the data storage computer to removable magnetic media at least once a month. This data is transported to Albany for analysis and archival storage. Discrete measurements include PM<sub>2.5</sub> filter samples, air toxics samples, and hydrocarbon canister samples. Filter sample and air toxic sample data acquisition is carried out as specified in the pertinent FRMs. Filter based (non-continuous) samplers such as the FRM mass instrument and the multi-filter speciation samplers produce data specific to each sampling event. The electronic data record from each sampling event is downloaded from each sampler by use of a direct serial connection to a local computer or to a palmtop computer. The data files are then sent electronically to a NYSDEC computer in Albany. The database is coordinated by NYS DEC. Hydrocarbon canister samples are labeled with canister sample tags at all times, and canister information is recorded in log books at the measurement site, and at the analysis laboratory at ASRC. Data generated when the sample is analyzed by the laboratory GC is recorded on a PC and backed up onto a workstation computer.

Special Study Measurements: Each of these special study instruments has associated with it 1) dedicated instrument software, 2) data acquisition system, and 3) data storage computer. Raw and analyzed data are stored on the computer; and both raw and analyzed data are copied to magnetic media or CD-ROM for backup and storage.

## **4.2 Control of Erroneous Data**

Power failures, instrument failures, operator intervention for maintenance and calibration purposes, or other reasons may compromise data validity. All principle investigators will be responsible for identifying those periods during which data should be considered unreliable. Data quality flags discussed in Section 4.3 will be used by all investigators. Power failures will be identified by status flags stored in the data loggers and many of the individual instruments, as well as by the site operator whenever possible. Instrument failures, operator interventions, external audits, etc. will be recorded in the site operator logbook and communicated to the data analyst directly. Data will be inspected graphically by the data analyst and/or principle investigator and all discrepancies and inconsistencies will be resolved by discussion with the site operator, and/or by reference to the raw data and the operator logbooks.

### 4.3 Initial Documentation of Data Quality

All data reporting forms will contain a column for flagging and indicating the validity and quality of the data. (See Data Management Handbook for details.) All problematic and missing data points will be highlighted in the form through the insertion of an appropriate coded flag. Table 8 lists and defines these flags. Invalid data will not be placed in the Reporting Form to avoid their possible inadvertent use.

**Table 8. Data Quality Flags**

<i>Code</i>	<i>Data Quality Flag Definition</i>
V0	Valid value
V1	Valid value but comprised wholly or partially of below-MDL data
V2	Valid estimated value
V3	Valid interpolated
V4	Valid value despite failing some statistical outlier tests
V5	“Valid value but qualified because of possible contamination (e.g., pollution source, laboratory contamination source)”
V6	“Valid value but qualified due to non-standard sampling conditions (e.g., instrument malfunction, sample handling)”
M1	Missing value because no value is available
M2	Missing value because invalidated by Data Originator
MDL	Value reported is below the minimum detection limit of the analysis method
H1	Historical data that have not been assessed or validated

### 4.4 Data Validation

Data acquired and verified by site operators, researchers and principle investigators will be subjected to written data validation procedures. Data will be checked for internal consistency, consistency with operator logbooks, and consistency with calibration zero and span checks. Internal consistency requires that data fall within normal operating ranges and do not exhibit excessive and rapid variations that are inconsistent with expected variations. Consistency with operator logbooks requires that all data acquired during calibration checks, instrument maintenance, and instrument outage periods be appropriately flagged. Consistency with calibration zero and span checks requires checking verified data against all calibration data to assure that reported data provides the most accurate possible measure of each parameter. All verified data that has been subjected to these tests will be designated as “validated data”.

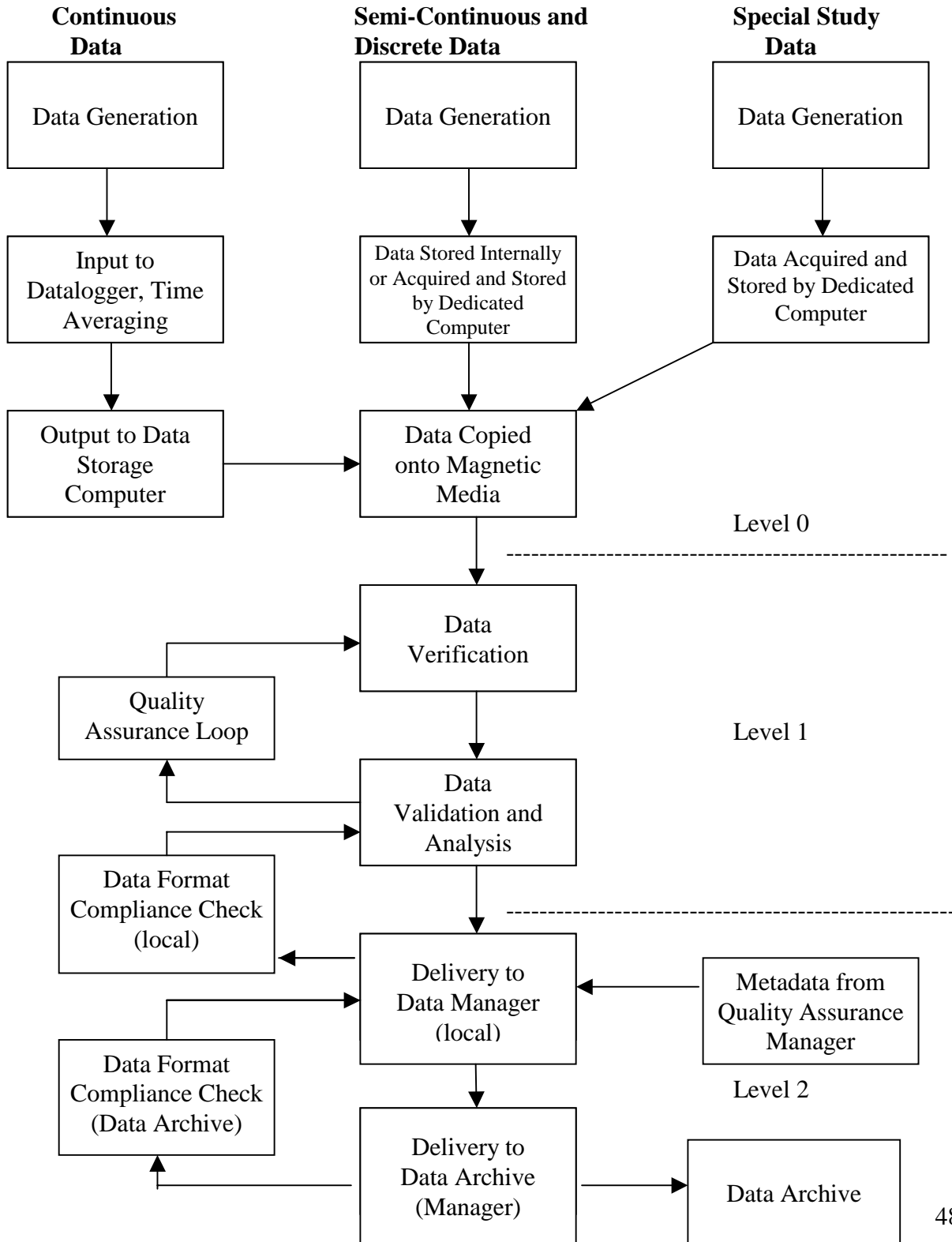
Data will be stored on electronic media for continuous and semi-continuous instruments. Separate CD-ROM and/or diskettes will be created for data storage.

## **5.0 Data Management and Archival**

PMTACS-NY regards data management and archival as a three stage process. In the first stage an investigator collects raw (level 0) data and stores it on the instrument or local computer.

After the level 0 data has been quality controlled by the investigator, and reviewed by the QAM, it becomes level 1 data and is moved to the second stage. In the second stage, the data is transferred to the PMTACS-NY intermediate database. At this stage the data will undergo further quality analysis and is assimilated with data from the other investigators (level 2). Finally, in the third and final stage the data will be transferred to the Permanent Data Archive (PDA). The location of the PDA will be determined by the EPA's Supersite coordinator, although the PDA is expected to be housed by the Carbon Dioxide Information Analysis Center (CDIAC) at the Oak Ridge National Laboratory (ORNL). A data flow chart is presented in Table 9.

**Table 9. Data Flow Chart**





Principally, PMTACS-NY will archive data using the procedures outlined in the NARSTO Data management Handbook (ORNL/CDIAC-112/R2) as amended by the Supersite Data Management Working Group. The Working Group will establish a set of naming and reporting conventions for all data produced at the fixed Supersites. Among the issues that are being worked out are:

- Chemical Speciation of Organic Compounds (IUPAC or agreed upon nomenclature by the Supersite data management working group where applicable)
- Encoding of sampling intervals and methods
- Site naming and identification standards
- Flagging Conventions
- Mobile monitoring
- New research and technology monitoring, such as data from the aerosol mass spectrometer.

PMTACS-NY will follow these amended conventions when submitting data to the PDA.

Within the PMTACS-NY Supersite, compatibility with the existing New York State Department of Environmental Conservation (NYS DEC) monitoring programs must be maintained. Currently, they release data in the AIRS format. Therefore, the PMTACS-NY data manager will accept data in either the amended NARSTO format or in the AIRS format for inclusion in the PMTACS-NY Interim database. Data submitted in other formats will NOT be accepted. Such data will be returned to the data originator, who must resubmit the data in an acceptable format. For data submitted in the AIRS format, it must include all the data and metadata necessary to reformat it into the amended NARSTO format. In all cases, it is the responsibility of the data originator to ensure that the data and metadata is complete and properly formatted. Incomplete or improperly formatted files will be returned to the data originator for corrections.

The interim PMTACS-NY database and archive consists of a set of network Unix workstations running the Sun Solaris operating system. Sufficient hard disk storage is available (or can be easily obtained) to hold the interim archive. The data files within the interim archive will be kept in the amended NARSTO format as jointly developed by all Supersite data managers. This allows files to be easily imported into a variety of analysis and graphing tools. On the local Unix cluster, SAS version 6.12 and Splus are available. Our SAS system will be upgraded to version 8.0 as soon as it is delivered. This is to maintain compatibility with the ORNL software.

The Unix system has a centralized tape backup system that performs incremental file backup on a nightly basis. All external access to the Unix system must be made by either selected encrypted protocols or via a secured anonymous ftp server. All unsecured access methods such as ftp, rlogin, rshell, have been disabled and removed. Security updates and patches are

regularly applied to the system.

All quality assurance reports will be stored as metadata files in the PMTACS-NY data base (including results of system and performance audits and QA experiments). SOPs for instruments operated under a RM-category will be posted on the web.

A website will be provided to Supersite investigators and the QAM who must have access to PMTACS-NY data.

## **5.1 Records Management**

Records identification, distribution and storage, retrieval and retention is described in Section 5 and in the appropriate SOPs.

All discrete and/or intermittent samples collected at the PMTACS-NY sites requiring preparation and/or analysis at a remote laboratory will be accompanied by a chain of custody (hard copy) and an electronic form. The chain of custody form will include the site name, sample identification number, data and time of collection, and signature of person responsible for the collection. The chain of custody form will be completed in triplicate; the original will accompany the sample to the laboratory, a copy will remain in the site log, and a copy will be forwarded to the PMTACS-NY Data Management Center. The appropriate SOPs describe the detailed procedures.

## **6.0 Routine Controls and Procedures**

A portion of the monitoring and research and development activities conducted under PMTACS-NY will use standard routine procedures based on FRMs and for which Standard Operating Procedures (SOPs) are already in place. These SOPs will be accepted by the QAM in their present form. They include all measurements at sites operated by the NYS Department of Environmental Conservation (DEC). Non-routine activities (research methods) will be covered by research protocols (RPs) and prepared by each investigator responsible for the measurements obtained from research methods and submitted to the QAM for approval. To the extent possible, the RPs will have a consistent format and include a summary of method, the applicable procedures for instrument/method calibration, interferences, sample collection, handling and preservation, sample preparation and analysis, data acquisition, calculations and data reduction, computer hardware and software (used to manipulate analytical results and report data) and local data management and records management.

Each of the investigators is responsible for quality control of the data set collected under their responsibility. Each investigator and sub-coordinator shall perform and document the required quality control calibrations and adjustments. The QA officer will review all data relating to the performance criteria. In addition, the QA officer will review the following

information provided by the data-generator:

- Calibration information
- Data handling information (i.e., chain of custody forms)
- Field and lab blank data
- Field notes
- Field data sheets
- The accuracy, bias, precision and MDLs will be calculated for the appropriate data sets
- Statistical trend analyses such as student's T-tests will be performed where applicable
- Results of instrument intercomparisons will be assessed on the basis of ISO-13752
- Any other tests results from QA experiments that the QAM has requested.

From this information, the QAM will be able to ascertain whether the operation of the instruments and systems were within the MQOs and acquired under adherence to the SOPs. If this review indicates a possible problem, the investigator will be contacted for further information. If the QAM is not satisfied with the results of the review, the QAM will contact the Supersite Project Director and explain the problems observed with the data set. The discussion of the Project Director and QAM will determine whether data collected for this project will remain in the database. The principle investigator will be informed of any data removal or invalidations that occur in the database.

## **7.0 Technical Assessment and Response**

For assessing the data quality from measurement systems for which FRMs or EPA-approved methods exist, a set of formal Technical Systems Audits (TSAs) and Performance Evaluations (PEs) will be implemented. Performance Evaluations will be performed on an annual basis at PMTACS\_NY sites by the auditing group of the NYS Department of Environmental Conservation (NYSDEC). We assume that TSAs will be coordinated and performed across all Supersite projects by EPA on a schedule to be decided. In the event that this is not the case, TSAs for PMTACS-NY will be performed in conjunction the PEs by the NYSDEC as defined in Table 3 (2000-2004). The TSAs and PEs cover all procedures and criteria outlined in Sections 3.3 and 3.4 as well as Sections 4.1-4.4 and further detailed in the appropriate SOPs. The results will be submitted to the QAM for assessment (compliance with all protocols and SOPs). Prior to issuance of the QA report, a draft of the report will be sent by the QAM to the site director for review and comment. The QAM will incorporate, where appropriate, the site directors comment, and submit the final report the PMTACS-NY Project Director with recommendations for actions, if necessary. The final QAM report will be made available as metadata file at the PMTACS-NY data bank.

For assessing the data quality of instruments/methods operated under RPs (included in Table 1) and of new measurement technologies (listed in Table 2) quality assurance experiments

will be designed and executed and where appropriate, instrument intercomparisons will be performed, both in the field and laboratory. The results from these activities will help define DQOs and MQOs and incorporated in the evolving SOPs. The ASRC has established a special aerosol facility where the particle related QA experiments will be conducted for the purpose of characterizing aerosol instrument response and addressing other quality assurance issues in aerosol physics and the chemistry of aerosols. Besides instrumentation for the generation and characterization of aerosols, the facility includes a large aerosol chamber along with support to provide controlled aerosol dilution and humidification. This facility has been designed to provide a capability that is as broad as possible to encompass a wide range of aerosol assessments in support of quality assurance. Aerosol generation includes spray atomization of solutions that are used for the generation of polydisperse aerosols in the 0.02 micrometer to 1 micrometer size range. Monodisperse aerosols over this size range can be produced by mobility classification. Production of larger monodisperse aerosols (0.5 micrometer to 20 micrometer) is accomplished through the use of a Vibrating Orifice Aerosol Generator (TSI Model 3450). Both inorganic and organic compounds can be used to generate test aerosols, and generation of secondary aerosols is planned.

Physical characterization of small test aerosols includes concentration measurement using several condensation nucleus counters as well as size distribution measurements with a mobility spectrometer (TSI Model 3080L). Concentrations and sizes of larger aerosols is obtained using optical scattering instruments (PMS ASASP-X) as well as an aerodynamic particle sizer (TSI Model 3220). The combination of these instruments allows a detailed size and concentration characterization over the size range 20 nanometers to greater than 1 micrometer that will be used to challenge aerosol instruments deployed in PMTACS-NY. Quality assurance experiments using the aerosol facility include the evaluation of TEOM mass monitors (Rupprecht & Patashnick Model 1400, R&P 5400 for carbon particulate monitoring, R&P 8400 for nitrate particulate monitoring and newly developed R&P instruments for monitoring sulfate aerosol.

The time schedule is shown in Table 3. The QAM will review the design of QA experiments and intercomparisons, assess the results, review the SOPs prepared by the principle investigators, and issue a QA report with findings and recommendations to the PMTACS-NY Project Director.

## Appendix 1

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