

# FINAL REPORT

## In Situ Characterization of Point-of-Discharge Fine Particulate Emissions

ESTCP Project WP-0420

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## List of Acronyms and Symbols

AMS	Aerosol Mass Spectrometer
ATC	Aberdeen Test Center
ARI	Aerodyne Research, Inc.
CPC	Condensation Particle Counter
DODIC	DoD_ Identification_ Code
DPW	Directorate of Public Works
EI	Electron_ Impact
ER	Emission_ Ratio
ESTCP	Environmental_ Security_ Technology_ Certification_ Program
EPA	Environmental Protection Agency
HR-ToF	High_ Resolution-Time_ Of_ Flight
MAAP	Multi-angle Aerosol Absorption Photometer
NDIR	Non-Dispersive Infrared
NEW	Net Explosive Weight
PAH	Polycyclic_ Aromatic_ Hydrocarbon
PM	Particulate Matter
PoD	Point of Detonation
PoF	Point-of-Fire
PTR-MS	Proton_ Transfer_ Reaction-Mass_ Spectrometer
SAW	Squad_ Automatic_ Weapon
SERDP	Strategic_ Environmental_ Research_ &_ Development_ Program
SOPC	Substances of Potential Concern
TBD	To be determined
TILDAS	Tunable Infrared Laser Differential Absorption Spectroscopy
ToF-AMS	Time-of-Flight Aerosol Mass Spectrometer
TSI	Name of Company that makes instrumentation
USACHPPM	U.S. Army Center for Health Promotion and Preventive Medicine
USAEC	U.S. Army Environmental Command (Formerly U.S. Army Environmental Center)



## Glossary

AMS	(Aerosol Mass Spectrometer) A real-time analytical instrument designed to measure the non-refractory chemical composition of submicron airborne particulate matter as a function of particle size from 50 to 1000 nm.)
MAAP	(Multi-Angle Aerosol Absorption Photometer) Used to characterize the elemental carbon PM component.
ToF-AMS	(Time-of-Flight Aerosol Mass Spectrometer) An AMS employing a Time-of-Flight mass spectrometer.)
TSI CPC	TSI condensation particle counter will be used to measure the total fine and ultrafine (10 to 1000 nm diameter) PM number density.

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The financial support of the Environmental Security Technology Certification Program is hereby acknowledged.

## **Abstract**

Fine particle and trace gaseous emissions from five weapons systems were characterized during routine training on firing ranges at Ft. Sill, OK between March 16<sup>th</sup> and March 24<sup>th</sup> 2007. Real-time trace gas and fine particulate matter (PM) instruments were deployed in the Aerodyne Research, Inc. mobile laboratory to measure muzzle plume and, where feasible, breech plume and soldier breathing zone munitions emission properties from the M109A5 155mm self-propelled howitzer, the M119 105mm howitzer, the M203 40mm grenade launcher, the M249 5.66mm SAW, and the M240 7.62mm machine gun. Fine particle number density, mass loading, black carbon content, and non-refractory chemical content were characterized along with carbon dioxide, carbon monoxide, nitric oxide, nitrogen dioxide, and selected toxic organic trace gas emissions. Emission indices (mass of pollutant/mass of propellant energetic material) for quantified gaseous and PM chemical species or species classes were computed from emission plume trace species and major carbon gas (CO + CO<sub>2</sub>) concentrations; propellant carbon mass balances were used to correct for plume dilution by ambient air. Time traces of soldier breathing zone trace gas and fine PM emissions concentrations for the relatively high wind conditions present during the sampled firing sequences are also reported along with representative ambient background measurements before and/or after firing sequences. The plume emission indices and breathing zone data have been transmitted to USACHPPM for evaluation of potential health risks for gun crews and/or individual weapons operators under real weapons training conditions.

# **1. Introduction**

## **1.1 Background**

The Strategic Environmental Research and Development Program (SERDP) recently sponsored field measurement and modeling programs designed to measure point-of-fire (PoF) and point-of-detonation (PoD) gaseous and fine particulate matter (PM) emissions from common weapons systems and munitions. The purpose of the measurements is to assess their impact on the health of military personnel engaged in training exercises as well as on the soil, air and water quality of training ranges and adjacent areas. In September 2002, as part of SERDP project CP-1197 lead by Battelle Columbus, PoF emissions were measured from a range of weapons fired in an enclosed facility operated by the Aberdeen Test Center (ATC). Under SERDP project, CP-1159, scientists from Aerodyne Research, Inc. (ARI) deployed an innovative aerosol mass spectrometer (AMS) to characterize the chemical composition of fine (diameters of 50 to 1000 nm) PM emitted in the muzzle plumes of the weapons tested.

The resulting AMS measurements showed that the PoF weapons tested emitted a high level of submicron PM in addition to a wide range of organic and inorganic materials, including ammonium compounds, sulfates, nitrates, carbonates, cyanide, potassium, zinc, lead, antimony, and polycyclic aromatic hydrocarbons (PAHs) (Onasch et al., 2003). They also demonstrated that “muzzle flash” afterburning had a strong impact on the chemical composition of the emitted PM.

Further evolution of the Aerodyne AMS, including the use of a time-of-flight (ToF) mass spectrometer now allows significantly faster data acquisition. The deployment of this faster AMS on a mobile laboratory equipped with real-time (1 s) instruments to measure key PoF gaseous emissions (Kolb et al., 2004; Herndon et al., 2005) allows the real-time analysis of unconfined PoF emission plumes; this eliminates the need for an expensive closed firing facility and allows measurements to be performed on real training ranges under ambient environmental conditions.

The Environmental Security Technology Certification Program (ESTCP) contracted the U. S. Army Environmental Command (USAEC) and ARI to perform PoF emission measurements for common Army weapons on current training ranges to demonstrate this new capability and to gain further knowledge about the composition of PoF emissions (particularly fine PM), so their potential impact on the health of gun training crews can be assessed.

This document presents a detailed test plan and the results for those proposed and actual field measurements.

## **1.2 Objectives of the Demonstration**

Aerodyne Research, Inc., in collaboration with the U.S. Army Environmental

caliber weapons at Ft. Sill, OK. Table 1-1 is a list of the weapon systems emissions that were measured as an objective of this demonstration.

**Table 1-1. Weapon Systems Investigated**

<b>Weapon Model #</b>	<b>Ammunition Model #</b>	<b>Ammunition Size</b>	<b>DODIC*</b>	<b>Measurement Zones</b>	<b>Measured Firing Rate</b>
M109A5	M4A1	155mm	D541	Muzzle	Single Rounds
M119	M1	105mm	C445	Muzzle, Breech, Breathing Zone	Single Rounds
M203	M781	40mm	B519	Muzzle, Breech, Breathing Zone	Single Rounds
M249	M855	5.56mm	A062	Muzzle, Breech, Breathing Zone	Single and Multiple Rounds
M240	M80	7.62mm	A143	Muzzle, Breech, Breathing Zone	Single and Multiple Rounds

**\*Department of Defense Identification Code**

### **1.3 Regulatory Drivers**

The interest in PoF emissions is primarily driven by concerns about the potential exposure of personnel to unhealthy emissions during training exercises. PoF emissions also may potentially contribute to the degradation of air, water, and soil quality on and near military training facilities. The Environmental Protection Agency generally delegates the enforcement of air, water and soil quality regulations to state environmental agencies.

### **1.4 Stakeholder/End-User Issues**

U.S. military personnel are the major stakeholders and end-users of the weapons being characterized. Within the Army, USACHPPM has the responsibility and authority to assess potential military personnel health hazards and to devise protective measures as required. The data obtained in the proposed field measurements was transmitted to USACHPPM and both ARI and USAEC worked with USACHPPM to assess their potential impact on gun crews and other training personnel.

## 2. Technology Description

### 2.1 Technology Development and Application

The main PM diagnostic is an Aerodyne time-of-flight aerosol mass spectrometer (ToF-AMS). The instrument has three main sections: the aerosol inlet, the particle sizing chamber, and the particle composition detection section. The aerosol inlet samples sub-micron aerosol particles into the AMS through an aerodynamic lens, forming a narrow particle beam that is transmitted into the detection chamber where non-refractory components are flash vaporized upon impact on a hot surface (500 - 1000 °C) under high vacuum ( $\sim 10^{-5}$  Pa) and subsequently chemically analyzed via electron impact ionization (EI) and mass spectrometry. The transmission of the beam to the particle detector can be modulated with a mechanical chopper that is operated at 100-150 Hz. The chopper is placed in a “closed” position which blocks the beam completely, an “open” position which transmits the beam continuously, or a “chopped” position which modulates the beam transmission with a 1-4% duty cycle that is determined by the width of the chopper slit. The chopped mode is used to measure particle flight times from the chopper to the detector (Jayne et al., 2000).

Three versions of the AMS (Q-AMS, ToF-AMS, and HR-ToF-AMS) are currently in use. These versions, which vary in the type of mass spectrometric detector, use either a quadrupole mass spectrometer (Q), a time-of-flight (ToF) mass spectrometer, or a high resolution ToF mass spectrometer (HR-ToF). The ToF AMS version that will be used in this work is described in detail in Drewnick et al. (2005).

In addition, a fast response ThermoElectron multi-angle aerosol absorption photometer (MAAP) will be deployed to characterize the elemental carbon PM component and a TSI condensation particle counter will be used to measure the total fine and ultrafine (10 to 1000 nm diameter) PM number density. A commercial optically scattering instrument (TSI Dustrak) that provides a secondary estimate of total fine PM mass will also be deployed to help assess the primary PM mass loading measurements provided by the primary AMS and MAAP data. Real-time trace gas instruments will be used to quantify the major carbon exhaust gases (CO and CO<sub>2</sub>) in the emission plumes and ambient background enabling the degree of plume dilution at the measurement point to be determined and propellant mass based PM component emission indices to be computed. The major nitrogen oxide emission gases (NO and NO<sub>2</sub>) will also be quantified and their emission indices computed.

Where appropriate, results for specific munitions PM emission characteristics will be compared with results from munitions characterized during the 2002 SERDP/USAEC sponsored point-of-fire tests in the Aberdeen Test Center (ATC) enclosed firing facility that were characterized by an earlier version of the Aerodyne AMS (Onasch et al., 2003).

The Ionicon Proton Transfer Reaction Mass Spectrometer (PTR-MS), was added to the mobile laboratory instrument suite after the Final Test Plan was prepared. We have previously used this instrument onboard the ARI mobile laboratory to measure selected volatile organic air toxic compounds emitted by aircraft and on-road motor vehicles. Details of its operation and typical data products can be found in Herndon et al. (2006) and Rodgers et al. (2006).

## **2.2 Previous Testing of the Technology**

The ARI mobile laboratory and its associated real-time trace gas and PM characterization technology has been used to measure emissions from aircraft in taxi and take-off modes (Herndon et al., 2004; 2005b) and on-road diesel emissions (Canagaratna et al., 2004; Herndon et al., 2005c). Other emissions and ambient air quality measurements are described in Kolb et al. (2004) and Herndon et al. (2005a). Several other manuscripts reporting either in-use aircraft, test cell mounted aircraft engine, or on-road vehicle emissions are either in press or under review. The earlier SERDP sponsored AMS measurements of PoF PM emissions have been reported by Onasch et al. (2003). Ambient PM measurements utilizing the TOF-AMS are described in Drewnick et al. (2005).

## **2.3 Factors Affecting Cost and Performance**

The major risk associated with the PoF planned field measurements is the possibility of extended periods of bad weather during the planned deployment period. Extended periods of heavy precipitation could postpone training or prevent the mobile laboratory from reaching the firing positions on training ranges with rough terrain or unpaved access roads. The measurement schedule could be extended under these circumstances, assuming that suitable weapons training sessions are available. A less likely threat is the failure of one or more critical instruments, which could delay measurements for two to three days while parts are obtained and repairs made.

## **2.4 Advantages and Limitations of the Technology**

The advantage of using this system is the ability to take measurements in real time. The technology's key limitation is the need to intercept the buoyant muzzle plume with a sampling line. The sampling strategy, which employs an easily movable, height adjustable sampling line, is described below.

# **3. Demonstration Design**

## **3.1 Performance Objectives**

Emission indices (mass of pollutant/mass of propellant energetic material) for quantified gaseous and PM chemical species or species classes were computed from ratios of emission plume trace species concentrations to plume carbon oxide ( $CO_x = CO + CO_2$ ) concentration using propellant carbon mass balance to correct for plume dilution at the measurement points. Some propellant carbon is present as gaseous and particulate organic compounds, but the sum of these is of order 0.01 (one percent) of the  $CO_x$  and can be ignored without significantly impacting the accuracy of the resulting emission indices. Time traces of soldier breathing zone trace gas and fine PM emissions concentrations for the relatively high wind conditions present during the sampled firing sequences are

also reported along with representative ambient background measurements before and after firing sequences. Data analysis and emission index computation procedures generally follow those developed in our previous data report on point-of-fire emissions measurements at the Aberdeen Test Chamber (Onasch et al., 2003). Detailed data analysis products are presented in Section 4 of this report. The following figures (Figures 3-1 – 3-3) show pictures of the laboratory, schematic of the Mobile Laboratory Deployment and Sampling Strategy in relationship to the weapon system, wind direction, etc, and a schematic of the setup of the laboratory. Figures 3-4 – 3-8 show the arrangements and setups that were used for each of the weapon systems that were investigated.



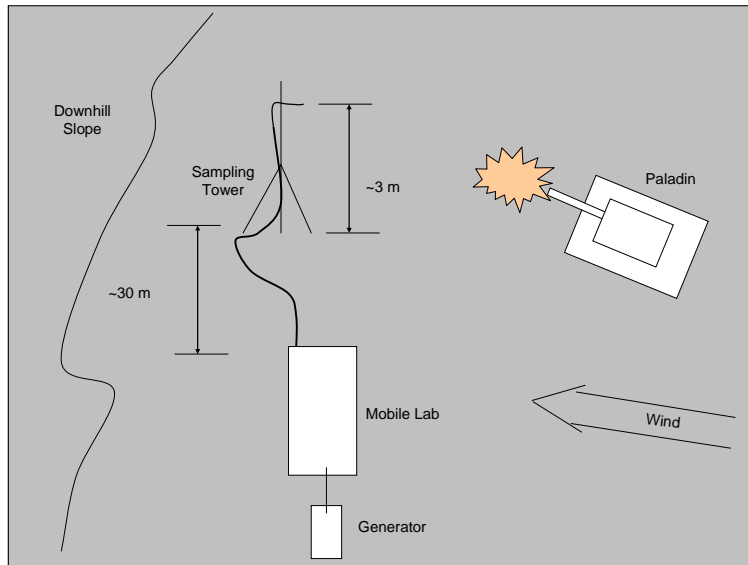
**Figure 3-1. Aerodyne Mobile Laboratory and Sampling Line Deployment.** The mobile laboratory was stationed within 30 meters of the weapons systems. The sampling probe was



located either fixed on a tripod or handheld during firing to obtain measurements at the desired locations (muzzle, breech, breathing zone).



## Sampling Schematic



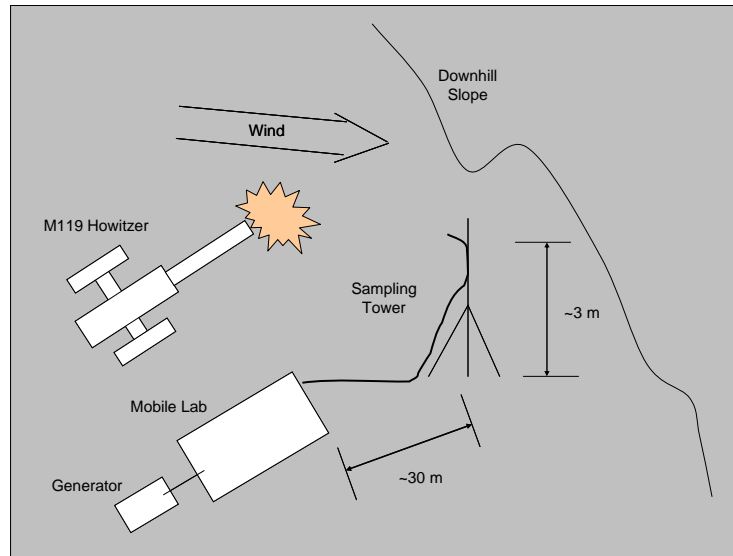
## 155mm Paladin Firing



**Figure 3-4. M109A5 Paladin Self Propelled Howitzer.** Four soldiers were located inside the Paladin during firing. Muzzle plume emissions were sampled downwind using the sampling tripod (shown in schematic). Twenty individual shots were fired (charge 7). Wind speed =  $2.9 \pm 1.2$  m/s



## Sampling Schematic

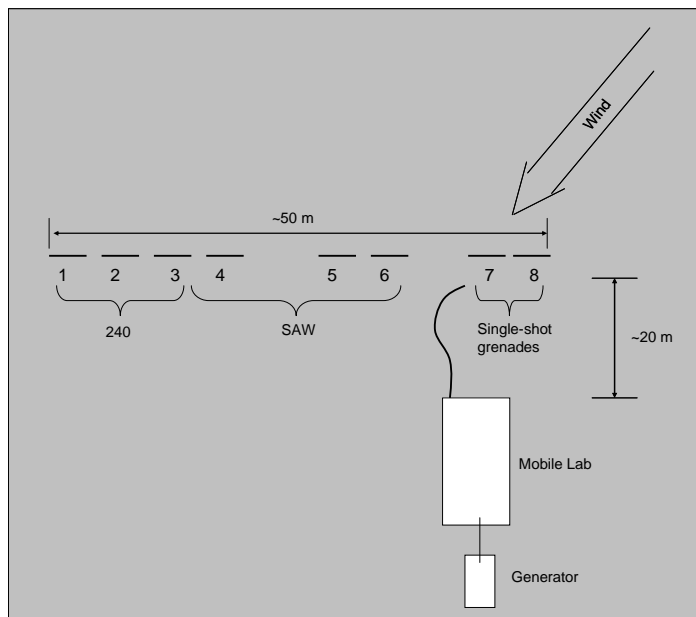


## 105mm Howitzer Firing



**Figure 3-5. M119 105mm Lightweight Towed Howitzer.** Four soldiers fired the M119 weapon, though several more were within 10 meters of the gun to help with ammunition supply and management. Muzzle emissions were sampled downwind using the sampling tripod (shown in schematic) and muzzle emissions/breech plumes in the breathing zone were sampled by attaching the sampling line to the wheel of the howitzer (shown in the picture). Approximately 150 rounds were fired. Wind speed =  $8.7 \pm 1.9$  m/s

## Sampling Schematic

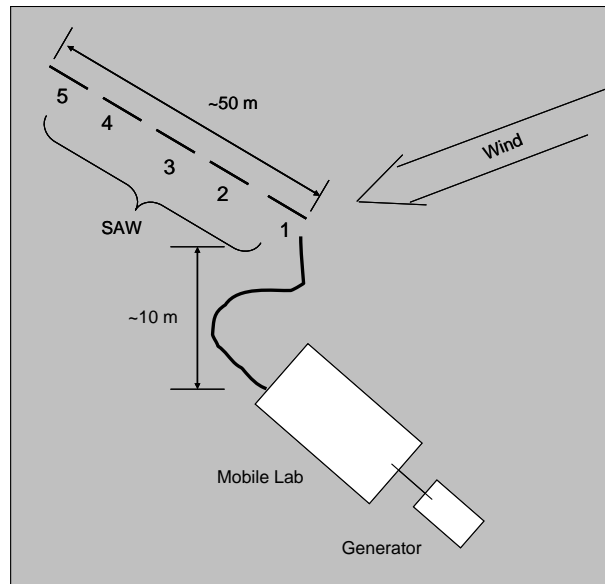


## M203 Grenade Launcher Firing



**Figure 3-6. M203 Grenade Launcher.** Individual soldiers fired the M203 from behind the wood posts from two side-by-side positions. Muzzle plume emissions/breech plumes were sampled in the breathing zone via a hand held sampling line (shown in the picture). Wind speed =  $9.9 \pm 1.6$  m/s.

### Sampling Schematic

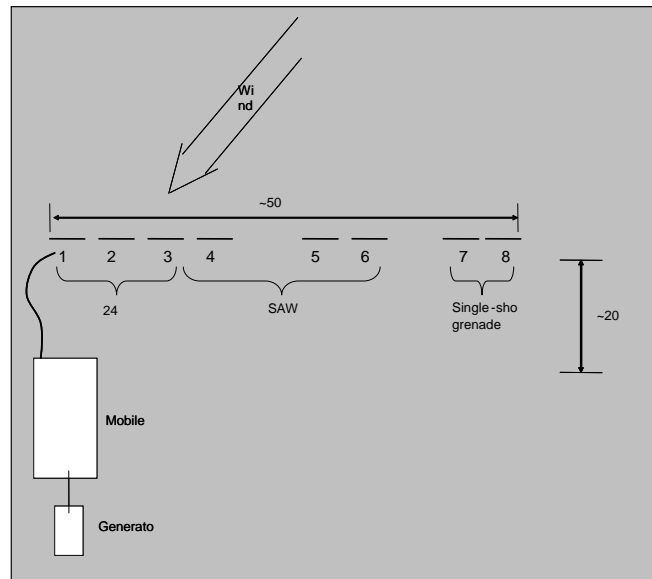


### SAW Machine Gun Firing



**Figure 3-7. M249 5.56mm Squad Automatic Weapon (SAW).** Individual soldiers fired the M249 (20-50 rounds per soldier) from prone positions from five firing positions located side-by-side. Muzzle plumes/breech plumes of one gun were measured in the breathing zone by handholding the sampling line near the breech (shown in the picture). Wind speed =  $5.6 \pm 1.4$  m/s.

## Sampling Schematic



## 7.62mm Machine Gun Firing



**Figure 3-8.** M240 7.62mm Machine Gun. Individual soldiers fired the M240 weapons (20-50 rounds per soldier) from prone positions with eight firing positions located side-by-side. The muzzle emissions/breech plumes of several individual guns (from the firing line) in the breathing zone were sampled during firing by placing the sampling line on a small tripod located just down wind of the breech (shown in the picture) and 3 meters further down wind (not shown). Wind speed =  $8.1 \pm 1.6$  m/s.



**Table 3-1. PM/Trace Gases Detected**

<b>Instrument</b>	<b>Species Name</b>	<b>m/z</b>	<b>Chemical Formula</b>	<b>Emission Ratio Units (per ppm COx)</b>
<b>PM Measurements</b>				
TSI 3025 CPC	Particle Count			#/cm <sup>3</sup>
TSI 8520 DustTrak	Particle Mass			ug/m <sup>3</sup>
Thermo MAAP	PM Black Carbon			ug/m <sup>3</sup>
Aerodyne CTOF-AMS	PM Org			ug/m <sup>3</sup>
Aerodyne CTOF-AMS	PM SO <sub>4</sub>		SO <sub>4</sub>	ug/m <sup>3</sup>
Aerodyne CTOF-AMS	PM NO <sub>3</sub>		NO <sub>3</sub>	ug/m <sup>3</sup>
Aerodyne CTOF-AMS	PM NH <sub>4</sub>		NH <sub>4</sub>	ug/m <sup>3</sup>
Aerodyne CTOF-AMS	PM PAH			ug/m <sup>3</sup>
Aerodyne CTOF-AMS	PM Pb		Pb	ug/m <sup>3</sup>
Aerodyne CTOF-AMS	PM HCN		HCN	ug/m <sup>3</sup>
<b>Trace Gas Measurements</b>				
LI-COR 820	Carbon dioxide		CO <sub>2</sub>	ppm
LI-COR 6262	Carbon dioxide		CO <sub>2</sub>	ppm
Thermo NOx Box 42I	Nitric oxide		NO	ppb
Aerodyne QCL	Carbon monoxide		CO	ppm
Aerodyne QCL	Nitrogen dioxide		NO <sub>2</sub>	ppb
Aerodyne QCL	Formaldehyde		HCHO	ppb
Ionicon PTR-MS	Acetonitrile	m/z 42	CH <sub>3</sub> CN	ppb
Ionicon PTR-MS	Acetaldehyde	m/z 45	C <sub>2</sub> H <sub>4</sub> O	ppb
Ionicon PTR-MS	Benzene	m/z 79	C <sub>6</sub> H <sub>6</sub>	ppb
Ionicon PTR-MS	C <sub>2</sub> Benzene	m/z 107	C <sub>8</sub> H <sub>10</sub>	ppb
Ionicon PTR-MS	Toluene	m/z 93	C <sub>7</sub> H <sub>8</sub>	ppb
Ionicon PTR-MS	Benzonitrile	m/z 104	C <sub>7</sub> H <sub>5</sub> N	ppb
Ionicon PTR-MS	Styrene	m/z 105	C <sub>8</sub> H <sub>8</sub>	ppb
Ionicon PTR-MS	Hydrogen cyanide	m/z 28	HCN	ppb
Ionicon PTR-MS	Alkene and acetic acid fragments	m/z 43		ppb
Ionicon PTR-MS	Acrylonitrile	m/z 54	C <sub>3</sub> H <sub>3</sub> N	ppb
Ionicon PTR-MS	Acetic acid	m/z 61	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	ppb
Ionicon PTR-MS	Furan	m/z 69	C <sub>4</sub> H <sub>4</sub> O	ppb
Ionicon PTR-MS	Ethyl acetate	m/z 89	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	ppb

### 3.2 Selecting Test Platforms/Facilities

Ft. Sill was selected as the site for the point-of-fire field measurements because of its continuous training schedule for a reasonably large number of weapons systems. A number of Ft. Sill's training ranges were projected to be in use during the last half of March, 2007 through the first half of April. Project staff visited Ft. Sill on March 6, 2007 to meet with Milton (Buddy) Leavell and Dave McGowan of Range Operations, who manage the training ranges, to tour active ranges and assess their suitability for mobile laboratory operations. It was determined that road access to most of the training ranges was feasible in relatively dry weather, but that terrain variations made deployment of the mobile laboratory within reasonable sampling line length of some firing sites could be problematical, especially in wet weather.

Extensive army and/or marine training activities on 155mm and 105mm howitzers, MK 19 40mm grenade machine guns, M203 40mm grenade launchers, 50 cal machine guns and numerous smaller caliber weapons were scheduled at accessible training range firing points from mid-March through early April. The decision was made to go ahead and take the measurements during this season to ensure easy mobility and access to the weapon systems.

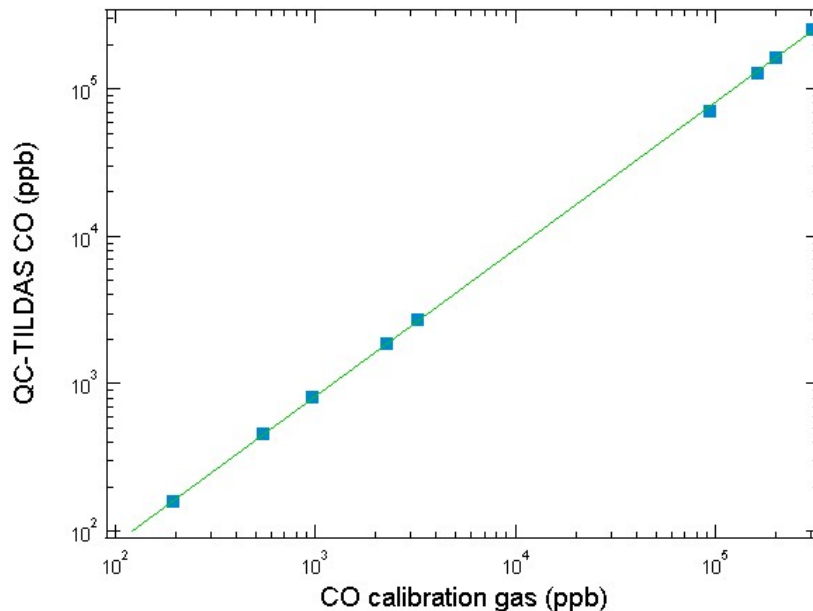
### **3.3 Test Platform/Facility History/Characteristics**

The test platform used was the instrumentation used in the mobile Aerodyne laboratory described below.

#### **3.3.1 Aerodyne QC-TILDAS (Tunable Infrared Laser Differential Absorption Spectroscopy)**

Measurements of carbon monoxide (CO), nitrogen dioxide (NO<sub>2</sub>), and formaldehyde (HCHO) were made with two separate QC-TILDAS instruments. The QC-TILDAS instruments recorded spectra of the sampled air every second. The raw spectra were fit in real-time with known spectroscopic parameters (line positions, line strengths, pressure broadened line widths) to derive species concentrations using proprietary Aerodyne software (TDL Wintel) to provide in-field initial data. In addition to this automated spectral fit to provide real-time data, the data were re-analyzed after the campaign and corrected to account for the high optical depths encountered. These re-fit numbers were finally corrected by the field calibration factors described below.

In principle, the QCL-TILDAS measures absolute concentrations based on molecule-specific spectroscopic parameters that have been published in peer-reviewed scientific literature. In practice, due to imperfections in the lasers used and the high optical depths encountered for the CO measurement, these instruments are field calibrated as well. The CO response was calibrated using a standard tank of CO (300 ppm, ± 2%, Scott Specialty Gases) and one of two dilution systems – 1) the dynamic gas calibrator described in Section 2) a combination of stainless steel critical orifices, which were useful for calibrating at the highest concentrations (>100 ppm) measured during the field campaign. Figure 10 shows the linearity of the QC-TILDAS response over three orders of magnitude in concentration.



**Figure 3-9. CO QC-TILDAS Calibration Plot**

To assess the sampling efficiency of NO<sub>2</sub> through the long metal inlet, a constant flow of NO<sub>2</sub> and CO<sub>2</sub> was introduced at the inlet. NO<sub>2</sub> calibrations were performed by quantitative ozonation of the same standard NO samples described below. The observed NO<sub>2</sub>/CO<sub>2</sub> ratio was compared to that observed when sampling the same flow with only a short (1 foot) inlet attached to the mobile laboratory. The calculated NO<sub>2</sub> sampling efficiency was 96% ± 5%.

### 3.3.2 ThermoElectron Nitric Oxide Chemiluminescence Analyzer (Model 42C)

The chemiluminescence analyzer was calibrated by dynamic dilution of a standard tank concentration using a dynamic gas calibrator (Model 146C, Thermo Environmental Instruments). This calibrator works by using two stainless steel mass flow controllers to mix known flows of NO in nitrogen (99.3 ± 2 ppm, Scott Specialty Gases) with a known flow of either nitrogen or dry “zero” air in order to create gas with concentrations ranging from ~20 ppb up to 1000 ppb. The stated accuracy and precision of the calibrator’s mass flow controllers is ± 2%. The accuracy and reproducibility of the readings was thus calculated, at the 2σ level (95%), to be ± 7% and ± 6% respectively. The calibration NO tank gas lines were purged several times prior to calibration and all calibration points were allowed to flow for several minutes through the chemiluminescence analyzer before a reading was taken in order to allow for passivation and settling time. Readings were taken at 4-6 different concentrations ranging between 20 and 1000 ppb. These readings were plotted versus calculated concentration and fit with a linear least squares routine. The instrumental background was periodically measured by overflowing the inlet with zero air or nitrogen.

NO, NO<sub>2</sub> and CO calibrations were performed at Ft Sill, at ARI prior to the field campaign, and at a subsequent field campaign at Tinker Air Force Base two weeks later. The calibrations at these three locations and time periods agreed within 5%.

### 3.3.3 LI-COR Carbon Dioxide Non-dispersive IR Detectors

Carbon dioxide measurements were made with a LI-COR model LI-6262 detector and by a higher range model 820 detector. The accuracy and linearity of the LI-COR detectors were periodically checked by overflowing the inlet with gas directly from one of two standard calibration tanks (400 ppm and 803 ppm, ± 1%, Scott Specialty Gases) and with CO<sub>2</sub>-free nitrogen.

### 3.3.4 Ionicon PTR-MS

The PTR-MS (Ionicon Analytic GmbH) is a chemical ionization based mass spectrometer that utilizes H<sub>3</sub>O<sup>+</sup> as a reagent ion. This instrument has been described elsewhere (Rodgers et al., 2006; Lindinger et al., 1998), so only a brief description of the relevant details is provided here. The instrument consists of an ion source, a drift tube reaction region and a quadrupole mass spectrometer. H<sub>3</sub>O<sup>+</sup> reagent ions formed in the hollow cathode discharge ion source are electrostatically injected into the drift tube through which the sampled air stream is continuously passed at reduced pressure, 2.0 mbar. These H<sub>3</sub>O<sup>+</sup> reagent ions are pulled through the air sample by an electric field where they can react via proton transfer reactions with those components in the sample having proton affinities greater than that of water. The reagent ions and the resulting proton transfer reaction products are mass selected and detected using the mass spectrometer.

Because the munition detonations produce short-lived plumes, the measurement of the emission products had to be accomplished rapidly in order to adequately capture the transient nature of the events. A maximum measurement time of 1.5 seconds was established and to meet this time requirement the PTR-MS was restricted to monitoring up to 7 ions at 0.1 sec per mass and the drift tube temperature and pressure. Two of the sample ion channels are dedicated to measuring the reagent ion intensities, H<sub>3</sub>O<sup>+</sup> (m/z 21 O-18 isotope) and H<sub>3</sub>O<sup>+</sup>-H<sub>2</sub>O (m/z 39 O-18 isotope), leaving 5 ion sample measurement channels available. A total of 14 ions were identified as signature species for anticipated emission products, which required splitting the measurements into 3 separate sets. We rotated through each of the measurement sets initially to determine which species were most active for a given weapon system. In general more time was spent measuring those sets which appeared to have the most signal. The different sets of the measured compounds were as follows: Set 1: m/z 28 (hydrogen cyanide), m/z 31 (formaldehyde), m/z 42 (acetonitrile), m/z 45 (acetaldehyde) and m/z 54 (acrylonitrile). Set 2: m/z 79 (benzene), m/z 93 (toluene), m/z 104 (benzonitrile), m/z 105 (styrene) and m/z 107 (C2-benzenes, sum of xylenes and ethylbenzene). Set 3: m/z 43 (multiple neutrals including propene, acetic acid and other larger alkenes), m/z 61 (acetic acid), m/z 69 (furan) and m/z 89 (ethyl acetate).

The sampled exhaust flow stream was periodically diverted through a heated platinum catalyst (400°C) to provide a VOC free gas stream for determining the instrumental background. In many cases the platinum catalyst appeared to be contaminated and did not efficiently remove the VOCs from the sample stream. Under circumstances where the catalyst appeared to be compromised,

instrumental background measurements were determined when the main inlet was purged with N<sub>2</sub>. The instrumental background is non-zero for most masses and the reported concentrations reflect the difference between the sample and background signals.

The concentrations of emission components are deduced from the measured ion signals using relationships derived either from simple reaction kinetics or from calibrated response factors. For a limited number of compounds calibrated response factors have been determined and the relationship between the response factors and the volumetric mixing ratio (VMR) are given by Eq. 1. (Rodgers et al., 2006)

$$VMR_R = \left( \frac{1}{S_R} \right) \left( \frac{I_{RH^+}}{I_{H_3O^+} + X_R \times I_{H_3O^+(H_2O)}} \right) \left( \frac{T^2}{P^2} \right) \quad (1)$$

Where  $I_{RH^+}$ ,  $I_{H_3O^+}$  and  $I_{H_3O^+(H_2O)}$  represent raw measured ion intensities, T is the drift tube temperature and P is the drift tube pressure.  $S_R$  represents the overall sensitivity, while  $X_R$  compensates for the reaction efficiency of the  $H_3O^+(H_2O)$  reagent ion. Sensitivity factors,  $S_R$ , are determined from the slopes of calibration curves created through dilution of certified high-pressure multi-component gas mixtures (Apel-Reimer Environmental Inc. Denver, CO) and were checked periodically throughout the measurement period. The calibration factors employed in this study are reported in Table 3-2.

For compounds where calibration gas standards were not available, concentrations were calculated assuming simple reaction kinetics apply (2) and the following relationship was used.

$$VMR_R = \left( \frac{I_{RH^+} / BF}{I_{H_3O^+} k_c t} \right) \left( \frac{1}{N_{tot}} \right) \quad (2)$$

$I_{RH^+}$  and  $I_{H_3O^+}$  are the respective transmission corrected ion intensities, BF is the product ion branching fraction, t is the drift time of the reagent ions,  $k_c$  is the reaction rate coefficient and  $N_{tot}$  is the total number density. For polar compounds capable of reacting with the  $H_3O^+(H_2O)$  via a ligand switching reaction,  $I_{H_3O^+}$  represents the sum of the  $H_3O^+$  and  $H_3O^+(H_2O)$ . Table 3-2 provides a summary of the proton transfer reaction rate coefficients and the calibration factors used in this study.

Due to the magnitude (and importance) of measured hydrogen cyanide (HCN), we put specific time and effort into calibrating the m/z 28 (HCN) signal in the PTRMS. Measuring HCN with a PTRMS is not straightforward due to the fact that HCN has a proton affinity close to that of water. Thus, HCN calibrations were done as a function of the sampling relative humidity. The details of this calibration are included in this report's Appendix F. An US Army Report on the "Combined Exposures to Hydrogen Cyanide and Carbon Monoxide in Army Operations: Initial Report" is included as Appendix H.

**Table 3-2. Compounds Monitored Table (compounds monitored, their proton transfer reaction products and relative abundance, including calibration factors and reaction rate coefficients used for quantification).**

Compound	Ions formed (abundance)	Quantification Method	S <sub>R</sub>	X <sub>R</sub>	k (mL/s) x 10 <sup>9</sup>
Hydrogen Cyanide	28 (100%)	Reaction kinetics	--	--	0.17 <sup>(a)</sup>
Formaldehyde	31 (100%)	Reaction kinetics	--	--	0.17 <sup>(b)</sup>
Acetonitrile	42 (100%)	Reaction kinetics	--	--	4.74 <sup>(c)</sup>
“Mass 43”	See note (d)	Reaction kinetics	--	--	2
Acetaldehyde	45 (100%)	Calibration	0.70	0.3	--
(e)Acrylonitrile	54 (100%)	Reaction kinetics	--	--	2
(e)Acetic Acid	43 (30%) 61 (70%)	Reaction kinetics	--	--	2
(e)Furan	69 (100%)	Reaction kinetics	--	--	2
Benzene	79 (100%)	Calibration	0.45	-0.4	--
(e)Ethyl acetate	43(20%) 61(50%) 89(30%)	Reaction kinetics	--	--	2
Toluene	93 (100%)	Calibration	0.60	-0.1	--
(e)Benzonitrile	104 (100%)	Reaction kinetics	-	-	2
(e)Styrene	105 (100%)	Reaction kinetics	-	-	2
C2-Benzenes	107 (100%)	Calibration	0.64	0.15	--

(a) See appendix for details.

(b) Reaction rate coefficients are dependent on the reverse reaction with H<sub>2</sub>O as described by Hansel et al. (1997) and the appendix of this report. The proton affinity of formaldehyde is sufficiently similar to that of HCN so that correction factor applied to the HCN measurement is also appropriate for formaldehyde.

(c) Reaction rate coefficient from Zhao and Zhang (2004)

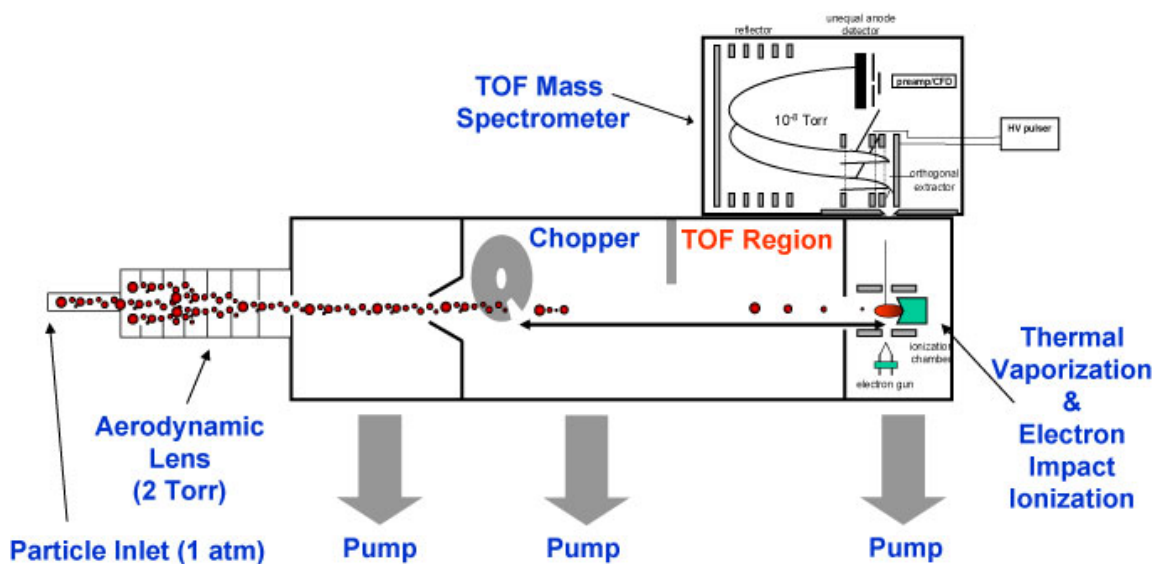
(d) A number of compounds contribute ion intensity to this mass including acetic acid, ethyl acetate, propene and larger (>C4 alkenes).

(e) Assumed compound identities based on molecular weight. Quantification of these components assumes a standard reaction rate coefficient of  $2 \times 10^{-9}$  molecules<sup>-1</sup> ml s<sup>-1</sup> and does not account for any loss of ion signal due to fragmentation.

### 3.3.5 Aerodyne TOF-AMS

The Aerodyne Aerosol Mass Spectrometer (AMS) was used during the PoF measurement campaign to characterize the chemical composition of non-refractory fine PM. A schematic of the AMS is shown in Figure 3-10 (Drewnick et al. 2005; Canagartna et al., 2007). The AMS design consists of three differentially pumped sections: (1) an aerosol inlet, (2) an aerodynamic sizing chamber, and (3) a particle composition detection chamber. Ambient particles are sampled through a 100 μm critical orifice (inlet pressure ~2 torr pressure and sample flow rate ~100 cm<sup>3</sup> min<sup>-1</sup>) and focused by an aerodynamic lens (Liu et al., 1995a,b) into a narrow beam (<1 mm diameter) as they enter into high vacuum. A mechanical beam chopper lets a burst of particles into the particle sizing chamber at a defined time. Particle aerodynamic diameter is determined by measuring the time a particle takes to reach the vaporization oven. Rapid vaporization of the particles provides sufficient time resolution for measurement of particle size distributions. Particle chemical composition is determined via flash vaporization followed by electron impact (EI) ionization and time-of-flight mass spectrometry. Since the AMS requires aerosol species to be vaporized, this technique does not detect refractory components which do

not vaporize at the temperature of the vaporizer (typically 600°C, *vide infra*), such as mineral dust or elemental carbon.



**Figure 3-10. Schematic of the time-of-flight aerosol mass spectrometer (TOF-AMS). Used to gather size resolved chemical information of the point-of-fire particles.**

The AMS operates in two modes. In time-of-flight (TOF) mode aerosol mass distributions (as a function of particle vacuum aerodynamic size) are determined using the beam-chopping technique. The AMS exhibits excellent particle collection efficiencies from 40 nm to 1 μm (near unity for particles in the size range 60 nm to 600 nm). In mass spectrum (MS) mode, the chopper is moved out of the particle beam and ensemble mass spectra (1-400 amu) are obtained for the sampled aerosol. Sensitivities of ~0.01 μg/m<sup>3</sup> (with several minute integration time) for individual volatile and semi-volatile chemical components have been demonstrated.

To operate the AMS near its highest possible data acquisition rate, we modified the standard operation procedure substantially (with the exception of the first day of experimentation - 155 mm howitzer data). First, the AMS is typically alternated between MS and TOF modes, with data being collected in each mode for 5 sec. During the PoF measurements, the AMS was operated in either MS or TOF for extended periods of time – on the order of 10 min. Second, the data acquisition periods were shortened to 1 sec for MS mode and 3 sec for TOF mode. These acquisition periods were selected to obtain reasonable mass/charge ( $m/z = 1-400$ ) and particle size (50-1000 nm) ranges. Shortening the acquisition time further would have resulted in loss of data. Third, the AMS typically acquires alternating “open” and “closed” spectra. During “closed” sampling, the mechanical chopper is placed directly in front of the detector to determine instrumental background. During PoF measurements, instrumental background was negligible compared to signal (signal to noise on the order of 100:1) so “closed” spectra were not taken. Instead, samples obtained during periods of weapon inactivity were used to remove the influence

of ambient air and instrument background simultaneously. Finally, we found in our previous PoF study (Aberdeen) certain semi-volatile metals (e.g., lead) in artillery smoke. These semi-volatile metals are only partially vaporized at the standard AMS oven temperature of 600°C. The majority of archival AMS data have been collected at 600°C and we used this as our base temperature to facilitate data inter-comparison; to capture and quantify semi-volatile metals, we operated the AMS at 750°C for some of the weapons systems. High temperature operation was not always possible. The Table 3-3 lists the data acquisition rates, modes, and oven temperatures used during each of the 5 weapons-systems experiments.

**Table 3-3.** AMS Operation Modes

Experiment	Date	Mode	Resolution (sec)	Oven Temp (°C)
155 mm	3/19	TOF <sup>a</sup> /MS <sup>b</sup>	12	600
5.56 mm & 7.62mm	3/20	TOF	3	600
		MS	1	600
105 mm	3/21	TOF	3	600
		MS	1	600
40mm (grenades)	3/21	TOF	3	600,750
		MS	1	600,750
5.56 mm (single shot)	3/22	AMS off-line for repairs		

<sup>a</sup> TOF = time-of-flight

<sup>b</sup> MS = mass spectrometer

The AMS data were subjected to careful post-processing. First, the mass/charge calibrations were re-checked for the entire data set. Second, the electronic noise in the baseline was fit to an empirical function:

$$\text{Intensity}(m) = R_0 \left\{ 1 - \frac{1}{1 + \exp\left[\frac{m - m_0}{\Delta m}\right]}\right\} \quad (3)$$

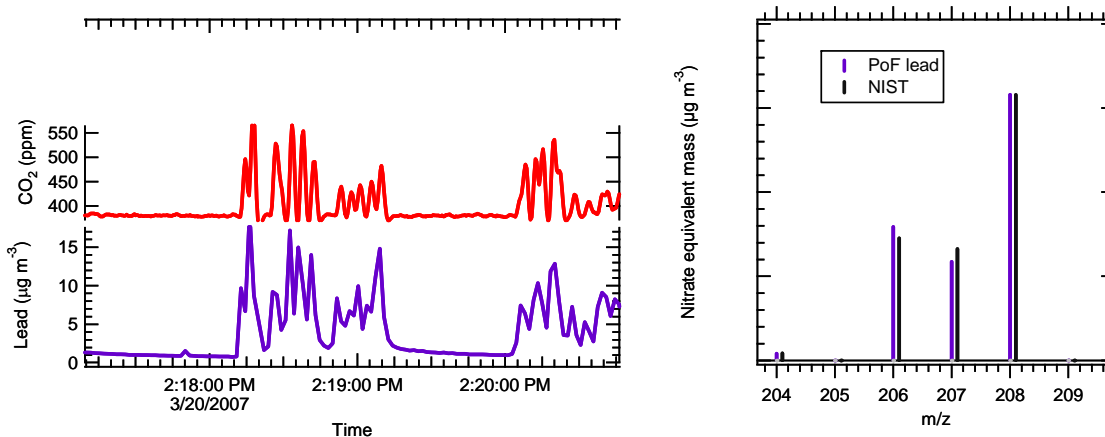
where  $m$  is the mass (or mass to charge ratio),  $R_0$  is a simple proportionality constant,  $m_0$  is the reference mass for the baseline, and  $\Delta m$  is the peak width. Third, we inspected the individual mass spectra and found that the potassium signals ( $m/z = 39$  and  $41$ ) were frequently saturated. When total mass loadings are calculated from the mass spectra,  $m/z = 39$  is assumed to be entirely potassium;  $m/z = 41$  is potassium's isotope, but it also receives a contribution from organic species ( $C_3H_5$ ). Because the  $m/z = 41$  peak was dominated by K-41 for the PoF data set, we removed its contribution to the overall organic mass. We estimate the organic mass loadings are under-estimated by no more than about 3-5% due to the  $m/z = 41$  omission.

AMS mass spectra are analyzed to identify and quantify categories of chemical compounds (nitrates, sulfates, organics, particle-bound cyanide, lead, PAHs) and, in some cases, specific



compounds in the fine particles. The analysis of mass spectral signatures (based on comparison with standard EI mass spectral libraries, as well as laboratory calibrations) easily distinguishes inorganic (e.g. ammonium, nitrate, sulfate) and organic species. Common inorganic compounds fragment in known patterns (e.g., nitrate forms fragments with  $m/z$ 's 30 and 46 in a roughly 2:1 ratio). Likewise, metals are readily identified by their unique isotopic ratios. For instance, lead occurs primarily as 3 isotopes: 206 (24%), 207 (22%), and 208 (52%). (A fourth isotope exists, 204, but its abundance is small, ~1%) Therefore, the presence of peaks at mass 206, 207, and 208 in roughly a 1:1:2 ratio is indicative of lead. Figure 3-11 shows AMS PM lead signatures compared with expected lead isotope ratios and a time series of the particulate lead concentrations compared with gas phase  $\text{CO}_2$  which indicates time intervals during which M240 shots were sampled. PM lead was clearly correlated with  $\text{CO}_2$  indicating its presence in the plume and formation during the detonation process.

After all of the inorganic peaks have been identified, the remaining peaks are attributed to organic species. Detailed identification of individual organic components is not always possible from EI mass spectra, due to overlapping ion fragmentation patterns from complex mixtures. However, some important compounds such as PAHs, tend not to fragment and have been successfully identified and quantified by the AMS in past work (Dzepina et al., 2007).

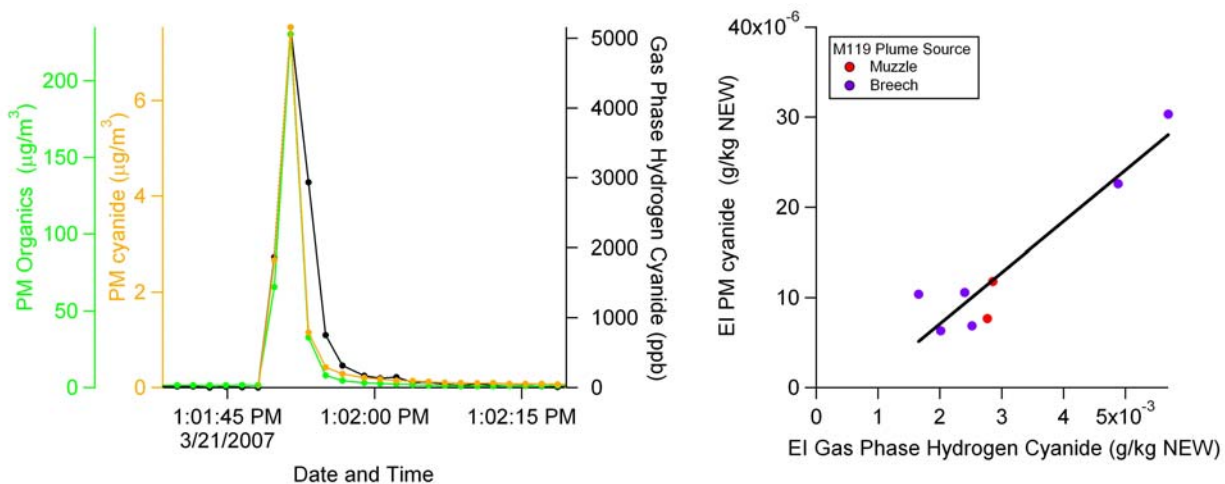


**Figure 3-11. Particulate lead measured during PoF activities: (a) particulate lead concentrations measured during training periods showing coincidence of lead with carbon dioxide; (b) comparison of AMS mass spectrum with NIST library.**

In addition to significant gas phase cyanide concentrations, particle-bound cyanide was detected in the muzzle plumes of most of the weapons studied during the PoF tests. Due to high vapor pressures, cyanide in the form of HCN and its neutralized  $\text{NH}_4^+$  salt are likely present only in the gas phase unless there is significant particulate water ( $\text{NH}_4\text{CN}$  is highly water soluble). The source of particulate-bound cyanide detected by the AMS is likely the  $\text{Na}^+$  and  $\text{K}^+$  salts of  $\text{CN}^-$  which dissociate on the  $600^\circ\text{C}$  AMS vaporizer and evolve HCN gas that is subsequently detected via electron impact ionization inside the instrument. The vapor pressures of both KCN and NaCN are negligible at temperatures close to  $20^\circ\text{C}$  and would be present as particulate solids during the PoF tests. Moreover, all cartridges contain either potassium (M109A5, M119, and

M203) or sodium (M240 and M249), providing the cation sources for the particulate cyanide observed during the PoF mission.

As was done for the analysis of the Aberdeen test data (Onasch et al., 2003), particulate cyanide mass loadings and EIs were estimated based on the NIST fragmentation pattern of gaseous HCN. The NIST mass spectrum shows the majority of signal from HCN at  $m/z$ 's 26 ( $CN^+$ ) and 27 ( $HCN^+$ ), with  $m/z$  26 about 17% of the  $m/z$  27 signal. A complicating factor was that the hydrocarbon fragment ( $C_2H_3^+$ ) contributes to the AMS  $m/z$  27 signal. Due to the hydrocarbon interference, the uncertainty in the mass loadings determined for particulate cyanide were larger than for the other measured particulate chemical species. The hydrocarbon contribution to  $m/z$  27 was estimated from the background organic signals observed at  $m/z$  29 following the procedure recommended by Onasch et al. (2003). The enrichment of the  $m/z$  27/29 signal ratio in the weapons' muzzle plumes during firing compared to the background ratio was used to estimate the HCN concentration at  $m/z$  27. This assignment is supported by strong correlations between the  $m/z$ 's 27 and 26 signals during plume measurements (consistent with the NIST HCN spectrum) and weaker correlations with other organic signals as  $m/z$  12, 29, 55, and 57. Furthermore, the derived particulate cyanide concentrations were observed to drop slower in concentration than the organic PM after each shot as expected for refractory compounds. Figure 3-12 (left plot) shows a single, representative M119 shot with corresponding PM cyanide and organic and gas phase hydrogen cyanide concentrations. Figure 3-12 (right plot) shows the positive correlation between the particulate bound cyanide emission indices and the gas phase hydrogen cyanide emission indices.



**Figure 3-12. (Left plot) M119 single shot breach plume with corresponding particulate organic and cyanide concentrations and gas phase hydrogen cyanide concentrations. (Right plot) Positive correlation between measured particulate cyanide and gas phase hydrogen cyanide emission indices (EI).**

Chemical mass loadings are determined from the mass spectra and sample flow rate using the knowledge of electron impact (EI) ionization fragmentation patterns and two additional factors (discussed below). Direct laboratory calibrations and EI-MS databases provide the EI

fragmentation patterns for a particular species, subject to three complicating factors: 1) signal to noise of each fragment ion; 2) saturation of the signal at a given mass fragment; and 3) interference between the fragmentation signals of two or more different chemical species. The first of these complicating factors only plays a significant role when a given species is present in low concentrations (typically not an issue for ambient particles and not an issue for these tests). The second factor is an issue when the amount of a given species is present in very high concentrations (typically not an issue for ambient particles, but sometimes a problem for these test). The final complicating factor is when the amount of organic compounds is much greater than the concentrations of an inorganic or metallic compound (also encountered during PoF tests, e.g. for particulate HCN).

Quantifying AMS data required two additional factors.

The first of the additional factors was the ionization efficiency of a vaporized molecule, i.e., the likelihood that a molecule will be ionized by electron impact. Aerodyne has found that species belonging to similar chemical categories have similar ionization efficiencies. Critically, the ionization efficiencies of typical ambient particle-bound inorganic and organic molecules are quasi-linear as functions of molecular weight. Moreover, calibrations between AMS signal and mass loading show a linear relationship between the nitrate equivalent cross section (ionization efficiency relative to ammonium nitrate) and molecular weight for a range of inorganic and organic compounds. For more precise work, ionization efficiencies can be determined through specific laboratory calibrations for the desired species; in practice, the uncertainties associated with assuming that ionization efficiency scales with molecular weight are small. Typical uncertainties for total non-refractory inorganic and organic loadings are within 20%.

The second factor was the collection efficiency of the AMS. The aerodynamic lens employed in the AMS focuses spherical particles ranging in size from 60 to 600 nm in diameter such that nearly 100% of the spherical particles in this size range strike the vaporizer. Particles smaller than 60 nm are lost to diffusion and particles greater than 600 nm are lost due to impaction on the inlet of the AMS. Essentially no particles smaller than about 30 nm or larger than 1  $\mu\text{m}$  reach the detector. The collection efficiencies of non-spherical particles are reduced due to particle lift. Furthermore, we have found that nearly 100% of the liquid particles which strike the vaporizer are detected, but only about half of the solid particles which are focused onto the vaporizer are detected. The remaining solid particles “bounce” off the vaporizer prior to vaporization. The likelihood of bounce depends on the mechanical, physical, and chemical properties of the particles and can not be determined *a priori*. For this reason, no correction for particle bounce was applied to the PoF data and the AMS mass loadings reported here may be systematically low by about 50%. Based on an assessment of these uncertainties, the mass loadings reported in this report are representative lower limits of their particulate loadings.

### **3.3.6 Facility History/Characteristics**

The site of Fort Sill was staked out on January 8, 1869 by Maj. Gen. Philip H. Sheridan who led a Campaign into Indian Territory to stop hostile tribes from raiding border settlements in Texas and Kansas. At first the garrison was called "Camp Wichita" and referred to by the Indians as

"the Soldier House at Medicine Bluffs." Sheridan later named it in honor of his West Point classmate and friend, Brigadier General Joshua W. Sill, who was killed during the Civil War. The Last Indian lands in Oklahoma opened for settlement in 1901 and 29,000 homesteaders registered at Fort Sill during July for the land lottery. On August 6 the town of Lawton sprang up and quickly grew to become the third largest city in Oklahoma.

With the disappearance of the frontier, the mission of Fort Sill gradually changed from cavalry to field artillery. The first artillery battery arrived at Fort Sill in 1902 and the last cavalry regiment departed in May 1907. The School of Fire for the Field Artillery was founded at Fort Sill in 1911 and continues to operate today as the world renowned U.S. Army Field Artillery School.

Because of this background this installation was chosen as the site for the measurement of weapon's emissions during training. Part of this testing was to determine if measurements of emissions could be separated from any background ambient airborne material due to natural entrainment of emissions that have been deposited on this installation over the last 105 years. These weapons, mainly artillery, but have also included small arms type weapons including rifles, pistols and shotguns and the machine gun.

### **3.4 Present Operations**

Presently Fort Sill continues as the "Home of the Field Artillery" and hosts much of their training there in addition to the training of the assigned units to Fort Sill, as well as local Army and Marine reserve units. This includes field artillery and standard infantry weapons.

### **3.5 Pre-Demonstration Testing and Analysis**

The main pre-deployment analysis and testing involved the use of a suitable muzzle plume sampling system.(Discussed in the next paragraph) A range of buoyant plume rise calculations (See Appendix C) show that under low wind (1-2 mph) conditions the emission plume may rise as much as five meters above discharge height before traveling more than a few meters downwind from the weapon. This effect is much less severe at moderate (~5 mph) wind conditions. To intercept the anticipated range of muzzle plumes the sampling line inlet must be adjustable in height between one and five meters. Obviously, the higher sampling heights are applicable to the lowest wind speeds and to the largest caliber weapons which produce the most buoyant plume rise. We anticipated that the sampling heights for most weapons would be between two and four meters but in practice most of the sampling heights were right at the muzzle or breech of the weapon except for the M109 (155mm) and some initial measurements from the M119 (105mm).

We had built, tested and used a sturdy wood sampling mast that was assembled to extend up to ~16 ft (~5m) to serve as the sampling line inlet adjustable support. For muzzle emissions plumes, measurement of an estimate of where the mast must be placed and how high the sampling line inlet mounted to intercept on the downwind muzzle plume were based on visual observations of prior firing plume trajectories and ongoing wind velocity and direction measurements supplied by anemometers mounted on the mobile laboratory. The anticipated length of the sampling line depended on wind speed and direction and varied from 10-15 m for smaller weapons and as

long as 30 m (~100 ft) for the 155mm weapon. Ambient temperature, wind speed, wind direction, and relative humidity were measured before, during and after each measurement was taken. Precipitation was not encountered during the testing phase.

Our sampling methodology for fine airborne PM does not conform to normal US Environmental Protection Agency (EPA) methods because EPA methods were developed for traditional filter sampling measurements, not real-time instrumental analysis, and are therefore not suitable. Instead, the techniques for real-time sampling and analysis to be used in these field measurements are based on those used previously for PoF weapons emissions, aircraft emissions, and on-road vehicle emissions by ARI and collaborating institutions. They have proven well suited in a variety of field fine PM measurement programs sponsored by the EPA (Cangaratna, 2004; Herndon et al., 2004; 2005b;2005c; Shorter et al., 2005), as well as the National Aeronautics and Space Administration (Kolb et al., 2004, Herndon et al., 2005a), the Federal Aviation Agency (manuscripts in press), the Department of Energy (manuscripts in press), the National Science Foundation (Kolb et al., 2004, Herndon et al., 2005a), Army Research Laboratory (C.C. Wy et al., 2006), and the Strategic Environmental Research and Development Program (Onasch et al., 2003).

A TFIA-F high volume air-sampling blower capable of moving up to 2 STP m<sup>3</sup> of air per minute was deployed to draw the plume and background air samples through the sampling system to the mobile lab inlet. This was sufficient to move sampled air through the sampling line in ~10 s. Turbulent flow calculations indicated that the resulting pressure drop in the sampling line was minimal (less than 1%) and that less than ~10% of the fine particles (50 to 1000 nm diameter) of interest will be lost to agglomeration or deposition to the sampling line walls. The actual loss of fine PM and trace gases was determined by sample line calibrations. Particles temporarily lost to walls will generally be quickly re-entrained, due to the high air flow rate, and exhausted in the blower out flow. The sampling line was made of non-conducting materials to avoid static electrical fields that can cause enhanced deposition. It consisted of a 1 inch diameter flexible aluminum sampling section that was hoisted up and down the sampling mast and mated to a 3/4 inch copper sampling line that ran along the ground from the sampling mast to a sampler that will divert the flow analysis portion into the mobile laboratory's sample distribution flow system. A cyclone will remove particles with diameters larger than 2.5 microns to avoid contamination of the sampling system with large airborne dust particles while passing all submicron particles.

Periodically zero air was run through the lines to check the background readings of the instrumentation every three to five minutes of operation with an approximate ten second burst of zero air (Additional calibration information is in Appendix F).

### **3.6 Testing and Evaluation Plan**

#### **3.6.1 Demonstration Set-Up and Start-Up**

The original plan called for a field measurement campaign that started on Saturday, March 17 and ended Thursday, March 28. The actual operation was completed on 24

March due to the speed of testing being much faster than originally planned. The mobile laboratory left Aerodyne on Wednesday, March, 13 and arrived in Oklahoma City on Friday, March 16. It picked up the generator early on the morning of March 17 in Oklahoma City and towed it to Ft. Sill, arriving before noon on March 17. The measurement crew members flew from Boston to Oklahoma City on March 17<sup>th</sup> and arrived at Ft. Sill via rental car on March 17. The team assembled at the airfield hanger where the mobile lab was unpacked and instruments were turned on, pumped down and tested. Starting on March 19, the mobile lab was deployed from the airfield hanger each morning to the training range firing points selected for each day's measurements in consultation with range operations personnel and the military unit firing the weapons.

The mobile laboratory was originally to be parked 5-10 meters behind stationary firing sites at each range. Based on wind directions and speeds changes were made in this arrangement as seen in the previous figures of the positions of the laboratory relative to the weapon emissions being measured. No attempt was made to sample vehicle mounted weapons "on the fly" since this would have likely violated range safety rules. A 1 inch diameter flexible sampling section coupled to a 3/4 inch copper sampling line was deployed from the mobile lab inlet to an extendable mast sited beside and downwind from the weapon. Electrical power for the mobile laboratory and its sampling system were supplied by a 20 KW trailer mounted diesel generator that was towed to each range by the mobile laboratory and sited downwind of the mobile laboratory and the weapons being sampled. A schematic of the overall measurement set-ups are shown previously in Figure 3-2, 3-4, 3-5, 3-6, 3-7, & 3-8.

The main measurement focus for each weapons system was to be the interception and characterization of the muzzle emissions plume so that chemically speciated emissions indices can be calculated for this major emissions source. In addition, breech emissions plumes were characterized from breech loaded weapons by placing the line adjacent to the breech. (In one case the line had to be moved away from the breech because too much particulate and gases were being collected). Finally, as requested by USACHPPM, the atmosphere behind the weapon in the region where the weapons personnel operate was also sampled to determine how much muzzle, breech or other weapons associated airborne emissions were present.

Each specific test deployment configuration for the mobile laboratory and the sampling system was determined by the weapons platform and system being tested, the wind speed, the wind direction, and the specific measurement (muzzle plume, breech plume, or simulation of gun crew exposure) being performed as shown previously in Figure 3-1.

Sampling the muzzle plume from the howitzers was a relatively straight forward except for the distance we were from the M109A6 muzzle and the wind speed when we measured the M119 (caused the breakup of the plume before it could be adequately measured). Even with the distance from the M109A6 adequate measurements were able to be taken and the line was moved (for the M119) next to the breech to get the breech

plume. The M240 7.62mm machine gun and the M249 5.56mm machine gun produced lower buoyant plume rises than the larger caliber weapons allowing lower sampling heights but did require some adjustments during the measurements; i.e. for example the line for the 7.62mm had to be moved away from the breech because of overlap from the adjacent firing position.

Rapid-fire weapons like the machine guns produced pseudo-continuous plumes that will merge the emissions from multiple shots. This will make sample interception easier and instrument measurement signals higher than for equivalent caliber single shot weapons, but estimates of the firing rate (number of rounds fired per unit time) were obtained from the gun crews to allow accurate computation of emission indices per shot.

For sampling breech plumes and crew breathing zone simulations the sampling mast was positioned as close to the firing position as possible and the sampling height lowered to catch the breech plume or to simulate the crew breathing zone. (Small arms weapons) For ground-deployed weapons, the crew breathing simulation sampling height recommended by USACHPPM is 5 feet when firing from a standing position.

The mobile lab was deployed each day from the Airfield hanger and proceeded to the training range of interest. It returned each night to the hanger.

### **3.6.2 Period of Operation**

The mobile laboratory arrived at Ft. Sill on Saturday, March 17 and its instrumentation was powered up overnight and tested/calibrated on Sunday, March 18. Field measurements commenced on Monday, March 19 and continued until Saturday, March 24.

### **3.6.3 Amount/Treatment Rate of Material to be Treated**

Because real time training range measurements of weapons' emission plumes had never before been made it was difficult to firmly predict how many weapons could have been characterized in a typical measurement day. We had originally estimated we could do one to two weapon systems a day. Based on the testing we were able to complete one weapon system a day.

### **3.6.4 Operating Parameters for the Technology**

Training firings are normally under the command of a master gunner. Mobile laboratory deployment at each training range was originally to fall under their direction. During the testing at Fort Sill we fell under the control of the Firing Range Safety Officer for that particular team firing. No mobile team member accessed the firing lines to deploy or re-deploy sampling lines without their express permission. Mobile laboratory personnel wore substantive ear protection and safety glasses during firings and the mobile lab was positioned behind or at an angle to the range firing positions.

### **3.6.5 Experimental Design**

Not applicable.

### **3.6.6 Product Testing**

The ToF-AMS and associated measurement instruments have been extensively used in mobile laboratory missions measuring of jet engine exhaust and on-road vehicle exhaust emissions. The instruments worked well during the measurement phase of this test.

### **3.6.7 Demobilization**

Once the appropriate number weapons systems emissions had been characterized the monitoring crew returned to Billerica, MA. The driver transported the mobile laboratory back to Tinker AFB for scheduled aircraft engine emission measurements after dropping off the rental generator in Oklahoma City.

### **3.6.8 Health and Safety Plan**

The firing units' safety plans were used while making the measurements. Training firings are normally under the command of a master gunner or the Range Safety Officer. Mobile laboratory deployment at each training range was under their control and direction. No mobile team member accessed the firing lines or deployed or re-deployed sampling lines without their express permission. Mobile laboratory personnel wore substantive ear protection and safety glasses during firings and the mobile lab was positioned well behind or at an angle to the range firing positions.

A more detailed discussion of health and safety issues is presented in Appendix B.

## **3.7 Selection of Analytical /Testing Method**

As detailed above the project will utilize real-time instrumental methods, not traditional grab sample collection and separate laboratory analysis methods.

## **3.8 Selection of Analytical/Testing Laboratory**

Not applicable

## **3.9 Management and Staffing**

The principal investigator (PI) for this project was Howard M. Beardsley. The CO-PI for this project was Dr. Charles E. Kolb.

Dr. Charles E. Kolb managed and led the Aerodyne team. Dr. Kolb is a physical and atmospheric chemist with over 35 years of post-doctoral experience in atmospheric and combustion chemistry and the measurement of pollutant emissions and radiation from military and civilian systems. As PI and president/CEO of ARI Dr. Kolb planned and coordinated the field measurements addressed in this document and was responsible for their successful execution. He also oversaw data analyses and data evaluation tasks and supervised the preparation of reports and presentations.



The ARI field measurement team was led by Dr. Timothy B. Onasch of ARI's Center for Aerosol and Cloud Chemistry and is a veteran of numerous mobile laboratory field measurement missions. Dr. Onasch, who has 8 years of relevant post-doctoral experience, was also the Quality Assurance leader. He was assisted by Dr. Ezra C. Wood, who oversaw gas phase NO, NO<sub>2</sub>, CO and CO<sub>2</sub> measurements and Dr. Michael Timko, who assisted in PM emission measurements. Dr. Wood is a physical and atmospheric chemist and Dr. Timko is a chemical engineer, both with two years of post-doctoral experience. Mr. Robert Prescott drove the mobile laboratory and oversaw operation of the on-board and trailer mounted electrical generating systems.

The CHPPM team will be led by Dr. David Reed.

### **3.10 Demonstration Schedule**

The schedules shown below for the Ft. Sill training ranges were used in the planning and the Actual Range Weapons Training was what actually occurred.

#### **Scheduled Range Weapons Training**

155mm howitzers: 03/19, 20, 21, 22, 26, 27, 28  
105mm howitzers: 03/19, 20, 21, 22, 23, 26, 27,28  
Mk19 40mm grenade machine gun: 03/22, 26, 27  
M203 40mm grenade launcher: 03/21, 22, 26, 27, 28  
M2 50 cal machine gun: not scheduled in advance

#### **Actual Range Weapons Training**

155mm howitzers: 03/19, 20, 21, 22, 26, 27, 28  
105mm howitzers: 03/19, 20, 21, 22, 23, 26, 27,28  
Mk19 40mm grenade machine gun: Wind Direction came out of wrong direction.  
M203 40mm grenade launcher: 03/21, 22, 26, 27, 28  
M2 50 cal machine gun: Training Cancelled  
M240 7.62mm machine gun: 22  
M249 5.56mm machine gun: 23

## **4. Performance Assessment**

### **4.1 Performance Criteria**

This program was a straightforward field measurement project to obtain PoF emissions data, focusing on fine PM chemical composition as a function of particle size and PM emission indices, from at least four common Army weapons systems (actually measured five weapon systems). Multiple calibrations were performed before, during and after the taking of emissions to ensure the data was correct and of the highest quality. The quality of the emissions data was assured by the well developed instrument and sampling system calibration procedures and data archiving and evaluation procedures that were detailed in Appendix A. The data presented in this report has been forwarded to the U.S. Army's Center for Health Promotion and Preventive Medicine (CHPPM), to determine how these data can be used to assess health risk and the associated reliability of health risk estimates. The data has been used to provide an assessment of the health risk and its reliability for each of the weapon systems tested. The health risk evaluations are presented in Appendix E of this report.

### **4.2 Performance Confirmation Methods**

The mobile laboratory instruments that were deployed for the field measurements are real-time instruments with data analysis and display software that provides a reliable readout of the nature and quality of the trace gas and fine PM characteristics in real-time. This allows immediate assessment of whether a representative portion of a weapon's muzzle emissions plume or background ambient air sample (for comparison) has been obtained and whether each individual instrument performed adequately to characterize that sample. If a significant level of combustion gases (CO<sub>2</sub>, CO, NO<sub>2</sub>, NO) are detected above background levels (we anticipated that measured CO and/or the CO<sub>2</sub> "in plume" concentrations will need to exceed measured ambient background measurements by 10% or more), a clear emissions plume event were recognized.

Since the emissions plumes were turbulent they tended to be very well mixed and it can be safely assumed that submicron PM detection in any part of the plume is representative of the whole plume. As noted above, the concentration of CO and CO<sub>2</sub> above background will be used to compute the level of dilution that has occurred for the portion of the plume that is intercepted during the measurement period. This allows the concentrations in the diluted plume to be corrected back to the concentrations in the undiluted plumes. Thus, each time a weapon fires the field measurement team will be able to determine if enough valid plume measurements have been obtained and adjust the instruments and/or the sampling system, as required.

Measurements on a given weapons systems/munitions type continued until adequate individual firing data were obtained to characterize the emissions and compute statistically significant emissions indices. The number of samples required depended on three factors: 1. The plume to plume variability; 2. The statistical significance of each plume measurement; and 3. The limited ability of the PTR-MS to measure more than three species at a time. As noted in our prior PoF measurement report (Onasch, et. al., 2003), there can be significant plume to plume pollutant variation if there is muzzle flash afterburning for some projectiles but not for others. The degree of afterburning would have been indicated by variations in the measured plume CO/CO<sub>2</sub> ratio.

If the CO/CO<sub>2</sub> ratio varies significantly a larger number of measurements were not needed to address this intrinsic plume variability. (Afterburning did not appear to affect the plumes we measured) The second factor was determined by how well we intercepted each plume, based on prior analysis of combustion plume emissions three or four good plume intercepts yielded a significant measurement of the major pollutants present. Additional measurements were taken to ensure statistical correlation of the results and to allow the PTR-MS to obtain additional measurements of the other species.

### **4.3 Data Analysis, Interpretation and Evaluation**

After quality assurance of the basic instrumental data emissions indices for muzzle and breech plumes and above background concentrations for breathing zone measurements were computed and average and standard deviation values were tabulated. The statistical significance of each measurement was evaluated and used to flag the data reliability. The interpretation and evaluation of the data in terms of possible health impacts for the gun crews was determined by USACHPPM (Appendix E) as they and the measurement team proceeded with the planned health impacts analysis.

Selected trace gas and fine PM emissions were measured during the Ft. Sill Point of Fire (PoF) campaign. For trace gas emissions: carbon dioxide was quantified with two separate LI-COR NDIR instruments, carbon monoxide, formaldehyde, and nitrogen dioxide were measured with ARI quantum cascade TILDAS instruments, nitric oxide was measured with a ThermoElectron chemiluminescent detector, and selected toxic organic species were measured with an Ionicon PTR-MS. Fine PM properties measured included fine (~7-700 nm diameter) particle number density with a TS I 3025 CPC, PM<sub>2.5</sub> mass loading with a TSI 8520 DustTrak, PM<sub>2.5</sub> black carbon mass loading with a ThermoElectron MAAP, and submicron PM nonrefractory organic and inorganic composition with an Aerodyne Aerosol Mass Spectrometer (AMS).

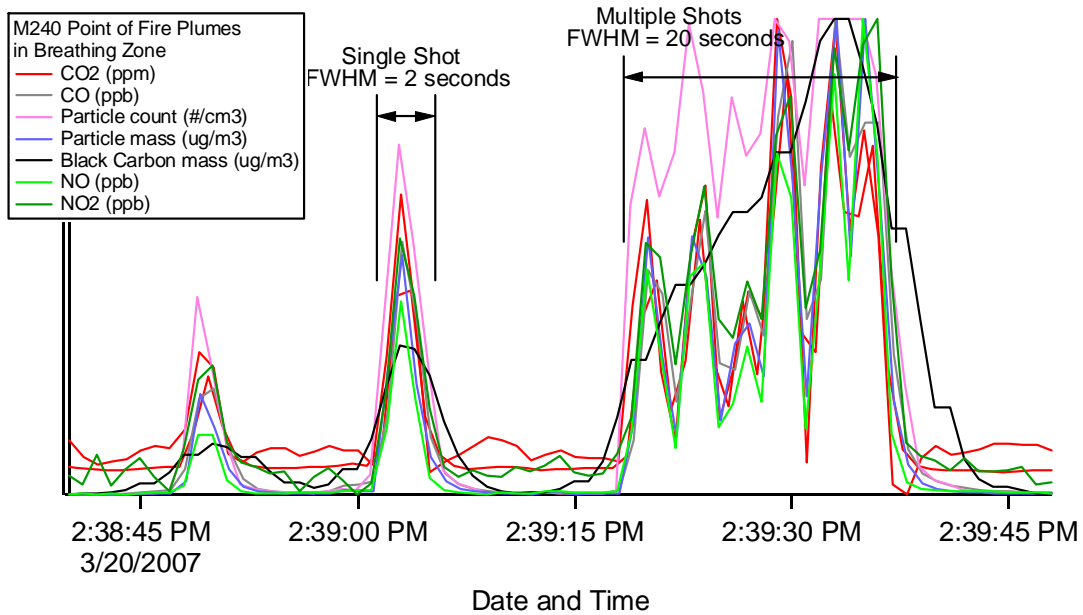
The Aerodyne Time-of-Flight Aerosol Mass Spectrometer (TOF-AMS) is a core instrument for this project; its operation is described in Drewnick et al. (2005) and Canagaratna et al. (2007). One major instrument, the Ionicon Proton Transfer Reaction Mass Spectrometer (PTR-MS), was added to the mobile laboratory instrument suite after the detailed test plan was prepared. We have previously used this instrument onboard the ARI mobile laboratory to measure selected volatile organic air toxic compounds emitted by aircraft and on-road motor vehicles. Details of its operation and typical data products can be found in Herndon et al. (2006) and Rodgers et al. (2006).

The chemical species, species classes, or PM properties measured by each instrument are summarized in Tables 3-1 and 3-2.

#### **4.3.1 Typical Data**

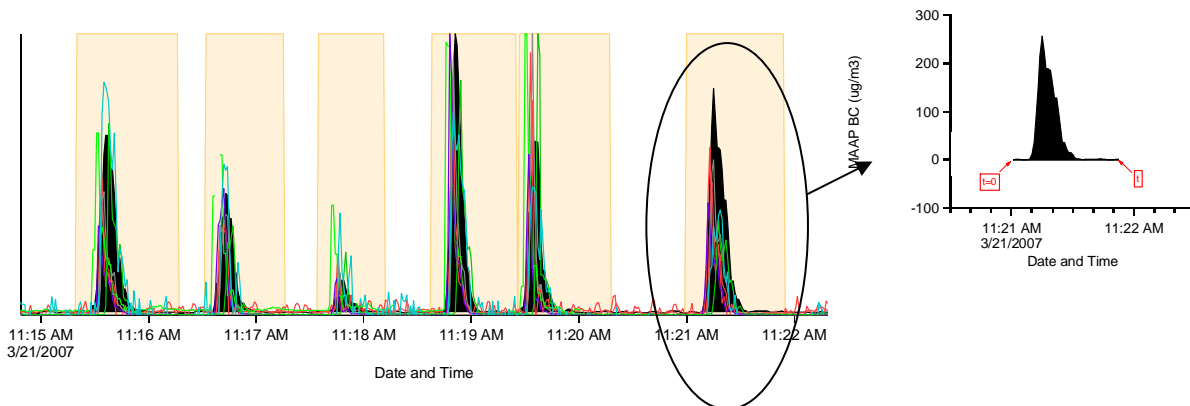
An example of typical data representing single shot and a multiple shot burst from the M240 machine gun is shown in Figure 4-1. The relatively high wind speeds (3-10 m/s) encountered during the Ft. Sill measurements ensured that single shot plumes would be advected past the sampling point in just a few seconds. Variable intensity plumes from multiple shot bursts could persist for several tens of seconds. This places a premium on correctly accounting for the variation in the time it takes for sample flow to reach each of the mobile lab instrument so data

from each instrument are properly time registered and aligned. Since not all instrumentation could be operated at the same response time, some of the measurement plumes are slightly broader than others. This required that plume integrations, as illustrated in Figure 4-2, be performed to compute accurate species ratios for each plume.



**Figure 4-1. M240 Point-of-Fire Plume Shapes and Durations**

An illustration of the data peak integration process performed is shown in Figure 4-2. An explanation of the general data quality assurance protocols used for the mobile laboratory instrumentation is presented in the project’s detailed test plan (Kolb et al., 2007) and Appendix A of this document. Overviews of these procedures for key instruments are presented below.



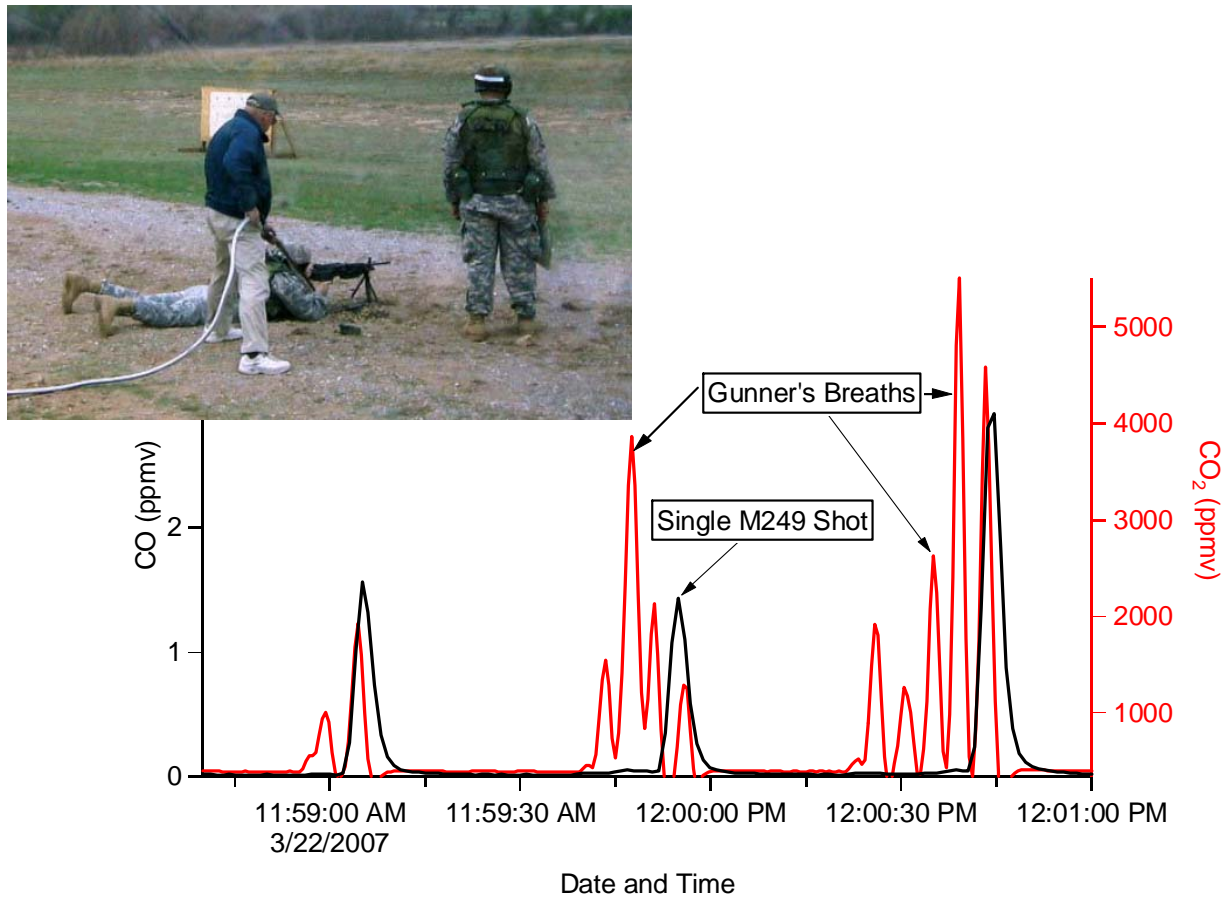
**Figure 4-2. Analysis – Peak Integrations.**

$$\frac{\int_{t=0}^t BC \cdot dt}{\left( \int_{t=0}^t CO_2 \cdot dt + \int_{t=0}^t CO \cdot dt \right)} = ER_{BlackCarbon} \left( \frac{\mu g / m^3 BC}{ppm CO_x} \right) \quad (4)$$

### 4.3.2 Breathing Zone Measurement Data

In addition to analyzing individual and multiple shot muzzle plumes in terms of pollutant emission ratios (plume excess concentration of pollutant/plume excess concentration of CO<sub>x</sub>), we also measured breech plumes and soldier breathing zone data. Two additional data analysis issues needed to be addressed for the breathing zone measurements.

Typical breathing zone measurements are depicted in Figure 4-3. They illustrate the point that, for medium and small caliber weapons, soldiers' exhaled breath can produce CO<sub>2</sub> concentrations larger than the CO<sub>2</sub> from breech plumes blown into the breathing zone. To calculate emission ratios and emission indices from these plumes it is necessary to correct emission CO<sub>x</sub> ratios for any breath CO<sub>2</sub> contamination. Fortunately soldiers' breath contains negligible amounts of CO, as illustrated in Figure 4-3, so only data with CO/CO<sub>2</sub> ratios consistent with muzzle emissions were used to compute (CO + CO<sub>2</sub>) values for ER and EI analyses. Figure 4-3 also illustrates the point that soldiers may take several measured breaths and then hold their breath while firing their training shots. This has interesting implications for computations of exposure/dose evaluations, particularly during brisk wind conditions when weapons emissions plumes are rapidly advected away.



**Figure 4-3. M249 Breathing zone measurements.**

A second breathing zone data issue was the need to identify adequate fine PM and trace gas weapons emissions and ambient background state so that the incremental impact of inhaled weapons emissions can be properly evaluated. USACHPPM has requested that we supply high time resolution fine PM and trace gas data for breathing zone dose analyses rather than processing the data to produce time averaged exposures. Accordingly we have produced one-second resolution data (EXCEL spreadsheets) that provide 5-15 minutes of breathing zone data for the M109A5, M119, M203, M249 and M240 weapons. We note that in some cases the exhaled breath  $\text{CO}_2$  markers shown for the M240 data in Figure 4-3 may be useful in identifying when the soldier firing the weapon may be inhaling (at least it identifies when he exhales.) These breathing data spreadsheets are displayed in Appendix G of this report.

#### **4.3.3 Calculation of Emission Ratios and Emission Indices (Emission Factors)**

Pollutant emissions are traditionally quantified by emission indices (also termed emission factors). In the case of munitions point-of-fire studies these are usually dimensionless ratios defined as mass of pollutant emitted per mass of net explosive weight (NEW) in the munitions propellant. Since the emissions index or factor is dimensionless it does not matter if the

calculation is done in Imperial (lbs) or metric (g or kg) units as long as the same mass units are used for both the pollutant emitted and the NEW.

As noted above we can calculate emission indices from specific pollutant emission ratios using a carbon mass balance approach by calculating the concentrations of a plume pollutant (above background) divided by the sum of plume CO + CO<sub>2</sub> (CO<sub>x</sub>) (above background). This approach is based on the observation that all but a few percent of the carbon in the munitions propellant is oxidized to either CO or CO<sub>2</sub> during detonation and that the major effect of any unsuppressed afterburning (muzzle flash) is to convert emitted CO (or other incompletely oxidized carbon) to CO<sub>2</sub>. We note that in our previous PoF measurements in the Aberdeen test chamber, we observed that the degree of unsuppressed afterburning affected the emission ratios of some species, decreasing emission ratios for incompletely oxidized species and increasing them for more fully oxidized species, as expected (Onasch et al., 2003).

The emission index (EI, mass emitted material per mass NEW) is determined from the measured emission ratio, defined as the ratio of the emitted component concentration (e.g., particle number/mass concentration or a trace gas concentration) to the emitted Carbon ([C] = [CO<sub>x</sub>] = [CO] + [CO<sub>2</sub>]) concentration, and a calculated Carbon EI. The EI for a given emitted PM component concentration, X (μgm<sup>-3</sup>), is calculated as,

$$EI(X) = (\Delta X/\Delta CO_x) \times EI(C) \times M_{AIR}/MC \times (1/\rho_{AIR})$$

and the EI for a given emitted gas phase component concentration, X (ppm), is calculated as,

$$EI(X) = (\Delta X/\Delta CO_x) \times EI(C) \times M_X/MC$$

where  $\Delta X/\Delta CO_x$  is the emission ratio for the emitted component,  $M_{AIR}$  is the molecular mass of air,  $MC$  is the atomic mass of C,  $M_X$  is the molecular mass of the gas phase component, X,  $\rho_{AIR}$  is the density of air at ambient conditions, and the EI(C) used for this work in g C per g propellant is determined from the DODIC information for a given munition. This method of calculating the emission index makes the assumption that propellant carbon is converted to CO<sub>x</sub> during combustion with 100% efficiency. Measured carbon species other than CO and CO<sub>2</sub> contain, at most, a few percent of propellant C, making this a reasonably accurate assumption given the uncertainties in quantifying emission ratios.

The elemental compositions of the five munitions studied, computed from the chemical species listed in the DODIC tables for these munitions, is shown in Table 4-1 along with the bulk materials associated with the physical structure of the projectiles, primers and weapons tubes.

**Table 4-1. Propellant Atomic Composition (g) & Projectile/Primer/Weapons Tube Materials**

Weapon Model	M109A5	M119	M203	M240	M249
Munition	M4A1	M1	M781	M80	M855
Element	155mm	105mm	40mm	7.62mm	5.56mm
H	1.67E+02	4.21E+01	7.98E-03	7.99E-02	4.24E-02
C	1.76E+03	4.10E+02	7.50E-02	7.98E-01	4.20E-01
O	3.32E+03	8.01E+02	2.09E-01	1.70E+00	8.55E-01
N	8.17E+02	2.02E+02	5.53E-02	4.08E-01	4.37E-01
K	3.94E+01	8.59E+01	1.96E-03	0.00E+00	0.00E+00
S	1.68E+01	3.12E+01	6.07E-04	5.01E-03	3.05E-03
Ba	0.00E+00	0.00E+00	2.48E-03	6.55E-03	4.26E-03
Pb	0.00E+00	1.01E+01	5.20E-03	6.61E-03	4.29E-03
Sb	0.00E+00	1.21E-01	1.53E-03	4.18E-03	2.71E-03
Fe	0.00E+00	0.00E+00	1.28E-05	0.00E+00	0.00E+00
Zn	0.00E+00	0.00E+00	6.41E-06	0.00E+00	0.00E+00
Si	0.00E+00	0.00E+00	6.41E-06	0.00E+00	0.00E+00
Ca	0.00E+00	0.00E+00	0.00E+00	2.98E-03	1.75E-03
Na	0.00E+00	0.00E+00	0.00E+00	4.83E-03	2.83E-03
Al	0.00E+00	0.00E+00	2.11E-03	2.72E-03	1.77E-03
Cl	0.00E+00	1.52E-01	0.00E+00	0.00E+00	0.00E+00
TOTAL (g)	6.12E+03	1.58E+03	3.61E-01	3.02E+00	1.77E+00

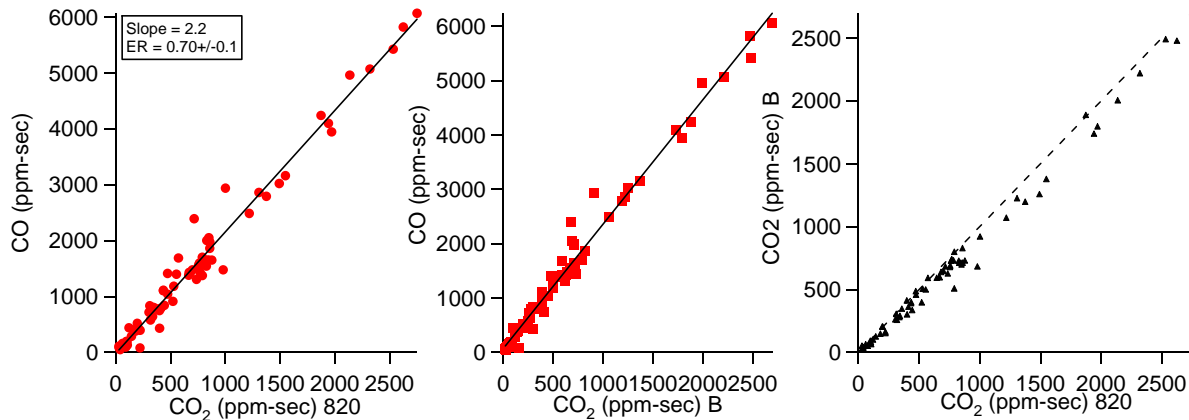
Munition	M3A1	M1	M781	M80	M855
Bulk Material	155mm	105m	40mm	7.62mm	5.56mm
Aluminum Alloy		x			
Brass		x			
Copper Alloy		x	x	x	x
Lead Antimony				x	x
Nylon			x		
Plastic Shield					
Steel		x		x	
Zinc Alloy					

Emissions ratios used to compute emission indices are determined by plotting measured emission plume pollutant concentrations (above ambient background) against excess CO<sub>x</sub> for all of the interference free intercepted muzzle plumes from a given weapon type. By combining data from multiple shots we can determine a better average emission ratio for each detected pollutant for each weapon/munitions combination.

As noted in Section 4.3 and Table 3-1, we deployed two LI-COR CO<sub>2</sub> instruments to provide multiple plume timing markers; a model 6262, which is more precise for relatively low CO<sub>2</sub> concentrations, and a model 820, which is more accurate for very high CO<sub>2</sub> concentrations (>1000 ppm). Plots of the integrated QC-TILDAS CO measurements versus the integrated LI-

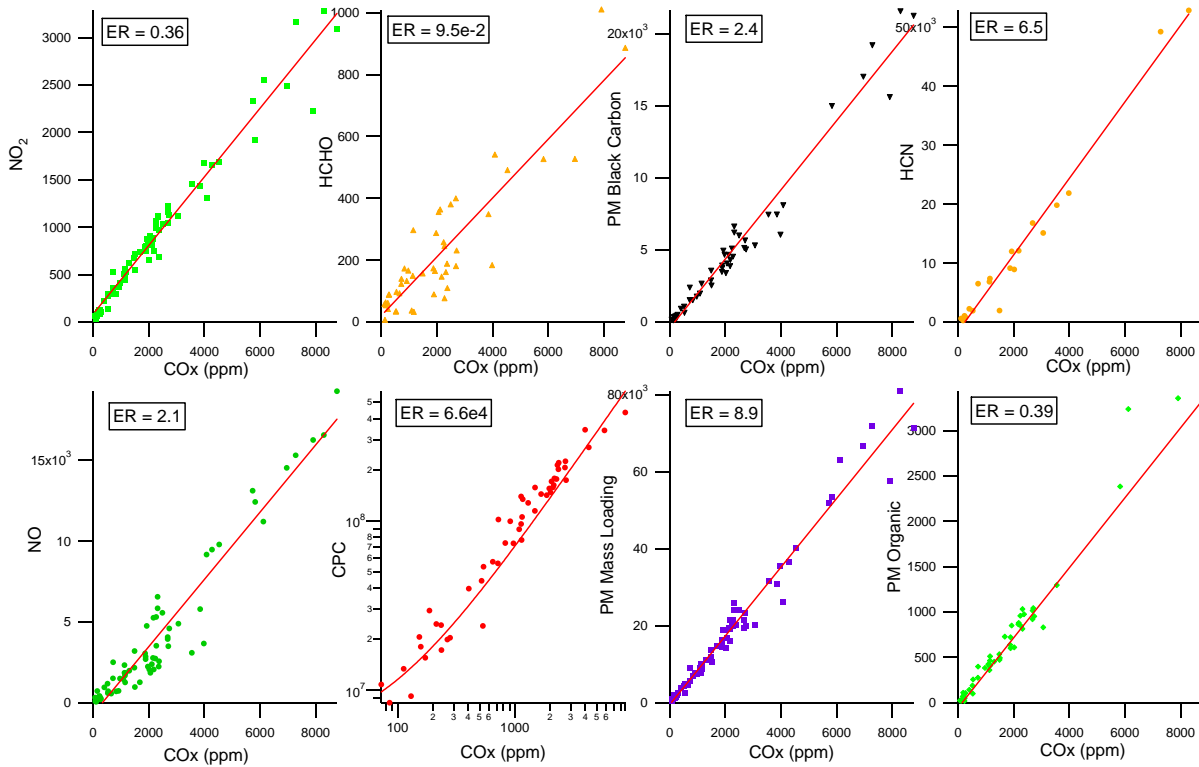


COR 820 and the LI-COR 6262 (labeled instrument B) CO<sub>2</sub> measurements for M240 muzzle plume measurements are shown in Figure 4-4. Slopes of the two plots are very similar and both indicate an average CO emission ratio of  $0.70 \pm 0.10$ . Also shown in Figure 4-4 is a correlation plot of the integrated CO<sub>2</sub> measurements from the two LI-COR models along with a dashed 1/1 line that would be produced if the two instruments were identically sensitive over the full measurement range. As expected, the major deviations from the 1/1 line occur at CO<sub>2</sub> concentrations above 500 ppmv (>1000 ppm-sec) where the accuracy of the 6262 model is decreased.



**Figure 4-4. M240 CO emission ratios and LI-COR CO<sub>2</sub> measurement correlation.**

Figure 4-5 shows representative M240 emission ratio data for selected muzzle plume species and fine PM properties. Despite the short duration of the individual shot plumes the correlations are reasonably tight ( $R^2 > 0.8$ ) and they produce accurate emission indices.



**Figure 4-5. Example M240 muzzle plume species and fine PM property emission ratios. Units: ppbv/ppmv CO<sub>x</sub> for trace gases, μgm<sup>-3</sup>/ppmv CO<sub>x</sub> for PM chemical components, particles cm<sup>-3</sup>/ppmv CO<sub>x</sub> for CPC particle number density.**

The composition data shown in Table 4-1 and emission ratios like those shown in Figure 4-5 have been used to calculate the emissions indices for each weapons/munitions combination tested. These are presented in Section 4.3.4.

#### 4.3.4 Emission Index and Breathing Zone Data

##### 4.3.4.1 Emission Indices

Muzzle and breech (averaged together) plume emission indices for detected species from each of the five weapons/munitions combinations measured during the Ft. Sill campaign are displayed in Table 4-2. Not all species listed in Table 3-1 are available for each weapon. The slow AMS response achieved on the first measurement day (03/19) allowed only partial quantification of the fine PM non-refractory composition. The co-firing of the M240 and M249 weapons on 03/20 made it difficult to isolate M249 plumes for TOF-AMS data. Finally, as expected, not all weapons/munitions combinations produce measurable amounts of all of the toxic species targeted.

As detailed in Table 1-1, we were successful at measuring muzzle and breech emission plumes (either down field and/or in the breathing zones of soldiers operating the weapons) for four out of the five weapon systems investigated. The M109A5 was the only fully enclosed weapon system and sampling from inside the vehicle without disrupting the training of the soldiers was

impractical. For the small weapons (M203, M249, and M240), we were able to identify and measure breech and muzzle plumes individually on occasion. However, due to the large number of shots fired on these weapons, the fact that typically more than one weapon was fired nearly simultaneously up wind from our sampling system, and the relatively short distances in distance (and time) between the exhausted muzzle and breech plumes for these small weapons, we were unable to readily distinguish between muzzle and breech plumes during analysis. With a bit more patience and careful application of sampling technique, lessons learned from this initial test can readily be used to make confident measurements of muzzle and breech plumes on small fire arms during future studies.

The one weapon system where we were readily able to distinguish between muzzle and breech emission plumes was the M119 system. Table 4-2 lists the average emission indices for the muzzle and breech plumes determined independently. Differences are evident between muzzle and breech plumes, a few of which will be discussed in more detail in Section 4.3.4.2 below. The fact that the muzzle and breech plumes are different for the M119 weapon has implications for measurement testing and reporting. For example, the emission plume measurements conducted at the Aberdeen test facility for weapons fully enclosed in a sampling chamber cannot distinguish between the emission from muzzle and breech plumes.

As the first real-time measurements of PoF emissions on active open air training ranges, the data shown in Table 4-1 represent a significant achievement. We note that the high wind conditions encountered at Ft. Sill resulted in very fast moving plumes with concomitant short measurement times, producing a stringent test of real-time measurement capabilities. Calmer wind conditions and slower moving emission plumes would improve measurement accuracy.

**Table 4-2. Average Emission Indices (g / g propellant)**

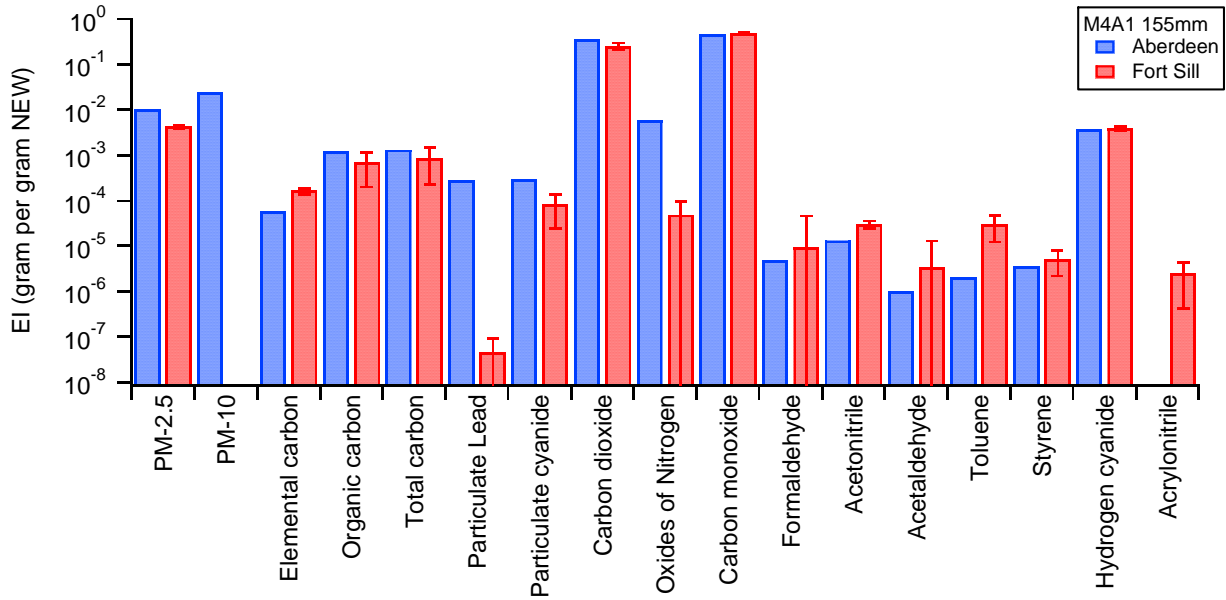
Species Name	Weapon Model #	M109A5			M119			M203			M240			M249		
		Emission Index Units (per g propellant)			Average	Standard deviation	# shots	Average	Standard deviation	# shots	Average	Standard deviation	# shots	Average	Standard deviation	# shots
<b>PM Measurements</b>																
Particle Count	#	1.20E+13	1.8E+12	14	5.76E+12	3.6E+12	57	2.57E+13	2.2E+13	66	5.07E+13	1.3E+13	51	8.08E+12	5.4E+12	28
Particle Mass	g	4.27E-03	2.97E-04	19	5.71E-03	3.23E-03	60	5.62E-03	2.85E-03	73	4.85E-03	8.05E-04	72	1.32E-03	8.91E-04	25
PM Black Carbon	g	1.63E-04	2.59E-05	19	1.51E-03	1.07E-03	54	1.53E-03	7.71E-04	64	1.20E-03	2.54E-04	50	3.85E-04	2.25E-04	22
PM Org	g	6.68E-04	4.75E-04	5	2.55E-04	2.09E-04	35	3.05E-04	2.37E-04	33	2.14E-04	9.71E-05	50	0.00E+00	0.00E+00	0
PM SO4	g	3.20E-05	2.99E-05	6	1.37E-05	1.18E-05	26	3.69E-05	3.39E-05	35	7.15E-07	1.45E-06	46	0.00E+00	0.00E+00	0
PM NO3	g	1.28E-05	1.26E-05	6	5.80E-06	4.56E-06	33	1.10E-05	1.05E-05	34	2.61E-06	7.39E-07	50	0.00E+00	0.00E+00	0
PM NH4	g	1.02E-05	6.65E-06	5	-5.30E-05	9.38E-05	35	-3.06E-05	5.49E-05	38	1.34E-06	6.89E-07	53	0.00E+00	0.00E+00	0
PM PAH	g	3.00E-07	2.30E-07	6	2.93E-06	3.38E-06	30	0.00E+00	0.00E+00	0	-8.46E-06	9.65E-06	50	0.00E+00	0.00E+00	0
PM Pb	g	4.53E-08	3.34E-08	8	7.43E-07	7.28E-07	27	6.22E-05	5.08E-05	35	2.64E-05	6.74E-06	48	0.00E+00	0.00E+00	0
PM HCN	g	8.00E-05	5.53E-05	5	1.72E-05	1.58E-05	35	8.32E-06	5.19E-06	38	9.27E-06	3.03E-06	53	0.00E+00	0.00E+00	0
<b>Trace Gas Measurements</b>																
Carbon dioxide	g	2.88E-01	3.77E-02	19	2.52E-01	1.04E-01	58	4.97E-01	1.92E-01	71	3.42E-01	9.80E-02	72	4.05E-01	1.52E-01	32
Carbon dioxide	g	2.18E-01	1.78E-02	19	2.41E-01	9.09E-02	60	4.10E-01	9.88E-02	74	2.87E-01	5.36E-02	72	3.98E-01	1.30E-01	32
Nitrogen monoxide	g	4.10E-05	1.65E-05	3	2.79E-03	2.61E-03	60	8.71E-03	4.13E-03	69	1.10E-03	5.03E-04	72	1.64E-03	7.04E-04	32
Carbon monoxide	g	4.88E-01	2.40E-02	19	4.51E-01	5.79E-02	60	2.23E-01	6.29E-02	74	4.34E-01	3.41E-02	72	3.00E-01	8.30E-02	32
Nitrogen dioxide	g	3.30E-05	3.08E-05	9	2.31E-04	2.59E-04	52	8.07E-04	3.58E-04	73	4.42E-04	9.83E-05	72	3.16E-04	3.04E-04	20
Formaldehyde	g	9.08E-06	3.65E-05	19	1.41E-04	1.42E-04	25	2.40E-04	1.24E-04	46	9.13E-05	6.39E-05	47	6.43E-04	7.81E-04	13
Acetonitrile	g	2.95E-05	5.20E-06	7	7.84E-04	1.17E-03	16	3.64E-05	1.66E-05	33	3.85E-05	2.80E-05	24	4.42E-05	3.02E-05	17
Acetaldehyde	g	3.37E-06	9.61E-06	4	1.75E-04	8.73E-05	14	9.81E-05	4.65E-05	3	5.30E-05	3.76E-05	6	4.29E-05	6.05E-05	5
Benzene	g	9.50E-05	9.08E-05	2	1.59E-03	7.67E-04	18	4.26E-04	2.95E-04	30	1.15E-04	1.00E-04	19	1.42E-04	7.79E-05	7
C2Benzene	g	2.30E-05	7.61E-06	4	2.11E-05	8.45E-06	2	3.39E-05	2.65E-05	10	5.08E-06	3.61E-06	3	3.13E-03	7.32E-03	6
Toluene	g	2.94E-05	1.70E-05	4	2.54E-04	1.56E-04	18	4.61E-05	1.75E-05	10	8.19E-06	1.68E-06	2	7.35E-03	1.38E-02	4
Benzonitrile	g	0.00E+00	0.00E+00	0	8.11E-05	6.78E-05	11	9.71E-06	7.33E-06	9	5.51E-06	3.04E-06	2	5.79E-04	1.28E-03	6
Styrene	g	5.13E-06	2.96E-06	3	3.53E-05	4.16E-05	10	1.89E-05	1.38E-05	9	4.94E-06	1.59E-06	4	8.14E-04	2.13E-03	8
Hydrogen cyanide	g	3.90E-03	4.27E-04	7	3.26E-03	1.33E-03	16	2.15E-04	1.57E-04	33	3.03E-03	1.08E-03	20	1.05E-03	7.01E-04	15
Alkene & acetic acid frags	g	2.39E-05	2.08E-05	4	1.27E-04	5.31E-05	9	1.26E-04	1.08E-04	3	0.00E+00	0.00E+00	0	0.00E+00	0.00E+00	0
Acrylonitrile	g	2.41E-06	1.99E-06	5	1.06E-03	2.01E-03	16	8.39E-05	4.08E-05	35	1.03E-05	5.11E-06	23	1.31E-05	3.93E-06	9
Acetic acid	g	1.52E-05	1.36E-05	2	1.94E-05	1.76E-05	3	3.49E-05	1.37E-05	3	1.18E-05	0.00E+00	1	0.00E+00	0.00E+00	0
Furan	g	9.45E-06	2.35E-06	3	5.95E-05	6.23E-05	6	4.11E-05	2.05E-05	6	7.66E-07	0.00E+00	1	4.96E-04	5.00E-04	9
Ethyl acetate	g	-2.96E-06	0.00E+00	1	6.10E-06	1.64E-06	4	3.30E-05	1.57E-05	3	2.13E-06	4.82E-07	2	0.00E+00	0.00E+00	0

**Table 4-3. M119 emission indices from muzzle and breech plumes (g / g propellant).**

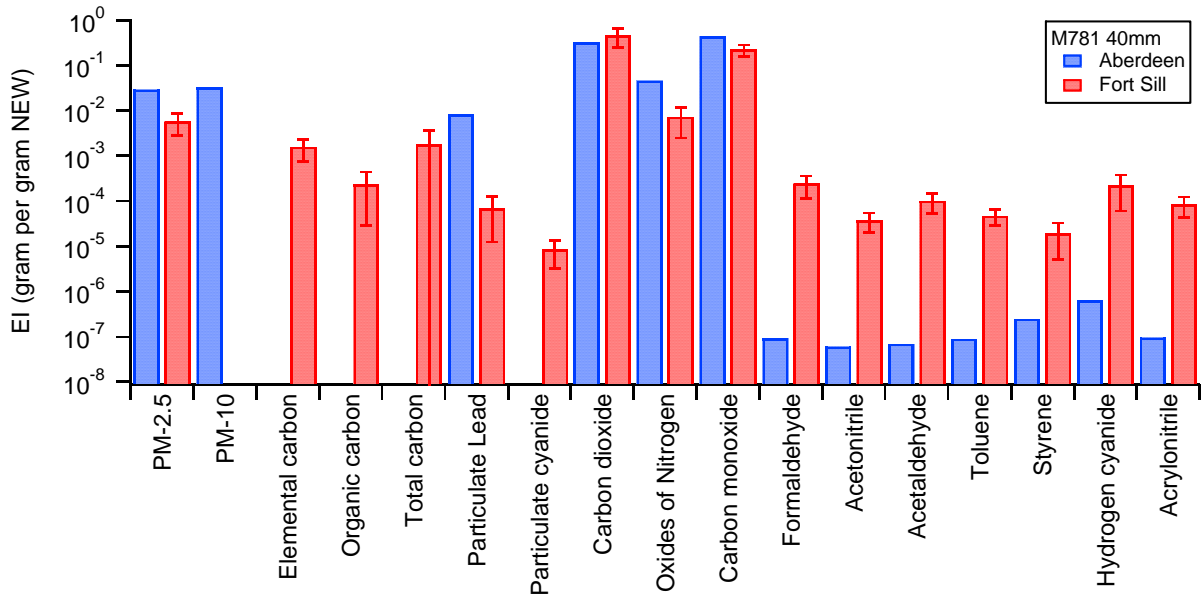
Species Name	Weapon Model # Emission Index Units (per g propellant)	M119 - Combined			M119 - Breech Plumes			M119 - Muzzle Plumes		
		Standard			Standard			Standard		
		Average	deviation	# shots	Average	deviation	# shots	Average	deviation	# shots
<b>PM Measurements</b>										
Particle Count	#	5.76E+12	3.6E+12	57	3.06E+12	2.9E+12	25	7.86E+12	2.5E+12	32
Particle Mass	g	5.71E-03	3.23E-03	60	7.52E-03	4.31E-03	25	4.42E-03	9.20E-04	35
PM Black Carbon	g	1.51E-03	1.07E-03	54	2.05E-03	1.59E-03	20	1.20E-03	3.00E-04	34
PM Org	g	2.36E-04	2.20E-04	35	3.24E-04	2.46E-04	21	1.04E-04	4.33E-05	14
PM SO4	g	1.37E-05	1.18E-05	26	1.48E-05	1.31E-05	20	1.00E-05	5.52E-06	6
PM NO3	g	5.80E-06	4.56E-06	33	6.03E-06	4.75E-06	20	5.44E-06	4.41E-06	13
PM NH4	g	-5.30E-05	9.38E-05	35	-5.11E-05	4.02E-05	21	-5.59E-05	1.43E-04	14
PM PAH	g	2.93E-06	3.38E-06	30	3.97E-06	3.86E-06	19	1.14E-06	8.23E-07	11
PM Pb	g	8.39E-07	7.94E-07	27	5.66E-07	2.89E-07	20	1.62E-06	1.23E-06	7
PM HCN	g	1.72E-05	1.58E-05	35	2.37E-05	1.75E-05	21	7.60E-06	4.25E-06	14
<b>Trace Gas Measurements</b>										
Carbon dioxide	g	2.52E-01	1.04E-01	58	3.09E-01	1.17E-01	23	2.15E-01	7.64E-02	35
Carbon dioxide	g	2.41E-01	9.09E-02	60	3.01E-01	1.11E-01	25	1.98E-01	3.30E-02	35
Nitrogen monoxide	g	2.79E-03	2.61E-03	60	3.92E-03	3.76E-03	25	1.98E-03	5.12E-04	35
Carbon monoxide	g	4.51E-01	5.79E-02	60	4.13E-01	7.08E-02	25	4.78E-01	2.10E-02	35
Nitrogen dioxide	g	2.31E-04	2.59E-04	52	2.88E-04	3.68E-04	24	1.82E-04	7.68E-05	28
Formaldehyde	g	1.41E-04	1.42E-04	25	8.74E-05	6.03E-05	3	1.49E-04	1.49E-04	22
Acetonitrile	g	7.84E-04	1.17E-03	16	1.45E-03	1.38E-03	8	1.18E-04	1.00E-04	8
Acetaldehyde	g	1.75E-04	8.73E-05	14	1.96E-04	1.16E-04	7	1.54E-04	4.54E-05	7
Benzene	g	1.59E-03	7.67E-04	18	2.44E-03	7.34E-04	6	1.16E-03	2.71E-04	12
C2Benzene	g	2.11E-05	8.45E-06	2	0.00E+00	0.00E+00	0	2.11E-05	8.45E-06	2
Toluene	g	2.54E-04	1.56E-04	18	4.44E-04	1.12E-04	6	1.59E-04	4.55E-05	12
Benzonitrile	g	8.11E-05	6.78E-05	11	1.30E-04	8.41E-05	4	5.32E-05	4.02E-05	7
Styrene	g	3.53E-05	4.16E-05	10	6.48E-05	6.55E-05	3	2.27E-05	2.33E-05	7
Hydrogen cyanide	g	3.21E-03	1.25E-03	16	3.36E-03	1.53E-03	8	3.06E-03	9.84E-04	8
Alkene & acetic acid frags	g	1.27E-04	5.31E-05	9	1.52E-04	4.23E-05	6	7.66E-05	3.25E-05	3
Acrylonitrile	g	1.06E-03	2.01E-03	16	2.05E-03	2.53E-03	8	6.02E-05	5.91E-05	8
Acetic acid	g	1.94E-05	1.76E-05	3	2.83E-05	1.22E-05	2	1.69E-06	0.00E+00	1
Furan	g	5.95E-05	6.23E-05	6	5.95E-05	6.23E-05	6	0.00E+00	0.00E+00	0
Ethyl acetate	g	6.10E-06	1.64E-06	4	6.10E-06	1.64E-06	4	0.00E+00	0.00E+00	0

Three of the munitions measured at Ft. Sill, the 155mm M4A1, the 40mm M781 and the 7.62mm M80 were also characterized in a firing point emissions study funded by USAEC and conducted by the Aberdeen Test Center in an enclosed test chamber at the Aberdeen Proving Ground, MD (USAEC, 2006).

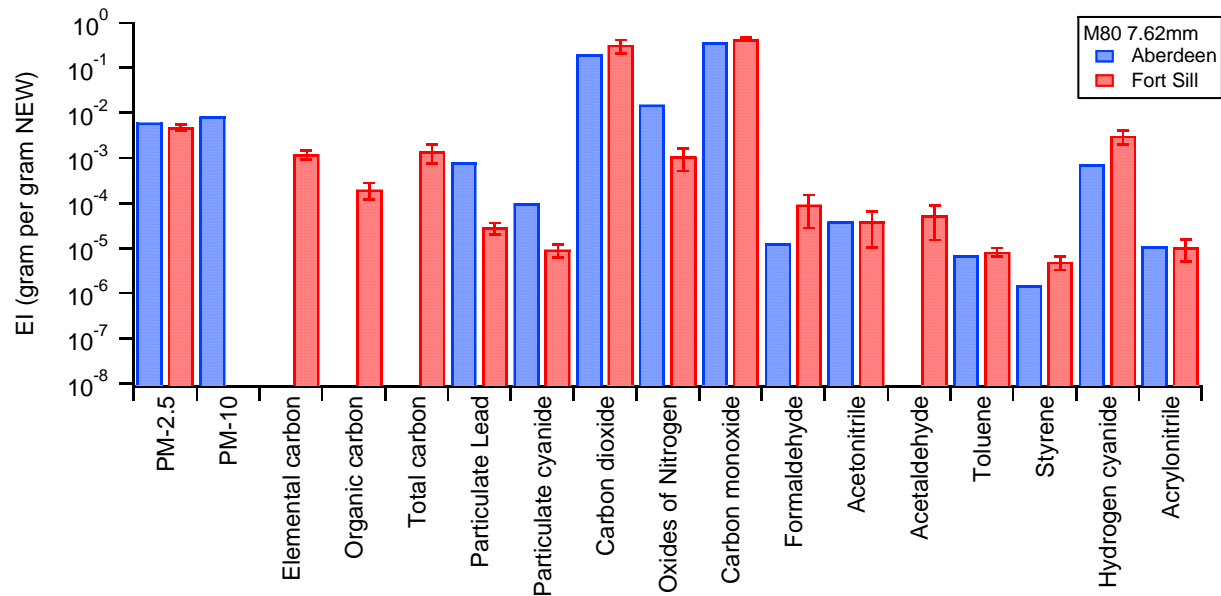
Comparisons of measured emission indices (emission factors) reported for the Aberdeen tests with those derived from the Ft. Sill measurements are presented in Figures 4-6 – 4-8. Statistical ( $1\sigma$ ) error bars due to the variations in emission ratio measurements (see Figure 4-5) are shown for the Ft. Sill data. Error bars that are larger than the mean value indicate that species concentrations were near or below the detection limit and can be regarded as non-detects.



**Figure 4-6. Comparison of Aberdeen and Ft. Sill Emission Indices for the 155mm M4A1**



**Figure 4-7. Comparison of Aberdeen and Ft. Sill Emission Indices for the 40mm M781**



**Figure 4-8. Comparison of Aberdeen and Ft. Sill Emission Indices for the 7.62mm M80**

Error estimates for the Aberdeen measurements are not available, but most have been assigned an “average” reliability rating (USAEC, 2006).

The differences in Ft. Sill and Aberdeen fine PM and trace gas emission indices may be due to differences in either measurement techniques or test conditions. Measurement techniques can capture part, but not all of a species, or they may be sensitive to interfering species that are incorrectly attributed to the target species. An example of the first type is particulate Pb, which, is not fully flash vaporized at the normal AMS of 600°C. Thus, the fine PM lead EIs reported represent a lower limit measurement, not a full quantification.

However, lower measurement values do not always represent partial measurements. While many species comparisons in Figures 4-6 – 4-8 are well within measurement uncertainties, the nitrogen oxides (generally termed NO<sub>x</sub> and defined as the sum of NO and NO<sub>2</sub>, reported as NO<sub>2</sub>) measured at Aberdeen greatly exceed those measured at Ft. Sill. The measurements of nitrogen oxides (NO<sub>x</sub>) at Fort Sill were made with a chemiluminescence analyzer for NO and a QC-TILDAS spectrometer for NO<sub>2</sub>, whereas the measurements at Aberdeen were made using a chemiluminescence sensor with a heated molybdenum converter to reduce NO<sub>2</sub> to NO (TEI model 10AR). These converters are not specific to NO<sub>2</sub> and are known to convert other oxidized nitrogen-containing compounds such as organic nitrates, nitric acid and particulate nitrate into a measured NO signal. If any of these compounds were produced by the measured munitions then one would expect the converter-based measurements to be higher than the measurements at Fort Sill. A similar difference in the measurements would be expected if even a small fraction of other nitrogen-containing compounds such as HCN and NH<sub>3</sub>, which are known to be emitted by common propellant combustion, were converted into NO in the molybdenum converter. We

suspect the nitrogen oxide (NO<sub>x</sub>) emissions reported for the Aberdeen experiments (USAEC, 2006) are too large and at least part of the error is due to the measurement method employed.

One obvious difference in Aberdeen and Ft. Sill test conditions may be responsible for differences in measured emission indices for several of the trace gas and PM chemical components compared above. At Ft. Sill weapons emissions plumes were sampled in open air within a few seconds of each shot, while at Aberdeen plumes from single shots or multiple shot bursts were confined in a chamber, mixed into a limited amount of chamber background air with a fan and then sampled over an approximately twenty minute time period. These differences in sample time and dilution conditions may significantly impact the gas to particle conversion processes for semi-volatile inorganic and organic species.

For instance, acid vapors like sulfuric acid, nitric acid and hydrogen cyanide are often surface reactive and can be converted to PM constituents either by direct reaction with PM surfaces or by interacting with ammonia vapor (often produced by nitrogen propellant combustion) to form water soluble ammonium bisulfate, ammonium nitrate, or ammonium cyanide. These are both kinetic heterogeneous processes that require the reactant gases to diffuse to and interact with existing particle surfaces. Similarly, semi-volatile or surface reactive organic species can condense on smoke particles after they have mixed with enough ambient air to cool. These heterogeneous processes take time and the much longer residence times and controlled dilution conditions of the trapped emission plume gases and particles in the Aberdeen chamber may allow them to proceed more completely.

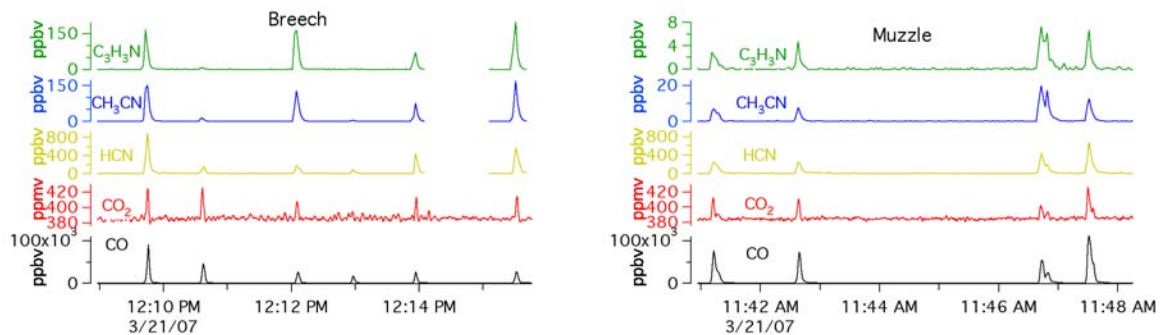
These differences in gas/particle interaction times and dilution rates may explain why the Ft. Sill gaseous hydrogen cyanide measurements are consistently higher than the Aberdeen measurements (155 mm M4A1, 40 mm M78 and 7.62 mm M80) while the Ft. Sill particulate cyanide measurements (155 mm M4A1 and 7.62 mm M80) measurements are lower than the available Aberdeen measurements. Similarly, the generally higher gaseous toxic organic compound measurements at Ft. Sill may be due to lower heterogeneous loss rates due to absorption or reaction on smoke particles as well as the absence of absorptive or reactive loss on chamber walls. The Ft. Sill data indicate that measurements of semivolatile gun exhaust plume species in open air conditions may differ significantly from those in enclosed test chambers due to losses on chamber surfaces and enhanced gas to particle heterogeneous chemistry under chamber conditions.

#### **4.3.4.2 M119 Breech versus Muzzle Emissions**

The trace gas emission profiles for the breech and the muzzle plumes were found to be very different for the M119 towed howitzer weapon system (Table 4-3). For example, two organic cyanide compounds, acetonitrile and acrylonitrile, were found to have concentrations 10-20 times greater in the breech plumes than in the muzzle plumes. The larger gas phase concentrations of the organic cyanide compounds in the breech versus muzzle plumes is clearly shown in Figure 4-9 where time series traces for selected measured species are plotted for several muzzle and breech plumes. The scales for the organic cyanide compounds differ appreciably between the left and right plots in Figure 4-9. This artillery weapon fired a round approximately once every several minutes and each round fired and subsequent plume are easily

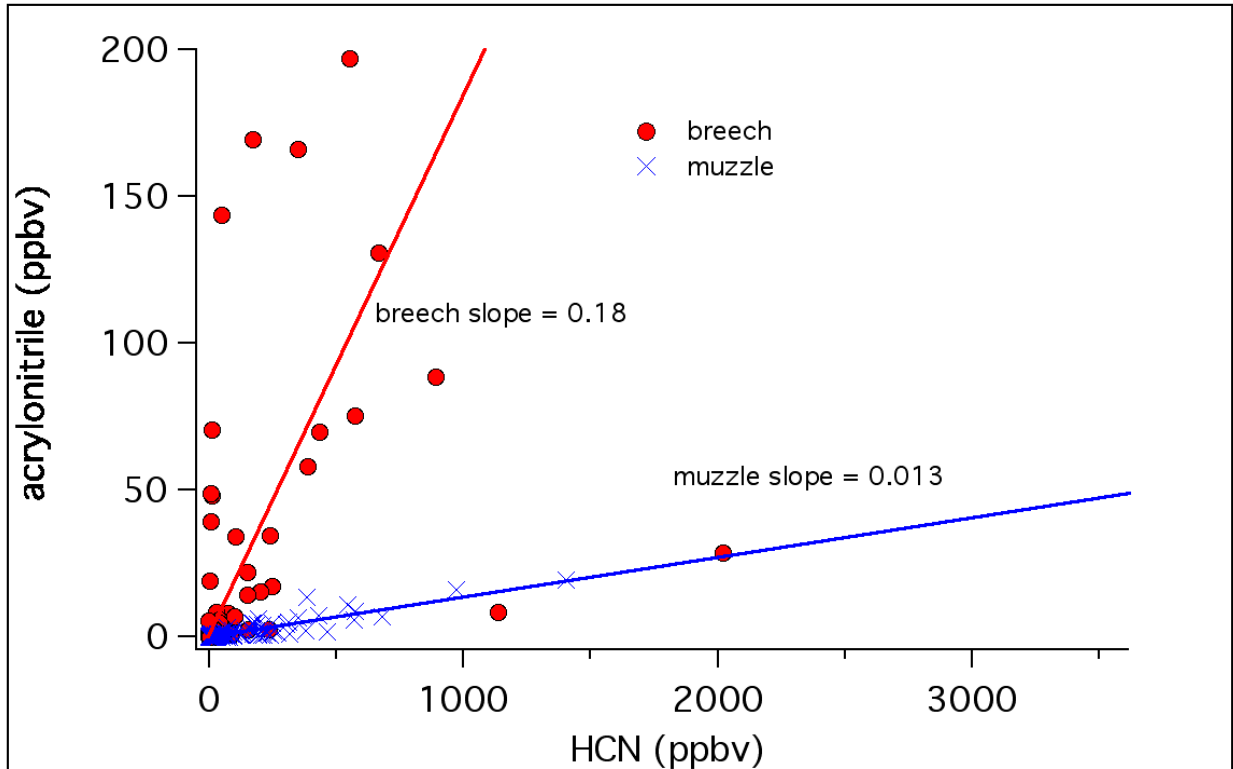
identified on these graphs. We note that with the exception of the acetonitrile and acrylonitrile species the other emission products are present at similar levels for both muzzle and breech plumes. This indicates that the increased concentration of these organic cyanide compounds was not the result of sampling a more concentrated plume. While the organic cyanides appear to differ significantly in concentration between the breech and muzzle plumes, Figure 4-9 shows that the gas phase hydrogen cyanide concentrations are larger and do not exhibit a similar dependence on the plume source. Figure 4-10 shows the correlation between gas phase acrylonitrile and hydrogen cyanide and highlights the significant increase in organic cyanide compounds in breech plumes compared with muzzle plumes.

Enhanced breech emissions are of primary concern since these emissions have a greater impact on the soldiers breathing zone. Because of this, more analysis time was spent trying to understand the origin and behavior of these emission products. It was noted that the measured emission ratios for these organic cyanide compounds exhibit much more variability than that of the other emission trace gas species. This variability of emission ratios coupled with the low concentrations of these species in the muzzle plume implies that these species are not produced directly from the detonation of the propellant. We hypothesize that acetonitrile and acrylonitrile may be volatile decomposition products from the residue left in the barrel of the weapon after firing.



**Figure 4-9. Trace gas emission profiles for breech and muzzle plumes from the M119. Note the large differences in the top two scales in both plots.**



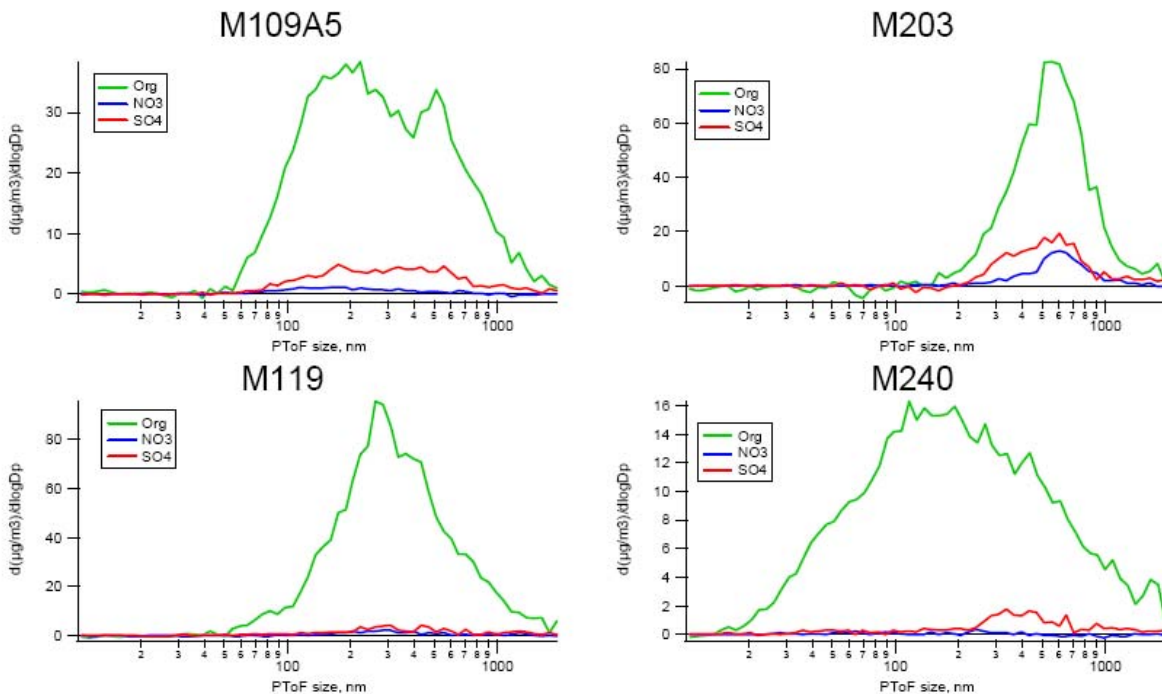


**Figure 4-10. Correlation plot of acrylonitrile versus hydrogen cyanide for both breach and muzzle plumes. The organic cyanide compounds were greatly enhanced in the breach plumes compared with muzzle plumes. Hydrogen cyanide concentrations were similar for both plumes.**

#### 4.3.4.3 PM Size Distributions

Particulate matter size distributions can be important in assessing the potential health and environmental impacts of PM emissions. At Ft. Sill the AMS was operated in the particle TOF to measure the vacuum aerodynamic diameter of weapons plume PM chemical components. Figure 4-11 shows the measured size distributions for PM organic, nitrate, and sulfate components. The AMS measures approximately PM<sub>1.0</sub> (e.g. particles less than 1 micron in diameter). Representative distributions shown are for the M109A5, M119, M203, and M240 weapons systems. Distinctly different size distributions were measured for the different weapons. The rapid fire M240 shows the widest particle size distribution with the smallest particle sizes. The M203 emissions show only large particles, greater than ~200 nm  $D_{va}$  and the M109A5 particles appear to have a bimodal size distribution. Note that the aerodynamic nozzle used in the TOF-AMS deployed at Ft. Sill has an ~100% transmission factor for particles between ~60 and 600 nm, so the size distributions shown above and below this size range may be significantly attenuated. The PM organic content is the largest non-refractory portion of the weapons emissions particles measured at Ft. Sill. The sulfate and nitrate component signals plotted in Figure 4-11 are too low to produce reliable size distributions but the similar peak widths shown

for the M109A5 155mm and the M203 40mm data indicate that the organic and inorganic components are internally mixed, consistent with earlier AMS PoF measurements at the Aberdeen facility (Onasch et al., 2003).

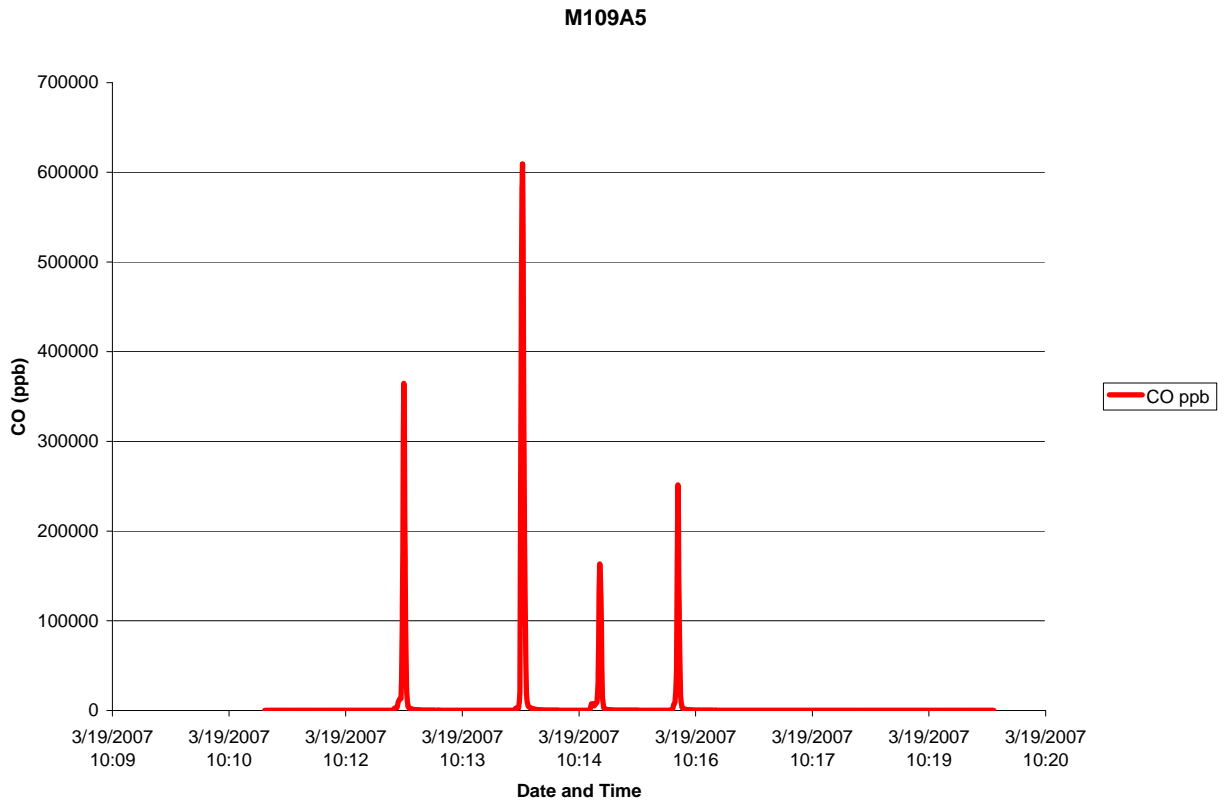


**Figure 4-11. PM Vacuum Aerodynamic Size Distributions**

The PM size distributions measured at Ft. Sill in open-air conditions are probably more representative of training range exposure and inhalation dosage than those measured in the Aberdeen chamber. Our previous AMS PM size distribution measurements at Aberdeen showed significant PM growth during the twenty-minute sampling period, likely due to both particle agglomeration and the heterogeneous growth by vapor deposition processes described in Section 4.3.4.1 above.

#### 4.3.4.4 Breathing Zone Data

As discussed in Section 4.3.2 breathing zone data were taken and reported as specified by USACHPPM. EXCEL spreadsheets were prepared that provide 5-15 minutes of breathing zone data for the M109A5, M119, M203, M249 and M240 weapons. Plots of CO emissions versus time are also included to clearly indicate when weapons emissions plumes are being detected. An example time period for the M109A5 is shown in Figure 4-12, showing background (ambient) levels broken by several shot plumes. The submitted breathing zone data are included in Appendix G of this report.



**Figure 4-12. CO concentrations during a five minute period while sampling four shots fired from a M109A5 paladin.**

## **5. Cost Assessment**

### **5.1 Cost Reporting**

Since the planned two-week field measurement mission was of limited duration, there was no cost breakdown reports prepared while the field team was deployed. The field measurements were carefully costed, in consultation with USAEC, before the project was funded. ARI has adhered to their original cost estimate. Full financial reporting of the costs of preparing for and executing the planned field measurements were included in the monthly project reports prepared for ESTCP

### **5.2 Cost Analysis**

Not applicable.

## **6. Implementation Issues**

### **6.1 Environmental Checklist**

The mobile laboratory operation produces no extraordinary emissions or other environmental impacts that require permits. Since we measured emissions from regularly scheduled training exercises at Fort Sill the Fort Sill operations and training were not impacted in any significant matter that will require modifications to any existing environmental permits.

### **6.2 Other Regulatory Issues**

Not applicable.

### **6.3 End-User/Original Equipment Manufacturer (OEM) Issues**

Not Applicable.

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## 8. Points of Contact

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## **Appendix A – Quality Assurance Plan**

### **A.1 Purpose and Scope**

The scope of this data quality assurance (QA) plan is to ensure that the real-time trace gas and fine PM data taken to characterize and quantify muzzle plume emissions are adequately recorded, quality assured, and archived for final analysis. Data characterizing both PoF emission plumes and ambient background conditions will be required, since the relevant quantities are the difference in concentration between the intercepted plume measurements and the ambient background concentrations immediately before and after plume intercepts. Plume and background data will be recorded, automatically reduced, quality assured, and electronically archived in the same way.

### **A.2 Data Quality Assurance Responsibilities**

The measurement team leader, Dr. John T. Jayne, will be the data quality assurance leader. Measurement team members will bear direct responsibility for assuring data quality for the real-time instruments they operate and calibrate. Dr. Ezra Wood will be responsible for QA of gas phase data for CO and NO<sub>2</sub> from the ARI Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) instruments, CO<sub>2</sub> from the LI-COR Non-Dispersive Infrared (NDIR) instrument and NO from the Thermo Environmental chemiluminescence instrument. Dr. Jayne and Dr. Michael Timko will be responsible for the ARI TOF-AMS, Thermo Environmental MAAP, and TSI CPC particle number density instruments.

### **A.3 Data Quality Parameters**

Key data parameters for the trace gas measurements are measured concentration, expressed as a molecular mixing ratio (e.g. parts-per-million by volume, ppmv, or parts-per-billion-by-volume, ppbv). The standard output is the mixing ratio and an estimate of its uncertainty based on the standard deviation of repetitive one second time averaged measurements of known trace gas levels and estimates of any systematic errors introduced by uncalibrated sampling losses, instrument drift or other instrumental errors.

Key data parameters for the major fine PM measurements (the TOF-AMS and MAAP) are measured mass loadings of specific PM components expressed in  $\mu\text{g}/\text{m}^3$  or  $\text{ng}/\text{m}^3$  along with estimated uncertainties based on measurement precision as determined by standard deviations from known particle calibration measurements and estimates of systematic errors of the specific measurement instrument. However, for the TSI Condensation Particle Counter (CPC) instrument the key data parameter is the number density of particles within the instruments measurement range (~10 to 1000 nm diameter) expressed as particles/cm<sup>3</sup>.



#### **A.4 Data Quality Indicators, Quality Assurance and Data Format**

As noted in section 3.7 of the test plan this project will utilize only real time instrumentation methods and there will be no traditional grab sample collection and analyses. The quality assurance procedures for real time instrumentation methods involve inspection of the fundamental instrumentation measurement data (infra red spectra, mass spectra, etc.) to assure detection of target species and computation of the average and statistical variance for each species measurement. These data quality assurance assessments will be made by doctoral level scientists with extensive experience in analyzing data from the real time instruments used in this measurement campaign. Analysis of absolute species concentration requires the incorporation of calibration procedures performed during the field campaign and described in detail in section A.5, for each instrument, directly below. After analysis of absolute in plume (above background) concentrations plume emission indices (pounds of pollutants/pounds of NEW) will be computed along with standard deviation. These data will be evaluated based on computed statistical significance and flagged as either robust and reliable, questionable and/or unreliable. The data will be entered into an excel spread sheet sorted by munition type (Propellant Train) (DODIC) and transmitted by both hard copy and electronic format to USAEC and USACHPPM.

#### **A.5 Calibration Procedures**

Each real-time instrument operates on different physical principles; however, they all require established baselines for quantitative measurements. True “no signal” baselines are established periodically during mobile lab operation by introducing zero air into the mobile laboratory-sampling manifold, exposing all instruments to a “no pollutant” stable air sample. Background ambient air and plume pollutant levels are measured from the zero air baseline. Each instrument can then be calibrated by introducing known levels of gaseous or PM species into the sampling manifold. In the case of the major trace gases (NO, CO and CO<sub>2</sub>), calibration gas cylinders with no trace gas levels, traceable to NIST standards are used for absolute calibration. Calibrations are periodically performed using calibration gas cylinders carried onboard the mobile laboratory.

Some commercial instruments (LI-COR CO<sub>2</sub>, Thermo Environmental NO) have standard calibration procedures prescribed by their manufacturers that will be implemented during the field campaign. For example, the carbon dioxide measurements are made by two LI-COR model LI-6262 detectors and by a higher range model 820 detector. The accuracy and linearity of the LI-COR detectors are periodically checked by overflowing the inlet with gas directly from one of two standard calibration tanks (400 ppm and 803 ppm,  $\pm 1\%$ , Scott Specialty Gases) or with CO<sub>2</sub>-free nitrogen. The NO chemiluminescence analyzer is calibrated by dynamic dilution of a standard tank concentration using a dynamic gas calibrator (Model 146C, Thermo Environmental Instruments). This calibrator works by using two stainless steel mass flow controllers to mix known flows of NO in nitrogen ( $99.3 \pm 2$  ppm, Scott Specialty Gases) with a known flow of either nitrogen or dry “zero” air in order to create gas with concentrations ranging from ~20 ppb up to 1000 ppb. The stated accuracy and precision of the calibrator’s mass flow controllers is  $\pm$

2%. The accuracy and reproducibility of the readings is thus calculated, at the 2 $\sigma$  level (95%), to be  $\pm 7\%$  and  $\pm 6\%$  respectively. The calibration NO tank is purged several times prior to calibration and all calibration points are allowed to flow for several minutes through the chemiluminescence analyzer before a reading is taken in order to allow for passivation and settling time. Readings are taken at 4-6 different concentrations ranging between 20 and 1000 ppb. These readings are plotted versus calculated concentration and fit with a linear least squares routine. The instrumental background is periodically measured by overflowing the inlet with zero air or nitrogen.

The commercial TSI CPC and Thermo Environmental MAAP instruments are factory calibrated and are periodically returned for refurbishment and recalibration.

The ARI TILDAS instruments are based on a primary spectral method that measures absolute molecular concentrations provided the appropriate absorption coefficients are available. We use well-recognized, certified spectral databases to provide this information. We will also use calibrated sources (CO) or reference cells (NO<sub>2</sub>) to aid in the calibration and performance evaluation of the sampling system.

The calibration of the ARI AMS is a more complex procedure. In order to minimize uncertainties in the reported mass concentrations it is desirable that the fluctuations of the detection efficiency of the AMS are closely monitored and properly corrected throughout the whole campaign. The parameters that capture the AMS detection efficiency are  $IE_{NO_3^-}$ , which is the ionization efficiency of a reference compound—NO<sub>3</sub><sup>-</sup>, and the air beam signal ( $AB$ ), which is the ion rate (Hz) detected for a major air signal, e.g. N<sub>2</sub><sup>+</sup> in this study [Allan et al., 2003; Jimenez et al., 2003]. While  $AB$  can be monitored continuously during instrument operation, the determination of  $IE_{NO_3^-}$  requires interruption of sampling to perform a calibration experiment (typically 1 – 2hrs). Given this restriction and the expectation (based on previous experience) that  $IE$  would not be highly variable, periodic  $IE_{NO_3^-}$  calibrations will be conducted during this study. Because the ratios of  $IE_{NO_3^-}$  to  $AB$  remains remarkably constant (r.s.d. < 1%) the continuous  $AB$  signal can be used to correct for the variations in the AMS detection efficiencies to a very good approximation.

Two other AMS parameters significantly influence the absolute values of its PM measurements: the collection efficiency (CE) and relative ionization efficiency (RIE). CE is introduced to correct for incomplete detection of non refractory particles, NR-PM, by the AMS, e.g., due to irregularly shaped particles that do not completely reach the vaporizer [Jayne et al., 2000]. Although strictly speaking CE should be a function of particle size and shape, at present it is defined as the correction factor for the bulk mass concentrations, i.e., the fraction of the particle mass that is measured by the AMS. A CE value of 0.5 is assigned to sulfate, based on extensive observations from several laboratory and field tests for sulfate aerosols. The same CE value (i.e., 0.5) is applied to particles containing nitrate and ammonium, because they appear to be internally mixed with sulfate particles most of the time.

The CE value for total NR-PM<sub>1</sub> organics is estimated based on their size distributions, which often show two modes – a larger accumulation mode of ambient background particles that appears to be internally mixed with SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, and a smaller ultra fine mode that seems to be mainly emitted from combustion-related sources. A CE value of 0.5 is thus applied to the accumulation mode organics (due to the internal mixing with SO<sub>4</sub><sup>2-</sup>) and CE for the smaller mode is assumed to be 1.0 because laboratory studies have shown close to 100 % AMS transmission for sooty combustion particles. By studying the size distributions of total organics, as well as individual organics mass fragments, averaged over the whole sampling period we have found that these two modes can be best separated at  $D_{iva} = 160$  nm and that the mass ratio of the smaller ( $D_{va} < 160$  nm) to the larger mode ( $D_{va} > 160$  nm) is roughly 2/3. The CE value of the bulk organics is therefore set at 0.7.

Relative ionization efficiency (RIE) is the ratio of the electron impact ionization efficiency of a given species to  $IE_{NO_3^-}$  on a per unit mass basis. Note that  $IE_{NO_3^-}$  is the IE of NO<sub>3</sub><sup>-</sup> measured based on two major ions,  $m/z$ 's 30 and 46, instead of all the mass fragments. RIE values of individual species representative have been determined in a range of laboratory measurements and tabulated [Zhang et al., 2006].

Finally, two other key AMS parameters require calibration. The AMS volumetric sampling flow rate and the particle velocity. The sample flow rate will be determined using a Gilibrator (flow calibrator). The particle aerodynamic size reported by the AMS is based on measured particle velocities. The size – velocity calibration is performed using NIST traceable polystyrene latex spheres (PSLs) in the size range 100 – 1000 nm. Particles generated from an atomizer and differential mobility analyzer combination will also be used to check the AMS size calibration.

The calibration schedule for the various instruments will vary. For example, the commercial trace gas instruments (LI-COR CO<sub>2</sub> and Thermo Environmental NO) calibrations have proven to be very stable in previous field measurements and will be made at the beginning of the measurement campaign and then checked every two to three days.

Likewise, the ARI TILDAS CO and NO<sub>2</sub> frequency calibrations are generally stable and can typically be done at the beginning of the mission and repeated every two to three days. In the case of the TILDAS instruments, however, we store actual spectral data and the theoretical lineshape fits to the recorded spectra. These are reviewed during the course of the measurement to insure that frequency drift is not occurring and re-calibration is performed sooner, if indicated. Approximately every 3 to 5 minutes, depending on operating conditions, the sample flow is diverted and zero air (commercial, particle free nitrogen/oxygen gas mixtures) is introduced into the mobile laboratory sampling manifold for about 10 seconds to create a “zero signal” baseline for the instrument suite.

As noted above the calibration of the AMS is more complex. To verify the overall molecular detection efficiency the absolute and relative strengths of the  $N_2^+$  and  $O_2^+$  signals from the air beam are monitored continuously. The particle vaporization and ionization efficiency, which varies slowly, is calibrated by introducing known ammonium nitrate particle samples at the beginning, mid-point and end of each two to three week field mission. The particle time-of-flight aerodynamic diameter measurement is calibrated at the beginning and end of each mission using polystyrene spheres of known diameter.

Note, that since all measurements are made in real-time, no actual samples are retained for post verification analysis. In practice, since the fine PM that are the focus of this mission contain semi-volatile materials and undergo significant agglomeration during and sample retention procedure, it is virtually impossible to take and archive a sample that retains all of its important physical and chemical characteristics. Thus, the need for real-time measurements that minimize sampling perturbations.

## **A.5 Data Acquisition and Storage**

Data from the mobile laboratory real-time instruments is collected in real-time by their control computers and stored on hard drives that are interfaced to the mobile laboratory's computer network. The highest data rates are associated with the TILDAS and TOF-AMS instruments. The TILDAS data acquisition system is based upon ARI's commercial software, "TDL Wintel". The data acquisition system drives the QC laser, monitors the infrared detector, calculates infrared spectra, analyzes these spectra to derive molecular concentrations, and archives the data. The TOF-AMS control software ensures data are always saved with an identifier containing the date in which the data was taken plus a unique sequential "run number" for every field campaign. The data analysis software is always referenced to these identifiers. The data stored on the mobile laboratory hard drives are periodically backed up to removable hard drives and can also be downloaded to ARI's servers if a robust internet connection is available.

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## Appendix B – Health and Safety Plan

### B.1 Potential Hazards

All field measurements present some safety and health concerns for the field measurement team. In this case, since measurements will be made in the vicinity of active weapons systems, the most important concern is to avoid operating too closely or down range from a firing weapon. Other potential hazards include hearing damage from weapons report and inhalation of excess PoF emissions. Finally, very severe weather that might threaten the safe deployment of the mobile laboratory and its crew must be avoided.

### B.2 Hazard Control

Weapons training exercises with live ammunition are strictly controlled by the master gunners and training range managers. We have discussed our measurement procedures with the relevant Ft. Benning personnel, and with their input we have designed a measurement strategy that maximizes safety while minimizing interference with training activities. This measurement strategy is described in detail in section 3.4 above.

During weapons firing the measurement team will be in the mobile laboratory sited ~10 yards behind the firing position. Only the sampling system lines will be in the proximity of an active weapon. The most dangerous activity will occur when the measurement team needs to reposition the sampling line to better intercept a weapon's muzzle emission plume. **This will only occur when a weapon has ceased firing and the measurement team has permission from the Army personnel in charge to move the sampling line. The measurement teams' movements will be under the control of the relevant Army personnel when they are deployed on an active training range and they will conform with all health and safety regulations and advisories in effect.**

The ARI mobile laboratory has frequently been deployed to high noise and exhaust emission venues to measure emissions produced by military and commercial equipment, including jet engines and combustor test stands, aircraft on active runways, and previous PoF weapons tests. The mobile laboratory measurement team is equipped with appropriate industrial grade ear and eye protection and the air in the mobile laboratory is filtered by its HVAC system to minimize unhealthful pollution levels.

Finally weather forecasts are routinely monitored and field measurement schedules are adjusted to avoid serious weather threats to the mobile laboratory's mobility or safety.

These precautions have, to date, allowed the operation of two generations of ARI mobile laboratories and their associated field measurement teams without significant injury or health impacts from field deployments all over North America.

### **B.3 Environmental Impact**

The ARI mobile laboratory operates without the emission of any significant levels of hazardous chemicals or radiation. The most significant emissions associated with the planned measurements will be the exhaust from the trailer mounted diesel generator (20 Kilowatt) that will power the lab's operations at the training ranges. This generator will be located 10 yards or more downwind from the mobile laboratory and even further from any active weapons training site so it's health or environmental impact will be minimal.



## APPENDIX C – Plume Calculations

P. Yelvington, 27 September 2006

### Summary of Puff Rise Calculations for Point-of-Fire Sampling System Design

Methods. Calculations of the buoyant rise of a puff of hot gas in a crosswind were performed to estimate the size, height, and temperature of the puff. The motivation for these calculations was to help design the sampling system for the Point-of-Fire measurements of aerosol particles from machine guns and artillery. These calculations use the integral model for plume rise developed by Boughton and DeLaurentis (1986). The model is described by the following equations:

$$\frac{dm}{dt} = \rho_{\infty} E \quad (1)$$

$$\frac{dp_x}{dt} = \rho_{\infty} u_{\infty} E - F_{D_x} \quad (2)$$

$$\frac{dp_z}{dt} = V (\rho_{\infty} - \rho) g - F_{D_z} \quad (3)$$

$$\frac{dx}{dt} = \frac{p_x}{m} \quad (4)$$

$$\frac{dz}{dt} = \frac{p_z}{m} \quad (5)$$

$$\frac{dT}{dt} = \frac{1}{mc_p} (\rho_{\infty} E (h_{\infty} - h) - \rho_{\infty} g w V) \quad (6)$$

where  $m$  = mass,  $t$  = time,  $\rho$  = density,  $V$  = volume,  $u$  = horizontal velocity,  $w$  = vertical velocity,  $E$  = entrainment,  $F_D$  = pressure drag force,  $p$  = momentum,  $x$  = horizontal distance,  $z$  = vertical distance,  $g$  = acceleration due to gravity, and  $h$  = enthalpy. The subscript  $x$  denotes a horizontal component,  $z$  denotes a vertical component, and  $\infty$  denotes an ambient quantity.

The entrainment, relative velocity and pressure drag force are defined as follows:

$$E = 4\pi r^2 \alpha |\mathbf{V}_r|$$

$$\mathbf{V}_r = \mathbf{V} - \mathbf{V}_{\infty}$$

$$F_D = \frac{1}{2} \rho_{\infty} |\mathbf{V}_r|^2 \pi r^2 C_D (Re)$$

where  $r$  is the puff radius,  $\alpha$  is the entrainment coefficient,  $\mathbf{V}_r$  is the relative velocity vector, and  $C_D$  is drag coefficient of a sphere in crossflow. The entrainment coefficient can range from 0.15 to 0.33, and a value of 0.26 was used in these calculations. The drag coefficient was taken as 0.44, the limiting value at high Reynolds number. Equations 1-6 are a set of coupled ODE's that were integrated using VODE to obtain temporal profiles of  $m$ ,  $p_x$ ,  $p_z$ ,  $x$ ,  $z$ , and  $T$  for the puff. A version of this model was also implemented in the Source Characterization Model (SCM) that was developed at Aerodyne (Brown et al., 2004). The SCM implementation does not include some of the physics in the original model, namely,

the variation of  $c_p$  with temperature, the drag terms in momentum equations, and the work term in the energy balance. Those physics were included in these calculations, and the integral model was implemented as presented in the original paper by Boughton and DeLaurentis.

This model makes the following important assumptions:

- The puff is assumed to be spherical and spatially homogeneous.
- Heat release from chemical reactions in the puff is negligible. As a result, the model only applies once afterburning plumes burn out.
- The puff does not have any initial momentum. We assume that the initial momentum of the jet of hot gases leaving the muzzle simply displaces the origin of the puff, and this model is then valid for describing the subsequent buoyant rise and advection by wind.
- The atmosphere is assumed to have an ambient lapse rate of 6.5 K/km, the value used in the ICAO International Standard Atmosphere.
- The direction of the wind is purely horizontal (no vertical component).
- The initial puff is taken to be release at  $z = 0$  m. The actual height of the puff is effectively the rise calculated by the model plus the height of the release point.

Boughton and DeLaurentis compared the predictions of “cloud top heights”, the final height a buoyant puff reaches, with experimental data for explosive detonations and found that the agreement was on average with 10%. In my opinion, the largest source of uncertainty in our calculations is the treatment of the initial jet exiting the muzzle, which could affect the initial shape, temperature, and size of the puff. As a result, a number of different initial puff sizes and temperatures were examined.

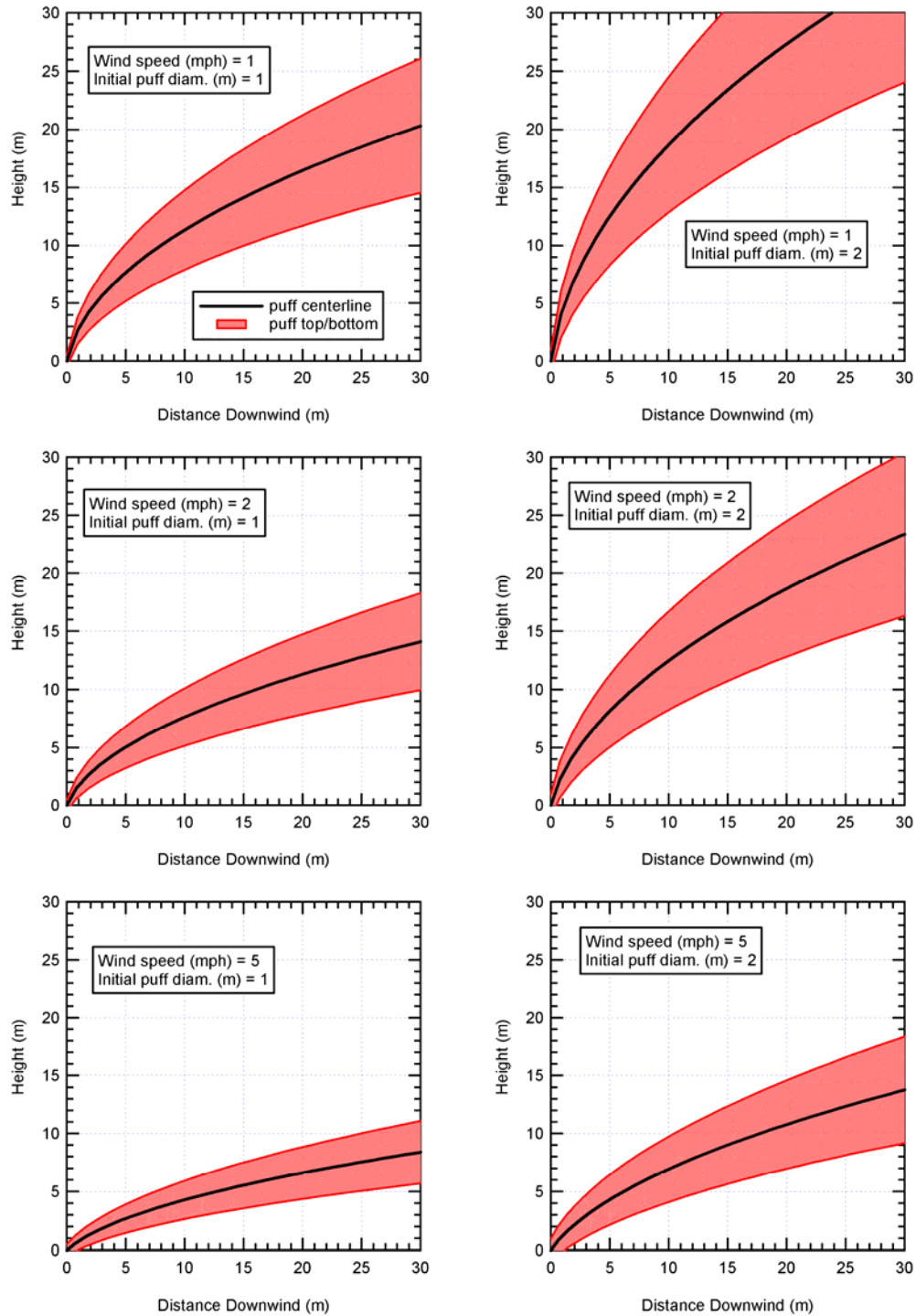
Boughton, B.A. and J.M. DeLaurentis, 1986: *An integral model of plume rise from high explosive detonations*, SAND-86-2553C, CONF-870816-1, Sandia National Laboratories, Albuquerque, NM, 19 pp.

Brown, R.C., C.E. Kolb, J.A. Conant, J. Zhang, and D.M. Dussault, 2004: *Source Characterization Model (SCM)*, ARI-RR-1384, Aerodyne Research, Inc., Billerica, MA, 91 pp.

Results. Because the initial diameter,  $d_o$ , and temperature,  $T_o$ , of the puff are not known and will depend on the type/size of the munition, a range of values were simulated. The initial diameters of 1, 2, 5, and 10 m and initial temperatures of 500, 1000, 1500, and 2000 K were used. Wind speeds,  $u_\infty$ , of 1, 2, 5, and 10 mi/hr were also tested to give a total of  $4^3 = 64$  cases. Initial temperature was observed to have a modest effect on the puff for initial temperatures above 1000 K, so the plots below only show results for  $T_o = 1000$  K. Also, the initial puff diameters of 5 m and 10 m are probably more relevant for the Howitzer, so those are not discussed. Finally, average winds in the southeast are less than 5 mi/hr, so the results for 10 mi/hr winds are not shown. Figure 1 shows the height and size of the puff as a function of distance downwind for  $d_o$  of 1 and 2 m and  $u_\infty$  of 1, 2 and 5 mi/hr. For a given

**downwind position, puff height decreases with wind speed and increases with initial radius.**

**Recommendations. Having some flexibility with the height of the sample inlet seems important. At a sampling location 10 m downwind of the gun, the centerline height of the puff is predicted to vary between about 5 m ( $u_{\infty} = 5$  mi/hr,  $d_o = 1$  m case) and 20 m ( $u_{\infty} = 1$  mi/hr,  $d_o = 2$  m case), assuming the muzzle exit is at a height of 1 m. Again at 10 m downwind, the predicted diameter of the puff varies from about 3 m ( $u_{\infty} = 5$  mi/hr,  $d_o = 1$  m case) to about 10 m ( $u_{\infty} = 1$  mi/hr,  $d_o = 2$  m case). At least a portion of the puff could be caught for most of these cases with a sampling stand that can reach 10 m high, if placed 10 m downwind of the gun. Even given the uncertainties of the calculation, having that range of flexibility seems adequate. In the absence of afterburning, the puff temperature drops off quickly as the puff mixes with ambient air and high temperatures should not be a problem for a sampling system placed even a few meters downwind.**



**Figure 1.** Predicted height and size of a buoyant puff for various wind speeds and initial puff radii (initial puff temperature = 1000 K)

## **Appendix D – Answers to Comments from ESTCP Review (November 2006)**

These comments were prepared in answer to a review that ESTCP provided.

### **General Comments**

1. See the third paragraph in 3.6.1; the original proposal and the test plan clearly state that the major focus of the plan measurements is the collection of data that allow the calculation of chemically speciated emissions indices for the muzzle emission plumes and where appropriate breech plumes from weapon systems. This is in agreement with previous talks with USACHPPM personnel, and at their request that breathing zone measurements will be made for the wind conditions prevailing if the permissions can be obtained to sample that close to the weapon. This prioritization of measurements was detailed in section 3.6.1 paragraph 3 as follows: “The main measurement focus for each weapons system will be the interception and characterization of the muzzle emissions plume so that chemically speciated emissions indices can be calculated for this major emissions source. In addition, breech emissions plumes will be characterized from breech loaded weapons, assuming that permission to deploy the sampling line close enough to the weapon to intercept this smaller emissions source. Finally, as requested by USACHPPM, the atmosphere behind the weapon in the region where the weapons personnel operate will be sampled to determine how much muzzle, breech or other weapons associated airborne emissions are present, assuming permission can be obtained to introduce the sampling line in the required proximity to the gun crew. These measurements will be taken at separate times.”

2. The plume rise estimates presented in Appendix C were calculated to show the span of potential plume heights as a function of wind speed. As shown in figure 1 of Appendix C the slower the wind speed the higher the buoyant plume rise is for a given distance from the weapon’s muzzle. The higher wind speeds noted for Fort Benning, GA in December mean that the sampling line placement will not have to be as high as the data in figure one indicate. That is why we use an adjustable line to adjust the height of the sampling line. If the wind speed is higher than 5 MPH the adjustable sampling line can be adjusted to lower and more convenient heights than shown in Appendix C and figure 1. Higher wind speeds will lead to somewhat higher emission plume dilution levels and shorter sampling times however the instruments deployed are sensitive enough to characterize plume emission indices over a wide range of plume dilution levels. In addition plume dilution can be reduced by moving the adjustable sampling line closer to the muzzle of the weapon as permitted by Range Safety personnel. Since most of the weapons scheduled for the measurements are small to moderate caliber we anticipate being able to place the sampling line quite close to the muzzle. So plume dilution should be manageable even at high wind speeds. Finally several of the weapons scheduled for the measurements are rapid fire and will produce a semi-continuous emission plume which will allow a significantly longer measurement time. Dilution of the emission plume does occur in the atmosphere before sampling. The additional dilution within the sampling line, is relevantly modest and has been fully characterized in sampling line calibration measurements made at

Aerodyne. These sampling line characterizations measurements will be repeated during the field measurements taken at Fort Benning, GA to ensure sample integrity as shown in Appendix Section A.4. However, since emissions plumes pollutant endices are computed from the ratio of the pollutant of interest to the excess carbon combustion gases (CO & CO<sub>2</sub>) in the sample dilution does not invalidate the measurement as long as pollutant levels above background and combustion gas levels above background are clearly discerned. As detailed on the last paragraph of page A-4 the suggestion of acquisition of selected grab samples is not feasible for the fine PM that is the focus of this study as explained in detail in the last paragraph on page A-4.

### **Specific Comments**

**Section 3.1 Performance Objectives:** An additional figure will be added to Appendix A to indicate the sample flow and the calibration sequences.

**Section 3.5 Pre-Demonstration Testing and Analysis:** As shown in Figure 1 in Appendix C plume rise of 5-7 meters at anticipated sampling locations will only occur for very large weapon systems under very low wind conditions, however for high wind speed conditions blowing into the face of the gun crew these same plumes could occur in the breathing zone of the gun crew (worst case scenario). That is why our primary measurement focus is to characterize plume emission endices for pollutants of concern since gun crew exposure depends both on plume chemical content and plume dynamics controlled by wind speed and wind direction. In a Finite measurements campaign it is impossible to sample all possible wind conditions therefore breathing zone measurements alone would not be sufficient.

**Section 3.5 Pre-Demonstration Testing and Analysis:** Completed as requested.

**Section 3.5 Pre-Demonstration Testing and Analysis:** Completed as requested.

**Section 3.5 Pre-Demonstration Testing and Analysis:** Added as requested in section 3.5 paragraph 2.

**Section 3.5 Pre-Demonstration Testing and Analysis:** Added as requested in previous comment to section 3.5 paragraph 2.

**Section 3.6.1 Demonstration Set-Up and Start-Up:** In the second paragraph of section 3.5 we've changed the second sentence to indicate that these measurements are only for emissions plume measurements, not for breathing zone measurements.

**Section 3.6.3 Amount/Treatment Rate of Material to be Treated:** See additional material in section 3.6.3.

**Section 4.1 Performance Criteria:** The below paragraph has been added to section 4.1 as further explanation: "As stated in the statement of work for the contract Aerodyne will calculate

fine particles species and nitrogen oxide emission factors for each measured muzzle and breech plume. In addition above background weapons associated CO and CO<sub>2</sub>, NO and NO<sub>2</sub> and fine particulate species measured in crew breathing zones will be tabulated and reported. These data will be supplied to USACHPPM in both hard copy and electronic format (Excell Sheet). After data quality assurance Aerodyne will calculate the air emission endices for each measured muzzle and breech emission plumes. In addition, for breathing zone measurement, the trace gas (CO, CO<sub>2</sub>, NO, NO<sub>2</sub>) and fine PM chemical speciation above background will also be reported. For breathing zone measurements, background pollutant levels, will be computed by averaging before firing and after firing background measurements. ('Wind cleared' before and after firing) The quality of all data delivered, as assessed in the quality assurance procedures, will be noted in both hard copy and electronic data reports. Further Aerodyne personnel will interact directly with USACHPPM personnel to explain the quality and limitations of the reported data set."

**Section 4.2 Performance Confirmation Methods:** To clarify this key measurement point we have added the following sentence to section 4.2: "As noted above, the concentration of CO and CO<sub>2</sub>, above background, will be used to compute the level of dilution that has occurred for the portion of the plume that is intercepted during the measurement period."

The authors do not assume that the absolute plume pollutant concentration are uniform over the entire plume, they are most certainly not. We only assume that the plume is well mixed enough that the relative concentrations of emitted pollutants are uniform (are diluted by the same amount over the portion of the plume being sampled). As discussed in sections 2.1 (paragraph 3) and 3.1 (paragraph 1), measurement of the above background major combustion gases (CO & CO<sub>2</sub>) allow the degree of dilution of the plume sample to be computed. This common emission plume characterization method is widely used in the pollution emission community and is discussed specifically in the context of emissions measurement for on-road motor vehicles and operational aircraft in several of the references provided in Section 7.0. In addition it is described in detail in Onasch, et.al. (2003), a previous PoF emissions report to SERDP. Also listed in Section 7.0.

**Section 4.2 Performance Confirmation Methods:** See response to previous comment. By using the relative concentrations of the pollutants of interest to the measured carbon combustion gas concentration to specify the level of plume dilution there is no need to estimate plume volume.

**Section 4.2 Performance Confirmation Methods:** The below paragraph has been added to the second paragraph of section 4.2: "The number of samples required depends on two factors: 1. The plume to plume variability; and 2. The statistical significance of each plume measurement. As noted in our prior PoF measurement report Onasch, et. al. (2003), there can be significant plume to plume pollutant variation if there is muzzle flash afterburning for some projectiles but not for others. The degree of afterburning will be indicated by variations in the measured plume CO/CO<sub>2</sub> ratio. If the CO/CO<sub>2</sub> ratio varies significantly a larger number of measurements will need to be made to address this intrinsic plume variability. The second factor will be determined by how well we can intercept each plume, based on prior analysis of combustion plume

emissions three or four good plume intercepts should yield a significant measurement of the major pollutants present.”

**Section 4.3 Data Analysis, Interpretation and Evaluation:** The section now reads: “After quality assurance of the basic instrumental data emissions indices for muzzle and breech plumes and above background concentrations for breathing zone measurements will be computed and average and standard deviation values will be tabulated. The statistical significance of each measurement will be evaluated and used to flag the data reliability. The interpretation and evaluation of the data in terms of actual or potential health impacts for the gun crews will be determined by USACHPPM as they and the measurement team proceed with the planned health impacts analysis.”

**Appendix A—Quality Assurance Plan:** We’ve added section: “**A.4 Data Quality Indicators, Quality Assurance and Data Format.** As noted in section 3.7 of the test plan this project will utilize only real time instrumentation methods and there will be no traditional grab sample collection and analyses. The quality assurance procedures for real time instrumentation methods involve inspection of the fundamental instrumentation measurement data (infra red spectra, mass spectra, etc.) to assure detection of target species and computation of the average and statistical variance for each species measurement. These data quality assurance assessments will be made by doctoral level scientists with extensive experience in analyzing data from the real time instruments used in this measurement campaign. Analysis of absolute species concentration requires the incorporation of calibration procedures performed during the field campaign and described in detail in section A.5, for each instrument, directly below. After analysis of absolute in plume (above background) concentrations plume emission indices (pounds of pollutants/pounds of NEW) will be computed along with standard deviation. These data will be evaluated based on computed statistical significance and flagged as either robust and reliable, questionable and/or unreliable. The data will be entered into an excel spread sheet sorted by munition type (Propellant Train) (DODIC) and transmitted by both hard copy and electronic format to USAEC and USACHPPM.”

Appendix A.3—Data Quality Parameters: **See additions and responses for sections 4.1, 4.2, 4.3 and Appendix A.4.**

**Appendix B.3 Environmental Impact:** Corrected as noted.

**Appendix C—Plume Calculations:** See additions and responses for General Comments Number 2 and Section 3.5. The major impacts of faster wind speeds are to limit the plume rise height for a given sampling offset position. The plume rise estimate reported in Appendix C was performed to indicate the worst case height plume intercept requirements. The secondary issue of shorter sampling times with increased wind speed and the resulting dilution issue are all discussed in the response to General Comment 2 and the additions made to the Test Plan.



## Appendix E

### EVALUATION OF THE HEALTH IMPACT OF MUNITIONS EMISSIONS AT THE POINT-OF-DISCHARGE USING THE AERODYNE SAMPLING SYSTEM

1. REFERENCES. See Appendix A for a list of references.
2. PURPOSE. To evaluate the potential for health impact on data provided. The USACHPPM agreed to be a third-party reviewer of the Aerodyne Research Inc. testing that was to be performed via an award by the Environmental Security Technology Certification Program (ESTCP). Of relevance to this document is that the USACHPPM agreed to perform a health impact analysis based on the results generated by Aerodyne on the five weapons systems described by the Aerodyne SOW paragraph C.3.1. This health impact analysis was specifically limited to data generated and obtained from the sampling in and around the point of fire breathing zone.
3. AUTHORITY. On the 26<sup>th</sup> of April 2006, the U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM) provided a statement of work to the U.S. Army Environmental Command concerning the point of discharge project. The USACHPPM statement of work was modified on 3 August 2006 by incorporating phased tasks for the work effort. This report addresses paragraph 2.f. of the revised scope of work in providing a health impact analysis of the Aerodyne test results.

#### 4. BACKGROUND.

Over the last few decades there has been an increasing body of technical evidence of the human and ecological health impacts of small particles. Regulations aimed at limiting emissions of particulate have become more stringent and addressed smaller and smaller sized particles since the inception of the Clean Air Act. During the late 90's and early 2000's, this focus continued on products of combustion and regulations for particles as small as 2.5 micrometers (microns) appeared. Continuing research has showed that even smaller particulate can play a significant health role, where the sources are primarily due to combustion. Further interest in this trend has focused on the impacts due to the development of nanotechnology and engineered particles on the molecular cluster scale.

Nanotechnology has been likened to the next industrial revolution (Office of the White House Press Secretary, 2000). Presently, in 2007, commercial applications are generally limited to the use of passive nanoscale materials including sunscreen, cosmetics, packaging, clothing disinfectants, appliance coatings, paints, varnishes and fuel catalysts (Oberdorster G., July, 2005). Further applications include using nano materials as the engines themselves to make nano applied materials and functions. Great concern about the implications of these materials on human health and the environment has arisen as industrial development has far outpaced health, safety and environmental research. There is a growing body of scientific research demonstrating that some nano materials could be toxic due to one, or a combination of, properties such as size, chemical composition, shape, surface structure, surface charge, aggregation and solubility. The

smaller size results in relatively rapid uptake by organic systems. Some literature has indicated that nano sized materials can accumulate in bacteria. (Westerhoff, Sept. 2007)

Governments, citizens and even industry have started to recognize the potential harm that fine particles can inflict. The United Kingdom's Royal Society seminal 2004 report (The Royal Academy of Engineering, 2004) "Nanoscience and Nanotechnologies: Opportunities and Uncertainties" recommended that nanomaterials be regulated as new chemicals. Watch groups include The Center for Responsible Nanotechnology, The International Council on Nanotechnology, and the Project on Emerging Nanotechnology; which currently lists over 500 products that manufacturers have voluntarily identified that use nanotechnology and also notes strongly that no labeling is required by the U.S. Food and Drug Administration.

In examining Aerodyne's test results USACHPPM followed conventional practices in risk assessment. Mainly that, in hazard identification and analysis, worst-case is used to determine if there is a health impact. When the exposures resulting from these assumptions are checked against accepted standards then, should the actual worst-case exposure be lower than the standards, there is a high probability and high confidence that there is no health impact. It can happen that exposures under worst-case conditions exceed accepted health exposure guidelines. In that case a re-examination of the assumptions is performed to determine if some assumptions can be relaxed or eliminated in order to meet or fall under the standards. This necessarily implies less confidence in the final conclusion of no health impact and is discussed as a significant uncertainty factor. Of course, it also happens that reasonable relaxation of the assumptions does not result in a lower exposure than the accepted standard: in these cases the risk assessment indicates that the exposure is unacceptable in accordance with current guidelines. These worst-case assumptions are necessary because health risk assessment incorporates, by its very nature, a number of aleatory and epistemic uncertainties. Included among them are: the variability of humans to be able to incur exposures at different levels based on their particular body response; impact and uncertainty from multiple chemical exposures; interspecies variability from laboratory testing performed on a animal species (usually using a single chemical) and then scaled to humans. As a general rule it is strongly believed that the worst-case assumptions account for these uncertainties in a conservative and safe manner. These assumptions were applied to the Aerodyne results, which are discussed in the next section.

## 6. RESULTS AND DISCUSSION.

Aerodyne characterized particle and trace gas emissions from five different weapons systems at Fort Sill Oklahoma between March 16 and March 24, 2007. The weapon systems included the M109A5 155 mm self-propelled howitzer, the M119 105 mm howitzer, the M203 40 mm grenade launcher, the M249 5.66 mm squad automatic weapon, and the M240 7.62 mm machine gun. For the health impact analysis, during the firing of these weapons (except for the M109A5) the air sample inlet was placed in the approximate breathing zone of the soldiers firing the

weapons and real-time measurements of the particulate and trace gas emissions were taken. During the M109A5 howitzer emissions measurements an extremely strong down range wind immediately swept exhaust emissions away from the weapon and no significant emissions reached the gun crew. In this case muzzle plume emissions for a series of consecutive firings were measured downwind of the weapon and supplied to CHPPM. These data approximate the exposure the gun crew would have received if the wind direction was reversed.

Breathing zone data was transmitted to USACHPPM for evaluation of potential health impact for gun crews and/or individual weapons operators under real weapons training conditions. Aerodyne supplied one second averaged raw data as requested and plots of CO concentration to better define the sampling times of interest (e.g., when the sample consisted of discharge emissions.) The data provided is a snapshot of breathing zone conditions for individual soldiers under the particular conditions at Fort Sill during the firing. They cannot be considered representative of total health risks to a soldier without sampling under a broader range of conditions to include the full multicomponent exposure conditions that could be encountered in combat or extensive training exercises. That data would include expected soldier exposure over lifetime conditions to determine if there were any long-term health effects. However, as communicated to the Army Environmental Command, the Aerodyne results can be evaluated to determine if this methodology and instrumentation package could begin to provide that complete characterization. It should be noted that the Aerodyne test was focused on muzzle and breach emissions and comparison of these real-life field conditions to the Aberdeen Test Center point-of-fire chamber results taken over the last five years. The muzzle and breech emission plume were assessed for loadings of fine particulate matter and selected trace gases. The results of these tests, and, in particular, the results of the carbon monoxide and carbon dioxide from the emissions, were then scaled to the Aberdeen Test Center results.

The raw data for each munitions item presented in Aerodyne's report was processed in the following manner. First, all data points for all substances of potential concern (SOPCs) were averaged to obtain the exposure concentration for the duration of the breathing zone test for that weapon system. Any SOPC that was not detected, or had a negative average concentration, was eliminated from further evaluation. Carbon dioxide values were based on the 820 analyzer since 1) this provided higher one second maximums and averages and 2) it is more accurate at higher concentrations according to the Aerodyne report. These exposure concentrations represent the maximum and average concentration of each SOPC that a soldier would be exposed to when firing that weapon under circumstances similar to the Aerodyne test. It is important to note this does not represent the environmental concentration that might be found during different uses of the weapon. For instance, under very low wind conditions the emissions from multiple shots of a single weapon can accumulate as a cloud around the gun crew and in some moderate wind conditions emissions plumes from multiple upwind weapons can sweep consistently across a firing position. (Multiple weapons emissions from two of the 7.62mm machine guns were collected because of a change in wind direction during the testing)

The one second maximum and average exposure concentration was compared to the Threshold Limit Value (TLV). TLVs are developed by the American Conference of Government Industrial Hygienists and are meant to be a guideline for the maximum concentration of a substance a typical worker can be repeatedly exposed to over their working life without adverse effects to their health. These values are very conservative for this particular evaluation, because it is a gross overestimation of the level of exposure a soldier would experience, however using these values will allow confidence that if the exposure concentration is indeed below the TLV, the soldier will not experience health effects. Any SOPCs that a TLV was not available for was dropped from further evaluation per standard risk assessment practice.

The following tables (Tables 1-5) represent the results of the screening evaluation of the munitions items. Each table contains the results for an individual munitions item. These results are limited by the fact that each substance and item is evaluated separately. Cumulative effects of SOPCs from each item and multiple items being fired during a training scenario would have to be evaluated in a more in depth study. However, these results indicate that no SOPC is anywhere close to its TLV. This allows a reasonable degree of certainty that under the tested use conditions, soldiers would not experience adverse health effects from the use of these items.

It should be noted that post test review indicated that hydrogen cyanide values may have been too low by a factor of about 6. This would have no impact on the SOPC screen and values. Also, the National Academy of Sciences is reviewing the combined exposure of HCN and CO from weapons discharge. Preliminary results indicate that air monitoring (rather than blood testing) is adequate for determining exposure and that further investigation into the combined effects should be performed. While the values below do show high spikes of CO, the average breathing zone concentration is well below worker exposure values. As noted, the USACHPPM feels that this review is to validate proof of concept for the Aerodyne sampling system rather than definitive health risk determination. The HCN and CO considerations will need to be accounted for as further information and protocols for the data are developed.

**Table 1: Results of Analysis of M109A5**

SOPC	Maximum 1s Conc.	Average Conc.	TLV	SOPC Passes Screen?
	ppm	ppm	ppm	
Carbon dioxide	1174	787	5000	YES
Carbon monoxide	607	6	25	YES
Black carbon	0.2	0.005	7.12	YES
Nitric oxide	0.003	0.001	25	YES
Nitrogen dioxide	0.005	0.001	3	YES
Benzene	0.06	0.003	0.5	YES
Toluene	0.009	0.0002	20	YES
Styrene	0.001	0.00003	20	YES
Acetic Acid	0.006	0.001	10	YES
PM Sulfuric acid	0.002	0.0002	0.05	YES
PM Nitric acid	0.0008	0.00007	2	YES
PM Lead	0.000002	0.000002	0.006	YES

**Table 2: Results of Analysis of M119**

SOPC	Maximum 1s Conc.	Average Conc.	TLV	SOPC Passes Screen?
	ppm	ppm	ppm	
Carbon dioxide	1051	766	5000	YES
Carbon monoxide	1187	6	25	YES
Black carbon	1	0.02	7.12	YES
Nitric oxide	2	0.02	25	YES
Nitrogen dioxide	0.03	0.002	3	YES
Formaldehyde	0.002	0.005	0.3	YES
Acetonitrile	0.2	0.002	20	YES
Acetaldehyde	0.1	0.003	25	YES
Hydrogen cyanide	0.2	0.002	4.7	YES
Acrylonitrile	0.1	0.002	2	YES
Acetic acid	0.003	0.001	10	YES
Ethylacetate	0.001	0.0004	400	YES
PM Sulfuric acid	0.002	0.0002	0.05	YES
PM Nitric acid	0.002	0.00004	2	YES
PM Lead	0.00004	0.000002	0.006	YES
PM Lead chloride	0.000005	0.0000001	0.006	YES

**Table 3: Results of Analysis of M203**

SOPC	Maximum 1s Conc.	Average Conc.	TLV	SOPC Passes Screen?
	ppm	ppm	ppm	
Carbon dioxide	878	763	5000	YES
Carbon monoxide	53	2	25	YES
Black carbon	0.2	0.04	7.12	YES
Nitric oxide	3	0.083	25	YES
Nitrogen dioxide	0.1	0.005	3	YES
Formaldehyde	0.0001	0.002	0.3	YES
Acetaldehyde	0.003	0.003	25	YES
Benzene	0.02	0.003	0.5	YES
Toluene	0.002	0.0003	20	YES
Styrene	0.0004	0.00005	20	YES
PM Sulfuric acid	0.01	0.001	0.05	YES
PM Nitric acid	0.0007	0.00008	2	YES
PM Lead	0.002	0.0001	0.006	YES

**Table 4: Results of Analysis of M249**

<b>SOPC</b>	<b>Maximum 1s Conc.</b>	<b>Average Conc.</b>	<b>TLV</b>	<b>SOPC Passes Screen?</b>
	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	
Carbon dioxide	1795	805	5000	YES
Carbon monoxide	423	15	25	YES
Black carbon	0.4	0.02	7.12	YES
Nitric oxide	2	0.06	25	YES
Nitrogen dioxide	0.03	0.003	3	YES
Formaldehyde	0.04	0.02	0.3	YES
Acetonitrile	0.03	0.001	20	YES
Acetaldehyde	0.02	0.005	25	YES
Benzene	0.03	0.005	0.5	YES
Toluene	0.001	0.002	20	YES
Styrene	0.0004	0.0001	20	YES
Hydrogen cyanide	0.1	0.004	4.7	YES
Acrylonitrile	0.005	0.0002	2	YES

**Table 5: Results of Analysis of M240**

<b>SOPC</b>	<b>Maximum 1s Conc.</b>	<b>Average Conc.</b>	<b>TLV</b>	<b>SOPC Passes Screen?</b>
	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	
Carbon dioxide	932	764	5000	YES
Carbon monoxide	245	7	25	YES
Black carbon	2	0.06	7.12	YES
Nitric oxide	0.7	0.03	25	YES
Nitrogen dioxide	0.1	0.008	3	YES
Formaldehyde	0.05	0.003	0.3	YES
Acetonitrile	0.01	0.001	20	YES
Acetaldehyde	0.01	0.003	25	YES
Hydrogen cyanide	0.1	0.007	4.7	YES
Acrylonitrile	0.002	0.0001	2	YES
PM Sulfuric acid	0.002	0.0003	0.05	YES
PM Nitric acid	0.0004	0.00008	2	YES
PM Lead	0.001	0.0001	0.006	YES

Little research has been done on the health and environmental impacts of specific fine, ultrafine and nanoscale materials. Existing studies on larger fine particle sized materials have only shown trends: in general, the smaller particles get the more toxic they become. This is primarily due to the larger surface area and subsequent dose effects, in terms of particle numbers, that is incurred as particle size decreases. Studies of the health impact of airborne products of combustion are the closest thing we have for a tool for assessing potential health risks. These studies do not

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segregate the individual chemical effects that the Aerodyne results would allow. As such, current risk assessment methodologies are not suited to these fine or nano sized particles and health risk assessment. Exposure evaluation expressed as quantity of particles and/or surface area rather than mass simply do not exist. Regulatory bodies such as the U.S. EPA, the U.S. Food and Drug Administration or the Health and Consumer Protection Directorate of the European Commission have started looking at the potential risk posed by nano particles. This would require developing data that would identify particles and more complex formulations which are likely to have special toxicological properties. A precautionary approach would be unwise given the huge economic impact from these materials both in the economic and military security of the nations involved.

Most studies examining fine ultrafine and nanoscale materials and their health impacts relate to the effects of higher levels of diesel and other vehicle exhausts in highly populated areas. These studies are showing that exhaust characteristics contribute to adverse health effects in a population generally via respiratory tract as well as extrapulmonary organ effects.

Epidemiological studies are showing that morbidity and mortality both increase in susceptible parts of the population during the studies for the most part; however, there are studies that have not seen such associations (Pekkanen J., 1997).

## 7. CONCLUSIONS.

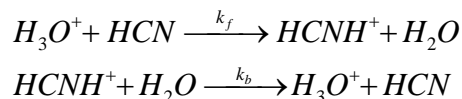
The Aerodyne test results are beyond the current ability of particle toxicology to assess the health impact at the point of discharge. Only estimates based on total mass exposure can be performed. These values indicate that the exposure to the soldier, if they were exposed to the concentration of the sampled SOPC's in a similar manner to a civilian worker, would not result in a negative health impact based on current exposure guidelines. That said, there is value in the use of the Aerodyne technology in determining these size and chemical specific speciated exposures to the soldiers. Relevant toxicological testing is expected to occur over the next few decades. As this happens, health impact determinations can be made and checked against health records to epidemiologically form a more realistic and robust database.

8. TECHNICAL ASSISTANCE. For further assistance, contact Dr. David Reed at commercial 410-436-5969 or e-mail [dave.reed@us.army.mil](mailto:dave.reed@us.army.mil).

## Appendix F

### Quantification of HCN by PTR-MS

The following derivation provides a method for evaluating of the influence of water vapor concentration on the response of the PTR-MS to HCN. When the proton affinity (PA) of a substrate, such as HCN (PA = 170.4 kcal/mole) is close to that of water PA = 165 kcal/mole both the forward and reverse proton transfer reactions need to be considered when interpreting the PTR-MS response (Hansel et al., 1997).



Starting with these two chemical reactions the concentration of  $HCNH^+$  formed within the drift tube can be deduced by solving the differential equation for this species. For simplicity  $[HCN]$  and  $[HCNH^+]$  are represented as  $[R]$  and  $[RH^+]$  respectively.

$$[RH^+] = \frac{k_f [R][H_3O^+]}{k_b [H_2O]} (1 - e^{-k_b t [H_2O]}) \quad (A-1)$$

Rearranging eq A-1 to solve for  $[R]$  while substituting ion concentrations with measured ion intensities yields eq A-2.

$$[R] = \frac{I_{RH^+} k_b [H_2O]}{I_{H_3O^+} k_f (1 - e^{-k_b t [H_2O]})} \quad (A-2)$$

Note that in the limit as  $[H_2O]$  goes to zero eq A-2 simplifies to the traditional form of the equation used to calculate  $[R]$ , eq A-3. However in the present context we will use this equation to reflect the “observed” concentration, which indicates that this is the concentration calculated ignoring the influence of water.

$$[R]_{obs} = \frac{I_{RH^+}}{k_f t I_{H_3O^+}} \quad (A-3)$$

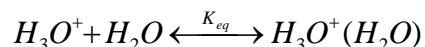
The detection efficiency (ratio of observed response to the response that would be observed in the absence of water) can then be described as  $\frac{[R]_{obs}}{[R]}$ , which is shown in eq A-4.

$$\frac{[R]_{obs}}{[R]} = \frac{1 - e^{-k_b t [H_2O]}}{k_b t [H_2O]} \quad (A-4)$$

Equation A-4 shows that  $k_b$ ,  $t$  ( $HCNH^+$  drift time) and the water concentration (expressed a number density in units of molecules  $ml^{-1}$ ) are needed to evaluate the magnitude of the loss of  $HCNH^+$  signal due to the presence of water.



At present none of the variables in eq A-4 are explicitly known, however only the water concentration is expected to change significantly between experiments. While we do not have a direct measure of the concentration of water in the drift tube this quantity can be estimated from the  $H_3O^+$  cluster ion distribution.

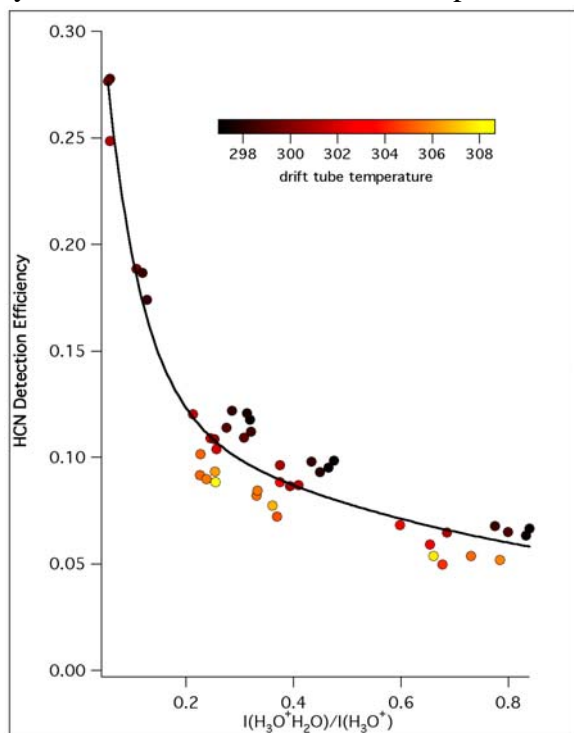


Equation A-5 shows that the partial pressure of water can be determined from the measured ion intensities of  $H_3O^+$  and  $H_3O^+(H_2O)$  if the value of the equilibrium constant,  $K_{eq}$ , is known.

$$P_{H_2O} = \frac{I_{H_3O^+H_2O}}{K_{eq} I_{H_3O^+}} \quad (A-5)$$

While the enthalpy and entropy for the  $H_3O^+$  clustering reaction are known, calculation of the relevant  $K_{eq}$  is not possible because the effective temperature of the reaction is dependent on both the electric field and actual gas temperature. Since values for a number of the variables shown in eq A-4 and eq A-5 are not explicitly known, a series of calibration experiments were conducted under a wide range of humidities with the goal of empirically evaluating a relationship between detection efficiency and the ratio of the  $H_3O^+(H_2O)$  and  $H_3O^+$  ion intensities.

Figure A-1 shows the observed detection efficiency plotted against the measured  $H_3O^+(H_2O)$  to  $H_3O^+$  ion intensity ratio, surrogate measurement for the concentration of water, recorded at different temperatures and humidities. Figure clearly demonstrates that the detection efficiency (observed response HCN) decreases as the concentration of increases. The reagent ion clustering equilibrium reaction is sensitive to the changes in temperature and the influence temperature is clearly seen in Figure A-1. The humidity of the drift gas was varied mixing a small flow of the HCN calibrated gas standard with one of three diluent gases; dry air, room air or room air saturated with water vapor by bubbling the air through a column of water. The hollow cathode ion source uses water vapor as a reagent gas and a small portion of this water vapor from the ion source diffuses into drift tube so that truly dry conditions cannot be achieved. The water flow to the



**Figure A-2. Influence of water vapor concentration expressed as the ratio of reagent ion cluster distribution on the detection of HCN.**

hollow cathode ion source was also varied in this experiment. At the lowest hollow cathode water flow and using dry air as the drift gas the detection sensitivity is still only about 30%. Using normal hollow cathode water flows and typical ambient humidities the detection efficiencies are lower ~8-12%. These results can be compared with those of other PTR-MS evaluations of the HCN response. Christian et al. (2004) compared the concentrations derived from their PTR-MS measurements to those obtained using FTIR and found that PTR-MS concentrations were about 5 times lower (detection efficiency = 0.2) than the FTIR results. Jobson et al. (2004) using a PTR-MS report sensitivity factors derived from HCN calibration experiments as a function of sample humidity and report significant humidity dependence. Similar to our results, they observe low detection efficiencies even under their driest conditions. At 0% relative humidity they report a sensitivity factor of about 2.8 ncps/ppbv (normalized counts per second per ppbv) for HCN while other compounds like methanol and acetonitrile ranged from 15 – 35 ncps/ppbv. This implies that their detection efficiency under dry conditions is probably somewhere between 0.08 and 0.2, which is consistent with our value of 0.18 measured here with dry air and a small hollow cathode ion source water vapor flow. At their highest humidity level 80% RH, the sensitivity factor for HCN dropped to about 1 ncps/ppbv, indicating a detection sensitivity of in the range of 0.03 – 0.07, which is comparable to the values obtained with humidified air shown in Figure A-1.

Our goal was to develop an empirical relationship between detection efficiency and the observed  $H_3O^+(H_2O)$  and  $H_3O^+$  ion ratios. As a substituted the concentration of water described in eq A-5 into eq A-4 and A-2 shows a plot of the measured

efficiencies versus 
$$1 - \frac{e^{\left(\frac{-k_b t I_{(H_3O^+ H_2O)}}{K_{eq} I_{H_3O^+}}\right)}}{K_{eq} I_{H_3O^+}}$$

and the effective temperature (in  $K_{eq}$  used calculate the water concentration) were fitting variables. Effective temperature the magnitude of  $K_{eq}$ , which in conjunction with observed proton hydrate ion distribution is used to evaluate the concentration of water in the drift tube. fit was found using  $k_b = 2 \times 10^{-11}$  molecules<sup>-1</sup> ml s<sup>-1</sup> and an effective temperature of (474K + Tdrift) where the measured drift tube temperature. While the plot in Figure A-2 is reasonably linear we note that temperature dependence in the detection efficiency still remains. We also note that the intercept is non-zero, but we are less concerned about this result. Numerous studies have questioned the integrity of the PTR-MS measurements of weakly bound cluster ions. This is because there is evidence that a fraction  $H_3O^+(H_2O)$  ions undergo dissociative collisions within the expansion region,

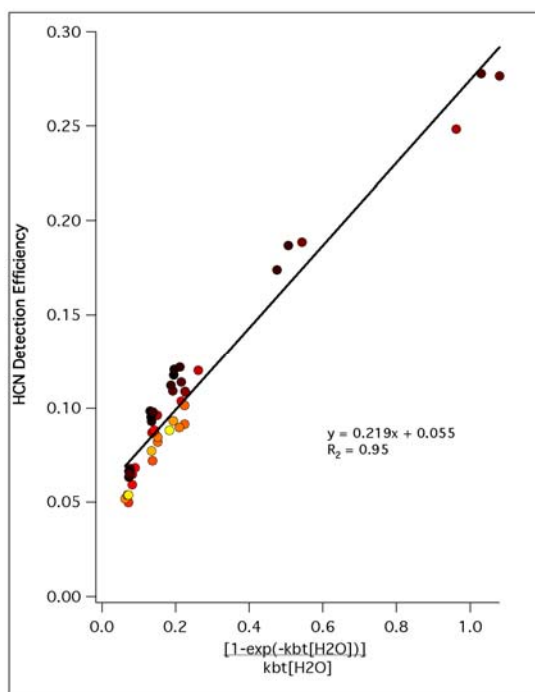


Figure A-3. Best fit of the HCN detection efficiency to the expression given in eq A-

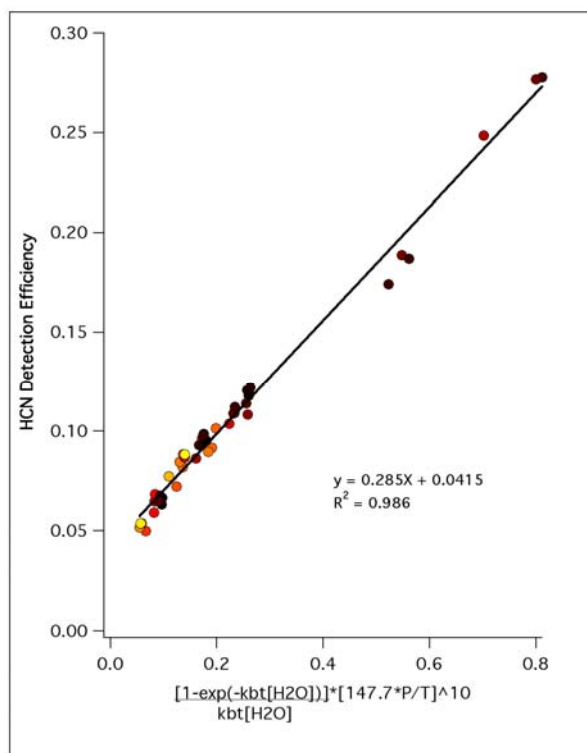
4

between the drift tube and entrance aperture to the mass spectrometer, and are detected as  $H_3O^+$ . This result led us to consider adding another adjustable temperature dependent term to our expression. To accomplish this we added the term  $\left(\frac{P_1 T_2}{P_2 T_1}\right)^n$ , which accounts for any variation in number density with due to changes in temperature and pressure. We define  $P_2$  (2.048 mbar) and  $T_2$  (302.5 K) the midpoint experimental pressures and temperatures to be our reference state, while  $P_1$  and  $T_1$  are the actual recorded experimental temperatures and pressures.

$$\frac{[R]_{obs}}{[R]} = \frac{1 - e^{-k_b t [H_2O]}}{k_b t [H_2O]} \left(\frac{P_1 T_2}{P_2 T_1}\right)^n \quad (A-6)$$

The exponent (n) then becomes the experimental fitting parameter. The results of adding this additional fitting parameter are shown in Figure A-3, where  $n = 10$ . The best-fit parameters used for the plot shown in Figure A-3 are included in Table A-1. Inspection of the plot shown in Figure A-3 illustrates that eq A-6 effectively accounts for the observed temperature dependence. While we do not have any explanation for the physical significance of this correction factor, we have achieved our desired result in obtaining a well defined relationship between detection efficiency and typical experimentally measured parameters.

We have now used eq A-6 and the best fit parameters in Table A-1 to correct the measurements for the influence of water were made during the Point of Fire field campaign conducted in March 2007. The actual data have been corrected on a point-by-point basis, but because the temperature and sample humidity were reasonably constant during the field campaign a single correction factor could be applied. This is demonstrated in Figure where the evaluated HCN concentration has been plotted versus the observed concentration (shown as mass 28 concentration) where the influence of water has been ignored. This plot shows a large correction factor (~11) results in determining the HCN concentration using a standard PTR-MS. Better detection limits could be achieved if less water was present in the drift tube. One means to accomplish this is by virtually eliminating the water flow to the hollow cathode ion source.



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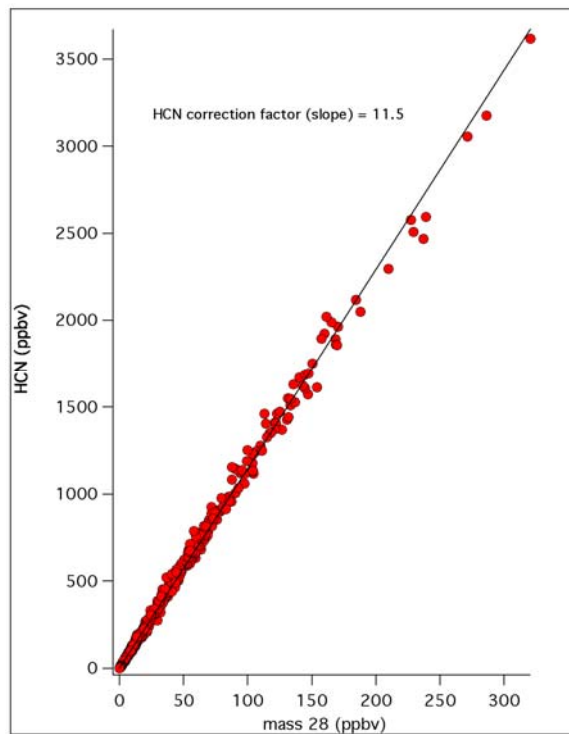
Figure A-4. Best fit of the HCN detection efficiency to the expression given in eq A-6

**Table A-1.** Best-Fit parameters determined for the HCN detection efficiency via eq A-6.

Fitting parameter	Value		
$k_b$	$2 \times 10^{-11} \text{ molecules}^{-1} \text{ ml s}^{-1}$		
$t$	$1 \times 10^{-4} \text{ s}$		
$^{(a)}K_{eq}$	$\Delta H = -31.6 \text{ kcal mol}^{-1}$	$\Delta S = -24 \text{ cal K}^{-1} \text{ mol}^{-1}$	$T = 474 \text{ K} + T_{drift}$
$n$	10		

(a)  $K_{eq} = \exp^{-(\Delta G/RT)}$  where  $\Delta G = \Delta H - T\Delta S$  Thermodynamic values are taken from Keesee and Castleman (1986).

This modification reduces the water content within the drift tube significantly without sacrificing any reagent ion intensity and so a significant improvement to detection of can be expected. The downside to operating the hollow cathode in this that the  $O_2^+$  impurity reagent ion is very which severely complicates the identification and quantification of molecular weight species.



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**Figure A-4.** Computed HCN concentration versus uncorrected HCN concentration (mass 28) for Point of Fire campaign.

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3/19/2007 10:16:02	4.01E+02	3.84E+02	1.67E+02	4.51E+03	2.64E-01	2.99E-01	5.81E-01	1.52E+00	2.19E-01	-3.60E-01	4.45E-01	1.63E-02	2.25E-03	3.36E+00	8.17E-01	1.79E-01	-1.46E-02	5.19E+03	0.00E+00
3/19/2007 10:16:03	4.04E+02	3.86E+02	6.58E+03	4.30E+03	6.29E-01	1.61E+00	5.81E-01	2.36E+00	2.34E+00	-5.00E-01	5.52E-02	9.71E-02	1.73E-01	3.36E+00	8.17E-01	1.79E-01	-1.46E-02	5.19E+03	0.00E+00
3/19/2007 10:16:04	4.01E+02	3.87E+02	1.08E+04	1.17E+04	5.38E+00	4.14E+00	5.81E-01	1.29E+00	2.17E+00	7.06E-02	-8.66E-02	-8.30E-02	2.95E-03	3.36E+00	8.17E-01	1.79E-01	-1.46E-02	5.19E+03	0.00E+00
3/19/2007 10:16:05	4.41E+02	3.95E+02	4.95E+04	6.89E+04	3.78E+00	1.67E+01	5.81E-01	1.50E+00	4.79E+00	-8.36E-02	8.59E-02	1.45E-02	-9.70E-02	3.36E+00	8.17E-01	1.79E-01	-1.46E-02	5.19E+03	0.00E+00
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3/19/2007 10:16:07	4.14E+02	4.19E+02	1.08E+05	1.25E+06	4.00E-01	3.11E+01	5.81E-01	1.99E+00	5.41E+00	-8.25E-02	8.64E-02	-8.30E-02	9.73E-04	3.36E+00	8.17E-01	1.79E-01	-1.46E-02	5.19E+03	0.00E+00
3/19/2007 10:16:08	3.99E+02	3.84E+02	1.71E+02	4.51E+03	1.49E-01	2.99E-01	5.81E-01	1.59E+00	1.75E+00	3.00E-01	1.59E-01	1.35E-02	9.60E-02	3.36E+00	8.17E-01	1.79E-01	-1.46E-02	5.19E+03	0.00E+00
3/19/2007 10:16:09	3.94E+02	3.87E+02	4.03E+03	2.73E+06	4.70E+02	2.22E-01	5.81E-01	1.64E+00	4.45E+00	7.18E-02	6.49E-01	1.17E-01	3.13E-03	3.36E+00	8.17E-01	1.79E-01	-1.46E-02	5.19E+03	0.00E+00
3/19/2007 10:16:10	3.99E+02	3.85E+02	1.98E+03	1.10E+06	6.30E+02	1.11E+01	5.81E-01	1.99E+00	4.45E+00	7.18E-02	6.49E-01	1.17E-01	3.13E-03	3.36E+00	8.17E-01	1.79E-01	-1.46E-02	5.19E+03	0.00E+00
3/19/2007 10:16:11	4.00E+02	3.84E+02	1.41E+03	2.05E+05	4.40E+02	1.11E+01	5.81E-01	1.55E+00	2.28E+00	-3.80E-01	3.15E-02	4.32E-03	-9.70E-02	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:12	3.97E+02	3.84E+02	1.09E+03	1.10E+05	3.80E+02	4.93E+00	5.81E-01	1.44E+00	3.56E+00	4.15E-02	7.50E-02	-8.30E-02	-1.10E-03	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:13	3.97E+02	3.84E+02	8.47E+02	6.62E+04	3.50E+02	2.20E+00	5.81E-01	1.69E+00	1.05E+00	1.46E-01	2.16E-01	-8.30E-02	-9.70E-02	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:14	3.99E+02	3.84E+02	6.98E+02	4.37E+03	2.10E+02	6.64E-01	5.81E-01	2.06E+00	1.75E+00	1.46E-01	2.16E-01	-8.30E-02	-9.70E-02	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:15	3.99E+02	3.84E+02	5.64E+02	2.17E+04	3.20E+02	8.64E-01	5.81E-01	1.66E+00	6.41E-01	-2.37E-01	3.94E-01	1.06E-01	-9.70E-02	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:16	4.01E+02	3.84E+02	4.87E+02	1.58E+04	3.40E+02	5.34E-01	5.81E-01	1.42E+00	4.13E+00	-3.64E-01	-9.73E-02	1.37E-02	-2.55E-04	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:17	4.01E+02	3.84E+02	4.35E+02	1.30E+04	2.90E+02	8.31E-01	5.81E-01	2.24E+00	4.03E+00	4.67E-01	-9.37E-02	-8.30E-02	6.85E-04	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:18	3.98E+02	3.84E+02	3.87E+02	9.70E+03	2.90E+02	1.24E+00	5.81E-01	1.82E+00	4.03E+00	4.67E-01	-9.37E-02	-8.30E-02	6.85E-04	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:19	3.98E+02	3.84E+02	3.31E+02	8.70E+03	2.80E+02	1.24E+00	5.81E-01	1.75E+00	9.81E-01	1.98E-01	2.63E-01	-8.30E-02	2.18E-03	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:20	3.99E+02	3.84E+02	2.89E+02	8.30E+03	2.50E+02	1.30E-01	5.81E-01	2.09E+00	2.35E+00	-2.29E-01	2.54E-01	1.03E-01	8.93E-02	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:21	3.99E+02	3.85E+02	2.67E+02	8.70E+03	2.80E+02	1.24E+00	5.81E-01	2.44E+00	2.35E+00	-2.39E-01	-1.05E-01	1.03E-01	8.93E-02	2.06E+00	7.89E-01	1.32E-01	-1.75E-02	4.12E+03	0.00E+00
3/19/2007 10:16:																			





Date and Time	CO2 (820)	CO2 (B)	CO	Number	PM2.5	PM Carbon	NO	NO2	HCHO	Acetonitrile	Acetaldehyde	Benzene	C2Benzene	Toluene	Benzonitrile	Styrene	Hydrogen	Propene+alkene+acetic acid	Acetic	Furan	Ethylacetate	PM Org	PM SO4	PM NO3	PM PAH	PM Pb	PM Zn
	ug/m3	ug/m3	ug/m3	ppb	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3
3/21/2007 12:56:00	3.83E+02	3.78E+02	1.63E+02	1.84E+03	1.10E-02	7.72E-01	1.32E+00	1.52E+00	1.50E+00	-5.40E-02	1.80E+00											6.40E-02					
3/21/2007 12:56:01	3.84E+02	3.78E+02	1.64E+02	1.86E+03	1.80E-02	5.63E-01	1.86E+00	6.15E+01	-5.40E-02	1.80E+00												-6.40E-02					
3/21/2007 12:56:02	3.83E+02	3.78E+02	1.62E+02	1.86E+03	4.50E-02	1.98E-01	1.27E+00	5.04E-01	-2.69E+00	1.32E-01	2.35E+00											-6.40E-02					
3/21/2007 12:56:03	3.82E+02	3.78E+02	1.64E+02	1.84E+03	1.90E-02	8.65E-02	1.36E+00	8.24E-01	-1.42E+00	1.32E-01	2.35E+00											-6.40E-02					
3/21/2007 12:56:04	3.82E+02	3.78E+02	1.64E+02	1.83E+03	2.10E-02	4.80E-01	1.24E+00	1.37E+00	3.47E-02	-1.13E-01	1.78E+00											8.78E-02					
3/21/2007 12:56:05	3.83E+02	3.78E+02	1.62E+02	1.85E+03	1.90E-02	1.01E+00	1.54E+00	2.83E-01	6.73E-01	3.47E-02	1.78E+00											8.78E-02					
3/21/2007 12:56:06	3.84E+02	3.78E+02	1.65E+02	1.83E+03	1.90E-02	1.27E+00	1.56E+00	-1.39E-01	-5.76E+00	6.11E-01	1.61E-01											-6.40E-02					
3/21/2007 12:56:07	3.85E+02	3.78E+02	1.65E+02	1.86E+03	1.70E-02	1.21E+00	1.29E+00	2.24E-01	-2.21E+00	3.13E-01	6.11E-01											-6.40E-02					
3/21/2007 12:56:08	3.84E+02	3.78E+02	1.60E+02	1.86E+03	1.80E-02	9.80E-01	1.33E+00	1.07E+00	-5.95E+00	2.32E-01	1.47E+00											-6.40E-02					
3/21/2007 12:56:09	3.83E+02	3.78E+02	1.64E+02	1.88E+03	1.90E-02	5.98E-01	1.11E+00	3.16E-01	-1.35E+00	2.32E-01	1.47E+00											-6.40E-02					
3/21/2007 12:56:10	3.83E+02	3.78E+02	1.65E+02	1.86E+03	1.70E-02	1.19E-02	1.51E+00	-8.41E-01	-5.11E+00	1.51E-01	2.08E+00											-4.26E-01					
3/21/2007 12:56:11	3.82E+02	3.78E+02	1.61E+02	1.87E+03	1.90E-02	-4.85E-01	1.17E+00	1.10E-01	-6.36E+00	1.51E-01	2.08E+00											-6.40E-02					
3/21/2007 12:56:12	3.81E+02	3.78E+02	1.64E+02	1.87E+03	2.10E-02	-6.10E-01	1.57E+00	7.67E-01	-2.81E+00	2.30E-01	8.47E-01											9.80E-02					
3/21/2007 12:56:13	3.82E+02	3.78E+02	1.65E+02	1.88E+03	1.80E-02	-4.04E-01	1.83E+00	1.12E-01	-3.12E+00	3.58E+00	8.47E-01											9.80E-02					
3/21/2007 12:56:14	3.83E+02	3.78E+02	1.61E+02	1.87E+03	1.90E-02	-1.54E-01	1.01E+00	1.20E+00	-3.13E+00	1.39E-01	2.39E+00											-4.30E-01					
3/21/2007 12:56:15	3.82E+02	3.78E+02	1.65E+02	1.89E+03	1.80E-02	3.16E-02	1.55E+00	-5.51E-01	1.34E+00	1.39E-01	2.39E+00											9.89E-02					
3/21/2007 12:56:16	3.83E+02	3.78E+02	1.62E+02	1.89E+03	1.60E-02	2.39E-01	1.47E+00	-5.10E-01	-6.11E+00	1.53E+00												-6.40E-02					
3/21/2007 12:56:17	3.84E+02	3.78E+02	1.64E+02	1.86E+03	2.10E-02	5.37E-01	1.73E+00	-4.96E-02	4.26E+00	2.36E-01	1.53E+00											-6.40E-02					
3/21/2007 12:56:18	3.84E+02	3.78E+02	1.69E+02	1.87E+03	1.80E-02	5.37E-01	1.24E+00	-8.96E-01	-2.04E+00	-5.40E-02	7.30E-01											-6.40E-02					
3/21/2007 12:56:19	3.83E+02	3.78E+02	1.62E+02	1.85E+03	1.80E-02	8.88E-01	1.29E+00	-2.02E-01	3.63E-01	-5.40E-02	7.30E-01											-6.40E-02					
3/21/2007 12:56:20	3.83E+02	3.78E+02	1.63E+02	1.84E+03	1.90E-02	9.21E-01	1.65E+00	3.72E-01	-3.92E+00	-5.40E-02	7.30E-01											-6.40E-02					
3/21/2007 12:56:21	3.83E+02	3.78E+02	1.63E+02	1.88E+03	1.90E-02	5.78E-01	1.17E+00	-4.90E-01	-7.33E+00	6.40E-02	2.50E+00											1.05E-01					
3/21/2007 12:56:22	3.82E+02	3.78E+02	1.64E+02	1.90E+03	1.70E-02	5.78E-01	1.05E+00	1.12E+00	-3.08E+00	-5.40E-02	2.50E+00											1.05E-01					
3/21/2007 12:56:23	3.81E+02	3.78E+02	1.65E+02	1.90E+03	2.20E-02	1.67E-01	9.35E-01	8.89E-01	-1.90E-01	-5.40E-02	2.62E+00											2.35E-01					
3/21/2007 12:56:24	3.83E+02	3.78E+02	1.61E+02	1.91E+03	1.60E-02	-1.11E-01	1.17E+00	3.97E-01	-6.39E+00	-5.40E-02	2.62E+00											2.35E-01					
3/21/2007 12:56:25	3.83E+02	3.78E+02	1.68E+02	1.87E+03	1.90E-02	1.70E+00	2.03E+00	1.37E+00	1.76E+00	1.81E+01	9.64E-01											-6.40E-02					
3/21/2007 12:56:26	3.83E+02	3.78E+02	1.65E+02	1.89E+03	1.80E-02	-7.8E-01	1.31E+00	1.29E+00	1.81E+01	9.64E-01	9.64E-01											-6.40E-02					
3/21/2007 12:56:27	3.79E+02	3.79E+02	1.59E+02	1.92E+03	1.90E-02	-2.97E-02	1.43E+00	1.01E+00	-3.18E+00	4.03E-01	3.22E+00											9.21E-02					
3/21/2007 12:56:28	3.83E+02	3.79E+02	1.67E+02	1.92E+03	1.70E-02	4.75E-01	1.63E+00	-5.69E-01	-8.97E+00	4.03E-01	3.22E+00											9.21E-02					
3/21/2007 12:56:29	3.83E+02	3.79E+02	1.61E+02	1.96E+03	1.70E-02	4.75E-01	1.46E+00	-1.41E+00	-3.22E+00	4.41E-01	6.56E-01											2.61E-01					
3/21/2007 12:56:30	3.83E+02	3.79E+02	1.64E+02	1.97E+03	1.80E-02	1.09E+00	8.51E-01	-1.14E+00	-1.84E+00	4.22E-01	6.56E-01											2.61E-01					
3/21/2007 12:56:31	3.84E+02	3.79E+02	1.67E+02	1.94E+03	1.80E-02	-5.68E-01	1.10E+00	-8.47E-01	-3.24E+00	1.24E+00												-6.40E-02					
3/21/2007 12:56:32	3.85E+02	3.79E+02	1.65E+02	1.93E+03	1.80E-02	8.26E-01	1.55E+00	4.02E-01	4.13E-01	2.19E-01	2.20E+00											-6.40E-02					
3/21/2007 12:56:33	3.86E+02	3.80E+02	1.65E+02	1.92E+03	1.60E-02	8.26E-01	1.21E+00	8.10E-01	-5.22E+00	1.37E-01	3.31E+00											-6.40E-02					
3/21/2007 12:56:34	3.84E+02	3.79E+02	1.60E+02	1.95E+03	1.70E-02	1.90E-01	1.56E+00	2.10E-02	-2.26E+00	1.37E-01	3.31E+00											-6.40E-02					
3/21/2007 12:56:35	3.83E+02	3.79E+02	1.60E+02	1.97E+03	1.80E-02	-3.52E-01	1.65E+00	-1.44E+00	-3.55E+00	3.86E-02	1.24E+00											-6.40E-02					
3/21/2007 12:56:36	3.83E+02	3.79E+02	1.67E+02	1.94E+03	1.80E-02	-5.68E-01	1.10E+00	-8.47E-01	-3.24E+00	1.24E+00												-6.40E-02					
3/21/2007 12:56:37	3.81E+02	3.78E+02	1.63E+02	1.96E+03	1.80E-02	-5.68E-01	1.41E+00	2.33E+00	-8.38E+00	1.27E-01	3.84E+00											-6.40E-02					
3/21/2007 12:56:38	3.85E+02	3.78E+02	1.63E+02	1.93E+03	2.00E-02	-3.68E-01	1.43E+00	-3.78E-01	-2.58E+00	1.27E-01	3.84E+00											-6.40E-02					
3/21/2007 12:56:39	3.85E+02	3.78E+02	1.64E+02	1.94E+03	1.80E-02	2.14E-02	8.69E-01	-4.72E-01	-1.93E+00	1.34E-01	3.93E-01											-6.40E-02					
3/21/2007 12:56:40	3.83E+02	3.78E+02	1.65E+02	1.98E+03	1.80E-02	2.14E-02	1.49E+00	-4.22E-01	-4.88E+00	1.34E-01	3.93E-01											-6.40E-02					
3/21/2007 12:56:41	3.82E+02	3.79E+02	1.62E+02	1.95E+03	1.90E-02	4.70E-01	1.47E+00	1.42E-01	3.17E+00	1.42E-01	3.17E+00											1.03E-01					
3/21/2007 12:56:42	3.82E+02	3.79E+02	1.63E+02	2.00E+03	1.80E-02	9.20E-01	1.58E+00	5.30E-01	-2.95E+00	1.17E-01	3.74E+00											1.03E-01					
3/21/2007 12:56:43	3.84E+02	3.79E+02	1.63E+02	1.98E+03	1.90E-02	1.12E+00	1.98E+00	-2.58E-01	-4.39E+00	1.42E-01	3.17E+00											1.03E-01					
3/21/2007 12:56:44	3.81E+02	3.79E+02	1.63E+02	2.02E+03	1.90E-02	7.75E-01	1.31E+00	5.16E-01	-2.27E+00	-5.40E-02	2.30E+00											-6.40E-02					
3/21/2007 12:56:45	3.81E+02	3.79E+02	1.63E+02	2.03E+03	1.60E-02	1.50E-01	1.01E+00	4.47E-01	9.71E-01	-5.40E-02	2.30E+00											-6.40E-02					
3/21/2007 12:56:46	3.84E+02	3.79E+02	1.63E+02	2.02E+03	1.80E-02	-3.92E-01	1.31E+00	9.96E-01	-2.32E+00	1.37E-01	2.52E+00											-6.40E-02					
3/21/2007 12:56:47	3.85E+02	3.79E+02	1.65E+02	1.98E+03	1.80E-02	5.33E-01	1.37E+00	-8.83E-01	-3.93E+00	1.50E-01	2.52E+00											-6.40E-02					
3/21/2007 12:56:48	3.84E+02	3.78E+02	1.66E+02	2.03E+03	2.00E-02	-3.56E-01	1.40E+00	8.67E-01	3.24E+00	1.29E-01																	

3/21/2007 12:57:33	3.80E+02	3.79E+02	1.63E+02	2.73E+03	1.80E-02	5.00E-01	1.18E+00	1.23E+00	-3.51E+00	3.86E-02	2.66E+00	-4.30E-01	-4.39E-01	-6.40E-02	1.76E+00	7.64E-01	6.54E-02	-1.03E-02	8.59E-03	0.00E+00
3/21/2007 12:57:34	3.82E+02	3.79E+02	1.68E+02	2.72E+03	1.80E-02	5.99E-01	1.20E+00	1.60E+00	8.99E-01	-5.40E-02	1.73E+00	-4.39E-01	-4.39E-01	-6.40E-02	1.76E+00	7.64E-01	6.54E-02	-1.03E-02	8.59E-03	0.00E+00
3/21/2007 12:57:35	3.81E+02	3.79E+02	1.63E+02	2.73E+03	1.80E-02	5.49E-01	1.20E+00	1.32E+00	1.43E+00	-5.40E-02	1.73E+00	-4.39E-01	-4.39E-01	-6.40E-02	1.76E+00	7.64E-01	6.54E-02	-1.03E-02	8.59E-03	0.00E+00
3/21/2007 12:57:36	3.85E+02	3.80E+02	1.65E+02	2.70E+03	1.60E-02	7.44E-01	1.08E+00	1.64E-01	4.03E+00	-5.40E-02	1.47E+00	-4.17E-01	-4.17E-01	-6.40E-02	1.81E+00	8.41E-01	6.77E-02	-1.04E-02	8.18E-03	0.00E+00
3/21/2007 12:57:37	3.82E+02	3.79E+02	1.62E+02	2.64E+03	1.90E-02	7.44E-01	1.13E+00	8.83E-01	-6.26E+00	-5.40E-02	1.47E+00	-4.17E-01	-4.17E-01	-6.40E-02	1.86E+00	9.13E-01	7.60E-02	-1.43E-02	8.56E-03	0.00E+00
3/21/2007 12:57:38	3.81E+02	3.79E+02	1.62E+02	2.61E+03	1.90E-02	9.36E-01	1.12E+00	6.37E-01	1.01E+00	3.85E-02	2.45E+00	-4.23E-01	-4.23E-01	-6.40E-02	1.96E+00	9.79E-01	1.23E-01	-1.10E-02	1.09E-02	0.00E+00
3/21/2007 12:57:39	3.83E+02	3.79E+02	1.62E+02	2.52E+03	1.90E-02	1.12E+00	1.46E+00	-4.99E-01	-3.17E+00	3.85E-02	2.45E+00	-4.23E-01	-4.23E-01	-6.40E-02	1.96E+00	9.79E-01	1.23E-01	-1.10E-02	1.09E-02	0.00E+00
3/21/2007 12:57:40	3.83E+02	3.79E+02	1.61E+02	2.43E+03	1.80E-02	1.12E+00	1.46E+00	3.43E-02	-3.69E+00	-5.40E-02	1.92E+00	-4.15E-01	-4.15E-01	-6.40E-02	1.79E+00	7.67E-01	7.05E-02	-4.07E-03	8.26E-03	0.00E+00
3/21/2007 12:57:41	3.81E+02	3.79E+02	1.68E+02	2.33E+03	1.60E-02	1.03E+00	1.09E+00	8.93E-02	-3.85E+00	-5.40E-02	1.92E+00	-4.15E-01	-4.15E-01	-6.40E-02	1.79E+00	7.67E-01	7.05E-02	-4.07E-03	8.26E-03	0.00E+00
3/21/2007 12:57:42	3.82E+02	3.79E+02	1.66E+02	2.33E+03	1.70E-02	8.93E-01	8.76E-01	-1.32E-01	-3.55E+00	1.20E-01	1.66E+00	-4.12E-01	-4.12E-01	-6.40E-02	1.77E+00	7.93E-01	7.50E-02	-9.53E-03	9.49E-03	0.00E+00
3/21/2007 12:57:43	3.84E+02	3.79E+02	1.61E+02	2.32E+03	1.70E-02	9.35E-01	1.04E+00	5.98E-01	-2.16E+00	1.20E-01	1.66E+00	-4.12E-01	-4.12E-01	-6.40E-02	1.77E+00	7.93E-01	7.50E-02	-9.53E-03	9.49E-03	0.00E+00
3/21/2007 12:57:44	3.82E+02	3.79E+02	1.61E+02	2.33E+03	1.80E-02	1.13E+00	1.07E+00	2.74E-01	1.48E+00	-5.40E-02	2.11E+00	-4.50E-01	-4.50E-01	-6.40E-02	1.77E+00	7.93E-01	7.50E-02	-9.53E-03	9.49E-03	0.00E+00
3/21/2007 12:57:45	3.82E+02	3.79E+02	1.64E+02	2.28E+03	1.60E-02	1.12E+00	1.43E+00	-3.88E-01	-3.79E-01	4.13E-02	2.11E+00	-4.50E-01	-4.50E-01	-6.40E-02	1.77E+00	7.93E-01	7.50E-02	-9.53E-03	9.49E-03	0.00E+00
3/21/2007 12:57:46	3.84E+02	3.79E+02	1.63E+02	2.30E+03	1.80E-02	5.92E-01	1.48E+00	1.88E+00	-5.40E-02	9.65E-01	-4.18E-01	-4.18E-01	-4.18E-01	-6.40E-02	2.00E+00	6.81E-01	6.71E-02	-8.47E-03	1.04E-02	0.00E+00
3/21/2007 12:57:47	3.85E+02	3.80E+02	1.62E+02	2.28E+03	2.30E-02	1.38E-01	1.00E+00	1.25E+00	-3.10E+00	-5.40E-02	9.65E-01	-4.18E-01	-4.18E-01	-6.40E-02	2.00E+00	6.81E-01	6.71E-02	-8.47E-03	1.04E-02	0.00E+00
3/21/2007 12:57:48	3.84E+02	3.80E+02	1.63E+02	2.28E+03	2.00E-02	9.77E-02	9.35E-01	7.64E-01	-3.33E+00	3.97E-02	1.03E+00	-4.35E-01	-4.35E-01	-6.40E-02	2.18E+00	7.38E-01	6.64E-02	-5.56E-03	9.27E-03	0.00E+00
3/21/2007 12:57:49	3.84E+02	3.79E+02	1.63E+02	2.24E+03	1.50E-02	2.52E-01	1.19E+00	2.53E-01	-1.08E+00	-4.35E-01	1.03E+00	-4.35E-01	-4.35E-01	-6.40E-02	2.18E+00	7.38E-01	6.64E-02	-5.56E-03	9.27E-03	0.00E+00
3/21/2007 12:57:50	3.82E+02	3.80E+02	1.63E+02	2.23E+03	2.00E-02	3.63E-01	1.12E+00	1.01E+00	-9.72E-01	3.97E-02	1.03E+00	-4.35E-01	-4.35E-01	-6.40E-02	2.13E+00	7.38E-01	6.64E-02	-5.56E-03	9.27E-03	0.00E+00
3/21/2007 12:57:51	3.82E+02	3.79E+02	1.62E+02	2.22E+03	1.90E-02	5.01E-01	1.22E+00	7.65E-01	-8.61E-01	1.36E-01	2.19E+00	-4.29E-01	-4.29E-01	-6.40E-02	2.22E+00	7.97E-01	8.12E-02	-1.60E-02	8.35E-03	0.00E+00
3/21/2007 12:57:52	3.83E+02	3.79E+02	1.64E+02	2.23E+03	1.80E-02	7.09E-01	8.20E-01	-3.65E+00	-3.65E+00	-4.29E-01	2.19E+00	-4.29E-01	-4.29E-01	-6.40E-02	2.22E+00	7.97E-01	8.12E-02	-1.60E-02	8.35E-03	0.00E+00
3/21/2007 12:57:53	3.83E+02	3.79E+02	1.63E+02	2.19E+03	1.70E-02	8.11E-01	1.27E+00	-8.89E-02	-2.02E+00	3.09E-01	2.59E+00	-4.49E-01	-4.49E-01	-6.40E-02	2.17E+00	8.09E-01	6.53E-02	-3.08E-03	8.24E-03	0.00E+00
3/21/2007 12:57:54	3.84E+02	3.79E+02	1.65E+02	2.10E+03	1.90E-02	6.55E-01	1.24E+00	-2.40E+00	-2.40E+00	3.09E-01	2.59E+00	-4.49E-01	-4.49E-01	-6.40E-02	2.17E+00	8.09E-01	6.53E-02	-3.08E-03	8.24E-03	0.00E+00
3/21/2007 12:57:55	3.83E+02	3.79E+02	1.64E+02	2.07E+03	1.70E-02	3.75E-01	1.45E+00	2.55E-01	-6.25E+00	3.80E-02	2.72E+00	-4.22E-01	-4.22E-01	-6.40E-02	2.07E+00	7.39E-01	6.85E-02	-1.85E-02	6.28E-03	0.00E+00
3/21/2007 12:57:56	3.81E+02	3.79E+02	1.68E+02	2.11E+03	1.70E-02	1.40E-01	1.95E-01	2.48E-01	-3.83E+00	3.80E-02	2.72E+00	-4.22E-01	-4.22E-01	-6.40E-02	2.07E+00	7.39E-01	6.85E-02	-1.85E-02	6.28E-03	0.00E+00
3/21/2007 12:57:57	3.82E+02	3.79E+02	1.63E+02	2.11E+03	1.70E-02	3.64E-01	1.31E+00	1.54E+00	-3.23E-01	3.80E-02	2.72E+00	-4.22E-01	-4.22E-01	-6.40E-02	2.11E+00	7.96E-01	6.53E-02	-4.97E-03	9.51E-03	0.00E+00
3/21/2007 12:57:58	3.84E+02	3.79E+02	1.66E+02	2.25E+03	1.70E-02	3.07E-03	1.74E+00	4.59E-01	-3.82E+00	3.30E-01	2.23E+00	-4.35E-01	-4.35E-01	-6.40E-02	2.11E+00	7.96E-01	6.53E-02	-4.97E-03	9.51E-03	0.00E+00
3/21/2007 12:57:59	3.85E+02	3.79E+02	1.65E+02	2.25E+03	1.80E-02	0.00E+00	1.89E+00	2.50E+00	-8.31E-01	1.36E-01	2.74E+00	-4.10E-01	-4.10E-01	-6.40E-02	1.83E+00	7.56E-01	6.04E-02	-1.13E-02	8.60E-03	0.00E+00
3/21/2007 12:58:00	3.84E+02	3.79E+02	1.65E+02	2.14E+03	2.10E-02	0.00E+00	1.94E+00	6.23E-01	-2.96E+00	1.36E-01	2.74E+00	-4.10E-01	-4.10E-01	-6.40E-02	1.83E+00	7.56E-01	6.04E-02	-1.13E-02	8.60E-03	0.00E+00
3/21/2007 12:58:01	3.82E+02	3.79E+02	1.63E+02	2.15E+03	2.00E-02	0.00E+00	1.94E+00	1.28E+00	-3.47E+00	3.42E-02	1.16E+00	-4.05E-01	-4.05E-01	-6.40E-02	1.79E+00	7.81E-01	6.95E-02	-1.33E-02	8.35E-03	0.00E+00
3/21/2007 12:58:02	3.81E+02	3.79E+02	1.62E+02	2.09E+03	2.00E-02	3.25E-03	1.17E+00	8.40E-02	-3.17E+00	3.42E-02	1.16E+00	-4.05E-01	-4.05E-01	-6.40E-02	1.79E+00	7.81E-01	6.95E-02	-1.33E-02	8.35E-03	0.00E+00
3/21/2007 12:58:03	3.81E+02	3.79E+02	1.64E+02	2.13E+03	2.10E-02	3.22E-02	1.22E+00	6.80E-01	-3.23E+00	3.72E-02	5.95E-01	-4.18E-01	-4.18E-01	-6.40E-02	1.84E+00	8.19E-01	7.86E-02	-8.48E-03	6.97E-03	0.00E+00
3/21/2007 12:58:04	3.82E+02	3.79E+02	1.64E+02	2.10E+03	1.70E-02	1.41E-01	1.82E+00	6.90E-01	-4.14E+00	3.72E-02	5.95E-01	-4.18E-01	-4.18E-01	-6.40E-02	1.69E+00	6.61E-01	8.78E-02	-1.61E-02	9.74E-03	0.00E+00
3/21/2007 12:58:05	3.84E+02	3.79E+02	1.65E+02	2.17E+03	1.60E-02	3.53E-01	1.47E+00	-5.43E-01	-3.80E+00	3.77E-02	9.47E-01	-4.30E-01	-4.30E-01	-6.40E-02	1.69E+00	6.61E-01	8.78E-02	-1.61E-02	9.74E-03	0.00E+00
3/21/2007 12:58:06	3.85E+02	3.79E+02	1.63E+02	2.12E+03	2.00E-02	5.31E-01	1.79E+00	-1.71E-01	-3.35E+00	3.77E-02	9.47E-01	-4.30E-01	-4.30E-01	-6.40E-02	1.82E+00	7.98E-01	1.17E-01	-1.73E-02	9.55E-03	0.00E+00
3/21/2007 12:58:07	3.86E+02	3.80E+02	1.60E+02	2.05E+03	2.00E-02	4.19E-01	7.85E-01	1.24E+00	4.61E+00	1.89E-01	1.89E+00	-4.47E-01	-4.47E-01	-6.40E-02	1.82E+00	7.98E-01	1.17E-01	-1.73E-02	9.55E-03	0.00E+00
3/21/2007 12:58:08	3.85E+02	3.81E+02	1.67E+02	2.07E+03	2.60E-02	0.00E+00	1.46E+00	3.04E-01	6.06E-01	1.35E-01	1.89E+00	-4.47E-01	-4.47E-01	-6.40E-02	1.75E+00	7.79E-01	6.84E-02	-1.52E-02	7.71E-03	0.00E+00
3/21/2007 12:58:09	3.84E+02	3.80E+02	1.63E+02	2.08E+03	2.40E-02	-4.20E-01	1.29E+00	2.07E-01	-1.96E+00	-5.40E-02	3.19E+00	-4.31E-01	-4.31E-01	-6.40E-02	1.73E+00	7.70E-01	6.72E-02	-8.69E-03	9.97E-03	0.00E+00
3/21/2007 12:58:10	3.84E+02	3.79E+02	1.62E+02	2.10E+03	2.10E-02	-3.55E-01	1.29E+00	2.07E-01	-1.96E+00	-5.40E-02	3.19E+00	-4.31E-01	-4.31E-01	-6.40E-02	1.82E+00	7.70E-01	6.72E-02	-8.69E-03	9.97E-03	0.00E+00
3/21/2007 12:58:11	3.82E+02	3.79E+02	1.61E+02	2.10E+03	1.90E-02	-3.52E-01	7.92E-01	1.11E+00	-1.64E+00	-5.40E-02	3.19E+00	-4.31E-01	-4.31E-01	-6.40E-02	1.73E+00	7.70E-01	6.72E-02	-8.69E-03	9.97E-03	0.00E+00
3/21/2007 12:58:12	3.84E+02	3.79E+02	1.63E+02	2.15E+03	3.30E-02	-1.40E-01	1.98E+00	1.03E-01	-5.40E-02	1.61E+00	9.05E-02	-4.28E-01	-4.28E-01	-6.40E-02	1.83E+00	7.98E-01	1.01E-01	-7.97E-03	8.54E-03	0.00E+00
3/21/2007 12:58:13	3.85E+02	3.79E+02	1.65E+02	2.15E+03	1.50E-02	-3.21E-02	9.44E-01	-3.15E-01	2.00E+00	-5.40E-02	1.61E+00	-4.28E-01	-4.28E-01	-6.40E-02	1.83E+00	7.98E-01	1.01E-01	-7.97E-03	8.54E-03	0.00E+00
3/21/2007 12:58:14	3.86E+02	3.79E+02	1.65E+02	2.13E+03	1.90E-02	-3.23E-03	1.21E+00	-1.88E-01	-2.03E+00	-5.40E-02	3.53E+00	-4.41E-01	-4.41E-01	-6.40E-02	1.74E+00	7.20E-01	6.68E-02	-1.27E-02	9.06E-03	0.00E+00
3/21/2007 12:58:15	3.85E+02	3.79E+02	1.66E+02	2.16E+03	2.00E-02	0.00E+00	1.30E+00	-7.98E-01	1.03E-01	-5.40E-02	3.53E+00	-4.41E-01	-4.41E-01	-6.40E-02	1.74E+00	7.20E-01	6.68E-02	-1.27E-02	9.06E-03	0.00E+00
3/21/2																				









3/21/2007 13:03:57	3.83E+02	3.79E+02	1.63E+02	2.06E+03	2.00E-02	-6.69E-01	1.81E+00	1.08E+00	1.33E-01	1.53E+00	-4.47E-01	9.61E-02	1.78E+00	6.58E-01	5.49E-02	1.07E-02	3.23E+03	0.00E+00
3/21/2007 13:03:58	3.82E+02	3.79E+02	1.68E+02	2.09E+03	2.10E-02	-9.47E-01	1.10E+00	-6.67E-01	6.96E+01	1.33E-01	-4.47E-01	9.61E-02	1.69E+00	6.63E-01	5.39E-02	1.56E-03	4.22E+03	0.00E+00
3/21/2007 13:03:59	3.83E+02	3.79E+02	1.68E+02	2.09E+03	2.10E-02	-9.47E-01	1.10E+00	-6.67E-01	6.96E+01	1.33E-01	-4.47E-01	9.61E-02	1.69E+00	6.63E-01	5.39E-02	1.56E-03	4.22E+03	0.00E+00
3/21/2007 13:04:00	3.87E+02	3.81E+02	1.62E+02	2.06E+03	2.10E-02	-7.75E-01	1.58E+00	2.56E+00	6.74E+00	1.30E-01	3.20E+00	-6.40E-02	1.79E+00	6.60E-01	1.02E-01	4.86E-04	6.27E+03	0.00E+00
3/21/2007 13:04:01	3.82E+02	3.80E+02	1.62E+02	2.07E+03	2.00E-02	-7.58E-01	1.42E+00	2.11E+00	6.68E+00	2.06E-01	2.14E+00	-6.40E-02	1.79E+00	6.60E-01	1.02E-01	4.86E-04	6.27E+03	0.00E+00
3/21/2007 13:04:02	3.82E+02	3.79E+02	1.62E+02	2.04E+03	1.90E-02	-9.34E-01	1.13E+00	1.95E+00	9.58E+00	2.06E-01	2.14E+00	-6.40E-02	1.71E+00	6.31E-01	7.00E-02	-1.45E-02	7.47E+03	0.00E+00
3/21/2007 13:04:03	3.83E+02	3.79E+02	1.64E+02	1.98E+03	1.80E-02	-9.34E-01	1.22E+00	1.09E+01	1.04E+01	2.25E-01	3.75E+00	-6.40E-02	1.63E+00	6.74E-01	6.04E-02	-2.10E-03	3.00E+03	0.00E+00
3/21/2007 13:04:04	3.85E+02	3.80E+02	1.61E+02	1.95E+03	2.20E-02	-1.36E+00	1.41E+00	2.19E+00	7.01E+00	1.23E-01	3.75E+00	-6.40E-02	1.63E+00	6.74E-01	6.04E-02	-2.10E-03	3.00E+03	0.00E+00
3/21/2007 13:04:05	3.83E+02	3.79E+02	1.68E+02	1.94E+03	2.40E-02	-1.15E+00	1.79E+00	3.27E-01	5.00E+00	1.35E-01	3.82E+00	-6.40E-02	1.75E+00	6.10E-01	7.01E-02	-1.67E-02	8.17E+03	0.00E+00
3/21/2007 13:04:06	3.87E+02	3.80E+02	1.59E+02	1.92E+03	2.20E-02	-9.64E-01	1.52E+00	1.83E+00	1.10E+01	1.23E-01	4.10E+00	-6.40E-02	1.82E+00	6.75E-01	7.01E-02	-1.67E-02	6.17E+03	0.00E+00
3/21/2007 13:04:07	3.93E+02	3.85E+02	1.60E+02	1.91E+03	1.90E-02	-2.04E-01	1.23E+00	2.49E+00	1.16E+01	-5.40E-02	1.50E+00	-6.40E-02	1.65E+00	6.73E-01	7.00E-02	3.20E-03	4.14E+03	0.00E+00
3/21/2007 13:04:08	3.85E+02	3.83E+02	1.62E+02	1.94E+03	2.00E-02	4.08E-01	1.81E+00	2.56E+00	4.88E+00	-5.40E-02	1.50E+00	-6.40E-02	1.57E+00	6.54E-01	5.53E-02	-1.26E-02	7.40E+03	0.00E+00
3/21/2007 13:04:09	3.80E+02	3.80E+02	1.65E+02	1.98E+03	2.10E-02	4.42E-01	1.42E+00	2.03E+00	9.19E+00	-5.40E-02	3.65E+00	-6.40E-02	1.57E+00	6.54E-01	5.53E-02	-1.26E-02	7.40E+03	0.00E+00
3/21/2007 13:04:10	3.87E+02	3.82E+02	1.65E+02	2.06E+03	2.60E-02	-4.73E-01	1.66E+00	1.15E+00	8.68E+00	1.57E+01	1.29E+00	-6.40E-02	1.57E+00	6.54E-01	5.53E-02	-1.26E-02	7.40E+03	0.00E+00
3/21/2007 13:04:11	3.87E+02	3.81E+02	1.62E+02	2.03E+03	1.80E-02	-5.79E-01	1.91E+01	1.27E+00	8.36E+00	3.64E-02	1.29E+00	-6.40E-02	1.57E+00	6.54E-01	5.53E-02	-1.26E-02	7.40E+03	0.00E+00
3/21/2007 13:04:12	3.88E+02	3.81E+02	1.61E+02	2.01E+03	2.20E-02	-3.88E-01	1.59E+00	1.41E+00	8.50E+00	3.64E-02	1.29E+00	-6.40E-02	1.78E+00	6.78E-01	6.51E-02	-1.96E-02	5.12E+03	0.00E+00
3/21/2007 13:04:13	3.85E+02	3.79E+02	1.64E+02	2.04E+03	2.00E-02	-1.50E-01	1.45E+00	4.46E-01	6.32E+00	1.42E-01	1.95E+00	-6.40E-02	1.79E+00	6.78E-01	6.51E-02	-1.96E-02	5.12E+03	0.00E+00
3/21/2007 13:04:14	3.80E+02	3.79E+02	1.63E+02	2.11E+03	2.00E-02	1.43E-01	1.85E+00	2.52E+00	6.21E+00	3.64E-01	2.53E+00	-6.40E-02	1.79E+00	6.78E-01	6.51E-02	-1.96E-02	5.12E+03	0.00E+00
3/21/2007 13:04:15	3.81E+02	3.79E+02	1.65E+02	2.07E+03	2.40E-02	3.15E-01	1.36E+00	2.36E+00	6.59E+00	3.64E-01	2.53E+00	-6.40E-02	1.66E+00	6.73E-01	6.27E-02	-7.95E-03	7.68E+03	0.00E+00
3/21/2007 13:04:16	3.82E+02	3.79E+02	1.65E+02	2.08E+03	2.30E-02	3.15E-01	1.54E+00	1.96E+00	1.21E+01	3.86E-02	2.69E+00	-6.40E-02	1.60E+00	6.00E-01	5.55E-02	-1.91E-02	4.86E+03	0.00E+00
3/21/2007 13:04:17	3.83E+02	3.79E+02	1.64E+02	2.08E+03	2.30E-02	5.08E-01	1.47E+00	1.89E+00	8.02E+00	3.86E-02	2.69E+00	-6.40E-02	1.60E+00	6.00E-01	5.55E-02	-1.91E-02	4.86E+03	0.00E+00
3/21/2007 13:04:18	3.84E+02	3.78E+02	1.61E+02	2.10E+03	2.60E-02	5.18E-01	1.50E+00	2.40E+00	3.22E+00	3.12E-01	1.38E+00	-6.40E-02	1.60E+00	6.19E-01	5.72E-02	-5.59E-03	5.97E+03	0.00E+00
3/21/2007 13:04:19	3.84E+02	3.79E+02	1.65E+02	2.13E+03	2.40E-02	5.81E-01	1.46E+00	1.81E+00	3.98E+00	1.72E-01	1.65E+00	-6.40E-02	1.72E+00	7.14E-01	9.41E-02	-6.69E-03	7.40E+03	0.00E+00
3/21/2007 13:04:20	3.83E+02	3.79E+02	1.65E+02	2.14E+03	2.30E-02	4.05E-01	1.57E+00	1.48E+00	1.16E+01	1.40E-01	1.96E+00	-6.40E-02	1.72E+00	7.14E-01	9.41E-02	-6.69E-03	7.40E+03	0.00E+00
3/21/2007 13:04:21	3.83E+02	3.80E+02	1.64E+02	2.14E+03	1.90E-02	4.93E-01	1.13E+00	1.70E+00	5.24E+00	-4.33E-01	1.96E+00	-6.40E-02	1.72E+00	7.14E-01	9.41E-02	-6.69E-03	7.40E+03	0.00E+00
3/21/2007 13:04:22	3.86E+02	3.81E+02	1.61E+02	2.14E+03	1.90E-02	7.48E-01	1.36E+00	2.34E+00	8.24E+00	3.78E-02	1.52E+00	-6.40E-02	1.72E+00	7.14E-01	9.41E-02	-6.69E-03	7.40E+03	0.00E+00
3/21/2007 13:04:23	3.87E+02	3.81E+02	1.65E+02	2.17E+03	2.10E-02	1.55E+00	1.55E+00	8.43E+00	5.28E+00	3.78E-02	1.52E+00	-6.40E-02	1.56E+00	6.46E-01	5.27E-02	2.79E-03	5.96E+03	0.00E+00
3/21/2007 13:04:24	3.83E+02	3.79E+02	1.65E+02	2.20E+03	1.81E-01	1.51E+00	1.81E+00	1.51E+00	3.79E+00	1.51E+00	3.79E+00	-6.40E-02	1.51E+00	1.81E+00	1.51E+00	3.79E+00	3.79E+00	0.00E+00
3/21/2007 13:04:25	3.82E+02	3.79E+02	1.63E+02	2.16E+03	2.30E-02	5.88E-01	1.48E+00	2.68E+00	8.78E+00	1.34E-01	1.59E+00	-6.40E-02	1.59E+00	5.96E-01	6.11E-02	-2.13E-02	8.29E+03	0.00E+00
3/21/2007 13:04:26	3.81E+02	3.79E+02	1.65E+02	2.13E+03	1.90E-02	1.80E-01	1.65E+00	2.83E+00	8.58E+00	3.46E+00	1.93E-01	-6.40E-02	1.58E+00	6.82E-01	5.92E-02	-2.05E-02	6.67E+03	0.00E+00
3/21/2007 13:04:27	3.83E+02	3.79E+02	1.64E+02	2.12E+03	2.40E-02	1.80E-01	1.66E+00	1.80E+00	6.36E+00	3.46E+00	1.93E-01	-6.40E-02	1.58E+00	6.82E-01	5.92E-02	-2.05E-02	6.67E+03	0.00E+00
3/21/2007 13:04:28	3.85E+02	3.81E+02	1.68E+02	2.15E+03	2.10E-02	9.07E-01	1.85E+00	8.77E-01	9.05E+00	4.66E-01	1.49E+00	-6.40E-02	1.58E+00	6.82E-01	6.10E-02	-1.37E-02	7.18E+03	0.00E+00
3/21/2007 13:04:29	3.84E+02	3.80E+02	1.63E+02	2.11E+03	1.80E-02	7.94E+00	1.63E+00	1.79E-01	3.16E+00	4.98E-02	3.34E+00	-6.40E-02	1.62E+00	1.63E+00	4.30E-01	1.25E-02	1.79E+03	0.00E+00
3/21/2007 13:04:30	3.83E+02	3.80E+02	1.67E+02	2.13E+03	5.40E-02	3.10E+01	1.68E+00	3.36E-01	8.74E+00	5.88E+00	1.55E-01	-6.40E-02	1.62E+00	1.63E+00	4.30E-01	1.25E-02	1.79E+03	0.00E+00
3/21/2007 13:04:31	3.85E+02	3.80E+02	2.74E+02	2.12E+03	2.71E+00	3.10E+01	1.31E+00	2.70E+00	6.52E+00	5.88E+00	1.55E-01	-6.40E-02	1.62E+00	1.63E+00	4.30E-01	1.25E-02	1.79E+03	0.00E+00
3/21/2007 13:04:32	4.32E+02	3.97E+02	8.02E+03	2.80E+03	9.24E+00	8.43E+01	1.43E+00	1.49E+01	8.06E+00	5.88E+00	1.55E-01	-6.40E-02	1.62E+00	1.63E+00	4.30E-01	1.25E-02	1.79E+03	0.00E+00
3/21/2007 13:04:33	4.91E+02	4.57E+02	1.11E+05	1.27E+05	4.50E+00	1.63E+02	1.48E+00	3.04E+01	1.40E+01	3.83E+01	3.82E+01	-6.40E-02	3.34E+01	2.19E+00	7.63E-01	5.23E-02	4.32E-02	0.00E+00
3/21/2007 13:04:34	4.39E+02	4.46E+02	4.57E+05	5.69E+05	1.39E+00	2.53E+02	1.56E+00	2.17E-01	9.92E+00	3.83E+01	3.82E+01	-6.40E-02	3.34E+01	2.19E+00	7.63E-01	5.23E-02	4.32E-02	0.00E+00
3/21/2007 13:04:35	3.75E+02	3.99E+02	1.53E+05	7.25E+05	4.61E-01	2.53E+02	4.95E+01	1.44E+01	1.85E+01	1.37E+01	1.40E+01	-6.40E-02	3.34E+01	2.19E+00	7.63E-01	5.23E-02	4.32E-02	0.00E+00
3/21/2007 13:04:36	3.74E+02	3.86E+02	3.23E+04	2.20E+05	1.57E-01	2.67E+02	9.16E+02	6.53E+00	1.24E+01	1.37E+01	1.40E+01	-6.40E-02	3.34E+01	2.19E+00	7.63E-01	5.23E-02	4.32E-02	0.00E+00
3/21/2007 13:04:37	3.79E+02	3.82E+02	7.08E+03	1.16E+05	8.50E-02	2.01E+02	2.38E+03	1.53E+00	7.22E+00	3.17E+00	3.48E+00	-6.40E-02	2.45E+00	1.31E+00	2.89E-02	-5.93E-03	3.96E+03	0.00E+00
3/21/2007 13:04:38	3.83E+02	3.80E+02	2.77E+03	6.39E+04	5.20E-02	1.24E+02	1.67E+03	3.20E+00	7.50E+00	3.17E+00	3.48E+00	-6.40E-02	2.45E+00	1.31E+00	2.89E-02	-5.93E-03	3.96E+03	0.00E+00
3/21/2007 13:04:39	3.87E+02	3.81E+02	1.71E+02	2.66E+04	3.90E-02	1.24E+02	3.54E+02	1.39E+00	1.07E+01	1.13E+00	2.73E+00	-6.40E-02	1.66E+00	1.25E+00	2.24E-03	-3.98E-03	1.51E+03	0.00E+00
3/21/2007 13:04:40	3.88E+02	3.81E+02	1.61E+03	1.93E+04	3.40E-02	5.79E+01	6.58E-01	6.81E-01	7.21E+00	6.43E-01	1.02E+00	-6.40E-02	1.66E+00	1.25E+00	2.24E-03	-3.98E-03	1.51E+03	0.00E+00
3/21/2007 13:04:41	3.89E+02	3.83E+02	9.20E+02	1.46E+04	2.80E-02	2.40E+01	2.12E+01	1.85E+00	1.10E+01	6.50E-01	3.18E+00	-6.40E-02	1.34E+00	1.17E+00	2.02E-02	-2.81E-03	4.43E+03	0.00E+00
3/21/2007 13:04:42	3.86E+02	3.81E+02	7.19E+02	1.17E+04	2.80E-02	2.40E+01	1.31E+01	2.50E+00	1.08E+01	6.50E-01	3.18E+00	-6.40E-02	1.22E+00	9.78E-01	2.94E-02	6.43E-04	7.35E+03	0.00E+00
3/21/2007 13:04:43	3.84E+02	3.81E+02	5.70E+02	7.70E+03	2.60E-02	7.41E+00	9.91E+00	1.05E+00	6.24E+00	3.15E-01	1.20E+00	-6.40E-02	1.22E+00	9.78E-01	2.94E-02	6.43E-04	7.35E+03	0.00E+00
3/21/2007 13:04:44	3.86E																	







3/21/2007 14:50:09	3.89E+02	3.79E+02	2.43E+02	3.41E+03	4.57E-01	2.37E+01	3.76E+00	2.73E-01	3.12E+00	-9.99E-01	4.88E-01	2.58E-01	-2.50E-02	5.86E-02	2.13E+01	3.03E+00	2.56E-01	-2.90E+00	6.34E+00	0.00E+00
3/21/2007 14:50:10	3.90E+02	3.84E+02	3.38E+03	4.70E+05	1.77E-01	4.01E+01	2.09E+00	7.20E+00	5.63E+00	6.10E+00	-2.72E-01	1.10E-02	-2.50E-02	6.11E-02	6.71E+00	9.78E-01	8.65E-02	-5.95E-01	1.23E+00	0.00E+00
3/21/2007 14:50:11	3.89E+02	3.76E+02	3.83E+02	4.22E+04	1.13E-01	5.12E+01	1.23E+01	1.62E+01	1.75E+01	6.10E+01	1.23E+01	2.50E-02	6.11E-02	2.23E+02	6.17E+01	1.78E+01	3.85E+02	-1.35E+01	8.45E+00	0.00E+00
3/21/2007 14:50:12	3.84E+02	3.80E+02	4.35E+03	3.28E+06	1.48E-01	5.41E+01	1.45E+00	1.04E+01	3.00E+00	5.10E+00	1.08E+00	5.11E-01	-2.50E-02	6.14E-02	5.07E+00	8.54E-01	8.03E-02	-3.85E-01	7.55E-01	0.00E+00
3/21/2007 14:50:13	3.82E+02	3.78E+02	1.34E+03	1.34E+06	9.70E-02	4.44E+01	8.88E+00	4.79E+00	3.00E+00	5.10E+00	1.08E+00	5.11E-01	-2.50E-02	6.14E-02	4.57E+00	8.77E-01	1.67E-01	-3.39E-01	6.68E-01	0.00E+00
3/21/2007 14:50:14	3.83E+02	3.78E+02	1.01E+03	5.22E+05	1.63E-01	3.19E+01	1.16E+02	5.07E+00	6.29E+00	6.18E+00	6.79E-01	-2.32E-01	1.12E-01	6.29E-02	4.57E+00	8.77E-01	1.67E-01	-3.39E-01	6.68E-01	0.00E+00
3/21/2007 14:50:15	3.83E+02	3.77E+02	1.22E+03	2.35E+05	1.45E-01	1.81E+01	4.17E+01	5.63E+00	-2.77E+00	6.18E+00	6.79E-01	-2.32E-01	1.12E-01	6.29E-02	3.89E+00	7.45E-01	1.91E-01	-2.57E-01	5.14E-01	0.00E+00
3/21/2007 14:50:16	3.83E+02	3.77E+02	1.18E+03	8.53E+04	9.50E-02	1.40E+01	4.17E+01	5.65E+00	4.92E+00	5.14E+00	2.79E-01	2.32E-01	2.38E-01	-7.40E-02	3.89E+00	7.45E-01	1.91E-01	-2.57E-01	5.14E-01	0.00E+00
3/21/2007 14:50:17	3.81E+02	3.77E+02	1.44E+03	7.52E-01	1.40E+01	2.18E+01	3.47E+00	2.38E+00	2.38E+00	6.30E+00	1.44E+01	2.38E-01	2.38E-01	-7.40E-02	6.39E+00	1.14E+00	9.08E-01	-6.80E-01	1.41E+00	0.00E+00
3/21/2007 14:50:18	3.82E+02	3.77E+02	1.07E+03	4.51E+04	7.27E-01	1.60E+01	4.06E+01	4.68E+00	4.28E+00	3.01E+00	4.56E-01	4.53E-01	1.07E-01	5.75E-02	6.39E+00	1.14E+00	9.08E-01	-6.80E-01	1.41E+00	0.00E+00
3/21/2007 14:50:19	3.85E+02	3.80E+02	1.72E+03	2.87E+04	2.06E-01	1.90E+01	4.06E+01	8.40E+00	1.98E+00	3.01E+00	4.56E-01	4.53E-01	1.07E-01	5.75E-02	3.65E+00	1.76E-01	1.48E-01	-2.76E-01	5.45E-01	0.00E+00
3/21/2007 14:50:20	3.84E+02	3.79E+02	6.47E+03	2.57E+04	6.80E-02	2.07E+01	4.86E+01	2.12E+01	9.56E+00	3.01E+00	4.56E-01	4.53E-01	1.07E-01	5.75E-02	3.15E+00	1.75E-01	5.68E-02	-1.85E-01	3.39E-01	0.00E+00
3/21/2007 14:50:21	3.80E+02	3.77E+02	3.58E+03	2.21E+04	3.80E-02	2.07E+01	5.16E+01	1.46E+01	1.11E+01	1.27E+00	-9.71E-02	2.07E-01	1.01E-01	3.05E-01	3.15E+00	1.75E-01	5.68E-02	-1.85E-01	3.39E-01	0.00E+00
3/21/2007 14:50:22	3.78E+02	3.76E+02	8.93E+02	1.46E+04	2.60E-02	2.13E+01	3.22E+01	5.04E+00	7.86E+00	2.92E+00	4.73E-01	2.07E-01	1.01E-01	3.05E-01	2.92E+00	1.73E-01	5.02E-02	-1.49E-01	3.01E-01	0.00E+00
3/21/2007 14:50:23	3.80E+02	3.76E+02	3.18E+02	1.18E+03	2.02E-02	1.63E+01	1.74E+02	1.48E+00	4.00E+00	2.82E+00	2.73E-01	2.64E-01	1.11E-01	-7.40E-02	2.78E+00	1.75E-01	4.81E-02	-1.50E-01	2.66E-01	0.00E+00
3/21/2007 14:50:24	3.81E+02	3.76E+02	2.39E+02	1.05E+04	2.00E-02	8.86E+00	2.61E+02	1.24E+00	3.54E+00	2.04E+00	3.09E-01	2.64E-01	1.11E-01	-7.40E-02	2.82E+00	1.73E-01	5.02E-02	-1.49E-01	3.01E-01	0.00E+00
3/21/2007 14:50:25	3.80E+02	3.76E+02	2.21E+02	9.10E+03	2.60E-02	8.86E+00	5.80E+01	1.95E+00	1.35E+00	2.35E+00	2.48E-01	4.21E-01	2.25E-01	5.11E-02	2.85E+00	1.32E-01	5.12E-02	-1.52E-01	2.76E-01	0.00E+00
3/21/2007 14:50:26	3.82E+02	3.76E+02	2.16E+02	7.60E+03	1.80E-02	4.36E+00	8.52E+00	2.96E-01	3.97E+00	2.35E+00	2.48E-01	4.21E-01	2.25E-01	5.11E-02	2.78E+00	1.75E-01	4.81E-02	-1.50E-01	2.66E-01	0.00E+00
3/21/2007 14:50:27	3.79E+02	3.76E+02	2.06E+02	6.40E+03	2.10E-02	1.73E+00	2.89E+00	-1.46E-01	-2.04E+00	2.78E+00	1.75E-01	4.81E-02	-1.50E-01	2.66E-01	2.75E+00	1.75E-01	5.01E-02	-1.44E-01	2.60E-01	0.00E+00
3/21/2007 14:50:28	3.81E+02	3.76E+02	2.06E+02	6.40E+03	2.10E-02	1.73E+00	2.89E+00	-1.46E-01	-2.04E+00	2.78E+00	1.75E-01	4.81E-02	-1.50E-01	2.66E-01	2.82E+00	1.75E-01	5.35E-02	-1.38E-01	2.56E-01	0.00E+00
3/21/2007 14:50:29	3.83E+02	3.77E+02	1.97E+02	8.79E+03	1.80E-02	3.58E-01	2.48E+00	1.58E-01	-4.79E+00	3.16E-01	-9.34E-02	-2.32E-01	-2.50E-02	-7.40E-02	2.82E+00	1.75E-01	5.35E-02	-1.38E-01	2.56E-01	0.00E+00
3/21/2007 14:50:30	3.82E+02	3.76E+02	1.93E+02	7.99E+03	1.90E-02	1.05E+00	2.05E+00	1.62E-01	-3.58E+00	3.16E-01	-9.34E-02	-2.32E-01	-2.50E-02	-7.40E-02	2.82E+00	1.75E-01	5.35E-02	-1.38E-01	2.56E-01	0.00E+00
3/21/2007 14:50:31	3.81E+02	3.76E+02	1.92E+02	7.12E+03	1.90E-02	3.01E+00	1.80E+00	1.32E+00	-1.83E+00	3.05E+00	1.04E-01	7.25E-01	1.08E-01	5.91E-02	2.65E+00	6.84E-01	4.49E-02	-1.51E-01	2.50E-01	0.00E+00
3/21/2007 14:50:32	3.81E+02	3.76E+02	1.95E+02	6.33E+03	2.00E-02	3.01E+00	2.05E+00	7.64E-01	2.79E+00	3.05E+00	1.04E-01	7.25E-01	1.08E-01	5.91E-02	2.65E+00	6.84E-01	4.49E-02	-1.51E-01	2.50E-01	0.00E+00
3/21/2007 14:50:33	3.80E+02	3.76E+02	1.98E+02	5.60E+04	1.38E-01	4.01E+04	1.38E+01	1.13E+01	1.77E+01	1.19E+00	1.19E+00	1.24E-01	1.13E+01	1.77E+01	2.55E+01	3.78E+00	2.21E-01	-2.94E+00	5.78E+00	0.00E+00
3/21/2007 14:50:34	3.80E+02	3.76E+02	1.89E+02	4.88E+03	2.24E+00	3.73E+01	2.05E+00	5.94E-01	5.98E+00	1.19E+00	4.44E-01	2.24E-01	1.02E-01	-7.40E-02	2.55E+01	3.78E+00	2.21E-01	-2.94E+00	5.78E+00	0.00E+00
3/21/2007 14:50:35	4.04E+02	3.89E+02	6.64E+02	2.68E+03	8.10E-01	3.73E+01	1.09E+00	5.42E-01	3.06E+00	1.21E+00	5.10E-02	1.13E+00	-2.50E-02	-7.40E-02	2.55E+01	3.78E+00	2.21E-01	-2.94E+00	5.78E+00	0.00E+00
3/21/2007 14:50:36	4.13E+02	4.03E+02	2.05E+04	4.21E+06	2.47E-01	7.57E+01	1.33E+00	1.73E+01	4.90E+00	1.21E+01	9.56E-02	1.13E+00	-2.50E-02	-7.40E-02	9.57E+00	1.24E+00	4.43E-02	-6.79E-01	1.24E+00	0.00E+00
3/21/2007 14:50:37	3.85E+02	3.85E+02	4.33E+02	8.21E+06	1.01E+01	1.05E+02	1.47E+00	3.35E+01	1.25E+01	1.41E+01	8.84E-01	1.82E+00	1.03E-01	1.81E-01	9.57E+00	1.24E+00	4.43E-02	-6.79E-01	1.24E+00	0.00E+00
3/21/2007 14:50:38	3.79E+02	3.76E+02	1.33E+04	1.89E+06	6.50E-02	1.00E+02	1.89E+02	8.49E+01	8.49E+01	7.02E+00	8.90E-02	6.43E-01	1.01E-01	5.16E-02	9.57E+00	1.24E+00	4.43E-02	-6.79E-01	1.24E+00	0.00E+00
3/21/2007 14:50:39	3.81E+02	3.77E+02	1.03E+03	1.83E+06	4.30E-02	1.00E+02	6.52E+01	4.96E+00	6.69E-01	7.02E+00	-9.79E-02	6.43E-01	1.01E-01	5.16E-02	6.75E+00	8.90E-01	2.22E-02	-3.81E-01	6.44E-01	0.00E+00
3/21/2007 14:50:40	3.82E+02	3.76E+02	6.56E+02	6.95E+05	9.20E-02	7.96E+01	4.48E+02	3.29E+00	-2.94E+00	7.20E+00	-9.79E-02	6.43E-01	1.01E-01	5.16E-02	9.14E+00	2.91E+00	4.84E-01	-8.04E-01	1.59E+00	0.00E+00
3/21/2007 14:50:41	3.80E+02	3.77E+02	6.13E+02	3.55E+05	1.40E+00	5.35E+01	2.79E+02	3.05E+00	8.89E-01	5.84E+00	1.12E-01	7.51E-01	1.10E-01	6.14E-02	9.14E+00	2.91E+00	4.84E-01	-8.04E-01	1.59E+00	0.00E+00
3/21/2007 14:50:42	3.93E+02	3.81E+02	3.00E+03	1.21E+05	1.15E+00	3.86E+01	7.28E+01	1.80E+01	3.58E+00	5.84E+00	1.12E-01	7.51E-01	1.10E-01	6.14E-02	7.33E+00	1.82E+00	3.15E-01	-7.96E-01	1.52E+00	0.00E+00
3/21/2007 14:50:43	4.17E+02	3.95E+02	8.90E+02	2.47E+04	2.30E-01	1.38E+01	5.26E+01	1.10E+01	5.14E-02	5.84E+00	1.12E-01	7.51E-01	1.10E-01	6.14E-02	4.84E+00	9.14E+00	4.85E-02	-3.42E-01	5.79E-01	0.00E+00
3/21/2007 14:50:44	4.03E+02	3.97E+02	6.98E+03	7.26E+04	8.30E-02	3.15E+01	2.31E+01	4.10E+01	8.97E+00	4.12E+00	-9.15E-02	4.44E-01	-2.50E-02	1.89E-01	4.84E+00	9.14E+00	4.65E-02	-3.42E-01	5.79E-01	0.00E+00
3/21/2007 14:50:45	3.77E+02	3.81E+02	1.30E+03	4.68E+04	4.10E-02	2.71E+01	1.69E+01	1.05E+01	1.79E+00	3.52E+00	-9.15E-02	4.44E-01	-2.50E-02	1.89E-01	4.13E+00	6.70E-01	6.22E-02	-2.51E-01	4.26E-01	0.00E+00
3/21/2007 14:50:46	3.78E+02	3.78E+02	4.01E+02	3.64E+04	2.90E-02	2.71E+01	7.80E+01	1.39E+00	8.95E+00	3.52E+00	6.79E-01	6.79E-01	4.85E-01	3.08E-01	4.13E+00	6.70E-01	6.22E-02	-2.51E-01	4.26E-01	0.00E+00
3/21/2007 14:50:47	3.82E+02	3.77E+02	2.81E+02	2.97E+04	2.20E-02	2.19E+01	7.98E+02	1.23E+00	-2.57E+00	3.73E+00	8.04E-01	6.79E-01	4.85E-01	3.08E-01	3.73E+00	6.68E-01	3.44E-02	-2.06E-01	3.76E-01	0.00E+00
3/21/2007 14:50:48	3.83E+02	3.76E+02	2.52E+02	2.47E+04	2.30E-02	1.41E+01	8.62E+02	1.30E+01	3.01E+00	3.73E+00	8.04E-01	6.79E-01	4.85E-01	3.08E-01	3.73E+00	6.68E-01	3.44E-02	-2.06E-01	3.76E-01	0.00E+00
3/21/2007 14:50:49	3.80E+02	3.76E+02	2.31E+02	1.84E+04	2.20E-02	7.54E+00	1.62E+02	8.48E-01	-1.77E+00	3.73E+00	8.04E-01	6.79E-01	4.85E-01	3.08E-01	3.48E+00	7.67E-01	4.06E-02	-1.91E-01	3.56E-01	0.00E+00
3/21/2007 14:50:50	3.81E+02	3.76E+02	2.20E+02	1.69E+04	2.00E-02	7.54E+00	1.69E+01	1.04E-01	-7.40E+00	2.06E+00	8.21E-01	2.32E-01	1.04E-01	-7.40E+00	3.48E+00	7.49E-01	4.48E-02	-1.81E-01	3.37E-01	0.00E+00
3/21/2007 14:50:51	3.83E+02	3.77E+02	2.14E+02	1.40E+04	2.00E-02	3.08E+00	7.53E+00	1.82E-02	-5.72E+00	2.06E+00	8.21E-01	2.32E-01	1.04E-01	-7.40E+00	3.48E+00	7.49E-01	4.48E-02	-1		

3/21/2007 14:51:45	3.81E+02	3.77E+02	1.96E+02	7.78E+03	2.20E-02	4.88E-01	1.62E+00	7.78E-01	-3.73E+00	2.22E+00	-2.72E-01	1.47E-02	1.18E-01	2.12E-01	2.79E+00	6.68E-01	4.72E-02	-1.60E-01	3.05E-01	0.00E+00
3/21/2007 14:51:46	3.79E+02	3.77E+02	1.93E+02	9.41E+03	1.90E-02	-4.48E-01	1.09E+00	4.48E-02	-8.08E-02	3.03E+00	9.97E-01	2.24E-01	-2.50E-02	-7.40E-02	2.78E+00	7.08E-01	3.33E-02	-1.69E-01	3.04E-01	0.00E+00
3/21/2007 14:51:47	3.81E+02	3.77E+02	1.87E+02	7.69E+03	2.30E-02	-1.43E+00	1.15E+00	-1.22E+00	-2.65E+00	3.03E+00	9.97E-01	2.24E-01	-2.50E-02	-7.40E-02	2.78E+00	7.08E-01	3.33E-02	-1.69E-01	3.04E-01	0.00E+00
3/21/2007 14:51:48	3.84E+02	3.77E+02	1.86E+02	5.85E+03	2.00E-02	-1.43E+00	1.19E+00	2.05E+00	3.15E-01	1.71E+00	-2.72E-01	2.14E-01	1.04E-01	-7.40E-02	2.63E+00	6.70E-01	4.82E-02	-1.56E-01	3.08E-01	0.00E+00
3/21/2007 14:51:49	3.84E+02	3.77E+02	1.87E+02	4.67E+03	1.80E-02	-2.16E+00	1.71E+00	-1.36E-01	-4.49E+00	1.71E+00	-2.72E-01	2.14E-01	1.04E-01	-7.40E-02	2.75E+00	7.31E-01	5.26E-02	-1.58E-01	2.99E-01	0.00E+00
3/21/2007 14:51:50	3.81E+02	3.77E+02	1.85E+02	3.87E+03	1.90E-02	-1.86E+00	1.93E+00	8.89E-01	5.89E-01	1.71E+00	-2.72E-01	2.14E-01	1.04E-01	-7.40E-02	2.75E+00	7.31E-01	5.26E-02	-1.58E-01	2.99E-01	0.00E+00
3/21/2007 14:51:51	3.81E+02	3.77E+02	1.87E+02	3.39E+03	2.00E-02	-1.86E+00	1.04E+00	3.70E-01	-1.55E+00	3.47E-01	-9.10E-02	-3.32E-03	-2.50E-02	5.56E-02	2.72E+00	8.36E-01	5.57E-02	-1.44E-01	2.96E-01	0.00E+00
3/21/2007 14:51:52	3.83E+02	3.77E+02	1.89E+02	3.12E+03	1.60E-02	0.00E+00	1.67E+00	8.15E-02	-2.89E+00	3.47E-01	-9.10E-02	-3.32E-03	-2.50E-02	5.56E-02	2.72E+00	8.36E-01	5.57E-02	-1.44E-01	2.96E-01	0.00E+00
3/21/2007 14:51:53	3.83E+02	3.77E+02	1.84E+02	2.96E+03	1.80E-02	1.74E+00	1.14E+00	1.02E+00	4.41E+00	1.49E+00	5.01E-02	1.68E-01	9.29E-02	4.39E-02	2.63E+00	6.79E-01	4.05E-02	-1.45E-01	2.95E-01	0.00E+00
3/21/2007 14:51:54	3.83E+02	3.77E+02	1.92E+02	2.74E+03	2.00E-02	2.16E+00	1.41E+00	9.86E-01	-1.33E+00	1.49E+00	5.01E-02	1.68E-01	9.29E-02	4.39E-02	2.63E+00	6.79E-01	4.05E-02	-1.45E-01	2.95E-01	0.00E+00
3/21/2007 14:51:55	3.81E+02	3.77E+02	1.83E+02	2.59E+03	1.90E-02	2.16E+00	1.76E+00	2.80E-01	3.24E+00	3.67E+00	1.13E-01	5.05E-01	-2.50E-02	-7.40E-02	2.56E+00	6.61E-01	5.12E-02	-1.66E-01	2.90E-01	0.00E+00
3/21/2007 14:51:56	3.83E+02	3.77E+02	1.85E+02	2.54E+03	2.00E-02	1.44E+00	1.45E+00	-5.69E-01	-2.45E+00	3.67E+00	1.13E-01	5.05E-01	-2.50E-02	-7.40E-02	2.56E+00	6.61E-01	5.12E-02	-1.66E-01	2.90E-01	0.00E+00
3/21/2007 14:51:57	3.84E+02	3.77E+02	1.89E+02	2.47E+03	1.70E-02	6.14E-01	1.41E+00	1.22E+00	2.19E+00	1.26E+00	-7.42E-02	7.81E-01	-2.50E-02	6.53E-02	2.58E+00	7.02E-01	4.46E-02	-1.52E-01	2.91E-01	0.00E+00
3/21/2007 14:51:58	3.82E+02	3.77E+02	1.86E+02	2.40E+03	2.10E-02	6.14E-01	1.33E+00	-5.56E-01	1.70E+00	1.26E+00	-7.42E-02	7.81E-01	-2.50E-02	6.53E-02	2.58E+00	7.58E-01	4.54E-02	-1.37E-01	2.84E-01	0.00E+00
3/21/2007 14:51:59	3.83E+02	3.77E+02	1.85E+02	2.34E+03	1.90E-02	0.00E+00	1.10E+00	7.57E-01	-1.20E+00	2.92E+00	3.23E-01	-2.32E-01	1.11E-01	1.98E-01	2.58E+00	7.58E-01	4.54E-02	-1.37E-01	2.84E-01	0.00E+00
3/21/2007 14:52:00	3.82E+02	3.77E+02	1.85E+02	2.27E+03	1.80E-02	-5.72E-01	1.16E+00	-2.80E-01	-2.55E+00	2.92E+00	3.23E-01	-2.32E-01	1.11E-01	1.98E-01	2.47E+00	7.41E-01	4.70E-02	-1.44E-01	2.85E-01	0.00E+00

Date and Time	CO2 (820)	CO2 (P)	CO	Particle Number	PM2.5	Carbon	NO	NO2	HCHO	Acetonitrile	Acetaldehyde	Benzene	C2Benzene	Toluene	Benzonitrile	Styrene	Hydrogen Cyanide	Propene+alkene+acetic acid fragments	Acrylonitrile	Acetic Acid	Furan	Ethylacetate	PM Org	PM SO4	PM NO3	PM PAH	PM Pb	PM Zn		
	ppb	ppb	ppb	ug/m3	ug/m3	ug/m3	ug/m3	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3		
3/22/2007 11:15:00	3.94E+02	3.81E+02	1.62E+02	2.04E+03	1.60E-02	1.81E-01	1.80E+00	1.77E+00	2.68E+01	2.50E-01	4.88E+00	3.61E+00	4.77E-02	2.48E+01	2.81E+00	2.81E+00	2.07E+01	3.59E-02	3.44E+00	3.28E-01										
3/22/2007 11:15:01	3.93E+02	3.81E+02	1.58E+02	2.08E+03	1.40E+02	1.34E+00	1.43E+00	2.81E+00	2.48E+01	4.77E-02	3.65E+00	3.13E+00								-8.70E-02										
3/22/2007 11:15:02	3.92E+02	3.81E+02	1.57E+02	2.05E+03	1.60E-02	1.26E+00	1.45E+00	2.28E+00	2.57E+01	4.77E-02	3.65E+00	3.13E+00								-8.70E-02										
3/22/2007 11:15:03	3.92E+02	3.81E+02	1.59E+02	2.10E+03	1.50E-02	7.01E-01	1.23E+00	1.25E+00	1.80E+01	1.42E-01	3.39E+00	3.55E-01								-8.70E-02										
3/22/2007 11:15:04	3.91E+02	3.81E+02	1.61E+02	2.05E+03	1.60E-02	2.98E-01	1.25E+00	1.04E+00	1.87E+01	1.42E-01	3.39E+00	-3.55E-01								-8.70E-02										
3/22/2007 11:15:05	3.92E+02	3.81E+02	1.59E+02	2.04E+03	1.30E-02	1.30E-01	1.83E+00	2.30E+01	3.59E-02	5.01E+00	2.80E+01	6.94E-02								-8.70E-02										
3/22/2007 11:15:06	3.92E+02	3.81E+02	1.58E+02	2.02E+03	1.50E-02	2.35E+00	1.65E+00	3.08E+00	2.61E+01	-3.59E-02	4.72E+00	-3.93E-01								-8.70E-02										
3/22/2007 11:15:07	3.93E+02	3.81E+02	1.60E+02	2.01E+03	1.50E-02	3.53E+00	9.16E-01	2.13E+00	2.27E+01	5.99E-02	4.72E+00	-3.93E-01								-8.70E-02										
3/22/2007 11:15:08	3.92E+02	3.81E+02	1.59E+02	2.03E+03	1.40E-02	2.82E+00	1.21E+00	3.08E+00	2.30E+01	5.99E-02	4.72E+00	-3.93E-01								-8.70E-02										
3/22/2007 11:15:09	3.92E+02	3.80E+02	1.59E+02	1.98E+03	1.30E-02	4.19E-01	1.38E+00	2.37E+00	1.97E+01	6.01E-02	6.69E+00	-3.52E-01								-8.70E-02										
3/22/2007 11:15:10	3.92E+02	3.80E+02	1.59E+02	2.00E+03	1.20E-02	-1.50E+00	1.81E+00	2.18E+00	1.83E+01	6.01E-02	6.69E+00	-3.52E-01								-8.70E-02										
3/22/2007 11:15:11	3.90E+02	3.81E+02	1.58E+02	2.05E+03	1.30E-02	-1.60E+00	1.80E+00	2.89E+00	2.19E+01	-3.59E-02	4.41E+00	-3.43E-01								-8.70E-02										
3/22/2007 11:15:12	3.91E+02	3.81E+02	1.59E+02	2.03E+03	1.60E-02	-5.55E-01	1.50E+00	1.26E+00	2.19E+01	-3.59E-02	4.41E+00	-3.43E-01								-8.70E-02										
3/22/2007 11:15:13	3.93E+02	3.81E+02	1.60E+02	2.02E+03	1.10E-02	2.18E-01	1.53E+00	1.51E+00	2.00E+01	-3.59E-02	3.44E+00	-3.68E-01								-8.70E-02										
3/22/2007 11:15:14	3.94E+02	3.81E+02	1.58E+02	2.04E+03	1.40E-02	3.09E-01	1.14E+00	2.43E+00	2.21E+01	-3.59E-02	3.44E+00	-3.68E-01								-8.70E-02										
3/22/2007 11:15:15	3.93E+02	3.81E+02	1.58E+02	2.04E+03	1.40E-02	8.00E-02	1.44E+00	2.06E+00	1.98E+01	6.00E-02	4.11E+00	-3.56E-01								-8.70E-02										
3/22/2007 11:15:17	3.91E+02	3.81E+02	1.60E+02	2.06E+03	1.20E-02	3.11E-01	1.50E+00	2.59E+00	1.89E+01	6.00E-02	4.11E+00	-3.56E-01								-8.70E-02										
3/22/2007 11:15:18	3.93E+02	3.81E+02	1.61E+02	2.05E+03	1.40E-02	8.81E-01	1.20E+00	8.49E-01	1.97E+01	4.79E-02	3.11E+00	-3.57E-01								-8.70E-02										
3/22/2007 11:15:19	3.93E+02	3.81E+02	1.58E+02	2.10E+03	1.40E-02	1.69E+00	1.94E+00	1.87E+00	1.81E+01	4.79E-02	3.11E+00	-3.57E-01								-8.70E-02										
3/22/2007 11:15:20	3.93E+02	3.81E+02	1.58E+02	2.09E+03	1.50E-02	2.54E+00	1.28E+00	2.43E+00	2.34E+01	1.42E-01	3.37E+00	-3.48E-01								-8.70E-02										
3/22/2007 11:15:21	3.93E+02	3.81E+02	1.57E+02	2.04E+03	1.30E-02	1.61E+00	1.46E+00	1.18E+00	1.95E+01	1.42E-01	3.37E+00	-3.48E-01								-8.70E-02										
3/22/2007 11:15:22	3.93E+02	3.81E+02	1.57E+02	2.06E+03	1.20E-02	2.23E+00	1.21E+00	2.15E+00	2.62E+01	-3.59E-02	3.49E+00	-3.79E-01								-8.70E-02										
3/22/2007 11:15:23	3.94E+02	3.81E+02	1.59E+02	2.08E+03	1.20E-02	6.33E-01	1.50E+00	1.17E+00	1.99E+01	-3.59E-02	3.49E+00	-3.79E-01								-8.70E-02										
3/22/2007 11:15:24	3.94E+02	3.81E+02	1.59E+02	2.02E+03	1.40E-02	6.33E-01	1.40E+00	2.22E+00	2.20E+01	5.77E-02	4.51E+00	-3.79E-01								-8.70E-02										
3/22/2007 11:15:25	3.93E+02	3.81E+02	1.57E+02	2.05E+03	1.40E-02	-1.30E+00	1.21E+00	2.16E+00	1.62E+01	5.77E-02	4.51E+00	-3.79E-01								-8.70E-02										
3/22/2007 11:15:26	3.92E+02	3.81E+02	1.59E+02	2.07E+03	1.50E-02	-2.33E+00	1.47E+00	1.58E+00	2.17E+01	4.01E+00	3.70E+00	-3.56E-01								-8.70E-02										
3/22/2007 11:15:27	3.91E+02	3.81E+02	1.61E+02	2.02E+03	1.60E-02	-1.88E+00	1.66E+00	2.38E+00	2.38E+01	2.30E-01	4.01E+00	-3.76E-01								-8.70E-02										
3/22/2007 11:15:28	3.92E+02	3.81E+02	1.60E+02	2.08E+03	1.20E-02	-1.09E+00	1.57E+00	1.83E+00	2.14E+01	5.60E-02	3.29E+00	-3.62E-01								-8.70E-02										
3/22/2007 11:15:29	3.92E+02	3.81E+02	1.58E+02	2.02E+03	1.40E-02	-1.09E+00	1.71E+00	1.48E+00	5.60E-02	3.29E+00	-3.62E-01									-8.70E-02										
3/22/2007 11:15:30	3.93E+02	3.81E+02	1.58E+02	1.98E+03	1.60E-02	-8.82E-02	1.25E+00	2.54E+00	1.94E+01	3.10E-01	4.39E+00	-3.56E-01								-8.70E-02										
3/22/2007 11:15:31	3.94E+02	3.81E+02	1.58E+02	1.99E+03	1.30E-02	7.43E-01	1.62E+00	6.76E-01	2.20E+01	3.19E-01	3.66E+00	-3.56E-01								-8.70E-02										
3/22/2007 11:15:32	3.94E+02	3.81E+02	1.58E+02	1.92E+03	1.30E-02	7.43E-01	1.31E+00	8.41E-01	1.21E+01	6.15E-02	3.72E+00	-3.96E-01								-8.70E-02										
3/22/2007 11:15:33	3.94E+02	3.81E+02	1.57E+02	1.96E+03	1.30E-02	1.14E+00	1.52E+00	2.59E+00	2.22E+01	6.15E-02	3.72E+00	-3.96E-01								-8.70E-02										
3/22/2007 11:15:34	3.94E+02	3.81E+02	1.55E+02	1.95E+03	1.50E-02	1.20E+00	1.44E+00	1.51E+00	1.47E+01	6.15E-02	3.72E+00	-3.96E-01								-8.70E-02										
3/22/2007 11:15:35	3.91E+02	3.81E+02	1.58E+02	1.98E+03	1.40E-02	1.50E+00	1.11E+00	3.07E+00	2.01E+01	1.48E-01	2.97E+00	-3.48E-01								-8.70E-02										
3/22/2007 11:15:36	3.93E+02	3.81E+02	1.58E+02	1.97E+03	1.60E-02	1.50E+00	1.11E+00	2.26E+00	2.61E+01	1.48E-01	2.97E+00	-3.48E-01								-8.70E-02										
3/22/2007 11:15:37	3.94E+02	3.81E+02	1.59E+02	1.94E+03	1.40E-02	1.66E+00	1.40E+00	1.15E+00	1.88E+01	1.41E-01	4.10E+00	-3.60E-01								-8.70E-02										
3/22/2007 11:15:38	3.94E+02	3.81E+02	1.59E+02	1.96E+03	1.40E-02	1.10E+00	1.18E+00	2.32E+00	2.30E+01	1.41E-01	4.10E+00	-3.60E-01								-8.70E-02										
3/22/2007 11:15:39	3.95E+02	3.81E+02	1.57E+02	1.97E+03	1.30E-02	1.10E+00	1.59E+00	1.68E+00	2.02E+01	1.53E-01	5.65E+00	-3.82E-01								-8.70E-02										
3/22/2007 11:15:40	3.93E+02	3.81E+02	1.55E+02	1.93E+03	1.30E-02	-5.95E-01	1.37E+00	2.95E+00	2.11E+01	1.53E-01	5.65E+00	-3.82E-01								-8.70E-02										
3/22/2007 11:15:41	3.93E+02	3.81E+02	1.59E+02	1.92E+03	1.40E-02	-1.86E+00	8.99E-01	2.65E+00	1.85E+01	-3.59E-02	4.79E+00	-3.40E+00								-8.70E-02										
3/22/2007 11:15:42	3.93E+02	3.81E+02	1.57E+02	1.90E+03	1.80E-02	-1.86E+00	1.25E+00	2.42E+00	1.78E+01	-3.59E-02	4.79E+00	-3.40E+00								-8.70E-02										
3/22/2007 11:15:43	3.91E+02	3.81E+02	1.56E+02	1.86E+03	1.20E-02	-1.86E+00	1.25E+00	1.98E+00	2.06E+01	1.42E-01	2.64E+00	-3.40E-01								-8.70E-02										
3/22/2007 11:15:44	3.91E+02	3.81E+02	1.58E+02	1.85E+03	1.60E-02	-8.55E-01	1.13E+00	1.73E+00	1.58E+01	1.42E-01	2.64E+00	-3.40E-01								-8.70E-02										
3/22/2007 11:15:45	3.93E+02	3.81E+02	1.58E+02	1.81E+03	1.40E-02	7.76E-02	1.48E+00	2.26E+00																						

3/22/2007 11:16:33	3.93E+02	3.81E+02	1.55E+02	1.66E+03	1.40E-02	2.17E-03	1.12E+00	1.18E+00	2.47E+01	1.51E-01	4.51E+00	-3.77E-01	-8.70E-02
3/22/2007 11:16:34	3.92E+02	3.81E+02	1.53E+02	1.72E+03	1.70E-02	0.00E+00	1.26E+00	1.41E+00	1.74E+01	5.34E-02	3.34E+00	-3.74E-01	-8.70E-02
3/22/2007 11:16:35	3.93E+02	3.81E+02	1.54E+02	1.67E+03	1.40E-02	0.00E+00	1.26E+00	1.53E+00	2.46E+01	5.34E-02	3.34E+00	-3.74E-01	-8.70E-02
3/22/2007 11:16:36	3.93E+02	3.81E+02	1.53E+02	1.66E+03	1.80E-02	0.00E+00	1.22E+00	4.71E-01	1.58E+01	-3.59E-02	6.22E+00	-3.64E-01	-8.70E-02
3/22/2007 11:16:37	3.93E+02	3.81E+02	1.56E+02	1.67E+03	1.30E-02	0.00E+00	1.22E+00	1.56E+00	1.60E+01	-3.59E-02	6.22E+00	-3.64E-01	-8.70E-02
3/22/2007 11:16:38	3.91E+02	3.81E+02	1.58E+02	1.69E+03	1.30E-02	0.00E+00	1.24E+00	1.64E+00	1.58E+01	-3.59E-02	5.40E+00	-3.53E-01	-8.70E-02
3/22/2007 11:16:39	3.90E+02	3.81E+02	1.52E+02	1.68E+03	1.30E-02	0.00E+00	1.33E+00	1.49E+00	2.18E+01	-3.59E-02	5.40E+00	-3.53E-01	-8.70E-02
3/22/2007 11:16:40	3.96E+02	3.81E+02	1.55E+02	1.69E+03	1.30E-02	0.00E+00	1.28E+00	2.27E+00	2.25E+01	1.49E-01	3.85E+00	-3.32E+00	-8.70E-02
3/22/2007 11:16:41	3.91E+02	3.81E+02	1.55E+02	1.69E+03	1.50E-02	0.00E+00	1.16E+00	1.01E+00	1.99E+01	1.49E-01	3.85E+00	-3.32E+00	-8.70E-02
3/22/2007 11:16:42	3.92E+02	3.81E+02	1.54E+02	1.70E+03	1.20E-02	0.00E+00	8.99E-01	8.56E-01	2.77E+01	5.57E-02	5.05E+00	-3.63E-01	-8.70E-02
3/22/2007 11:16:43	3.93E+02	3.81E+02	1.55E+02	1.74E+03	1.40E-02	0.00E+00	1.31E+00	4.11E-01	2.40E+01	5.57E-02	5.05E+00	-3.63E-01	-8.70E-02
3/22/2007 11:16:44	3.92E+02	3.81E+02	1.53E+02	1.69E+03	1.30E-02	0.00E+00	1.41E+00	2.11E+00	1.94E+01	-3.59E-02	4.70E+00	-3.74E+00	-8.70E-02
3/22/2007 11:16:45	3.92E+02	3.81E+02	1.56E+02	1.70E+03	1.30E-02	0.00E+00	1.36E+00	1.52E+00	1.65E+01	-3.59E-02	4.70E+00	-3.74E+00	-8.70E-02
3/22/2007 11:16:46	3.93E+02	3.81E+02	1.53E+02	1.70E+03	1.40E-02	0.00E+00	1.00E+00	6.68E-01	1.93E+01	-3.59E-02	4.70E+00	-3.74E+00	-8.70E-02
3/22/2007 11:16:47	3.92E+02	3.81E+02	1.52E+02	1.71E+03	1.30E-02	0.00E+00	1.16E+00	2.15E+00	1.93E+01	1.37E-01	3.46E+00	-3.72E-01	-8.70E-02
3/22/2007 11:16:48	3.92E+02	3.81E+02	1.52E+02	1.68E+03	1.30E-02	0.00E+00	8.30E-01	1.59E+00	2.34E+01	1.37E-01	3.46E+00	-3.72E-01	-8.70E-02
3/22/2007 11:16:49	3.94E+02	3.81E+02	1.58E+02	1.69E+03	1.30E-02	0.00E+00	1.09E+00	1.23E+00	1.65E+01	1.42E-01	4.70E+00	-3.62E-01	-8.70E-02
3/22/2007 11:16:50	3.95E+02	3.81E+02	1.55E+02	1.68E+03	1.60E-02	0.00E+00	1.42E+00	1.16E+00	1.80E+01	1.42E-01	4.70E+00	-3.62E-01	-8.70E-02
3/22/2007 11:16:51	3.94E+02	3.81E+02	1.57E+02	1.69E+03	1.20E-02	1.68E-02	1.27E+00	2.27E+00	2.25E+01	2.54E-01	7.57E+00	-3.86E-01	-8.70E-02
3/22/2007 11:16:52	3.94E+02	3.81E+02	1.58E+02	1.71E+03	1.40E-02	1.67E-01	1.09E+00	1.91E+00	2.55E+01	2.54E-01	7.57E+00	-3.86E-01	-8.70E-02
3/22/2007 11:16:53	3.93E+02	3.81E+02	1.58E+02	1.70E+03	1.40E-02	7.65E-01	1.44E+00	5.28E-01	2.08E+01	-3.59E-02	3.46E+00	-3.90E+00	-8.70E-02
3/22/2007 11:16:54	3.92E+02	3.81E+02	1.54E+02	1.66E+03	1.40E-02	1.98E+00	1.07E+00	2.02E+00	1.99E+01	-3.59E-02	3.46E+00	-3.90E+00	-8.70E-02
3/22/2007 11:16:55	3.92E+02	3.81E+02	1.55E+02	1.66E+03	1.40E-02	3.11E+00	1.54E+00	2.35E+01	2.39E+01	2.39E-01	4.23E+00	-3.76E-01	-8.70E-02
3/22/2007 11:16:56	3.93E+02	3.81E+02	1.57E+02	1.70E+03	1.20E-02	2.76E+00	1.03E+00	2.22E+00	2.29E+01	2.39E-01	4.23E+00	-3.76E-01	-8.70E-02
3/22/2007 11:16:57	3.93E+02	3.81E+02	1.57E+02	1.70E+03	1.50E-02	6.03E-01	6.65E-01	9.14E-01	1.56E+02	1.72E+01	1.78E+01	-3.54E-01	-8.70E-02
3/22/2007 11:16:58	3.93E+02	3.81E+02	1.56E+02	1.68E+03	1.50E-02	-1.78E+00	1.40E+00	1.47E+00	1.51E+01	1.48E-01	3.85E+00	-3.54E-01	-8.70E-02
3/22/2007 11:16:59	3.93E+02	3.81E+02	1.58E+02	1.70E+03	1.50E-02	-2.43E+00	1.26E+00	3.26E-01	1.93E+01	-3.59E-02	4.59E+00	-3.79E-01	-8.70E-02
3/22/2007 11:17:00	3.93E+02	3.81E+02	1.55E+02	1.73E+03	1.40E-02	-1.38E+00	1.33E+00	1.40E+00	2.28E+01	-3.59E-02	4.59E+00	-3.79E-01	-8.70E-02
3/22/2007 11:17:01	3.93E+02	3.81E+02	1.54E+02	1.69E+03	1.40E-02	-6.31E-02	1.01E+00	7.05E-01	1.87E+01	5.81E-02	5.46E+00	-3.75E+00	-8.70E-02
3/22/2007 11:17:02	3.92E+02	3.81E+02	1.50E+02	1.73E+03	1.30E-02	6.54E-01	3.90E+00	1.49E+00	1.78E+01	2.17E+01	5.78E+00	-3.42E+00	-8.70E-02
3/22/2007 11:17:03	3.91E+02	3.81E+02	1.52E+02	1.74E+03	1.70E-02	3.43E-01	9.51E-01	1.57E+00	1.89E+01	5.06E-02	3.23E+00	-3.46E-01	-8.70E-02
3/22/2007 11:17:04	3.90E+02	3.81E+02	1.55E+02	1.74E+03	1.40E-02	-3.44E-01	1.15E+00	6.35E-01	1.67E+01	5.06E-02	3.23E+00	-3.46E-01	-8.70E-02
3/22/2007 11:17:05	3.91E+02	3.81E+02	1.54E+02	1.72E+03	1.20E-02	-9.35E-01	1.24E+00	1.99E+00	2.65E+01	1.48E-01	4.46E+00	-3.58E-01	-8.70E-02
3/22/2007 11:17:06	3.93E+02	3.80E+02	1.55E+02	1.74E+03	1.30E-02	-8.02E-01	1.24E+00	1.32E+00	1.50E+01	1.48E-01	4.46E+00	-3.58E-01	-8.70E-02
3/22/2007 11:17:07	3.93E+02	3.80E+02	1.55E+02	1.73E+03	1.50E-02	1.72E+00	1.08E+00	1.72E+00	1.49E+00	1.72E+01	3.42E+00	-3.42E+00	-8.70E-02
3/22/2007 11:17:08	3.93E+02	3.80E+02	1.54E+02	1.72E+03	1.60E-02	1.45E+00	1.69E+00	4.13E-01	2.29E+01	-3.59E-02	3.05E+00	-3.42E+00	-8.70E-02
3/22/2007 11:17:09	3.92E+02	3.80E+02	1.53E+02	1.71E+03	1.20E-02	2.30E+00	1.44E+00	7.79E-01	2.28E+01	-3.59E-02	3.05E+00	-3.42E+00	-8.70E-02
3/22/2007 11:17:10	3.93E+02	3.80E+02	1.52E+02	1.71E+03	1.50E-02	2.19E+00	1.37E+00	1.73E+00	1.91E+01	1.47E-01	6.25E+00	-3.71E-01	-8.70E-02
3/22/2007 11:17:11	3.92E+02	3.80E+02	1.56E+02	1.73E+03	1.40E-02	1.09E+00	1.37E+00	1.50E+00	2.22E+01	1.47E-01	6.25E+00	-3.71E-01	-8.70E-02
3/22/2007 11:17:12	3.91E+02	3.80E+02	1.55E+02	1.72E+03	1.40E-02	-3.48E-01	8.57E-01	1.74E+00	2.19E+01	5.38E-02	5.50E+00	-3.65E-01	-8.70E-02
3/22/2007 11:17:13	3.92E+02	3.80E+02	1.53E+02	1.76E+03	1.40E-02	-1.16E+00	1.48E+00	6.90E-01	2.24E+01	5.38E-02	5.50E+00	-3.65E-01	-8.70E-02
3/22/2007 11:17:14	3.91E+02	3.80E+02	1.56E+02	1.74E+03	1.50E-02	-6.54E-01	9.51E-01	9.72E-01	2.53E+01	-3.59E-02	3.15E+00	-3.58E-01	-8.70E-02
3/22/2007 11:17:15	3.91E+02	3.80E+02	1.55E+02	1.75E+03	1.30E-02	1.11E+00	8.39E-01	6.60E-01	2.31E+01	-3.59E-02	3.15E+00	-3.58E-01	-8.70E-02
3/22/2007 11:17:16	3.92E+02	3.80E+02	1.56E+02	1.74E+03	1.60E-02	3.18E+00	1.08E+00	1.12E+00	2.22E+01	-3.59E-02	2.73E+00	-3.58E-01	-8.70E-02
3/22/2007 11:17:17	3.93E+02	3.80E+02	1.56E+02	1.74E+03	1.40E-02	4.30E+00	1.44E+00	1.84E+00	2.29E+01	-3.59E-02	2.73E+00	-3.58E-01	-8.70E-02
3/22/2007 11:17:18	3.94E+02	3.80E+02	1.56E+02	1.72E+03	1.40E-02	2.84E+00	1.88E+00	9.63E-01	2.47E+01	1.44E-01	3.39E+00	-3.73E-01	-8.70E-02
3/22/2007 11:17:19	3.92E+02	3.80E+02	1.56E+02	1.70E+03	1.40E-02	3.71E-01	1.10E+00	1.48E+00	2.04E+01	1.44E-01	3.39E+00	-3.73E-01	-8.70E-02
3/22/2007 11:17:20	3.91E+02	3.80E+02	1.56E+02	1.75E+03	1.30E-02	-1.44E+00	1.19E+00	1.07E+00	2.05E+01	5.56E-02	3.43E+00	-3.65E-01	-8.70E-02
3/22/2007 11:17:21	3.92E+02	3.80E+02	1.54E+02	1.78E+03	1.50E-02	-1.44E+00	9.86E-01	1.46E+00	2.46E+01	5.56E-02	3.43E+00	-3.65E-01	-8.70E-02
3/22/2007 11:17:22	3.92E+02	3.80E+02	1.53E+02	1.77E+03	1.70E-02	-1.88E+00	1.30E+00	1.36E+00	2.20E+01	5.86E-02	4.20E+00	-4.00E-01	-8.70E-02
3/22/2007 11:17:23	3.93E+02	3.80E+02	1.57E+02	1.76E+03	1.50E-02	-8.69E-01	1.17E+00	7.32E-01	1.98E+01	-3.59E-02	4.20E+00	-4.00E-01	-8.70E-02
3/22/2007 11:17:24	3.92E+02	3.80E+02	1.56E+02	1.72E+03	1.80E-02	-8.69E-01	1.21E+00	1.28E+00	2.20E+01	4.84E-02	6.10E+00	-3.83E-01	-8.70E-02
3/22/2007 11:17:25	3.91E+02	3.80E+02	1.55E+02	1.76E+03	1.50E-02	9.84E-01	4.85E-01	1.54E+00	2.58E+01	4.84E-02	6.10E+00	-3.83E-01	-8.70E-02
3/22/2007 11:17:26	3.92E+02	3.80E+02	1.57E+02	1.77E+03	1.30E-02	2.61E+00	8.99E-01	1.93E+00	1.83E+01	1.47E-01	5.53E+00	-3.70E-01	-8.70E-02
3/22/2007 11:17:27	3.93E+02	3.80E+02	1.56E+02	1.76E+03	1.70E-02	2.46E+00	1.09E+00	1.78E+00	2.59E+01	1.47E-01	5.53E+00	-3.70E-01	-8.70E-02
3/22/2007 11:17:28	3.92E+02	3.80E+02	1.58E+02	1.76E+03	1.50E-02	1.33E+00	1.25E+00	1.30E+00	1.93E+01	-3.59E-02	3.05E+00	-3.88E-01	-8.70E-02
3/22/2007 11:17:29	3.91E+02	3.80E+02	1.56E+02	1.74E+03	1.40E-02	1.33E+00	8.49E-01	1.70E+00	2.17E+01	-3.59E-02	3.05E+00	-3.88E-01	-8.70E-02
3/22/2007 11:17:30	3.91E+02	3.80E+02	1.59E+02	1.78E+03	1.30E-02	2.74E-01	1.05E+00	4.94E-01	2.07E+01	5.39E-02	6.70E+00	-3.48E+00	-8.70E-02
3/22/2007 11:17:31	3.93E+02	3.80E+02	1.58E+02	1.74E+03	1.60E-02	3.11E-01	1.06E+00	2.21E+00	2.04E+01	5.39E-02	6.70E+00	-3.48E+00	-8.70E-02
3/22/2007 11:17:32	3.92E+02	3.80E+02	1.58E+02	1.75E+03	1.50E-02	3.11E-01	1.45E+00	1.77E+00	1.94E+01	5.39E-02	6.70E+00	-3.48E+00	-8.70E-02
3/22/2007 11:17:33	3.91E+02	3.80E+02	1.59E+02	1.71E+03	1.40E-02	6.75E-01	1.25E+00	3.16E+00	1.82E+01	5.70E-02	5.25E+00	-3.85E-01	-8.70E-02
3/22/2007 11:17:34	3.92E+02	3.80E+02	1.57E+02	1.74E+03	1.40E-02	3.62E-01	1.10E+00	2.00E+00	2.33E+01	5.70E-02	5.25E+00	-3.85E-01	-8.70E-02
3/22/2007 11:17:35	3.92E+02	3.80E+02	1.57E+02	1.76E+03	1.60E-02	-5.87E-03	1.53E+00	1.31E+00	1				









3/22/2007 11:22:57	3.92E+02	3.81E+02	1.54E+02	1.58E+03	1.30E-02	-1.25E-01	1.30E+00	1.74E+00	2.64E+01	-3.59E-02	3.31E+00	-3.73E-01	-8.70E-02
3/22/2007 11:22:58	3.93E+02	3.81E+02	1.54E+02	1.59E+03	1.50E-02	-5.47E-01	1.22E+00	1.93E+00	1.87E+01	-3.59E-02	3.31E+00	-3.73E-01	-8.70E-02
3/22/2007 11:22:59	3.93E+02	3.80E+02	1.54E+02	1.59E+03	1.30E-02	-1.81E-01	1.22E+00	1.93E+00	1.87E+01	-3.59E-02	3.31E+00	-3.73E-01	-8.70E-02
3/22/2007 11:23:00	3.90E+02	3.80E+02	1.51E+02	1.56E+03	1.40E-02	-1.28E+00	1.50E+00	6.38E-01	2.44E+01	1.36E-01	4.07E+00	3.24E+00	-8.70E-02
3/22/2007 11:23:01	3.90E+02	3.80E+02	1.51E+02	1.54E+03	1.40E-02	-1.88E+00	1.33E+00	6.09E-01	2.61E+01	6.23E-02	5.11E+00	3.87E+00	-8.70E-02
3/22/2007 11:23:02	3.92E+02	3.80E+02	1.53E+02	1.52E+03	1.30E-02	-1.51E+00	1.15E+00	5.72E-01	1.43E+01	6.23E-02	5.11E+00	3.87E+00	-8.70E-02
3/22/2007 11:23:03	3.93E+02	3.80E+02	1.54E+02	1.51E+03	1.40E-02	0.00E+00	1.00E+00	8.99E-01	2.03E+01	5.51E-02	5.45E+00	3.66E+00	-8.70E-02
3/22/2007 11:23:04	3.92E+02	3.80E+02	1.54E+02	1.52E+03	1.70E-02	0.00E+00	1.17E+00	3.92E-01	2.37E+01	5.51E-02	5.45E+00	3.66E+00	-8.70E-02
3/22/2007 11:23:05	3.92E+02	3.80E+02	1.53E+02	1.56E+03	1.30E-02	2.06E+00	1.23E+00	9.21E-01	2.08E+01	5.51E-02	5.45E+00	3.66E+00	-8.70E-02
3/22/2007 11:23:06	3.91E+02	3.80E+02	1.54E+02	1.53E+03	1.30E-02	2.59E+00	6.88E-01	-2.74E-01	2.19E+01	1.60E-01	4.81E+00	3.85E+00	-8.70E-02
3/22/2007 11:23:07	3.91E+02	3.80E+02	1.53E+02	1.52E+03	1.40E-02	1.88E+00	1.19E+00	2.87E+00	2.14E+01	1.60E-01	4.81E+00	3.85E+00	-8.70E-02
3/22/2007 11:23:08	3.93E+02	3.80E+02	1.56E+02	1.55E+03	1.30E-02	7.39E-01	1.30E+00	-3.38E-01	1.74E+01	-3.59E-02	5.08E+00	3.76E+00	-8.70E-02
3/22/2007 11:23:09	3.93E+02	3.80E+02	1.53E+02	1.52E+03	1.40E-02	1.66E-01	1.31E+00	1.82E+00	1.55E+01	-3.59E-02	5.08E+00	3.76E+00	-8.70E-02
3/22/2007 11:23:10	3.94E+02	3.80E+02	1.54E+02	1.51E+03	1.40E-02	1.65E-02	1.31E+00	2.71E+00	1.80E+01	6.46E-02	3.63E+00	1.25E+01	-8.70E-02
3/22/2007 11:23:11	3.92E+02	3.80E+02	1.51E+02	1.51E+03	1.30E-02	0.00E+00	1.24E+00	4.85E-02	2.39E+01	6.46E-02	3.63E+00	1.25E+01	-8.70E-02
3/22/2007 11:23:12	3.91E+02	3.80E+02	1.53E+02	1.50E+03	1.20E-02	0.00E+00	1.09E+00	7.65E-01	2.51E+01	2.39E-01	4.29E+00	3.76E+00	-8.70E-02
3/22/2007 11:23:13	3.93E+02	3.80E+02	1.52E+02	1.52E+03	1.30E-02	-1.32E-02	1.18E+00	9.67E-01	2.50E+01	2.39E-01	4.29E+00	3.76E+00	-8.70E-02
3/22/2007 11:23:14	3.92E+02	3.80E+02	1.54E+02	1.53E+03	1.30E-02	-1.28E-01	6.23E-01	5.96E-01	2.33E+01	-3.59E-02	6.84E+00	3.70E+00	-8.70E-02
3/22/2007 11:23:15	3.91E+02	3.80E+02	1.52E+02	1.52E+03	1.40E-02	-5.49E-01	1.08E+00	6.09E-01	2.35E+01	-3.59E-02	6.84E+00	3.70E+00	-8.70E-02
3/22/2007 11:23:16	3.91E+02	3.80E+02	1.52E+02	1.52E+03	1.80E-02	-1.31E+00	1.61E+00	-2.08E-01	2.34E+01	-3.59E-02	4.70E+00	6.62E-02	-8.70E-02
3/22/2007 11:23:17	3.93E+02	3.80E+02	1.51E+02	1.55E+03	1.40E-02	-1.85E+00	9.86E-01	2.29E+00	2.30E+01	-3.59E-02	4.70E+00	6.62E-02	-8.70E-02
3/22/2007 11:23:18	3.93E+02	3.80E+02	1.52E+02	1.52E+03	1.70E-02	-1.09E+00	1.28E+00	1.51E+00	2.43E+01	5.90E-02	5.08E+00	3.81E-01	-8.70E-02
3/22/2007 11:23:19	3.89E+02	3.80E+02	1.54E+02	1.50E+03	1.50E-02	-1.13E-01	1.24E+00	1.21E-01	2.58E+01	5.90E-02	5.08E+00	3.81E-01	-8.70E-02
3/22/2007 11:23:20	3.90E+02	3.80E+02	1.54E+02	1.51E+03	1.60E-02	1.93E-01	1.03E+00	-5.82E-01	3.10E+01	5.87E-02	6.09E+00	3.77E+01	-8.70E-02
3/22/2007 11:23:21	3.93E+02	3.80E+02	1.54E+02	1.50E+03	1.60E-02	1.93E-01	1.03E+00	1.64E-01	2.47E+01	5.87E-02	6.09E+00	3.77E+01	-8.70E-02
3/22/2007 11:23:22	3.92E+02	3.80E+02	1.57E+02	1.52E+03	1.50E-02	-3.87E-01	1.00E+00	6.26E-01	2.42E+01	1.46E-01	3.58E+00	3.54E+00	-8.70E-02
3/22/2007 11:23:23	3.92E+02	3.80E+02	1.55E+02	1.50E+03	1.30E-02	-1.08E+00	1.33E+00	9.81E-02	2.74E+01	1.46E-01	3.58E+00	3.54E+00	-8.70E-02
3/22/2007 11:23:24	3.91E+02	3.80E+02	1.55E+02	1.52E+03	1.50E-02	-8.49E-01	1.51E+00	2.34E-01	2.73E+01	5.66E-02	3.31E+00	-3.59E-01	-8.70E-02
3/22/2007 11:23:25	3.91E+02	3.80E+02	1.53E+02	1.53E+03	1.40E-02	-8.49E-01	1.59E+00	7.69E-01	3.54E-01	5.66E-02	3.31E+00	-3.59E-01	-8.70E-02
3/22/2007 11:23:26	3.92E+02	3.80E+02	1.54E+02	1.52E+03	1.20E-02	4.25E-02	1.08E+00	7.77E-01	1.81E+01	5.66E+00	3.31E+00	3.55E-01	-8.70E-02
3/22/2007 11:23:27	3.92E+02	3.80E+02	1.55E+02	1.53E+03	1.60E-02	7.75E-01	1.21E+00	7.03E-01	2.44E+01	-3.59E-02	5.60E+00	3.76E-01	-8.70E-02
3/22/2007 11:23:28	3.91E+02	3.80E+02	1.54E+02	1.56E+03	1.40E-02	1.81E+00	1.33E+00	2.35E-03	2.30E+01	-3.59E-02	5.60E+00	3.76E-01	-8.70E-02
3/22/2007 11:23:29	3.91E+02	3.80E+02	1.54E+02	1.54E+03	1.50E-02	1.81E+00	6.58E-01	3.32E-01	1.97E+01	-3.59E-02	5.47E+00	3.77E-01	-8.70E-02
3/22/2007 11:23:30	3.90E+02	3.80E+02	1.54E+02	1.53E+03	1.50E-02	2.58E+00	1.28E+00	9.43E-01	1.95E+01	-3.59E-02	5.47E+00	3.77E-01	-8.70E-02
3/22/2007 11:23:31	3.91E+02	3.80E+02	1.53E+02	1.53E+03	1.30E-02	2.43E+00	1.11E+00	1.49E+00	2.08E+01	1.49E-01	3.58E+00	3.48E+00	-8.70E-02
3/22/2007 11:23:32	3.94E+02	3.80E+02	1.54E+02	1.56E+03	1.30E-02	1.81E+00	1.12E+00	3.46E-01	1.95E+01	1.48E-01	5.66E+00	3.48E+00	-8.70E-02
3/22/2007 11:23:33	3.92E+02	3.80E+02	1.51E+02	1.54E+03	1.50E-02	1.81E+00	1.41E+00	-8.54E-01	1.71E+01	1.50E-01	4.25E+00	7.18E-02	-8.70E-02
3/22/2007 11:23:34	3.92E+02	3.80E+02	1.51E+02	1.55E+03	1.40E-02	1.24E+00	1.07E+00	3.10E-01	2.63E+01	1.50E-01	4.25E+00	7.18E-02	-8.70E-02
3/22/2007 11:23:35	3.93E+02	3.80E+02	1.54E+02	1.55E+03	1.30E-02	1.06E+00	1.35E+00	1.62E+00	2.10E+01	-3.59E-02	4.77E+00	7.50E+00	3.66E-01
3/22/2007 11:23:36	3.94E+02	3.81E+02	1.54E+02	1.55E+03	1.50E-02	1.06E+00	9.51E-01	3.55E-01	2.70E+01	-3.59E-02	4.77E+00	7.50E+00	3.66E-01
3/22/2007 11:23:37	3.94E+02	3.81E+02	1.51E+02	1.55E+03	1.50E-02	8.05E-01	1.20E+00	-1.80E-01	2.47E+01	3.40E-01	3.88E+00	2.34E-01	-8.70E-02
3/22/2007 11:23:38	3.92E+02	3.80E+02	1.54E+02	1.58E+03	1.50E-02	2.52E-01	1.13E+00	1.10E+00	2.37E+01	3.40E-01	3.88E+00	2.34E-01	-8.70E-02
3/22/2007 11:23:39	3.90E+02	3.80E+02	1.55E+02	1.61E+03	1.30E-02	-2.46E-01	1.29E+00	4.14E-01	2.17E+01	5.67E-02	5.45E+00	3.70E-01	-8.70E-02
3/22/2007 11:23:40	3.91E+02	3.80E+02	1.54E+02	1.58E+03	1.50E-02	-2.46E-01	1.22E+00	-6.53E-01	2.04E+01	5.67E-02	5.45E+00	3.70E-01	-8.70E-02
3/22/2007 11:23:41	3.92E+02	3.80E+02	1.53E+02	1.59E+03	1.50E-02	-1.95E-01	1.59E+00	-3.48E-01	2.73E+01	2.42E-01	3.80E+00	3.80E+00	-8.70E-02
3/22/2007 11:23:42	3.93E+02	3.80E+02	1.53E+02	1.59E+03	1.20E-02	5.78E-01	1.28E+00	1.54E-01	1.74E+01	2.42E-01	3.80E+00	3.80E+00	-8.70E-02
3/22/2007 11:23:43	3.92E+02	3.80E+02	1.53E+02	1.52E+03	1.40E-02	1.35E+00	1.05E+00	8.65E-01	2.14E+01	5.66E-02	2.94E+00	-3.83E-01	2.29E-01
3/22/2007 11:23:44	3.90E+02	3.80E+02	1.52E+02	1.59E+03	1.50E-02	1.35E+00	1.24E+00	-5.28E-01	2.49E+01	5.66E-02	2.94E+00	-3.83E-01	2.29E-01
3/22/2007 11:23:45	3.91E+02	3.80E+02	1.55E+02	1.53E+03	1.40E-02	1.73E+00	1.61E+00	-2.86E-01	2.66E+01	5.72E-02	4.28E+00	3.58E+00	-8.70E-02
3/22/2007 11:23:46	3.92E+02	3.80E+02	1.53E+02	1.58E+03	1.40E-02	1.79E+00	1.24E+00	9.02E-01	1.87E+01	5.72E-02	4.28E+00	3.58E+00	-8.70E-02
3/22/2007 11:23:47	3.93E+02	3.80E+02	1.52E+02	1.60E+03	1.40E-02	1.91E+00	2.00E+00	1.77E-01	1.98E+01	5.52E-02	4.02E+00	3.79E-01	-8.70E-02
3/22/2007 11:23:48	3.93E+02	3.80E+02	1.52E+02	1.57E+03	1.60E-02	1.33E+00	1.33E+00	1.01E+00	1.83E+01	4.30E-01	4.33E+00	-3.79E-01	-8.70E-02
3/22/2007 11:23:49	3.94E+02	3.80E+02	1.54E+02	1.60E+03	1.30E-02	3.65E-01	7.87E-01	8.59E-01	2.46E+01	4.30E-01	4.33E+00	-3.79E-01	-8.70E-02
3/22/2007 11:23:50	3.93E+02	3.80E+02	1.52E+02	1.62E+03	1.10E-02	-8.48E-01	1.06E+00	6.46E-01	2.42E+01	2.44E-01	6.71E+00	7.26E-02	-8.70E-02
3/22/2007 11:23:51	3.95E+02	3.80E+02	1.55E+02	1.58E+03	1.40E-02	-8.48E-01	1.06E+00	1.83E+00	2.37E+01	2.44E-01	6.71E+00	7.26E-02	-8.70E-02
3/22/2007 11:23:52	3.96E+02	3.82E+02	1.52E+02	1.66E+03	1.40E-02	-1.91E+00	2.00E+00	1.77E-01	1.98E+01	5.52E-02	4.02E+00	3.79E-01	-8.70E-02
3/22/2007 11:23:53	3.93E+02	3.81E+02	1.53E+02	1.62E+03	1.20E-02	-1.65E+00	2.13E+00	-5.38E-01	1.89E+01	5.52E-02	4.02E+00	3.79E-01	-8.70E-02
3/22/2007 11:23:54	3.92E+02	3.80E+02	1.52E+02	1.57E+03	1.30E-02	2.56E-03	2.54E+00	4.98E-01	1.94E+01	5.41E-02	4.40E+00	-3.77E-01	-8.70E-02
3/22/2007 11:23:55	3.92E+02	3.80E+02	1.53E+02	1.60E+03	1.60E-02	2.56E-03	1.93E+00	1.00E+00	2.08E+01	5.41E-02	4.40E+00	-3.77E-01	-8.70E-02
3/22/2007 11:23:56	3.93E+02	3.80E+02	1.54E+02	1.64E+03	1.80E-02	1.52E+00	1.93E+00	8.75E-01	2.38E+01	2.31E-01	4.28E+00	-3.55E-01	6.52E-02
3/22/2007 11:23:57	3.93E+02	3.81E+02	1.54E+02	1.69E+03	3.00E-02	2.23E+00	1.44E+00	2.38E-01	2.34E+01	2.31E-01	4.28E+00	-3.55E-01	6.52E-02
3/22/2007 11:23:58	3.95E+02	3.81E+02	1.54E+02	2.05E+03	1.90E-02	1.71E+00	2.83E+00	1.38E+00	2.03E+01	4.94E-02	2.98E+00	2.03E-01	-8.70E-02
3/22/2007 11:23:59	3.94E+02	3.82E+02	1.54E+02	2.40E+03	1.60E-02	7.10E-01	2.83E+00	1.92E+00	2				



3/22/2007 11:26:09	3.89E+02	3.80E+02	1.56E+02	1.74E+03	1.70E-02	2.83E+00	8.48E-01	1.12E-01	2.25E+01
3/22/2007 11:26:10	3.94E+02	3.81E+02	1.56E+02	1.80E+03	1.50E-02	1.72E-02	1.46E+00	3.75E-01	1.99E+01
3/22/2007 11:26:11	3.95E+02	3.83E+02	1.56E+02	1.75E+03	1.60E-02	2.69E+00	9.09E-01	2.04E-01	1.85E+01
3/22/2007 11:26:12	3.98E+02	3.85E+02	1.59E+02	1.91E+03	1.40E-02	-3.46E+00	1.18E+00	-1.80E-01	2.18E+01
3/22/2007 11:26:13	3.98E+02	3.85E+02	1.55E+02	2.11E+03	1.30E-02	-1.71E+00	1.15E+00	2.74E-01	2.46E+01
3/22/2007 11:26:14	3.96E+02	3.85E+02	1.56E+02	2.26E+03	1.50E-02	8.10E-01	1.74E+00	6.42E-01	2.14E+01
3/22/2007 11:26:15	3.95E+02	3.84E+02	1.55E+02	2.27E+03	1.50E-02	1.73E+00	3.04E+00	1.13E+00	2.64E+01
3/22/2007 11:26:16	3.95E+02	3.84E+02	1.53E+02	2.30E+03	1.50E-02	6.85E-01	3.09E+00	1.24E+00	2.79E+01
3/22/2007 11:26:17	3.95E+02	3.83E+02	1.55E+02	2.33E+03	1.50E-02	5.24E+02	2.98E+00	4.22E-01	2.71E+01
3/22/2007 11:26:18	3.97E+02	3.84E+02	1.56E+02	2.44E+03	1.60E-02	1.44E+00	2.58E+00	1.34E+00	1.94E+01
3/22/2007 11:26:19	3.97E+02	3.84E+02	1.58E+02	2.58E+03	1.50E-02	1.44E+00	3.20E+00	1.20E+00	2.40E+01
3/22/2007 11:26:20	3.95E+02	3.84E+02	1.55E+02	2.58E+03	1.50E-02	3.89E+00	3.29E+00	9.17E-01	2.65E+01
3/22/2007 11:26:21	3.97E+02	3.84E+02	1.56E+02	3.00E+03	1.50E-02	4.91E+00	3.83E+00	9.94E-01	2.34E+01
3/22/2007 11:26:22	3.96E+02	3.84E+02	1.55E+02	3.51E+03	1.70E-02	2.87E+00	4.09E+00	1.73E+00	2.16E+01
3/22/2007 11:26:23	3.96E+02	3.85E+02	1.56E+02	3.91E+03	1.40E-02	2.87E+00	5.35E+00	3.26E-01	2.50E+01
3/22/2007 11:26:24	3.96E+02	3.85E+02	1.56E+02	3.78E+03	1.50E-02	-6.39E-01	7.58E+00	2.31E+00	2.13E+01
3/22/2007 11:26:25	3.96E+02	3.84E+02	1.59E+02	3.43E+03	1.20E-02	-3.14E+00	8.43E+00	1.98E+00	2.11E+01
3/22/2007 11:26:26	3.97E+02	3.85E+02	1.57E+02	3.19E+03	1.40E-02	-2.59E+00	8.16E+00	2.67E+00	2.59E+01
3/22/2007 11:26:27	3.85E+02	3.85E+02	1.57E+02	3.01E+03	1.40E-02	-2.59E+00	6.12E+00	2.08E+00	2.22E+01
3/22/2007 11:26:28	3.97E+02	3.85E+02	1.56E+02	2.83E+03	1.30E-02	-1.08E+00	5.51E+00	5.90E-01	2.50E+01
3/22/2007 11:26:29	3.96E+02	3.84E+02	1.56E+02	2.58E+03	1.70E-02	1.42E-01	4.60E+00	1.32E+00	2.56E+01
3/22/2007 11:26:30	3.97E+02	3.84E+02	1.55E+02	2.51E+03	1.40E-02	6.79E-01	4.08E+00	1.01E+00	2.25E+01
3/22/2007 11:26:31	3.97E+02	3.84E+02	1.57E+02	2.41E+03	1.40E-02	6.79E-01	4.02E+00	1.05E+00	2.31E+01
3/22/2007 11:26:32	3.95E+02	3.83E+02	1.58E+02	2.39E+03	1.50E-02	6.79E-01	3.01E+00	-1.06E-01	2.54E+01
3/22/2007 11:26:33	3.95E+02	3.83E+02	1.56E+02	2.45E+03	1.40E-02	5.08E-01	3.23E+00	1.94E-01	1.92E+01
3/22/2007 11:26:34	3.98E+02	3.83E+02	1.56E+02	2.43E+03	1.60E-02	5.08E-01	3.98E+00	1.74E-01	1.84E+01
3/22/2007 11:26:35	3.97E+02	3.83E+02	1.58E+02	2.39E+03	1.40E-02	3.03E-01	3.47E+00	-1.98E-01	2.38E+01
3/22/2007 11:26:36	3.95E+02	3.83E+02	1.55E+02	2.41E+03	1.40E-02	2.65E-01	3.52E+00	-1.29E+00	2.21E+01
3/22/2007 11:26:37	3.95E+02	3.83E+02	1.56E+02	2.44E+03	1.30E-02	5.34E-01	4.31E+00	-6.98E-01	1.95E+01
3/22/2007 11:26:38	3.96E+02	3.83E+02	1.55E+02	2.46E+03	1.60E-02	6.34E-01	4.31E+00	-5.86E-01	1.59E+01
3/22/2007 11:26:39	3.94E+02	3.83E+02	1.58E+02	2.57E+03	1.40E-02	1.04E+00	3.47E+00	-3.29E-01	1.79E+01
3/22/2007 11:26:40	3.93E+02	3.83E+02	1.53E+02	2.70E+03	1.50E-02	1.46E+00	3.92E+00	-1.41E+00	2.24E+01
3/22/2007 11:26:41	3.96E+02	3.83E+02	1.57E+02	2.91E+03	1.40E-02	1.37E+00	4.46E+00	4.28E-01	2.20E+01
3/22/2007 11:26:42	4.12E+02	3.91E+02	1.55E+02	3.09E+03	1.50E-02	1.37E+00	5.17E+00	-4.46E-01	1.58E+01
3/22/2007 11:26:43	4.20E+02	4.04E+02	1.56E+02	2.97E+03	1.20E-02	8.99E-01	5.29E+00	2.46E-01	2.13E+01
3/22/2007 11:26:44	4.04E+02	3.97E+02	1.60E+02	2.63E+03	1.40E-02	1.80E-01	5.76E+00	-5.29E-01	1.96E+01
3/22/2007 11:26:45	3.89E+02	3.85E+02	1.55E+02	2.30E+03	1.40E-02	-3.21E-02	5.76E+00	2.89E-02	2.00E+01
3/22/2007 11:26:46	3.91E+02	3.81E+02	1.58E+02	1.99E+03	1.40E-02	2.53E-01	3.92E+00	-2.79E-02	1.87E+01
3/22/2007 11:26:47	3.94E+02	3.80E+02	1.57E+02	1.82E+03	1.30E-02	3.43E-01	2.57E+00	-7.12E-01	1.72E+01
3/22/2007 11:26:48	3.92E+02	3.80E+02	1.51E+02	1.73E+03	1.40E-02	-3.48E-02	2.21E+00	-4.17E-01	1.80E+01
3/22/2007 11:26:49	3.92E+02	3.80E+02	1.55E+02	1.62E+03	1.60E-02	-4.78E-01	1.22E+00	-1.77E-01	2.01E+01
3/22/2007 11:26:50	3.92E+02	3.80E+02	1.55E+02	1.63E+03	1.50E-02	-4.78E-01	1.37E+00	-7.84E-01	2.06E+01
3/22/2007 11:26:51	3.91E+02	3.79E+02	1.56E+02	1.57E+03	1.40E-02	3.85E-03	8.90E-01	-2.79E-01	1.55E+01
3/22/2007 11:26:52	3.91E+02	3.79E+02	1.54E+02	1.60E+03	1.50E-02	5.12E-01	1.00E+00	-1.52E+00	1.84E+01
3/22/2007 11:26:53	3.91E+02	3.79E+02	1.54E+02	1.59E+03	1.60E-02	6.89E-01	1.00E+00	-1.39E+00	1.26E+01
3/22/2007 11:26:54	3.91E+02	3.79E+02	1.57E+02	1.55E+03	1.30E-02	6.43E-01	1.18E+00	-1.41E+00	1.75E+01
3/22/2007 11:26:55	3.92E+02	3.79E+02	1.53E+02	1.50E+03	1.40E-02	7.28E-01	1.52E+00	-1.52E+00	1.90E+01
3/22/2007 11:26:56	3.91E+02	3.79E+02	1.55E+02	1.55E+03	1.60E-02	9.83E-01	8.65E-01	-5.52E-01	1.75E+01
3/22/2007 11:26:57	3.92E+02	3.79E+02	1.55E+02	1.52E+03	1.40E-02	9.47E-01	1.52E+00	-9.15E-01	1.82E+01
3/22/2007 11:26:58	3.93E+02	3.80E+02	1.55E+02	1.57E+03	1.40E-02	4.32E-01	1.29E+00	-1.91E+00	1.68E+01
3/22/2007 11:27:00	3.91E+02	3.80E+02	1.56E+02	1.56E+03	1.40E-02	8.21E-02	1.30E+00	-4.52E-01	1.29E+01
3/22/2007 11:27:01	3.92E+02	3.80E+02	1.53E+02	1.56E+03	1.30E-02	-8.22E-02	1.25E+00	-5.42E-01	1.51E+01
3/22/2007 11:27:02	3.94E+02	3.80E+02	1.54E+02	1.56E+03	1.40E-02	1.28E-01	1.28E+00	-1.26E+00	1.39E+01
3/22/2007 11:27:03	3.93E+02	3.80E+02	1.54E+02	1.55E+03	1.40E-02	4.11E-01	1.42E+00	-1.09E+00	9.17E+00
3/22/2007 11:27:04	3.91E+02	3.80E+02	1.56E+02	1.59E+03	1.50E-02	6.59E-01	7.10E-01	-1.30E+00	1.73E+01
3/22/2007 11:27:05	3.92E+02	3.80E+02	1.52E+02	1.57E+03	1.40E-02	6.94E-01	1.08E+00	-1.45E+00	1.64E+01
3/22/2007 11:27:06	3.91E+02	3.80E+02	1.54E+02	1.57E+03	1.40E-02	5.94E-01	1.47E+00	-1.32E+00	1.54E+01
3/22/2007 11:27:07	3.90E+02	3.80E+02	1.56E+02	1.57E+03	1.40E-02	7.02E-01	9.08E-01	-5.70E-01	1.60E+01
3/22/2007 11:27:08	3.92E+02	3.80E+02	1.53E+02	1.58E+03	1.60E-02	1.08E+00	1.18E+00	-1.71E+00	2.20E+01
3/22/2007 11:27:09	3.92E+02	3.80E+02	1.54E+02	1.60E+03	1.50E-02	1.37E+00	8.99E-01	-8.22E-01	1.27E+01
3/22/2007 11:27:10	3.93E+02	3.80E+02	1.52E+02	1.57E+03	1.50E-02	1.14E+00	1.18E+00	-3.33E-01	1.90E+01
3/22/2007 11:27:11	3.93E+02	3.80E+02	1.54E+02	1.58E+03	1.40E-02	5.39E-01	1.28E+00	-2.59E+00	1.71E+01
3/22/2007 11:27:12	3.92E+02	3.80E+02	1.55E+02	1.56E+03	1.40E-02	1.07E-01	1.37E+00	-3.86E-01	1.34E+01
3/22/2007 11:27:13	3.91E+02	3.80E+02	1.55E+02	1.58E+03	1.40E-02	1.81E-01	1.51E+00	-1.10E+00	1.27E+01
3/22/2007 11:27:14	3.90E+02	3.80E+02	1.51E+02	1.56E+03	1.30E-02	4.73E-01	1.56E+00	-9.55E-01	1.73E+01
3/22/2007 11:27:15	3.92E+02	3.80E+02	1.56E+02	1.59E+03	1.20E-02	5.71E-01	1.46E+00	-7.99E-01	1.34E+01
3/22/2007 11:27:16	3.96E+02	3.82E+02	1.56E+02	1.58E+03	1.60E-02	4.93E-01	1.51E+00	-1.07E+00	1.88E+01
3/22/2007 11:27:17	4.02E+02	3.87E+02	1.54E+02	1.59E+03	1.20E-02	5.55E-01	1.00E+00	-1.80E+00	1.65E+01
3/22/2007 11:27:18	4.00E+02	3.87E+02	1.55E+02	1.58E+03	1.50E-02	1.02E+00	1.02E+00	-6.34E-01	1.28E+01
3/22/2007 11:27:19	4.00E+02	3.88E+02	1.56E+02	1.59E+03	1.80E-02	3.22E+00	1.00E+00	-5.10E-01	1.07E+01
3/22/2007 11:27:20	3.95E+02	3.88E+02	1.58E+02	1.59E+03	1.41E-01	1.18E+01	1.51E+00	-1.10E+00	1.22E+01
3/22/2007 11:27:21	4.00E+02	3.87E+02	1.55E+02	1.55E+03	1.54E+00	1.18E+01	7.52E-01	-1.98E+00	1.66E+01
3/22/2007 11:27:22	5.58E+02	4.20E+02	1.56E+02	1.50E+03	1.92E+00	3.26E+01	7.17E-01	-1.01E+00	9.44E+00
3/22/2007 11:27:23	6.17E+02	5.59E+02	2.22E+02	3.82E+05	2.32E+00	6.86E+01	1.20E+00	-1.91E+00	1.72E+01
3/22/2007 11:27:24	6.26E+02	5.68E+02	2.26E+02	2.56E+06	2.30E+00	1.29E+02	2.02E+00	7.89E-01	1.78E+01
3/22/2007 11:27:25	5.14E+02	5.23E+02	2.91E+04	6.05E+06	1.76E+00	1.29E+02	1.26E+01	1.59E+00	1.70E+01
3/22/2007 11:27:26	4.71E+02	4.87E+02	9.75E+04	6.59E+06	1.57E+00	1.75E+02	2.55E+02	8.07E+00	1.73E+01
3/22/2007 11:27:27	5.33E+02	4.99E+02	2.00E+05	8.84E+06	1.44E+00	1.88E+02	1.28E+03	1.63E+01	1.19E+01
3/22/2007 11:27:28	5.13E+02	5.25E+02	3.00E+05	7.89E+06	2.37E+00	1.88E+02	1.28E+03	2.18E+01	2.04E+01
3/22/2007 11:27:29	6.24E+02	5.17E+02	3.17E+05	7.29E+06	1.65E+00	1.88E+02	1.40E+03	2.56E+01	1.91E+01
3/22/2007 11:27:30	7.50E+02	7.03E+02	2.71E+05	7.01E+06	8.23E-01	1.92E+02	1.01E+03	2.25E+01	2.25E+01
3/22/2007 11:27:31	5.79E+02	5.96E+02	2.14E+05	7.48E+06	3.35E-01	1.69E+02	8.10E+02	2.02E+01	2.28E+01
3/22/2007 11:27:32	4.62E+02	5.17E+02	1.97E+05	7.62E+06	1.86E-01	1.27E+02	6.43E+02	1.81E+01	2.33E+01
3/22/2007 11:27:33	4.91E+02	4.77E+02	2.18E+05	4.55E+06	1.42E-01	1.27E+02	7.14E+02	1.69E+01	2.59E+01
3/22/2007 11:27:34	5.06E+02	5.11E+02	2.11E+05	2.49E+06	4.66E-01	9.60E+01	1.15E+03	1.64E+01	2.72E+01
3/22/2007 11:27:									

3/22/2007 11:27:45	3.90E+02	3.89E+02	1.29E+05	3.66E+06	3.30E+02	9.44E+01	4.61E+02	1.60E+01	1.81E+01	1.25E+01	2.22E-01	2.58E-01	5.91E-02	9.71E-02
3/22/2007 11:27:46	3.89E+02	3.82E+02	9.51E+04	9.30E+05	2.80E+02	5.69E+01	2.82E+02	1.14E+01	2.87E+01	6.98E+00	5.63E-02	2.60E-01	5.98E-02	-2.30E-02
3/22/2007 11:27:47	3.80E+02	6.94E+04	3.80E+02	3.80E+02	2.00E+02	3.24E+01	3.24E+01	2.74E+02	1.01E+01	5.80E+01	5.63E-02	2.60E-01	5.98E-02	-2.30E-02
3/22/2007 11:27:48	3.84E+02	3.80E+02	4.65E+04	1.95E+05	2.20E+02	1.60E+01	1.48E+02	6.66E+00	2.14E+01	7.57E+00	-1.08E-01	2.73E-01	6.18E-02	-2.30E-02
3/22/2007 11:27:49	3.92E+02	3.80E+02	2.80E+04	1.05E+05	1.80E+02	7.16E+00	2.87E+01	3.77E+00	1.99E+01	7.57E+00	-1.08E-01	2.73E-01	6.18E-02	-2.30E-02
3/22/2007 11:27:50	3.93E+02	3.80E+02	1.58E+04	5.12E+04	1.90E+02	2.97E+00	9.58E+00	-1.03E-01	2.18E+01	7.57E+00	-1.08E-01	2.73E-01	6.18E-02	-2.30E-02
3/22/2007 11:27:51	3.94E+02	3.80E+02	9.27E+03	3.93E+04	1.40E+02	1.03E+00	7.41E+00	4.63E-01	2.16E+01	3.95E+00	3.43E-01	3.10E+02	5.05E-01	4.29E-01
3/22/2007 11:27:52	3.92E+02	3.80E+02	6.11E+03	3.16E+04	1.70E+02	2.72E-01	5.55E+00	-2.06E-01	2.45E+01	3.95E+00	3.43E-01	3.10E+02	5.05E-01	4.29E-01
3/22/2007 11:27:53	3.91E+02	3.80E+02	4.43E+03	2.12E+04	1.80E+02	1.12E+02	4.65E+00	-1.00E-01	1.78E+01	4.34E+00	-1.03E-01	2.85E-01	5.70E-01	-2.30E-02
3/22/2007 11:27:54	3.92E+02	3.80E+02	3.39E+03	1.79E+04	1.60E+02	4.25E+02	4.06E+00	-1.63E+00	1.91E+01	4.34E+00	-1.03E-01	2.85E-01	5.70E-01	-2.30E-02
3/22/2007 11:27:55	3.92E+02	3.80E+02	2.65E+03	1.60E+04	1.50E+02	1.95E-01	4.03E+00	-2.15E-01	2.37E+01	2.58E+00	5.76E-02	5.05E-02	5.91E-02	2.17E-01
3/22/2007 11:27:56	3.92E+02	3.80E+02	2.11E+03	1.25E+04	1.40E+02	5.80E+01	2.57E+00	-2.10E+00	2.22E+01	2.58E+00	5.76E-02	5.05E-02	5.91E-02	2.17E-01
3/22/2007 11:27:57	3.92E+02	3.80E+02	1.70E+03	1.20E+04	1.60E+02	1.14E+00	3.06E+00	-7.15E-01	1.50E+01	1.85E+00	4.24E-02	-1.64E-01	5.54E-02	9.34E-02
3/22/2007 11:27:58	3.92E+02	3.80E+02	1.39E+03	1.16E+04	1.50E+02	1.60E+00	2.69E+00	-8.49E-01	1.85E+01	1.85E+00	4.24E-02	-1.64E-01	5.54E-02	9.34E-02
3/22/2007 11:27:59	3.93E+02	3.80E+02	1.15E+03	1.08E+04	1.70E+02	1.61E+00	2.29E+00	-2.56E-01	2.24E+01	1.05E+00	-1.11E-01	-1.64E-01	3.03E-01	2.20E-01
3/22/2007 11:28:00	3.94E+02	3.80E+02	9.57E+02	1.06E+04	1.60E+02	1.14E+00	2.09E+00	-7.73E-01	1.97E+01	1.05E+00	-1.11E-01	-1.64E-01	3.03E-01	2.20E-01
3/22/2007 11:28:01	3.92E+02	3.80E+02	8.07E+02	1.01E+04	1.40E+02	5.59E-01	1.37E+00	-1.38E+00	1.39E+01	1.03E+00	-1.09E-01	5.06E-02	4.32E-01	-2.30E-02
3/22/2007 11:28:02	3.92E+02	3.80E+02	6.93E+02	1.00E+04	1.40E+02	1.84E-01	1.88E+00	-4.36E-01	1.79E+01	1.03E+00	-1.09E-01	5.06E-02	4.32E-01	-2.30E-02
3/22/2007 11:28:03	3.94E+02	3.80E+02	5.99E+02	9.00E+03	1.40E+02	7.54E-02	2.25E+00	-6.74E-01	1.55E+01	7.76E-01	4.18E-01	5.61E-02	6.42E-02	2.27E-01
3/22/2007 11:28:04	3.93E+02	3.80E+02	5.21E+02	8.40E+03	1.40E+02	2.02E-01	1.54E+00	-1.21E+00	1.87E+01	7.76E-01	4.18E-01	5.61E-02	6.42E-02	2.27E-01
3/22/2007 11:28:05	3.90E+02	3.80E+02	4.62E+02	8.30E+03	1.50E+02	5.76E-01	1.60E+00	-6.39E-01	1.98E+01	1.67E+00	3.97E-01	4.72E-01	6.19E-02	2.23E-01
3/22/2007 11:28:06	3.92E+02	3.80E+02	4.15E+02	7.00E+03	1.30E+02	1.14E+00	1.90E+00	-1.80E+00	2.01E+01	1.67E+00	3.97E-01	4.72E-01	6.19E-02	2.23E-01
3/22/2007 11:28:07	3.91E+02	3.80E+02	3.76E+02	6.90E+03	1.60E+02	1.56E+00	1.74E+00	-4.66E-01	1.72E+01	2.61E+00	4.14E-01	4.92E-01	-6.10E-02	-2.30E-02
3/22/2007 11:28:08	3.93E+02	3.80E+02	3.47E+02	6.00E+03	1.60E+02	1.56E+00	2.10E+00	-1.58E+00	1.37E+01	2.61E+00	4.14E-01	4.92E-01	-6.10E-02	-2.30E-02
3/22/2007 11:28:09	3.93E+02	3.80E+02	3.19E+02	6.40E+03	1.20E+02	1.23E+02	1.30E+00	2.12E+00	2.76E+01	2.61E+00	4.14E-01	4.92E-01	-6.10E-02	-2.30E-02
3/22/2007 11:28:10	3.92E+02	3.80E+02	2.99E+02	8.93E+03	1.40E+02	5.62E-01	1.63E+00	-5.47E-01	2.11E+01	6.38E-01	5.66E-02	2.60E-01	-6.10E-02	-2.30E-02
3/22/2007 11:28:11	3.91E+02	3.80E+02	2.81E+02	8.44E+03	1.50E+02	1.90E-01	1.58E+00	-1.94E-01	2.59E+01	2.03E+00	4.28E-01	6.04E-02	1.91E-01	-2.30E-02
3/22/2007 11:28:12	3.90E+02	3.80E+02	2.63E+02	8.16E+03	1.60E+02	8.13E+02	1.48E+00	3.27E-01	1.47E+01	2.03E+00	4.28E-01	6.04E-02	1.91E-01	-2.30E-02
3/22/2007 11:28:13	3.91E+02	3.80E+02	2.52E+02	7.89E+03	1.40E+02	2.20E-01	1.60E+00	-1.04E+00	2.02E+01	2.03E+00	4.28E-01	6.04E-02	1.91E-01	-2.30E-02
3/22/2007 11:28:14	3.93E+02	3.80E+02	2.42E+02	7.96E+03	1.60E+02	1.18E+01	1.50E+00	2.02E+00	2.02E+01	2.05E+00	2.31E-01	4.90E+02	4.33E-01	1.00E-01
3/22/2007 11:28:15	3.94E+02	3.80E+02	2.30E+02	7.76E+03	1.70E+02	1.10E+00	1.68E+00	-1.26E-01	1.79E+01	2.05E+00	2.31E-01	4.90E+02	4.33E-01	1.00E-01
3/22/2007 11:28:16	3.92E+02	3.80E+02	2.25E+02	7.32E+03	1.40E+02	1.20E+00	1.53E+00	-1.48E-01	2.24E+01	2.79E+00	8.45E-01	-1.64E-01	7.17E-02	1.10E-01
3/22/2007 11:28:17	3.92E+02	3.80E+02	2.15E+02	6.85E+03	1.50E+02	5.28E-01	8.22E-01	-8.64E-02	2.07E+01	2.79E+00	8.45E-01	-1.64E-01	7.17E-02	1.10E-01
3/22/2007 11:28:18	3.93E+02	3.80E+02	2.09E+02	6.47E+03	1.40E+02	-4.28E-01	1.41E+00	-6.18E-01	1.85E+01	2.44E+00	-2.80E-01	-1.64E-01	2.02E-01	2.40E-01
3/22/2007 11:28:19	3.92E+02	3.80E+02	2.11E+02	6.50E+03	1.40E+02	1.21E+02	1.29E+00	-2.44E-01	1.50E+01	2.44E+00	-2.80E-01	-1.64E-01	2.02E-01	2.40E-01
3/22/2007 11:28:20	3.92E+02	3.80E+02	2.01E+02	5.82E+03	1.40E+02	-7.60E-01	1.25E+00	-1.28E+00	1.69E+01	1.34E+00	8.14E-02	2.95E-01	6.78E-02	1.06E-01
3/22/2007 11:28:21	3.92E+02	3.80E+02	1.97E+02	5.60E+03	1.30E+02	-7.60E-01	1.10E+00	-1.18E+00	2.45E+01	1.34E+00	8.14E-02	2.95E-01	6.78E-02	1.06E-01
3/22/2007 11:28:22	3.95E+02	3.80E+02	1.95E+02	5.53E+03	1.40E+02	-3.07E-01	1.95E+00	-7.50E-01	1.78E+01	2.77E+00	2.36E-01	2.65E-01	6.45E-02	1.02E-01
3/22/2007 11:28:23	3.91E+02	3.80E+02	1.92E+02	5.26E+03	1.30E+02	2.15E-01	1.40E+00	-1.35E+00	2.23E+01	2.77E+00	2.36E-01	2.65E-01	6.45E-02	1.02E-01
3/22/2007 11:28:24	3.90E+02	3.80E+02	1.90E+02	5.04E+03	1.30E+02	7.12E-01	1.29E+00	-2.36E-01	1.92E+01	1.47E+00	-1.27E-01	2.15E-01	1.64E-01	8.96E-02
3/22/2007 11:28:25	3.92E+02	3.80E+02	1.86E+02	4.92E+03	1.20E+02	7.12E-01	1.29E+00	-6.00E-01	1.95E+01	1.47E+00	-1.27E-01	2.15E-01	1.64E-01	8.96E-02
3/22/2007 11:28:26	3.91E+02	3.80E+02	1.84E+02	4.91E+03	1.60E+02	1.39E+00	1.05E+00	-1.09E-01	1.93E+01	1.78E-01	4.81E-01	7.91E-02	2.08E-01	2.46E-01
3/22/2007 11:28:27	3.91E+02	3.80E+02	1.85E+02	4.60E+03	1.40E+02	2.07E+00	1.38E+00	-7.57E-01	2.16E+01	7.88E-01	4.81E-01	7.91E-02	2.08E-01	2.46E-01
3/22/2007 11:28:28	3.90E+02	3.80E+02	1.80E+02	4.45E+03	1.40E+02	2.28E+00	1.43E+00	-1.84E-01	2.56E+01	2.06E+00	2.71E-01	5.49E-01	6.66E-02	1.05E-01
3/22/2007 11:28:29	3.91E+02	3.80E+02	1.78E+02	4.23E+03	1.30E+02	2.28E+00	1.43E+00	-6.22E-01	2.13E+01	2.06E+00	2.71E-01	5.49E-01	6.66E-02	1.05E-01
3/22/2007 11:28:30	3.91E+02	3.80E+02	1.80E+02	4.09E+03	1.80E+02	2.24E+00	1.19E+00	-6.98E-01	1.69E+01	2.16E+00	8.15E-02	4.72E-02	6.10E-02	9.44E-02
3/22/2007 11:28:31	3.91E+02	3.80E+02	1.77E+02	3.92E+03	1.60E+02	1.50E+00	1.46E+00	-8.69E-01	2.20E+01	2.16E+00	8.15E-02	4.72E-02	6.10E-02	9.44E-02
3/22/2007 11:28:32	3.94E+02	3.80E+02	1.75E+02	3.78E+03	1.20E+02	1.50E+00	1.42E+00	-6.54E-01	2.44E+01	4.05E+00	2.65E-01	-1.64E-01	3.20E-01	1.04E-01
3/22/2007 11:28:33	3.94E+02	3.80E+02	1.74E+02	3.72E+03	1.60E+02	4.96E-01	1.21E+00	-1.19E-01	1.70E+01	4.05E+00	2.65E-01	-1.64E-01	3.20E-01	1.04E-01
3/22/2007 11:28:34	3.92E+02	3.80E+02	1.74E+02	3.64E+03	1.30E+02	-9.15E-02	1.47E+00	-1.30E+00	2.17E+01	4.05E+00	2.65E-01	-1.64E-01	3.20E-01	1.04E-01
3/22/2007 11:28:35	3.91E+02	3.80E+02	1.68E+02	3.55E+03	1.50E+02	1.68E-01	1.47E+00	-3.07E-01	2.75E+01	4.05E+00	2.65E-01	-1.64E-01	3.20E-01	1.04E-01
3/22/2007 11:28:36	3.92E+02	3.80E+02	1.71E+02	3.48E+03	1.30E+02	1.68E-01	1.65E+00	-2.66E-01	2.16E+01	4.05E+00	2.65E-01	-1.64E-01	3.20E-01	1.04E-01
3/22/2007 11:28:37	3.94E+02	3.80E+02	1.69E+02	3.34E+03	1.40E+02	6.72E-01	1.81E+00	2.53E-01	2.01E+01	1.39E+00	2.01E-01	4.35E-01	5.63E-02	-2.30E-02
3/22/2007 11:28:38	3.94E+02	3.80E+02	1.66E+02	3.30E+03	1.10E+02	8.01E-01	1.20E+00	-5.13E-01	2.37E+01	1.39E+00	2.01E-01	4.35E-01	5.63E-02	-2.30E-02
3/22/2007 11:28:39	3.91E+02	3.80E+02	1.69E+02	3.25E+03	1.60E+02	8.01E-01	1.10E+00	8.05E-01	1.87E+01	1.75E+00	7.99E-02	6.49E-02	6.68E-02	-2.30E-02
3/22/2007 11:28:40	3.91E+02	3.80E+02	1.68E+02	3.15E+03	1.30E+02	5.78E-01	1.40E+00	9.60E-01	2.02E+01	1.75E+00	7.99E-02	6.49E-02	6.68E-02	-2.30E-02
3/22/2007 11:28:41	3.93E+02	3.80E+02	1.68E+02	3.04E+03	2.00E+02	2.50E-01	1.03E+00	9.12E-01	1.98E+01	1.39E+00	2.01E-01	4.35E-01	5.63E-02	-2.30E-02
3/22/2007 11:28:42	3.92E+02	3.80E+02	1.67E+02	3.08E+03	1.40E+02	1.47E-01	9.34E-01	-7.77E-02	1.70E+01	1.72E+00	2.32E-01	2.64E-01	1.86E-01	1.01E-01
3/22/2007 11:28:43	3.92E+02	3.80E+02	1.64E+02	2.99E+03	1.30E+02	1.47E-01	1.55E+00	5.65E-01	1.82E+01	4.12E+00	5.90E-01	5.53E-02	4.38E-01	-2.30E-02
3/22/2007 11:28:														

3/22/2007 11:29:21	5.48E+02	5.43E+02	4.59E+04	4.39E+06	1.60E+00	1.43E+02	1.90E+02	8.00E+00	2.45E+01	7.81E+00	6.77E-02	2.80E-01	3.08E-01	3.46E-01
3/22/2007 11:29:22	5.18E+02	5.34E+02	9.27E+04	6.25E+06	1.33E+00	1.43E+02	6.23E+02	1.26E+01	1.93E+01	7.81E+00	6.77E-02	2.80E-01	3.08E-01	3.46E-01
3/22/2007 11:29:23	4.78E+02	4.74E+02	1.89E+05	6.19E+06	2.09E+00	1.69E+02	7.10E+02	1.65E+01	2.42E+01	2.41E+01	-9.91E-02	7.57E-01	1.96E-01	2.34E-01
3/22/2007 11:29:24	6.33E+02	5.84E+02	2.49E+05	6.52E+06	2.79E+00	2.07E+02	1.29E+03	1.80E+01	2.51E+01	2.41E+01	-9.91E-02	7.57E-01	1.96E-01	2.34E-01
3/22/2007 11:29:25	8.98E+02	7.43E+02	2.95E+05	5.52E+06	1.98E+00	2.14E+02	1.00E+03	2.12E+01	2.00E+01	2.37E+01	-1.11E-01	9.03E-01	-6.10E-02	-2.30E-02
3/22/2007 11:29:26	7.91E+02	7.77E+02	2.74E+05	6.79E+06	1.05E+00	2.14E+02	1.05E+03	2.14E+01	2.64E+01	2.37E+01	-1.11E-01	9.03E-01	-6.10E-02	-2.30E-02
3/22/2007 11:29:27	4.87E+02	7.77E+02	2.43E+05	7.51E+06	7.28E-01	1.85E+02	6.98E+02	1.93E+01	2.95E+01	1.80E+01	2.20E-01	1.32E+00	5.69E-02	2.13E-01
3/22/2007 11:29:28	4.30E+02	5.67E+02	2.59E+05	7.68E+06	6.07E-01	1.66E+02	1.16E+03	2.07E+01	3.01E+01	1.80E+01	2.20E-01	1.32E+00	5.69E-02	2.13E-01
3/22/2007 11:29:29	6.70E+02	6.02E+02	3.01E+05	5.29E+06	1.98E-01	1.66E+02	1.16E+03	2.22E+01	3.10E+01	2.00E+01	3.11E-02	2.25E-01	1.65E-01	8.99E-02
3/22/2007 11:29:30	6.02E+02	6.01E+02	2.85E+05	3.79E+06	6.40E-02	1.28E+02	1.11E+03	2.32E+01	2.66E+01	2.00E+01	3.11E-02	2.25E-01	1.65E-01	8.99E-02
3/22/2007 11:29:31	3.62E+02	4.28E+02	2.07E+05	2.51E+06	3.10E-02	8.95E+01	6.44E+02	2.17E+01	2.82E+01	1.34E+01	7.11E-02	1.17E+00	6.43E-02	-2.30E-02
3/22/2007 11:29:32	3.69E+02	3.93E+02	1.35E+05	5.89E+05	2.20E-02	5.09E+01	3.52E+02	1.63E+01	2.46E+01	1.34E+01	7.11E-02	1.17E+00	6.43E-02	-2.30E-02
3/22/2007 11:29:33	3.81E+02	3.84E+02	8.84E+04	2.66E+05	2.20E-02	5.09E+01	2.40E+02	1.38E+01	2.19E+01	7.83E+00	6.87E-02	9.48E-01	1.86E-01	3.47E-01
3/22/2007 11:29:34	3.93E+02	3.80E+02	5.71E+04	1.40E+05	2.20E-02	2.30E+01	3.05E+01	1.07E+01	2.59E+01	7.83E+00	6.87E-02	9.48E-01	1.86E-01	3.47E-01
3/22/2007 11:29:35	3.93E+02	3.80E+02	3.51E+04	8.37E+04	1.80E-02	9.87E+00	3.05E+01	7.28E+00	2.82E+01	4.43E+00	2.61E-01	6.42E-02	6.80E-02	2.35E-01
3/22/2007 11:29:36	3.94E+02	3.80E+02	2.07E+04	4.10E+04	1.80E-02	3.87E+00	1.06E+01	3.14E+00	2.35E+01	4.43E+00	2.61E-01	6.42E-02	6.80E-02	2.35E-01
3/22/2007 11:29:37	3.95E+02	3.80E+02	1.25E+04	3.18E+04	1.80E-02	3.87E+00	8.12E+00	2.55E+00	3.01E+01	2.13E+00	-1.09E-01	5.11E-02	3.10E-01	1.01E-01
3/22/2007 11:29:38	3.94E+02	3.80E+02	8.27E+03	2.57E+04	1.40E-02	1.48E+00	6.62E+00	2.86E+00	2.02E+01	2.13E+00	-1.09E-01	5.11E-02	3.10E-01	1.01E-01
3/22/2007 11:29:39	3.93E+02	3.80E+02	5.95E+03	1.75E+04	1.40E-02	5.45E-01	5.50E+00	2.08E+00	2.89E+01	7.80E-01	2.30E-01	2.69E-01	-6.10E-02	9.73E-02
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3/22/2007 11:29:41	3.91E+02	3.80E+02	3.48E+03	1.30E+04	1.60E-02	7.79E-01	3.78E+00	1.62E+00	2.18E+01	7.80E-01	2.30E-01	2.69E-01	-6.10E-02	9.73E-02
3/22/2007 11:29:42	3.91E+02	3.80E+02	2.74E+03	1.06E+04	1.60E-02	1.88E+00	3.37E+00	1.73E+00	1.97E+01	2.05E+00	7.09E-01	-1.64E-01	1.75E-01	2.13E-01
3/22/2007 11:29:43	3.90E+02	3.80E+02	2.18E+03	9.80E+03	1.30E-02	2.93E+00	2.98E+00	1.16E+00	2.97E+01	2.05E+00	7.09E-01	-1.64E-01	1.75E-01	2.13E-01
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3/22/2007 11:29:51	3.93E+02	3.80E+02	5.34E+02	6.80E+03	1.50E-02	4.01E-01	2.46E+00	2.78E+00	2.32E+01	4.33E+00	2.55E-01	-1.64E-01	3.22E-01	-2.30E-02
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3/22/2007 11:29:55	3.95E+02	3.80E+02	3.50E+02	8.25E+03	1.50E-02	1.64E+00	1.34E+00	1.41E+00	2.14E+01	4.82E+00	8.68E-02	7.11E-02	6.79E-02	3.64E-01
3/22/2007 11:29:56	3.93E+02	3.80E+02	3.26E+02	7.77E+03	1.70E-02	5.29E-01	1.26E+00	1.92E+00	1.67E+01	8.81E-01	7.21E-02	5.99E-02	6.41E-02	-2.30E-02
3/22/2007 11:29:57	3.92E+02	3.80E+02	3.01E+02	7.47E+03	1.30E-02	-3.73E-01	1.92E+00	2.02E+00	2.62E+01	8.81E-01	7.21E-02	5.99E-02	6.41E-02	-2.30E-02
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3/22/2007 11:30:00	3.92E+02	3.80E+02	2.39E+02	6.47E+03	1.80E-02	-1.20E+00	1.74E+00	1.71E+00	2.35E+01	9.85E-01	-1.04E-01	2.89E-01	1.86E-01	1.00E-01















## Appendix H



### **Combined Exposures to Hydrogen Cyanide and Carbon Monoxide in Army Operations: Initial Report**



NATIONAL RESEARCH COUNCIL

Committee on Combined Exposures to Hydrogen Cyanide and Carbon Monoxide in Army Operations, Committee on Toxicology, National Research Council

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# **Combined Exposures to Hydrogen Cyanide and Carbon Monoxide in Army Operations: Initial Report**

Committee on Combined Exposures to Hydrogen Cyanide and  
Carbon Monoxide in Army Operations

Committee on Toxicology

Board on Environmental Studies and Toxicology

Division on Earth and Life Studies

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## Preface

In support of the Health Hazard Assessment (HHA) for the U.S. Marine Corps Advanced Amphibious Assault Vehicle (AAAV), the U.S. Army's Center for Health Promotion and Preventive Medicine (CHPPM) performed weapons-emissions testing for various firing scenarios. CHPPM evaluated emissions of carbon monoxide, hydrogen cyanide, oxides of nitrogen, sulfur dioxide, ammonia, and carbon dioxide. Generally, CHPPM evaluates the concentrations of these gases against the permissible exposure limits established by various agencies and organizations. Because military personnel in the AAAV will be exposed to a mixture of gases, concerns were raised about potential additive or synergistic toxic effects, specifically the combined effects of simultaneous exposures to hydrogen cyanide and carbon monoxide, because both gases produce similar toxic effects. Because of these concerns, the Army prepared a report that provides guidance on assessing combined exposures to low levels of carbon monoxide and hydrogen cyanide. The Department of Defense (DOD) then requested that the National Research Council (NRC) independently evaluate the Army's proposed guidance on assessing combined exposures to hydrogen cyanide and carbon monoxide and recommend exposure limit guidelines for combined exposures to these chemicals. The NRC was asked to prepare two reports. For the initial report, the task was to determine whether the hazard presented from simultaneous exposures to hydrogen cyanide and carbon monoxide warrants a combined exposure assessment, and if so, whether the use of the hazard quotient approach is a reasonable method of assessment. The committee's second report, to be completed next year, will address the remainder of the task assigned to it (the complete statement of task is described in the summary of the report).

In response to DOD's request, the NRC convened the Committee on Combined Exposures to Hydrogen Cyanide and Carbon Monoxide in Army Operations. The members of the committee were selected by the NRC for their expertise in occupational health and medicine, physiology, pharmacokinetics, toxicology, inhalation toxicology, epidemiology, physiologically-based pharmacokinetic modeling, and risk assessment. Biographical information on the committee members is provided in Appendix A.

A draft of this initial report was reviewed by individuals selected for their diverse perspectives and technical expertise, in accordance with procedures approved by the NRC's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report: Robert Goyer, University of Western Ontario; Sam Kacew, University of Ottawa; David Macys, Island County Health Department; and Deepak Bhalla, Wayne State University.

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations nor did they see the final draft of the report before its release. The review of this report was overseen by Edward Bishop, HDR Engineering, Inc., appointed by the Division on Earth and Life Studies, who was responsible for making certain that an



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*Preface*

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independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.

The committee gratefully acknowledges the valuable assistance provided by the following persons: Glenn Leach, Mathew Bazaar, Steve Kistner, and Col. John Rowe (all from the U.S. Army, Department of Defense). We are grateful to James J. Reisa, director of the Board on Environmental Studies and Toxicology (BEST), for his helpful comments. Other staff members who contributed to this effort are Ruth Crossgrove, senior editor; Aida Neel, program associate and Radiah Rose, senior editorial assistant. The committee particularly acknowledges Kulbir Bakshi, project director for the committee, for bringing the report to completion. Finally, we would like to thank all members of the committee for their expertise and dedicated effort throughout the development of this report.

William E. Halperin, *Chair*  
Committee on Combined Exposures to Hydrogen  
Cyanide and Carbon Monoxide in Army Operations

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# **Combined Exposures to Hydrogen Cyanide and Carbon Monoxide in Army Operations: Initial Report**

## Summary

The U.S. Army's Health Hazard Assessment (HHA) Program is a Medical Department initiative that supports the Army acquisition process by evaluating potential health hazards during the design and development of materiel systems. Weapons emissions evaluated by the program include carbon monoxide (CO), hydrogen cyanide (HCN), oxides of nitrogen, sulfur dioxide, ammonia, and carbon dioxide. Typically, these chemicals are evaluated on an individual basis against their respective medical criteria that may include military-specific standards. However, additive or synergistic toxic effects among the chemicals must also be considered. Therefore, the Army is considering the simultaneous exposures of crew members in enclosed vehicles to CO and HCN generated from firing of conventional munitions from a 30-mm cannon.

Both CO and HCN are well known toxicants with established guidelines for safe levels of exposure. Adherence to these guidelines for either of these toxicants alone leads to engineering designs, administrative controls, and use of personal protective devices to ensure an acceptable working environment. However, safe levels of exposure to each of the toxicants may need to be lower if the combined effects of exposure are additive or more than additive. Hypothetically, the design requirements could be based upon the toxicologic mechanisms of CO and HCN being independent, additive, or synergistic. The three different scenarios would lead to differences in the resulting designs for ventilation systems, etc.

The potential for combined exposures results from firing of guns in enclosed (but ventilated) spaces in a military environment such as armored tanks. Because of concerns for the health effects of the personnel simultaneously exposed to HCN and CO, the Army's HHA program prepared a report titled *Assessment of Combined Health Effects of Hydrogen Cyanide and Carbon Monoxide at Low Levels for Military Occupational Exposures*. That report provides guidance to assess combined exposures in HHAs of military systems.

The weight of available evidence indicates that the toxic effects of inhaled CO and HCN at lethal and incapacitating levels are additive. Whether similar additive effects hold true at lower concentrations and longer time periods that military personnel may experience, while also in the presence of other combustion gases, is not known. No relevant chronic or low-level exposure studies were found in the literature. In 1981, a military standard established the Army's COHb limits of 5% for aviation crew members to protect against visual effects and 10% for all other military personnel. The exposure criterion for HCN is the current American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLC) ceiling of 4.7 ppm on the basis of anoxia, central-nervous-system, irritation, lung, and thyroid effects.

In addition to singular or individual evaluations of CO and HCN, the following hazard quotient (HQ) approach using singular benchmarks was employed in the Army's HHA report.

$$\frac{\text{COHb}\%}{10\%} + \frac{15\text{-min avg. HCN (ppm)}}{4.7 \text{ ppm}} = \text{HQ.}$$

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It assumed the effects at low levels were additive. An HQ equal to or greater than 1.0 indicated an overexposure.

The Army used the following criteria to evaluate the data involving combined exposures to CO and HCN: if both or either of the 10% COHb and 4.7 ppm HCN limits is exceeded, then the scenario fails and the HQ calculation is essentially not applicable. If COHb and HCN are within acceptable limits, then the HQ calculation is performed.

In 2005, the Department of Defense requested that the National Research Council evaluate the Army's proposed guidance for assessing the adverse effects resulting from combined exposures to low-levels of HCN and CO, and recommend exposure limit guidelines for combined exposures to these chemicals. In response, the National Research Council convened the Committee on Combined Exposures to Hydrogen Cyanide and Carbon Monoxide in Army Operations with oversight from the Committee on Toxicology to address the task assigned to it.

The committee's Statement of Task is as follows:

An ad hoc committee under the oversight of the standing Committee on Toxicology (COT) will assess potential toxic effects from combined exposures to low-levels of HCN and CO. In its first report (i.e., this report), the committee will evaluate the Army's proposed guidance on assessing combined exposures. The ad hoc committee will specifically determine the following in its initial report:

1. Does the hazard presented from combined exposure to HCN and CO at low levels warrant their combined assessment or is the individual assessment of each chemical sufficiently protective?
2. If the combined exposure assessment of HCN and CO is warranted at low levels, is the hazard quotient approach, discussed in the technical context section, a reasonable method of assessment? Should it be modified or improved (i.e., use of a blood CN benchmark instead of the ACGIH TLV-C)?

In its second report, to be completed next year, the committee will determine the following:

1. Is the approach discussed in the technical context section appropriate or an alternative assessment method should be developed and validated through either field or laboratory study?
2. What improvements are needed in the Army's proposed methodology for assessing these combined exposures? The committee will also provide recommendations that will yield more precise measurements of gases which might be useful in hazard assessment.
3. What exposure limit guidelines are appropriate for combined exposures to these chemicals?

### **THE COMMITTEE'S MAJOR CONCLUSIONS AND RECOMMENDATIONS OF THE INITIAL REPORT**

After receiving a briefing from the Army and evaluating published literature on the adverse effects of CO and HCN, both individually and in combination, in animals and in humans, the committee arrived at the following overall conclusions and recommendations for its initial report.

## Summary

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### Conclusions

- Based on the mechanisms of action of toxicity of CO and HCN and the supporting literature, it is likely that the toxicities of these two chemicals are additive, and therefore, the hazard presented from combined exposures to these chemicals should be assessed as a mixture and not singularly or individually.
- The use of the HQ approach proposed by the Army is reasonable in establishing exposure limits for personnel simultaneously exposed to CO and HCN.
- CO is assessed as an individual chemical in HHAs using the Coburn-Forster-Kane (CFK) equation for predicting the percent of COHb in blood. The use of the CFK model for the prediction of COHb levels related to air concentrations of CO is justified. The CFK model has been validated; however it has not been tested in environments with dynamically changing air concentrations, such as in an armored vehicle.
- The use of an air concentration for HCN in the HQ equation, as opposed to a blood level, is reasonable.

### Recommendations

- The Army should conduct further neurological studies on sensory and motor performance at lower concentrations of HCN and CO because most studies on the combined toxicity of CO and HCN have been carried out at high concentrations and have focused on lethality and/or incapacitation; this makes it difficult to use those data to extrapolate to low-levels of exposures and more subtle toxicity end points of interest to the Army. The committee recommends that the Army assess the validity of the CFK model in the context of armored vehicles both using instantaneous measured data and various running averages.
- While the toxicity of combined exposures to HCN and CO is important to understand, the Army should also consider concurrent exposures to other chemicals, e.g., other combustion gases, diesel exhaust, which may have additional effects on the tank crew.

# 1

## Introduction

The U.S. Army's Center for Health Promotion and Preventive Medicine (CHPPM) evaluates health hazards of materiel systems and considers that information in the design and development of materiel systems. CHPPM evaluates weapons emissions, including carbon monoxide (CO), hydrogen cyanide (HCN), oxides of nitrogen (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), ammonia (NH<sub>3</sub>), and carbon dioxide (CO<sub>2</sub>). Generally, these emission gases are evaluated on an individual basis. CHPPM also considers additive or synergistic toxic effects among the chemicals. The Army is specifically concerned about the combined exposures to low-levels of CO and HCN of crew members in an enclosed armored vehicles from the firing of 30 mm cannons.

The literature (Levin et al. 1987; Levin et al. 1988; Chaturvedi et al. 1995) indicates that the toxic effects of inhaled CO and HCN are additive at lethal and incapacitating levels. Whether similar additive effects hold true at the lower concentrations and for longer time periods (lasting from several weeks to several years in worst-case scenarios) that military personnel may experience, while also in the presence of other combustion gases, is not known. No relevant chronic or low-level exposure studies were found in the literature. CO is assessed as an individual chemical in HHAs using the Coburn-Forster-Kane (CFK) equation (Smith et al. 1996) for predicting the percent of carboxyhemoglobin (COHb) in blood. A 1981 military standard (DOD 1981) established the U.S. Army's COHb limits of 5% for aviation crew members to protect against visual effects and 10% for other effects. This level was considered to be a safe level for healthy young people and had previously been used by the American Conference of Governmental Industrial Hygienists (ACGIH) (Smith et al. 1996; DOD 1972). Adverse motor neuron effects such as decreased coordination, tracking, and driving ability, were not present when COHb was below 10% of hemoglobin (ACGIH 2002). The exposure criterion for HCN is the current ACGIH Threshold Limit Value (TLV) ceiling of 4.7 ppm to minimize the potential for headache; nausea; nasal, throat, and pulmonary irritation; and enlargement of the thyroid gland, which can result from low concentration exposure (ACGIH 2001).

The following hazard quotient (HQ) approach using the singular benchmarks was employed, which assumed the effects at low levels were additive. An HQ equal or greater than 1.0 indicated an overexposure.

$$\frac{\text{COHb}\%}{10\%} + \frac{\text{15-min avg. HCN (ppm)}}{4.7 \text{ ppm}} = \text{HQ}.$$

When evaluating an actual test scenario using the stream of test data, the COHb level was calculated at the end of each data interval (3 or 5 seconds) using the instantaneous CO level and the COHb concentration from the end of the previous interval. The 15-minute HCN average was a running average calculated at the end of each data interval.

The 15-minute HCN average concentration was used because HCN exposures were observed to be transient and to quickly clear after a round is fired. CO concentrations exhibit a spike when a round is fired and also quickly decline but will begin to accumulate in the blood of exposed subjects after several rounds.



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In addition to evaluating test data, the Army also provides predictions for proposed training and operational scenarios. The predictions are used for adjusting the proposed training and operational scenarios. The predictions are used for adjusting the proposed firing rates and patterns to keep weapons emissions exposure below the desired levels or verifying the need for use of personnel protective equipment. The predictions are based on the worst-case CO exposure levels per round (expressed in ppm-minutes) from the proposed hatch position/ventilation configuration. The build-up and decay of COHb is calculated over the course of the scenario. The HQ is then calculated with the highest estimated COHb value and highest value of the 15-minute running HCN average from the relevant scenario.

In summary, the Army used three criteria to evaluate the data. If one or both of the 10% COHb and 4.7 ppm HCN limits is exceeded, then the scenario fails and the HQ calculation is essentially not applicable. If COHb and HCN are within acceptable limits, then the HQ calculation is performed as the third criterion. The method employed allowed the HQ results to be consistent with the singular results. Although the Army assumes a linear relation between biological effects and COHb and HCN concentrations that may not be true, it was successful in providing an additional degree of protection above the singular benchmarks.

In 2005, the Department of Defense requested that the National Research Council assess the Army's proposed guidance for assessing the adverse effects resulting from the combined simultaneous exposures to low-levels of CO and HCN. The potential for combined exposures results from routine firing of guns in enclosed but ventilated spaces in the military environment such as armored tanks. In response, the National Research Council convened the Committee on Combined Exposures to Hydrogen Cyanide and Carbon Monoxide in Army Operations under the oversight of the Committee on Toxicology to assess the Army's proposed guidance.

Both CO and HCN are well known intoxicants with established guidelines for safe levels of exposure. Adherence to these guidelines for either of these intoxicants alone would lead to engineering designs, administrative controls, and use of personal protective devices. These controls would ensure an acceptable working environment. Safe levels of exposure to each of the intoxicants may be lower if the combined effects of exposure are additive to more than additive. Hypothetically the design requirements could be predicated based upon the toxicological mechanisms of CO and HCN being independent, additive, or synergistic. The three different scenarios would lead to variation in the resulting designs for ventilation systems, etc.

The committee's Statement of Task is as follows:

A committee of the National Academies' Committee on Toxicology will assess potential toxic effects from combined exposures to low-levels of CO and HCN and evaluate the Army's proposed guidance on assessing combined exposures in Health Hazard Assessments (HHAs) of military systems. The committee will specifically determine the following:

- Does the hazard presented from combined exposure to HCN and CO at low levels warrant their combined assessment or is the individual assessment of each chemical sufficiently protective of health?
- If the combined exposure assessment of HCN and CO is warranted at low levels, is the HQ approach, discussed in the technical context section, a reasonable method of assessment? Should it be modified or improved (i.e., use of a blood CN benchmark instead of the ACGIH TLV-C)?
- Is the approach discussed in the technical context section appropriate or an alternative assessment method should be developed and validated through either field or laboratory study?

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- The committee will also provide recommendations for making improvements in the Army's proposed methodology for assessing these combined exposures. The committee will also provide recommendations that will yield more precise measurements of gases which might be useful in hazard assessment.

### **THE COMMITTEE'S FIRST REPORT**

The committee divided its work into two reports. In the first report due by September 2007, the committee considers whether the hazards presented from combined exposures at low levels warrant a combined assessment. The committee then considers whether the HQ approach is a reasonable approach to assessment of the combined exposures. The committee approached its task by reviewing the toxicity data on CO and HCN singularly and in combination. The committee also heard presentations from representatives of academe, EPA, and ATSDR. The committee relied primarily on published peer reviewed data.

### **THE COMMITTEE'S SECOND REPORT**

In the second report, the committee will determine the following:

1. Is the approach discussed in the technical context section appropriate or an alternative assessment method should be developed and validated through either field or laboratory study?
2. What improvements are needed in the Army's proposed methodology for assessing these combined exposures? The committee will also provide recommendations that will yield more precise measurements of gases which might be useful in hazard assessment.
3. What exposure limit guidelines are appropriate for combined exposures to these chemicals?

## 2

# Mechanisms of Carbon Monoxide and Hydrogen Cyanide Toxicity

Carbon monoxide (CO) binds to reduced hemoglobin with a much higher affinity (200 times greater) than does O<sub>2</sub>. The formation of carboxyhemoglobin (COHb) results in a shift of the oxyhemoglobin (O<sub>2</sub>Hb) dissociation curve (this plots increases in O<sub>2</sub>Hb versus the partial pressure of O<sub>2</sub> [PO<sub>2</sub>]), which inhibits delivery of O<sub>2</sub> from peripheral capillaries into tissues thus producing a decrease in the PO<sub>2</sub> inside cells (tissue hypoxia). Molecular O<sub>2</sub> has numerous functions in cells, but the major function is that it binds to the mitochondrial terminal cytochrome, cytochrome C oxidase (a complex that includes cytochrome a<sub>3</sub>), and accepts electrons that flow through a series of different cytochromes (electron chain transport) coupled to oxidative phosphorylations, formation of adenosine triphosphate (energy formation) and oxidation of reduced compounds like nicotinamide adenine dinucleotide-reduced (NADH) which control the redox state. The cytoplasmic redox state is coupled to many cellular metabolic functions including acid formation (lactic acid). A COHb-evoked decrease in mitochondrial PO<sub>2</sub> below a threshold level limits or inhibits O<sub>2</sub> binding to cytochrome a<sub>3</sub> and electron chain transport. Mechanisms of CO toxicity, therefore, include decreases in energy formation and changes in the redox state which results in cellular metabolic acidosis. CO also binds to reduced cytochrome a<sub>3</sub>, but the binding affinity is so low that this does not occur in intact humans or animals.

The Coburn-Forster-Kane (CFK) equation allows calculation of rates of pulmonary uptake resulting from increases in ambient PCO, and reversal when CO is removed from inspired air, as well as steady state COHb values. The major factors are alveolar ventilation, a term that defines rate of uptake from alveolar gas to pulmonary capillary blood (the pulmonary diffusing capacity). Because CO has a relatively low solubility in water and a low diffusion coefficient, uptake is limited by diffusion, a major reason for the slow uptake of inhaled CO. Following a sudden steady state increase or decrease in inhaled CO at a normal PO<sub>2</sub> and resting ventilation, it takes 4 to 5 hours to reach a steady state COHb. For an exercising human, CO uptake is increased and steady state COHb values are achieved more rapidly. Under conditions where CO exposures are rapidly changing, such as occurs in the enclosed environment of the tank cabin during gun firing, spike changes in CO concentration are buffered both by the high lung volume compared to tidal volumes, as well as the slow uptake into pulmonary capillary blood. Under conditions where ambient CO concentrations are changing rapidly, the use of the CFK equation to calculate COHb levels needs to be verified with blood COHb measurements. There is evidence for effects of small but biologically significant increases in COHb in the range of 5 to 10% saturation on human mental functions including automobile driving reflexes and visual function. In some animal experiments time-dependent tolerance to large increases in COHb occurred and it is possible that military personnel exposed to CO over several days or weeks might develop tolerance. There is evidence for tolerance to CO toxicity, and, of course, altitude hypoxia, so it is likely tolerance to CO would develop. There are no data, human or animal studies, on tolerance to small concentrations of hydrogen cyanide (HCN). Whether or not tolerance is important during combined exposures of CO and HCN at concentrations found in the tank cabin should be given a high priority for future research.

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HCN is a weak acid with a pKa of 9.3; therefore at physiological pH ionization is minimal. Although HCN is a highly reactive compound and is known to form simple salts with alkali earth cations and ionic complexes of varying strengths with metal cations, the major mechanism of toxicity arises from its reversible binding to an iron containing heme group of cytochrome a3 with resulting inhibition of mitochondrial electron chain transport, decreased energy formation and changes in the cellular redox state producing metabolic acidosis. As with O<sub>2</sub>, HCN binds to heme Fe<sup>2+</sup> in reduced cytochrome a3. However, in the presence of O<sub>2</sub> when the iron in cytochrome a3 is rapidly oxidized, its affinity for binding of HCN increases markedly. Threshold HCN concentrations that inhibit mitochondrial electron chain transport are not known. Unlike CO, HCN does not induce tissue hypoxia defined as a decrease in tissue PO<sub>2</sub>. Indeed, under conditions of HCN-evoked inhibition of O<sub>2</sub> consumption, tissue PO<sub>2</sub> must increase, explaining the known decrease of O<sub>2</sub> extraction from capillary blood during HCN poisoning. HCN is miscible with water and has a high effective "solubility" in body fluids and tissues. Thus, ambient HCN is absorbed via the skin as well as the lung. However, pulmonary uptake is most important. Pulmonary uptake is determined by ventilation and blood flow and its high effective solubility in blood. Since the kinetics of HCN uptake have not been accurately determined, our knowledge is based on a few measurements of blood HCN levels in animals and humans which suggest rapid uptake reaching steady state values in minutes rather than hours as occurs with CO. Because some HCN taken up in pulmonary capillary blood binds to methemoglobin (MetHb) forming cyanmethemoglobin, blood levels reflect the presence of MetHb as well as free HCN. Since MetHb content (usually only a few "percent" of total hemoglobin content) is variable in different humans, one can not precisely equate blood content to the partial pressure of HCN which determines peripheral tissue HCN concentrations and should most closely relate to the toxicity of this gas. HCN is rapidly metabolized via several pathways, the most important being the irreversible reaction of HCN with thiosulphate to form thiocyanate. Thiocyanate is then rapidly excreted in urine. Thiocyanate itself has tissue toxicity. The relatively small "percent" of body HCN excreted via the lungs indicates a very low partial pressure of this gas in pulmonary capillary blood and that most absorbed HCN is bound. After humans suffered from smoke inhalation, half of the peak HCN content in blood was lost over 20 to 60 minutes. Unlike the case for CO toxicity there are no reports that relate small HCN exposures, such as measured in tank cabins, to human abilities.

The apparent additivity of CO and HCN toxicity is explained by CO binding to hemoglobin evoking tissue hypoxia plus HCN binding to both reduced and oxidized cytochrome a3. There are possible interactions that occur during combined CO and HCN poisoning which influence their apparent additivity: (a) Does the presence of one of the gases influence pulmonary uptake of the other gas? In animal experiments large concentrations of HCN stimulated carotid body-driven ventilation which would increase uptake of CO. There is evidence that CO, as well, may stimulate the carotid body. (b) Since HCN-evoked inhibition of mitochondrial O<sub>2</sub> consumption results in increases in tissue and mitochondrial PO<sub>2</sub>, HCN might blunt effects of concomitant CO poisoning which operates by evoking decreases in tissue PO<sub>2</sub>.

### **RECOMMENDATIONS**

Tests should be conducted to determine blood COHb and air CO concentrations before and after multiple test firings over several days; pre- and concurrent-exposure to CO from other sources such as smoking and engine exhaust, should be considered in evaluating test exposures. There is evidence for tolerance to CO toxicity, and, of course, altitude hypoxia, so it is likely tolerance to CO would develop. There are no data, human or animal studies, on tolerance to small concentrations of hydrogen cyanide (HCN). Whether or not tolerance is important during combined exposures of CO and HCN at concentrations found in the tank cabin should be given a high priority for future research.

### 3

## A Brief Review of Hydrogen Cyanide and Carbon Monoxide Toxicity

Data on sublethal exposures and time to incapacitation for HCN and CO gases alone and combined are available for experimental animals and humans. However, data addressing subtle differences (e.g. attention deficits, decreases in hand and eye coordination, and decreases in fine movements) in performance, relevant to setting guidelines for human exposure, are sparse. For HCN, inhalation toxicity studies that involve human exposures are old, often anecdotal, and lack analytically measured concentrations. Human exposures with measured concentrations are limited to occupational reports, but these studies lack correlation between exposure concentrations and symptoms. Animal studies were generally conducted at high concentrations and also lack good dose-response information (NRC 2000, 2002). Few studies measured cyanide concentration in the blood.

Concentrations of CO that produce incapacitation are extremely high, and it is difficult to correlate exposure concentrations with COHb formation. Data for combined exposure to HCN-CO involve laboratory animal studies and were generally conducted at high concentrations, i.e., concentrations that produce incapacitation or death. Recent inhalation studies, considered relevant to setting human exposure guidelines for military unique occupational exposures, i.e., performance degradation rather than incapacitation or death, are reviewed below.

### HYDROGEN CYANIDE

Selected occupational monitoring studies show that exposures have been to concentrations up to an average of 10 ppm (Hardy et al. 1959; Maehly and Swensson 1970; El Ghawabi et al. 1975). Although many of these studies did not address health effects, symptoms that were reported appeared attributable to the long-term effect of cyanide on the thyroid gland. In animal studies, times to incapacitation for the monkey ranged from 8 to 19 minutes at concentrations of 156 to 100 ppm, respectively (Purser et al. 1984). A concentration of 60 ppm for 30 minutes had only a non-biologically significant depressive effect on the central nervous system of monkeys (Purser 1984). For the rat, incapacitation ( $EC_{50}$  for loss of righting reflex) occurred at 10 minutes at an exposure concentration of 170 ppm (Levin et al. 1987) and, in another study, at 5 minutes at 184 ppm and at 35 minutes at 64 ppm (Chaturvedi et al. 1995; see also Crane et al. 1989; Sanders et al. 1994). Respective blood cyanide concentrations in the Chaturvedi et al. (1995) study were 2.3 and 4.2  $\mu\text{g/mL}$ . In a third study, incapacitation of rats exposed to 95 ppm HCN occurred at 44 minutes (Hartzell et al. 1985a,b). Lethal ( $LC_{50}$ ) values in the rat range from approximately 500 ppm for a 5-minute exposure to 100-140 ppm for a 60-minute exposure (NRC 2002).

There are studies that show that HCN can be absorbed through the skin, with effects up to and including lethality. For that reason, the ACGIH has used a skin notation since 1961, stating that a significant fraction of the total absorbed dose of HCN can occur via this route to produce systemic effects. However, the committee concludes that exposure from this route of exposure is not likely to be significant

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so as to be considered in the development of allowable concentrations used in the hazard index calculation.

Guidelines for human exposure to HCN have been developed by several agencies. Following a review of the literature on occupational exposures, a National Research Council Subcommittee concluded that a 1-hour exposure to HCN at 8 ppm should cause no more than mild headache in healthy adults (NRC 2000). The American Conference of Governmental Industrial Hygienists Ceiling value, a concentration that should not be exceeded during any part of a working exposure, is 4.7 ppm (ACGIH 1996). The National Institute for Occupational Safety and Health (NIOSH) short-term exposure limit is also 4.7 ppm, and the Immediately Dangerous to Life and Health (IDLH), a 30-minute exposure, is 50 ppm (NIOSH 2007). The Occupational Safety and Health Administration Permissible Exposure Limit (OSHA) is 10 ppm (NIOSH 2007). A guideline value considered safe for the general public includes the 1-hour Acute Exposure Guideline Level-1 (AEG1-1) of 2.0 ppm (NRC 2002).

### **CARBON MONOXIDE**

Data on correlations between exposure concentrations and levels of blood COHb are lacking. A number of sources including Coburn and Forman (1987), WHO (1999), and NRC (2007) reviewed COHb levels in the blood of smokers and symptoms in healthy adults associated with COHb levels in the blood. A physiologic background concentration of 0.5-0.8% is due to endogenous formation. A concentration of 5% COHb may be found in one pack/day smokers, and concentrations of 10-15% in two and three pack/day smokers. Up to 10% COHb has no appreciable effect except shortness of breath on vigorous exertion. Concentrations of 10-20% may result in symptoms such as headache. As concentrations of COHb increase from 30 to 70%, successive symptoms reported are headache, fatigue, dizziness, confusion, unconsciousness, and possibly death. A concentration of 80% COHb is rapidly fatal. Clinical studies with humans indicate that a COHb of about 35-56% are not lethal in healthy adults (NRC 2007). CO levels in homes are usually lower than 9 ppm, but may range up to 30 ppm in homes with wood stoves. Levels inside motor vehicles are generally around 9-25 ppm, but may range up to 35 ppm (NRC 2007).

In a study with cynomolgus monkeys exposed to 900 ppm CO, no signs of intoxication occurred during the first 20-25 minutes (corresponding to COHb of about 16-21%) (Purser and Berrill 1983). At 25 minutes, the animals' performance in a behavioral test was significantly decreased. At 30 minutes the monkeys were lying down. In rodent studies, incapacitation in rats exposed to CO occurred at 5 and 35 minutes at concentrations of 5706 and 1902 ppm, respectively. Blood COHb values were 81 and 71%, respectively (Chaturvedi et al. 1995). Hartzell et al. (1985a,b) reported a higher value, incapacitation at 8000 ppm at 5.1 minutes. Blood levels were not reported. Lethal (LC<sub>50</sub>) data in the rat ranges from a 5-minute value of 10,000-14,000 ppm to a 60-minute value of approximately 4000 ppm (NRC 2007).

Guidelines for human exposure to carbon monoxide include the following: ACGIH 8-hour TLV-TWA of 25 ppm; NIOSH 8-hour TWA of 35 ppm and IDLH of 1200 ppm; OSHA PEL of 50 ppm; 1-hour Emergency Response Planning Guidelines (ERPG-1) of 200 ppm; and the NRC Emergency Exposure 1-hour Guidance Level of 400 ppm.

## 4

# Summary of the Effects of Combined Exposure to Carbon Monoxide and Hydrogen Cyanide and Recommendation for Combined-Exposure Risk Assessment

As discussed previously, certain Army operations such as firing ammunition generate toxic gases. In a confined environment, exposure of Army personnel to these gases could pose a health concern. CO and HCN are the toxic gases of major concern, but analyses show that the time-weight-average concentrations of these two gases are low and generally do not exceed OSHA's permissible exposure limit or ACGIH's Threshold Limit Value for these two gases (Bazar 2006). However, since both compounds can induce hypoxia in tissue and the primary targets are the brain and the heart (Pitt et al. 1979), the U.S. Army is concerned about the potential for the combined effects of exposures to low concentrations of these gases to produce performance decrements. The present assessment of the toxicity of CO + HCN co-exposures could provide a guideline to the Army for evaluating the hazard of exposures in a confined environment and implementing mitigation procedures.

CO and HCN are two of the toxic gases of major concern produced in fires and other combustion events (Esposito and Alarie 1988, Sanders et al. 1994). Smoke can kill victims outright or produce physical incapacitation. Postmortem analyses of blood samples collected from victims revealed that in some victims, inhalation of either CO or HCN could not have been the sole cause of death (Esposito and Alarie 1988). The effects of combined exposure to CO and HCN have been subjected to intensive investigation. Investigations have centered on lethality or incapacitation, and these were assessed by exposing animals simultaneously to both gases at concentrations below their individual effect levels (at concentrations of CO and HCN, which produce no effects), or by studying the shortening of time to death (Td) or incapacitation (Ti) when animals were exposed to the effect levels of both gases. The biological interaction of combined exposure to CO and HCN can be studied by investigating the fractional effective concentrations (FECs) of the two compounds (Crane et al. 1989). If the sum ( $\Sigma$ FEC) is equal or close to 1, the combined effects are said to be additive; if the sum is greater than 1, the effects are said to be synergistic; if the sum is less than 1, the effects are said to be antagonistic or less than additive, or to have no interaction (Crane et al. 1989).

The results of examining the CO + HCN interaction in a very large rodent study conducted by the National Bureau of Standards (NBS) under the sponsorship of the U.S. Army Medical Research Institute led the investigators to conclude that the lethal effects of combined exposure were additive (Levin et al. 1987, 1988). These results were consistent with the conclusions of earlier NBS studies (Levin et al. 1988). In a study similar to the NBS investigations, Esposito and Alarie (1988) also demonstrated that the combined lethal effects of CO + HCN were additive. Additive effects were also observed by Lynch (1975) and Kaplan (1988) in animals exposed to CO + HCN. Instead of testing the combined effects by exposing animals to predetermined durations (T) and gaseous concentrations (C), Yamamoto and

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Kuwahara (1981) exposed rats to various combinations of CO and HCN concentrations and recorded the C x T values when animal deaths occurred; the results also led these authors to conclude that the combined effects were additive.

Several studies were carried out by the Civil Aerospace Medical Institute (CAMI) of the Federal Aviation Administration (Oklahoma City, OK); Sanders et al. (1994) and Chaturvedi et al. (1995) reported that the Ti for combined CO + HCN exposure in rodents was shortened compared with the Ti for individual gas exposures; these observations led the authors to conclude that the combined effects were additive. The results of an earlier study conducted at CAMI led Smith et al. (1974) to come to the same conclusion.

Higgins et al. (1971) observed no additive toxicity in animals exposed to CO followed by HCN. However, additive lethal effects might not have been detected because of the great variation in the data points; the large confidence limits may have prevented detection of the combined biological effects of CO + HCN.

Moore's group concluded that the combined lethal effects in CO-exposed mice given lethal doses of cyanide salt by intraperitoneal injection were synergistic (Norris et al. 1986). However, the fact that the two compounds were given by different routes, resulting in different toxicokinetics, coupled with the fact that the data were not rigidly analyzed. A similar study by Moore's group examining biochemical variables in blood showed that some results were additive and others were synergistic (Moore et al. 1991). Pitt et al. (1979) studied effects of CO and cyanide on cerebral blood flow (CBF) and oxygen consumption in anesthetized and CO-exposed dogs, to which cyanide was given by slow intravenous infusion. The exposure concentrations were comparable to those that produce physical incapacitation. These authors concluded that the combined effects of co-exposure on CBF and cerebral conductance were additive.

The weight of evidence on combined exposures to CO and HCN supports the conclusion that the effects of these toxic gases are additive. However, the exposure concentrations that were used to investigate the combined effects were high in efforts to observe lethality or physical incapacitation. As pointed out above, the U.S. Army is concerned about the potential for the combined effects of exposures to low concentrations of these gases to produce performance decrements. In assessing the toxicity of these two compounds, it is prudent to expect that the additive effects of combined exposure observed with high concentrations would occur in subjects exposed to low concentrations. The hazard quotient or hazard index should be used for calculating the risk of the CO+HCN combined exposures.

$$\text{Hazard Quotient or Hazard Index} = \frac{[\text{CO}]_{\text{exp}}}{[\text{CO}]_{\text{al}}} + \frac{[\text{HCN}]_{\text{exp}}}{[\text{HCN}]_{\text{al}}}$$

where [CO]exp and [HCN]exp are exposure concentrations, and [CO]al and [HCN]al are allowable concentrations.

For the blood, COHb% and the 15-min average [HCN] are the variables measured and 10% COHb and 4.7 ppm HCN are the Army's current allowable values, and the equation becomes

$$\text{Hazard Quotient} = \frac{\text{COHb}\%}{10\%} + \frac{15 \text{ min avg. HCN (ppm)}}{4.7 \text{ ppm}}$$

The appropriateness of the Army's current level of 10% for CoHb and 4.7 ppm for HCN will be evaluated in the committee's final report, which is likely to be finalized in September 2008.



## 5

# Pharmacokinetics and Mathematical Modeling for Assessing Toxicity of Mixtures of Chemicals

Several approaches exist that could be used to evaluate the hazard presented by co-exposure to CO and HCN. It is commonly believed that the chemicals act independently if exposure to Chemical B does not change the severity of the toxic response to a given exposure to Chemical A. This is normally the case if the two chemicals cause their respective toxicities following entirely unrelated modes of action, the physiological, biochemical, or other series of processes that cumulatively cause toxic responses. When the modes of action share common elements, potential for non-independence in the combined dose response curve exists. Where this occurs, the non-independence can take a form of sub-additive, additive, or super-additive (also sometimes called synergistic effects). An additive response generally occurs when the dose response curves to the individual chemicals are parallel and can be added together to predict the combined response. A sub-additive response occurs when the combined response is somewhat less than expected through simple addition but greater than the response expected from either chemical alone. The super-additive response occurs when the combined response is greater than simple addition of the individual responses occurs. Mathematical approaches have been developed for these respective approaches; however, the choice of which approach to use is driven by the review of literature indicating which mode of interaction occurs.

As reviewed earlier in this report, there are several studies that indicate that high doses of HCN and CO may exert additive toxic responses. The underlying mode of action for toxicity of CO and HCN share some common elements; therefore, additive responses are plausible. Few reports suggested super-additive, sub-additive, or independent responses. However, these toxicity studies conducted were generally at very high exposure levels and extrapolation to relatively low levels is required. It is uncertain whether the response to the mixture would be additive at the levels germane to the assessment of combined exposures at low levels. For pharmacokinetic as well as pharmacodynamic reasons, potential for super-additive responses for any mixture is more likely as dose increases; thus, when additive responses may exist at high dose, it is unlikely that super-additive responses would occur in the range of extrapolation. The possibility that independence or sub-additive responses may occur cannot be discounted. However, in light of the weak database of relevant studies, the committee agrees that assuming an additive response is the most reasonable approach.

While other mathematical approaches may exist, by far the most common approach for assessing the combined hazard to chemical mixtures is the “hazard quotient” (HQ), which is also called the “hazard index” (HI). This approach is endorsed for use in applications such as this application by the U.S. Environmental Protection Agency (EPA 2000), American Conference of Governmental Industrial Hygienists (ACGIH 2006), the U.S. Occupational Safety and Health Administration (29 CFR 1910.1000 [2007]), and the Agency for Toxic Substances and Disease Registry (ATSDR 2004). EPA recommends the HQ for mixtures where toxicity is dose additive, which is consistent with the current hazard evaluation. Specifically, EPA (2000) defines a HI for the assessment of combined exposure to components of a mixture as the sum of quotients of exposure to each component divided by the Acceptable Level for that chemical. The generic formula for the HI is:

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$$HI = \sum_{i=1}^n \frac{E_i}{AL_i}$$

where HI = hazard index, E = exposure level to component i, and AL = acceptable level to component i.

If the HI exceeds 1.0, overexposure is indicated. ACGIH, OSHA and ATSDR's formulations are mathematically identical. The assumption that underlies the validity of the use of this model is that the shapes of the dose response curves (or more precisely, the exposure-response curves) are similar.

One unique aspect of the Army's proposed implementation of the HQ is the use of an internal measure of dose (COHb) with an external measure of dose (HCN in air). However, as COHb is a measure of dose rather than response, the combination of an internal and external measure of dose appears to be consistent with EPA guidance.

The Army proposes using the Coburn-Foster-Kane (CFK) equation to calculate carboxyhemoglobin (COHb) levels from CO air data that can be measured in real-time. The real time monitoring of CO provides an exceptional ability to observe the pulsatile spikes (seconds) in the ambient air in the armored vehicle after the cannon is fired. The changes in COHb are much slower, on the order of minutes to a few hours. Factors controlling the rate of change of CO binding to hemoglobin are CO concentration in the air, breathing rate (workload), and the diffusion rate of CO into lung blood. The CFK model has been validated, but as with any model, is not always accurate and typically has not been tested in environments such as in armored vehicles where the air concentration changes dynamically. Due to the fact that COHb changes over a slower time course than air concentrations, use of a running fifteen minute average for air CO would likely be more appropriate although has not been thoroughly analyzed. The committee recommends that the Army assess the validity of the CFK in the context of armored vehicles both using instantaneous measured data and various running averages. This should take into account the typical firing intervals, including the rapid firing sequences and the sequences of infrequent firing that are representative of actual conditions. After firing a round, the gases are at a peak and decline in concentration due to ventilation. When rounds are fired more frequently, exposures increase in parallel. Thus, the exposure is rarely if at all at steady state, and almost always subject to short peaks and declining levels. The ability of the exposure assessment strategy to detect a potential overexposure will therefore depend in large part on the appropriate selection of an averaging interval. The use of running averages for HCN exposure assessment copes with this difficulty by ensuring that a short peak exposure is not missed, i.e., selection of start and stop times for averaging are essentially moot since every configuration is calculated. The use of the internal measure of dose, via the CFK equation's calculation of % COHb likewise copes with the highly intermittent exposure by calculating an integrated measure of dose through the biomarker, wherein the biological process serves as the means of integration.

An alternate to mathematical models such as the HQ is the use of physiologically based pharmacokinetic (PBPK) modeling. PBPK has been used to understand interactions between individual chemicals found in a chemical mixture once the chemical mixture has entered the body of laboratory animals or humans. Inhaled solvents have received the greatest attention with PBPK modeling. Solvent toxicity of a chemical mixture such as central nervous system effects may be governed by the brain: blood partition coefficient for each chemical, while other toxicities are mediated by the formation of reactive metabolites. The use of PBPK models to predict the metabolic clearance of solvent mixtures from the body has received the greatest attention (Haddad et al. 2001) by quantitatively describing the competitive metabolism of each solvent by the same enzymatic system (e.g., P450 isoforms). The impact of solvent mixtures on individual solvent pharmacokinetics is governed by the exposure level of each solvent in the solvent mixture, chemical specific properties of each solvent such as its affinity for the metabolizing enzyme and thermodynamic properties (blood: air and tissue: blood partition coefficients).

While a PBPK model has addressed CO as a byproduct of solvent metabolism, currently there are no PBPK models for CO and HCN mixtures. In the case of CO and HCN, a computational research effort designed to understand possible mechanistic interactions (hypothesis generation) between CO and HCN is warranted.

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The Army reports that exposures to HCN appear to be low most of the time such that HCN may not contribute substantially to the HQ calculation for HCN and CO. By implication, if this is true, then HCN exposures may not warrant assessment. In practice if a chemical is 5% or less of occupational exposure limit as a maximum exposure, the chemical may be considered as minor contributor to the toxicity of a mixture of chemicals. In the current assessment, it is not clear that HCN exposure is low enough to warrant the elimination of monitoring activities, and as long as HCN is monitored, it should be included in the HQ calculation.

## 6

# Appropriateness of Measurement of Blood or Air Levels of Cyanide

The question has been asked if blood cyanide levels would be a more appropriate biomarker of toxicity risk than ambient air cyanide levels. It should first be noted that there is little human data for non-lethal endpoints with good measurements of either air or blood levels (reviewed in ATSDR 2006; NRC 2002). Most of the data on these gases are old and based on chronic occupational exposures to low levels of airborne hydrogen cyanide. In most of these reports symptoms were either absent or minor in nature. There are considerable data on blood cyanide levels in lethalties, primarily from fire victims where carbon monoxide was also present. Most authorities conclude that whole blood cyanide levels >1 mg/L may cause major symptoms or lethality, although reported levels in deaths have ranged from 0.4 to 230 mg/L (Rehling 1967). In summary, there is not good human data relating either blood levels or air levels to relevant endpoints of interest in the present situation.

That said there appear to be several reasons to think that measurement of air levels is a better benchmark to use in assessing the combined toxicity of cyanide and carbon monoxide in a hazard quotient model. First, measurement of hydrogen cyanide in air can apparently be done in real time as judged by the data presented by the military. There are no reported rapid or simple methods for the determination of cyanide in biological fluids (ATSDR 2006). Second, using blood cyanide levels as a biological marker for sub-lethal effects is complicated by the rapid metabolism of cyanide in vivo. The initial half-life of cyanide in humans is estimated to be 20-60 minutes (ATSDR 2006). When levels are very high, as in potentially lethal exposures, there is an initial rapid decline followed by a slow terminal elimination with half-lives ranging from 19-66 hours for the terminal phase (ATSDR 2006). Thus timing of blood sampling would be crucial in interpreting the results. Cyanide undergoes first pass metabolism that further complicates the interpretation of blood levels. Third, there is a problem with which blood fraction to use in analysis. Whole blood (WB) samples are more stable than plasma or serum samples, where there can be a significant decline in cyanide levels in stored samples over a period of hours (Alarie 2002; Ballantyne 1976). In WB most cyanide resides within the red blood cell. Thus WB levels may be a poorer marker of toxicity if obtained before equilibrium has been reached between the plasma cyanide and red blood cell cyanide (Alarie 2002). Plasma cyanide levels appear to correlate better with clinical effects, but suffer from the stability problem, even if stored at appropriate temperature. In any case virtually all authorities recommend that cyanide levels be measured as soon as possible after collection in order to avoid declining values. This would create a significant logistical problem if blood levels were to be used as the biomarker.

Finally it should be noted that factors other than acute environmental exposure may influence cyanide levels measured in blood. The most important of these is smoking history. There are numerous reports in the literature documenting variable increases in cyanide in blood as a result of smoking (Cailleux et al. 1988). There are also reports of increased blood cyanide levels in some populations whose diet includes large proportions of certain cyanogenic foods (Mlingi et al. 1992).

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*Appropriateness of Measurement of Blood or Air Levels of Cyanide*

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In summary, there seems to be no compelling reason why blood measurements of cyanide would be a better predictor of toxicity than measurement of ambient air levels. The added difficulties associated with the measurement and interpretation of blood cyanide levels would suggest that this measurement should not be selected as a routine monitoring methodology.

## 7

# Conclusions and Recommendations

In requesting that this project be carried out, the major concern of the army is the health of personnel during certain military operations, particularly the firing of guns in tanks which can result in the generation of toxic gases. The most relevant of these are carbon monoxide (CO) and hydrogen cyanide (HCN). The questions being asked are whether the adverse effects of these chemicals are additive or synergistic in nature and whether an assessment of their combined risk can be calculated using the hazard quotient approach (HQ) with the equation:

$$HQ = \frac{\text{COHb}\%}{10\%} + \frac{15 \text{ min avg. HCN (ppm)}}{4.7 \text{ ppm}} .$$

If so, this approach would be used to establish limits of exposure for these personnel; that would be important in the design and operation of the tanks.

As noted above, the mechanisms by which CO and HCN exert their toxic effects are multiple, have been well studied as individual agents, and continue to be investigated. While their exact mechanisms and characteristics for absorption, distribution, metabolism and excretion may be different, nevertheless, it is not unreasonable to suspect that the effects of these two chemicals on oxygen delivery and utilization would have an additive effect.

Based on the extensive review of the literature of studies in animals on this interaction, the committee concluded based on the weight of evidence that the effects of the two chemicals were additive. The committee recommends that the hazard quotient approach be utilized. However, one of the limitations in making this conclusion is that most of the studies were carried out in animals using high levels of cyanide, which were greater than 100 ppm or high levels of CO that were in the range of one to several thousand parts per million compared with low levels of interest with cyanide at less than 5 ppm or CO at less than 100 ppm and extreme end points, such as incapacitation or death. Thus there needs to be a caveat in the extrapolation of these results to low levels of exposure (less than 5 ppm for HCN and less than 100 ppm for CO) and more subtle effects such as decrements in performance of the tank crew. While a theoretical case could be made perhaps for a less than additive effect based on, for example, changes in respiration and gas uptake, the committee believes that it is prudent to expect that the additive effect of the combined exposure observed with high concentrations would occur if subjects were exposed to low concentrations (less than 4 ppm for HCN and concentrations of CO producing carboxyhemoglobin [COHb] levels of 10%).

While there have been a number of reports on the interaction of cyanide and CO and the potential interaction has been well recognized in respect to fires, the human literature is not helpful in defining adverse blood levels of cyanide alone or in combination with CO. In most cases, either the exposures were very high and/or the measurements of exposure, particularly cyanide, were questionable. It is difficult to find studies which carefully correlated exposures, blood levels and adverse effects. Furthermore, available studies do not address subtle effects, such as decrements in performance, relevant to setting guidelines for human exposure. While guidelines for limiting exposure to CO and cyanide have

## *Conclusions and Recommendations*

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been published by governmental and professional groups, they have the same limited databases, especially for the interaction.

As noted, since the actions of the two toxicants apparently are additive, the use of the hazard quotient approach proposed by the army is appropriate. The use of the Coburn-Foster-Kane (CFK) model for the prediction of COHb levels related to air concentrations appears to have a solid scientific basis. Since the spikes observed in air levels of CO within the tank during firing scenarios were of such short duration taking into account respiratory rate and tidal volume, the committee concluded that it was not overly concerned about them in comparison with longer, possibly increasing, COHb levels. However, because of conditions where ambient CO concentrations are changing rapidly, it is recommended that the use of CFK equation to calculate COHb levels needs to be verified with blood COHb measurements. It was also noted by the Army that their monitoring data from gun firing scenarios would suggest that cyanide levels would be expected to be below levels of concern most of the time. That, is they would normally not be expected to add substantially to the hazard quotient.

An ancillary question was whether or not the blood level of cyanide, rather than air exposure, should be used in the hazard quotient calculation. The committee concluded that use of a blood level would be problematical based on the lack of good data to support a model such as the CFK model for CO. Furthermore, there is no simple method for determining cyanide levels in blood, and there are a number of technical difficulties in obtaining and handling blood samples. In addition, the rapid metabolism of cyanide makes correlation of air levels and blood levels difficult. Finally there are a host of confounding environmental factors which may influence cyanide levels. The committee, therefore, recommends that the Army continue to use the air level for cyanide rather than a blood level.

Because most studies on the combined toxicity of CO and HCN have been carried out at high concentrations and have focused on lethality and/or incapacitation, which makes extrapolation to the low-levels of exposure and more subtle toxicity end points of interest to the Army is difficult. Therefore, the Army should conduct neurological studies of sensory and motor performance at lower concentrations of HCN and CO.

In conducting its review and evaluation, the committee provides the following additional recommendations for the army to consider. One is to search relevant military documents regarding exposure and biological monitoring that may not be in the open, published literature, especially with regard to cyanide levels. A second is that the Army should consider that, while the binary system is important, other potential exposures such as exposure to diesel combustion products may need to be considered with respect to health of the tank crew.

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## Appendix

### Biographical Information on the Committee on Combined Exposures to Hydrogen Cyanide and Carbon Monoxide in Army Operations

**William E. Halperin** is professor and chairman of the Department of Preventive Medicine and Community Health at the UMDNJ New Jersey Medical School. He received his M.D., M.P.H., and Dr.P.H. from Harvard University. Previously, Dr. Halperin was deputy director of the National Institute for Occupational Safety and Health. His research interests are in occupational medicine, occupational epidemiology, and public health surveillance. Dr. Halperin was a member of the NRC Committee on Risk Assessment Methodology, and served as a member of the Committee on Toxicology's Subcommittee on Spacecraft Water Exposure Guidelines, Subcommittee on Ethylene Oxide, and Subcommittee on Jet Fuels, Panel on Emergency Exposure Guidance Levels. He also served as a member of the IOM Committee to Survey the Health Effects of Mustard Gas and Lewisite. Dr Halperin is certified by the American Board of Preventive Medicine and the American Board of Occupational Medicine. He is currently the chair of the NRC Committee on Toxicology.

**Gary P. Carlson** is professor of toxicology and associate head of the School of Health Sciences at Purdue University. He received his Ph.D. in pharmacology from the University of Chicago. He was chairman of the NRC Subcommittee on Toxicologic Assessment of Low-Level Exposures to Chemical Warfare Agents. He is currently serving on the NRC's Committee on Toxicology. He is chairman of the Society of Toxicology's Board on Publications, and previously served as chairman of its Education Committee. Dr. Carlson is currently the secretary of the Society of Toxicology. He has served on EPA's Joint Advisory Board/Science Advisory Panel Committees on (1) Cholinesterase Inhibition and (2) Cholinesterase and Aldicarb and on the EPA Science Advisory Board's Panel on Drinking Water. Dr. Carlson has also served on the board of scientific counselors of the National Toxicology Program (NTP), and as chair of the NTP Technical Reports Review Committee. He is an associate editor of the Journal of Toxicology and Environmental Health and serves on the editorial board of the Journal of Toxicology.

**Ronald F. Coburn** is professor of physiology at the University of Pennsylvania. He received his M.D. from North Western University in 1957. He has done extensive research on carbon monoxide. He was the chairman of the Panel on Carbon Monoxide from 1972-1975. He received the N.I.H. merit award in 1997. He previously served on the NRC Committee on Medical and Biological Effects of Air Pollutants (1972-1976). Dr. Coburn is on the editorial boards of American Journal of Physiology, Journal of Applied Physiology, Pulmonary Pharmacology, and Lung.

**James E. Dennison** is a Certified Industrial Hygienist and owner of Century Environmental Hygiene LLC, Fort Collins, CO. Dr. Dennison received his Ph.D. in Environmental Health Toxicology from Colorado State University. His doctoral thesis involved physiologically-based pharmacokinetic modeling (PBPK) of complex mixtures of gasoline in rats. He has worked with the National Advisory Committee on Acute Exposure Guideline Levels (AEGs) committee performing PBPK modeling of CNS

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*Combined Exposures to Hydrogen Cyanide and Carbon Monoxide in Army Operations*

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depressants to help establish AEGL values for several chemicals. He performs consulting work as a Certified Industrial Hygienist providing advice on testing, evaluation, and control of chemical agents such as heavy metals, solvents, pesticides, and biological materials. He currently serves as the vice chair of the Biological Monitoring Committee of the American Industrial Hygiene Association.

**Chiu-Wing Lam** is a senior toxicologist at Wyle Laboratories in Houston, TX. He received his Ph.D. in toxicology from the University of Rochester in 1983. He is a diplomate of the American Board of Toxicology. He has drafted numerous toxicological risk assessment documents on spacecraft maximum allowable concentrations (SMACs) since 1990. The SMAC values (for time durations ranging from 1 hr to 180 days) are valuable guidelines to NASA for their space station and space shuttle documents. He also drafted the hydrogen cyanide SMAC document. Dr. Lam has conducted numerous toxicological assessments of payload and utility chemicals used in Space Shuttle and Space Station, providing consultations to NASA flight surgeons, safety engineers, and payload customers on toxicological issues.

**James J. McGrath** is professor emeritus at Texas Tech University Health Sciences Center, Lubbock, TX. He received his Ph.D. from Indiana University in 1968. Dr. McGrath served at EPA's Office of Risk Assessment and was awarded a Silver Star in recognition of work in evaluating the world's health and toxicology literature for relevancy to standard setting for diesel exhausts and worked on Air Quality Criteria for Carbon Monoxide, and also served as a consultant for Indoor Air Quality for the EPA's new campus. He served as a principal author for the EPA's Air Quality Criteria for Particulate Matter for several chapters. He is serving (or has served) on the editorial boards of American Journal of Physiology, Science, Molecular Pharmacology, Journal of Applied Toxicology, Journal of Toxicology and Environmental Health, Toxicology Letters, and CRC Press. He has served on the Society of Toxicology's Inhalation Toxicology specialty section.

**George C. Rodgers** is professor of pediatrics at the University of Louisville, Kentucky. He received his Ph.D. in 1964 from Yale University and received his M.D. in 1975 from the State University of New York, Syracuse. He is board certified in pediatrics and medical technology. He is a member of the National Advisory Committee on Acute Exposure Guideline Levels; he was the chemical manager for the carbon monoxide AEGLs document that was reviewed by the NRC. He also served on the American Society of Safety Engineers, Z390: Accredited Standards Committee on Hydrogen Sulfide Safety Training. He is a fellow of the American College of Medical Toxicology. He is on the editorial board of Poisindex. He was a member of the Firefighters Safety Act Technical Committee. He was president of the American Association of Poison Control Centers. He has served on committees of governmental agencies, such as EPA, ATSDR, and CDC.

**Sylvia Talmage** is a senior toxicologist at Summitec Corporation, a contractor for Oak Ridge National Laboratory. She received her Ph.D. from the University of Tennessee. She is a diplomate of the American College of Toxicology. She served on the NRC Subcommittee for the Review of the Risk Assessment of Methyl Bromide. She previously served for 26 years at Oak Ridge National Laboratory, where she performed numerous toxicological risk assessments for hazardous chemicals. She is the author of numerous acute exposure guideline level (AEGL) documents that were reviewed by the NRC. She also drafted the hydrogen cyanide AEGL document. She has also provided advice to EPA and the U.S. Army on matters related to toxicology and risk assessment.

**Raymond S. H. Yang** is a professor of Toxicology and Cancer Biology, and the leader of the Quantitative and Computational Toxicology Group at the Colorado State University. He received his Ph.D. in toxicology/entomology from the North Carolina State University. Dr. Yang's research focuses on the toxicology of chemical mixtures, physiologically-based pharmacokinetic/pharmacodynamic modeling, and biochemical reaction network modeling. Dr. Yang is the editor/co-editor of several textbooks, including *Toxicology of Chemical Mixtures: Case Studies, Mechanisms, and Novel*

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*Appendix*

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Approaches (1994), Physiologically-Based Pharmacokinetic/Pharmacodynamic Modeling: Principles, Methods, and Applications. Dr. Yang currently serves on the Board of Scientific Counselors for the National Center for Environmental Health, Center for Disease Control and Prevention, and Agency for Toxic Substances and Disease Registry, and the Pacific Northwest National Laboratory Environmental Technology Directorate Review Committee. He was a member of the IOM Committee on Interactions of Drugs, Biologics, and Chemicals in Deployed U.S. Military Forces, and the NRC Safe Drinking Water Subcommittee on Mixtures. He is serving on the NRC Committee on Human Biomonitoring of Environmental Toxicants.