FINAL REPORT

to

STRATEGIC ENVIROMENTAL RESEARCH AND DEVELOPMENT PROGRAM (SERDP)

on

A FIELD PROGRAM TO IDENTIFY TRI CHEMICALS AND DETERMINE EMISSION FACTORS FROM DOD MUNITIONS ACTIVITIES
(CP 1197)

by

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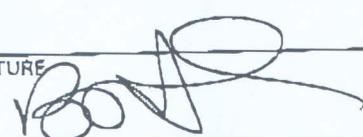if mailed: ATTN: Jennifer Rusk, 1155 Herndon Parkway, Suite 900, Herndon, VA 20170

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EXECUTIVE SUMMARY

This project was initiated in 2001 to respond to SERDP Statement of Need (SON) CPSON-01-01 to develop and apply an approach to measure emission factors of Toxic Release Inventory chemicals from munitions under realistic conditions of outdoor use on testing and training ranges. This need was driven by Title III of the Superfund Amendments and Reauthorization Act (SARA), which established the Emergency Planning and Community Right-To-Know Act (EPCRA) requiring the U.S. Environmental Protection Agency (EPA) to inform communities and citizens of chemical hazards in their areas. Under this legislation certain businesses are required to submit reports each year on the amount of toxic chemicals their facilities release into the environment, either routinely or as the result of accidents. Executive Orders 12856 and 13148 directed previously exempt federal facilities, including military installations, to adhere to EPCRA, including the toxic release inventory (TRI) requirements. A particularly difficult reporting issue for DoD concerns air emissions resulting from use of munitions. DoD facilities, specifically testing and training ranges, need reliable air emissions data for TRI chemicals from munitions activities to (1) meet EPCRA reporting requirements, and/or (2) demonstrate that emissions are below de minimis concentrations and therefore do not need to be reported.

Currently, emission factors for munitions activities have come primarily from burning and detonating energetic materials under enclosed conditions as well as from theoretical calculations using thermodynamic principles. These activities have provided valuable information for emissions estimation: they have indicated the types of chemicals that are emitted and they have provided initial estimates of emission factors. However, regulatory agencies often prefer or even require field verification of emission factors. Consequently, field measurements of emissions under realistic outdoor conditions on a range are desired to enhance the credibility of existing emission factors.

To meet this need, a team from Battelle, Aberdeen Test Center, the Naval Surface Warfare Center, Brookhaven National Laboratory, Pacific Northwest National Laboratory and Vexcel developed, evaluated and applied approaches to determine directly the TRI chemical emissions discharged by munitions on a range under realistic conditions.

To determine an emission factor for a specified chemical, it is necessary to have an estimate of the mass of that chemical released per munitions item or per mass of energetic material in the munitions. The mass of the chemical of interest is usually determined from measurement of the chemical's concentration in the diluted emissions, along with an estimate of the degree to which it has been diluted in the emission cloud. There are four major elements that must be addressed in determining emission factors from munitions:

1. Determination of target chemical concentrations in the diluted emissions.
2. Verification that the combustion process (from weapon discharge or munition detonation) was normal (not second order or dud).
3. Replication to assure representativeness of emission factors.
4. Estimation of dilution at the time of chemical sampling.

We reviewed data on the usage, composition and expected emissions for a large number of munitions items and selected representative munitions for testing. We also reviewed experimental and theoretical studies of munitions emissions and developed a list of 80 target TRI chemicals to measure during the field tests. Chemical measurement tools were then selected that had the capability to measure the target chemicals in the ppt to ppb concentration range, with high specificity, in a moving cloud of a few tens of seconds duration. Our measurement approach utilizes an array of instruments and samplers including highly sensitive and specific real-time air sampling mass spectrometers, whole air collectors, aerosol samplers, and individual monitors for specific chemical species.

The primary methodology we selected to account for dilution of the target chemicals in the emission cloud was carbon mass balance. The carbon balance approach is logical, appears to meet all the requirements for tracking dilution, and has been used successfully in related OB/OD applications. However, it has not been used for estimating emissions during field use of ordnance. Therefore, we also examined three other approaches to account for dilution of the emissions in the expanding plume. Two of these approaches attempted to measure the volume of the emissions cloud during the sampling period. They are aerosol lidar and 3-D photogrammetry. The other approach involved use of an external chemical tracer, xenon, to track dilution.

Two types of tests were carried out to characterize emissions from munitions. The Point of Discharge tests were designed to measure the emissions from the firing of a weapon. A major goal of those tests was a comparison of our measurement methods with standard methods used by the Army for emissions measurements.

The most important component of the project was the outdoor emissions testing on a range, and consequently much of our planning focused on this aspect of the project. The Point of Impact tests required 1) accurate and representative measurements of the concentrations of numerous chemicals in a relatively small, moving cloud of emissions, and 2) accurate estimates of the dilution of the emissions or the volume of the emissions cloud at the time of sampling. Unlike laboratory tests or the Point of Discharge tests, the Point of Impact tests were performed outdoors on a test range, where the meteorology was highly variable. The location of the emissions cloud and the time available for sampling the moving cloud were dependent on wind speed, wind direction and atmospheric stability conditions. Under the best of conditions, sample collection times of just a few seconds were expected. This short sampling time put great constraints on the measurement methods that were employed. These severe constraints required a strategy that would provide the greatest chance of success for measuring TRI chemicals in the expanding, fast-moving emissions cloud with sufficient sensitivity to calculate emissions factors, as well as multiple approaches for measuring the dilution factor and/or volume of the cloud to permit calculation of emission factors. Our approach involved monitoring and sampling the emissions from munitions using the facilities shown in the following figure.

To minimize safety concerns, we employed static detonations in which the ordnance was either detonated on the ground or as an air burst. An aerosol lidar system was positioned to the side of the test area behind a shield, and oriented to scan a vertical plane in front of the sampling towers. Three 10 m "tipping" towers were erected in the prevailing downwind direction from the detonation point. The towers were mounted on three open trailers, so they could be moved to

accommodate changes in wind direction. Three sampling towers were used in order to maximize the probability that the emissions cloud would encounter at least one of the towers, even if there were sudden shifts in wind direction, and to provide sampling from multiple points in the cloud to improve the representativeness of the samples. The towers were hinged to allow the upper portion to be "tipped" down to the ground. Each tower had hardened sample probes mounted on each side of the tower at heights of 7 m and 10 m above the ground. The towers were placed 8 m apart with probes mounted on arms extending 2 m from each side of the towers. This configuration provided 12 sampling probes along a 20 m line that was perpendicular to the wind direction and 20 to 80 m downwind of the detonation point. The sampling system was located closer to the ordnance (~20 m) for small items and further out (~80 m) for the more energetic munitions. Two bombproof shelters contained the sampling and monitoring systems and project scientists.

The Point of Impact study measured emissions of numerous TRI and related chemicals from 10 different types of ordnance. Replicate tests were conducted in order to estimate the reproducibility of the emission factors. Some tests were conducted over two different surfaces, to assess the effects of soil entrainment on emission factors. In addition to carbon balance, three other approaches to account for dilution were examined. The results from these tests provided a comparison of these approaches with the carbon mass balance approach. We found that aerosol lidar is not ideal for determining emission cloud volume primarily because of constraints imposed on the physical location of the lidar due to laser safety issues. The lack of flexibility in repositioning the laser to accommodate changing wind direction was also detrimental to the successful application of aerosol lidar for measuring emission cloud volumes. The photogrammetry approach was straightforward to deploy in the field, although it required significant attention to download and process images after each test, recharge batteries, and reposition cameras. We found this approach to be suitable for future emissions testing requiring cloud volume estimates with the following provisos:

- this method is best suited to relatively opaque emission clouds which are discernable in the photographic images
- this approach should not be relied upon if the use of munitions is likely to cause vegetation fires on the test range.

Based on our experience with the use of xenon as an external gaseous tracer, we found that this approach is well suited for ordnance emissions studies for exploding ordnance. Its use with slow release or dispersed release munitions (e.g. smoke and illumination items) is problematic and requires further study.

The data from the Point of Impact tests show that the reproducibility of emission factors measured under realistic outdoor conditions is variable. For a given chemical, the relative standard deviation (RSD) can range from near zero (perfectly reproducible) to over 100%. Overall, the relative standard deviation was better than 80% for two-thirds of the conditions. When reproducibility was compared for six chemicals that were measured above detection limits for most tests, the emission factor reproducibility was quite consistent, with the average RSD ranging from 47% for copper to 69% for benzene. When averaged across all six chemicals, the most reproducible test/condition was for a 4.2" mortar round fired over soil, with an average RSD of 24%. The least reproducible test/condition was a smoke grenade, with an average RSD of 80%. When averaged across all tests/conditions and all six example chemicals, the RSD was 60%.

During the Point of Impact study we conducted tests to explore the effects of entrainment of soil into the exploding fireball on emission factors. Two tests with a 4.2" mortar round were carried out over soil and two other tests were conducted over a steel plate. The entrained soil resulted in a reduction in the emission factors for oxidized nitrogen compounds, presumably due to a reduction in maximum combustion temperature caused by quenching of chain reactions by the soil particles. At the same time the entrainment of soil resulted in increases in products of incomplete combustion such as benzene, carbon monoxide and 1,3-butadiene.

The results from the Point of Impact study show that the majority of the TRI and related chemicals were not found in the emissions from the munitions we tested. A direct comparison of emission factors from our outdoor tests and indoor chamber (BangBox) tests was possible for 155 mm howitzer illumination rounds. Given all the difficulties in measuring emission factors, both in the BangBox and in outdoor air, the agreement for most of the chemicals is reasonable, i.e. within a factor of five. Some comparisons that stand out are naphthalene, where the BangBox result is almost three times greater than the upper limit from the outdoor tests; carbon disulfide where the chamber tests report 12 times the emissions of the outdoor test; benzene and toluene, which are 3.8 and 4 times higher than the outdoor results; and nitrogen dioxide, which was about 65 times higher in the chamber tests compared to the outdoor tests. Some of these comparisons may be influenced by the way the tests are conducted. Factors such as local oxygen depletion have been cited as potentially affecting emissions from chamber tests, and may have lead to differences in emission factors. Nevertheless, with a few exceptions, the consistency between the two sets of emission factors is quite good.

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August, 2005

1.0 OBJECTIVE

The overall objective of this project is to demonstrate a methodology for measuring emissions of

Toxic Release Inventory (TRI) and related chemicals, and to apply the method to determine

emission factors from munitions activities at a Department of Defense (DoD) facility. In order to

achieve this objective, several specific goals had to be met. One specific goal was to devise a

methodology for measuring emission factors during munitions testing at an outdoor test range.

Another goal was to assemble and test an instrumentation package capable of measuring pertinent TRI chemicals. A third specific goal was to measure "point of discharge" TRI chemical emissions from a variety of munitions used in training activities. A fourth goal was to measure "point of impact" TRI emissions from munitions at an outdoor range under realistic conditions. Our project emphasized munitions used for training and testing activities, because TRI emissions from these activities have received relatively little attention.

2.0 BACKGROUND

In 1986, Congress passed the Superfund Amendments and Reauthorization Act (SARA). Title III of SARA established the Emergency Planning and Community Right-To-Know Act (EPCRA) that requires the U.S. Environmental Protection Agency (EPA) to inform communities and citizens of chemical hazards in their areas. Under Section 313 of EPCRA certain businesses are required to submit reports each year on the amount of toxic chemicals their facilities release into the environment, either routinely or as the result of accidents. The purpose of this reporting requirement is to inform government officials and the public about releases of toxic chemicals into the environment. The reports must be sent to the U.S. EPA and designated state agencies by July 1 each year. Those who fail to report as required are subject to civil penalties of up to $27,500 a day.

Executive Orders 12856 and 13148 directed previously exempt federal facilities, including military installations, to adhere to EPCRA, including the toxic release inventory (TRI) requirements of Section 313. EPCRA does not explicitly exempt military ranges from this reporting requirement. A particularly difficult reporting issue for DoD concerns air emissions resulting from use of munitions. Many DoD sites utilize munitions in activities that could generate reportable emissions. Furthermore, because of the large number of munitions activities, and the numerous DoD sites involved with these activities, the accurate reporting of TRI emissions is a very formidable task. DoD facilities, specifically testing and training ranges, need reliable air emissions data for TRI chemicals from munitions activities to (1) meet Section313 reporting requirements, and/or (2) demonstrate that emissions are below de minimis concentrations and therefore do not need to be reported.

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Currently, emission factors for munitions activities have come primarily from burning and detonating energetic materials under enclosed conditions as well as from theoretical calculations using thermodynamic principles. The experimental studies have included the BangBox tests conducted at Sandia National Laboratories[1] and Dugway Proving Grounds[2,3], underground detonations at the Department of Energy's Nevada Test Site[4], and recent extensive tests performed by Aberdeen Test Center and Dugway Proving Ground for the Army Environmental Center.[5-7] Key theoretical studies have been done using software generated at the U.S Naval Surface Warfare Center at Indian Head, Maryland.[8] Such information has been a very valuable starting point for emissions estimation, because it suggests the types of chemicals that are emitted and provides an initial estimate of emission factors.

However, there have been some concerns raised about the above data. First of all, the computer modeling has been criticized because it is based upon theoretical calculations. The experimental results have been criticized because (1) for some tests the small size of the charge may not provide a representative example of the reaction products formed under realistic field conditions and (2) the volume of air used in chambers may not be sufficient to accurately simulate conditions in the open field. Regulatory agencies often prefer or even require field verification of emission factors. The class of weapon that the munitions are used in can influence actual emissions, and external factors, such as meteorological conditions, can also affect results. For these reasons, field measurements of emissions from a variety of munitions activities would be very useful to enhance the credibility of existing emission factors. However, collection of actual field samples from a detonation plume is very difficult. Several attempts have been made to launch balloons or fly airplanes through the plume to capture meaningful data, with only very limited success.

This report describes activities and results of a project to develop and apply methodology to measure emission factors from outdoor munitions testing and training activities. During the first year of the project, we laid the foundation for conducting this program; we reviewed munitions and selected priority items for testing based on usage in training and testing, chemical composition, mass of energetic material, etc.; we also reviewed literature on previous emissions tests of munitions, and identified 124 chemicals and chemical classes from the TRI list that are

potential emissions from munitions use; we performed atmospheric modeling to estimate the dimensions of the expected emissions cloud under various weather conditions; we made some preliminary selections of measurement methods; we carried out detailed planning for a field test of four methods to estimate the dilution of the emission cloud or the volume of the cloud at the time of sampling; and we successfully completed a field test of those four methods at Aberdeen Test Center. During the second year of the project, we solidified key elements for carrying out emission factor calculations. We developed plans for the two general approaches (Tracer and Volume) that can be used to account for the dilution of the emissions, and applied those approaches to the data that were collected during the first year field tests of methods to determine emission cloud volume. We implemented two tracer methods (carbon mass and xenon) and two volumetric methods (aerosol lidar and 3-D photogrammetry). Results from these four techniques showed consistency and demonstrated that plume volumes could be determined within a factor of two or better. This degree of consistency provided confidence that these approaches could be used to compute emission factors for TRI chemicals during outdoor Point of Impact (POI) testing. Also, during Year 2, we selected, optimized and evaluated the measurement methods to be employed for the emission measurements studies, and we continued planning for two different emissions measurement tests. These tests are referred to as the Point of Discharge tests and the Point of Impact tests. We completed the Point of Discharge campaign during the second year of the project. The third year of the project was devoted to instrument testing, preparation and conduct of for the outdoor Point of Impact tests.

3.0 MATERIALS AND METHODS

3.1 Introduction to Approach

The ultimate goals of this project are to develop and validate a methodology for measuring TRI chemicals emitted by munitions used on training and testing ranges, to characterize the performance of the methodology under actual field conditions, and to develop emission factors for TRI chemicals for a set of priority munitions items. Two types of tests were planned to characterize emissions from munitions. The Point of Discharge tests are designed to measure the emissions from the firing of a weapon. These tests were conducted in September 2002 in an

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indoor facility, where the emissions were captured and sampled over a 20 minute period of time. The Army Environmental Center conducts such tests at the Aberdeen Test Center facilities, and our point of discharge tests were piggybacked on their tests.[9] The other type of testing involved measurement of emissions of ordnance items at their Point of Impact. These tests were conducted on a test range at the Aberdeen Proving Ground.

The most important component of the project is the outdoor emissions testing on a range, and consequently much of our planning has focused on this aspect of the project. The point of Impact tests require 1) accurate and representative measurements of the concentrations of numerous chemicals in a relatively small, moving cloud of emissions, and 2) accurate estimates of the dilution of the emissions or the volume of the emissions cloud at the time of sampling. Unlike previous BangBox tests or the point of discharge tests, the Point of Impact tests were performed outdoors on a test range, where the meteorology was highly variable. The location of the emissions cloud and the time available for sampling the moving cloud were dependent on wind speed, wind direction and atmospheric stability conditions. Under the best of conditions, sample collection times of just a few seconds were expected. This short sampling time put great constraints on the measurement methods that were employed. Considerable effort was devoted to understanding the behavior of an emissions cloud following the detonation of an ordnance item, devising a strategy that would provide the greatest chance of success for measuring TRI chemicals in that cloud with sufficient sensitivity to calculate emissions factors, and developing approaches for measuring the dilution factor and/or volume of the cloud to permit calculation of emission factors.

In the following sections we describe some of the considerations that led to our experimental approach for determining emission factors for TRI chemicals from munitions under realistic use conditions.

3.2 Important Elements for Emission Factor Calculation

To determine an emission factor for a specified chemical, it is necessary to have an estimate of the mass of that chemical released per munitions item or per mass of energetic material in the

munition. The mass of the chemical of interest is usually determined from measurement of the chemical's concentration in the diluted emissions, along with an estimate of the degree to which it has been diluted in the emission cloud. There are four major elements that must be addressed in determining emission factors from munitions:

1. Determination of target chemical concentrations in the diluted emissions.
2. Verification that the combustion process (from weapon discharge or munition detonation) was normal (not second order or dud).
3. Replication to assure representativeness of emission factors.
4. Estimation of dilution at the time of chemical sampling.

The next four subsections of the report describe our approach for obtaining the data to address these four elements.

3.2.1 Measurement of Target Chemicals

Measurement of concentrations of the target TRI chemicals in the emissions cloud is a primary requirement for determining emission factors. We reviewed potential measurement methods and selected methods that are compatible with our sampling approach and that provide sensitivity sufficient to measure the target chemicals in dilute emission clouds. We selected methods that have the potential to measure 80 of the TRI chemicals we identified as possibly emitted by munitions. These methods are discussed in Section 3.4.

3.2.2 Verification of Normal Weapon Operation

We wish to produce emissions factors that are representative of normal operation of ordnance items. One source of non-representative behavior is low order detonation. Low order detonations could produce unrealistic and non-representative levels of emissions. The outdoor tests were set up by an experienced ordnance technician, who witnessed each test and examined the site after each test for evidence of improper ordnance operation. We also video taped each test from multiple angles and reviewed the tapes for visual evidence of improper discharge.

3.2.3   Replication to Assess Variability

Another important element in our strategy for determining emission factors was an assessment of the accuracy and precision of the data used to calculate the factors. The accuracy of the measurement methods was assessed through comparisons with standard methods (e.g. EPA or NIOSH) methods) during the Point of Discharge tests, and by measuring a small number of the chemicals by more than one measurement method during the Point of Impact tests. The precision was assessed through replication of each munitions test.

3.2.4   Determination of Dilution Factor/Plume Volume

There are two general approaches that can be used to account for dilution of the emissions. We will refer to the two approaches as the Tracer Method and the Volume Method. Each approach imposes different requirements on the sampling strategy. Because neither approach is expected to be valid under all circumstances, we implemented both approaches for the outdoor Point of Impact tests.

The Tracer Method requires measurement of a tracer chemical in the dilute plume at the same time and position as the sample collected for the target chemicals. The tracer may be a material that is initially present in the ordnance, the combustion product of a material that was initially present, or a material artificially added to the emissions cloud. The mass of the tracer released must be known, and the tracer must be distributed and must behave similarly in the dispersing plume to the target chemical whose emission factor is to be estimated. Finally, the tracer mass must be conserved; either the chemical must be inert or its degradation products must be measurable. If an artificial substance is added to the cloud as a tracer, it is necessary that it be introduced in such a manner to assure that it is mixed throughout the cloud in the same manner as the target chemicals, that is, the relative distribution of the target chemical and the tracer should be nearly constant throughout the cloud. If these conditions are met, then the ratio of the target chemical to the tracer can be used, together with the emitted tracer mass, to estimated the emitted mass of the target chemical (Equation 1).

$$\frac{[A] - [A_{back}]}{[T] - [T_{back}]} \, x \, M_T = M_A \qquad\qquad (1)$$

where [A] is the measured concentration of the target chemical, [A_{back}] is the atmospheric background concentration of A, [T] is the measured tracer concentration in the plume, [T_{back}] is the atmospheric background concentration of the tracer, and M is the emitted mass. The tracer approach does not require an estimate of the plume volume. Obviously, the key to the success of the tracer approach is not only in meeting all of the conditions noted above, but also in selecting a tracer that can be measured accurately at the levels present in the diluted plume.

The Volume Method involves measuring the average concentration of the target chemical in the cloud (e.g. in µg per m^3) and estimating the volume of the cloud through external means. These two pieces of information yield the mass of target chemical in the cloud, from which an emission factor can be calculated. This approach requires an estimate of the mean concentration of the target chemical in the cloud, so it is important to sample enough locations within the cloud to estimate a concentration that is representative of the entire emission cloud. Estimation of the volume of the emissions cloud is not straightforward, and one method may not be suitable for all emissions clouds.

Because there is uncertainty about the accuracy of these two approaches, and because neither approach is expected to be valid under all emissions scenarios, we implemented two variations of each approach. Under the Tracer Method we evaluated and applied both a carbon mass balance method and an external chemical tracer method employing xenon as the tracer. Under the Volume Method we tested and implemented both three-dimensional photogrammetry and aerosol lidar to estimate cloud volumes. These four techniques are discussed in the following sections.

3.2.4.1 Carbon Mass Balance. The U.S. Army demonstrated the usefulness of the Carbon Mass Balance approach[2] for estimating the plume volume during open burning/open detonation activities. Essentially, this is a chemical tracer approach which makes use of the combustion products of carbon in the ordnance item. The assumptions underlying this approach are:

1. All of the carbon in the munitions item is converted to gaseous CO_2, CO, and hydrocarbons.
2. The carbon in the munitions item is conserved, i.e. the carbon may change chemical form during the combustion, but the total mass of carbon is unchanged.
3. The carbon combustion products are distributed in the plume similarly to the other emitted chemicals whose emission factors are to be measured. That is, while the absolute concentrations may vary dramatically within the plume, the relative concentration of target chemical to the sum of carbon combustion products is nearly constant.

For purposes of estimating emission factors from use of munitions during military training and testing activities, the assumptions are expected to be valid for most activities. With one exception, good carbon mass balances were obtained ($100 \pm 18\%$) for 23 items studied under OB/OD conditions.[10] One circumstance which may cause errors in the carbon mass balance approach is combustion which converts a significant fraction of the carbon to soot. Soot may be lost from the plume by settling or deposition, so the assumption of mass conservation in the plume may be violated. But in any case, because soot is generally not quantified in these tests, if a significant amount of soot is produced, then emission factor estimates will be higher than actual values. This is most likely to occur in confined detonations where the formation of a fireball is inhibited.[11] Thus, soot formation could cause errors in the carbon mass balance approach for tests on soil, some of which are planned for our Point of Impact tests.

The emission factor for a target chemical, A, using the carbon mass balance approach is given by:

$$EF(A) = M_c \; x \; \frac{([A]_p - [A]_{back})}{([CO_2]_p - [CO_2]_{back}) + ([CO]_p - [CO]_{back}) + ([HC]_p - [HC]_{back})} \quad (2)$$

where

EF(A) is the emission factor for target chemical A

M_c is the mass of carbon in the ordnance item

[A] is either the concentration of target chemical in the plume (p) or background air (back)

[HC] is the concentration of organic carbon in the plume (p) or background air (back). The concentrations of the carbon species are in mass of carbon per unit volume of air.

To put the carbon mass balance approach into practice, it is necessary to measure the CO_2, CO, and volatile organic species concentrations in the emissions cloud and in background air.

We implemented the carbon mass balance approach in two ways for the Point of Impact studies. We monitored the carbon-containing gases CO_2, CO, and total hydrocarbons in the plume in real time, and we collected integrated samples of plume air in Tedlar bags and analyzed the bag samples for the carbon species.

We considered carbon mass balance to be the primary approach for emission factor calculations and the standard against which the other approaches were judged. Carbon mass balance was selected as the primary approach for estimating emission factors for the following reasons:

- This approach was successfully demonstrated for related applications[10].
- It is based on the ratio of target chemical to carbon in the emissions cloud, and does not depend on collecting a representative sample of the cloud, as required by the Volume Approaches.
- Because the carbon is present in situ in munitions, the carbon products are expected to be distributed in the cloud similarly to the target chemicals. The requirement for similar distribution is difficult to assure with an external tracer, especially for slow-release munitions (e.g. smoke and illumination items) or those that distribute their releases over an area (e.g. certain smoke releasing items).

3.2.4.2 Xenon Tracer. As described above, carbon is naturally present in most munitions items and can be used as a dilution tracer. Because carbon is not present at significant levels in some munitions, and because the carbon mass balance could be in error for munitions or conditions that produce substantial amounts of soot, a separate chemical tracer was also employed to

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account for plume dilution. The approach for this external chemical tracer is to release an accurately known amount of the chemical at the point of detonation and then measure the resulting concentration downwind at the sampling location. A fast response instrument (e.g. PAH monitor) connected to the sampling system was used to indicate the presence of the plume and triggered the collection of a time-integrated Tedlar bag sample for the subsequent analysis of chemical tracer gas. The tracer sampling time corresponds to the amount of time that an elevated signal is observed by the fast response analyzer.

Several candidate chemical tracer gases have been considered. Sulfur hexafluoride (SF_6) is one of the most widely used tracer gases for determining ventilation rates and air movement of plumes. However, for this study, we were concerned that SF_6 would partially dissociate within the fireball of the detonation. Carbon tetrafluoride (CF_4) was also considered. Although it is more stable than SF_6, there is still concern that partial dissociation will occur and thus limit its usefulness. Furthermore, CF_4 is very difficult to measure when using standard gas chromatographic techniques.

Xenon and krypton were considered as candidate tracers because they are both inert gases and will be stable within the fireball of the detonation. Xenon has an atmospheric background concentration of ~0.09 ppm, while krypton has a background concentration at the low ppm level. Analytically, xenon is more easily resolved by gas chromatographic techniques. Although the cost per liter for xenon gas is ten times more expensive than krypton gas, the atmospheric concentration level of xenon gas is approximately twenty times lower than krypton. Because of their relative atmospheric background levels, the amount of xenon needed for the initial release during the detonations of the various ordnances is twenty times smaller than krypton. Based on this analysis, xenon was chosen as a second tracer to estimate emission factors for TRI chemicals. Our approach was to release an accurately measured volume of xenon gas at the point of detonation and then measure the resulting concentration downwind at the sampling tower. The assumptions underlying this approach are:

1. Xenon gas will be distributed in the plume similarly to other emitted chemicals from the detonation.

2. Xenon gas will be conserved throughout the combustion and dilution processes.

The modeling results that are discussed in Section 3.4 show predicted downwind tracer concentrations as a function of the following variables: initial puff size, atmospheric stability and wind speed. These model calculations were carried out using an assumed release of one gram of xenon (the gas density of xenon is 5.9 grams per liter). In order to assure that adequate concentrations of xenon above background are present at the downwind sampling location, a minimum centerline concentration of at least 1 ppm was targeted. The initial volume of xenon gas needed to achieve this target concentration will vary since the downwind concentration will be primarily a function of atmospheric stability and wind speed. Model predictions suggested that between 1 and 10 liters of xenon gas should be released per test run.

3.2.4.3 Photogrammetry. Defining the emission cloud dimensions during the outdoor Point of Impact tests is a key part of this study. Three-dimensional photogrammetry is one of the four approaches we implemented to address this problem. The approach involves using a multiple angle photographic system and software to create dimensionally accurate 3D CAD models of the emission clouds. The diagram shown below (Figure 3.1) is a top view of an irregular plume, captured from a number of viewpoints. Since the plume is not stationary it is important to be able to synchronize the captured images from the various viewpoints and to determine the position of the cameras relative to the plume and to each other. Using scale markers placed in the area of the sampling tower (the little circles shown below) the relative camera positions and the bounding emission cloud dimensions can be determined.

An example of the synchronized input images is shown in Figure 3.2 from a test we conducted early in the project to evaluate the four plume dimensioning approaches. These images were taken at the instant of detonation of a C4 charge. Our sampling tower is seen in the four images. Multiple angle views of the emissions cloud from this C4 detonation are seen in Figure 3.3 The very irregular shape of the evolving cloud is clearly pictured.

The photogrammetry approach is best suited for visible emissions clouds, that is clouds having moderate or higher opacity. In this sense it is complementary to the lidar approach described in
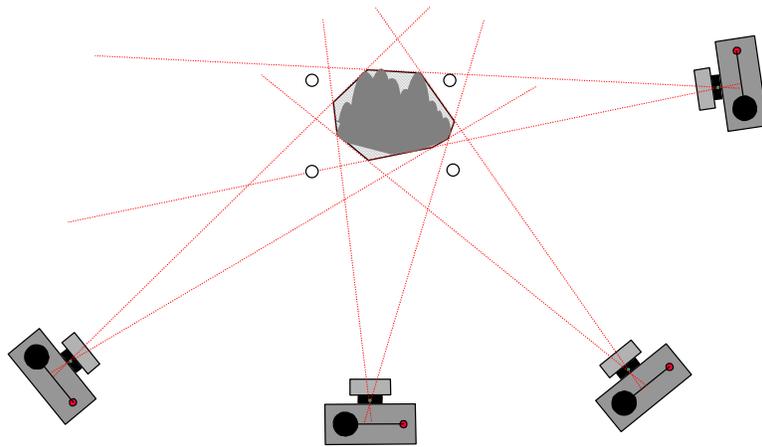
Figure 3.1. Illustration of Photogrammetry Approach for
Estimating Emissions Cloud Volume

Figure 3.2. Multiple-Angle Views of the Instant of Detonation for a C4 Charge

Figure 3.3. Multiple-Angle Views of Emission Cloud from C4 Detonation

the next section. Because different munitions can produce emissions of vastly different opacities, both photogrammetry and lidar approaches were evaluated as Volume Methods during this project.

3.2.4.4 Aerosol Lidar. The second Volume Method evaluated during the project was aerosol lidar. Aerosol lidar was employed for the estimation of the volume of the emissions cloud, as well as to provide information on the internal non-homogeneous structure of the emissions plumes. The aerosol lidar measurements utilized the fact that the emissions cloud possesses a different aerosol burden than that of the surrounding background atmosphere. This abrupt aerosol loading change results in a large transient increase in the strength of the elastically scattered laser light. This range-resolved signal enabled cross-sectional mapping of the developing plume's diameter. As noted earlier, lidar is best suited to low to moderate opacity

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clouds, because of the necessity for the laser beam to penetrate to the far side of the cloud. Thus the method is best suited to situations where photogrammetry is problematic, and vice versa.

3.3 Selection of Target Toxic Release Inventory (TRI) Chemicals

There are over 600 chemicals that are reportable as TRI chemicals. However, not all TRI chemicals are expected to be emitted by munitions activities. In selecting the target TRI chemicals to measure during this project, we first narrowed the list to those TRI species that may be emitted by munitions during training and testing activities. Our goal in selecting target chemicals was to include all TRI chemicals that might reasonably be expected to be emitted by munitions. We then selected measurement methods with the capability to measure as many of the target chemicals as possible. The approach used for down selecting TRI chemicals has involved determining which chemicals have been identified in past studies, by reviewing available literature on munitions firing studies, exploding ordnance studies, open burning-open detonation studies, and bang-box tests. The extensive data base developed by Mitchell and colleagues[10,11] at EPA has been a rich source of information. We prepared a listing of all emitted chemicals that have been reported in the emissions from munitions testing. This list was then compared to the current (March 2001) list of TRI chemicals (available at www.epa.gov/tri/chemicals/htm) which contains 582 individual chemicals and 30 chemical categories. Each TRI chemical that has been reported in previous studies of munitions emissions has been included on our list of potential target chemicals. Some of these chemicals were not quantified by earlier studies and others were present at very low levels. We included such chemicals on our initial target list with the philosophy that our emissions measurement program should not prejudge the emission factors for these "trace" emissions, but rather be exhaustive in the search for and quantification of any TRI-listed chemical for which appropriate measurement methods exist. Our list of target chemicals is provided in Table 3.1. It includes 123 chemicals and chemical groups. Two of the entries represent groups of chemicals:

1. Dioxin and dioxin-like compounds (17 specific chemicals)
2. Polycyclic aromatic compounds (21 specific chemicals).

Table 3.1. Initial List of Target Chemicals for TRI Screening

Compound	CAS Number	Reason Listed	Reference
acetaldehyde	75-07-0	A	12, 13, 10, 14, 15
acetonitrile	75-05-8	A	10, 13, 14
acrolein	107-02-8	A	3, 13
acrylonitrile	107-13-1	A	10, 13, 15, 16, 17
allyl alcohol	107-18-6	A	16, 17
allyl chloride	107-05-1	A	10
aluminum	7429-90-5	A	14, 18
4-aminobiphenyl	92-67-1	A	10
aniline	62-53-3	A	10
anthracene	120-12-7	A	10, 13, 15, 17
antimony	7440-36-0	A	13, 14
arsenic	7440-38-2	A	3, 13, 14
barium	7440-39-3	A	13, 14, 17, 18
benzene	71-43-2	A	3, 10, 12, 13, 14, 15, 16, 17
benzidine	92-87-5	A	10
benzyl chloride	100-44-7	A	10
beryllium	7440-41-7	A	13
biphenyl	92-52-4	A	10
bromoform	75-25-2	A	10
bromomethane	74-83-9	A	10
1,3-butadiene	106-99-0	A	3, 10, 13, 17
cadmium	7440-43-9	A	13, 14
carbon disulfide	75-15-0	A	13, 16, 17
carbon tetrachloride	56-23-5	A	10, 12
carbonyl sulfide	463-58-1	A	13, 16
chlorine	7782-50-5	A	14
chlorobenzene	108-90-7	A	10, 12, 13, 17
chlorobenzilate	510-15-6	A	10
chlorodifluoromethane	75-45-6	A	10
chloroethane	75-00-3	A	10, 12, 14
chloroform	67-66-3	A	3, 10, 12, 13
chloromethane	74-87-3	A	10, 13, 18
chloroprene	126-99-8	A	10
chromium	7440-47-3	A	13, 14, 17, 18
cobalt	7440-48-4	A	13
copper	7440-50-8	A	3, 13, 14, 17, 18, 20
o-cresol	95-48-7	A	19
m-cresol	108-39-4	C	
p-cresol	106-44-5	A	17
cyclohexane	110-82-7	A	16, 17
cyanide Species		A	16, 17
diallate	2303-16-4	A	10

Compound	CAS Number	Reason Listed	Reference
dibenzofuran	132-64-9	A	10, 14, 18
1,2-dibromoethane	106-93-4	A	12
dibutyl phthalate	84-74-2	A	13
1,2-dichlorobenzene	95-50-1	A	10, 12, 14
1,3-dichlorobenzene	541-73-1	A	10, 12
1,4-dichlorobenzene	106-46-7	A	10, 12, 19
3,3'-dichlorobenzidine	91-94-1	A	10
1,2-dichloroethane	107-06-2	A	10
2,4-dichlorophenol	120-83-2	A	10
1,2-dichloropropane	78-87-5	A	12
diethylphthalate	84-66-2	A	14
3,3'-dimethylbenzidine	119-93-7	A	10
2,4-dimethylphenol	105-67-9	A	10
dimethylphthalate	131-11-3	A	14
o-dinitrobenzene	528-29-0	C	
m-dinitrobenzene	99-65-0	A	13
p-dinitrobenzene	100-25-4	C	
4,6-dinitro-o-cresol	534-52-1	C	
2,4-dinitrophenol	51-28-5	A	10, 14
2,4-dinitrotoluene	121-14-2	A	10, 13, 19
2,6-dinitrotoluene	606-20-2	A	10, 13
dioxin and dioxin-like compounds		A	10, 13, 14
diphenyl amine	122-39-4	B	
ethylbenzene	100-41-4	A	10, 12, 13, 15, 16, 17
ethylene	74-85-1	A	3, 10, 13
formaldehyde	50-00-0	A	13, 15, 20
formic acid	64-18-6	C	
hexachloroethane	67-72-1	B	
hydrochloric acid	7647-01-0	A	14
hydrogen cyanide	74-90-8	A	13, 14, 15, 16, 17, 21
isosafrole	120-58-1	A	10
lead	7439-92-1	A	3, 13, 14, 17, 18, 20
manganese	7439-96-5	A	13
mercury	7439-97-6	A	3, 13, 14
methacrylonitrile	126-98-7	A	16, 17
methyl ethyl ketone	78-93-3	A	17
methyl tert-butyl ether	1634-04-4	A	10
naphthalene	91-20-3	A	3, 10, 13, 14, 15, 16, 17, 18
nickel	7440-02-0	A	13
nitric acid	7697-37-2	A	13
nitrobenzene	98-95-3	A	10, 13, 16, 17, 19
nitroglycerin	55-63-0	B	
2-nitrophenol	88-75-5	A	3, 10, 14, 18
4-nitrophenol	100-02-7	A	10, 14

Compound	CAS Number	Reason Listed	Reference
5-nitro-o-toluidine	99-55-8	A	10
N-nitrosodiethylamine	55-18-5	A	10
N-nitrosodimethylamine	62-75-9	A	10
N-nitrosodiphenylamine	86-30-6	A	10
N-nitrosomorpholine	59-89-2	A	10
N-nitrosopiperidine	100-75-4	A	10
m-xylene	108-38-3	C	
o-xylene	95-47-6	A	12, 13
p-xylene	106-42-3	C	
pentachloroethane	76-01-7	A	10
pentachlorophenol	87-86-5	A	10, 19
phenol	108-95-2	A	10, 13, 14, 16, 18
phosphorous (yellow or white)	7723-14-0	A	14
polycyclic aromatic compounds		A	13, 16, 17
pronamide	23950-58-5	A	10
propylene	115-07-1	A	10, 13, 14
pyridine	110-86-1	A	10, 15, 16, 17, 19
quinoline	91-22-5	A	16, 17
safrole	94-59-7	A	10
selenium	7782-49-2	A	13, 14
silver	7440-22-4	A	3, 13, 14
styrene	100-42-5	A	3, 10, 12, 13, 15, 16
1,1,2,2-tetrachloroethane	79-34-5	A	10, 12
tetrachloroethylene	127-18-4	A	16
thallium	7440-28-0	A	13
toluene	108-88-3	A	10, 12, 13, 15, 16, 17
o-toluidine	95-53-4	A	10
1,2,4-trichlorobenzene	120-82-1	A	10, 12
1,1,1-trichloroethane	71-55-6	A	10, 12. 17
1,1,2-trichloroethane	79-00-5	A	10, 12
trichloroethylene	79-01-6	A	10, 13, 17
2,4,5-trichlorophenol	95-95-4	A	10, 18, 19
2,4,6-trichlorophenol	88-06-2	A	10, 14, 19
1,2,4-trimethylbenzene	95-63-6	A	12, 13
vinyl acetate	108-05-4	A	10
vinyl chloride	75-01-4	A	10
xylene (mixed isomers)	1330-20-7	A	16, 17
zinc	7440-66-6	A	14, 17, 19

A Reported from previous emissions study.

B Potential munitions constituent.

C Potential combustion or transformation product.

Note: Chemicals in bold print are from EPA's highest priority list of 33 urban air toxics.

The second column of Table 3.1 gives the CAS number of the chemical. The third column provides a code giving the rationale for that chemical's inclusion on the list. Most are listed because they were reported in one or more previous emission studies. A few are included because they are constituents of some munitions, and therefore have the potential to be emitted, or because we consider them to be potential combustion or transformation products of munitions constituents. The fourth column lists the reference to the measurement of the chemical in munitions emissions.

The chemicals listed in Table 3.1 represent those TRI chemicals which have been measured in munitions emissions or which are likely to be present in the emissions. The list is extensive and covers a wide range of chemicals, both in terms of the nature of the chemicals and their potential risk to human health and the environment. It is desirable to measure emission factors for as many of the chemicals in Table 3.1 as possible. However, it is not cost effective to attempt to measure every chemical on the list. Therefore, we prioritized the target chemicals in order to focus on the most important species. In this regard we adopted EPA's prioritization of the most important hazardous air pollutants. EPA has selected 33 highest priority chemicals from the list of 188 hazardous air pollutants. These chemicals, known as the "33 Urban Air Toxics" were selected because of the risk they pose to human health, and high priority is being given to reducing this risk by controlling the emissions of these chemicals. Twenty-eight chemicals in Table 3.1 are listed as high priority Urban Air Toxics.[*] These chemicals are listed in bold in Table 3.1. These chemicals were given highest priority as we selected measurement methods for the Point of discharge and Point of Impact testing programs.

3.4 Measurement Methods

As part of the process to select appropriate measurement methods, we estimated the magnitude of emission factors that should be detectable using different measurement techniques. The dispersion of a gram of neat material was modeled using the Hazard Prediction Assessment Capability model (HPAC) assuming a range of puff sizes, wind speeds, receptor locations, and

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[*] Anthracene and naphthalene are included, along with polycyclic aromatic compounds, as members of the polycyclic organic matter Urban Air Toxics designation.

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meteorological stabilities. The results of this modeling allowed concentration estimates for each of the target analytes to be calculated at the various receptor sites. For example, Figure 3.4 illustrates the expected on-axis concentration profiles (in ppb) at 20, 50, 75, and 100 meters downwind of the release of 1 gram of neat material. Figure 3.5 illustrates the concentrations on-axis as well as 2,5, and 10 meters off-axis, at receptor locations 20 meters downwind. The downstream concentration estimates were used along with the estimated detection limits for the respective measurement techniques to determine the approximate amount of each target analyte that would need to be released from the detonation in order to be detected at the various receptor locations. Based on these estimates of the amount of material emitted and the amount of explosive material in the various munitions, the emission factors necessary to generate the downstream concentrations were calculated, in grams of analyte emitted per gram of explosive material.

These estimated emission factors were compared with available literature values for emissions from similar munitions to assist our selection of sampling strategies for the POI field tests. For most of the munitions to be tested, these calculations suggest that our sampling strategy can successfully establish emission factors for many of the target TRI chemicals. However, these results also suggested that resources should not be expended in an attempt to measure emissions of a number of species that are not likely to be detectable. These results were taken into consideration in developing the final list of TRI chemicals to be measured during munitions testing, and in selecting appropriate measurement methods.

Table 3.2 provides a range of minimum emission factors that are likely to be detectable for representative species measured by various techniques. These ranges take into consideration sampling duration and downwind location for the array of munitions to be evaluated. Included in Table 3.2 are reported values of emission factors for these species that can be used to gauge the likelihood of successful detection of the respective target chemicals. In most cases, the measurement techniques chosen should have sufficiently low detection limits to allow estimates of emission factors for the target chemicals. However, in the case of one method we considered, polyurethane foam (PUF) adsorbent/filter sampling and high-resolution mass spectrometry for dioxin compounds, the detection limits are approximately 1-2 orders of magnitude above the
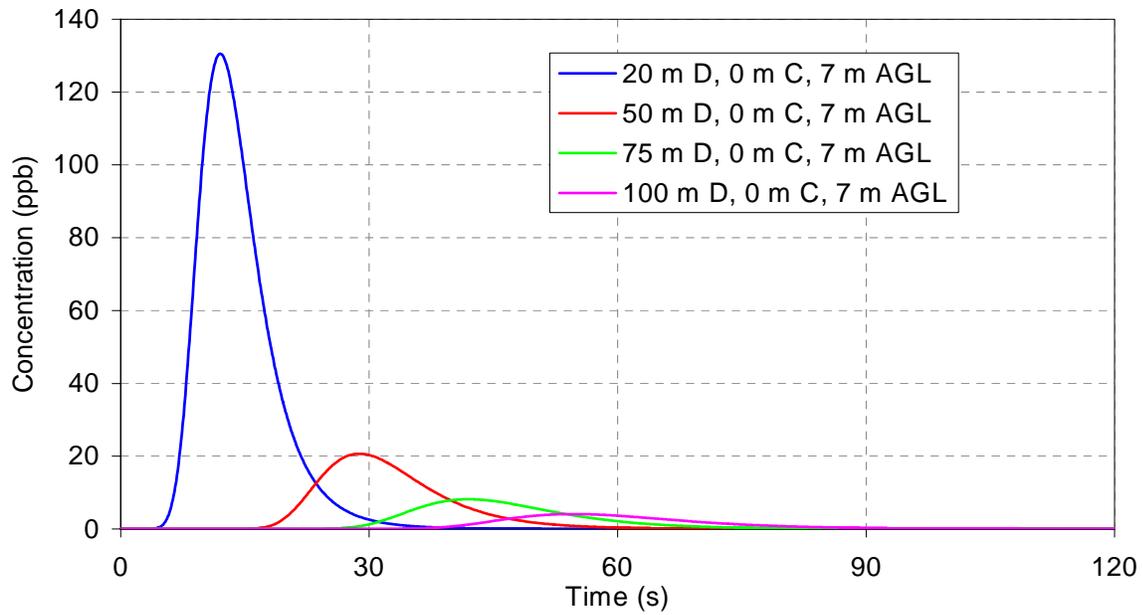
Figure 3.4.   Calculated Concentration Profiles at Downwind Receptor Locations. These
               Profiles were Calculated Assuming a 3 Meter PUFF Diameter, 2 m/s w Wind
               Speed, and D Stability. The Profiles are for Receptors Located 7 Meters Above
               Ground Level (AGL), on-Axis, at 20, 50, 75, and 100 Meters Downwind.
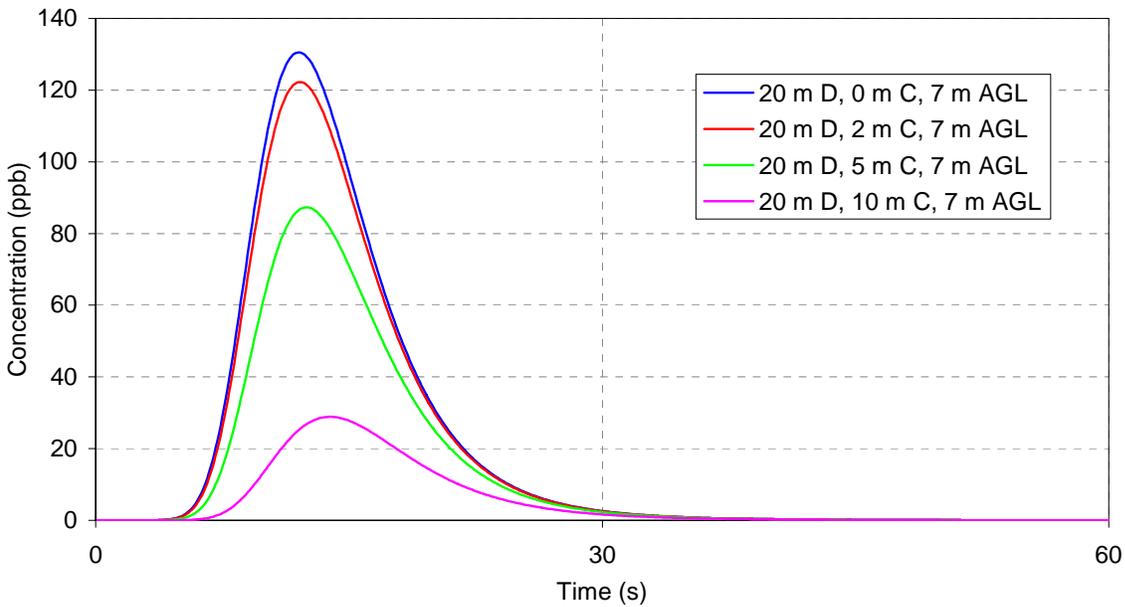
Figure 3.5.   Calculated Concentration Profiles at On-Axis and Off-Axis Receptor Locations,
               20 Meters Downwind of Release. These Profiles were Calculated Assuming a 3
               Meter PUFF Diameter, 2 m/s Wind Speed, and D Stability. The Profiles are for
               Receptors Located 7 Meters Above Ground Level (AGL), at 0, 2, 5, and 10
               Meters Off-Axis.

potential concentrations for the target chemicals. Because this technique is unlikely to provide useful data for outdoor POI testing, it was not deployed for the POI studies. In general, adsorbent sampling techniques (e.g. Tenax and XAD-2) for semi-volatiles and analyses with low-resolution mass spectrometry were considered but rejected because these methods can not provide sufficient sensitivity due to the expected short sampling times.

Table 3.2. Summary of Estimated Minimum Detectable Emission Factors and Reported Emission Factors for Various Target Chemicals

Target Chemical	Measurement Technique	Minimum Detectable Emission Factor	Reported Emission Factors
benzene	Canister/GC-MSD	$0.1\text{-}1 \times 10^{-5}$	2.8×10^{-5}
dioxins	PUF/HRMS	$0.4\text{-}4 \times 10^{-7}$	1.9×10^{-9}
Lead	Filter/ICP-MS	$0.1\text{-}1 \times 10^{-5}$	3.7×10^{-4}
diethyl phthalate	APCI-MS	$0.5\text{-}5 \times 10^{-7}$	7.7×10^{-5}
dimethylnitrosamine	APCI-MS	$0.5\text{-}5 \times 10^{-7}$	8.5×10^{-7}
quinoline	PTR-MS	$0.5\text{-}5 \times 10^{-7}$	1.4×10^{-7}
particle-bound PAH	Photo-ionization	$0.1\text{-}1 \times 10^{-6}$	1.2×10^{-6} (a)
formaldehyde	Fluorescence	$0.1\text{-}1 \times 10^{-7}$	1.3×10^{-6} (b)
mercury	Atomic absorption	$0.2\text{-}2 \times 10^{-6}$	

(a) Calculated from the sum of reported PAH emission factors from particulate samples.
(b) Calculated from reported CO/CH_2O molar ratio.

The measurement methods that were used during the emissions testing field campaigns are listed in Table 3.3. Under each method are the targeted TRI chemicals that were measured by that method. The chemicals designated as high priority are shown in bold. We attempted to measure all the chemicals listed in Table 3.3 during the Point of Discharge tests, where relatively long (20 minute) sampling times were available because the emissions were confined in a test chamber. However, sampling times for the POI study were often only 10-20 seconds, and several of the real-time measurement methods required one or more seconds to measure each chemical. To assure representative sampling we desired measurements of each chemical at several times as the emission cloud passed the sampling tower, and in order to achieve this requirement we reduced the number of chemicals measured by the two real-time mass spectrometric instruments (APCI-MS/MS and PTR-MS) during the POI testing to increase the number of times each measured

Table 3.3. TRI Targeted Chemicals and Associated Methods[a]

Whole Air Sampling/ GC-MS	Filter Sampling/ ICP-MS	Atm. Pressure Chemical Ionization Tandem MS[b]	Proton Transfer Reaction-MS[b]	UV Photo-ionization Monitoring	Derivatization/ Fluorescence Monitoring	Carbon Mass Balance Monitors
acetaldehyde	**arsenic**	nitroglycerine*	**anthracene***	**PAHs**	**formaldehyde**	CO_2
acrolein	**beryllium**	formic acid	**naphthalene**			CO
acrylonitrile	**cadmium**	dinitrobenzene*	**quinoline***			hydrocarbons
benzene	**chromium**	dinitrotoluene*	nitrobenzene			
1,3-butadiene	**lead**	N-nitroso diphenylamine*	dinitrobenzene			
carbon tetrachloride	**manganese**	N-nitroso dimethylamine*	dinitrotoluene			
chloroform	**nickel**	N-nitroso diethylamine*	phenol*			
1,2-dibromoethane	**mercury**	aniline*	nitrophenol			
1,2-dichloroethane	aluminum	dimethylphthalate*	dinitrophenol			
1,2-dichloropropane	antimony	diethylphthalate	benzidine			
1,1,2,2-tetrachloroethane	barium	dibutylphthalate	biphenyl			
tetrachloroethylene	cobalt	chlorine*	dibenzofuran			
trichloroethylene	copper	diphenylamine*	4-aminobiphenyl			
Vinyl chloride	selenium		hydrogen cyanide*			
toluene	silver		toluene*			
allyl chloride	thallium					
bromomethane	zinc					
carbon disulfide						
acetonitrile						
chlorobenzene						
chloromethane						
chloroprene						
ethylbenzene						
methyl tert-butyl ether						
vinyl acetate						
bromoform						
o-xylene						
m-xylene						
p-xylene						
styrene						
benzyl chloride						
1,2-dichlorobenzene						
1,4-dichlorobenzene						
1,3-dichlorobenzene						
hexachloroethane						
1,2,4-trichlorobenzene						
carbonyl sulfide						
naphthalene						

(a) Items in bold are high priority hazardous air pollutants.
(b) For the POI studies, the real time mass spectrometers monitored only the compounds with asterisks.

chemical was sampled in the cloud. The chemicals targeted for measurement by the real time mass spectrometers during the POI study are marked with an asterisk in Table 3.3.

Some chemicals appear under two methods in Table 3.3. This redundancy was intentional and provided a QC measure of instrument calibration and performance during the field tests. Each of the methods listed in Table 3.3 is described in the following sections.

3.4.1 Whole Air Sampling/GC-MS

For both the POD (chamber) study and POI (outdoor range) program, whole air samples were collected for analysis of volatile organic TRI chemicals. These samples were also used to determine xenon tracer gas in the POI samples. Collection of a representative sample was critical to the accurate determination of emission factors. During the POD testing, the emissions were well mixed in the chamber and a sampling time of 20 minutes permitted us to collect time integrated whole air samples directly into sampling canisters. However, for the POI field tests the sampling times, i.e. the period when the emissions cloud passed by the sampling probes, depended on wind speed and other local conditions and was not known in advance of each test. The variable nature of the sampling period did not lend itself to collection in a fixed-volume vessel such as a canister. Therefore, time integrated whole air samples were collected in pre-cleaned Tedlar bags. Bag collection were conducted while the plume passed by the sampling tower. The contents of the bag were immediately transferred to a cleaned, evacuated, and passivated stainless steel canister.

Upon receipt of the sampled canisters in the laboratory, the analyst filled the canisters with hydrocarbon free air to a known pressure. The pressurization step facilitated the extraction and analysis of sample aliquots. The dilution factor resulting from this pressurization step was incorporated into the data processing calculations.

Canister analyses for VOCs during the POD and POI field tests were accomplished with the use of a Fisons MD 800 gas chromatographic (GC) system equipped with parallel flame ionization (FID) and mass spectrometric detectors (MSD). The system is pictured in Figure 3.6. The GC

was connected to a Nutech 3600 pre-concentrator that contained a cryogenic pre-concentration trap. The trap was a 1/8-inch by 8-inch coiled stainless steel tube packed with 60/80 mesh glass beads. The trap was cooled to –165°C for sample collection and heated to 120°C during sample desorption. A six-port valve was used to control sample collection and injection. Analytes were chromatographically resolved on a Restek RTX-1, 60 m by 0.5 mm i.d. fused silica capillary column (1 µm film thickness). Optimal analytical results were achieved by temperature programming the GC oven from –60°C to 220°C at 10°/min. The column exit flow was split to direct one-half of the flow to the MSD and the remaining flow passed through the FID. The mass spectrometer was operated in the full scan mode so that all masses were scanned between 25 and 230 AMU at a rate of 1 scan per 0.4 seconds.

Figure 3.6. GC/MS System for VOC Analysis of Canisters

Calibration of the GC/MS was performed by preparing dilute mixtures in canisters. The stock mixture (1 ppm) was a 62 component TO-15 certified cylinder from Restek. Calibration levels of 1, 2, 5, and 10 ppb were prepared by injecting known gaseous amounts of the stock mixture into cleaned and evacuated canisters and then pressurizing the canisters to a positive pressure with humidified zero air. The compounds acetonitrile, acrylonitrile, acrolein, acetaldehyde, and naphthalene were not present in the TO-15 cylinder. Calibration response factors for these compounds were determined by preparing gas mixtures of these chemicals by injecting the neat materials, along with benzene, into a 17.3 m^3 environmental chamber. GC/MS response factors relative to benzene were then established for each compound.

3.4.2 Filter Sampling/ICP-MS

During the POD and POI studies, trace metals were quantified by filter sampling and laboratory analysis using inductively coupled plasma-mass spectrometry (ICP-MS). The filters were 90mm Teflon disks. For the POD tests, filter sampling was conducted by drawing air through a single Teflon filter located in front of a Metal Bellows pump and heat trace sampling line. The total flow rate through the filter was approximately 80 lpm (20 minute collection time). For the POI testing, air was drawn through four separate filters positioned on each sampling tower. A single Metal Bellows pump pulled air through all four filters of a given tower, with a total flow rate of approximately 98 lpm. The samples were prepared by acid digestion using EPA SW-846 Method 3050B (modified), and the extracts analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using EPA SW-846 Method 6020 (modified). The analytical reporting limit of this method, in µg per filter, was:

Be 0.025, Al 12.5, Cr 0.125, Mn 0.125, Co 0.125, Ni 1.25, Cu 0.25, Zn, 12.5, As 0.0625, Se 0.25, Ag 0.125, Cd 0.0625, Sb 0.125, Ba 1.25, Tl 0.0625, and Pb 0.625.

3.4.3 Atmospheric Pressure Chemical Ionization Tandem MS

Atmospheric pressure chemical ionization (APCI) tandem mass spectrometry (MS) was used to characterize the emissions of a number of TRI chemicals that are particularly difficult to measure

by traditional methods under the conditions of the POI tests. The API 365 instrument used for this project is pictured in Figure 3.7. This technique involves air sampling at atmospheric pressure followed by chemical ionization (CI) via charge transfer from ions produced in a corona discharge. The target analyte ions are mass selected by a quadrupole mass spectrometer (QMS) and subsequently fragmented through collisions with a collision gas. Specific daughter ions produced from fragmentation are mass selected in a second QMS and monitored as unique indicators of the parent ion. Quantitative determination of parent ion concentration is possible through laboratory calibration using appropriate standards. This technique is applied, in real time, to species forming either positive or negative ions and consequently can be used to characterize species covering a broad range of chemical properties. Typical detection limits for this technique for the TRI chemicals of interest are in the range of 2-100 ppt.

In order to maximize the effectiveness of this tool to achieve the greatest possible sensitivity and selectively, we evaluated the most appropriate ionization modes and parent/daughter ion combinations to use for each chemical. The approach used for each chemical was optimized experimentally through extensive laboratory testing using gaseous samples of the authentic chemicals. Details of this work are included in Appendix A and Reference 22.

Calibration of the tandem mass spectrometer was performed by preparing low concentration gas standards of the actual target chemicals using the procedures described in Appendix A. Because of the difficulty and time requirements for preparing such standards in the field, two of the target chemicals were designated as transfer standards. Laboratory tests developed response ratios for each target chemical relative to one of the two transfer standards. Methylethyl ketone was the transfer standard for chemicals measured as positive ions, and chlorine served this role for target chemicals measured as negative ions. During the field tests the APCI-MS/MS was calibrated each sampling day with highly dilute, known concentrations of methylethyl ketone and chlorine generated by permeation tubes (VICI Metronics). The daily response factors for these two species were combined with the relative response factors for the other target chemicals to derive daily response factors for each target chemical.

Figure 3.7. Battelle's Atmospheric Pressure Chemical Ionization Tandem Mass Spectrometer

3.4.4 Proton Transfer Reaction MS

Proton transfer reaction mass spectrometry (PTR-MS) was used during the POD and POI studies to monitor the sub-set of TRI chemicals shown in Table 3.3. PTR-MS involves chemical ionization of trace atmospheric species by proton transfer from H_3O^+ ions. Many of the TRI species of interest have proton affinities greater than that of water, and will readily accept a proton during a collision with a protonated water molecule. The ionized species are mass selected using QMS and quantified based on electron counting techniques. Typical detection limits for this technique are in the range of 0.05 – 0.5 ppb but are dependent on the background concentrations of species with the same mass. Additional details of our evaluation of this method are included in Appendix A. The instrument is shown in Figure 3.8.

Figure 3.8. Proton Transfer Reaction Mass Spectrometer

3.4.5   UV Photoionization for Particle-Bound Polycyclic Aromatic Hydrocarbons (PAH)

Polycyclic aromatic hydrocarbons (PAH) are included in the TRI list as a class and as selected individual chemicals. A number of these species are carcinogenic. During the POD and POI studies, some individual PAH species were determined with the PTR-MS. The sum of all particle-bound PAH was determined with a commercial instrument.

The operating principle of the instrument is photoionization. Particle-bound PAH species are monitored using photoionization and subsequent charge counting. This approach is based on the principle that particle-bound PAHs will ionize selectively over gaseous PAHs when exposed to high-intensity ultraviolet radiation. The ionized particles are counted to quantify the particle-bound PAH concentration, and are measured in real time. Typical detection limits for the technique are approximately 0.5-2 ng/m^3.

3.4.6 Derivatization/Fluorescence Monitoring for Formaldehyde

Formaldehyde is a suspected human carcinogen and is one of the high priority TRI chemicals to be measured. During the POD and POI studies, a Battelle-developed continuous monitor[23] was used to measure formaldehyde emissions. The instrument uses a coil scrubber to continuously remove formaldehyde from the sample air stream. The sampled formaldehyde reacts with a β-diketone and an amine at a prescribed temperature to produce a fluorescent derivative. The fluorescence from the derivative is measured by a fluorometer following excitation at 254 nm with light from a mercury lamp. Extensive testing in our laboratory has demonstrated that the monitor is highly specific and has a detection limit of 0.2 ppb and a precision of $\pm$ 7 percent. The rise time of the instrument is slow, about 80 seconds, which was acceptable for the POD studies, in which the sampling period was 20 minutes. However, for the POI studies, this long response time would complicate real-time monitoring of formaldehyde because the emission clouds were only available for monitoring for 20-30 seconds. Consequently, for the POI studies, formaldehyde was measured in whole air samples collected in the Tedlar bags used for VOC and tracer analysis. Within minutes following a test, air from the sample bag was used to fill a passivated 1-L canister for GC and GC/MS analysis. The remainder of the integrated sample was analyzed for formaldehyde, CO_2, CO, and total hydrocarbon using real time monitors. Formaldehyde calibrations were performed daily during the POD and POI studies by challenging the instrument with a known formaldehyde concentration in a standard solution that was prepared each test day.

3.4.7 Carbon Mass Balance Monitors

Two carbon dioxide monitors were used during the POD and POI studies. The Draeger Polytron CO_2 monitor makes use of non-dispersive infrared absorption technology and operated over a detection range of 50 to 10,000 ppm. The Fuji CO_2 monitor uses the same detection technology and operated in one of two ranges, either 0 to 2,000 ppm or 0 to 5,000 ppm.

CO was measured using a model 48C Thermo Environmental analyzer. The measurement principle is cross filter correlation spectroscopy. The operating ranges were either 0 to 2 ppm or 0 to 1,000 ppm.

A VIG Model 20 monitor was used to measure total hydrocarbons. A heated probe and a flame ionization detector were used to obtain a total hydrocarbon concentration on a per carbon basis using propane as the calibrant gas. The operating range was either 0 to 10 ppm C or 0 to 100 ppm C.

Calibration of the continuous monitors was done using NIST-traceable gas cylinders from Matheson and Scott Specialty Gases, and an Environics Series 100 gas phase dilution system.

3.4.8 Xenon Sampling/Analysis

An external chemical tracer, xenon, was employed to quantify emission cloud dilution during the Point of Impact study. Xenon was measured in the integrated whole air samples that were collected in Tedlar bags and transferred to stainless steel canisters. These are the same air samples used to determine VOCs by GC-MS, as described earlier. Upon receipt in the laboratory, each canister was checked to make sure that the canister was at atmospheric pressure. A 250-µl sample was withdrawn from the canister with a syringe and analyzed by an Agilent gas chromatograph/mass spectrometer (6890-5973). The mass spectrometer was operated in the selective ion-monitoring mode in order to enhance the signal/noise ratio for xenon. The two ions that were monitored are at 129 amu and 132 amu. The analytical column is a Porapak Q fused silica plot column (30 meters by 0.53 mm i.d.). A column oven initial temperature of –20 C and a temperature ramp rate of 30 C/minute result in a GC run time of less than 10 minutes. Figure 3.9 shows a GC/MS tracing of the 0.16 ppm calibration standard. The two mass ions selected for identification and quantification are 129 and 132. Atmospheric background levels are approximately 0.09 ppm. A multi-point calibration of xenon at concentrations ranging from 0.1 to 2 ppm is shown in Figure 3.10. Calibration mixtures were generated by injecting neat xenon (microliters) into a Tedlar bag and then carrying out secondary dilutions into additional Tedlar bags.
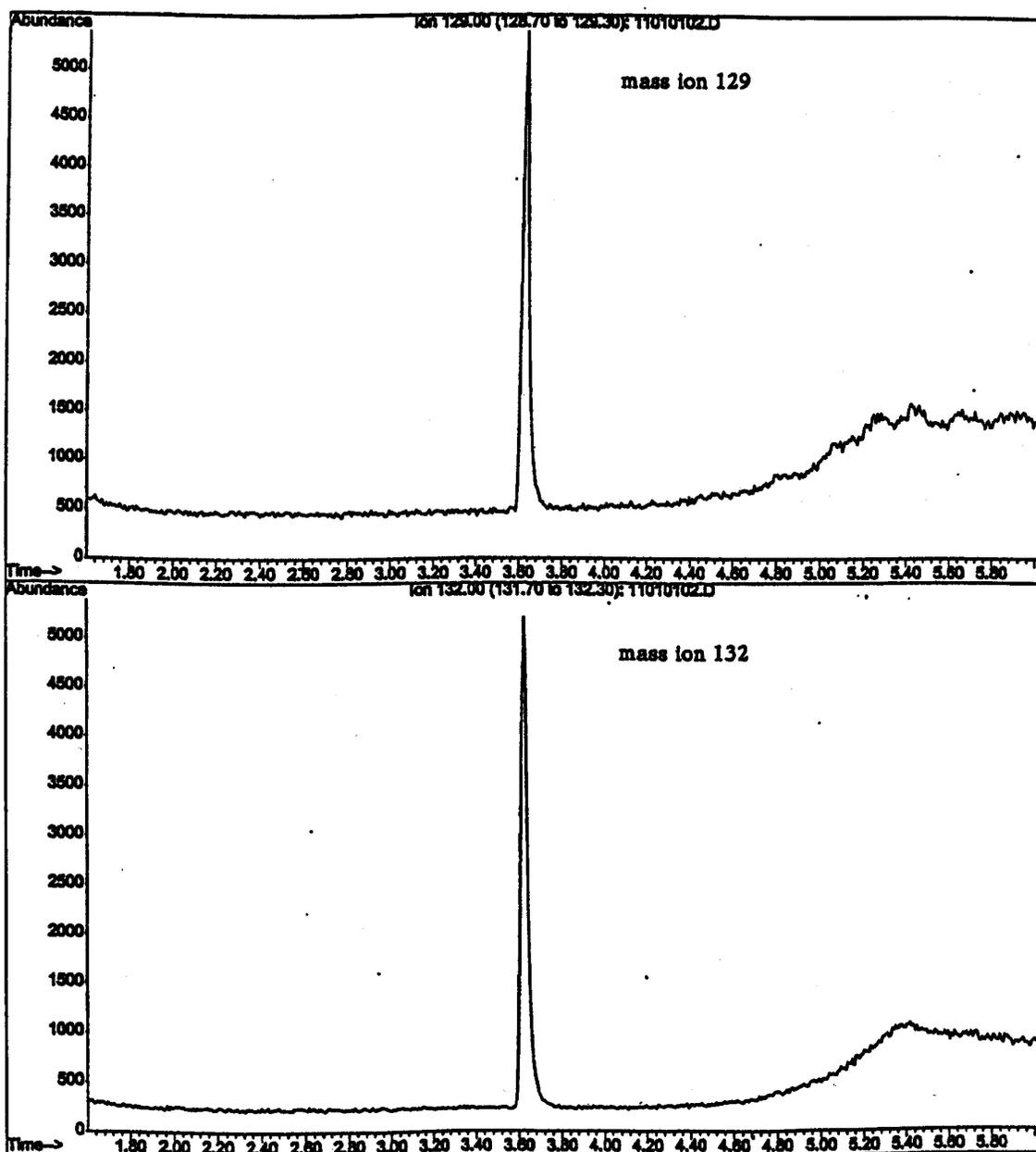
Figure 3.9. Gas Chromatogram of 0.16 ppm Xenon Calibration Standard
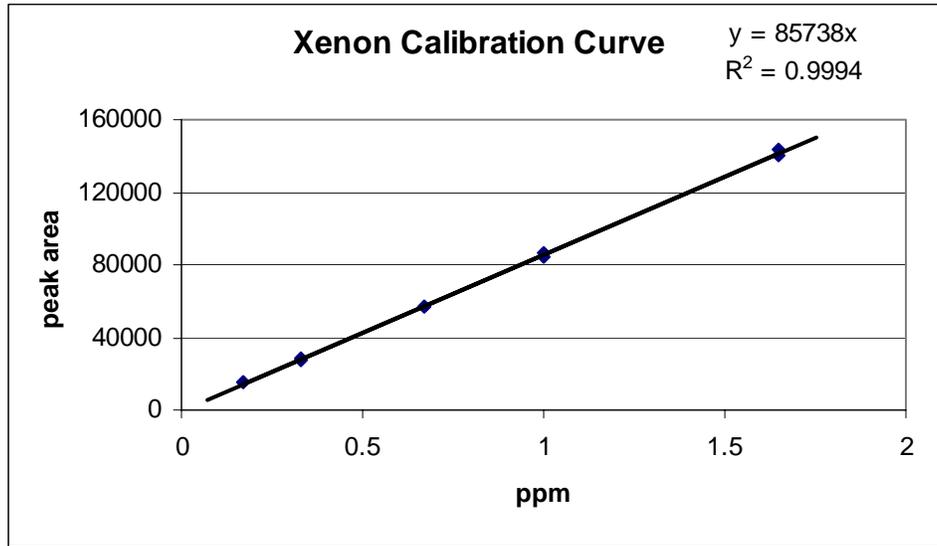
Figure 3.10. Xenon Calibration Curve from 0.1 to 1.7 ppm

3.4.9 Photogrammetry Methods

To visually define the dimensions of the emissions cloud during the point of impact tests, we employed a multiple angle photographic system and proprietary software to create 3-dimensional CAD images of the emission cloud. As shown below, for an irregular plume captured from a number of viewpoints, the outside bounding volume can be calculated. Since the plume is not stationary it is important to be able to synchronize the captured images from the various viewpoints and to calibrate the position of the cameras relative to the plume and to each other. By the use of scaled measurements of several points on the sampling tower and mathematical triangulation, the position of each camera relative to the tower can be determined. These measurements in turn are used to reline the photo images to the same measurement scale. Four JVC GRM-DVM55 digital video cameras were used to capture the emission cloud images as it passed the sampling towers. The four cameras were time synchronized before being placed at different viewpoints facing the sampling tower (Figure 3.1).

To calculate the plume volume, the cross Section area of the plume, as viewed by each of the four cameras, was determined. This was done by averaging ten plume-on-tower images (3.3 seconds) from each camera. All background images including clouds from the photo images

were removed by electronically subtracting a baseline image taken just prior to detonation from each of the plume-on tower images. The remaining color image was converted to a gray scale and light intensity measurements determined. Pixels with a light intensity greater than the threshold of the mean plus one standard deviation were retained, thus forming a limit of the cross sectional area of the plume at that angle. This process was repeated for the same instances of time for each of the remaining camera viewpoints. Each of the image plane plume outlines from each camera angle were imported into a 3-D solid modeling program. The intersection of the extruded plume outlines centered on the tower image plane provide the photogrammetric plume bounding volume measurements. The plume volume in cubic meters was then mathematically calculated from the bounding volume measurements.

3.4.10 Aerosol Lidar Method

Aerosol lidar was selected as one of four methods for estimating the volume of the emissions cloud. Lidar should allow an estimate of cloud volume even when the cloud is visually transparent. In that sense lidar is complementary to photogrammetry, in that lidar should perform best with low opacity clouds, while the opposite is true for photogrammetry. During the first year of this project, modifications were made to an existing lidar system, and software was developed, to enable rapid scanning of emission clouds in the field. The system was tested in the field as part of a preliminary test of the four plume volume estimating techniques. The methodology was modified slightly and used during the POI outdoor testing program. Details of the development and testing of the scanning lidar system devised for this project are included in Appendix B. A brief overview is presented below.

The lidar measurements utilize the fact that the emission cloud will possess a different aerosol burden than the surrounding background atmosphere. This abrupt aerosol loading change will result in a large transient increase in the strength of the elastically scattered laser light. This range-resolved signal will, in turn, allow cross-sectional mapping of the developing plume's diameter. The aerosol lidar used in this study provided estimates of the volume of the emissions clouds during the POI testing, and also provided information on the internal structure of the munitions clouds.

For this application, a high-precision stepper motor was used to provide a constant sinusoidal motion to the lidar unit via a push rod assembly. Since the master oscillator for the lidar is a 20 Hz laser system, the rotation of the stepper motor is kept to integrals of 20Hz thereby ensuring that each lidar image will be made-up of the same number of laser shots and that integral number of laser pulses probes the same atmospheric volume. Preliminary field tests utilized scan rates from 0.25 Hz to 1 Hz which translates to 80 laser pulses to 20 laser pulses for each image. Tests showed that higher temporal resolution was more important than high vertical spatial resolution. Hence, most tests were carried out at the 1 Hz or 0.5 Hz scan rates. The laser source is a single frequency 266 nm Nd:YAG laser (New Wave, Lase II, 7 mJ/pulse at 20 Hz). The use of a UV solar blind laser (λ <300 nm), rather than a visible or near-infrared wavelength, allows signal acquisition to be conducted in daylight without interference from ambient light. The backscattered elastic return signals are collected by a 6-inch, f/4 Newtonian telescope that is coaxial with the transmitted laser beam and outfitted with a ~300 MHz, solar-blind photomultiplier tube (PMT; Hamamastu, R1657). The elastic return signal is tracked as a function of distance (via time-of-flight) for plume-edge detection.

Due to the nature of the lidar scanning process, one complete cross-sectional image of the plume is generated when the unit scans from bottom to top and another is captured when the unit went from the top to the bottom. This means that any two adjacent lidar images are out-of-phase (i.e. reversed). Therefore, the initial step in the data reduction process was to correct all images for this bi-directionality. The next step was to convert the raw images, which were in polar coordinates, to Cartesian coordinates. This action greatly simplified area estimation since in cartesian coordinates, each pixel making up the image has the same area. Consequently, the area of the emission cloud was estimated by counting the number of pixels associated with the plume and multiplying by the area of a pixel. To insure that the spatial transform image was representative of the raw (polar-based) image, a test image was synthesized and validated against the original image.

Before estimating plume cross-sectional areas, we removed background signal caused by fixed objects (i.e., trees, the towers) so that these items are not misinterpreted as plume during the pixel counting process. This was accomplished by determining the median signal for each pixel

over all background scans. This "background" signal was then subtracted from each plume image, giving a background corrected plume image. Once this final correction was applied, all the images were reviewed, and any pixel that exceeded median + 3 sigma was considered to be part of the plume. As shown in Figure 3.11, this procedure appears to be quite robust and is able to capture the fine structure inside the plume as well as the plume's outer edges. Once the plume cross-sectional area was estimated for each time interval, measured wind speed was used to convert plume area to plume volume.
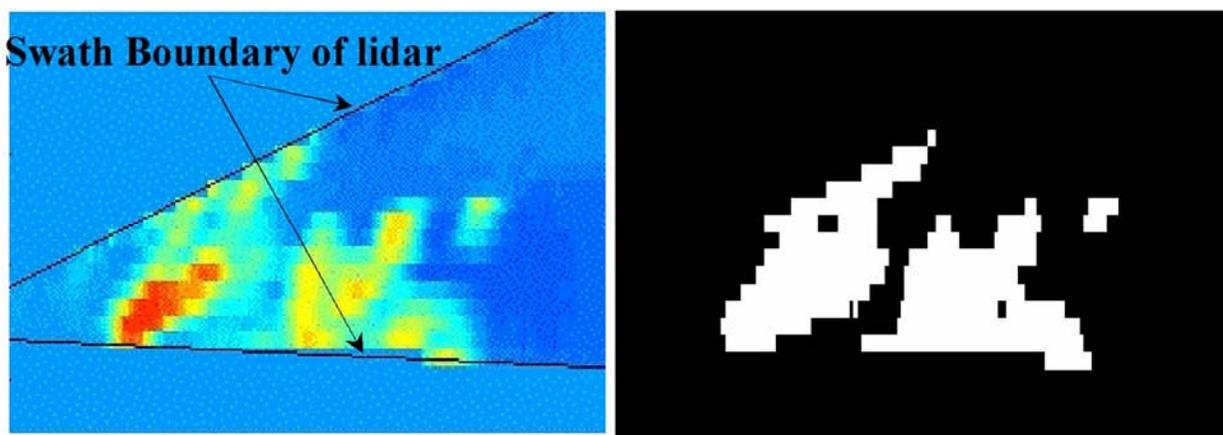
Figure 3.11. Left Frame Shows a Lidar Image. Right Frame Shows the
Statistically Determined Plume Cross Section

3.4.11 Xenon Tracer Release Methods

To estimate plume dilution by the xenon tracer method, it was necessary to distribute a known volume of Xe into the cloud. For detonating munitions, we used Tedlar bags that were accurately filled with a known amount of xenon gas. For these tests, 26.5 L of xenon gas was metered into a bag through a calibrated mass flow controller. The bag was attached to or placed as near as possible to the ordnance. Xenon has an atmospheric background concentration of ~0.09 ppm. Modeling results discussed earlier in this Section estimated downwind xenon concentrations as a function of the following variables: initial puff size, atmospheric stability and wind speed. In order to assure that xenon would be measurable above background at the downwind sampling location, a minimum centerline concentration of at least 0.3 ppm was targeted. The initial volume of xenon gas needed to achieve this target concentration was found

to vary as a function of atmospheric stability and wind speed. Model predictions suggested that at least 10 liters of xenon gas should be released per test. For the POI studies, 26.5 liters of gas were released to provide additional assurance that sufficient xenon was present.

For those munitions that involved a continuous release of material (e.g. illumination and smoke rounds), the xenon gas delivery system was as follows. The regulator from the high pressure cylinder of xenon was connected to a solenoid valve and mass flow controller (MFC). The exit of the MFC was connected with a 50-ft length of 1/4 inch o.d. polyethylene tubing to the center of a xenon dispersion manifold. The manifold was an aluminum tube 6 ft in length and 3/8 inch o.d., capped at the tube ends, but containing 16 drilled holes, each 0.03 inches in diameter, spaced evenly along the length of the tube. The manifold was placed on a tripod at ~ 3 feet above the ground. During the first part of the field study, xenon flow rate was set at 2.0 liters/minute. Beginning September 23, 2003, the flow rate was increased to 4.4 liters/minute. The mass flow controller was activated when the test material was initially released. The xenon flow was stopped when the sample bag collection had terminated.

3.5 Munitions Selected for Testing

3.5.1 Point of Discharge Tests

The POD testing was conducted in conjunction with a series of Aberdeen Test Center (ATC) tests supported by Army Environmental Center (AEC). The munitions items utilized during the POD tests were selected by AEC/ATC for purposes of their program. The munitions that were tested during the POD study are shown in Table 3.4.

3.5.2 Point of Impact Tests

Over 170 munitions types were reviewed as potential candidates for testing as a part of this project. Sources reviewed included Munitions Items Disposition Action System (MIDAS) Library and Toxic Release Inventory Data Delivery System (TRI-DDS). Factors considered during the selection process included: munitions size, potential for air emissions, explosive or

Table 3.4. Items Planned for Testing in Firing Point Series 08

Item	Designation
25 mm cartridge	M793 TP-T
25 mm cartridge	M910 TPDS-T
50 cal machine gun round	M2 AP
120 mm mortar round	M931 FRP, Zone 1
120 mm mortar round	M934 HE, Zone 1
120 mm mortar round	M931 FRP, Zone 4
120 mm mortar round	M934 HE, Zone 4
84 mm anti-tank projectile	M136 AT-4

energetic composition, and volume of munitions used during training activities. It was important to select a representative cross Section of munitions routinely used during training activities and still test the limits of the proposed sampling methodology. One of the first considerations was to limit the range of munitions sizes to be tested. Munitions below a certain size would not produce sufficient air emissions for testing. Munitions too large would put an undue risk to the test team, require additional safety measures, and limit the number of tests that could be successfully carried out. Based on these considerations, it was decided to limit testing to munitions between 40 mm and 155 mm. A review of available training usage data indicated that the most common munitions used during training activities fell into this range. Another important consideration is the opacity of the emissions cloud. The experimental approach for determining munitions emission factors should be able to accommodate the range of opacities generated by representative military ordnance. This is especially important with respect to determining emission factors using the "Volume Method" discussed in Section 3.2.4. Therefore, one munitions selection criterion focused on munitions that would provide a range of cloud opacities. The matrix of munitions selected for testing during the Point of Impact Study is shown in Table 3-5. In selecting munitions items for these tests, we reviewed the chemical compositions of the candidate items, to insure that our selections represented a wide range of compositions.

A description of many of the munitions used in the Point of Impact tests is included in Appendix C. This description includes: Munition Type, Identification Nomenclature and Department of Defense Identification Code (DODIC) number, average usage rate (based on 1995-1997 averages), and description of use.

Table 3.5. Primary TRI Munitions Selected for Testing

	Low Opacity → → → High Opacity		
Large Caliber	**1** 155 mm Howitzer (high explosive)	**2** 155 mm Howitzer (illumination)	**3** 155 mm Howitzer (smoke)
↑ **Medium Caliber**	**4** 66 mm Antitank Rocket (high explosive)	**5** 4.2 in Mortar (high explosive)	**6** 4.2 in Mortar (illumination)
↑	**7** 40 mm Cartridge (high explosive)	**8** 40 mm Grenade (illumination)	**9** 81 mm Mortar (smoke)
Small Caliber	**10** Hand Grenade (explosive)	**11** Hand Held Flare (illumination)	**12** Hand Grenade (smoke)

3.6 Strategy and Design

The test strategy and design of the two sets of emissions tests is described in this section.

3.6.1 Point of Discharge Tests

The POD tests were designed to measure the emissions from the firing of a weapon at the point of discharge. The Army Environmental Center carried out a series of such tests at the Aberdeen Test Center (ATC). These tests were conducted in an indoor facility, where emissions can be captured and sampled over an extended period of time. A goal of this SERDP project was to piggy-back on a subset of POD tests at ATC to allow a comparison between the standard techniques (EPA and NIOSH methods) for measuring chemical emissions from munitions, and the measurement techniques to be used for the POI tests. The standard techniques that have been employed by the Aberdeen Test Center are primarily time-integrated sample collection devices (e.g. filters, adsorbent tubes) followed by off-line analysis procedures; whereas several of the methods used for the POI studies involve real-time monitoring.

The POD tests were designed with two purposes in mind:

1. Allow comparison of the planned POI measurement methods with the standard methods employed by ATC/CHPPM.

2. Provide emission factors for the discharge of selected weapons (i.e. emissions from the propellant).

The tests were carried out in a large aluminum chamber that was installed inside one of the barricades at ATC. The chamber was equipped with several fans to mix the emissions throughout the chamber during a test. Large doors on one end of the chamber allowed access for weapon installation and maintenance of the emissions sampling systems. The doors were opened and the fans operated to purge the chamber between tests. Sulfur hexafluoride was added to the chamber before each test to measure dilution. Depending on the weapon being tested, an automated door on either the front or the top of the chamber was opened temporarily to allow the projectile to exit the chamber. The door opening was covered with a membrane to prevent leakage of chamber air. The projectile was fired through the membrane, and the door was then closed to seal the emissions in the chamber.

A typical testing sequence was as follows:

1. The chamber was cleaned from the previous test and sealed.
2. SF_6 was released into the chamber and mixed.
3. The weapon was fired.
4. The emissions were allowed to mix for 2 minutes.
5. Sampling was performed for 20 minutes.
6. The chamber was purged with outside air and checked for safety.

Background air samples were collected from the chamber in the same manner, but without weapon firing. A background sample was taken during each day of testing. A view of a 25 mm Bradley Fighting Vehicle cannon prepared for testing is shown in Figure 3.12. A photograph taken during firing of this weapon is given in Figure 3.13.

Figure 3.12. 25 mm Bushmaster Chain Gun in Mount Prepared for Testing

Figure 3.13. Interior of Test Chamber During Firing of 25 mm Cannon

For the POD tests, two of the instruments were installed just outside the test chamber. These included the PAH monitor and the temperature/dew point monitor. This location minimized the length of sample tubing needed to transmit chamber air to the instrument. All of the other instruments were located in a mobile laboratory parked outside of the barricade building. The sampling system consisted of two 90 mm filter holders and Teflon filters, two valves, a 50 ft. length of ½" heat traced Teflon tubing, a stainless steel Metal Bellows pump, a second 50 ft. length of ½" heat traced Teflon tubing, a heated multiport glass sampling manifold, and a high volume mass flow meter. The filter holders and valves were positioned inside the test chamber, with the valve controller inside the mobile laboratory. Sample air was drawn through one or the other Teflon filter, through the first length of ½ in. diameter tubing, through the pump, and then pushed through the second length of ½ in. diameter tubing and into the gas sampling manifold. Individual instruments and samplers pulled their samples from this manifold. Excess flow was vented from the manifold through a mass flow meter and then outside of the mobile laboratory. The sample lines and manifold were heated to 50ºC.

Trace metals were determined by analysis of the Teflon filter at the inlet of the air sampling probe. Two filters and valves were connected to the probe. One filter was used only during the 20 minute testing periods. This filter was replaced after each test and stored for later analysis. The other filter served as a by-pass. Chamber air flowed through this by-pass filter and supplied air to the mobile laboratory sampling manifold at all times other than the official sampling intervals. As noted above, the filter used for metals analysis collected samples for 20 minutes during each test. The flow rate through this filter was measured periodically between tests using a calibrated mass flow meter. The flow rate multiplied by the sampling time gives the volume of air sampled by the filter. However, some tests generated substantial amounts of particulate matter, which accumulates on the filter during sampling. This buildup can reduce the flow and thereby affect the volume sampled. To account for this, the mass flow meter was used to monitor the excess flow exhausted from the manifold during the 20-minute sampling period. The decrease in exhaust flow during a test was used to calculate an adjusted filter sample volume for each test.

3.6.2 Point of Impact Tests

The point of impact tests required measurements of the concentrations of numerous chemicals in a relatively small, expanding, moving cloud of emissions, and either accurate measurements of a stable tracer species that is distributed in the cloud in the same manner as the target chemicals, or accurate estimates of the volume of the emissions cloud at the time of sampling. Unlike previous BangBox tests or the Point of Discharge tests, the Point of Impact tests were performed outdoors on a test range, where variable meteorology is a factor. The location of the cloud and the time available for sampling the moving cloud was highly dependent on wind speed, wind direction and atmospheric stability conditions. Under the best of conditions, sample collection times of just a few tens of seconds were typically observed. This short sampling time put great constraints on the measurement methods that were employed. Also, because estimating emission factors by the Volume Method requires measurement of concentrations representative of the entire emissions cloud, samples must be collected from multiple locations within the cloud. There were substantial challenges in measuring the target chemical concentrations and also the cloud volume under actual test range conditions. Considerable effort during this project was focused on understanding the behavior of an emissions cloud following the detonation of an ordnance item, and devising a strategy that would provide the greatest chance of success for measuring TRI chemicals in that cloud with sufficient sensitivity to calculate emissions factors, and for measuring the volume of the cloud.

In developing a sampling approach for Point of Impact emissions testing, there was a compromise between distance and instrument sensitivity. The closer the measurement system was to the point of emissions, the higher the concentrations would be, so the less sensitive the measurement system needs to be. Sampling the emissions further downwind from the point of impact translated to greater dilution of the emissions and the need for more sensitive measurement tools. However, safety considerations provided a bound on how close the measurement system could be to the ordnance.

Our approach to measuring TRI chemicals during outdoor munitions tests is represented in the drawing in Figure 3.14. To minimize safety concerns, we employed static detonations in which

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the ordnance was either detonated on the ground or as an air burst. The lidar system was positioned to the side of the test area behind a shield, and oriented to scan a vertical plane in front of the sampling towers. Only minor changes could be made to the lidar orientation due to safety concerns with the Class 4 laser.
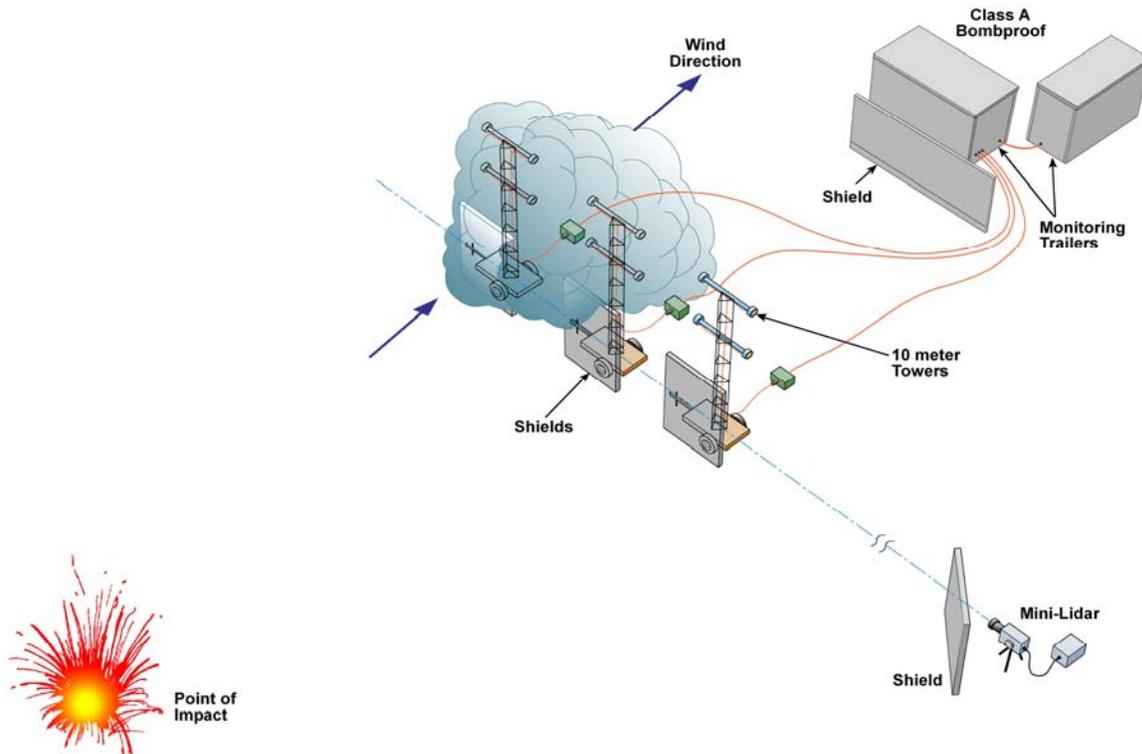
Figure 3.14. Overview of Sampling Design for Outdoor
Point of Impact Emissions Testing

Three 10 m "tipping" towers were erected in the prevailing downwind direction from the detonation point. The towers were mounted on three open trailers, so they could be moved to accommodate changes in wind direction. Three sampling towers were used in order to maximize the probability that the emissions cloud would encounter at least one of the towers, even if there were sudden shifts in wind direction, and to provide sampling from multiple points in the cloud to improve the representativeness of the samples. The towers were hinged to allow the upper portion to be "tipped" down to the ground. Following each test the towers were tipped to facilitate removing and replacing the filters in the 12 sampling probes. The towers also were

operated in the tipped configuration for some munitions tests, for which the type of munitions (e.g. smoke grenade) and/or meteorological conditions suggested that the emissions cloud would remain close to the ground. Each tower had hardened sample probes mounted on each side of the tower at heights of 7 m and 10 m above the ground. The towers were placed 8 m apart with probes mounted on arms extending 2 m from each side of the towers. This configuration provided 12 sampling probes along a 20 m line that was perpendicular to the wind direction and 20 to 80 m downwind of the detonation point. The sampling system was located closer to the ordnance (~20 m) for small items and further out (~80 m) for the more energetic munitions. Results from the preliminary modeling study indicated that the emissions cloud would be 24-40 m wide under expected conditions, so this sampling configuration was designed to maximize the chance that the probes from one or more of the towers would be in the path of the emissions cloud. Depending on wind direction on the testing days, the detonation point was moved and/or the sampling towers were relocated to maximize the chance of sampling the emissions cloud, as illustrated in Figure 3.15. Figure 3.16 is a photograph of the sampling towers and protective shields from the detonation point. The bombproof shelters containing the sampling and monitoring systems and project scientists are in the center background, partially hidden by the center tower and shield.

A more detailed schematic diagram of the sampling system is shown in Figure 3.17. The system consisted of the three sampling towers, three high capacity pumps, heated Teflon sample lines, and two Class A bombproof shelters. Shelter 1, shown in Figure 3.18, contained the sample distribution system, personnel performing the measurements, one of the continuous monitors (total hydrocarbon), laptop computer with real-time data display, communications links to the ordnance specialist and test coordinator, and video monitors. Shelter 2 contained the remaining air quality monitoring instrumentation and calibration equipment. The interior of this shelter is pictured in Figures 3.19 and 3.20. The two shelters were linked by heated ½ in. diameter Teflon tubing that transferred sample air to a stainless steel manifold.

Each sampling tower consisted of a 10 m heavy duty tower (Glenn Martin Engineering Model MF-1333) made up of a 3 m heavy duty galvanized base supporting a hinged 7 m aluminum top
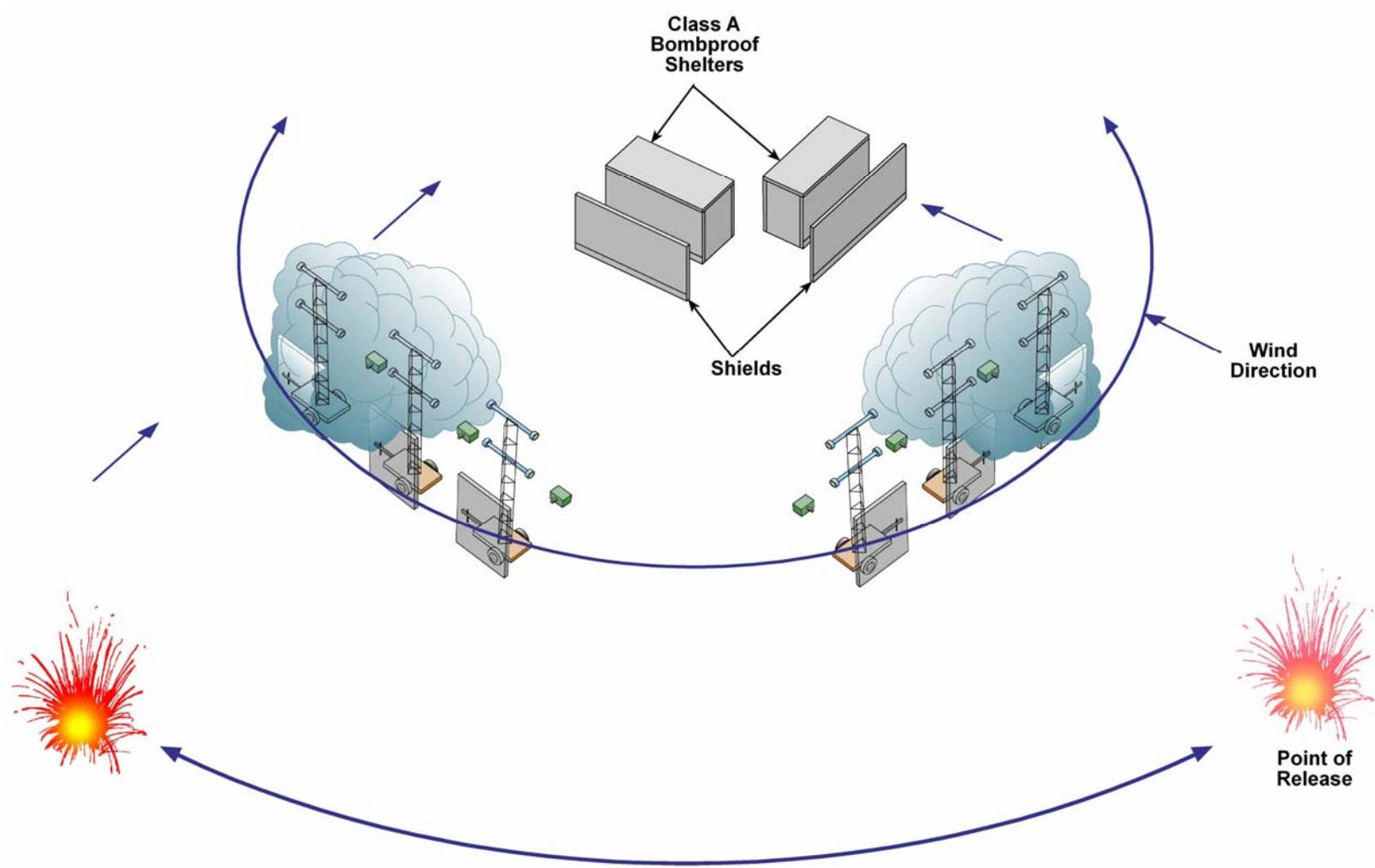
Figure 3.15. The Sampling System was Moveable to Allow for Changes in Wind Direction

Figure 3.16. POI Sampling Towers with Shields in Place. Photo Taken Near Location of Detonation Point. Bombproof Shelters are Visible in the Background Behind Center Tower. (Note: Vehicles and non-critical personnel were cleared from the range prior to each test.)

section. Hardened sample probes were mounted on each side of the tower at heights of 7 m and 10 m above the ground. These probes, extending 2 m from each side of the tower, supported a Teflon sample line and inlet filter holders (Savillex 90mm open face Teflon filter holder with a Teflon 1-2 micron pore size membrane filter). The 4 inlet filters on each tower were connected by a ½ inch diameter Teflon sample line to a high capacity pump (Metal Bellows Model MB-602) located on the trailer at the foot of the tower. A heated (50°C) ½ in. diameter Teflon sample tube (Apex Instruments) carried the sample air from the pump on each of the three trailers to a flow and control panel located inside bombproof shelter #1 positioned approximately 30 m behind the towers.
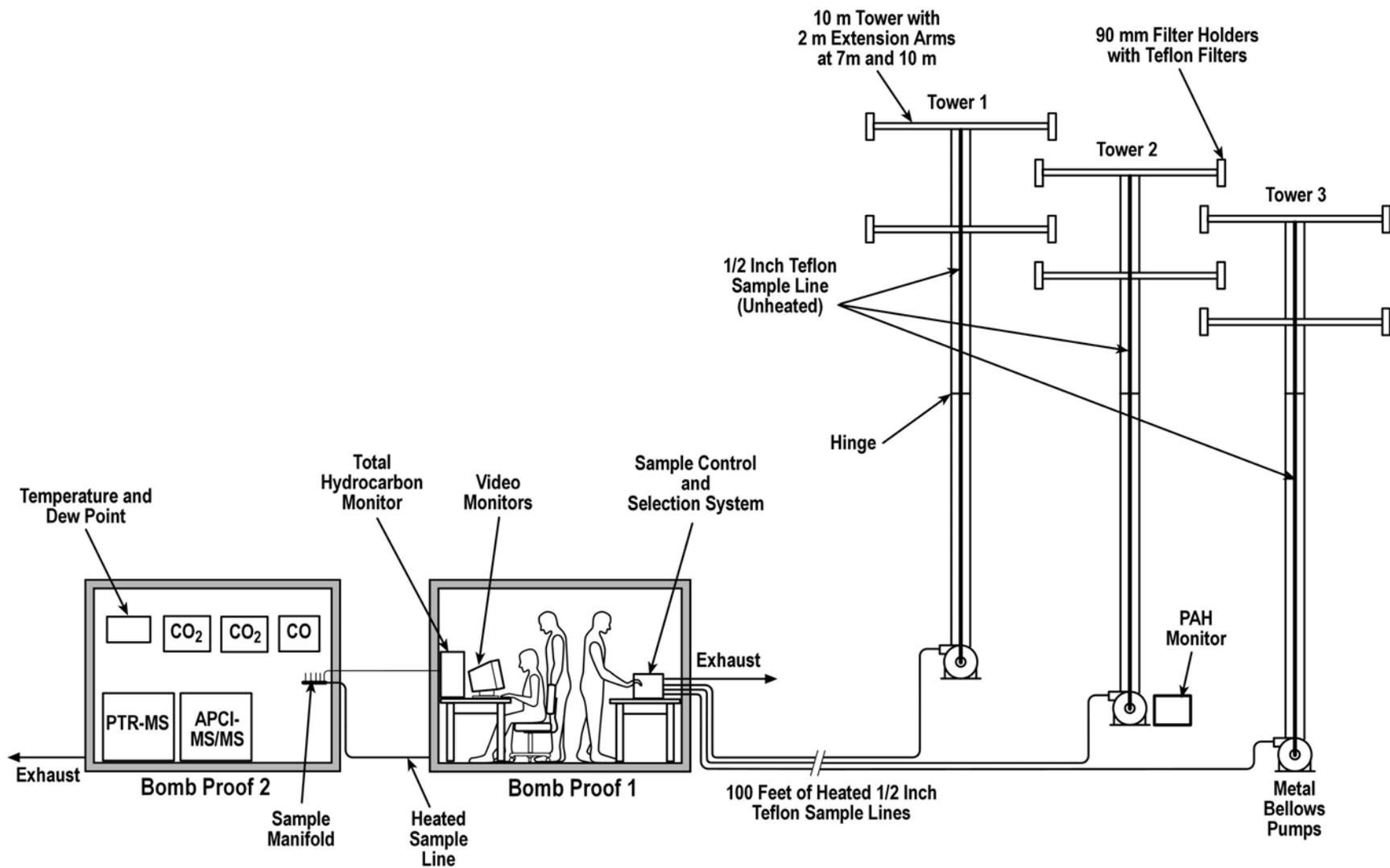
Figure 3.17. Point of Impact Sampling System
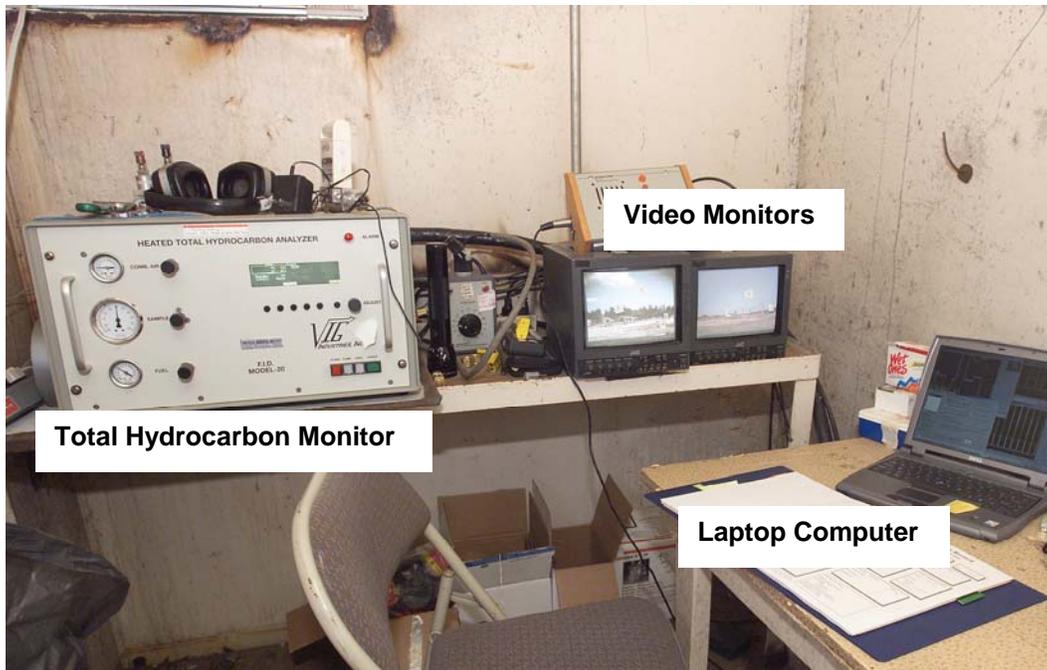
Figure 3.18. Interior View of Bombproof Shelter 1 During Point of Impact Tests
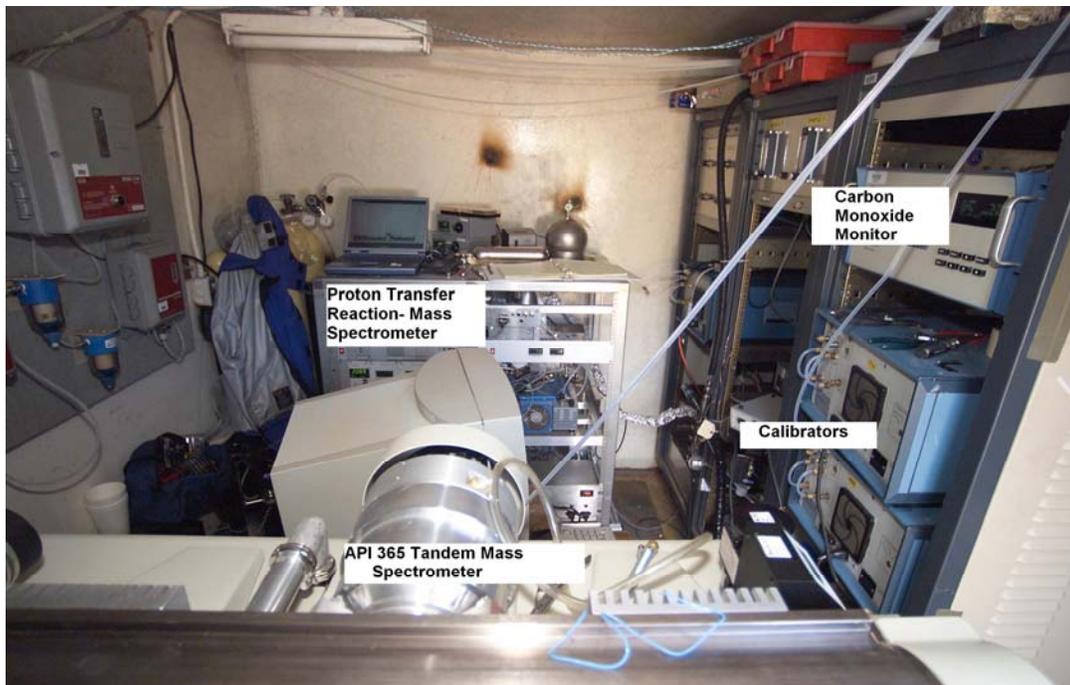
Figure 3.19. Interior View of Bombproof Shelter 2 from Entrance.
Some Measurement Systems are Noted
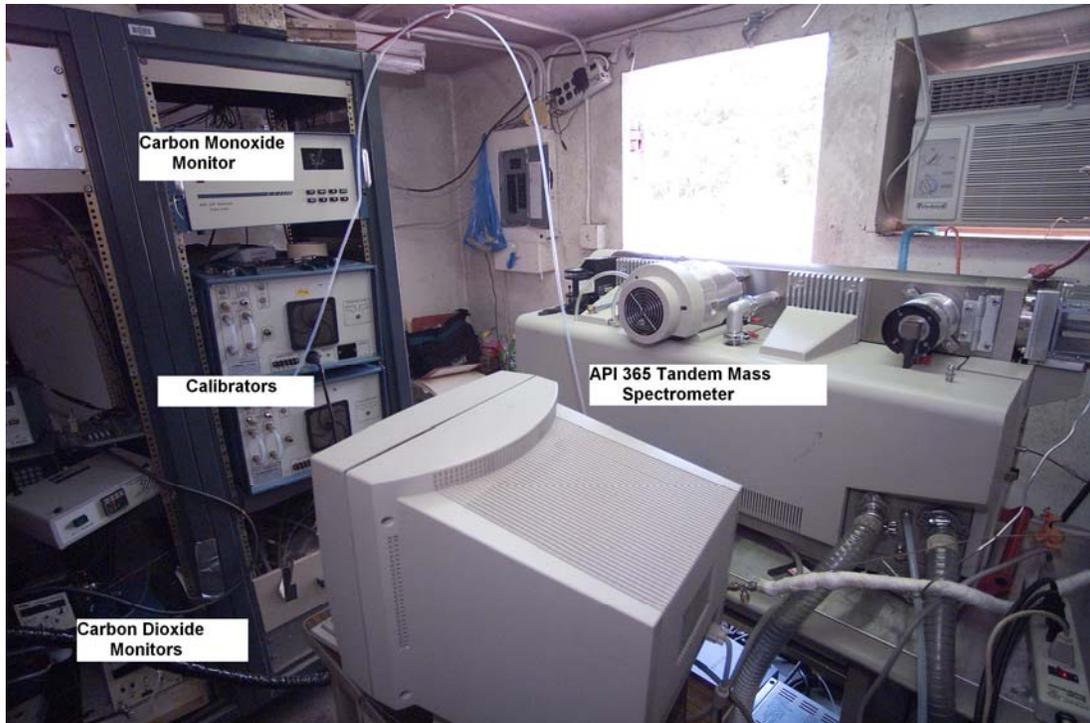
Figure 3.20. Interior View of Bombproof Shelter 2 from Rear.
Some Measurement Systems are Noted

Shelter 1 served as the sampling control center during each test. Strategically located video cameras allowed the sampling coordinator in the shelter to monitor the wind direction and speed prior to detonation, and the movement of the emissions cloud after detonation. Streamers on each tower and a wind vane were visible from two angles on the video monitors in Shelter 1, and these visual indicators of wind direction and speed were used by the coordinator to determine when the wind conditions were appropriate to initiate the test. Once the emissions were released, the wind transported the emissions cloud toward the towers (ideally), and the coordinator used the real-time video to select the tower to be used for sampling the cloud. When the most appropriate tower was identified, the flow from the other two towers was diverted to a vent, and only the sample air from the probes on the selected tower was transported to the monitoring instruments and sampling bag.

Sample pumps and sample flow were controlled using a flow and control panel shown schematically in Figure 3.21. This panel served to: turn on sample pumps, select the tower to be

sampled, control sample flow to the manifold, allow for the collection of an integrated sample in a 100 liter Tedlar bag. The bag was used to collect a sample of emissions cloud air. Because the bag is a variable volume sample container, it could collect small volumes of air from short duration tests (e.g. cloud from exploding ordnance) or large volumes from long duration tests (e.g. plume from smoke releasing munition or illumination rounds). Because the duration of cloud sampling was dependent on wind speed and munitions type, it was not known precisely beforehand, so the variable volume bag met the need. After sampling, a portion of the sample air in the bag was immediately transferred to a SUMMA canister and shipped to the laboratory for determination of the integrated amount of xenon and volatile TRI chemicals in the emissions cloud. The remaining sample in the bag was analyzed immediately on site by the carbon analyzers, the formaldehyde and NO/NO_2 monitors, and the PTR-MS. The results from the bag sample analyses provide one means of estimating emission factors. However, our laboratory tests established that some of the lower volatility or more polar TRI target chemicals were not amenable to collection in a Tedlar bag. For those chemicals the emission factors have been calculated based on the measurements made in real time by the continuous monitoring instruments.

To achieve the best chemical detection limits and therefore the best estimates of emission factors using the integrated bag samples, it is important to sample only the emissions cloud. Sample collected before or after the cloud passes the sampling tower dilutes the sample in the bag, reducing the likelihood of detecting low concentrations of target chemicals. To minimize collection of air outside of the emission cloud, a rapid response instrument (PAH monitor) was mounted at the base of the central tower and sampled through an unfiltered probe with short sample line. Tests were performed to define the delay from the time an emissions cloud was sampled at the tower until that sample reached the sample bag in Shelter 1. This delay time was factored into the start and stop times used for bag sampling.

Bombproof Shelter 2 housed the heated sampling manifold and most of the real time sampling instrumentation. These included a CO monitor, two continuous real time mass spectrometers, and two CO_2 monitors. Ambient temperature and relative humidity were also measured.
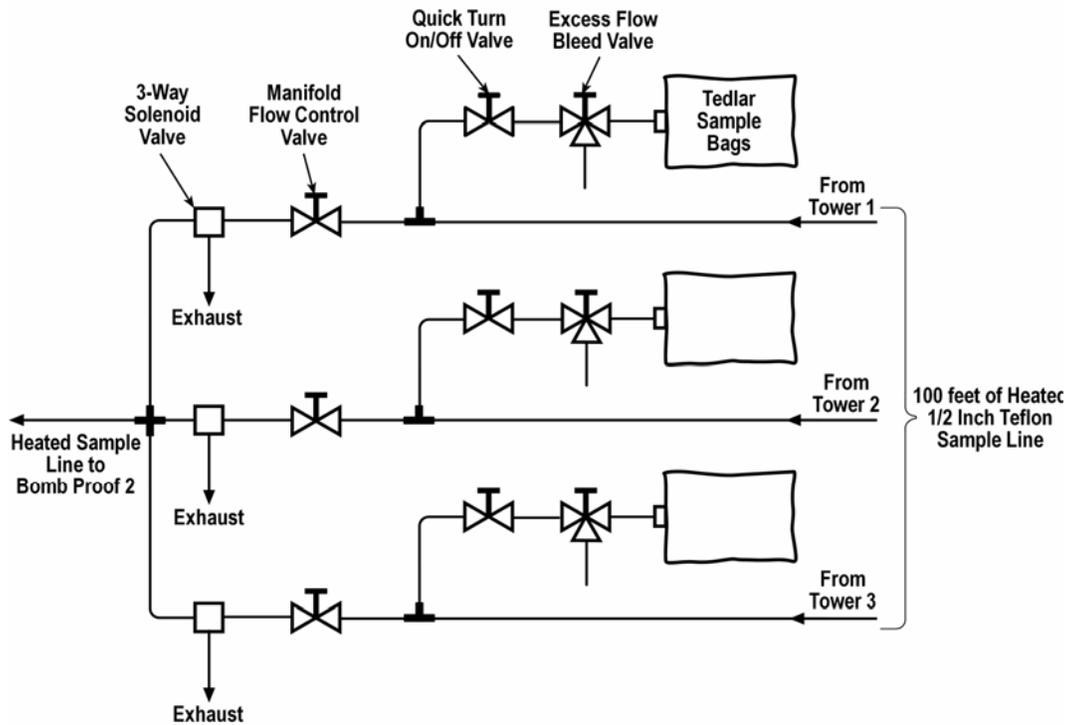
Figure 3.21. Sample Control and Selection System Flow Diagram

The following test sequence was used for the Point of Impact tests:

1. Place sampling towers dependent on wind direction, wind speed and type of munitions

2. Load filters into filter holders on tower.

3. Adjust tower angle tilt to place sampling inlets at optimal height above ground.

4. Place munitions and xenon tracer apparatus at point of detonation by test director and ordnance specialist. All activities dealing with the handling and detonation of munitions were under the direct control of the ATC Test Director.

5. Clear all nonessential personnel from test site. Test team closed in bombproof Shelter 1.

6. Ordnance specialist arms munitions.

7. Observe wind conditions.

8. Turn on sample pumps to measure background readings. Verify correct temperature for all sample lines. All three pumps were started simultaneously. Sample flow from only one tower was sent to the sample manifold in bombproof 2 with the sample flow from the other two towers being exhausted.

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9. Select tower most likely to be impacted. The sample air flowed to a heated manifold within the second bombproof , where the real-time monitors and sampling systems measured the TRI chemicals and other species required to determine emission factors.

10. Signal for firing when all systems are ready and appropriate wind conditions are observed.

11. Test director fired munitions.

12. Select tower to sample based on observation of plume.

13. Start to collect integrated bag sample as plume reaches tower. A 5 second lag time was used to account for transfer time in the sampling system.

14. Stop bag sample 5 seconds after plume passes sampling tower.

15. Continue sampling with continuous instruments until plume has cleared test area.

16. Open bombproof shelter upon instruction from test director.

17. Lower towers and recover sample filters.

18. Transfer bag sample to canister for volatile TRI chemical analysis and xenon determination; excess sample analyzed for CO, CO_2, NO, NO_x, formaldehyde, and PTR-MS chemicals on site.

All continuous analyzers were calibrated at the beginning and end of each test day.

3.6.2.1 Sampling System Testing. Prior to the POI field tests, the sampling system described in the previous section was tested in the laboratory for sample integrity and transmission efficiency. Due to safety requirements, the measurement instruments used for the POI tests needed to be located a considerable distance from the sampling towers, so the air samples passed through nearly 45 m of Teflon tubing, a Metal Bellows pump, and several stainless steel valves prior to the monitoring instruments. The possibility of losing some of the lower volatility or polar species in this sampling system was a concern. Therefore, as part of the sampling system testing and optimization, we conducted tests of the sample system transmission efficiency of a number of the semivolatile and polar chemicals that could present sampling problems. We assembled the entire sampling system that was to be used for the field tests, spiked target chemicals at ppt to ppb levels into a 17.3 m^3 environmental chamber, and measured the transfer

efficiency of the sampling system by comparing results for sampling directly from the chamber and through the sampling system. We tested dimethyl phthalate, diethyl phthalate, dibutylphthalate, dinitrobenzene, dinitrotoluene, aniline, nitrosodimethyl amine, nitrosodiethyl amine, nitrosodiphenyl amine, nitroglycerine, and diphenyl amine. All but two of the chemicals were transmitted through the sampling system (a filter, approximately 40 m of heat-traced Teflon tubing and a high flow sampling pump) with >94% efficiency. Only the two least volatile species, dibutylphthalate and nitrosodiphenylamine, showed lower transfer efficiencies, at 83 and 70% respectively. This test confirmed earlier observations that the sampling system efficiently transfers even these most difficult chemicals.

Separate tests were carried out on the integrity of samples containing the more difficult chemicals listed above following collection in large gas sampling bags. These tests were carried out to explore whether samples could be collected in bags and analyzed off-site (e.g. at a nearby mobile lab) shortly after each test, to augment the real-time measurements. Our results showed that these chemicals do not store well in large Tedlar bags, even over short (15 minute) periods. The recovery of most of the compounds was less than 65%, and half of them showed less than 25% recovery from the bag. Therefore, the possibility of analyzing collected whole air samples for these specific species was judged not feasible, due to the rapid loss to the surfaces of the sample container.

3.6.2.2 Test Strategy. An important consideration in designing the Point of Impact tests is the compromise between the need to provide statistical robustness to the emission factor estimates via replication versus the need to test a broad range of representative munitions (i.e., cover a wide range of different sizes and components). The primary constraint affecting this trade-off is the total number of tests that can be conducted. The sampling design for the Point of Impact testing was to conduct up to four weeks of testing (i.e., 20 days), running two tests per day, for a total of approximately 40 distinct munitions tests. In addition to the munitions tests, background ambient air monitoring and sampling were required each test day to allow for correction of the emissions data for background air concentrations.

In specifying the tests to be run, the design approach must recognize that not every test will be completed successfully. Some tests may be lost due to bad weather on planned test days. We also expected some loss of data due to unforeseen meteorological conditions such as short-term variation in local wind conditions. Likewise, given the complexity of the array of measurements to be made, instrument failure was another important factor that could lead to data loss. Since the nature and extent of data loss could not be completely known prior to actual field testing, our approach to Point of Impact testing was to employ a sequential test plan. Basically, after each test was conducted, we assessed the success of that test in order to determine the most appropriate subsequent test to be conducted.

Since the primary objective of the project was to demonstrate a method for measuring emission factors for TRI chemicals under realistic outdoor range conditions, an important outcome from these experiments should be estimates of the accuracy and precision of the resulting emission factors. The most appropriate and direct means for estimating accuracy and precision is through experimental replication. Therefore, one goal in sequential testing was to obtain a minimum of two complete (i.e., little to no data loss) test runs for each munitions item tested. Further replication was preferred, but was not practical when weighed against the constraints of 40 total munitions tests and the range of munitions that were tested.

The goal in selecting target munitions was to refine the target list to 12 different items that encompassed a broad, representative range of munitions. These were noted earlier in Table 3.5. Another important factor in developing a test strategy had to do with the surface over which or on which the ordnance was fired. The emissions from munitions detonated on or over soil, for example, are likely to be different than the emissions from the same type of munitions detonated in the air or over a hard surface. In the former case, entrained soil can contribute to the burden of TRI chemicals and can also affect the production of toxic chemicals by quenching chemical reactions in the initial fireball. To examine this effect, we planned to devote a few tests to measuring emissions from the same ordnance items fired over a hard surface (steel plate) and over soil.

Based on the various objectives of the Point of Impact tests, and considering the constraints on the number of available tests, we developed the prioritized list of tests shown in Table 3.6. These tests listed as "primary" were considered to be the highest priority. Those listed as "secondary" were to be completed as test time and conditions permitted.

Table 3.6. Prioritized Test Matrix for Point of Impact Testing

No.	Munitions	Type	Type of Detonation and Test Classification		
			Soil Surface	Hard Surface	Air Burst
1	155 mm Howitzer	high explosive	**primary**	**primary**	------
2	155 mm Howitzer	illumination	------	------	**primary**
3	155 mm Howitzer	smoke	secondary	secondary	------
4	66 mm Anti-tank	high explosive	------	secondary	------
5	4.2 in Mortar	high explosive	**primary**	**primary**	------
6	4.2 in Mortar	illumination	------	------	**primary**
7	81 mm Mortar	smoke	**primary**	**primary**	------
8	40 mm Cartridge	high explosive	**primary**	**primary**	------
9	40 mm Grenade	illumination	------	------	secondary
10	Hand Grenade	high explosive	secondary	secondary	------
11	Hand Held Flare	illumination	secondary	------	------
12	Hand Grenade	smoke	secondary	------	------

With the above test plan goals in mind, the experimental design for Point of Impact testing was implemented as follows:

1. Prepare munitions to conduct up to a total of four test runs for each of the tests on the top 10 list and second-tier list.
2. Starting with munitions and conditions of primary interest, conduct first test and assess the success of that test (i.e., determine whether meteorological conditions cooperated and whether instruments ran properly).
3. Conduct replicate test runs, assessing after each run, until a total of two successful outcomes have been observed. (Note that it may take two, three, or four test runs to obtain two successful outcomes depending on data loss.)
4. If two successful outcomes have not occurred after four test runs, move on to the next of the munitions/conditions on the top 10 list.

5. Proceed by cycling through the entire top 10 list. If the entire top 10 list is completed in less than 40 test runs, move on to the second-tier list and proceed similarly.

6. If both priority munitions lists are completed in less than 40 test runs, several options will be available. First, the experiment could simply be considered finished in less than 40 runs. Second, additional replicates could be obtained for those munitions that required less than four initial test runs to provide duplicates. Finally, depending on the logistics of obtaining more munitions for testing, those munitions that failed to produce two successful outcomes out of four attempts could be tested further (or additional munitions not yet tested could be considered).

Our conservative estimate going into the field study was that up to 20 percent of the possible tests would be lost due to weather (rain or inappropriate wind conditions) or to some manner of critical data loss, so we anticipated a total of approximately 32 successful test runs. Under this estimate, we expected our sequential testing approach to yield two successful replications for approximately 16 distinct test conditions.

3.6.2.3 Criteria for Field Assessment of the Success of a Test. The sequential test plan described above required rapid assessment of the success of each test in the field, shortly after the test was completed. The assessment was performed within about an hour of the test in order to provide sufficient time to set up for the next test. To be judged a success, a test had to meet the following minimum criteria.

1. Normal ordnance operation (e.g. detonation, smoke release, etc.). This was assessed visually in real time by the munitions technician and also through review of high speed video of the test, and examination of the residual ordnance item.

2. Valid data to apply carbon mass balance for emission factors. Successful measurement of CO_2 and CO and clear evidence that the emissions cloud was sampled (cloud measurements exceed background) were minimum requirements.

3. For munitions tests over soil, valid results for estimating cloud volume by a method other than carbon mass balance was required. Criteria for success were:
    - capture of the event by at least three cameras (photogrammetry) or

- collection and storage of lidar data showing cloud structure (aerosol lidar) or
- successful deployment of xenon tracer and collection of emissions cloud sample for analysis (see #4 below).

4. Valid collection of whole air cloud samples and successful transfer to sampling canister. This criterion assures a successful sample for volatile organic compound analysis. Collection of emissions cloud sample was judged by the filling of the sampling vessel when the continuous measurements show elevated levels of CO_2 and CO. Successful transfer of the sample to a canister was judged by a final canister pressure equivalent to atmospheric pressure or higher.

5. Valid collection of filter samples for trace element analysis and successful retrieval and storage of the filters. Collection will be judged by visual evidence and/or demonstration from the continuous monitors that emissions sample (above background levels) passed through the filter.

6. Valid operation of one of the real-time mass spectrometers. Success was judged by whether the instrument was operational, calibrated, collecting data during the test, and confirmation that the data had been archived for analysis.

If these minimum criteria were met, it should be possible to calculate emission factors for a large number of volatile and semivolatile organic compounds and inorganic species whose concentrations exceed the background levels. Thus the test would be judged a success.

4.0 RESULTS AND ACCOMPLISHMENTS

4.1 Point of Discharge Testing

The Point of Discharge tests were conducted between September 23, 2002 and October 3, 2002. We installed, tested and calibrated the instrumentation on September 23, and set up the sampling probes, filters, pump and heated sample lines. The actual emissions testing was initiated on September 25. Table 4.1 lists the dates and munitions tests that were carried out during the study, along with the test identifiers, and the nature of the samples collected.

4.1.1 Emissions Results

The test data for the Point of Discharge study are contained in Appendix D. Six tables are shown, one table for each munition that was tested. Each table shows the list of target chemicals, the emissions found for each compound per test in units of grams per round, the percent difference between repetitive test runs, and the average emission factors in units of grams per round. For some compounds in some tests, concentrations were measured but were below the background levels. These data are noted as "<BL". For other compounds, the concentrations were less than the method detection level. These data are noted in the tables as "<MDL". In instances where percent differences can not be calculated, a not applicable "NA" is listed. The compounds, acetonitrile, acrylonitrile, acrolein, benzene, toluene and naphthalene, are listed twice in the tables. The first entries are from data collected using the real time PTR mass spectrometer. The later entries are from data collected using time integrated canister sampling followed by off-line analyses with a gas chromatograph/mass spectrometer.

For the .50 caliber machine gun duplicate test runs (Table D-1), reasonably good agreement was observed for most of the target compounds.   In general percent differences of less than 30% were observed. For the 120 mm Mortar, M934 high explosive zone 1 duplicate test runs (Table D-2), very poor agreement was obtained for the duplicate tests. The second test run shows consistently less gaseous emissions. Logbook notes indicate that the concussion produced from

Table 4.1. List of Point of Discharge Emissions Tests

Date	Test Item	No. of Rounds	Comments
September 25, 2002	Background air sample	--	
September 25, 2002	25 mm cannon cartridge (tracer) M793TP-T	3	Excessive chamber dilution rate
September 25, 2002	25 mm cannon cartridge (tracer) M793TP-T	3	
September 26, 2002	Background air sample	--	
September 26, 2002	25 mm cannon cartridge (tracer) M793TP-T	3	Repeat 25 mm from previous day
September 26, 2002	25 mm cannon cartridge (tracer) M910TPDS-T	3	
September 26, 2002	25 mm cannon cartridge (tracer) M910TPDS-T	3	Muzzle fireball observed; test representativeness suspect
September, 27, 2002	.50 cal machine gun round M2 AP	20	
September, 27, 2002	.50 cal machine gun round M2 AP	20	
September, 27,2002	Background air sample	--	
September 30, 2002	Background air sample	--	
September 30, 2002	120 mm M931 FRP Zone 1	1	
September 30, 2002	120 mm M931 FRP Zone 1	1	Muzzle fireball observed
October 01, 2002	Background air sample	--	
October 01, 2002	120 mm mortar M934 HE Zone 1	1	
October 01, 2002	120 mm mortar M934 HE Zone 1	1	
October 02, 2002	Background air sample	--	
October 02, 2002	120 mm mortar M931 FRP Zone 4	1	ATC VOC line not connected; repeat test
October 02, 2002	120 mm mortar M931 FRP Zone 4	1	Chamber damaged
October 03, 2002	Background air sample	--	
October 03, 2002	120 mm mortar M934 HE Zone 4	1	Test cancelled due to chamber damage

these two rounds resulted in minor damage to the test chamber. Close inspection of the chamber after the second test revealed that the seam in the front wall and the roof of the chamber had actually come apart. Based upon this analysis, the data from the second test run is suspect. For the 120 mm Mortar, M931 full range practice zone 1 cartridge (Table D-3), the duplicate test runs likewise showed lower emissions for the second test, i.e. values were 50 to 75% lower for the second test. Emission factors for the 25 mm M793 target practice tracer cartridges (Table D-4) compare reasonably well for the three tests for those compounds in which measured concentrations were significantly above background levels. Percent differences across tests were in general ± 30%. Table D-5 shows the emissions from the 120 mm Mortar, M931 full practice zone 4 cartridge duplicate test runs. For most of the organic compounds, the first test shows much higher emissions (~50 to 100% higher). However, the emissions from the metals agree very well between to the two runs, with percent differences less than 30%.   The duplicate tests for the 25 mm M910 target practice discarding sabot-tracer are shown in Table D-6. Percent differences were in general ~50%. The first test showed consistently higher emissions for most of the organic compounds and the metals.

4.1.2 Measurement Methods Comparison

One of the primary objectives of the POD study was to compare our project's measurement methods with those employed by ATC/CHPPM. The latter groups utilized standard methods (e.g. EPA or NIOSH methods) which often involve collecting large sample volumes over several minutes. Because the ultimate objective of our project is to quantify emissions in uncontrolled outdoor situations, where only a few seconds may be available for sampling, we selected and developed several highly sensitive real time measurement approaches. One of the purposes of the POD study was to compare our novel methods with accepted measurement approaches.

The results of the AEC/ATC/CHPPM study are not publicly available at this time, but we have been given permission to present comparison data for four chemicals. These chemicals are total carbon, formaldehyde, benzene, and copper. Figures 4.1-4.4 show the side-by-side comparisons of our methods (Battelle) and the AEC/ATC/CHPPM (listed as ATC for convenience) results.

Carbon Mass Balance
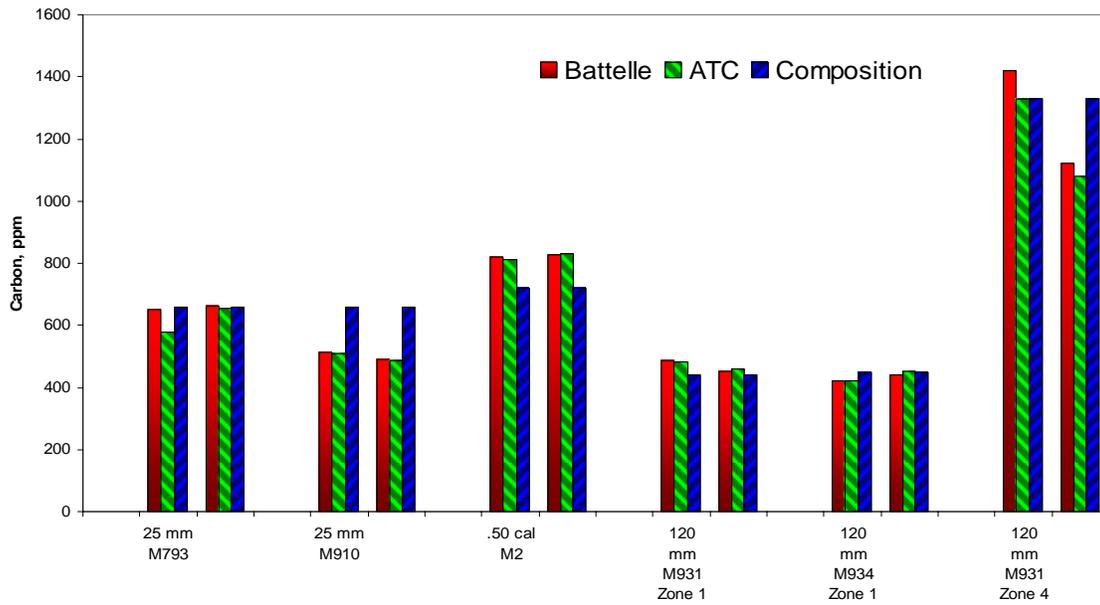
Figure 4.1. Comparison of Total Carbon Concentration in the ATC Test Chamber for Duplicate Tests of Six Munitions

BENZENE
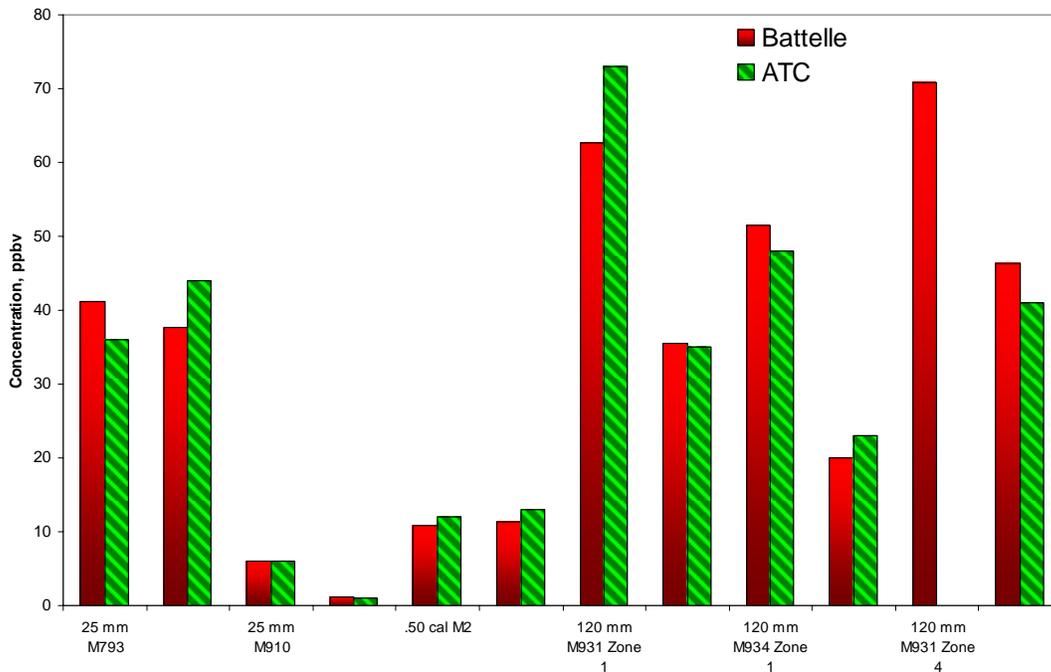
Figure 4.2. Comparison of Benzene Concentration in the ATC Test Chamber for Duplicate Tests of Six Munitions
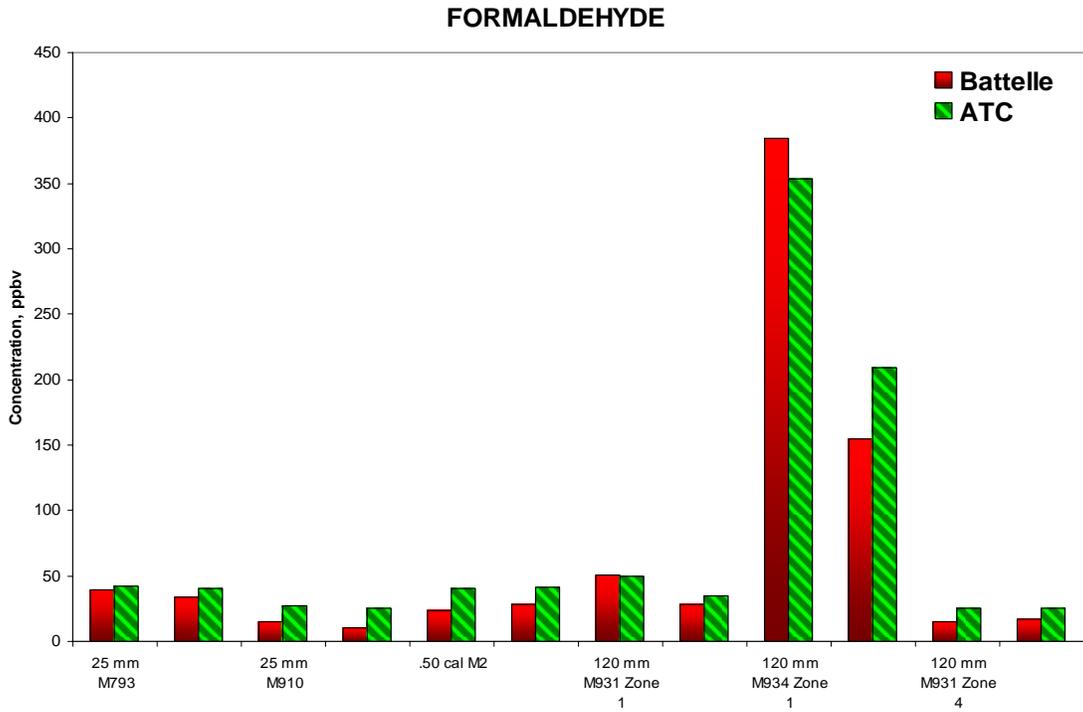
FORMALDEHYDE

Figure 4.3. Comparison of Formaldehyde Concentration in the ATC Test Chamber for Duplicate Tests of Six Munitions
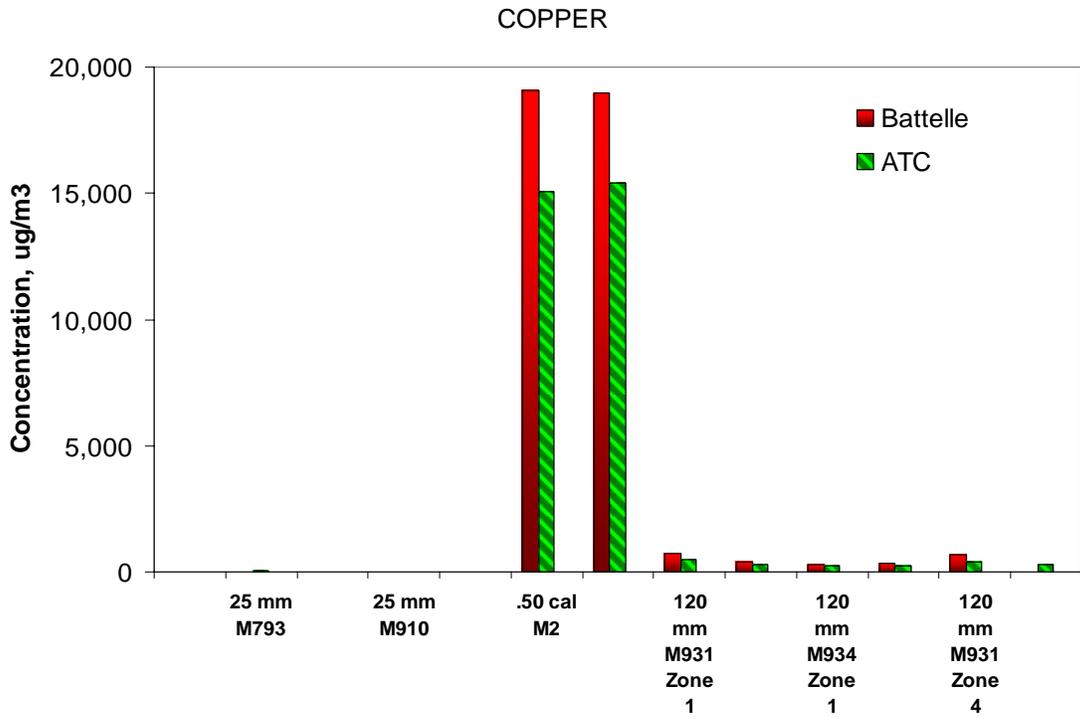
COPPER

Figure 4.4. Comparison of Copper Concentration in the ATC Test Chamber for Duplicate Tests of Six Munitions

The carbon mass results are shown in Figure 4.1. This is a particularly important comparison, because carbon mass is being used as a dilution tracer in the POI studies, so it is critical that carbon be measured correctly. Six sets of duplicate tests were performed. Each test is represented by three vertical bars in the figure. The first two bars show the concentration of total carbon measured by Battelle and ATC respectively. The third bar represents the concentration of carbon expected in the test chamber calculated from the amount of carbon available in the munitions item. It is evident from Figure 4.1 that the agreement between Battelle and ATC is quite good, and that both agree well with the theoretical carbon concentration. The total carbon in Figure 4.1 was calculated from the sum of the background-corrected concentrations of CO_2, CO, and hydrocarbons.

Results for benzene similarly show good agreement between the two teams. However, it is clear that the test reproducibility can vary widely. For example, results for the duplicate tests of the M910 cannon cartridge did not agree well at all. Also, the benzene values from the two M934 Zone 1 mortar round tests varied considerably. These variations are discussed later in this report.

The formaldehyde comparisons are shown in Figure 4.3. While the agreement is not perfect, the two sets of formaldehyde results agree well, except at the lowest levels. This may have to do with different time intervals used to define chamber background concentration.

Lastly, the trace metal copper, shown in Figure 4.4, agrees fairly well. Only low levels of copper were found in most tests. Only the .50 cal machine gun round showed high concentrations. These limited comparisons provided confidence in the respective methods we planned to use for the outdoor POI tests.

4.1.3 Comparison of Theoretical and Observed Masses for Conserved Species

It is of interest to compare the masses of conserved species measured during the POD tests with the expected masses of these materials based on munitions composition. One of the most important mass balance comparisons is for carbon, because we are using carbon mass balance in calculating emission factors for the outdoor POI studies, and it is critical to show that the

approach captures the majority of carbon released during munitions tests. Very good agreement was observed between the expected and measured mass of carbon in these tests, as noted in the previous section.

It is also possible to make such comparisons for metals used in the munitions. Metals contained in the propellants and primers are likely to vaporize during firing and then condense homogeneously, or more likely on other existing particles. The fraction of the metal that forms fine particles may remain airborne in the chamber and be subject to measurement during the 20 minute filter sampling. However, during the initial turbulence in the chamber, some fraction of the particles is expected to be deposited on the chamber surfaces, and any metal that is present in larger particles may be lost before sampling due to settling out from the air. Therefore it is expected that the observed mass of metals in the air will be less than the mass expected based on compositional data.

Of the 16 TRI metals that we measured, three are found in the primer used in all six munitions tested. These were: barium as barium nitrate, lead as lead styphnate, and antimony as antimony sulfide. A comparison of the expected mass of these metals (based on composition data) and the measured mass is provided in Table 4.2. Each munitions item tested is listed in column 1. The amounts of metals from duplicate tests are given in columns 2 and 3; the maximum expected mass based on composition is shown in column 4, and the observed masses are shown as a fraction of the maximum in columns 5 and 6.

The last two columns of Table 4.2 show the observed mass of the metals as a percentage of the maximum theoretical mass that could be present in the chamber air based on munitions composition. The observed mass is less than half of the theoretical maximum mass with few exceptions. Barium shows the lowest observed/theoretical ratio for nearly all tests, whereas lead and antimony were fairly similar for a given test. For the most part, the mass "recovery" was much lower for the mortar rounds than for the other munitions items.

Table 4.2. Metals Mass Balance

Munitions/Metal	Observed Mass		Maximum Theoretical Mass	Observed/Theoretical Mass	
	Test 1 (grams/round)	Test 2 (grams/round)	(grams/round)	Test 1 (percent)	Test 2 (percent)
25 mmTPDS-T M910					
barium	0.0060	0.0056	0.044	14	13
lead	0.0280	0.0235	0.044	64	53
antimony	0.0148	0.0132	0.028	53	47
25 mm TP-T M793					
barium	0.0082	0.0077	0.044	19	17
lead	0.0188	0.0224	0.044	43	51
antimony	0.0105	0.0115	0.028	38	41
.50 Caliber AP M2					
barium	B.L.*	B.L.*	0.034	0	0
lead	0.0101	0.0088	0.026	39	34
antimony	0.0046	0.0047	0.01	46	47
120 mm FRP M931 zone 1					
barium	0.0014	0.0033	0.105	1.3	3.1
lead	0.0073	0.0062	0.089	8.2	6.9
antimony	0.0024	0.0022	0.039	6.3	5.6
120 mm HT M934 zone 1					
barium	0.0030	0.0004	0.105	2.9	0.4
lead	0.0085	0.0081	0.089	9.6	9.1
antimony	0.0027	0.0028	0.039	6.9	7.1
120 mm FPR M931 zone 4					
barium	0.0246	0.0281	0.105	23	27
lead	0.0082	0.0070	0.089	9.2	7.9
antimony	0.0041	0.0032	0.039	10	8.1

* Below background.

4.2 Point of Impact Testing

The Point of Impact campaign was conducted at Aberdeen Test Center (ATC) in September, 2003. Tests were conducted with a variety of high explosive, smoke, and illuminating munitions, as noted in Table 3.6. Some items were tested over soil and also over a hard surface (large steel plate), to help distinguish the effect of soil entrainment in the fireball on emissions. The field campaign was carried out over the period September 3-30, 2003. Installation of instrumentation in three bombproof shelters, and setup of three 10-m sampling sampling towers and associated sampling systems took place during September 4-6, 2003. A pilot test was carried out on September 8, and full testing was initiated on September 9. Testing continued each weekday, and some weekend days, until September 29, except for the period

September 18-22 when the project was shut-down due to hurricane Isabel. Equipment was shut down and removed from the site on September 29-30. Altogether a total of 45 tests (munitions + background sampling) was conducted.

The munitions were obtained and prepared for testing by ATC. Preparation included developing a protocol and safety plan for each item, physically removing any propellant, if present, and rigging some of the munitions for electronic ignition. For some of the smaller items, our modeling results suggested that multiple items should be discharged simultaneously in order to improve the chances for detecting trace constituents in the dilute emissions cloud. ATC developed procedures for simultaneously firing these items.

An example of the test configuration is shown in Figures 4.5 and 4.6, taken from one of the photogrammetry cameras. Figure 4.5 shows the test site just after detonation of a 4.2 in. high explosive mortar round, and Figure 4.6 shows the emissions cloud impacting two of the sampling towers. The left-most tower was used for sampling during this test.

4.2.1 POI Test Matrix

The matrix of tests conducted during the POI campaign is provided in Table 4.3. The table lists the test number, the items tested, the munitions item designation and DODIC number, and brief comments on the test conditions. As noted in the table, background air samples were collected frequently throughout the POI campaign. These tests are designated "BKG" in column 1 of the table. Background gas and particle samples were collected for approximately 30 minutes, to provide sufficient material for metals analysis from the filters.

The tests noted in Table 4.3 are summarized in Table 4.4. The last two columns show the number of tests attempted for a given item/conditions, and the number of tests considered successful during the field campaign. Overall, we conducted 45 tests, comprised of 35 munitions tests noted in the next to last column of Table 4.4, and 10 Background tests. The number of successful tests is shown in the last column of the table. Overall, 25 of the 35 munitions tests were judged to have been successful. Of the unsuccessful tests, seven were due to the emissions

Table 4.3. Tests Conducted During the Point of Impact Campaign

Test No.	Item	Number	DODIC	Condition
POI090901	3 Flares	M49A1	L495	Ground level
POI090902	3 Flares	M49A1	L495	Ground level
POI090903	3 Flares	M49A1	L495	Ground level
POI0909BKG	None			
POI091001	3 Flares	M49A1	L495	Ground level
POI091002	3 Flares	M49A1	L495	Ground level
POI091003	40mm Illum	M583	B535	5 rounds--Air burst
POI091004	40mm Illum	M583	B535	5 rounds--Air burst
POI091005	40mm Illum	M583	B535	5 rounds--Air burst
POI091006	40mm Illum	M583	B535	5 rounds--Air burst
POI0911BKG	None			
POI091101	40mm Illum	M583	B535	5 rounds--Air burst
POI091102	Smoke Grenade	M18	G945	3 grenades--air burst
POI091103	Smoke Grenade	M18	G945	3 grenades--ground release
POI091104	Smoke Grenade	M18	G945	3 grenades--ground release
POI091601	81mm Smoke Mortar	M375A3	C276	Air release
POI091602	81mm Smoke Mortar	M375A3	C276	Air release
POI091603	81mm Smoke Mortar	M375A3	C276	Air release
POI0916BKG	None			
POI091701	155mm Illum	M485	D505	Air release
POI0917BKG	None			
POI091702	81mm Smoke Mortar	M375A3	C276	Air release
POI091703	81mm Smoke Mortar	M375A3	C276	Air release
POI0922BKG	None			
POI0923BKG	None			
POI092301	155mm Illum	M485	D505	Air release
POI092302	155mm Illum	M485	D505	Air release
POI0924BKG	None			
POI092401	66mm LAW Antitank Rocket	M72A2	H557	Fire into steel plate--3 rounds
POI092402	66mm LAW Antitank Rocket	M72A2	H557	Fire into steel plate--3 rounds
POI092403	40mm Cartridge HE	M430	B571	Fire into steel plate--5 rounds
POI0925BKG	None			
POI092501	4.2" Mortar HE	M329A2	C697	On steel plate
POI092502	4.2" Mortar HE	M329A2	C697	On steel plate
POI092503	4.2" Mortar HE	M329A2	C697	Over soil
POI092504	4.2" Mortar HE	M329A2	C697	Over soil
POI092601	155mm Howitzer HE	M107	D544	Over soil
POI0926BKG	None			
POI092602	155mm Howitzer HE	M107	D544	Over steel plate
POI092603	155mm Howitzer HE	M107	D544	Over steel plate
POI092701	155mm Howitzer Smoke	M825	D528	Over soil
POI092702	155mm Howitzer Smoke	M825	D528	Over soil
POI092703	155mm Howitzer Smoke	M825	D528	Over soil
POI092704A	155mm Howitzer Smoke	M825	D528	Over soil
POI092704B	155mm Howitzer Smoke	M825	D528	Over soil
POI0927BKG	None			

Figure 4.5. Test of 4.2 in. High Explosive Mortar Round Just After Detonation

Figure 4.6. Test of 4.2 in. High Explosive Mortar Round. Emissions Cloud is Being
Sampled by Tower 1 (left-most tower)

cloud missing our sampling towers and three were caused by duds or low order detonations. A close-up view of one of the 4.2 in. mortar (HE) tests is shown in Figure 4.7.

Table 4.4. Point of Impact Campaign Test Summary

Item	Type	Designation	Medium	No. Per Tests	No. of Tests	No. of Successful Tests
155 mm Howitzer	High Explosive	M107	Hard Surface	1	2	2
155 mm Howitzer	High Explosive	M107	Soil	1	1	0
4.2 in. Mortar	High Explosive	M329A2	Hard Surface	1	2	2
4.2 in. Mortar	High Explosive	M329A2	Soil	1	2	2
66 mm Rocket	Shaped Charge	M72A2	Steel Plate	3	2	2
40 mm Cartridge	High Explosive	M430	Steel Plate	5	1	0
155 mm Howitzer	Illumination	M485	Air	1	3	2
40 mm Grenade	Illumination	M583	Air	5	5	3
155 mm Howitzer	Smoke	M825	Soil	1	4	1
81 mm Mortar	Smoke	M375A3	Air	1	5	5
Grenade	Smoke	M18	Air	3	2	2
Grenade	Smoke	M18	Soil	3	1	1
Trip Flare	Illumination/Signaling	M49A	Air	3	5	3

4.2.2 Data Reduction for Point of Impact Tests

It was anticipated that many of the TRI chemicals would not be present in the emission clouds from the selected ordnance, so the treatment of "non-detects" is important. To maximize the usefulness of the data, we have are reporting upper limit values for the emission factors rather than reporting "Not Detected." The upper limit values are based on the detection limits of the various measurement methods used in conducting the POI tests. This section described the process used to compute upper limit emission factors for undetected chemicals.

4.2.1.1 Volatile Organic Compounds by GC/MSD. Volatile organic compounds determined by gas chromatography—mass spectrometry include species through hexachlorobutadiene in subsequent tables in this section. The analytical detection limit for these species by this method

Figure 4.7. Close-Up View of Fireball Formed During Test of High Explosive 4.2 in.
Mortar Round (Over Hard Surface)

is 0.05 ppbV. The detection limit for each of these species in concentration units ($\mu g/m^3$) is
provided in Table 4.5. . Many of these chemicals are present in ambient air, so it is necessary to
subtract background air concentrations from the test samples. A background air sample was
collected for each set of munitions tests, usually 1-2 hours before the test. The concentration of a
species in the background sample was subtracted from the concentration in the test sample to
obtain the background—corrected concentrations used to compute emission factors. The
methodology used for non-detects is as follows:

- If the concentration in the test sample is below the detection limit, the detection limit value is
  used as an upper limit, and this value carries a "less than" flag. The emission factor
  calculated using this upper limit concentration also is flagged as an upper limit.

Table 4.5. Detection Limits for Chemicals Measured by GC-MSD

Compound	Detection Limit, µg/m^3	Compound	Detection Limit, µg/m^3
Acetonitrile	0.39	1,2-dichloropropane	0.23
Acrolein	1.48	bromodichloromethane	0.33
Acrylonitrile	0.57	trichloroethene	0.34
Naphthalene	0.18	1,4-dioxane	0.18
Freon-12	0.25	heptane	0.2
methyl chloride	0.1	cis-1,3-dichloropropene	0.23
Freon 114	0.35	methyl isobutyl ketone	0.2
vinyl chloride	0.13	trans-1,3-dichloropropene	0.23
1.3-butadiene	0.11	1,1,2-trichloroethane	0.27
methyl bromide	0.19	toluene	0.19
ethyl chloride	0.13	methyl butyl ketone	0.2
Freon-11	0.28	dibromochloromethane	0.43
1,1-dichloroethene	0.2	1,2-dibromoethene	0.38
carbon disulfide	0.16	tetrachloroethene	0.34
Dichloromethane	0.17	chlorobenzene	0.23
Freon-113	0.38	ethylbenzene	0.22
trans-1,2-dichloroethene	0.2	m&p xylene	0.22
1,1-dichloroethane	0.2	bromoform	0.52
methyl tert butyl ether	0.18	styrene	0.21
methyl ethyl ketone	0.15	1,1,2,2-tetrachloroethane	0.34
cis-1,2-dichloroethene	0.2	o-xylene	0.22
Hexane	0.18	4-ethyltoluene	0.25
Chloroform	0.24	1,3,5-trimethylbenzene	0.25
ethyl acetate	0.18	1,2,4-trimethylbenzene	0.25
Chloroform	0.24	m-dichlorobenzene	0.3
ethyl acetate	0.18	p-dichlorobenzene	0.3
Tetrahydrofuran	0.15	o-dichlorobenzene	0.3
1,2-dichloroethane	0.2	1,2,4-trichlorobenzene	0.37
1,1,1-trichloroethane	0.27	hexachlorobutadiene	0.53
Benzene	0.16		
carbon tetrachloride	0.32		
Cyclohexane	0.17		

- If the concentrations of both the test and background air samples are above detection limit they are subtracted. If the result is positive it is reported without a flag. If the result is zero or negative, the detection limit is reported and the value carries a "less than" flag.
- If the concentration in the test sample is above the detection limit and the background air sample is below the detection limit, the detection limit is subtracted and the difference is reported without a flag.

4.2.1.2 Chemicals Measured by Atmospheric Pressure Chemical Ionization Tandem Mass Spectrometry (APCI MS/MS). The detection limits for the chemicals measured by real-time APCI MS/MS are shown in Table 4.6. .The data reduction process for the results from this real-time monitor is as follows:

- The instrumental signal for the ion pair representing each target chemical was averaged over the period when the emissions cloud was sampled. The corresponding signals for these chemicals were averaged for background air sampled a few minutes before each test. The background signal for each chemical was subtracted from the test signal, and the result converted to concentration units using the daily response factors for each target chemical.

- If the resulting concentration is at or below the detection limit, the detection limit is used and the value is assigned a "less than" flag. If it is above the detection limit, it is reported without a flag.

Table 4.6. Detection Limits for Chemicals Measured by APCI-MS/MS

Compound	Detection Limit, $\mu g/m^3$
chlorine	0.1
N-nitrosodimethylamine	0.3
Aniline	0.027
N-nitrosodiethylamine	0.56
dinitrobenzene	0.027
diphenyl amine	0.069
dinitrotoluene	0.045
dimethylphthalate	0.02
N-nitrosodiphenylamine	0.055
nitroglycerine	0.55

4.2.1.3 Chemicals Measured by Proton Transfer Reaction Mass Spectrometry (PTR-MS). The detection limits for the five chemicals measured in real-time by PTR-MS are listed in Table 4.7. We measured these chemicals in real-time during the munitions tests, and also in the integrated bag sample collected during each test. The bag samples were analyzed on site,

immediately following each test, and those data have been used to compute emission factors. The data reduction routine used for the PTR-MS data was as follows:

- For each target chemical, the signal measured in the background sample for a given test was subtracted from the signal obtained from the test sample. The background-corrected signal was then divided by the response factor for the target chemical to yield a concentration.

- If the concentration of the test sample is above the detection limit, it is reported without a flag.

- If the concentration of the test sample is at or below the detection limit, the detection limit is reported and the value is assigned a "less than" flag.

Table 4.7 Detection Limits for Chemicals Measured by PTR-MS

Compound	Detection Limit, $\mu g/m^3$
HCN	32
toluene	9.0
phenol	391
quinoline	1.2
anthracene	2.3
nitrobenzene	2.3
dibenzofuran	2.2

4.2.1.4 Carbon Oxides and Total Hydrocarbons. Measurements of CO_2, CO and total hydrocarbons were performed using two sampling approaches. The instruments were used to monitor the sample air continuously during each test, and they also were used to measure the CO_2, CO and total hydrocarbon levels in the integrated bag sample immediately after each test. Note that the sample volume collected by the 100 liter bag was sometimes insufficient to permit these on-site analyses. This occurred occasionally for exploding ordnance tests, when the sampling time was extremely short.

The primary data source for these three parameters was the continuous real-time measurement. The signal was integrated and the resulting dose was divided by the time interval over which the emissions cloud was sampled to yield an average concentration in the emission cloud. In a few instances the signal during a test was not significantly different from the background signal, so the integration could not be performed. In these cases we substituted the value measured in the integrated bag. Values measured in the bag were corrected by subtracting the values measured in the background air sample bag associated with each set of tests. If the concentration measured in the test sample was the same as or below the background sample, a background—corrected value of zero was used.

4.2.1.5 Nitrogen Oxides and Formaldehyde. Measurements of nitrogen oxides and formaldehyde were made on-site from the integrated bag sample collected during each munitions test and each associated background air sample. The response times of these instruments are slower than the other real-time monitors we employed, so that quantification of these species by real-time monitoring during the shorter tests would be problematic. Because these species are relatively stable for short periods (~1 hr) in Tedlar bags, we measured them from the bag samples only.

The data reduction process used for these chemicals is as follows.

- The concentration measured in the background air sample was subtracted from the concentration in the test sample. If the difference was positive it was reported without a flag. If the difference was zero or negative, a value of zero was reported.

The nitrogen oxides monitor measures nitric oxide (NO) and total nitrogen oxides (NO_x). For purposes of these tests NO_x is defined as the sum of NO and NO_2, so NO_2 was determined as (NO_x – NO). It should be noted that the NO_x measurement method involves catalytic reduction of NO_2 to NO, and some other oxidized nitrogen compounds (e.g. nitro compounds) can be reduced along with NO_2 and cause a positive bias to the NO_2 measurement. This effect could be significant if energetic materials containing nitro groups (e.g., TNT) are volatilized without being combusted during detonations.

4.2.1.6 Xenon. Xenon was measured on an aliquot from the integrated bag sample collected during each test and also from the background air samples collected each day of testing. The relative standard deviation of the xenon concentration in the background air samples was 8%. Because xenon is being used as a dilution tracer to compute emission factors, it is desirable to screen out samples that do not contain xenon above the background air level, to avoid biasing the emission factors. In this regard, we only used for emission factor calculations xenon values that exceeded the background air concentration by three times the standard deviation. This criterion ruled out 9 of 24 for using xenon to calculate emission factors.

4.2.1.7 Metals. Metals were determined from the four filter samples collected during each test, and from the filters collected during background air sampling. Each filter was extracted and analyzed separately by ICP-MS, with analytical detection limits noted in Section 3.4.2.

As noted earlier, four filter samples were collected at different positions in the emissions cloud to improve the representativeness of the results. Because multiple samples were involved, the data reduction process was a little more complicated. The results for each metal from the four test samples were averaged, and the results from the four associated background air samples also were averaged. If the result from one or more of the samples was below the detection limit, we substituted one-half the detection limit, summed the masses from the four samples, divided by the total flow rate, and flagged the result. The same process was used for the background air samples.

The background air samples were collected for ~30 minutes so much larger volumes of air (3-4 km^3) were sampled, so the detection limits were much lower than the test samples where only 0.02-0.08 m^3 of air was typically sampled. The very low concentrations of trace metals in the background air samples and the very short collection times and low sampling volumes of the emission cloud samples demonstrated that correction of the test samples for background air concentrations was unnecessary. The background air concentrations were so low relative to the detection limits for the emission samples that they would never cause the detection limit to be exceeded for the emission samples.

Because of the short sampling times and consequent low sample volumes for the emissions tests, the overall metals results are not sensitive to low levels of metals in the emissions cloud, and most of the results are non-detects. For tests in which metals concentrations were observed above the detection limit, we report the resulting emission factors. For tests in which the metals were not detected in all four filters, we report the emission factors as upper limits. Because the detection limits are so high due to the short sampling times, these upper limits should be used with caution, as the actual emission factors could be much lower than the upper limit values. In this regard, the upper limit emission factors for two of the metals, aluminum and zinc, are so high, due to the relatively high analytical detection limit, for these elements, that the results are not useful and are not reported.

4.2.3 Overview of Emissions Results

Table 4.8 summarizes the air concentrations from the Point of Impact emissions tests. The top four rows show the test designation, the ordnance item tested, and the number of items involved in that test. The next two rows list the temperature and relative humidity conditions during the test. Subsequent rows in the table give the background-corrected concentrations of the target chemicals in the emissions cloud, in units of $\mu g/m^3$. Values in shaded cells represent measurements that were below detection limit, as noted above.

The emissions tests were conducted at ambient temperatures from 23 to 28ºC, with humidities between 40 and 65%. The organic compounds that were frequently present in the emissions cloud above background concentrations include naphthalene, Freon 12, methyl chloride, Freon 11, carbon disulfide, methyl ethyl ketone, benzene, heptane, toluene, and formaldehyde. The TRI chemicals in this group include naphthalene, carbon disulfide, benzene, toluene, and formaldehyde. Benzene, toluene, and formaldehyde were the only organic TRI chemicals that were present above background levels in every emissions test.

Of the trace metals, only chromium, copper, and lead were often present at measurable levels. All three of these elements are on the TRI list. Other chemicals that were frequently or always present above background included CO_2, CO, NO, NO_2. particle-bound PAH, and hydrogen

Table 4.8.   Background-Corrected Concentrations of Chemicals Measured During Point of Impact Study. All Concentrations in µg/m³

	POI091001	POI091002	POI091005	POI091006	POI091101	POI091102	POI091103	POI091104	POI091601	POI091602	POI091603	POI091702	POI091703
	Signal Flare	Signal Flare	40mm Illumination	40mm Illumination	40mm Illumination	Grenade Smoke	Grenade Smoke	Grenade Smoke	81mm Mortar Smoke	81mm Mortar Smoke	81mm Mortar Smoke	81mm Mortar Smoke	81mm Mortar Smoke
Number of Items Tested	3	3	5	5	5	3	3	3	1	1	1	1	1
Temperature (avg), C			24.5	25.4	23.7	23.9	26.2	27.2	23.5	23.8	25.9	26.3	27.2
Rel Humidity (avg), %			46.1	48.5	50.7	53.1	45.2	40.4	49.1	43.4	39.2	43.1	42.2
Acetonitrile	0.04	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.16	0.39
Acrolein	1.48	1.48	0.94	1.48	1.48	1.34	5.78	3.81	1.48	1.01	0.49	1.48	1.48
Acrylonitrile	0.42	0.57	0.57	0.95	2.97	2.35	2.86	1.87	0.57	0.57	0.57	0.57	0.57
Naphthalene	0.19	0.12	0.11	0.18	0.28	0.40	0.23	0.18	0.18	0.18	0.05	0.19	0.45
Freon-12	0.61	0.04	0.00	0.04	0.11	0.08	0.01	0.25	0.39	0.25	0.04	0.06	0.43
Methyl Chloride	0.67	0.10	0.05	0.10	0.10	0.25	0.41	0.44	0.22	1.34	0.20	0.13	1.23
Freon 114	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Vinyl Chloride	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13
1,3-Butadiene	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.27	1.95
Methyl Bromide	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
Ethyl Chloride	0.14	0.13	0.13	0.13	0.13	0.19	0.16	0.13	0.18	0.13	0.13	0.21	0.13
Freon-11	0.06	0.02	0.28	0.28	0.01	0.04	0.06	0.28	0.17	0.06	0.28	0.16	0.35
1,1-Dichloroethene	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Carbon Disulfide	0.21	0.29	0.16	0.23	0.16	0.12	0.16	0.16	0.10	0.82	0.28	0.16	0.72
Dichloromethane	3.71	0.87	0.52	0.22	0.17	0.03	2.85	1.64	0.24	0.17	0.25	0.26	0.32
Freon-113	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
trans-1,2-Dichloroethene	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
1,1-Dichloroethane	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Methyl Tert Butyl Ether	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Methyl Ethyl Ketone	0.13	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.20	1.05	8.07
cis-1,2-Dichloroethene	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Hexane	0.18	0.18	0.18	0.18	0.32	0.18	1.27	0.34	0.18	0.08	0.18	0.33	0.18
Chloroform	0.24	0.24	0.24	0.24	0.24	0.24	0.30	0.24	0.24	0.24	0.24	0.24	0.24
Ethyl Acetate	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.48	0.18	0.18
Tetrahydrofuran	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
1,2-Dichloroethane	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
1,1,1-Trichloroethane	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
Benzene	0.16	0.16	0.16	0.09	0.36	9.24	11.11	9.63	0.81	1.88	0.84	2.63	8.36
carbon tetrachloride	0.32	0.32	0.32	0.32	0.17	0.09	0.32	0.32	0.32	0.52	0.32	0.32	0.32
Cyclohexane	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.28	0.17	0.17
1,2-Dichloropropane	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.38	0.35	0.24
Bromodichloromethane	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33
Trichloroethene	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
1,4-Dioxane	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Heptane	0.25	0.26	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.15	0.20	0.20
cis-1,3-Dichloropropene	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23
Methyl Isobutyl Ketone	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.27	0.20	1.00
trans-1,3-Dichloropropene	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23
1,1,2-Trichloroethane	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
Toluene	0.24	0.38	0.15	0.47	0.19	3.00	3.59	2.70	0.31	0.45	0.76	0.96	1.95

Shaded value = Upper limit   Stippled value = Lower limit

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Table 4.8.   (Continued)

	POI091001	POI091002	POI091005	POI091006	POI091101	POI091102	POI091103	POI091104	POI091601	POI091602	POI091603	POI091702	POI091703
	Signal Flare	Signal Flare	40mm Illumination	40mm Illumination	40mm Illumination	Grenade Smoke	Grenade Smoke	Grenade Smoke	81mm Mortar Smoke	81mm Mortar Smoke	81mm Mortar Smoke	81mm Mortar Smoke	81mm Mortar Smoke
Methyl Butyl Ketone	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.48	0.33	0.65
Dibromochloromethane	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43
1,2-Dibromoethane	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Tetrachloroethene	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Chlorobenzene	0.23	0.23	0.23	0.23	0.23	0.23	0.29	0.23	0.23	0.23	0.23	0.23	0.23
Ethylbenzene	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.23
m&p-Xylene	0.38	0.25	0.22	0.22	0.33	0.87	0.22	0.27	0.22	0.27	0.22	0.22	0.12
Bromoform	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52
Styrene	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.50
1,1,2,2-Tetrachloroethane	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
o-Xylene	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22
4-Ethyltoluene	0.25	0.25	0.25	0.25	0.25	0.26	0.25	0.25	0.25	0.25	0.25	0.25	0.25
1,3,5-Trimethylbenzene	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
1,2,4-Trimethylbenzene	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
m-Dichlorobenzene	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.44	0.30	0.30	0.30	0.30
p-Dichlorobenzene	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.43	0.30	0.30	0.30	0.30
o-Dichlorobenzene	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
1,2,4-Trichlorobenzene	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37
Hexachlorobutadiene	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53
chlorine	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.209	0.100
N-nitrosodimethylamine	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303
aniline	0.027	0.027	0.027	0.027	0.027	0.091	0.149	0.050	0.027	0.027	0.027	0.027	0.027
N-nitrosodiethylamine	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556
dinitrobenzene	0.027	0.027	0.027	0.027	0.027	0.027	0.123	0.027	0.027	0.027	0.027	0.027	0.027
diphenyl amine	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069
dinitrotoluene	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045
dimethylphthalate	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020
N-nitrosodiphenylamine	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055
nitroglycerine	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.645	0.551
Formaldehyde	6.3	5.3	8.2	6.5	5.4	47.8	89.4	70.6	2.7	4.1	3.1	7.0	14.3
hydrogen cyanide	NA	NA	NA	NA	NA	NA	32.09	32.09	32.09	56.43	76.35	69.71	161.56
toluene	NA	NA	NA	NA	9.05	9.05	9.05	9.05	9.05	9.05	9.05	9.05	9.43
phenol	NA	NA	NA	NA	NA	389.1	389.1	389.1	389.1	389.1	389.1	389.1	389.1
quinoline	NA	NA	NA	NA	NA	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22
anthracene	NA	NA	NA	NA	NA	2.33	2.33	2.33	2.33	2.33	2.33	2.33	2.33
nitrobenzene	NA	NA	NA	NA	NA	NA	2.27	2.27	2.27	2.27	NA	2.27	NA
dibenzofuran	NA	NA	NA	NA	NA	NA	2.20	2.20	2.20	2.20	NA	2.20	NA
beryllium	1.0	1.7	3.1	2.4	1.7	2.0	1.2	1.3	1.5	3.1	1.9	2.2	2.9
chromium	13.5	27.3	54.1	17.0	12.4	13.9	12.2	16.2	9.2	15.3	13.7	10.9	14.6
manganese	5.0	8.5	15.3	11.8	8.3	15.0	13.7	6.5	7.5	15.3	9.3	10.9	14.6
cobalt	5.0	8.5	15.3	11.8	8.3	9.9	7.4	6.5	7.5	15.3	9.3	10.9	14.6
nickel	50	85	195	121	171	99	98	74	75	153	231	124	194

Stippled value = Lower limit

Shaded value = Upper limit

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Table 4.8.   (Continued)

	POI091001 Signal Flare	POI091002 Signal Flare	POI091005 40mm Illumination	POI091006 40mm Illumination	POI091101 40mm Illumination	POI091102 Grenade Smoke	POI091103 Grenade Smoke	POI091104 Grenade Smoke	POI091601 81mm Mortar Smoke	POI091602 81mm Mortar Smoke	POI091603 81mm Mortar Smoke	POI091702 81mm Mortar Smoke	POI091703 81mm Mortar Smoke
copper	10	17	31	24	17	20	15	13	16	31	19	28	29
arsenic	2.5	4.3	7.7	5.9	4.1	4.9	3.1	3.3	3.7	7.7	4.6	5.6	7.3
selenium	10	17	31	24	17	20	12	13	15	31	19	22	29
silver	5.0	8.5	15.3	11.8	8.3	9.9	6.1	6.5	7.5	15.3	9.3	10.9	14.6
cadmium	3.6	4.3	7.7	5.9	6.5	4.9	3.4	3.3	3.7	7.7	4.6	5.5	7.3
antimony	5.0	8.5	15.3	11.8	8.3	9.9	6.1	6.5	16.0	17.9	10.1	11.2	14.6
barium	50	85	153	118	83	99	61	65	75	153	93	109	146
thallium	2.5	5.4	7.7	5.9	4.1	4.9	4.2	5.6	3.7	7.7	4.6	5.5	7.3
lead	110	162	349	130	102	99	58	101	40	77	46	55	73
PAH (particle-bound)	0.976	2.017	1.110	0.785	4.070	0.019	ND	4.940	ND	28.500	3.989	3.705	5.609
NO	41.8	4.3	6.1	4.9	336.9	4.9	1.2	3.7	4.3	23.4	46.1	46.1	41.8
NO2	66.9	31.1	58.4	66.9	49.0	16.0	32.0	13.2	61.3	11.3	105.6	45.2	36.8
CO2	110.0	0.0	541.0	6242.1	2339.4	349.0	4544.3	2532.3	45653.7	7032.8	13114.8	2704.9	8758.8
CO	0.0	0.0	0.0	177.4	107.9	533.1	349.8	0.0	1274.6	740.2	0.0	1640.2	1282.0
Total Hydrocarbons	6.5	84.4	475.1	505.0	502.4	105.7	514.6	759.7	335.4	185.9	203.0	303.5	345.7

Shaded value = Upper limit

Stippled value = Lower limit

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Table 4.8.   (Continued)

	POI092301	POI092302	POI092401	POI092402	POI092403	POI092501	POI092502	POI092503	POI092504	POI092602	POI092603	POI092704A	POI092704B
	155mm	155mm Howitzer	66mm Rocket	66mm Rocket	40mm	4.2" Mortar	4.2" Mortar	4.2" Mortar	4.2" Mortar	155mm Howitzer	155mm Howitzer	155mm Howitzer	155mm Howitzer
	Illumination	Illumination	High Explosive	High Explosive	High Explosive	High	High	High	High Explosive	High Explosive	High Explosive	Smoke	Smoke
Number of Items Tested	1	1	3	3	3	1	1	1	1	1	1	1	1
Temperature (avg), C	25	25.5	23.7	24	23.7	24.8	26.1	26.8	26.4	28	27.3	25.5	25.5
Rel Humidity (avg), %	52.3	43	50.4	45.5	46.5	64.1	61.3	56.7	58.6	60.1	63.5	77.7	77.7
Acetonitrile	0.39	0.39	0.39	0.14	0.39	0.39	0.04	0.39	0.39	0.39	0.39	0.39	0.39
Acrolein	1.48	1.48	1.86	1.48	1.48	0.10	0.81	1.48	4.78	1.48	2.44	1.02	2.10
Acrylonitrile	0.43	0.57	0.57	0.57	0.57	0.57	0.59	0.63	0.64	0.57	0.04	0.73	2.93
Naphthalene	0.18	0.18	0.16	0.19	0.05	0.18	0.50	0.16	0.54	0.18	0.58	0.18	3.15
Freon-12	0.43	0.25	0.27	0.19	0.16	0.25	0.25	0.25	0.25	0.50	0.04	0.25	0.25
Methyl Chloride	0.10	0.10	1.04	0.22	0.25	0.19	0.03	0.04	0.10	0.50	0.10	0.01	4.29
Freon 114	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Vinyl Chloride	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13
1,3-Butadiene	0.11	0.11	0.12	0.11	0.11	0.11	0.17	1.67	0.68	0.11	0.11	0.11	7.83
Methyl Bromide	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
Ethyl Chloride	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.14	0.13
Freon-11	0.28	0.28	0.35	0.11	0.20	0.04	0.28	0.05	0.06	0.28	0.18	0.28	0.28
1,1-Dichloroethene	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Carbon Disulfide	0.16	0.16	0.94	1.82	0.07	0.16	0.16	0.16	0.16	0.19	0.16	0.04	0.16
Dichloromethane	0.17	0.17	0.17	0.17	0.34	0.17	0.04	0.17	0.04	0.17	0.17	0.26	0.40
Freon-113	0.38	0.38	0.38	0.38	0.38	0.38	0.42	0.38	0.40	0.38	0.41	0.38	0.38
trans-1,2-Dichloroethene	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
1,1-Dichloroethane	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Methyl Tert Butyl Ether	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	3.69	0.18	0.18
Methyl Ethyl Ketone	0.98	1.87	0.71	9.46	1.08	0.15	0.80	0.15	2.26	5.66	1.67	0.15	0.15
cis-1,2-Dichloroethene	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Hexane	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	1.48	0.18	0.28
Chloroform	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Ethyl Acetate	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Tetrahydrofuran	0.15	0.15	0.15	12.78	0.15	0.15	0.15	0.19	0.15	0.15	0.15	0.15	0.15
1,2-Dichloroethane	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
1,1,1-Trichloroethane	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
Benzene	0.46	1.45	8.72	0.98	0.16	0.81	1.38	5.27	2.80	1.06	1.35	2.67	34.16
carbon tetrachloride	0.32	0.03	0.32	0.32	0.32	0.32	0.35	0.32	0.32	0.06	0.32	0.53	0.53
Cyclohexane	0.11	0.17	0.17	0.65	0.17	0.17	0.17	0.17	0.17	0.17	0.24	0.17	0.15
1,2-Dichloropropane	0.23	0.47	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.51	0.23	0.23
Bromodichloromethane	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33
Trichloroethene	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
1,4-Dioxane	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.38	0.18	0.18
Heptane	0.20	0.20	0.20	0.16	0.20	0.18	0.08	0.20	0.08	0.07	1.96	0.44	1.49
cis-1,3-Dichloropropene	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23
Methyl Isobutyl Ketone	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.45	0.20	0.20
trans-1,3-Dichloropropene	0.23	0.23	0.23	0.24	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23
1,1,2-Trichloroethane	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
Toluene	0.19	0.19	0.11	0.19	0.19	0.19	0.19	0.73	0.16	0.19	2.27	1.13	9.68

Shaded value = Upper limit

Stipled value = Lower limit

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Table 4.8. (Continued)

	POI092301	POI092302	POI092401	POI092402	POI092403	POI092501	POI092502	POI092503	POI092504	POI092602	POI092603	POI092704A	POI092704B
	155mm	155mm Howitzer	66mm Rocket	66mm Rocket	40mm	4.2" Mortar	4.2" Mortar	4.2" Mortar	4.2" Mortar	155mm Howitzer	155mm Howitzer	155mm Howitzer	155mm Howitzer
	Illumination	Illumination	High Explosive	High Explosive	High Explosive	High	High	High	High Explosive	High Explosive	High Explosive	Smoke	Smoke
Methyl Butyl Ketone	0.20	0.20	0.20	0.20	0.20	0.20	6.79	1.25	0.82	0.20	0.13	2.06	0.20
Dibromochloromethane	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43
1,2-Dibromoethane	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Tetrachloroethene	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Chlorobenzene	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23
Ethylbenzene	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.63	0.22	1.33
m&p-Xylene	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.23	0.22	0.22	2.32	0.22	0.99
Bromoform	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52
Styrene	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.73	0.21	0.21	0.21	0.21	3.50
1,1,2,2-Tetrachloroethane	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
o-Xylene	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	1.00	0.22	0.22
4-Ethyltoluene	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1.51	0.25	0.47
1,3,5-Trimethylbenzene	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
1,2,4-Trimethylbenzene	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1.47	0.25	0.25
m-Dichlorobenzene	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
p-Dichlorobenzene	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
o-Dichlorobenzene	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
1,2,4-Trichlorobenzene	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37
Hexachlorobutadiene	0.53	0.53	0.53	0.53	0.53	0.53	1.37	0.53	0.53	0.53	0.53	0.53	0.53
chlorine	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
N-nitrosodimethylamine	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.698	0.303	0.303	0.303
aniline	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.038	0.027	0.027	0.027
N-nitrosodiethylamine	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556	0.556
dinitrobenzene	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.027	0.034
diphenyl amine	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069
dinitrotoluene	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045
dimethylphthalate	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.062	0.020	0.020	0.020
N-nitrosodiphenylamine	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055
nitroglycerine	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.551	0.551
Formaldehyde	5.5	3.0	13.2	6.4	4.7	9.7	9.3	14.0	10.2	12.0	5.2	10.2	126.4
hydrogen cyanide	NA	NA	170.41	147.17	32.09	268.89	278.85	1878.93	686.07	904.06	36.52	32.09	362.95
toluene	NA	NA	9.05	10.93	9.05	9.05	9.05	9.05	9.05	9.05	9.05	9.05	14.33
phenol	NA	NA	389.1	389.1	389.1	389.1	389.1	389.1	389.1	389.1	389.1	389.1	389.1
quinoline	NA	NA	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22
anthracene	NA	NA	2.33	2.33	2.33	2.33	2.33	2.33	2.33	2.33	2.33	2.33	2.33
nitrobenzene	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
dibenzofuran	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
beryllium	1.4	1.0	12.2	11.9	3.8	3.4	2.9	3.1	2.4	2.0	1.1	1.3	1.3
chromium	11.8	9.3	187.3	109.0	34.1	32.2	24.9	20.0	19.9	15.5	7.3	12.3	12.3
manganese	7.1	4.8	91.7	58.8	19.1	21.9	21.4	20.3	12.6	40.9	7.8	6.5	6.5
cobalt	7.1	4.8	61.2	34.0	19.1	17.0	14.6	15.3	12.2	10.2	5.3	6.5	6.5
nickel	71	48	612	340	191	170	210	153	122	102	59	84	84.0

Shaded value = Upper limit   Stippled value = Lower limit

Table 4.8.   (Continued)

	POI092301	POI092302	POI092401	POI092402	POI092403	POI092501	POI092502	POI092503	POI092504	POI092602	POI092603	POI092704A	POI092704B
	155mm	155mm Howitzer	66mm Rocket	66mm Rocket	40mm	4.2" Mortar	4.2" Mortar	4.2" Mortar	4.2" Mortar	155mm Howitzer	155mm Howitzer	155mm Howitzer	155mm Howitzer
	Illumination	Illumination	High Explosive	High Explosive	High Explosive	High	High	High	High Explosive	High Explosive	High Explosive	Smoke	Smoke
nickel	71	48	612	340	191	170	210	153	122	102	59	84	84.0
copper	14	10	3706	1760	108	112	109	87	46	69	13	14	14.0
arsenic	3.6	2.4	306	17.0	9.6	8.5	7.3	7.7	6.1	5.1	2.6	3.3	3.3
selenium	14	10	122	68	38	34	29	31	24	20	11	13	13.0
silver	7.1	4.8	61.2	34.7	19.1	17.0	14.6	15.3	12.2	21.5	5.3	6.5	6.5
cadmium	3.6	2.4	30.6	19.9	9.6	8.5	7.3	7.7	6.1	5.1	2.6	3.3	3.3
antimony	7.1	4.8	61.2	34.0	19.1	17.0	14.6	15.3	12.2	10.2	5.3	6.5	6.5
barium	71	53	612	340	191	170	146	153	122	102	53	65	65.0
thallium	3.6	2.4	30.6	17.0	9.6	8.5	7.3	7.7	6.1	5.1	2.6	22.8	22.8
lead	69	57	1498	872	204	177	153	104	105	84	55	92	92.0
PAH (particle-bound)	5.595	2.522	0.396	ND	3.323	0.007	0.091	0.042	0.214	0.378	0.059	2.255	3.310
NO	293.2	296.3	290.2	135.2	0.0	35.0	69.5	7.4	0.6	180.1	0.6	4.3	104.5
NO_2	7.5	54.7	51.8	72.6	17.9	82.0	107.5	73.5	30.2	106.5	11.3	31.1	210.2
CO_2	7045.4	8621.9	51934.4	27650.3	5319.7	9617.5	41217.8	16229.5	8655.7	71770.5	14191.8	105531.0	154928.5
CO	139.3	102.2	1253.1	1407.7	146.3	1044.3	1689.2	7983.4	3723.5	6651.1	1346.2	4811.7	7064.0
Total Hydrocarbons	57.0	13.4	59.0	370.5	44.3	82.0	108.2	351.1	439.1	454.4	198.9	705.2	1035.3

Shaded value = Upper limit   Stipled value = Lower limit

cyanide. Among these species, hydrogen cyanide and PAH are TRI chemicals. Many of the chemicals, TRI and otherwise, were never observed above background in any test.

4.2.4 Comparison of Approaches for Estimating Plume Dilution/Plume Volume

The primary method used to account for dilution of the target chemicals in the emission cloud was carbon mass balance, for reasons noted in Section 3.2.4. The carbon balance approach is logical, appears to meet all the requirements for tracking dilution, and has been used successfully in related OB/OD applications.[10] However, it has not been used for estimating emissions during field use of ordnance. Therefore we also examined three other approaches to account for dilution of the emissions in the expanding plume. Two of these approaches attempted to measure the volume of the emissions cloud during the sampling period. There are aerosol lidar and 3-D photogrammetry. The other approach involved use of an external chemical tracer, xenon, to track dilution. The various approaches are compared in this section.

As mentioned above, carbon mass balance is the standard against which the other methods have been judged. The carbon approach was examined during the Point of Discharge tests (see Section 4.1.3 and Figure 4.1). For those chamber tests, the volume of the cloud was known (chamber volume) and the measured carbon was compared with the amount of carbon expected based on munitions composition. The agreement was very good.

In order to compare the methods that can be used to calculate emission factors, we selected one TRI chemical to illustrate the comparison. Benzene was selected because it is an important TRI chemical and it was present above the detection limit for all tests. Comparison of benzene emission factors calculated by the carbon tracer approach and the lidar volume method are shown in Figure 4.8.

For most of the emissions tests, the volume determined by lidar led to an underestimate of the benzene emission factor, as determined by carbon mass balance. This is especially true for tests with larger high explosive munitions (4.2" mortar and 155 mm howitzer—Tests POI092501 through POI092603). We suspect the reason for the underestimate is related to constraints in use
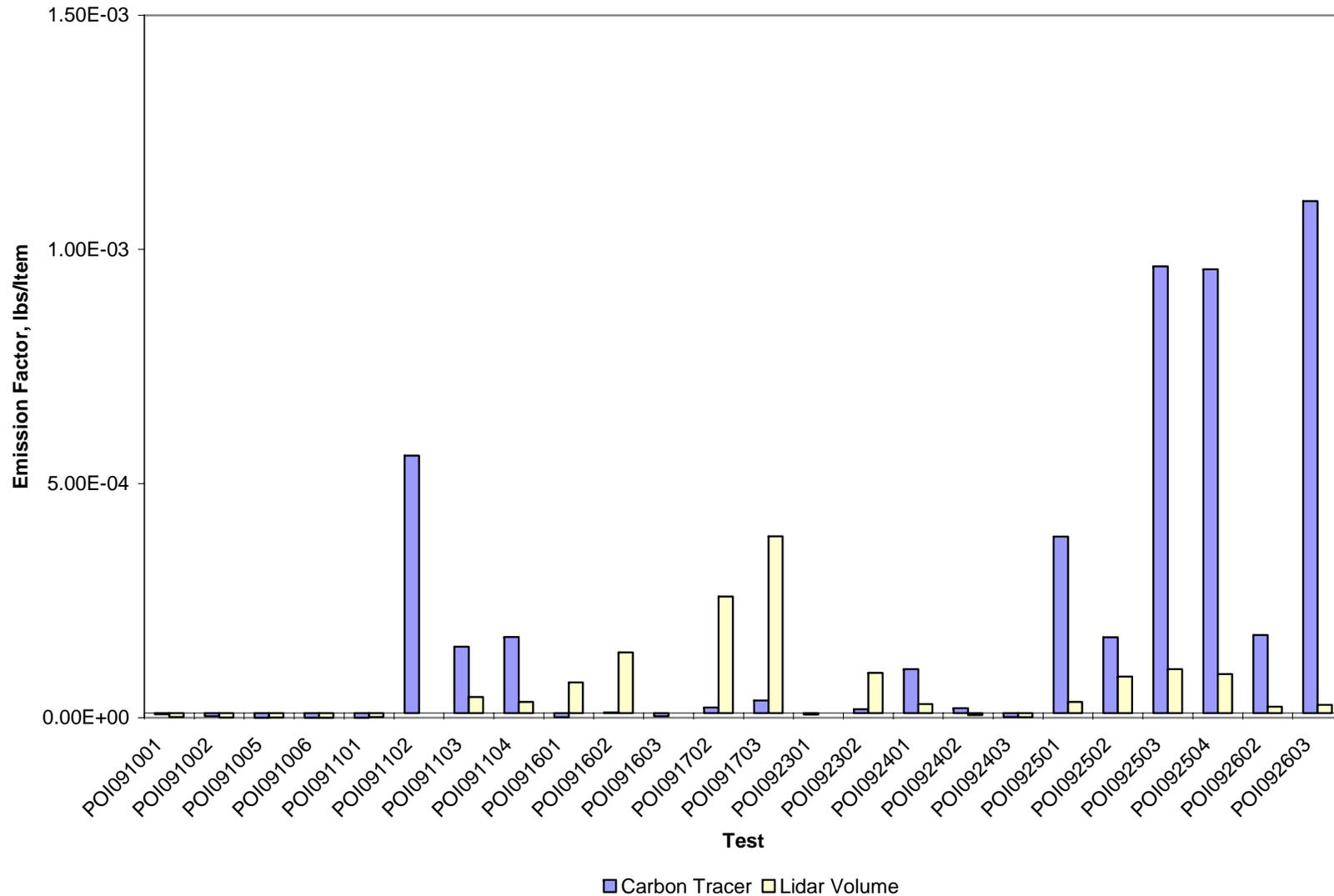
Figure 4.8. Benzene Emission Factors Calculated by Carbon Mass Balance and from
Cloud Volume Determined by Aerosol Lidar

of the lidar in the field. The system employs a Class 4 laser which presents eye safety problems. To eliminate risk, the laser was restricted to use in one direction, where the down-range area was cleared of personnel. Also, the scan angle was fixed for these tests so that portions of emission clouds that exceeded a certain height at the sampling point would not be measured. This effect can be seen in Figure 3.11, where it is evident that a portion of the cloud extended above the upper boundary of the lidar beam and was not measured. The larger the emission cloud, the more likely that a significant portion of the cloud would not be measured. A second factor that may have affected the volume measured by lidar is opacity. Very opaque emission clouds can prevent transmission of the beam through the complete cloud, and this can result in an underestimation of cloud volume.

In a few cases, the lidar approach overestimates the benzene emission factor, indicating that the cloud volume was overestimated. All but one of the tests in which this occurred involved the 81 mm smoke mortar (Tests POI091601-POI091703 in Figure 4.8). Field notes indicate that white phosphorous thrown out by the mortar round caused some burning of grass on the range. It is possible that the smoke from the burning phosphorous and the grass fires caused the lidar approach to overestimate the volume of the emissions cloud.

Because of the constraints imposed on the physical location of the lidar due to laser safety issues, and the lack of flexibility in repositioning the laser to accommodate changing wind direction for the same reason, we do not recommend aerosol lidar for future emissions testing of munitions on ranges.

Comparison of benzene emission factors determined by carbon mass balance and from cloud volumes measured by photogrammetry are shown in Figure 4.9. The number of comparisons are limited because photogrammetry was only deployed during 10 tests. Figure 4.9 shows that photogrammetry overestimated the benzene emission factor for the same 81 mm mortar tests that showed overestimates by the lidar approach (POI091601 to POI092302 in Figure 4.9). It is possible that smoke from the grass fires caused the same overestimate of cloud volume for photogrammetry as it did for lidar. For all but one of the remaining tests, the photogrammetry
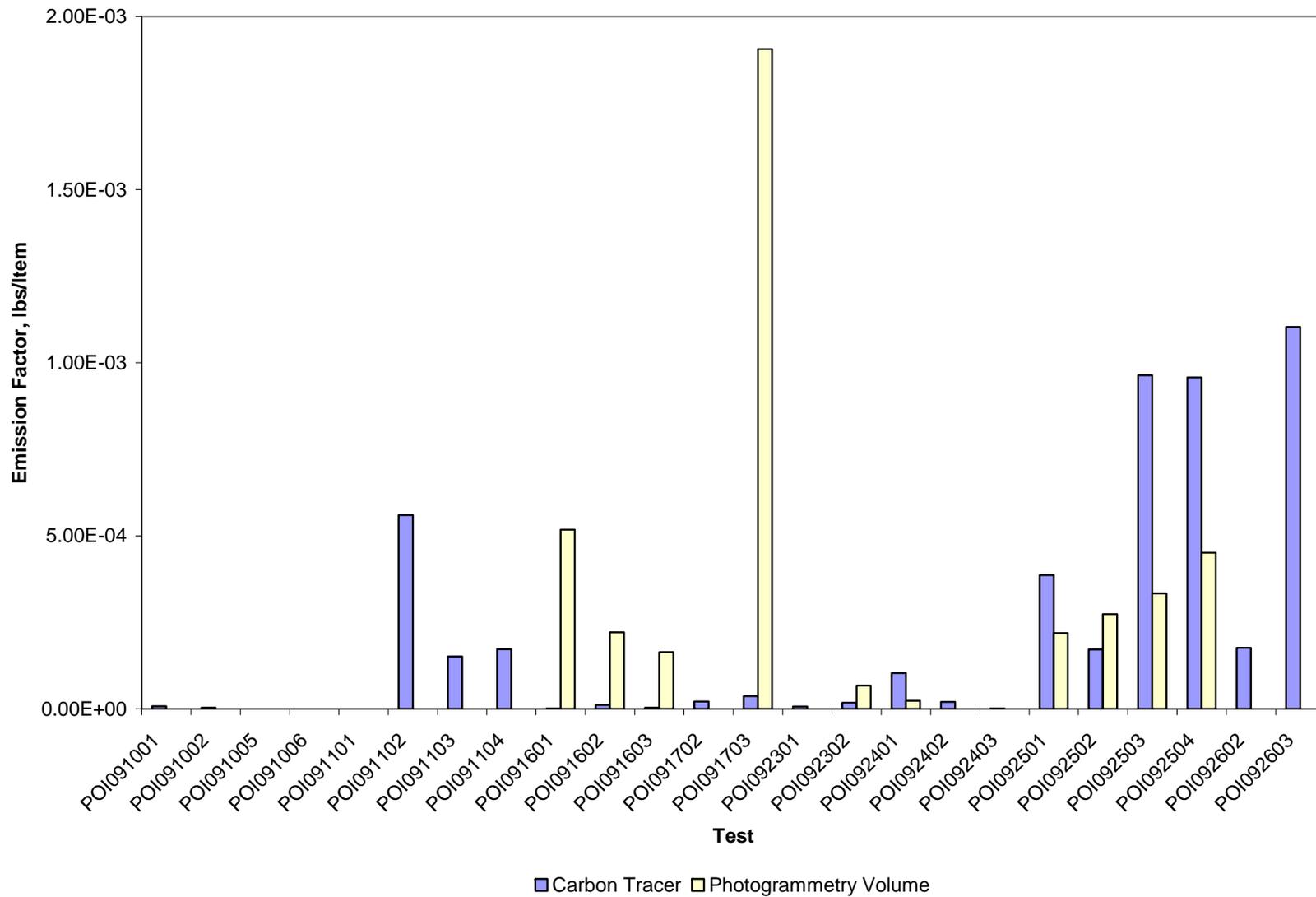
Figure 4.9. Benzene Emission Factors Calculated by Carbon Mass Balance and from
Cloud Volume Determined by Photogrammetry

approach underestimated the cloud volume and therefore the benzene emission factor. We believe that the main reason that the volume was underestimated is that portions of the emission cloud fell outside the view of one or more of the cameras whose images were used to develop three dimensional cloud images for the volume estimate. The most accurate volume estimates occur when the cloud is completely contained within the frame of all four camera views. Whenever the cloud is not contained in one or more images, the volume estimate will be less than actual.

The photogrammetry approach was straightforward to deploy in the field, although it required significant attention to download and process images after each test, recharge batteries, and reposition cameras. This approach also involved substantial data processing to convert the images from the four cameras to volume estimates. Some of this activity could no doubt be automated if the approach were to be used frequently for emissions measurements, but we anticipate that a significant amount of labor will still be required to assure the data quality. This approach is suitable for future emissions testing requiring cloud volume estimates with the following provisos:

- this method is best suited to relatively opaque emission clouds which are discernable in the photographic images
- this approach should not be relied upon if the use of munitions is likely to cause vegetation fires on the test range.

The final method used for estimating dilution in the emissions cloud was an external chemical tracer. We used xenon gas for this purpose for reasons described earlier. Figure 4.10 shows benzene emission factors estimated using both carbon and xenon as dilution tracers. The xenon results are missing for a number of tests because the measured concentration was so similar to the background air concentration that the difference did not meet our criteria for a robust dilution estimate.
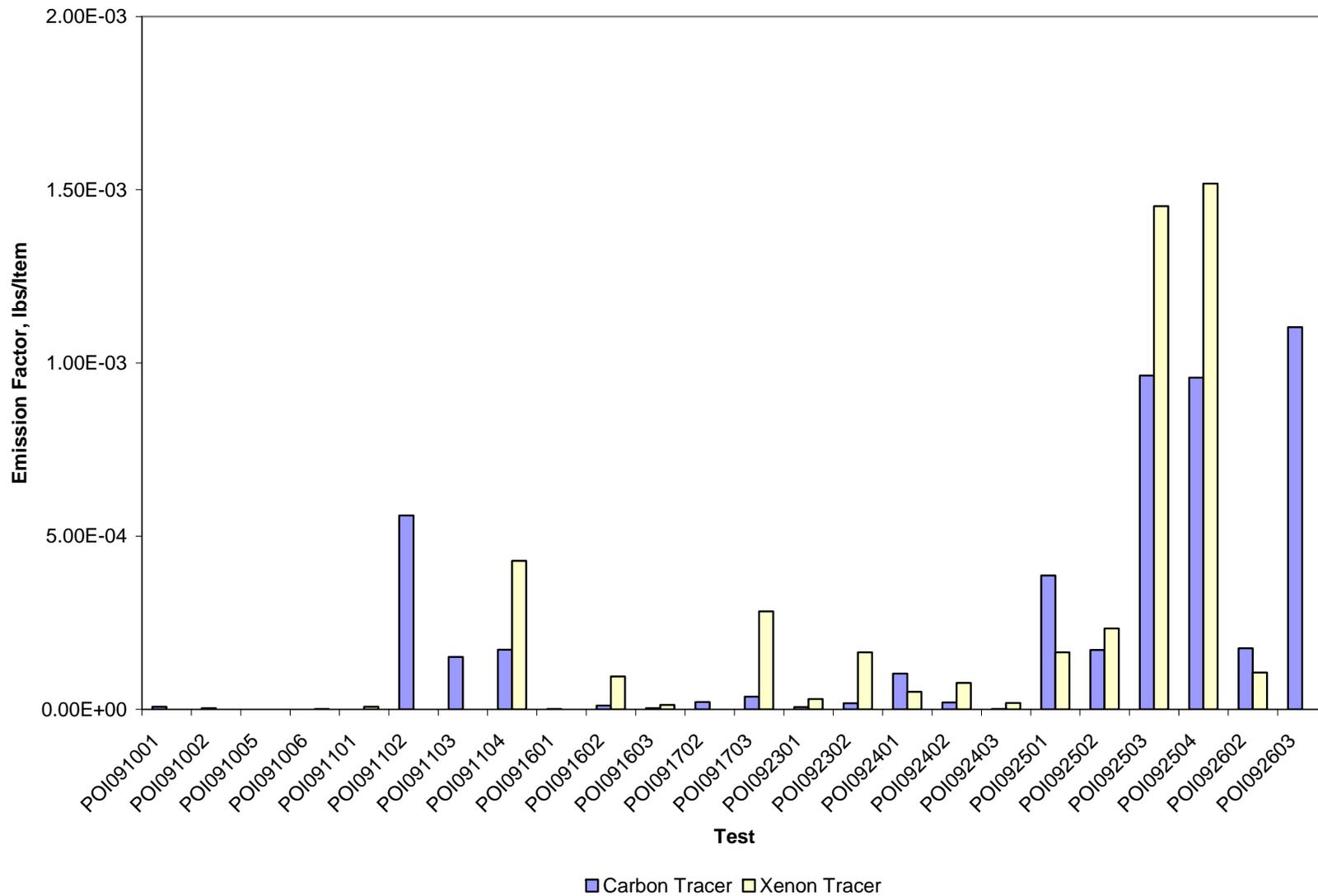
Figure 4.10. Benzene Emission Factors Calculated by Carbon Mass Balance and by Xenon Tracer

The most significant problem with the use of the external tracer had to do with distribution of the gas in the emission cloud. Recall that one of the requirements for an accurate dilution tracer is that it be distributed in the cloud in the same way as the chemicals whose emission factors are being measured. We believe that our approach for delivering xenon to the emission cloud met this criterion for explosive munitions, but meeting the distribution criterion was problematic for munitions that released their emissions slowly and/or non-uniformly over time, or released the emissions from multiple points. The smoke and illumination items are cases in point. Some of the smoke generating devices blow pads containing the smoke agent over a wide area, making it very difficult to assure that the external tracer is distributed in the same way as the emitted chemicals. Also, both smoke and illumination rounds often released non-uniformly over time, with periods of heavy release interspersed with periods of slower combustion and reduced emissions. On average, the ratio of benzene emission factors determined by carbon and xenon tracer techniques was 0.61.

Based on our experience with an external gaseous tracer, we recommend the use of xenon for future ordnance emissions studies for exploding ordnance. Its use with slow release or dispersed release munitions is problematic and requires further study.

4.2.5 *Emission Factors from Point of Impact Tests*

The primary objective of this project was to develop a methodology for measuring emission factors for TRI chemicals from use of munitions under realistic outdoor conditions, and to apply that methodology to measure emission factors for selected munitions. The Point of Impact study was the final step in this process. As described earlier, we selected a range of munitions to test, in terms of size, composition, function, and expected opacity of the emission cloud. We also selected, evaluated and optimized measurement methods for approximately 80 TRI chemicals, and developed and tested four approaches for converting chemical concentrations in the emission cloud into emission factors.

The Point of Impact study was conducted on a test range at Aberdeen Proving Ground in September, 2003. The concentrations of the target chemicals were reported in Section 4.2.3. For

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reasons noted earlier, the carbon mass balance approach is considered to be the most reliable and accurate method to account for dilution of chemicals in the emission cloud, and this approach has been used to compute emission factors for the TRI and other chemicals from the Point of Impact study data. Because it was likely that many of the target chemicals would not be emitted, or would be emitted at extremely low levels, from these munitions, care was taken to select sensitive measurement methods where possible, and within the constraints of field monitoring in a very short-lived emission cloud. For cases where a chemical was not detected in the emissions from a test, the detection limit of the measurement method has been used to provide an upper limit for the emission factor. Because of the very short sampling times (seconds), the detection limits for the trace metals were relatively high, so the upper limit estimate should be used with caution.

The emission factors derived from the Point of Impact study are given in Table 4.9. The table lists emission factors in pounds of emitted chemical per munitions item for 90 chemicals. At the top of each column is the test number and a brief description of the ordnance tested. A more complete description of the munitions was given in sections 3.5.2 and 4.2.1, and in Appendix C. The conditions under which the ordnance was used are listed in the last column of Table 4.3. Shaded entries in Table 4.9 are upper limit estimates based on the detection limit of the measurement method for that particular test. In three cases for particle-bound PAH, the emission factors are lower limits because the signal was off scale. These values are shown as stippled cells in the table.

The emission factors in Table 4.9 do not include emissions from propelling charges that may be used with these munitions. Emissions from some propelling charges have been examined in an ATC/AEC Firing Point study[13] and our Point of Discharge study (this report) conducted in conjunction with a component of the Firing Point study.

The Point of Impact study was designed to collect data that can be used to examine the reproducibility of emission factors from testing under realistic conditions, and also to explore the

Table 4.9. Emission Factors (lbs/test item) for Point of Impact Munitions Tests. Yellow Shaded Values are Upper Limits; Blue Shaded Values are Lower Limits

	POI091001	POI091002	POI091005	POI091006	POI091101	POI091102	POI091103	POI091104	POI091601	POI091602	POI091603	POI091702	POI091703	POI092301
	Signal Flare	Signal Flare	40mm Illumination	40mm Illumination	40mm Illumination	Grenade Smoke	Grenade Smoke	Grenade Smoke	81mm Mortar Smoke	81mm Mortar Smoke	81mm Mortar Smoke	81mm Mortar Smoke	81mm Mortar Smoke	155mm Howitzer Illumination
Temperature (avg), C			24.5	25.4	23.7	23.9	26.2	27.2	23.5	23.8	25.9	26.3	27.2	25
Rel Humidity (avg), %			46.1	48.5	50.7	53.1	45.2	40.4	49.1	43.4	39.2	43.1	42.2	52.3
Acetonitrile	1.74E-06	7.81E-06	2.30E-07	6.27E-08	1.21E-07	2.36E-05	5.32E-06	6.98E-06	4.23E-07	2.33E-06	1.49E-06	1.33E-05	1.72E-06	5.80E-06
Acrolein	6.85E-05	2.96E-05	5.55E-07	2.38E-07	4.58E-07	8.10E-05	7.90E-05	6.83E-05	1.60E-06	6.07E-06	1.87E-06	1.23E-05	6.52E-06	2.20E-05
Acrylonitrile	1.94E-05	1.15E-05	3.39E-07	1.53E-07	9.20E-07	1.42E-04	3.91E-06	3.34E-05	6.24E-07	3.44E-06	2.20E-06	4.77E-06	2.54E-06	6.47E-06
Naphthalene	8.99E-06	2.43E-06	6.38E-08	2.84E-08	8.58E-08	2.39E-05	3.13E-06	3.15E-06	1.92E-07	1.05E-06	2.09E-07	1.57E-06	2.01E-06	2.62E-06
Freon-12	2.81E-05	8.99E-07	1.48E-09	5.84E-09	3.32E-08	4.56E-06	1.40E-07	4.48E-06	4.23E-07	1.50E-06	1.55E-07	5.15E-07	1.89E-06	6.39E-06
Methyl Chloride	3.13E-05	2.01E-06	2.94E-08	1.61E-08	3.10E-08	1.50E-05	5.64E-06	7.82E-06	2.35E-07	8.00E-06	7.82E-07	1.04E-06	5.44E-06	1.49E-06
Freon 114	1.62E-05	7.02E-06	2.07E-07	5.64E-08	1.08E-07	2.12E-05	4.78E-06	6.27E-06	3.80E-07	2.10E-06	1.34E-06	2.91E-06	1.54E-06	5.21E-06
Vinyl Chloride	6.03E-06	2.61E-06	7.68E-08	2.09E-08	4.03E-08	7.87E-06	1.77E-06	2.33E-06	1.41E-07	7.78E-07	4.98E-07	1.08E-06	5.74E-07	1.94E-06
1,3-Butadiene	5.10E-06	2.21E-06	6.50E-08	1.77E-08	3.41E-08	6.66E-06	1.50E-06	1.97E-06	1.20E-07	6.58E-07	4.22E-07	2.28E-06	8.61E-06	1.64E-06
Methyl Bromide	8.81E-06	3.81E-06	1.12E-07	3.06E-08	5.89E-08	1.15E-05	2.59E-06	3.41E-06	2.07E-07	1.14E-06	7.29E-07	1.58E-06	8.39E-07	2.83E-06
Ethyl Chloride	6.52E-06	2.61E-06	7.68E-08	2.09E-08	4.18E-08	1.14E-05	2.15E-06	2.33E-06	1.94E-07	7.78E-07	4.98E-07	1.71E-06	5.74E-07	1.94E-06
Freon-11	2.64E-06	4.68E-07	1.65E-07	4.51E-08	1.86E-09	2.53E-06	8.38E-07	5.02E-06	1.80E-07	3.81E-07	1.07E-06	1.32E-06	1.57E-06	4.17E-06
1,1-Dichloroethene	9.28E-06	4.01E-06	1.18E-07	3.22E-08	6.20E-08	1.21E-05	2.73E-06	3.58E-06	2.17E-07	1.20E-06	7.67E-07	1.66E-06	8.83E-07	2.98E-06
Carbon Disulfide	9.73E-06	5.90E-06	9.45E-08	3.64E-08	4.96E-08	7.38E-06	2.18E-06	2.87E-06	1.12E-07	4.92E-06	1.07E-06	1.33E-06	3.16E-06	2.38E-06
Dichloromethane	1.72E-04	1.75E-05	3.06E-07	3.57E-08	5.27E-08	1.95E-06	3.90E-05	2.94E-05	2.63E-07	1.02E-06	9.70E-07	2.15E-06	1.42E-06	2.53E-06
Freon-113	1.76E-05	7.62E-06	2.25E-07	6.12E-08	1.18E-07	2.30E-05	5.19E-06	6.81E-06	4.13E-07	2.27E-06	1.46E-06	3.16E-06	1.68E-06	5.66E-06
trans-1,2-Dichloroethene	9.28E-06	4.01E-06	1.18E-07	3.22E-08	6.20E-08	1.21E-05	2.73E-06	3.58E-06	2.17E-07	1.20E-06	7.67E-07	1.66E-06	8.83E-07	2.98E-06
1,1-Dichloroethane	9.28E-06	4.01E-06	1.18E-07	3.22E-08	6.20E-08	1.21E-05	2.73E-06	3.58E-06	2.17E-07	1.20E-06	7.67E-07	1.66E-06	8.83E-07	2.98E-06
Methyl Tert Butyl Ether	8.35E-06	3.61E-06	1.06E-07	2.90E-08	5.58E-08	1.09E-05	2.46E-06	3.23E-06	1.96E-07	1.08E-06	6.90E-07	1.50E-06	7.94E-07	2.68E-06
Methyl Ethyl Ketone	5.86E-06	3.01E-06	8.86E-08	2.42E-08	4.65E-08	9.08E-06	2.05E-06	2.69E-06	1.63E-07	8.98E-07	8.94E-06	8.74E-06	3.56E-05	1.46E-06
cis-1,2-Dichloroethene	9.28E-06	4.01E-06	1.18E-07	3.22E-08	6.20E-08	1.21E-05	2.73E-06	3.58E-06	2.17E-07	1.20E-06	7.67E-07	1.66E-06	8.83E-07	2.98E-06
Hexane	8.35E-06	3.61E-06	1.06E-07	2.90E-08	9.93E-08	1.09E-05	1.74E-05	6.18E-06	1.96E-07	4.57E-07	6.90E-07	2.72E-06	7.94E-07	2.68E-06
Chloroform	1.11E-05	4.82E-06	1.42E-07	3.87E-08	7.44E-08	1.45E-05	4.11E-06	4.30E-06	2.61E-07	9.20E-07	9.20E-07	1.99E-06	1.06E-06	3.57E-06
Ethyl Acetate	8.35E-06	3.61E-06	1.06E-07	2.90E-08	5.58E-08	1.09E-05	2.46E-06	3.23E-06	1.96E-07	1.08E-06	1.83E-06	1.50E-06	7.94E-07	2.68E-06
Tetrahydrofuran	6.96E-06	3.01E-06	8.86E-08	2.42E-08	4.65E-08	9.08E-06	2.05E-06	2.69E-06	1.63E-07	8.98E-07	5.75E-07	1.25E-06	6.62E-07	2.23E-06
1,2-Dichloroethane	9.28E-06	4.01E-06	1.18E-07	3.22E-08	6.20E-08	1.21E-05	2.73E-06	3.58E-06	2.17E-07	1.20E-06	7.67E-07	1.66E-06	8.83E-07	2.98E-06
1,1,1-Trichloroethane	1.25E-05	5.42E-06	1.60E-07	4.35E-08	8.37E-08	1.63E-05	3.69E-06	4.84E-06	2.94E-07	1.62E-06	1.04E-06	2.24E-06	1.19E-06	4.02E-06
Benzene	7.42E-06	3.21E-06	9.46E-08	1.53E-08	1.11E-07	5.60E-04	1.52E-04	1.73E-04	8.81E-07	1.12E-05	3.21E-06	2.18E-05	3.69E-05	6.80E-06
carbon tetrachloride	1.48E-05	6.42E-06	1.89E-07	5.15E-08	5.42E-08	5.68E-06	4.37E-06	5.73E-06	3.48E-07	3.13E-06	1.23E-06	2.66E-06	1.41E-06	4.77E-06
Cyclohexane	7.89E-06	3.41E-06	1.00E-07	2.74E-08	5.27E-08	1.03E-05	2.32E-06	3.05E-06	1.85E-07	1.02E-06	1.09E-06	1.41E-06	7.50E-07	1.68E-06
1,2-Dichloropropane	1.07E-05	4.61E-06	1.36E-07	3.71E-08	7.13E-08	1.39E-05	3.14E-06	4.12E-06	2.50E-07	1.38E-06	1.46E-06	2.89E-06	1.08E-06	3.43E-06
Bromodichloromethane	1.53E-05	6.62E-06	1.95E-07	5.32E-08	1.02E-07	2.00E-05	4.51E-06	5.91E-06	3.59E-07	1.98E-06	1.27E-06	2.74E-06	1.46E-06	4.91E-06
Trichloroethene	1.58E-05	6.82E-06	2.01E-07	5.48E-08	1.05E-07	2.06E-05	4.64E-06	6.09E-06	3.70E-07	2.04E-06	1.30E-06	2.83E-06	1.50E-06	5.06E-06
1,4-Dioxane	8.35E-06	3.61E-06	1.06E-07	2.90E-08	5.58E-08	1.09E-05	2.46E-06	3.23E-06	1.96E-07	1.08E-06	6.90E-07	1.50E-06	7.94E-07	2.68E-06
Heptane	1.15E-05	5.16E-06	1.18E-07	3.22E-08	6.20E-08	1.21E-05	2.73E-06	3.58E-06	2.17E-07	1.20E-06	5.59E-07	1.66E-06	8.83E-07	2.98E-06
cis-1,3-Dichloropropene	1.07E-05	4.61E-06	1.36E-07	3.71E-08	7.13E-08	1.39E-05	3.14E-06	4.12E-06	2.50E-07	1.38E-06	8.82E-07	1.91E-06	1.02E-06	3.43E-06
Methyl Isobutyl Ketone	9.28E-06	4.01E-06	1.18E-07	3.22E-08	6.20E-08	1.21E-05	2.73E-06	3.58E-06	2.17E-07	1.20E-06	1.02E-06	1.66E-06	4.40E-06	2.98E-06
trans-1,3-Dichloropropene	1.07E-05	4.61E-06	1.36E-07	3.71E-08	7.13E-08	1.39E-05	3.14E-06	4.12E-06	2.50E-07	1.38E-06	8.82E-07	1.91E-06	1.02E-06	3.43E-06
1,1,2-Trichloroethane	1.25E-05	5.42E-06	1.60E-07	4.35E-08	8.37E-08	1.63E-05	3.69E-06	4.84E-06	2.94E-07	1.62E-06	1.04E-06	2.24E-06	1.19E-06	4.02E-06
Toluene	1.12E-05	7.70E-06	9.08E-08	7.52E-08	5.89E-08	1.82E-04	4.90E-05	4.84E-05	3.36E-07	2.66E-06	2.91E-06	7.99E-06	8.61E-06	2.83E-06

= Upper Limit
= Lower Limit

Table 4.9.　(Continued)

	POI091001 Signal Flare	POI091002 Signal Flare	POI091005 40mm Illumination	POI091006 40mm Illumination	POI091101 40mm Illumination	POI091102 Grenade Smoke	POI091103 Grenade Smoke	POI091104 Grenade Smoke	POI091601 81mm Mortar Smoke	POI091602 81mm Mortar Smoke	POI091603 81mm Mortar Smoke	POI091702 81mm Mortar Smoke	POI091703 81mm Mortar Smoke	POI092301 155mm Howitzer Illumination
Methyl Butyl Ketone	9.28E-06	4.01E-06	1.18E-07	3.22E-08	6.20E-08	1.21E-05	2.73E-06	3.58E-06	2.17E-07	1.20E-06	1.83E-06	2.75E-06	2.86E-06	2.98E-06
Dibromochloromethane	1.99E-05	8.63E-06	2.54E-07	6.93E-08	1.33E-07	2.60E-05	5.87E-06	7.71E-06	4.67E-07	2.57E-06	1.65E-06	3.57E-06	1.90E-06	6.40E-06
1,2-Dibromoethane	1.76E-05	7.62E-06	2.25E-07	6.12E-08	1.18E-07	2.30E-05	5.19E-06	6.81E-06	4.13E-07	2.27E-06	1.46E-06	3.16E-06	1.68E-06	5.66E-06
Tetrachloroethene	1.58E-05	6.82E-06	2.01E-07	5.48E-08	1.05E-07	2.06E-05	4.64E-06	6.09E-06	3.70E-07	2.04E-06	1.30E-06	2.83E-06	1.50E-06	5.06E-06
Chlorobenzene	1.07E-05	4.61E-06	1.36E-07	3.71E-08	7.13E-08	1.39E-05	3.89E-06	4.12E-06	2.50E-07	1.38E-06	8.82E-07	1.91E-06	1.02E-06	3.43E-06
Ethylbenzene	1.02E-05	4.41E-06	1.30E-07	3.54E-08	6.82E-08	1.33E-05	2.98E-06	3.94E-06	2.39E-07	1.32E-06	8.44E-07	1.83E-06	1.77E-06	3.28E-06
m&p-Xylene	1.77E-05	5.03E-06	1.30E-07	3.54E-08	1.03E-07	5.24E-05	3.00E-06	4.79E-06	2.39E-07	1.60E-06	8.44E-07	1.83E-06	5.27E-07	3.28E-06
Bromoform	2.41E-05	1.04E-05	3.07E-07	8.38E-08	1.61E-07	3.15E-05	7.10E-06	9.32E-06	5.65E-07	3.11E-06	1.99E-06	4.32E-06	2.30E-06	7.74E-06
Styrene	9.74E-06	4.21E-06	1.24E-07	3.38E-08	6.51E-08	1.27E-05	2.87E-06	3.76E-06	2.28E-07	1.26E-06	8.05E-07	1.75E-06	2.21E-06	3.13E-06
1,1,2,2-Tetrachloroethane	1.58E-05	6.82E-06	2.01E-07	5.48E-08	1.05E-07	2.06E-05	4.64E-06	6.09E-06	3.70E-07	2.04E-06	1.30E-06	2.83E-06	1.50E-06	5.06E-06
o-Xylene	1.02E-05	4.41E-06	1.30E-07	5.48E-08	6.82E-08	1.33E-05	4.64E-06	3.94E-06	2.39E-07	1.32E-06	8.44E-07	1.83E-06	9.71E-07	3.28E-06
4-Ethyltoluene	1.16E-05	5.02E-06	1.48E-07	4.03E-08	7.75E-08	1.55E-05	3.41E-06	4.48E-06	2.72E-07	1.50E-06	9.59E-07	2.08E-06	1.10E-06	3.72E-06
1,3,5-Trimethylbenzene	1.16E-05	5.02E-06	1.48E-07	4.03E-08	7.75E-08	1.51E-05	3.41E-06	4.48E-06	2.72E-07	1.50E-06	9.59E-07	2.08E-06	1.10E-06	3.72E-06
1,2,4-Trimethylbenzene	1.16E-05	5.02E-06	1.48E-07	4.03E-08	7.75E-08	1.51E-05	3.41E-06	4.48E-06	2.72E-07	1.50E-06	9.59E-07	2.08E-06	1.10E-06	4.47E-06
m-Dichlorobenzene	1.39E-05	6.02E-06	1.77E-07	4.83E-08	9.30E-08	1.82E-05	4.10E-06	5.38E-06	4.76E-07	1.80E-06	1.15E-06	2.49E-06	1.32E-06	4.47E-06
p-Dichlorobenzene	1.39E-05	6.02E-06	1.77E-07	4.83E-08	9.30E-08	1.82E-05	4.10E-06	5.38E-06	4.69E-07	1.80E-06	1.15E-06	2.49E-06	1.32E-06	4.47E-06
o-Dichlorobenzene	1.39E-05	6.02E-06	1.77E-07	4.83E-08	9.30E-08	1.82E-05	4.10E-06	5.38E-06	3.26E-07	1.80E-06	1.15E-06	2.49E-06	1.32E-06	4.47E-06
1,2,4-Trichlorobenzene	1.72E-05	7.42E-06	2.19E-07	5.96E-08	1.15E-07	2.24E-05	5.05E-06	6.63E-06	4.02E-07	2.21E-06	1.42E-06	3.07E-06	1.63E-06	5.51E-06
Hexachlorobutadiene	2.46E-05	1.06E-05	3.13E-07	8.54E-08	1.64E-07	3.21E-05	7.24E-06	9.50E-06	5.76E-07	3.17E-06	2.03E-06	4.40E-06	2.34E-06	7.89E-06
chlorine	4.66E-06	2.01E-06	5.93E-08	1.62E-08	3.11E-08	6.08E-06	1.37E-06	1.80E-06	1.09E-07	6.01E-07	3.85E-07	1.74E-06	4.43E-07	1.50E-06
N-nitrosodimethylamine	1.41E-05	6.08E-06	1.79E-07	4.89E-08	9.40E-08	1.84E-05	4.14E-06	5.44E-06	3.30E-07	1.82E-06	1.16E-06	2.52E-06	1.34E-06	4.52E-06
aniline	1.24E-06	5.35E-07	1.58E-08	4.30E-09	8.27E-09	5.54E-06	2.03E-06	8.88E-07	2.90E-08	1.60E-07	1.02E-07	2.22E-07	1.18E-07	3.97E-07
N-nitrosodiethylamine	2.58E-05	1.12E-05	3.28E-07	8.96E-08	1.72E-07	3.37E-05	7.59E-06	9.96E-06	6.04E-07	3.33E-06	2.13E-06	4.62E-06	2.45E-06	8.28E-06
dinitrobenzene	1.24E-06	5.36E-07	1.58E-08	4.30E-09	8.27E-09	1.66E-06	1.68E-06	4.78E-07	2.90E-08	1.60E-07	1.02E-07	2.22E-07	1.18E-07	3.98E-07
diphenyl amine	3.21E-06	1.39E-06	4.09E-08	1.12E-08	2.15E-08	4.19E-06	9.46E-07	1.24E-06	7.53E-08	4.15E-07	2.66E-07	5.76E-07	3.06E-07	1.03E-06
dinitrotoluene	2.06E-06	8.93E-07	2.63E-08	7.17E-09	1.38E-08	2.69E-06	6.08E-07	7.98E-07	4.84E-08	2.66E-07	1.71E-07	3.70E-07	1.96E-07	6.63E-07
dimethylphthalate	9.22E-07	3.99E-07	1.17E-08	3.20E-09	6.16E-09	1.20E-06	2.71E-07	3.56E-07	2.16E-08	1.19E-07	7.62E-08	1.65E-07	8.77E-08	2.96E-07
N-nitrosodiphenylamine	2.56E-06	1.11E-06	3.26E-08	8.89E-09	1.71E-08	3.34E-06	7.53E-07	9.89E-07	6.00E-08	3.30E-07	2.12E-07	4.59E-07	2.44E-07	8.22E-07
nitroglycerine	2.56E-05	1.11E-05	3.25E-07	8.87E-08	1.71E-07	3.34E-05	7.52E-06	9.87E-06	5.99E-07	3.30E-06	2.11E-06	5.36E-06	2.43E-06	8.20E-06
Formaldehyde	2.91E-04	1.06E-04	4.87E-06	1.05E-06	1.68E-06	2.90E-03	1.22E-03	1.26E-03	2.94E-06	2.43E-05	1.18E-05	5.82E-05	6.29E-05	8.24E-05
hydrogen cyanide	NA	NA	NA	NA	NA	NA	4.38E-04	5.75E-04	3.49E-05	3.38E-04	2.93E-04	5.79E-04	7.13E-04	NA
toluene	NA	NA	NA	NA	NA	5.48E-04	1.24E-04	1.62E-04	9.84E-06	5.42E-05	3.47E-05	7.52E-03	4.16E-05	NA
phenol	NA	NA	NA	NA	2.80E-06	NA	5.31E-03	6.97E-03	4.23E-04	2.33E-03	1.49E-03	3.23E-03	1.72E-03	NA
quinoline	NA	NA	NA	NA	NA	NA	1.66E-05	2.18E-05	1.32E-06	7.28E-06	4.66E-06	1.01E-05	5.37E-06	NA
anthracene	NA	NA	NA	NA	NA	NA	3.19E-05	4.18E-05	2.54E-06	1.40E-05	8.95E-06	1.94E-05	1.03E-05	NA
nitrobenzene	NA	NA	NA	NA	NA	NA	3.10E-05	4.07E-05	2.47E-06	1.36E-05	NA	1.89E-05	NA	NA
dibenzofuran	NA	NA	NA	NA	NA	NA	3.01E-05	3.95E-06	2.40E-06	1.32E-05	NA	1.83E-05	NA	NA
beryllium	4.66E-05	3.41E-05	1.81E-06	3.79E-07	5.13E-07	1.20E-04	1.67E-05	2.33E-05	1.62E-06	1.83E-05	7.11E-06	1.82E-05	1.29E-05	2.12E-05
aluminum	2.33E-02	1.71E-02	9.04E-04	1.90E-04	2.56E-04	5.98E-02	8.36E-03	1.17E-02	8.12E-04	9.16E-03	3.56E-03	9.08E-03	6.43E-03	1.06E-02
chromium	6.27E-04	5.47E-04	3.20E-05	2.74E-06	3.83E-06	8.42E-04	1.67E-04	2.91E-04	9.97E-06	9.16E-05	5.26E-05	9.08E-05	6.43E-05	1.75E-04
manganese	2.33E-04	1.71E-04	9.04E-06	1.90E-06	2.56E-06	9.11E-04	1.87E-04	1.17E-04	8.17E-06	9.16E-05	3.56E-05	9.08E-05	6.43E-05	1.06E-04
cobalt	2.33E-04	1.71E-04	9.04E-06	1.90E-06	2.56E-06	5.98E-04	1.01E-04	1.17E-04	8.12E-06	9.16E-05	3.56E-05	9.08E-05	6.43E-05	1.06E-04
nickel	2.33E-03	1.71E-03	1.15E-04	1.96E-05	5.29E-05	5.98E-03	1.33E-03	1.32E-03	8.12E-05	9.16E-04	8.84E-04	1.03E-03	8.56E-04	1.06E-03

= Upper Limit　　= Lower Limit

Table 4.9.   (Continued)

	POI091001 Signal Flare	POI091002 Signal Flare	POI091005 40mm Illumination	POI091006 40mm Illumination	POI091101 40mm Illumination	POI091102 Grenade Smoke	POI091103 Grenade Smoke	POI091104 Grenade Smoke	POI091601 81mm Mortar Smoke	POI091602 81mm Mortar Smoke	POI091603 81mm Mortar Smoke	POI091702 81mm Mortar Smoke	POI091703 81mm Mortar Smoke	POI092301 155mm Howitzer Illumination
copper	4.66E-04	3.41E-04	1.81E-05	3.79E-06	5.21E-06	1.20E-03	2.07E-04	2.33E-04	1.70E-05	1.83E-04	7.11E-05	2.36E-04	1.29E-04	2.12E-04
zinc	2.33E-02	1.71E-02	9.04E-04	1.90E-04	2.56E-04	5.98E-02	8.36E-03	1.17E-02	8.12E-04	9.16E-03	3.98E-03	9.08E-03	6.43E-03	1.06E-02
arsenic	1.16E-04	8.53E-05	4.52E-06	9.48E-07	1.28E-06	2.99E-04	4.18E-05	5.84E-05	4.06E-06	4.58E-05	1.78E-05	4.64E-05	3.22E-05	5.30E-05
selenium	4.66E-04	3.41E-04	1.81E-05	3.79E-06	5.13E-06	1.20E-03	1.67E-04	2.33E-04	1.62E-05	1.83E-04	7.11E-05	1.82E-04	1.29E-04	2.12E-04
silver	2.33E-04	1.71E-04	9.04E-06	1.90E-06	2.56E-06	5.98E-04	8.36E-05	1.17E-04	8.12E-06	9.16E-05	3.56E-05	9.08E-05	6.43E-05	1.06E-04
cadmium	1.66E-04	8.53E-05	4.52E-06	9.48E-07	2.02E-06	2.99E-04	4.67E-05	5.84E-05	4.06E-06	4.58E-05	1.78E-05	4.54E-05	3.22E-05	5.30E-05
antimony	2.33E-04	1.71E-04	9.04E-06	1.90E-06	2.56E-06	5.98E-04	8.36E-05	1.17E-04	1.74E-05	1.07E-04	3.88E-05	9.27E-05	6.43E-05	1.06E-04
barium	2.33E-03	1.71E-03	9.04E-05	1.90E-05	2.56E-05	5.98E-03	8.36E-04	1.17E-03	8.12E-05	9.16E-04	3.56E-04	9.08E-04	6.43E-04	1.06E-03
thallium	1.16E-04	1.08E-04	4.52E-06	9.48E-07	1.28E-06	2.99E-04	5.73E-05	9.96E-05	4.06E-06	4.58E-05	1.78E-05	4.54E-05	3.22E-05	5.30E-05
lead	5.12E-03	3.25E-03	2.06E-04	2.10E-05	3.17E-05	6.01E-03	7.87E-04	1.80E-03	4.39E-05	4.58E-04	1.78E-04	4.54E-04	3.22E-04	1.03E-03
PAH (particle-bound)	4.53E-05	4.05E-05	6.56E-07	1.26E-07	1.26E-06	1.17E-06	NA	8.85E-05	NA	1.71E-04	1.53E-05	3.08E-05	2.48E-05	8.33E-05
NO	1.94E-03	8.63E-05	3.63E-06	7.92E-07	1.04E-04	2.98E-04	1.68E-05	6.61E-05	4.68E-06	1.40E-04	1.77E-04	3.83E-04	1.85E-04	4.37E-03
NO2	3.10E-03	6.24E-04	3.45E-05	1.08E-05	1.52E-05	9.70E-04	4.38E-04	2.37E-04	6.66E-05	6.77E-05	4.05E-04	3.76E-04	1.62E-04	1.12E-04

= Upper Limit   = Lower Limit

Table 4.9.   (Continued)

	POI092302	POI092401	POI092402	POI092403	POI092501	POI092502	POI092503	POI092504	POI092802	POI092603	POI092704A	POI092704B
	155mm Howitzer	66mm Rocket	66mm Rocket	40mm Cartridge	4.2" Mortar	4.2" Mortar	4.2" Mortar	4.2" Mortar	155mm Howitzer	155mm Howitzer	155mm Howitzer	155mm Howitzer
	Illumination	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	Smoke	Smoke
Temperature (avg), C	25.5	23.7	24	23.7	24.8	26.1	26.8	26.4	28	27.3	25.5	25.5
Rel Humidity (avg), %	43	50.4	45.5	46.5	64.1	61.3	56.7	58.6	60.1	63.5	77.7	77.7
Acetonitrile	4.91E-06	4.61E-06	2.79E-06	3.61E-06	1.85E-04	4.78E-06	7.13E-05	1.33E-04	6.45E-05	3.18E-04	3.51E-07	2.39E-07
Acrolein	1.86E-05	2.20E-05	3.03E-05	1.37E-05	4.98E-05	1.01E-04	2.70E-04	1.63E-03	2.45E-04	1.99E-03	9.20E-07	1.29E-06
Acrylonitrile	7.24E-06	6.81E-06	1.18E-05	5.33E-06	2.73E-04	7.37E-05	1.15E-04	2.18E-04	9.52E-05	3.48E-05	6.59E-07	1.80E-06
Naphthalene	2.22E-06	1.94E-06	3.62E-06	4.52E-07	8.39E-05	6.18E-05	2.93E-05	1.85E-04	2.92E-05	4.75E-04	1.59E-07	1.93E-06
Freon-12	3.15E-06	3.19E-06	3.94E-06	1.47E-06	1.19E-04	3.11E-05	4.58E-05	8.53E-05	8.31E-05	3.15E-05	2.25E-07	1.53E-07
Methyl Chloride	1.26E-06	1.24E-05	4.51E-06	2.30E-06	9.21E-05	3.64E-06	7.78E-06	3.41E-05	8.34E-05	8.16E-05	1.31E-08	2.63E-06
Freon 114	4.41E-06	4.15E-06	7.19E-06	3.24E-06	1.67E-04	4.35E-05	6.41E-05	1.19E-04	5.80E-05	2.86E-04	3.15E-07	2.15E-07
Vinyl Chloride	1.64E-06	1.54E-06	2.67E-06	1.21E-06	6.19E-05	1.62E-05	2.38E-05	4.49E-05	2.15E-05	1.06E-04	1.17E-07	7.98E-08
1,3-Butadiene	1.39E-06	1.48E-06	2.26E-06	1.02E-06	5.24E-05	2.16E-05	3.05E-05	2.31E-04	1.82E-05	9.15E-05	9.91E-08	4.81E-06
Methyl Bromide	2.39E-06	2.25E-06	3.90E-06	1.76E-06	9.04E-05	2.36E-05	3.48E-05	6.49E-05	3.15E-05	1.55E-04	1.71E-07	1.17E-07
Ethyl Chloride	1.64E-06	1.54E-06	2.67E-06	1.21E-06	6.19E-05	1.62E-05	2.38E-05	4.44E-05	2.15E-05	1.06E-04	1.27E-07	7.98E-08
Freon-11	3.53E-06	4.13E-06	2.25E-06	1.88E-06	1.68E-05	3.48E-06	8.44E-06	2.10E-05	4.64E-05	1.44E-04	2.52E-07	1.72E-07
1,1-Dichloroethene	2.52E-06	2.37E-06	4.11E-06	1.85E-06	9.52E-05	2.49E-05	3.66E-05	6.83E-05	3.31E-05	1.63E-04	1.80E-07	1.23E-07
Carbon Disulfide	2.02E-06	1.11E-05	3.73E-05	6.90E-07	7.62E-05	1.99E-05	2.93E-05	5.46E-05	3.08E-05	1.31E-04	3.90E-08	9.82E-08
Dichloromethane	2.14E-06	2.02E-06	3.49E-06	3.15E-06	8.09E-05	5.00E-06	3.11E-05	1.36E-05	2.82E-05	1.39E-04	2.38E-07	2.45E-07
Freon-113	4.79E-06	4.50E-06	7.81E-06	3.52E-06	1.81E-04	5.27E-05	6.95E-05	1.37E-04	6.30E-05	3.33E-04	3.42E-07	2.33E-07
trans-1,2-Dichloroethene	2.52E-06	2.37E-06	4.11E-06	1.85E-06	9.52E-05	2.49E-05	3.29E-05	6.83E-05	2.98E-05	1.63E-04	1.80E-07	1.23E-07
1,1-Dichloroethane	2.52E-06	2.37E-06	4.11E-06	1.85E-06	9.52E-05	2.49E-05	3.29E-05	6.83E-05	2.98E-05	1.63E-04	1.80E-07	1.23E-07
Methyl Tert Butyl Ether	2.27E-06	2.13E-06	3.70E-06	1.67E-06	8.57E-05	2.24E-05	3.29E-05	6.14E-05	2.98E-05	3.01E-03	1.62E-07	1.10E-07
Methyl Ethyl Ketone	2.36E-05	8.44E-06	1.94E-04	1.00E-05	7.14E-05	9.90E-05	2.75E-05	7.71E-04	9.38E-04	1.36E-04	1.35E-07	9.20E-08
cis-1,2-Dichloroethene	2.52E-06	2.37E-06	4.11E-06	1.85E-06	9.52E-05	2.49E-05	3.66E-05	6.83E-05	3.31E-05	1.63E-04	1.80E-07	1.23E-07
Hexane	2.27E-06	2.13E-06	3.70E-06	1.67E-06	8.57E-05	2.24E-05	3.29E-05	6.14E-05	2.98E-05	1.21E-03	1.62E-07	1.71E-07
Chloroform	3.02E-06	2.84E-06	4.93E-06	2.23E-06	1.14E-04	2.98E-05	4.39E-05	8.19E-05	3.98E-05	1.96E-04	2.16E-07	1.47E-07
Ethyl Acetate	2.27E-06	2.13E-06	3.70E-06	1.67E-06	8.57E-05	2.24E-05	3.29E-05	6.14E-05	2.98E-05	1.47E-04	1.62E-07	1.10E-07
Tetrahydrofuran	1.89E-06	1.78E-06	2.63E-04	1.39E-06	7.14E-05	1.86E-05	3.52E-05	5.12E-05	2.49E-05	1.35E-04	1.35E-07	9.20E-08
1,2-Dichloroethane	2.52E-06	2.37E-06	4.11E-06	1.85E-06	9.52E-05	2.49E-05	3.66E-05	6.83E-05	3.31E-05	1.22E-04	1.53E-07	1.23E-07
1,1,1-Trichloroethane	3.40E-06	3.20E-06	5.55E-06	2.50E-06	1.29E-04	3.36E-05	4.94E-05	9.22E-05	4.47E-05	1.63E-04	1.80E-07	1.66E-07
Benzene	1.83E-05	1.03E-04	2.02E-05	1.48E-06	3.87E-04	1.72E-04	9.64E-04	9.57E-04	1.76E-04	2.20E-04	2.43E-07	2.10E-05
carbon tetrachloride	3.61E-07	3.79E-06	6.58E-06	2.97E-06	1.52E-04	4.40E-05	5.86E-05	1.09E-04	9.36E-06	1.10E-03	2.40E-06	3.26E-07
Cyclohexane	2.14E-06	2.02E-06	1.33E-05	1.58E-06	8.09E-05	2.11E-05	3.11E-05	5.80E-05	2.82E-05	2.61E-04	4.76E-07	9.44E-08
1,2-Dichloropropane	5.89E-06	2.73E-06	4.73E-06	2.13E-06	1.09E-04	2.86E-05	4.21E-05	7.85E-05	3.81E-05	1.99E-04	1.53E-07	1.41E-07
Bromodichloromethane	4.16E-06	3.91E-06	6.78E-06	3.06E-06	1.57E-04	4.10E-05	6.04E-05	1.13E-04	5.47E-05	4.20E-04	2.07E-07	2.02E-07
Trichloroethene	4.28E-06	4.03E-06	6.99E-06	3.15E-06	1.62E-04	4.23E-05	6.22E-05	1.16E-04	5.63E-05	2.69E-04	2.97E-07	2.09E-07
1,4-Dioxane	2.27E-06	2.13E-06	3.70E-06	1.67E-06	8.57E-05	2.24E-05	3.29E-05	6.14E-05	2.98E-05	2.77E-04	3.06E-07	2.09E-07
Heptane	2.52E-06	2.37E-06	3.27E-06	1.85E-06	8.70E-05	1.00E-05	3.66E-05	2.78E-05	1.11E-05	3.14E-04	1.62E-07	1.10E-07
cis-1,3-Dichloropropene	2.90E-06	2.73E-06	4.73E-06	2.13E-06	1.09E-04	2.86E-05	4.21E-05	7.85E-05	3.81E-05	1.60E-03	3.93E-07	9.15E-07
Methyl Isobutyl Ketone	2.52E-06	2.37E-06	4.11E-06	1.85E-06	9.52E-05	2.49E-05	3.66E-05	6.83E-05	3.31E-05	1.88E-04	2.07E-07	1.41E-07
trans-1,3-Dichloropropene	2.90E-06	2.73E-06	4.93E-06	2.13E-06	1.09E-04	2.86E-05	4.21E-05	7.85E-05	3.81E-05	3.68E-04	1.80E-07	1.23E-07
1,1,2-Trichloroethane	3.40E-06	3.20E-06	5.55E-06	2.50E-06	1.29E-04	3.36E-05	4.94E-05	9.22E-05	4.47E-05	1.88E-04	2.07E-07	1.41E-07
Toluene	2.39E-06	1.35E-06	3.90E-06	1.76E-06	9.04E-05	2.36E-05	1.33E-04	5.61E-05	3.15E-05	1.85E-03	2.43E-07	1.66E-07

= Upper Limit   = Lower Limit

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Table 4.9.   (Continued)

	POI092302	POI092401	POI092402	POI092403	POI092501	POI092502	POI092503	POI092504	POI092602	POI092603	POI092704A	POI092704B
	155mm Howitzer	66mm Rocket	66mm Rocket	40mm Cartridge	4.2" Mortar	4.2" Mortar	4.2" Mortar	4.2" Mortar	155mm Howitzer	155mm Howitzer	155mm Howitzer	155mm Howitzer
	Illumination	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	Smoke	Smoke
Methyl Butyl Ketone	2.52E-06	2.37E-06	4.11E-06	1.85E-06	9.52E-05	8.44E-04	2.28E-04	2.81E-04	3.31E-05	1.06E-04	1.86E-06	1.23E-07
Dibromochloromethane	5.42E-06	5.10E-06	8.84E-06	3.99E-06	2.05E-04	5.34E-05	7.87E-05	1.47E-04	7.12E-05	3.51E-04	3.87E-07	2.64E-07
1,2-Dibromoethane	4.79E-06	4.50E-06	7.81E-06	3.52E-06	1.81E-04	4.72E-05	6.95E-05	1.30E-04	6.30E-05	3.10E-04	3.42E-07	2.33E-07
Tetrachloroethene	4.28E-06	4.03E-06	6.99E-06	3.15E-06	1.62E-04	4.23E-05	6.22E-05	1.16E-04	5.63E-05	2.77E-04	3.06E-07	2.09E-07
Chlorobenzene	2.90E-06	2.73E-06	4.73E-06	2.13E-06	1.09E-04	2.86E-05	4.21E-05	7.85E-05	3.81E-05	1.88E-04	2.07E-07	1.41E-07
Ethylbenzene	2.77E-06	2.61E-06	4.52E-06	2.04E-06	1.05E-04	2.73E-05	4.03E-05	7.51E-05	3.65E-05	5.16E-04	1.98E-07	8.16E-07
m&p-Xylene	2.77E-06	2.61E-06	4.52E-06	2.04E-06	1.05E-04	2.73E-05	4.23E-05	7.51E-05	3.65E-05	1.89E-03	1.98E-07	6.09E-07
Bromoform	6.55E-06	6.16E-06	1.07E-05	4.82E-06	2.47E-04	6.46E-05	9.52E-05	1.78E-04	8.62E-05	4.24E-04	4.66E-07	3.19E-07
Styrene	2.65E-06	2.49E-06	4.31E-06	1.95E-06	1.00E-04	2.61E-05	1.33E-04	7.17E-05	3.48E-05	1.71E-04	1.89E-07	2.15E-06
1,1,2,2-Tetrachloroethane	4.28E-06	4.03E-06	6.99E-06	3.15E-06	1.62E-04	4.23E-05	6.22E-05	1.16E-04	5.63E-05	2.77E-04	3.06E-07	2.09E-07
o-Xylene	2.77E-06	2.61E-06	4.52E-06	2.04E-06	1.05E-04	2.73E-05	4.03E-05	7.51E-05	3.65E-05	8.19E-04	1.98E-07	1.35E-07
4-Ethyltoluene	3.15E-06	2.96E-06	5.14E-06	2.32E-06	1.19E-04	3.11E-05	4.58E-05	8.53E-05	4.14E-05	1.23E-03	2.25E-07	2.88E-07
1,3,5-Trimethylbenzene	3.15E-06	2.96E-06	5.14E-06	2.32E-06	1.19E-04	3.11E-05	4.58E-05	8.53E-05	4.14E-05	2.04E-04	2.25E-07	1.53E-07
1,2,4-Trimethylbenzene	3.15E-06	2.96E-06	5.14E-06	2.32E-06	1.19E-04	3.11E-05	4.58E-05	8.53E-05	4.14E-05	1.20E-03	2.25E-07	1.53E-07
m-Dichlorobenzene	3.78E-06	3.56E-06	6.16E-06	2.78E-06	1.43E-04	3.73E-05	5.49E-05	1.02E-04	4.97E-05	2.45E-04	2.70E-07	1.84E-07
p-Dichlorobenzene	3.78E-06	3.56E-06	6.16E-06	2.78E-06	1.43E-04	3.73E-05	5.49E-05	1.02E-04	4.97E-05	2.45E-04	2.70E-07	1.84E-07
o-Dichlorobenzene	3.78E-06	3.56E-06	6.16E-06	2.78E-06	1.43E-04	3.73E-05	5.49E-05	1.02E-04	4.97E-05	2.45E-04	2.70E-07	1.84E-07
1,2,4-Trichlorobenzene	4.66E-06	4.39E-06	7.60E-06	3.43E-06	1.76E-04	1.71E-04	6.77E-05	1.26E-04	6.13E-05	3.02E-04	3.33E-07	2.27E-07
Hexachlorobutadiene	6.68E-06	6.28E-06	1.09E-05	4.91E-06	2.52E-04	6.59E-05	9.70E-05	1.81E-04	8.78E-05	4.32E-04	4.77E-07	3.25E-07
chlorine	1.27E-06	1.19E-06	2.06E-06	9.31E-07	4.78E-05	1.25E-05	1.84E-05	3.43E-05	1.66E-05	8.19E-05	9.04E-08	6.16E-08
N-nitrosodimethylamine	3.82E-06	3.59E-06	6.23E-06	2.81E-06	1.44E-04	3.77E-05	5.55E-05	1.04E-04	1.16E-04	2.47E-04	2.73E-07	1.86E-07
aniline	3.36E-07	3.16E-07	5.48E-07	2.47E-07	1.27E-05	3.32E-06	4.88E-06	9.11E-06	6.32E-06	2.18E-05	2.40E-08	1.64E-08
N-nitrosodiethylamine	7.01E-06	6.59E-06	1.14E-05	5.15E-06	2.65E-04	6.91E-05	1.02E-04	1.90E-04	9.21E-05	4.54E-04	5.01E-07	3.41E-07
dinitrobenzene	3.36E-07	3.16E-07	5.48E-07	2.47E-07	1.27E-05	3.32E-06	4.88E-06	9.11E-06	4.42E-06	2.18E-05	2.40E-08	2.10E-08
diphenyl amine	8.73E-07	8.21E-07	1.42E-06	6.42E-07	3.30E-05	8.61E-06	1.27E-05	2.36E-05	1.15E-05	5.65E-05	6.24E-08	4.25E-08
dinitrotoluene	5.61E-07	5.28E-07	9.15E-07	4.13E-07	2.12E-05	5.53E-06	8.15E-06	1.52E-05	7.37E-06	3.63E-05	4.01E-08	2.73E-08
dimethylphthalate	2.50E-07	2.36E-07	4.08E-07	1.84E-07	9.46E-06	2.47E-06	3.64E-06	6.79E-06	1.03E-05	1.62E-05	1.79E-08	1.22E-08
N-nitrosodiphenylamine	6.95E-07	6.54E-07	1.13E-06	5.12E-07	2.63E-05	6.86E-06	1.01E-05	1.88E-05	9.14E-06	4.50E-05	4.97E-08	3.39E-08
nitroglycerine	6.94E-06	6.53E-06	1.13E-05	5.11E-06	2.62E-04	6.85E-05	1.01E-04	1.88E-04	9.13E-05	4.49E-04	4.96E-04	3.38E-07
Formaldehyde	3.72E-05	1.56E-04	1.31E-04	4.33E-05	4.62E-03	1.16E-03	2.57E-03	3.48E-03	2.00E-03	4.21E-03	9.19E-06	7.75E-05
hydrogen cyanide	NA	2.02E-03	3.02E-03	2.98E-04	1.28E-01	3.47E-02	3.44E-01	2.34E-01	1.50E-01	2.98E-02	2.89E-05	2.23E-04
toluene	NA	1.07E-04	2.25E-04	8.39E-05	4.31E-03	1.12E-03	1.66E-03	3.09E-03	1.50E-03	7.38E-03	8.15E-06	8.79E-06
phenol	NA	4.61E-03	7.99E-03	3.61E-03	1.85E-01	4.84E-02	7.12E-02	1.33E-01	6.45E-02	3.17E-01	3.50E-04	2.39E-04
quinoline	NA	1.44E-05	2.50E-05	1.13E-05	5.79E-04	1.51E-04	2.23E-04	4.15E-04	2.01E-04	9.92E-04	1.10E-06	7.46E-07
anthracene	NA	2.77E-05	4.80E-05	2.16E-05	1.11E-03	2.90E-04	4.27E-04	7.97E-04	3.87E-04	1.90E-03	2.10E-06	1.43E-06
nitrobenzene	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
dibenzofuran	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
beryllium	1.21E-05	1.45E-04	2.45E-04	3.55E-05	1.62E-03	3.62E-04	5.60E-04	8.36E-04	3.38E-04	8.61E-04	1.17E-06	7.98E-07
aluminum	6.03E-03	7.74E-02	1.40E-01	1.77E-02	8.09E-01	2.00E-01	3.15E-01	4.18E-01	5.44E-01	5.35E-01	5.87E-04	3.99E-04
chromium	1.17E-04	2.22E-03	2.24E-03	3.16E-04	1.53E-02	3.10E-03	3.66E-03	6.81E-03	2.57E-03	5.97E-03	1.10E-05	7.55E-06
manganese	6.03E-05	1.09E-03	1.21E-03	1.77E-04	1.04E-02	2.66E-03	3.72E-03	4.32E-03	6.78E-03	6.38E-03	5.87E-06	3.99E-06
cobalt	6.03E-05	7.26E-04	6.99E-04	1.77E-04	8.09E-03	1.81E-03	2.80E-03	4.18E-03	1.69E-03	4.31E-03	5.87E-06	3.99E-06
nickel	6.03E-04	7.26E-03	6.99E-03	1.77E-03	8.09E-02	2.61E-02	2.80E-02	4.18E-02	1.69E-02	4.85E-02	7.54E-05	5.15E-05

= Upper Limit   = Lower Limit

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Table 4.9.　　(Continued)

	POI092302	POI092401	POI092402	POI092403	POI092501	POI092502	POI092503	POI092504	POI092602	POI092603	POI092704A	POI092704B
	155mm Howitzer	66mm Rocket	66mm Rocket	40mm Cartridge	4.2" Mortar	4.2" Mortar	4.2" Mortar	4.2" Mortar	155mm Howitzer	155mm Howitzer	155mm Howitzer	155mm Howitzer
	Illumination	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	High Explosive	Smoke	Smoke
copper	1.21E-04	4.39E-02	3.62E-02	9.98E-04	5.31E-02	1.36E-02	1.59E-02	1.58E-02	1.14E-02	1.04E-02	1.23E-05	8.59E-06
zinc	6.03E-03	7.26E-02	6.99E-02	1.77E-02	8.09E-01	2.49E-01	2.80E-01	4.18E-01	1.69E-01	4.31E-01	5.87E-04	3.99E-04
arsenic	3.01E-05	3.63E-04	3.49E-04	8.87E-05	4.05E-03	9.06E-04	1.40E-03	2.09E-03	8.45E-04	2.15E-03	2.93E-06	2.02E-06
selenium	1.21E-04	1.45E-03	1.40E-03	3.55E-04	1.62E-02	3.62E-03	5.60E-03	8.36E-03	3.38E-03	8.61E-03	1.17E-05	7.98E-06
silver	6.03E-05	7.26E-04	7.13E-04	1.77E-04	8.09E-03	1.81E-03	2.80E-03	4.18E-03	3.56E-03	4.31E-03	5.87E-06	3.99E-06
cadmium	3.01E-05	3.63E-04	4.09E-04	8.87E-05	4.05E-03	9.06E-04	1.40E-03	2.09E-03	8.45E-04	2.15E-03	2.93E-06	2.02E-06
antimony	6.03E-05	7.26E-04	6.99E-04	1.77E-04	8.09E-03	1.81E-03	2.80E-03	4.18E-03	1.69E-03	4.31E-03	5.87E-06	3.99E-06
barium	6.66E-04	7.26E-03	6.99E-03	1.77E-03	8.09E-02	1.81E-02	2.80E-02	4.18E-02	1.69E-02	4.31E-02	5.87E-05	3.99E-05
thallium	3.01E-05	3.63E-04	3.49E-04	8.87E-05	4.05E-03	9.06E-04	1.40E-03	2.09E-03	8.45E-04	2.15E-03	2.05E-05	1.40E-05
lead	7.18E-04	1.78E-02	1.79E-02	1.89E-03	8.45E-02	1.91E-02	1.91E-02	3.60E-02	1.39E-02	4.46E-02	8.30E-05	5.64E-05
PAH (particle-bound)	3.18E-05	4.69E-06	NA	3.08E-05	3.17E-06	1.14E-05	7.69E-06	7.29E-05	6.26E-05	4.81E-05	2.03E-06	2.03E-06
NO	3.73E-03	3.44E-03	2.78E-03	0.00E+00	1.67E-02	8.63E-03	1.35E-03	2.10E-04	2.98E-02	5.02E-04	3.88E-06	6.41E-05
NO2	6.89E-04	6.15E-04	1.49E-03	1.66E-04	3.90E-02	1.34E-02	1.35E-02	1.03E-02	1.76E-02	9.23E-03	2.80E-05	1.29E-04

= Upper Limit

= Lower Limit

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effect of soil entrainment on emissions from high explosive munitions. The following sections discuss these two special topics.

4.2.5.1 Reproducibility of Emission Factors. The Point of Impact tests were designed to allow an examination of the reproducibility of emissions data. Replication was planned for all test conditions. Some tests were unsuccessful due to wind shifts blowing the emission cloud in the wrong direction or problems with the ordnance itself, but duplicate or greater replication was achieved for nine munitions/conditions.

To examine the reproducibility of emissions data from outdoor munitions testing, six chemicals were selected. The six chemicals are: benzene, toluene, formaldehyde, copper, lead, and nitrogen dioxide. Five of the six chemicals are on the TRI, and the sixth, NO_2, is a Criteria Air Pollutant regulated under the Clean Air Act. These chemicals were chosen because they are important representatives of TRI and criteria air pollutants and also because they were observed above the detection limit for nearly all tests. Table 4.10 lists the nine munitions and conditions for which replicate test data are available. Four successful tests were obtained for the 4.2" high explosive mortar round. Two of these tests were conducted over a steel plate, so that the effects of soil entrainment on emissions could be studied (see Section 4.2.5.2). The data for these two conditions are reported separately.

Table 4.10. Reproducibility of Emission Factors for Selected Chemicals from
Outdoor Point of Impact Tests

Munition	Number of Tests	Benzene	Toluene	Formaldehyde	Copper	Lead	NO_2
		Relative Standard Deviation					
Signal Flare	2	.56	.26	.66	--	.32	.94
40 mm Illumination	3	.70	.21	.81	--	1.21	.63
Smoke Grenade	3	.78	.83	.53	--	.97	.69
81 mm Smoke Mortar	5	1.00	.80	.85	--	.62	.76
155 mm Howitzer (illumination)	2	.65	.12	.53	--	--	1.02
66 mm Rocket	2	.95	.69	.12	.14	.01	.59
42" Mortar HE (over plate)	2	.55	.83	.85	.84	--	.69
42" Mortar HE (over soil)	2	.00	.58	.21	.01	--	.19
155 mm Howitzer HE (over plate)	2	1.02	1.37	.50	--	.74	.44

The table shows the relative standard deviation of the emission factor results for the six example chemicals and the nine munitions/conditions. In a few cases for copper and lead the relative

standard deviation is not reported because the test results were below the detection limit for one or more of the replications.

The data show that the reproducibility of emission factors measured under realistic outdoor conditions is variable. For a given chemical, the relative standard deviation can range from near zero (perfectly reproducible) to over 100%. Overall, the relative standard deviation is better than 80% for two-thirds of the conditions. When compared by chemical, the emission factor reproducibility is quite consistent, with the average RSD ranging from 47% for copper to 69% for benzene. When averaged across all six chemicals, the most reproducible test/condition was the 4.2" mortar fired over soil, with an average RSD of 0.24. The least reproducible test/condition was the smoke grenade, with an average RSD of 0.80. When averaged across all tests/conditions and all six chemicals, the RSD was 0.60.

4.2.5.2 Emission Factor Comparison—Over Soil versus On a Steel Plate. As indicated earlier, an important factor that was incorporated into our test strategy was to gather emissions data from the same munitions fired over two different surfaces. The surfaces selected were soil and a steel plate. The two munitions that were selected for the comparisons were the 4.2 inch mortar tested on 9/25/2003 and the 155 mm Howitzer high explosive detonated on 9/26/2003. Unfortunately, the 155 mm Howitzer high explosive detonation over the soil was not a successful run. As a result the only comparison data were two 4.2 inch mortar tests detonated on a steel plate and two tests conducted over the soil. The tabular emission factor results are contained in Table 4.9. The data clearly indicate that the emissions from munitions detonated over soil are different than the emissions from the same munitions detonated on a hard surface such as a steel plate. For example, in Figure 4.11 we show plots of total hydrocarbons and CO for the four tests. The y-axis shows the individual emission factors in pounds per item. On the x-axis, the four runs are identified as either on the hard surface or over soil. Both sets of emission factors are significantly lower when the mortar round was detonated over the steel plate than over the soil. The results are consistent with the fact that one would expect lower combustion temperatures and less complete combustion when soil is entrained into the fireball. As a consequence, emissions of products of incomplete combustion should be enhanced. The NO and NO_2 values are plotted similarly and are shown in Figure 4.12. In this case, one would

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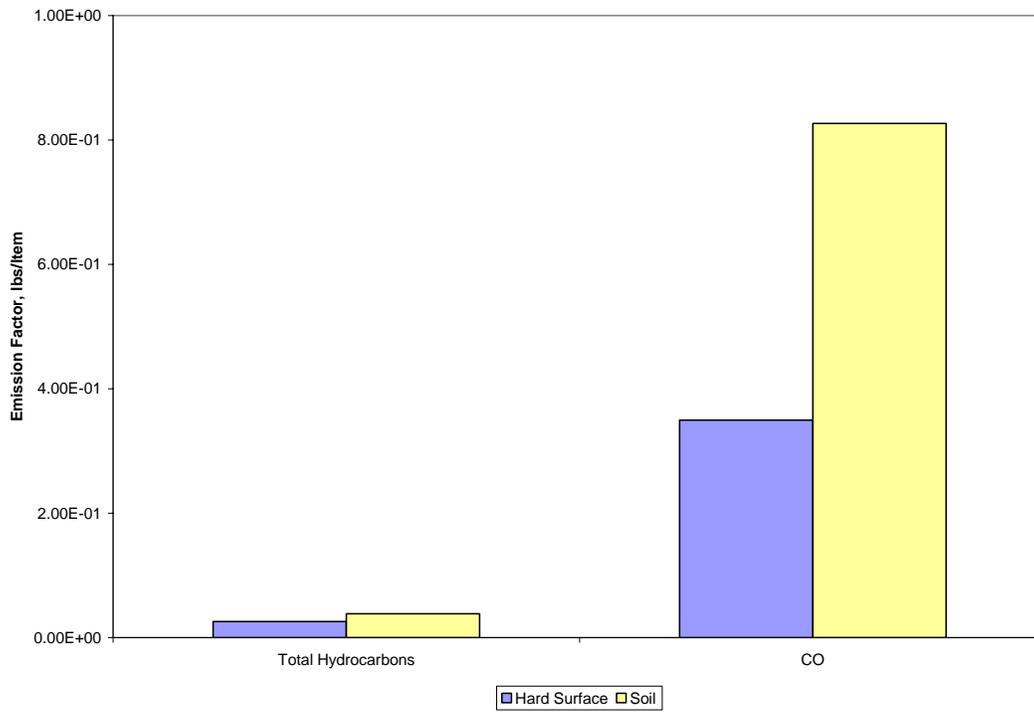
Figure 4.11. Total Hydrocarbons and CO Emission Factors With and
Without Entrained Soil
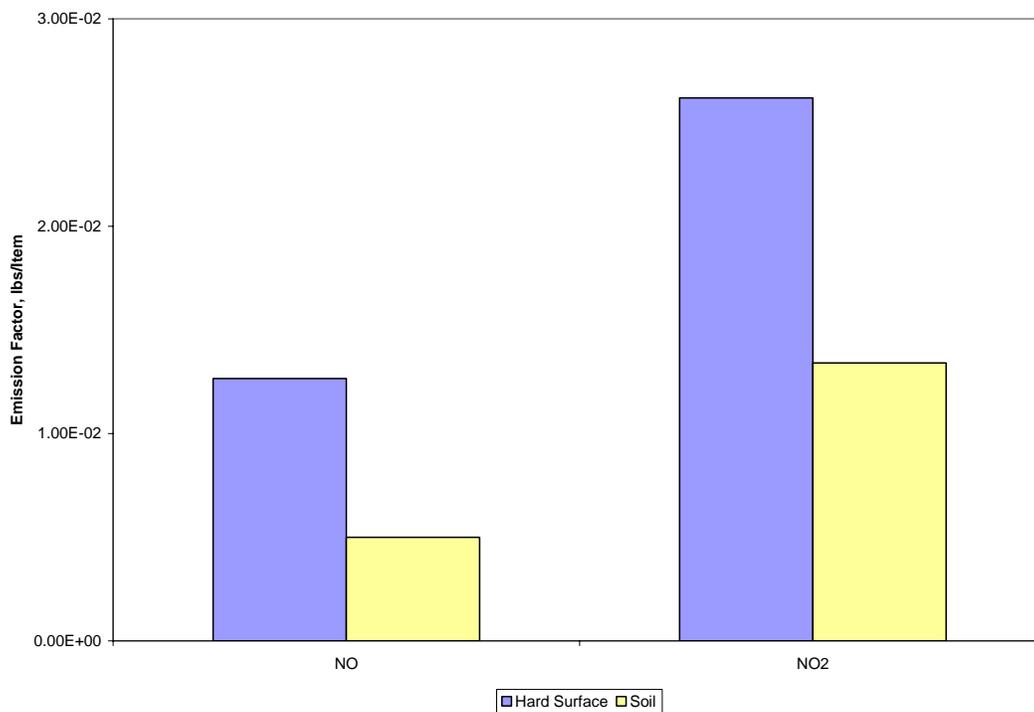
Figure 4.12. NO$_2$ and NO Emission Factors With and Without Entrained Soil

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expect higher levels of nitrogen oxides with higher combustion temperatures, and therefore the tests over the steel plate should show higher emission levels. The figure clearly confirms this expectation. Finally, we show plots of 1,3-butadiene and benzene in Figure 4.13. As the data indicate, higher levels of these species are observed from the two test runs conducted over soil. Clearly, the entrained soil contributes to an increased burden of TRI chemicals by quenching chemical reactions in the initial fireball.
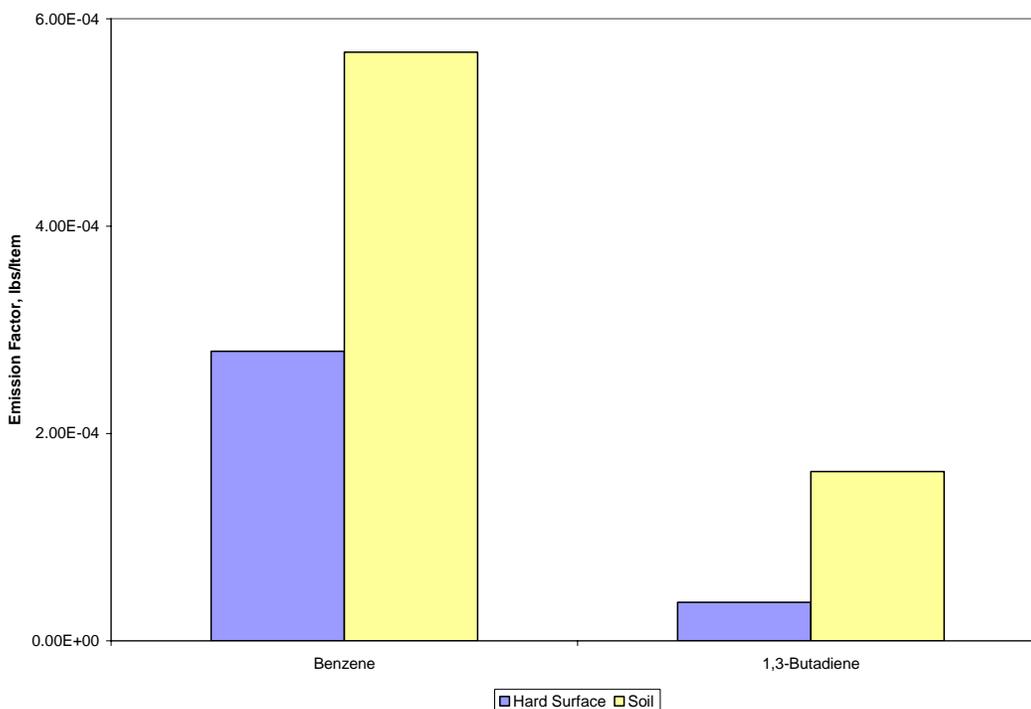
Figure 4.13. 1,3-Butadiene and Benzene Emission Factors With and Without Entrained Soil

4.2.5.3 Comparison with Data from Other Studies. Emission factors for one of the munitions tested in the Point of Impact study have recently been reported.[6] The Army Environmental Center supported a series of tests at Dugway Proving Ground in 50-foot diameter hemispherical chamber known as a BangBox. The chamber is constructed of plasticized fabric and is held in its hemispherical shape by constant injection of air from a blower.

The Dugway team tested the same 155 mm howitzer illumination round (DODIC D505) that was tested outdoors during the Point of Impact study, so a comparison of the resulting emission factors should be instructive.

Table 4-11 compares the emission factors from the two studies for many of the chemicals that both teams attempted to measure. All data are in units of pound of emitted chemical per munitions item. The Point of Impact results represent the average of two tests (POI092301 and POI092302). If the emission factor for a chemical was reported as an upper limit for either or both of the tests used to derive the average, then the average value is flagged as an upper limit value. The upper limit values are shown by shading the appropriate cells.

It is clear from Table 4-11 that the majority of these toxic chemicals were not found in the emissions from this item. Most of the results from the POI study are upper limits, and many of the chemicals were not detected in the Dugway tests. The detection limits for some species, especially metals, should be lower for the Dugway tests for two reasons: the emissions are confined in a fixed volume and are therefore more concentrated during the sampling period compared to the rapidly diluting concentrations in the outdoor emissions cloud, and the time available for sampling is much longer for the BangBox tests. For example, the metals were sampled for a minimum of 20 minutes in the BangBox tests, but could only be sampled for seconds in the moving outdoor emissions cloud. Because of these constraints on the outdoor tests, the detection limits for the metals are relatively high, and the upper limit emission factors are also relatively high. As a consequence, the emission factors for all of the metals detected in the Dugway tests are lower than the upper limit emission factors for those metals reported in the POI study. Thus the metals results are consistent but a careful comparison is not possible.

Selected results from Table 4.11 are shown in bar chart form in Figure 4.14. The data are plotted on a logarithmic scale, and upper limit values are noted by a "<" symbol above the corresponding bar. Given all the difficulties in measuring emission factors, both in the BangBox and in outdoor air, the agreement for most of the chemicals is reasonable. Some comparisons that stand out are naphthalene, where the BangBox result is almost seven times greater than the upper limit from the outdoor tests; carbon disulfide where the chamber tests report 29 times the

Table 4.11. Comparison of Emission Factors from Outdoor POI Study and Indoor BangBox Tests

Emission Factor, lbs/Item

Chemical	POI Average	BangBox
Acetonitrile	5.36E-06	2.60E-05
Acrolein	2.03E-05	2.90E-05
Acrylonitrile	6.87E-06	2.10E-05
Naphthalene	2.43E-06	1.60E-05
Methyl Chloride	1.38E-06	ND
Vinyl Chloride	1.79E-06	ND
1,3-Butadiene	1.51E-06	ND
Methyl Bromide	2.62E-06	ND
Ethyl Chloride	1.79E-06	ND
Carbon Disulfide	2.20E-06	6.40E-05
trans-1,2-Dichloroethene	2.75E-06	ND
1,1-Dichloroethane	2.75E-06	ND
Methyl Tert Butyl Ether	2.48E-06	2.10E-07
Methyl Ethyl Ketone	1.91E-05	1.60E-05
cis-1,2-Dichloroethene	2.75E-06	ND
Hexane	2.48E-06	2.60E-06
Chloroform	3.30E-06	ND
1,1,1-Trichloroethane	3.72E-06	ND
Benzene	1.26E-05	1.10E-04
carbon tetrachloride	2.57E-06	1.70E-07
Cyclohexane	1.91E-06	5.70E-07
Trichloroethene	4.68E-06	ND
1,4-Dioxane	2.48E-06	ND
trans-1,3-Dichloropropene	3.17E-06	ND
1,1,2-Trichloroethane	3.72E-06	ND
Toluene	2.62E-06	2.40E-05
1,2-Dibromoethane	5.23E-06	ND
Chlorobenzene	3.17E-06	ND
Ethylbenzene	3.03E-06	7.30E-06
m&p-Xylene	3.03E-06	4.20E-06
Styrene	2.89E-06	ND
1,1,2,2-Tetrachloroethane	4.68E-06	ND
o-Xylene	3.03E-06	4.50E-06
4-Ethyltoluene	3.44E-06	8.50E-07
1,2,4-Trimethylbenzene	3.44E-06	2.10E-06
m-Dichlorobenzene	4.13E-06	ND
p-Dichlorobenzene	4.13E-06	ND
o-Dichlorobenzene	4.13E-06	ND
1,2,4-Trichlorobenzene	5.09E-06	ND
Hexachlorobutadiene	7.30E-06	ND
chlorine	1.38E-06	2.00E-06
N-nitrosodimethylamine	4.17E-06	ND
aniline	3.67E-07	ND
N-nitrosodiethylamine	7.65E-06	ND
dinitrobenzene	3.67E-07	ND
dinitrotoluene	6.13E-07	ND
dimethylphthalate	2.74E-07	ND
beryllium	1.67E-05	2.10E-07
chromium	1.46E-04	7.00E-06
manganese	8.33E-05	5.40E-05
cobalt	8.33E-05	1.80E-06
nickel	8.33E-04	9.50E-06
copper	1.67E-04	7.60E-05
arsenic	4.16E-05	ND
selenium	1.67E-04	ND
silver	8.33E-05	ND
cadmium	4.16E-05	7.40E-05
antimony	8.33E-05	2.10E-05
barium	8.64E-04	3.90E-04
thallium	4.16E-05	ND
lead	8.75E-04	5.80E-05
NO	4.06E-03	3.90E-03
NO2	4.01E-04	5.90E-02

Shaded cell means upper limit
ND = Not Detected
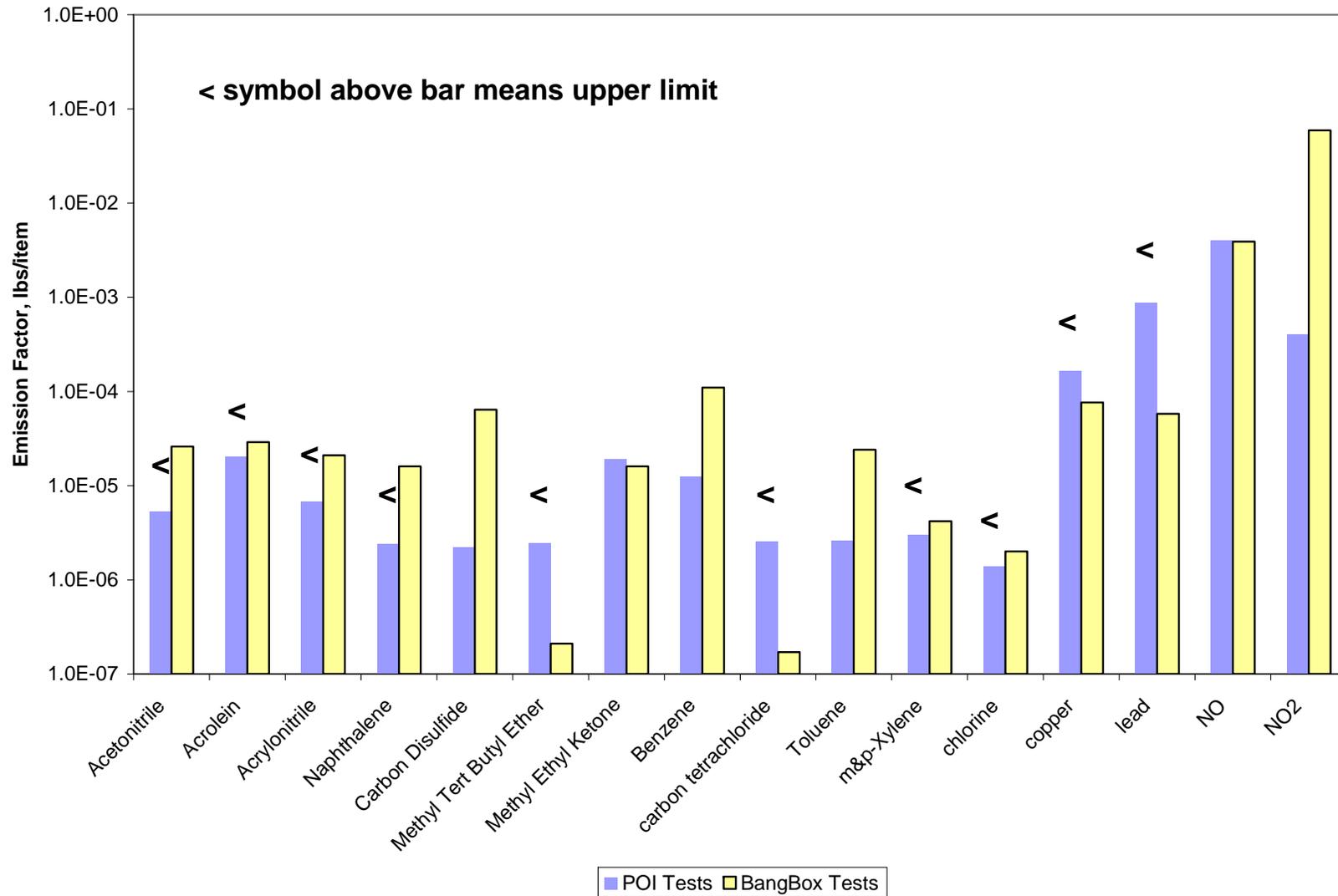
Figure 4.14. Comparison of Emission Factors from the Outdoor POI Tests and BangBox Tests
(upper limit values noted by "<" symbol)

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emissions of the outdoor test; benzene and toluene, which are nearly 9 times higher than the outdoor results; and nitrogen dioxide, which was about times higher in the chamber tests compared to the outdoor tests. Of course some of these comparisons may be influenced by the way the tests are conducted. For example NO can oxidize to NO_2 at the higher concentrations of the confined-volume chamber tests because the rate of the oxidation proceeds with the square of the NO concentration. Other factors such as local oxygen depletion have been cited as potentially affecting emissions from chamber tests, and could lead to differences in emission factors.

REFERENCES

1. Einfeld, W., Morrison, D. J., Mokler, B. V., An Experimental Study to Determine Gaseous and Particulate Products from Small-Scale TNT Detonations and Propellant Burns, Sandia Report—SAND90-0605, TTC-0975, UC-772, Sandia National Laboratories, 1991.

2. Johnson, M., Development of Methodology and Techniques for Identifying and Quantifying Products from Open Burning and Open Detonation Thermal Treatment Methods – Field Test Series A, B and C, Volume 1 (Test Summary), U.S. Army, Contract DAAD09-87-D-0008, 1992.

3. Radian International LLC, Sampling Results for C-3 and C-4 Propellant Emission Characterization, Doc. F9711301.MW97 prepared for Hill Air Force Base, UT, June 1998.

4. Watkins, B., Velsko, C. A., Pruneda, LLNL, Underground Detonations of Conventional Munitions at the Department of Energy's Nevada Test Site, presented at the 1998 Global Demilitarization Symposium and Exhibition, Coeur D'Alene, ID, May 11-14, 1998.

5. Rush, T. L., Firing Point Emissions Test Program, presented at Partners in Environmental Technology Technical Symposium and Workshop, November 30-December 2, 2004, Washington, D.C. Abstract available at www.SERDP.org.symposiums/2004/tech_abstracts_2004.pdf

6. MACTEC Federal Programs, Report on Creation of 5th Edition AP-42 Chapter 15-Ordnance Detonation, Emission Factors Developed Based on Phase I Testing Conducted at Dugway Proving Ground, Utah, Contract No. GS-IDF-0131K, August , 2004.

7. MACTEC Federal Programs, Report on Creation of 5th Edition AP-42 Chapter 15-Ordnance Detonation, Emission Factors Developed Based on Phase II Testing Conducted at Dugway Proving Ground, Utah, Contract No. GS-IDF-0131K, August, 2004.

8. Baroody, E. E., Computer Predictions of Pollution Products from Open Burn and Open Detonations, U.S. Naval Surface Warfare Center, Indian Head, MD, November 1999.

9. Spicer, C. W., Holdren, M. W., Wisbith, A. S., Cowen, K. A., Jobson, B. T., Satola, J., Mangaraj, R., Joseph, D. W., Bolt, W. R., Bach, J. C., Sedlacek, A. J., and Cramer, R. J., FY02 Annual Report to SERDP, "A Field Program to Identify TRI Chemicals and Determine Emission Factors from DoD Munitions Activities", December, 2002.

10. Mitchell, W. J. and Suggs, J. C., Emission Factors for the Disposal of Energetic Materials by Open Burning and Open Detonation (OB/OD), EPA/600/R-98/103, U.S. Environmental Protection Agency, 1998.

11. Mitchell, W. J., "State of the Science and Research Needs in the Characterization and Minimization of the Emissions from Ordnance Use and Disposal Activities", from Am. Academy of Environmental Engineers Workshop on Air Quality Issues—Diesel Engines, Gas Turbines and Ordnance, at www.enviro-engrs.org/newlook/air_quality_issues.htm.

12. Lindsay, M. L., McMorris, R., Baroody, E. E., and Watkins, J. W., Use of Blimps to Collect In-Situ Reaction Products from Detonation Plumes, U.S. Naval Surface Warfare Center, Indian Head, MD, 2000.

13. Schultz, M. P., Bolt, W. R., Report No. 1 for the Firing Point Emission Study Phase II, Propelling Charge, 155-mm, M3, Propelling Charge, 155-. <3A1, Prepared by Military Environmental Technology Demonstration Center, U.S. Army Aberdeen Test Center, Aberdeen Proving Ground, MD, 2100-5059.

14. Lipkin, J., Shaddix, C., Allendorf, S., Peabody, R., Summary and Final Results of the Rocket Motor Burn Test Series in X-Tunnel, Sandia National Laboratory, 2000 Global Demilitarization Symposium & Exhibition, 2000.

15. Snelson, A., Ase, P., Taylor, K., Gordon, S., Combustion Product Evaluation of Various Charge Sizes and Propellant Formulations, IIT Research Institute, Chicago, IL, Report No. IITRI-C06673, 1989.

16. Ase, P., Eisenberg, W., Gordon, S. Taylor, K., Snelson, A., Propellant Combustion Product Analyses on an M16 Rifle and a 105 mm Caliber Gun, Journal Environmental Science and Health, A20(3), 337-368, 1985.

17. Snelson, A., Ase, P., Bock, W., Butler, R., Characterization of Combustion Products of Military Propellants, Final Report, Volume II, IIT Research Institute, AD A167 417, Chicago, IL, 1983.

18. Watkins, B., Emission Characterization in the Contained Underground Demilitarization Laboratory at the Nevada Test Site, Lawrence Livermore National Laboratory, 2000.

19. Brennan, T., Report PEP Waste Combustion and Combustion Products Ten-Pound Pilot-Scale Confined Burn Facility (PCBF) Test Report, TCLP Semivolatile Organic Compound Analytical Results Summary Firing Chamber Particulate Sample, Composite Propellant Tests.

20. Chan, H., CPT, Jacobs, B., Schoffstall, L., Industrial Hygiene Study No. 55-35-0137-84, Determination of Composition of Combustion Products During Tracer Firing, Lake City Army Ammunition Plant, Independence, MO, U.S. Army Environmental Health Agency, APG, MD, November 29-December 2, 1983.

21. Menzies, K. T., Randel, M. A., Quill, A. L., Roberts, W. C., Evaluation of Weapons' Combustion Products in Armored Vehicles, Final Report on Contract No. DAMD17-86-C-6245, 1989.

22.   Spicer, C. W., Mangaraj, R., Cowen, K. A., Measurement of Nitrosoamines, Phthalates, Nitroglycerine and Other TRI Chemicals from Munitions Using Real-Time Atmospheric Pressure Ionization MS/MS, Symposium on Air Quality Measurement Methods and Technology—2002 VIP-115-CD, Air & Waste Mgmt. Assoc., 2002.

23.   Kelly, T. J. and Fortune, C. R., Continuous Monitoring of Gaseous Formaldehyde Using an Improved Fluorescence Approach, Intern. J. Environ. Anal. Chem., 54, 249-263 (1994).

APPENDIX A

EVALUATION AND OPTIMIZATION OF REAL-TIME MASS SPECTROMETRY FOR MEASUREMENT OF TRI CHEMICALS FROM MUNITIONS

(based on: Spicer, C. W. , Mangaraj, R., and Cowen, K. A., Measurement of Nitrosoamines, Phthalates, Nitroglycerine and Other TRI Chemicals from Munitions Using Real-Time Atmospheric Pressure Ionization MS/MS Symposium on Air Quality Measurement Methods and Technology—2002, VIP-115-CD, Air & Waste Mgmt. Assoc. (2002).)

EVALUATION AND OPTIMIZATION OF REAL-TIME MASS SPECTROMETRY FOR MEASUREMENT OF TRI CHEMICALS FROM MUNITIONS

INTRODUCTION

The objective of this project is to develop the tools and procedures for assessing emission factors for Toxic Release Inventory (TRI) chemicals from munitions activities conducted under realistic conditions. Measurement methods for the potential target chemicals were reviewed to determine which chemicals might be measurable under the conditions of the planned tests. The Point of Impact tests were performed outdoors on a military test range, so the measurement methods had to be highly sensitive. Also, for low volatility or very polar chemicals, extended storage in the gas phase for later analysis was not practical, and collection of integrated samples on adsorbent materials would not provide sufficient sensitivity due to the very short sampling times (tens of seconds). For such chemicals, highly sensitive real-time or near real-time measurement methods were desirable.

Our review of measurement methods suggested that a large number of the potential target chemicals, and 26 of the 27 high priority species, can be measured by six individual measurement methods. Two of the six methods involve real-time mass spectrometric monitoring. The two mass spectrometric techniques are atmospheric pressure chemical ionization tandem mass spectrometry (APCI MS/MS) and proton transfer reaction mass spectrometry (PTR-MS).

In theory the mass spectrometric instruments could each measure a large number of chemicals. However, for practical reasons it was necessary to target 5-8 chemicals for each instrument. Based on the characteristics of the two instruments, we selected 17-18 of the potential target chemicals for evaluation by each instrument. These species are shown in Table A-1. The dinitrobenzenes and dinitrotoluenes are common to both lists, because it was not clear which instrument would be most sensitive to these species. It should be noted that, although the TRI lists the dinitrobenzene and dinitrotoluene isomers individually, the mass spectrometric methods cannot separate the isomers, and can only report total dinitrobenzene and total dinitrotoluene.

Table A-1. Potential Target Chemicals Evaluated for
Mass Spectrometric Measurement

Atm. Pressure Chemical Ionization Tandem MS	Proton Transfer Reaction-MS
Nitroglycerine	Anthracene
formic acid	Naphthalene
chlorine	Quinoline
dinitrobenzene	Nitrobenzene
dinitrotoluene	Dinitrobenzene
N-nitrosodiphenylamine	Dinitrotoluene
N-nitrosodimethylamine	Phenol
N-nitrosodiethylamine	Nitrophenol
aniline	Dinitrophenol
dDimethylphthalate	Benzidine
diethylphthalate	Biphenyl
dibutylphthalate	Dibenzofuran
nitric acid	4-aminobiphenyl
hydrogen chloride	hydrogen cyanide

The first part of this document summarizes the results of the APCI MS/MS evaluation for the potential target chemicals listed in Table A-1, and the selection of final target chemicals for this instrument for emissions testing during this project. Considerations for selection of target chemicals for the PTR-MS are discussed at the end of the document.

APCI MS/MS Evaluation

The process of evaluating the APCI MS/MS instrument for the potential target compounds involved preparing test atmospheres of the chemicals at trace concentrations; optimizing the sensitivity of the instrument for each chemical by selection of parent and daughter ions, and by tuning the electrostatic lenses and other instrument parameters; and estimating the limit of detection for each chemical from monitoring of test atmospheres containing the target chemical at known, low concentration.

Five of the chemicals on the APCI MS/MS list have been evaluated previously with our current instrument (API 365) or with the previous version of this technology (TAGA). These chemicals are: formic acid, hydrogen cyanide, chlorine, nitric acid and hydrogen chloride. Selective measurement of HNO_3, HCl, and HCN by APCI requires the addition of a chlorine-

containing chemical to the ion source to utilize the chlorine adduct-forming properties of these acids to enhance selectivity. Because this ionization mode degrades the performance of the instrument for the other species listed in Table A-1, we did not include these three acids on the list of target chemicals for the APCI MS/MS method.

The daughter ion mass spectra for the remaining chemicals on the potential target list are provided in Figures A-1 through A-10. These spectra were used to select the parent/daughter ion pairs for sensitive, selective monitoring of these chemicals. Table A-2 lists the potential target chemicals, their CAS number, the ionization mode to be used, and the parent/daughter ion pair that will be used for quantification.
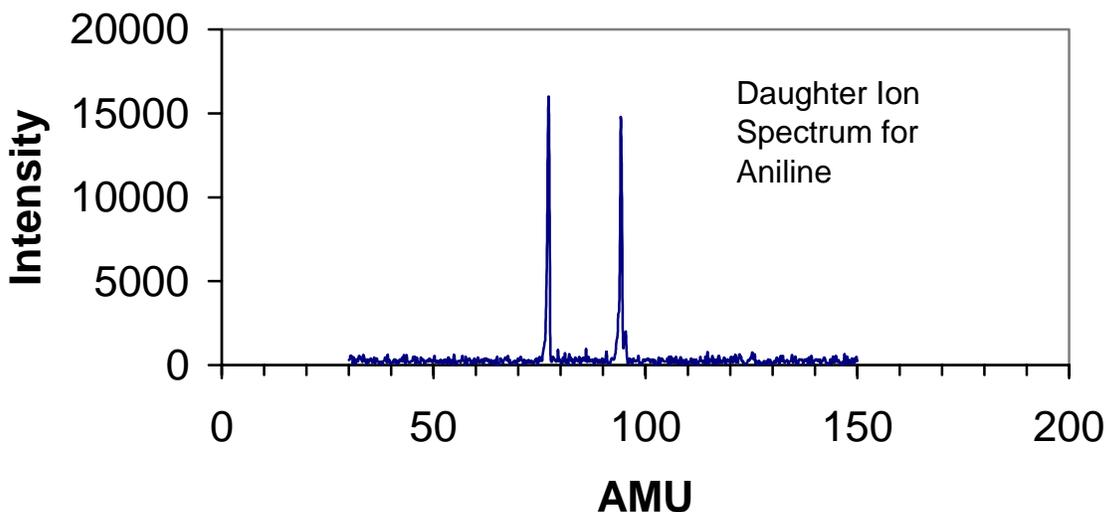
Figure A-1. Daughter Ion Spectrum for Aniline
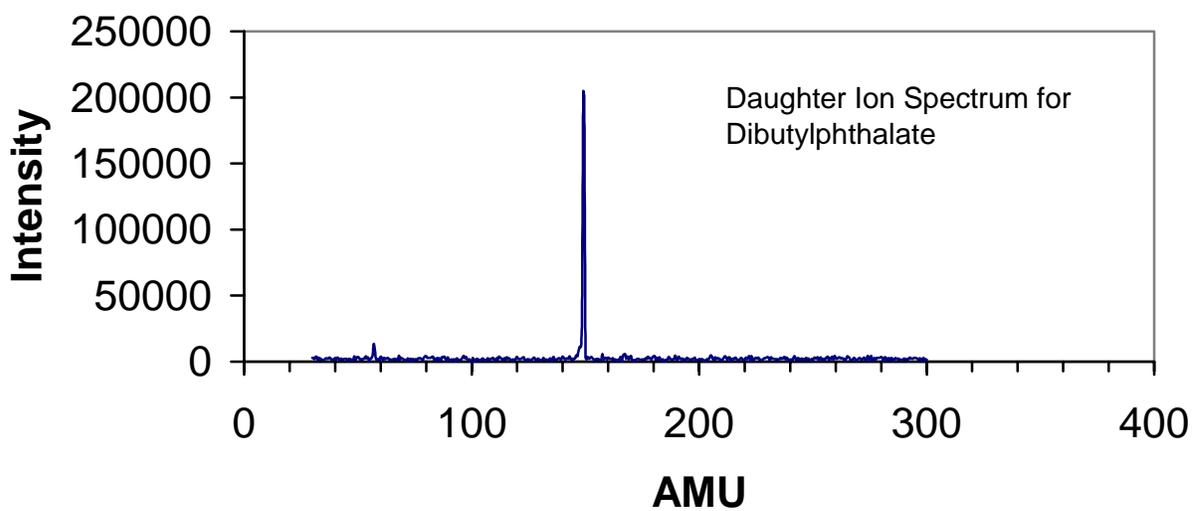
Figure A-2. Daughter Ion Spectrum for Dibutylphthalate
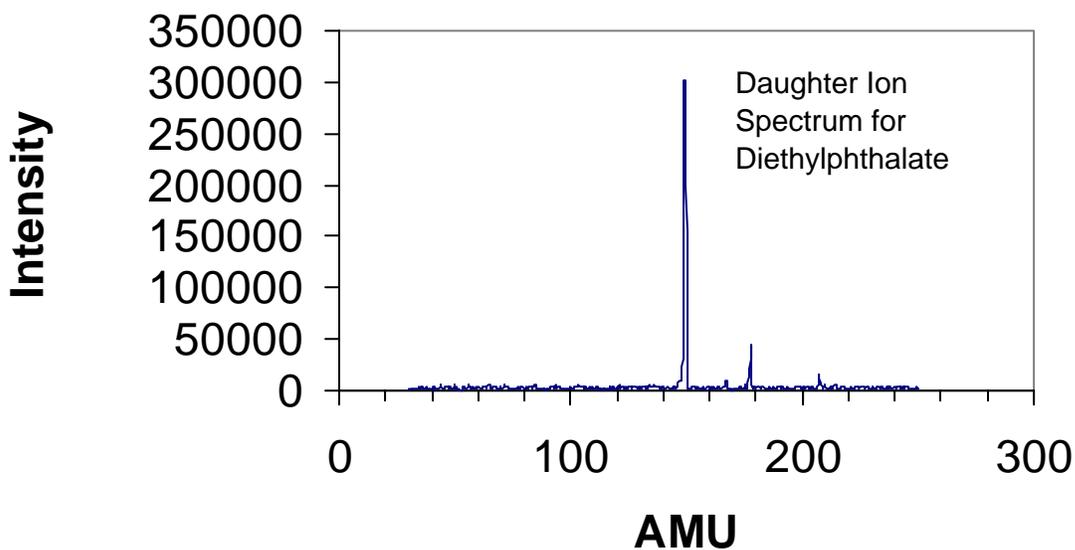
Figure A-3. Daughter Ion Spectrum for Diethylphthalate
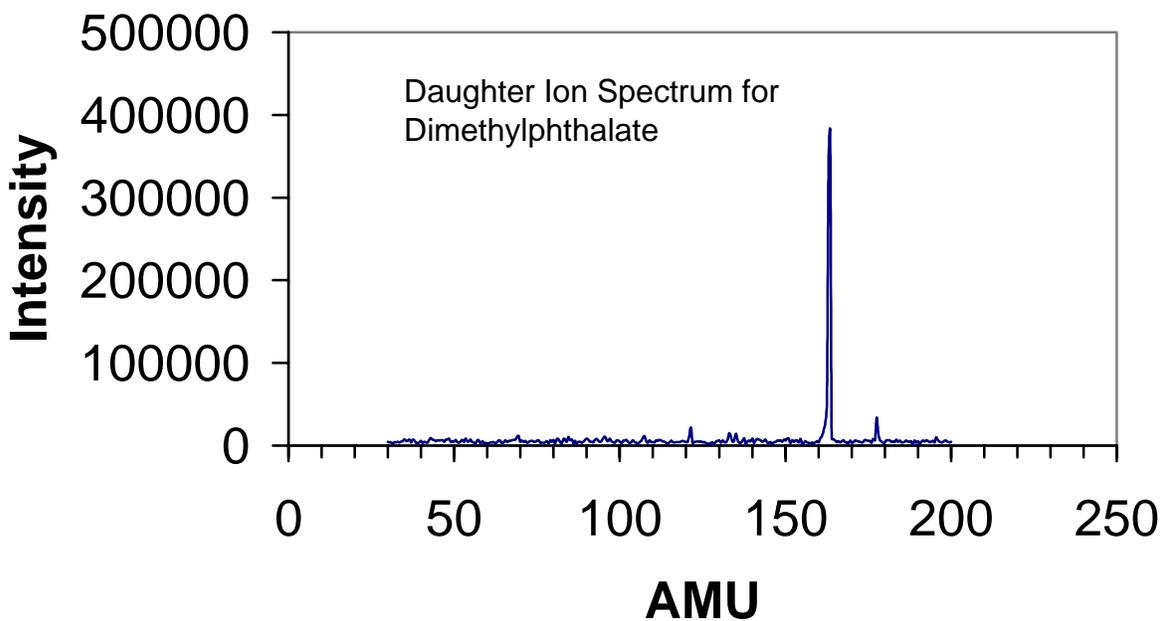
Figure A-4. Daughter Ion Spectrum for Dimethylphthalate
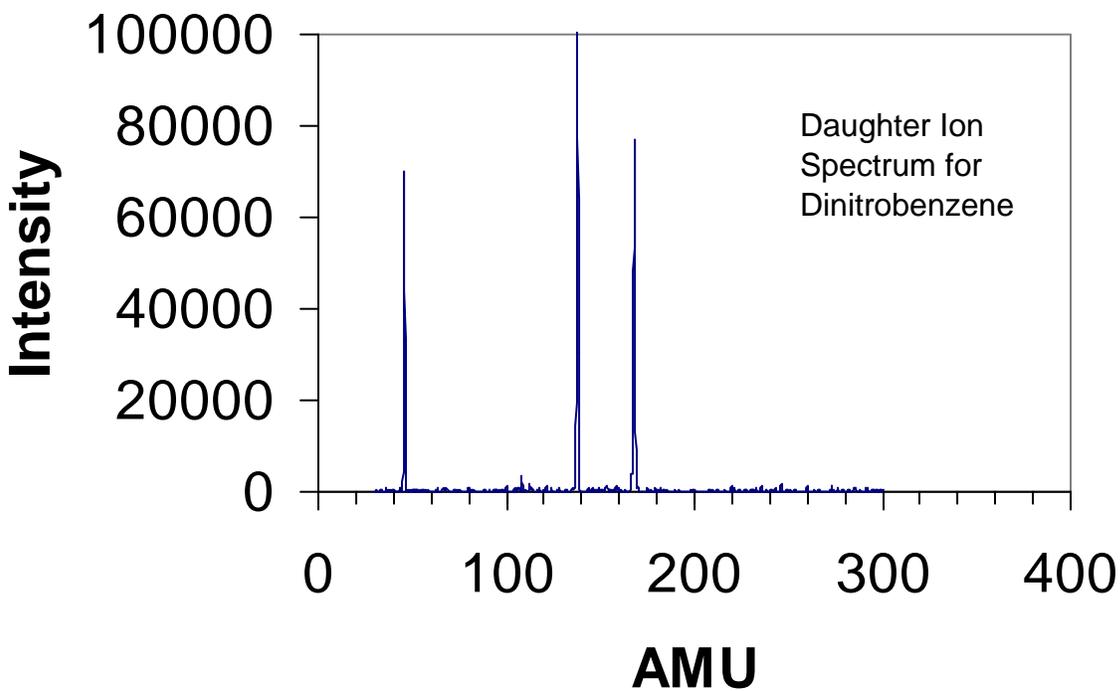
Figure A-5. Daughter Ion Spectrum for Dinitrobenzene
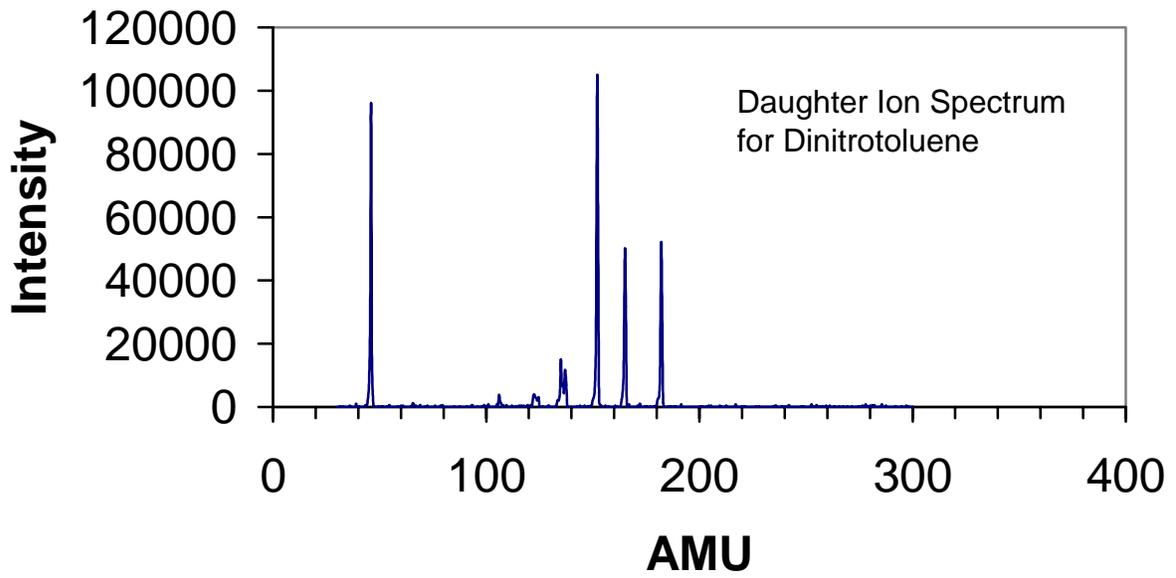
Figure A-6. Daughter Ion Spectrum for Dinitrotoluene
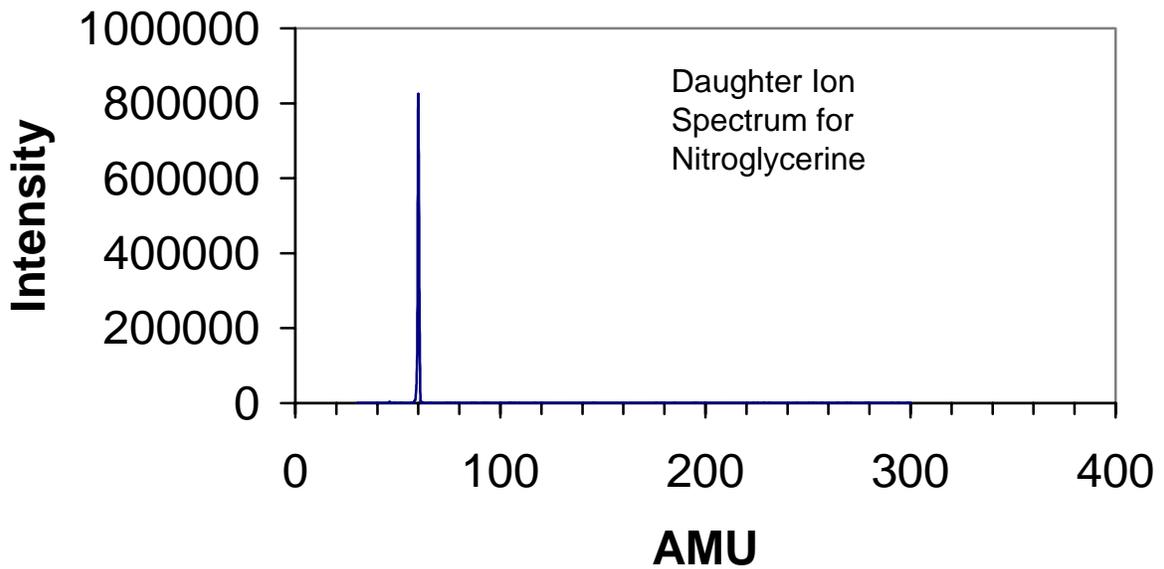
Figure A-7. Daughter Ion Spectrum for Nitroglycerine

Daughter Ion Spectrum for
Nitrosodiethylamine
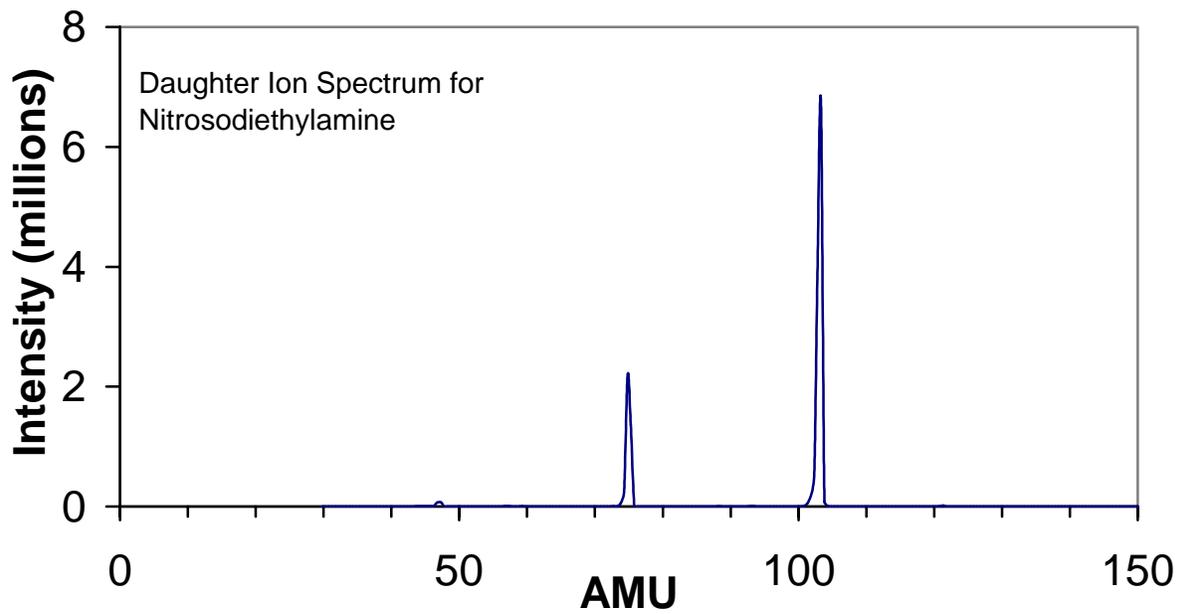
Figure A-8. Daughter Ion Spectrum for Nitrosodiethylamine

Daughter Ion
Spectrum for
Nitrosodimethylamine
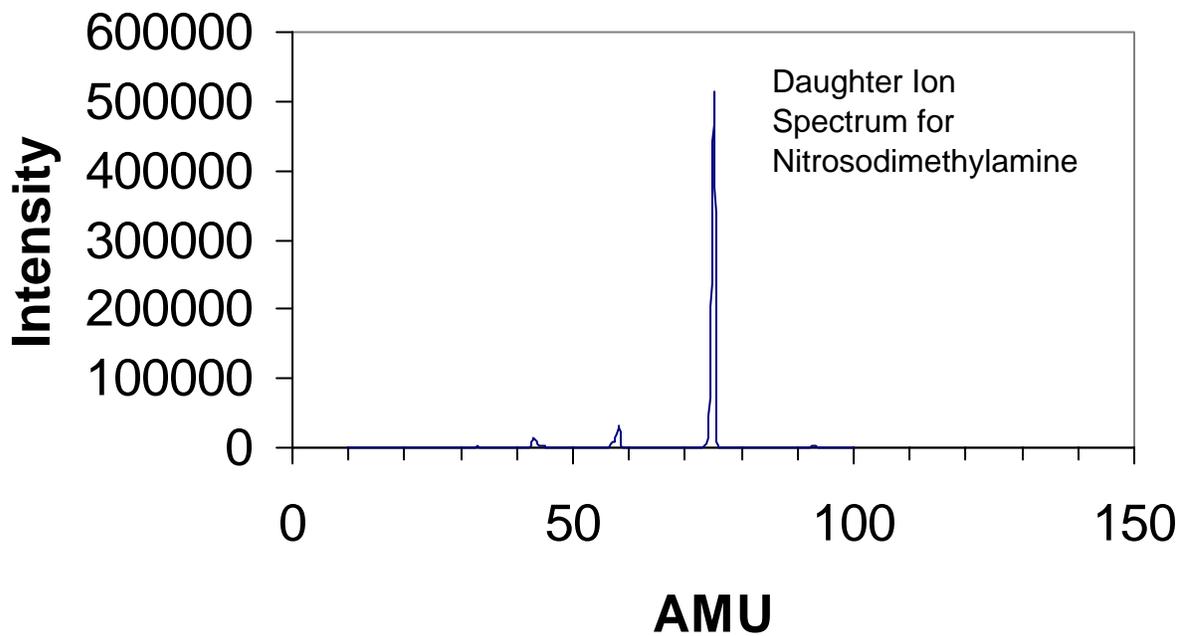
Figure A-9. Daughter Ion Spectrum for Nitrosodimethylamine
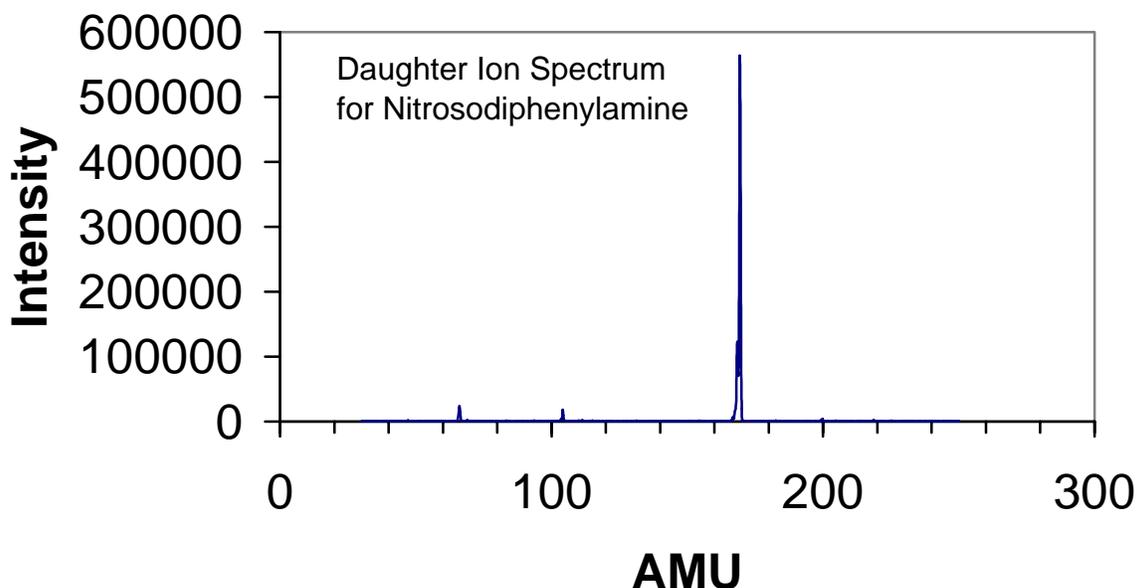
Figure A-10. Daughter Ion Spectrum for Nitrosodiphenylamine

Three of the chemicals in Table A-2 deserve special comment. Formic acid does not fragment under the CAD conditions used for other chemicals, so it was measured with less selectively than other species by using only the negative ion parent mass at 45 amu for quantification. Nitrosodimethylamine only fragments slightly under the CAD conditions, so MS/MS monitoring is possible, but greater sensitivity is achieved by monitoring at 75 amu in positive ion mode. Nevertheless. we measured this compound using the 75/58 parent/daughter ion combination, to assure maximum specificity for this species. Nitroglycerine also will be monitored using an unusual ion pair for quantification. As seen in Figure A-7 and noted by others, there is essentially no parent ion for nitroglycerine under APCI. The nitroglycerine reacts with $CO_3^=$ in the ion source to form an adduct at 287 amu. When this adduct undergoes CAD, the $CO_3^=$ ion at 60 amu is the dominant daughter ion. Thus we employed the 287/60 transition to quantify this chemical. The probability for interference from other chemicals under these conditions is very low.

Table A-2. Measurement Parameters for Target Chemicals

Chemical	CAS	Ionization Mode	Ion Pair
aniline	62-53-3	Pos	94/77
dibutylphthalate	84-74-2	Pos	279/149
diethylphthalate	84-66-2	Pos	223/149
dimethylphthalate	131-11-3	Pos	195/163
dinitrobenzene	528-29-0	Neg	168/46
dinitrotoluene	121-14-2	Neg	182/46
formic acid	64-18-6	Neg	45/45
nitroglycerine	55-63-0	Neg	287/60
N-nitrosodiethylamine	55-18-5	Pos	103/75
N-nitrosodimethylamine	62-75-9	Pos	75/58
N-nitrosodiphenylamine	86-30-6	Pos	199/169

Quantification

Converting the signal from the mass spectrometer in counts per second (cps) to concentration units requires calibration of the instrument. We have prepared known low concentration gas standards to calibrate the instrument by either of two procedures:

1.   Syringe injecting of dilute solutions (e.g. 1% in. methanol) of the target chemical into a 17 m^3 environmental chamber. Multiple injections can be used to generate multipoint calibrations.

2.   Placing a diffusion tube containing the real target chemical in a permeation oven at 30ºC and passing a known flow rate of air over the diffusion tube. This procedure has been useful for the nitioso- and nitro-containing chemicals, because the concentration of the target chemical in the output flow the permeation oven can be quantified using a total oxidized nitrogen monitor.

An example of a multipoint calibration for aniline is shown in Figure A-11, where the response of the 94/77 ion pair is shown as successive injections are made in the chamber. The curve resulting from this calibration is shown in Figure A-12. The response of the mass spectrometer is linear, and the slope provides the response factor for aniline.

API 365 Multipoint Aniline Calibration
June 27, 2002
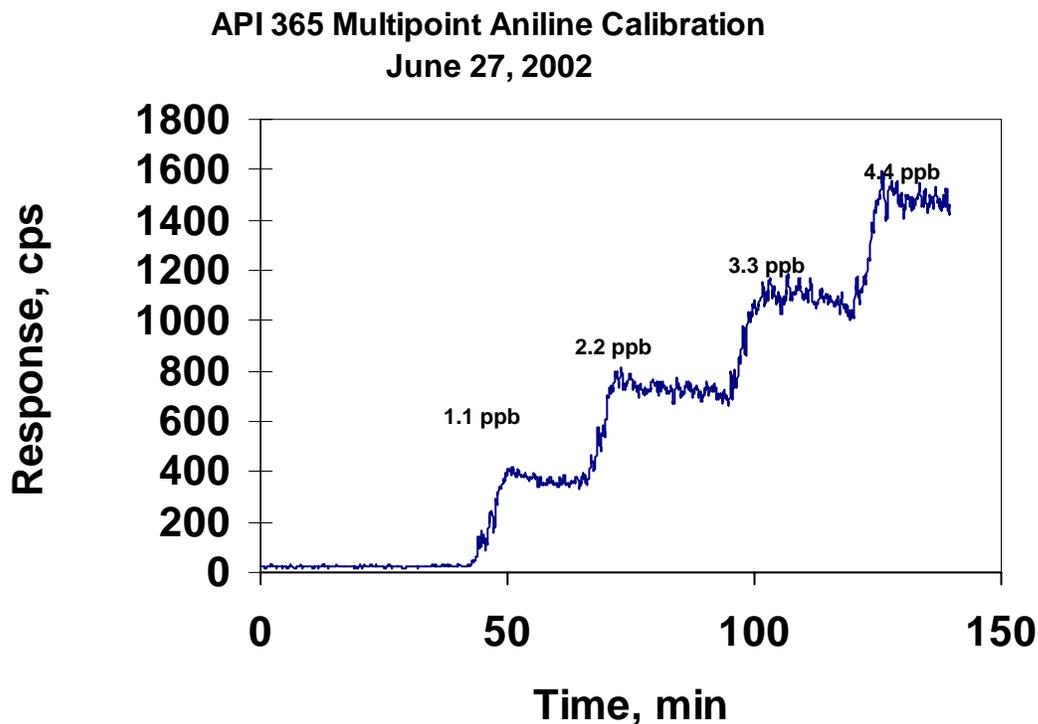
Figure A-11. Multipoint Calibration for Aniline in Positive Ion Mode Using 94/77 Ion Pair

$$y = 333.82x + 6.4$$
$$R^2 = 0.998$$
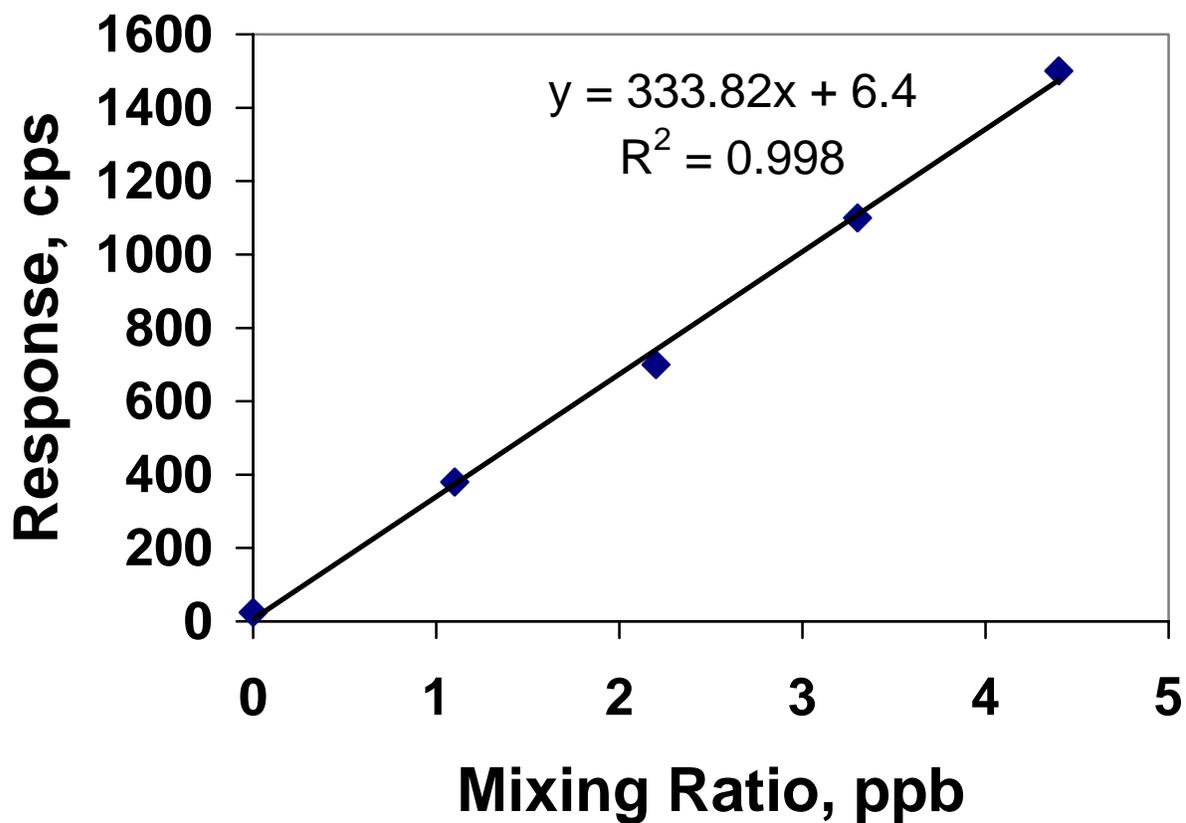
Figure A-12. Calibration Curve for Aniline Using 94/77 amu Ion Pair.

Another calibration example for nitrosodimethyl amine is provided in Figure A-13. In this case, the nitrosodimethyl amine is monitored in the positive ion mode using the 75/58 ion pair, as noted earlier. The calibration curve resulting from this calibration is given in Figure A-14.
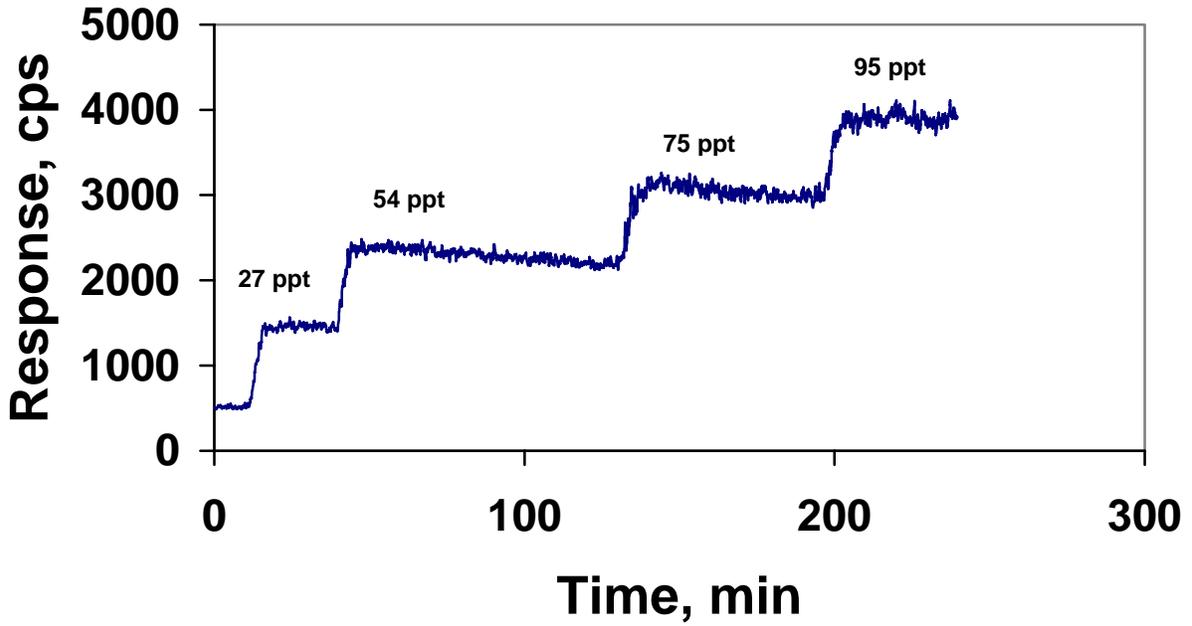
Figure A-13. Multipoint Calibration for Nitrosodimethylamine in
Positive Ion Mode Using 75/75 Ion Pair
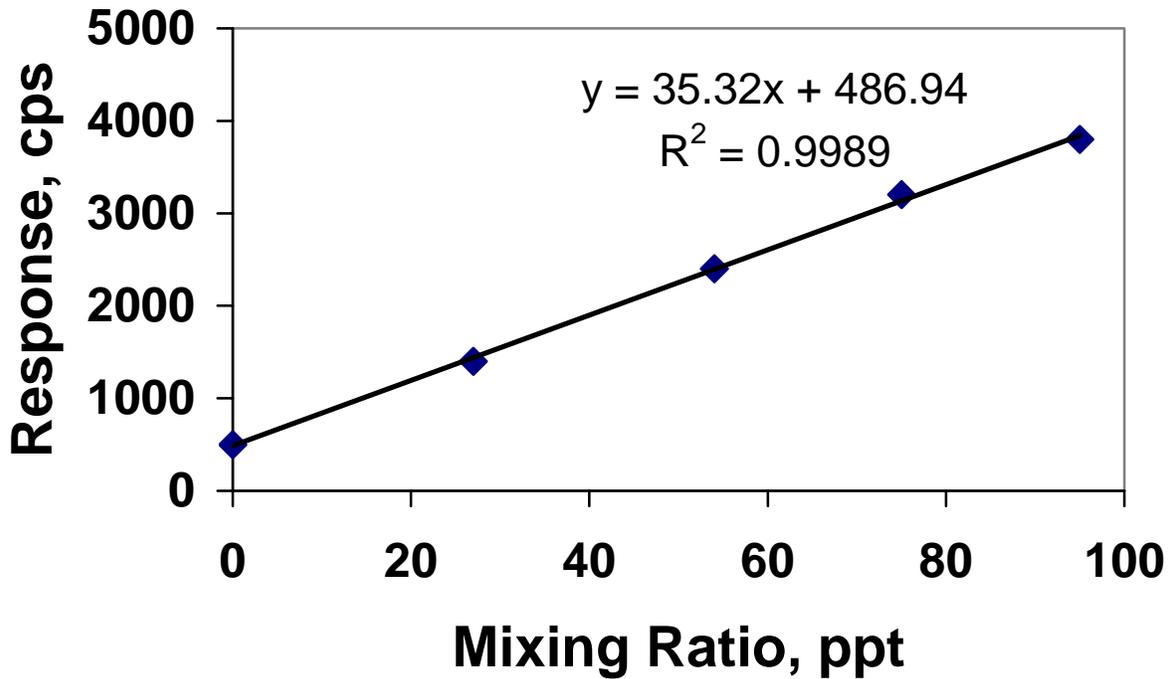
Figure A-14.   Multipoint Calibration for Nitrosodimethylamine
June 27, 2002 75/75 Ion Pair

An example of a single point calibration using the 103/75 ion pair of nitrosodiethyl amine in positive ion mode is shown in Figure A-15. For this calibration, the gas standard was generated using a diffusion tube via procedure (2) above.

Nitrosodiethylamine Calibration
June 24, 2002
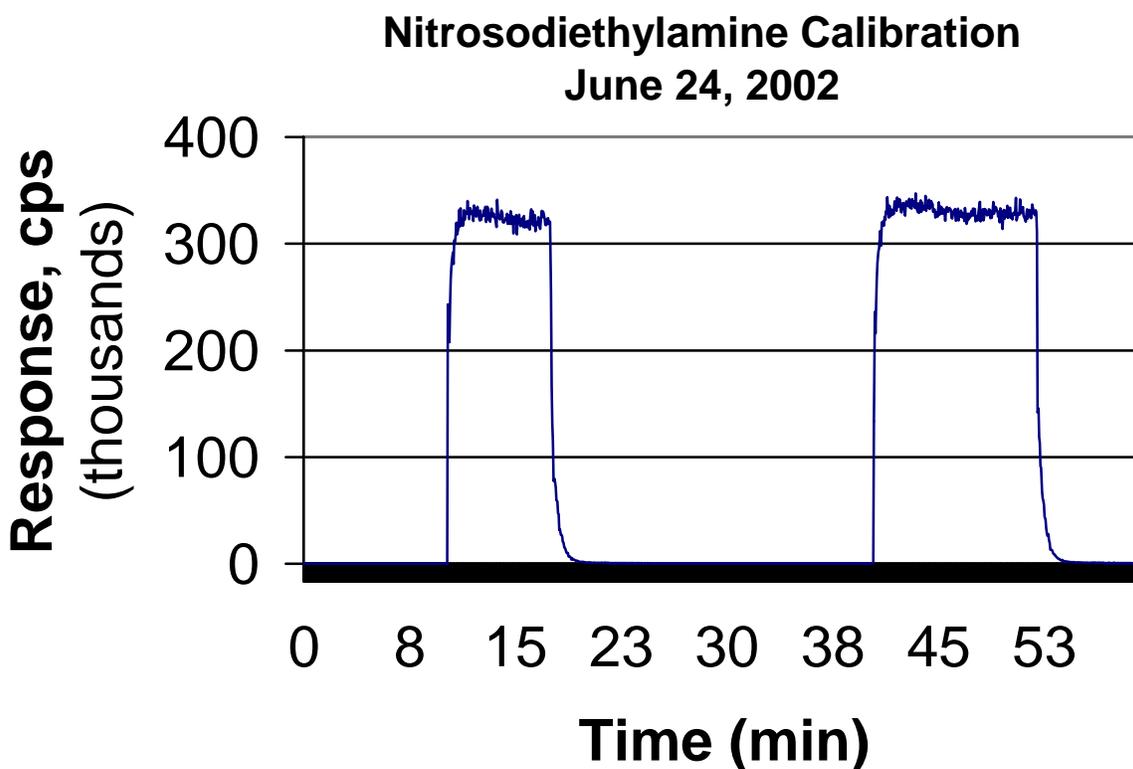
Figure A-15. Single Point Calibration for Nitrosodiethylamine Using 103/75 Ion Pair

Response factors, in units of cps/ppt, have been developed for the target chemicals shown in Table 2. These response factors were used, with estimates of signal noise for the appropriate ion pair, to estimate detection limits. Because the noise is affected by signal integration time, or "dwell time", we estimated detection limits for three dwell times of 1, 5, and 20 seconds. The noise signal is measured for the appropriate ion pair when the instrument is sampling clean air. The noise is determined as the square root of the signal for clean air at the ion pair of interest. We estimated the detection limit at a signal/noise of 3.0, so the signal at S/N = 3, divided by the response factor, yields the detection limits.

Table A-3 provides the detection limits for each of three dwell times for the target chemicals to be monitored by APCI-MS/MS. The table also lists the CAS number of each chemical, the ionization mode to be utilized, and the ion pair to be monitored.

Table A-3. Detection Limits at Various Integration Times for Target Chemicals

Chemical	CAS	Ionization Mode	Ion Pair	Detection Limit, pptv		
				1 sec	5 sec	20 sec
aniline	62-53-3	Pos	94/77	52	19	12
dibutylphthalate	84-74-2	Pos	279/149	40	25	
diethylphthalate	84-66-2	Pos	223/149	13	6	4
dimethylphthalate	131-11-3	Pos	195/163	8	3	1
dinitrobenzene	528-29-0	Neg	168/46	42	20	
dinitrotoluene	121-14-2	Neg	182/46	135	48	
formic acid	64-18-6	Neg	45/45	100		
nitroglycerine	55-63-0	Neg	287/60	9	3	1
N-nitrosodiethylamine	55-18-5	Pos	103/75	5	2	1
N-nitrosodimethylamine	62-75-9	Pos	75/58	6	3	2
N-nitrosodiphenylamine	86-30-6	Pos	199/169	2	0.8	0.4

These results are based on tests conducted in 2002. Changes in instrument configuration resulted in different detection limits for the Point of Impact study conducted in 2003.

Based on these results, the APCI MS/MS method has the ability to monitor all 11 of the target TRI chemicals with sufficient sensitivity and selectivity for the POI testing application. We attempted to monitor all 11 compounds during the POD tests, because there is sufficient time available to switch from compound to compound. However, during the outdoor POI tests, only 10-20 seconds were expected to be available for monitoring, so it was not considered practical to measure all 11 chemicals sensitively in such a short period. Therefore, it was necessary to "prune" the list of chemicals to be measured by this instrument to 5-8 species.

Another approach which we explored, involved collecting the emissions sample in a large Teflon bag, and then immediately measuring all 11 target chemicals over the following several minutes. This alternative approach allows the signal for each chemical to be integrated over a reasonable period (1-5 seconds) to achieve the necessary sensitivity, while minimizing sample storage time and potential loss of adsorptive species. It also offers the advantage that the sample in the bag would be integrated over the entire emissions cloud, which should improve the

reliability of the resulting emission factors. However laboratory tests showed that most of the target chemicals were lost to the surface of the Teflon sampling bag too rapidly to permit quantitation by this approach.

PTR-MS Considerations

The PTR-MS is a relatively new technology that seems well suited for measuring selected TRI chemicals in emissions clouds. The target compounds assigned to the PTR-MS were shown earlier in Table A-1. The PTR-MS is a single stage mass spectrometer, so chemicals are identified by their molecular weight. Two compounds of the same molecular weight may interfere with one another. However, this is not expected to be a serious problem with respect to most of the chemicals assigned to the PTR-MS for this study.

Calibration of the PTR-MS is, in theory, not required for neutral analytes. The concentration of the neutral [R] is calculated from the ratio of the RH+ count rate to the H_3O+ count rate, divided by the product of the reaction time (fixed) and the ion molecule rate coefficient: $[R] = [RH+]/[H_3O+]kt$. Exothermic proton transfer reactions occur at the collisional limit so the rate coeffiects are between 2×10^{-9} to 4×10^{-9} for most compounds (the range reflects the influence of the dipole moment strength; many rate coefficients have been measured but they can also be calculated from theory). We tested the theoretical response vs. the measured response for calibration standards for benzene, toluene, and isoprene. The agreement was reasonable, considering that the uncertainty in the rate coefficients is about $\pm 30\%$. Table A-4 shows the estimated detection limits for the target TRI chemicals for the PTR-MS. These limits were derived from literature or estimated rate constants, as noted above. The table also lists proton affinities where available, and the mass used for quantitation. Some interference among these chemicals is possible due to the single stage nature of the mass spectrometer. For example, both dibenzofuran and the dinitrobenzenes are measured at 169 amu, and benzidine and dinitrophenols are determined at 185 amu. As a consequence, we were unable to distinguish between these chemicals, and instrument response at these masses must be considered as the sum of all chemicals which yield a parent ion (M+1) at these masses.

Table A-4. Estimated Detection Limits for PTR-MS Target Chemicals

	Proton Affinity, KJ/mol	Mass Used for Quantitation	Estimated PTR-MS Detection Limit, ppb
Anthracene	877	179	0.05
naphthalene	803	129	0.1
Quinoline	953	130	0.05
nitrobenzene	800	124	0.3
dinitrobenzene	--	169	0.05
dinitrotoluene	--	183	0.05
Phenol	817	95	0.2
nitrophenol	--	140	0.05
2,4-dinitrophenol	--	185	0.05
Benzidine	--	185	0.05
Biphenyl	814	155	0.05
dibenzofuran	--	169	0.05
4-aminobiphenyl	--	170	0.05

APPENDIX B

**DEVELOPMENT AND TESTING OF AEROSOL
LIDAR FOR DETERMINING VOLUME OF
MUNITIONS EMISSIONS CLOUDS**

APPENDIX B

DEVELOPMENT AND TESTING OF AEROSOL
LIDAR FOR DETERMINING VOLUME OF
MUNITIONS EMISSIONS CLOUDS

The mapping of aerosol particles using lidar (Mie scattering) has a long and successful history.[1,2] Even in air that appears visually clear, the few but ever-present aerosol particles can be exploited as tracers to map atmospheric structure.[3] The mini-lidar system employed for this project exploits this elastic scattering channel. Specifically, the lidar measurements utilize the fact that the plume itself possesses a very different aerosol burden than that of the surrounding background atmosphere. This abrupt aerosol loading change results in a large transient increase in the strength of the elastically scattering laser light. This range-resolved signal can, in turn, allow cross-sectional mapping of the developing plume's diameter. Contained in Figure B-1 is a schematic of the deployment scenario for the aerosol lidar system.

Lidar is the laser analog of radar. Specifically, short pulses of laser light are scattered off a target and a receiver collects the backscattered signals. The distance to the target is calculated (typically by the system's computer) from the time required for the outgoing laser pulse to reach the target, scatter off the surface contaminants, and return to the receiver; similar to the range measurement process used by radar. Lidar platforms are typically composed of three main subsystems: (*i*) a laser system and beam transport optics, (*ii*) signal receiver telescope and signal detection unit, and (*iii*) equipment control and data acquisition/processing subsystem.

During the first year of this project, we reconfigured a mini-Raman lidar system (MRLS)[4] to meet our needs. This platform was chosen because it is specifically designed to work at
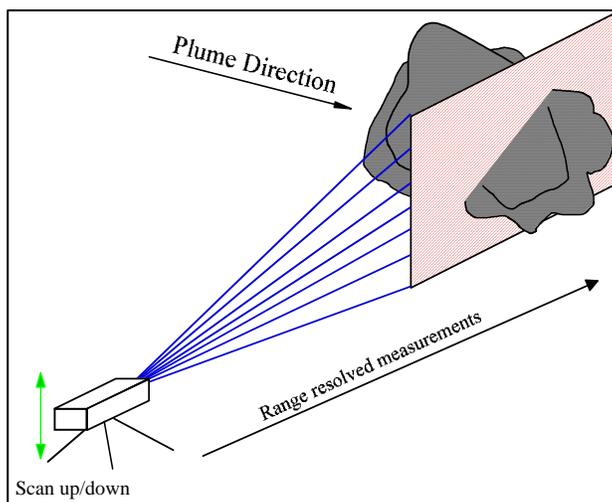
Figure B-1. Schematic of the Lidar Plume Dimensioning Deployment

distances far shorter than is typical for aerosol lidar (i.e., 100s of meters vs. 10s of kilometers). The leveraging of this specialized equipment eliminated issues such as signal loss due to shadowing of the secondary in the telescope at short standoff distances.[5,6] The reconfiguration of the lidar system was broken down into 3 categories: (i) optical components; (ii) software; and (iii) scanning hardware.

Figure B-2 shows the MRLS unit and Figure B-3 a schematic of the lidar optical network after reconfiguration of the MRLS platform to a Mie scattering platform. The laser source is a single frequency 266 nm Nd:YAG laser (New Wave, Lase II, 7 mJ/pulse at 20 Hz). The use of a UV solar blind laser ($\lambda < 300$ nm), rather than a visible or near-infrared wavelength, allows signal acquisition to be conducted in daylight without interference from ambient light. The backscattered elastic return signals are collected by a 6-inch, f/4 Newtonian telescope that is coaxial with the transmitted laser beam and outfitted with a ~ 300 MHz, solar-blind photomultiplier tube (PMT; Hamamastu, R1657). The elastic return signal is tracked as a function of distance (via time-of-flight) for plume-edge detection.

Figure B-2. The Mini-Raman Lidar System (MRLS)

The primary reconfiguration associated with the optical components involved the replacement of a spectrometer/ICCD (intensified charge coupled device) detector with a single-element PMT (photomultiplier tube) detector and associated coupling optics. The optical reconfiguration was accomplished using Zeemax® ray tracing software for choice and optimal placement of optical components.
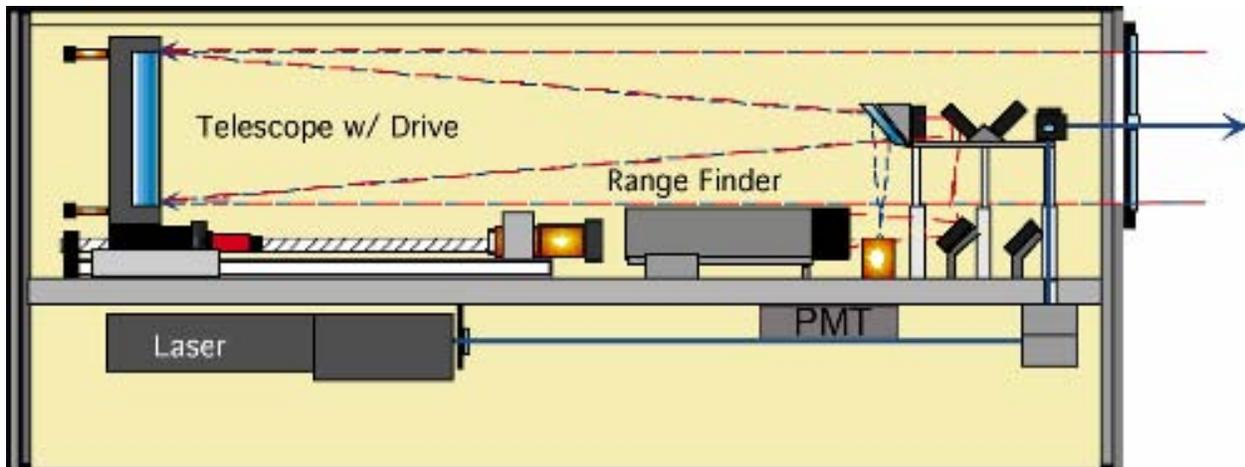
Figure B-3. Schematic of Optical Layout for the Reconfigured MRLS Unit. Reconfiguration
Involved the Replacement of a Spectrometer/ICCD Detection Subsystem with a
Single-Element PMT

Software development focused on two areas: instrumentation control and data analysis.
Development in the first area focused on interfacing of a laptop PC with a 500 MHz/500 Mega-
sample/sec LeCroy 9354AM digital oscilloscope (DSO), which served as the signal analog-to-
digital converter. This data acquisition configuration enables the collection of 500-point data
files every 50 ms for the duration of the experiment. The temporal resolution of an individual
dataset is 2-ns/pt. We have chosen as our interfacing software, Wavemetric's Igor Pro software
to write the GPIB-based instrument control hardware. The other software area is data analysis.
This issue required the programming of a unique set of "Macros" necessary for properly
reconstructing the data collected by the scanning lidar. Here the central issue is that the lidar
system will collect a series of 20 (or 40) individual data files in one scan direction (each file
representing a different interrogation angle and, hence, a varying height above the ground as a
function of distance). Therefore, once a complete set of 20 (or 40) files are collected, care *must*
be taken to insure that these data files are "spliced" together correctly when reconstructing the
plume image. To aid in completing this task, we used Mathwork's Matlab Image Processing
ToolBox® (see below).

The last reconfiguration issue that needed to be addressed was the scanning mechanism for the
lidar platform. It should be recalled that the objective of this scanning mechanism is to create a
plane through which the munition plume will pass thus allowing its dimension to be measured
via lidar. The scanning mechanism incorporated for the field tests utilizes a Pacific Scientific
5445 microstep motor and controller with embedded encoder. In order to invoke the desired
vertical motion with the lidar unit, a simple CAM-like arrangement was constructed. This
approach enabled the realization of either a sawtooth or sinusoidal scan profile (the former being
achieved by simply toggling the step motor direction after a set number of steps and the latter
through a free rotation of the stepper motor). Due to the recent acquisition of a video showing
examples of munition plumes, we expect that the sinusoidal scan profile will be employed due to
the expected size of the plume and the desired scan rate (1 or 2 second scan in one direction).

Despite the fact that the laser repetition rate and the scan rate are asynchronous, both systems can be made to operate at the sample scan rate to better than 1 part in 10^4.

Shown below in Figure B-4 for illustration is raw data collected with the modified mini-lidar in a laboratory test. This plot represents one 40-shot data set out of 10,000; that is, the image formed by scanning the lidar in one direction. The elastic returns from small water vapor plumes generated by a plant water atomizer, and hard body returns from a business card place on the floor at approximately 26-m standoff distance and the door at the end of the hallway (~ 110-m.) are easily discernable. The first thing to notice is that the height of the laser beam scales as the sine of the angle subtended by the lidar unit. Consequently, this means that the return signal from a given laser pulse will originate from a height that continuously varies as a function of standoff distance. Furthermore, each laser pulse, for a given data set (i.e., 20 or 40 laser shots for one scan direction) represents a new angle that, in turn, has it own unique set of heights as a function of standoff distance. Therefore, the data plotted in Figure B-4 show this angular dependence of the lidar signal height.

Finally, once the image has been correctly reconstructed, it is necessary to determine the location of the plume edges. While there are a variety of edge detection techniques, we have so far focused on a first-derivative zero-crossing technique provided by Matlab's Image Processor toolbox.
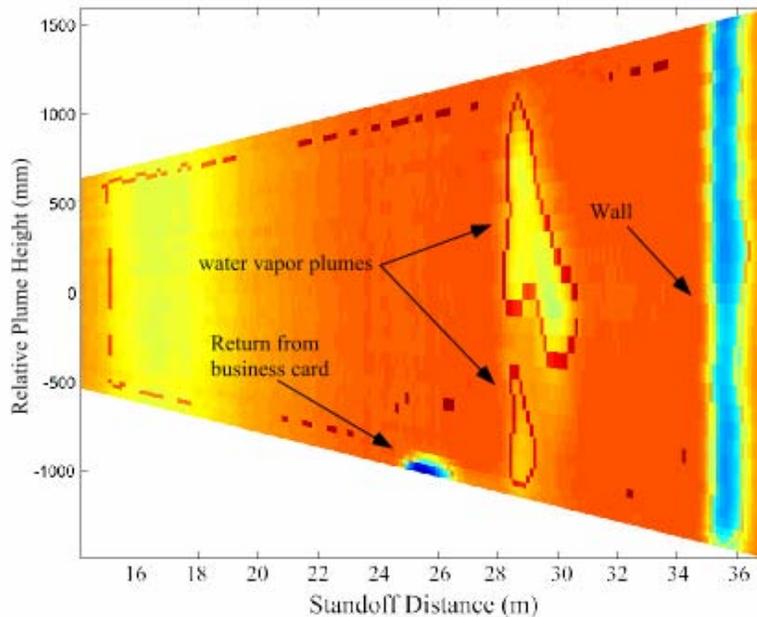
Figure B-4. Raw Data Collected Using the Modified MRLS as an Aerosol Lidar.
Water Vapor Plumes are Generated Using a Plant Water Atomizer.
Plume Edge Detection is Accomplished Using Matlab.
(See text for details)

Mie Lidar Sensitivity Estimate:

The high level of sensitivity achievable by elastic lidars is attributable to large Mie scattering cross-sections (10^{-10} - 10^{-8} cm^2/sr, in contrast the Rayleigh scattering term is typically on the order of $< 10^{-25}$ cm^2/sr – see *page 208 from reference 22*). Hence, the very large Mie scattering cross-sections translate to detection under very low particle loading conditions. As an example, we shall perform a calculation using the relevant form of the elastic-scattering lidar equation. where:

$$S = \left(\frac{E}{h\nu}\right)\varepsilon_D\varepsilon_T\varepsilon_R\left(\frac{A_o}{R^2}\right)\left[\eta_{aerosol}\left(\frac{d\sigma}{d\Omega}\right)_{aerosol}\right]\left(\frac{c\tau}{2}\right)\exp\left[-2\left(\sigma_{abs}\eta_{ozone}R\right)\right]$$

S   signal photons/pulse

E   pulse energy (7 mJ)

ν frequency of 266 nm laser (1.13×10^{15} s^{-1})

ε_D Quantum efficiency of detector (0.10)

ε_T Transmitter subsystem efficiency (0.80)

ε_R Receiver subsystem efficiency (0.10)

A_o Effective receiver area of telescope ($A_{primary}$-$A_{secondary}$) → π(58.1 cm^2 - 1.6 cm^2) = 178 cm^2

R   Stand off distance (10,000 cm)

$\eta_{aerosol}$ aerosol particle number density (100 particles/cc)

τ laser pulse width (7 ns)

σ_{abs} absorption cross-section of ozone (@ 266 nm → 9.44×10^{-18} cm^2/molecule)

η_{ozone} ozone loading (assume 35 ppb)

$(d\sigma/d\Omega)$ Mie scattering cross-section (assume 10^{-10} cm^2/molecule-sr)

This calculation reveals that for an aerosol loading of 100 particles/cc and a standoff distance of 100 meters; the number of signal photons collected is estimated to be on the order of 118 photons. Since these measurements will be conducted in the solar-blind (i.e., < 300 nm), the signal-to-noise ratio (SNR) will go as the square root of the signal photons; therefore, the above estimate translates to a SNR of ~ 10. Therefore, as this calculation reveals, the elastic lidar should provide plume edge discrimination sensitivity down to approximately 100 particles/cc above the ambient background levels. Preliminary experiments using a plant water atomizer qualitatively confirmed the reconfigured lidar's detection sensitivity at 100 and 150 meters. Since we are conducting the measurements in the solar blind, signal attenuation due to tropospheric ozone was accounted for in the sensitivity calculation.[7] For a standoff distance of 100 meters, attenuation due to ozone will be under 20% for ozone loading of 35 ppb.

Appendix B Referemces

1. Measures, R. M., Laser Remote Sensing: Fundamentals and Applications, Krieger Publishing Co., Malabar, FL, 1992, or Measures, R. M., Laser Remote Chemical Analysis, in Chemical Analysis Series, **94**, R. M. Measures, Ed., John Wiley and Sons: New York, 1988.

2. Grant, W. B., Browell, E. V., Menzies, R. T., Sassen, K., and She, C-Y., SPIE Milestone Series, Laser Applications in Remote Sensing, **141**, 1997.

3. Reagan, J. A., McCormick, M. P., and Spinhirne, MJ. D., Proceedings IEEE, **77** (3), 433, 1989.

4. Ray, M. D., Sedlacek, A. J., and Wu, M., Rev. of Sci. Instrum,, **71** (9), 3485, 2000.

5. Harms, J., Lahmann, W., and Weirkamp, C., Appl. Optics, **17**, 1131, 1978.

6. Harms, J., Appl. Optics, **18**, 1559, 1979.

7. Patterson, E. M. and Gillespie, J. B., Appl. Optics, **28**, 425, 1989.

APPENDIX C

INFORMATION ON MUNITIONS TESTED IN
POINT OF IMPACT STUDY

Appendix C

Information on Munitions Tested in
Point of Impact Study

LARGE CALIBER

1.   **Munitions Type:** 155 mm Howitzer (high explosive)
        Identification: PROJ 155MM HE M107, DODIC Number D544
        Average Usage Rate: 423,402 rounds per year
        Description of Use:
          ARMAMENT
          Towed and self-propelled howitzer.
          DEVELOPMENT
            Projectile, 155 mm, HE, M107 is probably the most widely used of all western artillery
          projectiles and is still one of the NATO "standard" projectiles by which all others are measured.
          Many nations continue to fire the 155 mm HE M107 as a training projectile rather than as
          an operational round as its ready availability due to production in volume often makes it far less
          costly to fire than some specialized training projectiles.
          DESCRIPTION
            The Projectile, 155 mm HE, M107 is a separately loaded munition, it has a hollow forged
          AISI 1045 steel shell of conventional design with a streamline ogive (6/12 cm) and a boat tall base
          to provide aerodynamic efficiency. A steel base cover is welded to the projectile base. A swaged
          gliding metal drive bend encircles the shell casing near the base and is normally protected by
          a grommet during storage, transport and handling. The fuze well is normally occupied by a
          threaded lifting plug during transit and handling; the plug can be replaced before firing by
          a wide range of standard and commercial fuzes.
            The 155 mm HEM107 filling may be either 6.62 kg of cast TNT or 6.985 kg of Composition
          B; 155 mm HE M107 projectiles manufactured in the USA since 1977 have been filled only with TNT.
                A TNT-filled 155 mm HE M107 will produce approximately 1,950 fragments on detonation.
          SPECIFICATION
          Weights:
            with lifting plug – 40.82-42.91 kg
            as fired – 43.88 kg
            filler – Comp B – 6.985 kg
            filler – cast TNT – 6.62 kg
            supplementary charge, TNT – 136 g
          Lengths:
            with lifting plug – 680.9 mm
            shell body – 605.3 mm
          Max body diameter: 154.89 mm
          Max diameter over drive band: 157.98 mm
          Operating temperature range: -32 to +52°C
          AUTHORIZED FUZES
          The 155 mm HE M107 has a standard 2-in. 12UN-1B thread in the fuze well and can thus
          accommodate a wide range of standard and commercial fuzes. Standard fuzes that can be
          used with the HE M107 include the following:
            PD M51A5, M728 series, M557, M572, M730
            MTSQ M564, M577, M582
            Prox M732, M728 (if fitted, the supplementary charge must be removed when the
            M728 is used).

2. **Munitions Type:** 155 mm Howitzer (illumination)
   Identification: PROJ 155MM ILLUM M485 SERIES, DODIC Number D505
   Average Usage Rate: 31,085 rounds per year
   Description of Use:

   ARMAMENT
   Towed and self-propelled howitzers.

   DEVELOPMENT
   The 155 m illumination M485A2 is now the standard 155 mm illumination projectile used by the US and most NATO armed forces.

   DESCRIPTION
   The M485 series of 155 mm illumination projectiles are separate loading munitions using a hollow forged steel body with a steel base plug press fitted to the rear of the projectile and held in place by shear pins and twist pins. The exterior is fitted with a single gliding metal drive band and a plastic obturating band. The shell interior contains a primary expulsion charge, a canister assembly, and a drogue parachute. The canister assembly contains a secondary expulsion charge, a delay holder, an illumination composition and the main parachute.

   In operating the nose-mounted time fuze functions at the preselected time and ignites the primary explusion charge. The resultant pressure forces the drogue parachute and canister against the baseplate, rupturing the base pins and expelling the canister assembly and its parachute. Once out of the shell body the drogue parachute deploys to decelerate the canister assembly while fins deploy to stop rotation. The primary explusion charge also ignites the delay element in the nose of the canister assembly. After an 8 second delay and once rotation has ceased, the secondary expulsion charge ignites the illuminating composition and expels the main parachute and the flare body from the canister assembly. The main parachute deploys and, with the flare candle suspended from shrouds, the illuminating body descends at a rate of 4.5 to 5 m/s. The flare will burn for up to 2 minutes, producing approximately 1 Mcd.

3. **Munitions Type:** 155 mm Howitzer (smoke)
   Identification: PROJ 155MM SMK WP M825, DODIC Number D528
   Average Usage Rate: 14,750 rounds per year
   Description of Use:

   ARMAMENT
   Towed and self-propelled howitzer.

   DEVELOPMENT
   The 155 mm Smoke WP M825A1 was developed to be a replacement for the venerable M110 family of WP/Smoke projectiles and is in production by Morton Thiokol Inc. (metal parts) for the U.S. Army and Marine Corps.

   DESCRIPTION
   The 155 mm Smoke WP M825A1 is a separate loading, base ejection, smoke-producing projectile which uses a body virtually identical to the 155 mm DPICM M483A1. The projectile uses a 155 mm DPICM M483A1 aluminum ogive section and explusion charge, a forged steel modified M483A1 body and a threaded steel ring and aluminum body base. Inside the body is a hermetically sealed canister containing 116 White Phosphorus (WP) saturated felt wedges each 190 mm thick and separated into four quadrants of 29 each. A burster charge containing 45 g of Composition B runs the entire length of the canister's center cavity.
   In operation, the nose-mounted time fuze is set to function at a selected point during the projectile's trajectory. When the fuze functions, it ignites a 51 g expulsion charge of M10 propellant which creates sufficient internal pressure to push off the body base and eject the canister. The expulsion charge also ignites a 100 ms pyrotechnic delay, enabling the canister to be

fully ejected from the carrier body before the burster charge (21.2 g of Composition A5) ignites to break open the canister and release the WP saturated felt wedges (total weight of WP in the wedges is 5.78 kg). A launch activated safe and arm module from a PD M739 fuze separates the forward end of the main burster charge from the heat sensitive pyrotechnic delay element.

Within 45 seconds of meeting the air the separated felt wedges start to burn and produces smoke. They continue to produce a dense and uniform smoke screen between 5 to 10 minutes.

MEDIUM CALIBER

4.   **Munitions Type:** 4.2 in Mortar (high explosive)
        Identification: CTG 4.2 IN HE M329A2 W/O FUZE, DODIC Number C697
        Average Usage Rate: 124,252 rounds per year
        Description of Use:
        ARMAMENT
            US M2 and M30 107 mm mortars.
        DESCRIPTION
            This represents the only major design change in the history of the 107 mm mortar. This projectile is boat tailed and even more like an artillery shell than the previous models, an appearance which is enhanced by the presence of a driving band.
            The rotating disk/pressure plate system described previously has been abandoned in this design. Instead, the projectile is provided with a pre-engraved driving band and, behind it, a neoprene obturating ring. A tubular cartridge container, similar to that used with earlier designs but shorter, is screwed into the base of the projectile.
            To load, the bomb is positioned so that the pre-engraved driving band engages in the rifling grooves of the mortar, and is then released to drop down the barrel. When the propelling charge fires, the gas pressure expands the neoprene obturating ring and provides the gas seal. The engagement of the driving band in the rifling generates the desired spin as the projectile moves up the barrel.

SMALL CALIBER

5.   **Munitions Type:** 40 mm Mortar (high explosive)
        Identification: CTG 40MM HE M430
        Average Usage Rate: 537,324 rounds per year
        Description of Use:
        ARMAMENT
            Automatic grenade launchers of he Mk 19 type.
        DESCRIPTION
            Whist adhering to the same general appearance as the low-velocity cartridge, the high-velocity is slightly larger, using a heavier and longer projectile, and has a different propulsion system, sometimes called the "single chamber system" though this is a misnomer.
            The cartridge is stronger and has a much thicker base, into which the forward part of the spherical high-pressure chamber is burned; the rear of the chamber is provided by the screw-in primer plug. Vents lead from the enlarged chamber to the interior of the cartridge case, and the empty space beneath the projectile is much less than that found in the low-velocity rounds.
            The projectile has a long, cylindrical body filled with high explosive and capped by a thin metal ballistic cap or ogive, beneath which is the impact fuze.
            On firing, the propellant burns at high pressure in the first chamber and the gas leaks out into the case, as with the low-velocity round. The difference lies in the larger quantity or propellant, the greater rate of high- to low-pressure space, and different venting.

6. **Munitions Type:** 40 mm Grenade cartridge (illumination)
   Identification: CTG 40MM ILLUM WHT STAR PARA M583, DODIC Number B535
   Average Usage Rate: 95,148 per year

7. **Munitions Type:** 81 mm Mortar (smoke)
   Identification: CTG 81MM SMK WP M75 W/PD FUZE, DODIC Number C276
   Average Usage Rate: 17,520 rounds per year
   Composition:

8. **Munitions Type:** Hand Held Flare
   Identification: FLARE SURF TRIP N149, DODIC C495
   Average Usage Rate: 57,789 per year
   Description of Use:
      Used for illuminating and signaling.

9. **Munitions Type:** Hand Grenade (smoke)
   Identification: GRENADE, HAND SMK YLW M18, DODIC Number G945
   Average Usage Rate: 4,201,610 per year
   Description of Use:
      The M18 colored smoke hand grenade is used for ground-to-air or ground-to-ground signaling. Grenades may be filled with any one of four smoke colors: red, green, yellow or violet. Each grenade will emit smoke for 50 to 90 seconds.
      Grenade body: The body, of thin sheet metal, is filled with red, green, yellow or violet smoke composition. The filler is topped with a starter mixture.
   Fuze, hand grenade, M201A1: fuze M201A1 is a pyrotechnic delay-igniting fuze. The body contains a primer, first-fire mixture, protechnic delay column and ignition mixture. Assembled to the body are a striker, striker spring, safety lever and safety pin with pull-ring. The split end of the safety pin has an angular spread.

APPENDIX D

EMISSION FACTORS FROM POINT OF DISCHARGE TESTS

APPENDIX D

EMISSION FACTORS FROM POINT OF DISCHARGE TESTS

TABLE D-1. .50 Caliber Machine Gun M2 - Armor Piercing (AP)

Chemical	Emission Factor		% Difference	Emission Factor
	grams per round			avg grams
	Test 1	Test 2		per round
Formaldehyde	3.19E-04	3.72E-04	14	3.45E-04
hydrogen cyanide,	4.24E-04	3.13E-04	36	3.69E-04
acetonitrile,	1.78E-04	1.60E-04	11	1.69E-04
acetaldehyde,	1.34E-04	1.24E-04	8	1.29E-04
acrylonitrile,	3.88E-05	3.56E-05	9	3.72E-05
Acrolein,	4.60E-05	5.77E-05	20	5.18E-05
benzene,	3.54E-04	3.36E-04	5	3.45E-04
Toluene,	7.80E-05	6.68E-05	17	7.24E-05
phenol,	3.10E-05	2.27E-05	36	2.69E-05
nitrobenzene,	1.65E-06	2.20E-06	25	1.93E-06
naphthalene,	3.60E-05	4.36E-05	17	3.98E-05
quinoline,	6.33E-06	5.78E-06	10	6.06E-06
2-nitrophenol+4-nitrophenol,	6.20E-07	6.23E-07	0	6.21E-07
dibenzofuran+nitrotoluenes,	7.50E-07	7.53E-07	0	7.51E-07
diphenylamine+4-aminobiphenyl,	<MDL	<MDL	NA	<MDL
anthracene,	<MDL	<MDL	NA	<MDL
2,4-dinitrotoluene,	<BL	8.15E-07	NA	8.15E-07
2,4-dinitrophenol,	<MDL	<MDL	NA	<MDL
biphenyl,	<MDL	<MDL	NA	<MDL
Aniline	3.73E-06	5.10E-06	27	4.41E-06
dibutylphthalate	<BL	2.62E-06	NA	2.62E-06
diethylphthalate	7.82E-06	3.88E-06	102	5.85E-06
dimethylphthalate	<BL	<BL	NA	<BL
dinitrobenzene	<MDL	<MDL	NA	<MDL
dinitrotoluene	9.01E-06	6.44E-06	40	7.73E-06
formic acid	<BL	<BL	NA	<BL
nitroglycerine	<BL	<BL	NA	<BL
N-nitrosodiethylamine	9.10E-07	8.23E-07	11	8.66E-07
N-nitrosodimethylamine	8.19E-06	9.75E-06	16	8.97E-06
N-nitrosodiphenylamine	5.30E-07	5.68E-07	7	5.49E-07
diphenylamine	3.55E-08	7.12E-08	50	5.34E-08
chloromethane	<BL	<BL	NA	<BL
vinyl chloride	<MDL	<MDL	NA	<MDL
1,3-butadiene	3.17E-05	3.90E-05	19	3.54E-05
bromomethane	<MDL	<MDL	NA	<MDL
allyl chloride	1.02E-05	4.90E-06	109	7.57E-06
chloroform	<MDL	<MDL	NA	<MDL
1,2-dichloroethane	3.26E-06	<MDL	NA	3.26E-06
benzene	3.76E-04	3.94E-04	5	3.85E-04

carbon tetrachloride	4.47E-08	9.59E-09	367	2.72E-08
1,2-dichloropropane	<MDL	<MDL	NA	<MDL
trichloroethene	<MDL	<MDL	NA	<MDL
Toluene	1.09E-04	9.81E-05	11	1.03E-04
1,2-dibromoethane	<MDL	<MDL	NA	<MDL
tetrachloroethene	<MDL	<MDL	NA	<MDL
chlorobenzene	<MDL	<MDL	NA	<MDL
ethylbenzene	7.62E-06	5.70E-06	34	6.66E-06
m&p-xylene	2.81E-05	1.80E-05	56	2.30E-05
Styrene	1.45E-05	1.14E-05	27	1.30E-05
1,1,2,2-tetrachloroethane	<MDL	<MDL	NA	<MDL
o-xylene	8.84E-06	5.14E-06	72	6.99E-06
benzyl chloride	2.61E-05	1.39E-05	89	2.00E-05
1,3-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,4-dichlorobenzene	3.85E-06	<MDL	NA	3.85E-06
1,2-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,2,4-trichlorobenzene	4.42E-06	<MDL	NA	4.42E-06
acetaldehyde	5.17E-06	<BL	NA	2.56E-06
carbonyl sulfide	6.21E-04	5.86E-04	6	6.03E-04
acetonitrile	1.97E-04	3.03E-04	35	2.50E-04
Acrolein (2-propenal)	1.81E-04	1.64E-04	10	1.72E-04
acrylonitrile	4.47E-05	4.77E-05	6	4.62E-05
carbon disulfide	<BL	3.51E-07	NA	3.51E-07
methyl tert-butyl ether	1.34E-05	1.16E-05	16	1.25E-05
vinyl acetate	9.69E-07	<MDL	NA	9.69E-07
chloroprene	<MDL	<MDL	NA	<MDL
bromoform	<MDL	<MDL	NA	<MDL
hexachloroethane	3.17E-06	4.75E-06	33	3.96E-06
naphthalene	4.11E-05	4.70E-05	14	4.41E-05
beryllium	<MDL	<MDL	NA	<MDL
Aluminum	2.77E-02	3.26E-02	15	3.01E-02
Chromium	3.32E-05	2.19E-05	51	2.76E-05
manganese	1.52E-05	6.44E-06	136	1.08E-05
Cobolt	5.87E-05	3.39E-05	73	4.63E-05
Nickel	1.10E-05	8.05E-06	36	9.52E-06
Copper	1.37E-01	1.34E-01	2	1.35E-01
Zinc	2.24E-02	1.96E-02	14	2.10E-02
Arsenic	5.23E-06	6.11E-06	14	5.67E-06
Selenium	6.24E-06	<BL	NA	6.24E-06
Silver	6.50E-06	6.93E-06	6	6.72E-06
Cadmium	3.16E-06	2.92E-06	8	3.04E-06
Antimony	4.64E-03	4.73E-03	2	4.68E-03
Barium	<BL	<BL	NA	<BL
Thallium	<MDL	<MDL	NA	<MDL
Lead	1.01E-02	8.79E-03	15	9.43E-03

NA = not applicable

<BL = less than background level

<MDL = less than method detection level

TABLE D-2. 120 mm Mortar M934 - High Explosive (HE) Zone 1 Cartridge

Chemical	Emission Factor grams per round		% Difference	Emission Factor avg grams per round
	Test 1	Test 2		
Formaldehyde	1.40E-01	4.95E-02	182	9.47E-02
hydrogen cyanide,	6.81E-03	2.56E-03	166	4.69E-03
acetonitrile,	2.15E-02	9.55E-03	125	1.55E-02
acetaldehyde,	5.69E-02	2.24E-02	154	3.97E-02
acrylonitrile,	1.28E-02	6.28E-03	103	9.52E-03
acrolein,	1.58E-02	5.46E-03	189	1.06E-02
Benzene,	3.52E-02	1.36E-02	159	2.44E-02
toluene,	5.22E-03	6.27E-04	733	2.93E-03
phenol,	2.83E-03	6.61E-04	328	1.74E-03
nitrobenzene,	6.86E-04	2.49E-04	176	4.68E-04
naphthalene,	4.18E-03	1.77E-04	2257	2.18E-03
Quinoline,	6.73E-04	9.62E-05	600	3.85E-04
2-nitrophenol+4-nitrophenol,	1.69E-04	8.88E-05	90	1.29E-04
dibenzofuran+nitrotoluenes,	2.04E-04	1.07E-04	90	1.56E-04
diphenylamine+4-aminobiphenyl,	4.10E-05	1.80E-05	128	2.95E-05
anthracene,	<MDL	<MDL	NA	<MDL
2,4-dinitrotoluene,	2.21E-05	<MDL	NA	2.21E-05
2,4-dinitrophenol,	2.23E-05	<MDL	NA	2.23E-05
biphenyl,	<MDL	<MDL	NA	<MDL
Aniline	1.13E-02	4.81E-03	135	8.07E-03
Dibutylphthalate	5.40E-04	5.06E-04	7	5.23E-04
Diethylphthalate	4.12E-04	3.59E-04	15	3.86E-04
Dimethylphthalate	4.00E-06	3.14E-05	87	1.77E-05
Dinitrobenzene	7.99E-05	2.49E-05	221	5.24E-05
Dinitrotoluene	1.50E-03	5.69E-04	163	1.03E-03
formic acid	2.49E-04	1.76E-04	41	2.13E-04
Nitroglycerine	6.47E-05	1.38E-04	53	1.01E-04
N-nitrosodiethylamine	7.09E-05	3.87E-05	83	5.48E-05
N-nitrosodimethylamine	2.15E-05	3.22E-05	33	2.68E-05
N-nitrosodiphenylamine	2.62E-04	2.61E-04	0	2.61E-04
Diphenylamine	<BL	3.39E-07	NA	3.39E-07
Chloromethane	<BL	<BL	NA	<BL
vinyl chloride	<MDL	6.38E-05	NA	6.38E-05
1,3-butadiene	1.29E-03	<MDL	NA	1.29E-03
Bromomethane	<MDL	<MDL	NA	<MDL
allyl chloride	<BL	1.29E-04	NA	1.29E-04
Chloroform	<MDL	<MDL	NA	<MDL
1,2-dichloroethane	<BL	<BL	NA	<BL
Benzene	4.88E-02	1.66E-02	194	3.27E-02
carbon tetrachloride	2.86E-05	3.72E-06	670	1.62E-05
1,2-dichloropropane	<MDL	<MDL	NA	<MDL
Trichloroethene	<MDL	<MDL	NA	<MDL

Toluene	1.16E-02	2.70E-03	330	7.15E-03
1,2-dibromoethane	<MDL	<MDL	NA	<MDL
Tetrachloroethene	<MDL	<MDL	NA	<MDL
Chlorobenzene	<MDL	<MDL	NA	<MDL
Ethylbenzene	7.98E-04	1.29E-04	518	4.64E-04
m&p-xylene	1.17E-03	<BL	NA	1.17E-03
Styrene	1.19E-03	3.54E-04	237	7.72E-04
1,1,2,2-tetrachloroethane	<MDL	<MDL	NA	<MDL
o-xylene	3.58E-04	<BL	NA	3.58E-04
benzyl chloride	<BL	<BL	NA	<BL
1,3-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,4-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,2-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,2,4-trichlorobenzene	<MDL	<MDL	NA	<MDL
Acetaldehyde	1.42E-04	2.23E-05	536	8.19E-05
Carbonyl sulfide	7.36E-04	7.86E-04	6	7.61E-04
Acetonitrile	2.13E-02	1.06E-02	101	1.60E-02
acrolein (2-propenal)	5.66E-02	1.92E-02	195	3.79E-02
Acrylonitrile	2.13E-02	9.77E-03	117	1.55E-02
carbon disulfide	3.10E-05	3.80E-04	92	2.05E-04
methyl tert-butyl ether	<BL	<BL	NA	<BL
vinyl acetate	<MDL	4.24E-05	NA	4.24E-05
Chloroprene	2.68E-05	1.80E-05	49	2.24E-05
Bromoform	<MDL	<MDL	NA	<MDL
Hexachloroethane	<BL	<BL	NA	<BL
Naphthalene	7.22E-03	8.59E-04	741	4.04E-03
	<MDL	<MDL	NA	<MDL
Beryllium	<MDL	<MDL	NA	<MDL
Aluminum	2.41E+00	8.89E-01	171	1.65E+00
Chromium	1.62E-03	2.67E-03	39	2.14E-03
Manganese	2.75E-03	3.25E-03	15	3.00E-03
Cobolt	1.63E-04	1.40E-04	16	1.52E-04
Nickel	1.44E-03	3.43E-03	58	2.44E-03
Copper	5.47E-02	5.97E-02	8	5.72E-02
Zinc	3.34E-02	3.13E-02	7	3.24E-02
Arsenic	5.48E-05	<BL	NA	5.48E-05
Selenium	<BL	<BL	NA	<BL
Silver	3.14E-04	1.89E-04	66	2.52E-04
Cadmium	3.33E-04	3.74E-04	11	3.54E-04
Antimony	2.71E-03	2.78E-03	2	2.75E-03
Barium	3.01E-03	4.06E-04	642	1.71E-03
Thallium	<MDL	<MDL	NA	<MDL
Lead	8.52E-03	8.06E-03	6	8.29E-03

NA = not applicable

<BL = less than background level

<MDL = less than method detection level

TABLE D-3. 120 mm Mortar M931- Full Range Practice (FRP) Zone 1 Cartridge

Chemical	Emission Factor		% Difference	Emission Factor
	grams per round			avg grams
	Test 1	Test 2		per round
Formaldehyde	1.39E-02	8.15E-03	70	1.10E-02
hydrogen cyanide,	5.54E-03	4.48E-03	24	5.01E-03
Acetonitrile,	<MDL	<MDL	NA	<MDL
acetaldehyde,	4.21E-03	2.09E-03	102	3.15E-03
acrylonitrile,	1.11E-03	6.56E-04	69	8.82E-04
acrolein,	4.10E-03	9.96E-04	312	2.55E-03
benzene,	3.56E-02	1.93E-02	84	2.75E-02
toluene,	6.27E-03	1.23E-03	411	3.75E-03
phenol,	5.48E-03	2.85E-03	92	4.16E-03
nitrobenzene,	2.26E-04	1.07E-04	111	1.66E-04
naphthalene,	6.81E-03	1.55E-03	340	4.18E-03
quinoline,	8.17E-04	1.87E-04	337	5.02E-04
2-nitrophenol+4-nitrophenol,	3.83E-05	1.34E-05	185	2.58E-05
dibenzofuran+nitrotoluenes,	4.62E-05	1.62E-05	185	3.12E-05
diphenylamine+4-aminobiphenyl,	1.55E-05	<BL	NA	1.55E-05
anthracene,	3.27E-05	<BL	NA	3.27E-05
2,4-dinitrotoluene,	5.01E-05	<MDL	NA	5.01E-05
2,4-dinitrophenol,	3.38E-05	1.78E-05	90	2.58E-05
biphenyl,	<MDL	<MDL	NA	<MDL
Aniline	<BL	4.36E-05	NA	4.36E-05
Dibutylphthalate	1.02E-04	1.61E-04	37	1.32E-04
Diethylphthalate	<BL	2.79E-05	NA	2.79E-05
Dimethylphthalate	<BL	8.63E-06	NA	8.63E-06
Dinitrobenzene	1.54E-07	<BL	NA	1.54E-07
Dinitrotoluene	1.67E-06	<BL	NA	1.67E-06
formic acid	<BL	<BL	NA	<BL
Nitroglycerine	1.85E-05	1.64E-04	89	9.13E-05
N-nitrosodiethylamine	1.87E-07	<BL	NA	1.87E-07
N-nitrosodimethylamine	<BL	<BL	NA	<BL
N-nitrosodiphenylamine	3.11E-05	8.38E-05	63	5.74E-05
Diphenylamine	<BL	<BL	NA	<BL
Chloromethane	<BL	<BL	NA	<BL
vinyl chloride	<MDL	<MDL	NA	<MDL
1,3-butadiene	2.96E-02	5.02E-03	489	1.73E-02
Bromomethane	<MDL	<MDL	NA	<MDL
allyl chloride	1.17E-04	<BL	NA	1.17E-04
Chloroform	<MDL	<MDL	NA	<MDL
1,2-dichloroethane	<BL	<BL	NA	<BL
Benzene	4.48E-02	2.68E-02	67	3.58E-02
carbon tetrachloride	1.36E-05	3.44E-05	60	2.40E-05
1,2-dichloropropane	<MDL	<MDL	NA	<MDL
Trichloroethene	<MDL	<MDL	NA	<MDL
Toluene	1.12E-02	2.82E-03	296	6.99E-03

1,2-dibromoethane	<MDL	<MDL	NA	<MDL
Tetrachloroethene	<MDL	<MDL	NA	<MDL
Chlorobenzene	<MDL	<MDL	NA	<MDL
Ethylbenzene	8.72E-04	1.23E-04	607	4.98E-04
m&p-xylene	2.20E-03	2.81E-04	684	1.24E-03
Styrene	4.93E-03	1.82E-03	171	3.37E-03
1,1,2,2-tetrachloroethane	<MDL	<MDL	NA	<MDL
o-xylene	7.64E-04	9.07E-05	742	4.28E-04
benzyl chloride	6.74E-03	9.71E-04	594	3.85E-03
1,3-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,4-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,2-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,2,4-trichlorobenzene	<MDL	<MDL	NA	<MDL
Acetaldehyde	2.74E-06	<BL	NA	2.74E-06
carbonyl sulfide	2.94E-03	3.24E-03	9	3.09E-03
Acetonitrile	3.01E-03	1.47E-03	105	2.24E-03
acrolein (2-propenal)	5.85E-03	2.64E-03	122	4.24E-03
Acrylonitrile	4.61E-03	1.49E-03	210	3.05E-03
carbon disulfide	1.13E-04	8.31E-05	36	9.81E-05
methyl tert-butyl ether	<BL	<BL	NA	<BL
vinyl acetate	<BL	<BL	NA	<BL
Chloroprene	9.08E-05	2.56E-05	254	5.82E-05
Bromoform	<BL	<BL	NA	<BL
Hexachloroethane	1.64E-04	<BL	NA	1.64E-04
Naphthalene	1.29E-02	3.45E-03	273	8.16E-03
beryllium	<MDL	<MDL	NA	<MDL
Aluminum	1.61E+00	5.45E-01	196	1.08E+00
Chromium	1.35E-03	6.90E-04	96	1.02E-03
Manganese	1.19E-02	4.36E-03	172	8.11E-03
Cobolt	1.35E-04	1.34E-04	1	1.35E-04
Nickel	1.77E-03	9.13E-04	94	1.34E-03
Copper	1.05E-01	6.20E-02	70	8.37E-02
Zinc	1.76E+00	1.09E+00	61	1.43E+00
Arsenic	7.51E-05	4.69E-05	60	6.10E-05
Selenium	3.57E-04	2.73E-04	31	3.15E-04
Silver	<BL	<BL	NA	<BL
Cadmium	5.50E-04	5.08E-04	8	5.29E-04
Antimony	2.44E-03	2.20E-03	11	2.32E-03
Barium	1.35E-02	3.28E-02	59	2.31E-02
Thallium	<MDL	<MDL	NA	<MDL
Lead	7.33E-03	6.16E-03	19	6.74E-03

NA = not applicable

<BL = less than background level

<MDL = less than method detection level

TABLE D-4. 25 mm M793 - Target Practice - Tracer (TP-T)

Chemical	Emission Factor grams per round			% Difference			Emission Factor avg grams
	Test 1	Test 2	Test 3	Test 1 vs 2	Test 2 vs 3	Test 1 vs 3	per round
Formaldehyde	3.44E-03	3.54E-03	3.07E-03	3	15	12	3.35E-03
hydrogen cyanide,	--	--	2.68E-02	NA	NA	NA	2.68E-02
acetonitrile,	0.00E+00	3.67E-03	3.94E-03	NA	7	NA	2.54E-03
acetaldehyde,	1.11E-03	1.17E-03	1.25E-03	5	6	11	1.18E-03
acrylonitrile,	--	--	--	NA	NA	NA	--
acrolein,	--	--	--	NA	NA	NA	--
Benzene,	5.89E-03	6.58E-03	6.23E-03	11	6	5	6.23E-03
Toluene,	3.06E-04	3.60E-04	2.93E-04	15	23	4	3.20E-04
Phenol,	3.49E-04	3.95E-04	1.95E-04	12	103	79	3.13E-04
nitrobenzene,	2.95E-05	2.57E-05	9.54E-06	15	169	209	2.16E-05
naphthalene,	3.99E-04	5.08E-04	3.97E-04	21	28	0	4.35E-04
Quinoline,	5.41E-05	6.54E-05	5.47E-05	17	20	1	5.81E-05
2-nitrophenol+4-nitrophenol,	<BL	4.15E-06	<BL	NA	NA	NA	4.15E-06
dibenzofuran+nitrotoluenes,	<BL	5.01E-06	2.02E-06	NA	148	NA	3.52E-06
diphenylamine+4-aminobiphenyl,	<BL	5.04E-06	7.21E-06	NA	30	NA	6.13E-06
anthracene,	5.33E-06	5.31E-06	1.98E-06	0	168	169	4.21E-06
2,4-dinitrotoluene,	5.45E-06	5.43E-06	4.92E-07	0	1003	1008	3.79E-06
2,4-dinitrophenol,	<BL	<BL	6.08E-07	NA	NA	NA	6.08E-07
Biphenyl,	<BL	<BL	<BL	NA	NA	NA	<BL
Aniline	<BL	<BL	1.75E-05	NA	NA	NA	1.75E-05
Dibutylphthalate	4.00E-05	<BL	<BL	NA	NA	NA	4.00E-05
Diethylphthalate	1.80E-05	1.46E-05	5.34E-06	23	173	236	1.26E-05
Dimethylphthalate	<BL	1.16E-06	<BL	NA	NA	NA	1.16E-06
Dinitrobenzene	4.53E-07	<BL	1.01E-07	NA	NA	349	2.77E-07
Dinitrotoluene	3.27E-06	3.26E-07	1.75E-06	904	81	87	1.78E-06
formic acid	<BL	<BL	<BL	NA	NA	NA	<BL
Nitroglycerine	4.08E-06	5.42E-07	3.00E-06	653	82	36	2.54E-06
N-nitrosodiethylamine	<BL	<BL	1.23E-06	NA	NA	NA	1.23E-06
N-nitrosodimethylamine	5.30E-05	7.22E-05	9.14E-05	27	21	42	7.22E-05
N-nitrosodiphenylamine	4.86E-05	5.14E-05	4.21E-05	5	22	16	4.74E-05
Diphenylamine	<BL	<BL	<BL	NA	NA	NA	<BL
Chloromethane	<BL	<BL	<BL	NA	NA	NA	<BL
vinyl chloride	<BL	<BL	<BL	NA	NA	NA	<BL
1,3-butadiene	2.07E-04	9.86E-05	1.77E-04	110	44	17	1.61E-04
Bromomethane	<BL	<BL	<BL	NA	NA	NA	<BL
allyl chloride	3.32E-06	3.44E-05	<BL	90	NA	NA	1.88E-05
Chloroform	<BL	<BL	<BL	NA	NA	NA	<BL
1,2-dichloroethane	<BL	<BL	<BL	NA	NA	NA	<BL
Benzene	7.84E-03	9.57E-03	8.82E-03	18	8	11	8.74E-03
Carbon tetrachloride	<BL	<BL	2.34E-05	NA	NA	NA	2.34E-05
1,2-dichloropropane	<BL	8.91E-06	<BL	NA	NA	NA	8.91E-06
Trichloroethene	<BL	<BL	<BL	NA	NA	NA	<BL
Toluene	5.64E-04	4.47E-04	4.69E-04	26	5	20	4.93E-04

1,2-dibromoethane	<BL	<BL	<BL	NA	NA	NA	<BL
Tetrachloroethene	<BL	<BL	<BL	NA	NA	NA	<BL
Chlorobenzene	<BL	<BL	<BL	NA	NA	NA	<BL
Ethylbenzene	3.35E-05	2.83E-05	1.73E-05	18	63	93	2.64E-05
m&p-xylene	1.28E-05	9.75E-06	2.11E-05	31	54	39	1.45E-05
Styrene	7.77E-05	5.63E-05	8.30E-05	38	32	6	7.23E-05
1,1,2,2-tetrachloroethane	<BL	<BL	<BL	NA	NA	NA	<BL
o-xylene	<BL	<BL	<BL	NA	NA	NA	<BL
benzyl chloride	<BL	<BL	<BL	NA	NA	NA	<BL
1,3-dichlorobenzene	<BL	<BL	<BL	NA	NA	NA	<BL
1,4-dichlorobenzene	<BL	<BL	<BL	NA	NA	NA	<BL
1,2-dichlorobenzene	<BL	<BL	<BL	NA	NA	NA	<BL
1,2,4-trichlorobenzene	<BL	<BL	<BL	NA	NA	NA	<BL
Acetaldehyde	5.29E-06	2.55E-06	<BL	108	NA	NA	3.92E-06
Carbonyl sulfide	2.08E-03	2.43E-03	2.36E-03	14	3	12	2.29E-03
Acetonitrile	4.85E-03	4.37E-03	6.33E-03	11	31	23	5.18E-03
acrolein (2-propenal)	8.32E-04	4.90E-04	<BL	70	NA	NA	6.61E-04
Acrylonitrile	4.16E-04	3.21E-04	4.41E-04	30	27	6	3.93E-04
Carbon disulfide	8.87E-06	1.22E-05	1.72E-06	27	608	416	7.58E-06
Methyl tert-butyl ether	<BL	2.44E-05	<BL	NA	NA	NA	2.44E-05
vinyl acetate	<BL	<BL	1.81E-06	NA	NA	NA	<BL
Chloroprene	8.87E-06	<BL	<BL	NA	NA	NA	8.87E-06
Bromoform	<BL	<BL	<BL	NA	NA	NA	<BL
Hexachloroethane	2.08E-05	1.82E-05	1.25E-06	15	1350	1561	1.34E-05
Naphthalene	3.38E-04	4.35E-04	6.00E-04	22	27	44	4.58E-04
	<BL	<BL	<BL	NA	NA	NA	<BL
Beryllium	<BL	<BL	<BL	NA	NA	NA	<BL
Aluminum	4.87E-01	4.70E-02	1.94E-01	936	76	151	2.43E-01
Chromium	8.71E-04	5.45E-04	1.21E-03	60	55	28	8.76E-04
manganese	3.43E-03	2.63E-03	3.42E-03	30	23	0	3.16E-03
Cobolt	6.30E-05	3.26E-05	2.51E-05	93	30	151	4.02E-05
Nickel	4.94E-04	1.48E-04	2.87E-04	233	48	72	3.10E-04
Copper	2.24E-03	1.26E-03	8.14E-04	78	55	176	1.44E-03
Zinc	6.00E-02	5.83E-02	1.04E-01	3	44	42	7.40E-02
Arsenic	9.97E-06	2.53E-05	2.64E-05	61	4	62	2.06E-05
Selenium	<BL	<BL	<BL	NA	NA	NA	<BL
Silver	1.21E-04	1.84E-05	2.58E-05	558	29	369	5.50E-05
Cadmium	1.92E-04	1.66E-04	1.63E-04	16	2	18	1.74E-04
antimony	1.12E-02	1.05E-02	1.15E-02	6	8	3	1.11E-02
Barium	1.25E-02	8.17E-03	7.65E-03	52	7	63	9.43E-03
Thallium	<BL	<BL	<BL	NA	NA	NA	<BL
Lead	1.86E-02	1.88E-02	2.24E-02	1	16	17	1.99E-02

NA = not applicable

<BL = less than background llevel

<MDL = less than method detection level

TABLE D-5. 120 mm Mortar M931 - Full Range Practice (FRP) Zone 4 Cartridge

Chemical	Emission Factor grams per round		% Difference	Emission Factor avg grams per round
	Test 1	Test 2		
formaldehyde	4.46E-03	5.66E-03	21	5.06E-03
hydrogen cyanide,	5.63E-03	3.84E-03	47	4.73E-03
acetonitrile,	1.75E-03	7.56E-04	131	1.25E-03
acetaldehyde,	2.74E-03	1.97E-03	39	2.35E-03
acrylonitrile,	3.65E-04	1.70E-04	115	2.67E-04
acrolein,	2.66E-03	7.85E-04	239	1.72E-03
benzene,	4.07E-02	2.43E-02	68	3.25E-02
toluene,	7.58E-03	1.95E-03	288	4.76E-03
phenol,	5.62E-03	5.98E-03	6	5.80E-03
nitrobenzene,	1.07E-04	2.72E-05	295	6.73E-05
naphthalene,	7.21E-03	2.09E-03	245	4.65E-03
quinoline,	7.88E-04	2.28E-04	246	5.08E-04
2-nitrophenol+4-nitrophenol,	2.70E-05	<MDL	NA	2.70E-05
dibenzofuran+nitrotoluenes,	3.26E-05	<MDL	NA	3.26E-05
diphenylamine+4-aminobiphenyl,	3.28E-05	1.87E-05	76	2.57E-05
anthracene,	6.91E-05	<BL	451	6.91E-05
2,4-dinitrotoluene,	3.53E-05	<MDL	NA	3.53E-05
2,4-dinitrophenol,	3.57E-05	<MDL	NA	3.57E-05
biphenyl,	7.32E-04	2.55E-04	187	4.93E-04
aniline	<BL	<MDL	NA	<BL
dibutylphthalate	4.10E-04	6.69E-04	39	5.39E-04
diethylphthalate	8.18E-05	3.92E-05	109	6.05E-05
dimethylphthalate	<BL	<BL	NA	<BL
dinitrobenzene	6.52E-07	<BL	276	6.52E-07
dinitrotoluene	<BL	<BL	NA	<BL
formic acid	<BL	1.76E-04	NA	1.76E-04
nitroglycerine	<BL	<BL	NA	<BL
N-nitrosodiethylamine	<BL	<BL	NA	<BL
N-nitrosodimethylamine	2.01E-05	2.21E-05	9	2.11E-05
N-nitrosodiphenylamine	<BL	<BL	NA	<BL
diphenylamine	7.71E-07	1.40E-06	45	1.09E-06
chloromethane	6.58E-05	1.04E-04	37	8.49E-05
vinyl chloride	<MDL	<MDL	NA	<MDL
1,3-butadiene	2.21E-02	3.59E-03	516	1.29E-02
bromomethane	<MDL	<MDL	NA	<MDL
allyl chloride	<BL	<BL	NA	<BL
chloroform	<MDL	<MDL	NA	<MDL
1,2-dichloroethane	<MDL	<MDL	NA	<MDL
benzene	5.36E-02	3.99E-02	35	4.68E-02
carbon tetrachloride	<BL	1.21E-05	NA	1.21E-05
1,2-dichloropropane	<MDL	<MDL	NA	<MDL
trichloroethene	<MDL	<MDL	NA	<MDL
toluene	1.51E-02	4.06E-03	273	9.60E-03

1,2-dibromoethane	<MDL	<MDL	NA	<MDL
tetrachloroethene	<MDL	<MDL	NA	<MDL
chlorobenzene	<MDL	<MDL	NA	<MDL
ethylbenzene	8.82E-04	1.87E-04	372	5.35E-04
m&p-xylene	2.39E-03	<BL	NA	2.39E-03
styrene	4.87E-03	1.47E-03	231	3.17E-03
1,1,2,2-tetrachloroethane	<MDL	<MDL	NA	<MDL
o-xylene	7.12E-04	<BL	NA	7.12E-04
benzyl chloride	4.62E-03	1.06E-03	335	2.84E-03
1,3-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,4-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,2-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,2,4-trichlorobenzene	<MDL	<MDL	NA	<MDL
acetaldehyde	2.80E-05	<MDL	NA	2.80E-05
carbonyl sulfide	1.05E-02	1.18E-02	11	1.11E-02
acetonitrile	2.26E-03	1.61E-03	41	1.93E-03
acrolein (2-propenal)	2.72E-03	1.22E-03	123	1.97E-03
acrylonitrile	3.69E-03	4.74E-04	679	2.08E-03
carbon disulfide	1.44E-04	5.66E-05	154	1.00E-04
methyl tert-butyl ether	<BL	<BL	NA	<BL
vinyl acetate	<BL	9.64E-05	NA	9.64E-05
chloroprene	8.68E-05	1.66E-05	422	5.17E-05
bromoform	<BL	<BL	NA	<BL
hexachloroethane	5.17E-04	1.22E-04	323	3.20E-04
naphthalene	1.37E-02	5.30E-03	159	9.51E-03
	<BL	<BL	NA	<BL
beryllium	<MDL	<MDL	NA	<MDL
aluminum	<BL	<BL	NA	<BL
chromium	1.48E-03	1.61E-03	8	1.55E-03
manganese	4.25E-03	3.78E-03	12	4.01E-03
cobolt	2.64E-04	2.26E-04	17	2.45E-04
nickel	2.51E-03	2.68E-03	7	2.60E-03
copper	9.29E-02	7.41E-02	25	8.35E-02
zinc	4.53E-02	3.35E-02	35	3.94E-02
arsenic	<BL	<BL	NA	<BL
selenium	<BL	<MDL	NA	<BL
silver	<BL	<BL	NA	<BL
cadmium	1.27E-03	1.25E-03	1	1.26E-03
antimony	4.06E-03	3.17E-03	28	3.62E-03
barium	2.46E-02	2.81E-02	12	2.63E-02
thallium	<MDL	<MDL	NA	<MDL
lead	8.23E-03	7.01E-03	17	7.62E-03

NA = not applicable

<BL = less than background level

<MDL = less than method detection level

TABLE D-6. 25 mm BUSHMASTER M910 - Target Practice Discarding Sabot-Tracer (TPDS-T)

Chemical	Emission Factor grams per round		% Difference	Emission Factor avg grams per round
	Test 1	Test 2		
Formaldehyde	1.36E-03	9.17E-04	32	1.14E-03
hydrogen cyanide,	1.74E-03	3.54E-04	80	1.05E-03
acetonitrile,	5.10E-04	2.03E-04	60	3.57E-04
acetaldehyde,	2.75E-04	1.84E-04	33	2.30E-04
acrylonitrile,	--	--	NA	--
acrolein,	--	--	NA	--
benzene,	1.07E-03	2.04E-04	81	6.36E-04
toluene,	1.41E-04	1.05E-04	26	1.23E-04
phenol,	<BL	<BL	NA	<BL
nitrobenzene,	<MDL	<MDL	NA	<MDL
naphthalene,	8.24E-05	1.58E-05	81	4.91E-05
quinoline,	1.19E-05	1.19E-05	1	1.19E-05
2-nitrophenol+4-nitrophenol,	<MDL	<MDL	NA	<MDL
dibenzofuran+nitrotoluenes,	<MDL	<MDL	NA	<MDL
diphenylamine+4-aminobiphenyl,	<MDL	<MDL	NA	<MDL
anthracene,	<MDL	<MDL	NA	<MDL
2,4-dinitrotoluene,	<MDL	<MDL	NA	<MDL
2,4-dinitrophenol,	<MDL	5.67E-06	NA	5.67E-06
biphenyl,	<MDL	<MDL	NA	<MDL
Aniline	1.61E-05	<BL	NA	1.61E-05
Dibutylphthalate	<BL	<BL	NA	<BL
Diethylphthalate	<BL	<BL	NA	<BL
Dimethylphthalate	<BL	<BL	NA	<BL
Dinitrobenzene	5.15E-07	4.14E-07	20	4.65E-07
Dinitrotoluene	4.75E-05	3.88E-05	18	4.32E-05
formic acid	<BL	<BL	NA	<BL
Nitroglycerine	<BL	1.61E-06	NA	1.61E-06
N-nitrosodiethylamine	2.19E-06	3.46E-06	58	2.82E-06
N-nitrosodimethylamine	1.70E-05	1.19E-05	30	1.44E-05
N-nitrosodiphenylamine	6.43E-06	4.70E-06	27	5.57E-06
Diphenylamine	<MDL	<MDL	NA	<MDL
Chloromethane	1.08E-05	4.31E-05	299	2.70E-05
vinyl chloride	<MDL	<MDL	NA	<MDL
1,3-butadiene	2.31E-04	6.15E-05	73	1.46E-04
Bromomethane	<MDL	<MDL	NA	<MDL
allyl chloride	<BL	<BL	NA	<BL
Chloroform	<MDL	<MDL	NA	<MDL
1,2-dichloroethane	<MDL	<MDL	NA	<MDL
Benzene	1.42E-03	2.74E-04	81	8.49E-04
carbon tetrachloride	2.57E-05	2.91E-05	13	2.74E-05
1,2-dichloropropane	<MDL	<MDL	NA	<MDL
Trichloroethene	<MDL	<MDL	NA	<MDL
Toluene	3.47E-04	1.69E-04	51	2.58E-04

1,2-dibromoethane	<MDL	<MDL	NA	<MDL
Tetrachloroethene	<MDL	<MDL	NA	<MDL
Chlorobenzene	<MDL	<MDL	NA	<MDL
Ethylbenzene	2.89E-05	2.36E-05	18	2.62E-05
m&p-xylene	4.01E-05	4.25E-05	6	4.13E-05
Styrene	4.74E-05	3.60E-05	24	4.17E-05
1,1,2,2-tetrachloroethane	<MDL	<MDL	NA	<MDL
o-xylene	<BL	8.38E-06	NA	8.38E-06
benzyl chloride	<BL	<BL	NA	<BL
1,3-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,4-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,2-dichlorobenzene	<MDL	<MDL	NA	<MDL
1,2,4-trichlorobenzene	<MDL	<MDL	NA	<MDL
Acetaldehyde	<BL	<BL	NA	<BL
carbonyl sulfide	5.09E-04	1.05E-04	79	3.07E-04
Acetonitrile	<BL	<BL	NA	<BL
acrolein (2-propenal)	<BL	<BL	NA	<BL
Acrylonitrile	2.97E-04	1.31E-04	56	2.14E-04
carbon disulfide	1.44E-05	1.68E-06	88	8.05E-06
methyl tert-butyl ether	3.79E-05	4.22E-05	11	4.01E-05
vinyl acetate	<BL	4.02E-06	NA	4.02E-06
Chloroprene	<BL	<BL	NA	<BL
Bromoform	<MDL	<MDL	NA	<MDL
Hexachloroethane	<BL	<BL	NA	<BL
Naphthalene	2.47E-04	1.34E-04	46	1.91E-04
beryllium	<MDL	<MDL	NA	<MDL
Aluminum	1.57E-01	1.31E-01	17	1.44E-01
Chromium	2.93E-03	2.63E-03	11	2.78E-03
Manganese	2.60E-03	1.48E-03	43	2.04E-03
Cobolt	3.07E-05	2.65E-05	14	2.86E-05
Nickel	3.43E-04	3.05E-04	11	3.24E-04
Copper	1.04E-03	8.61E-04	17	9.48E-04
Zinc	2.82E-01	2.80E-01	1	2.81E-01
Arsenic	5.17E-05	5.01E-05	3	5.09E-05
Selenium	4.37E-05	9.94E-05	128	7.16E-05
Silver	2.41E-05	7.06E-06	71	1.56E-05
Cadmium	1.22E-04	7.87E-05	36	1.01E-04
Antimony	1.48E-02	1.32E-02	11	1.40E-02
Barium	6.02E-03	5.59E-03	7	5.80E-03
Thallium	<MDL	<MDL	NA	<MDL
Lead	2.80E-02	2.35E-02	16	2.57E-02

NA = not applicable

<BL = less than background level

<MDL = less than method detection level