FINAL REPORT

Exploratory Development of Energetic and Pyrotechnic Combustion Characterization Apparatus

SERDP Project WP-2612

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A sampling platform was designed and constructed with enough flexibility that it could be adapted to contained detonation or combustion test facility, as well as to take ground-level ambient samples of plumes from OB/OD activities or live-fire tests. Testing consisted of the detonation of thirteen test articles and one blank in a confined detonation test chamber (DTC), followed by sampling of the plume with the measurement platform. Twelve of the test articles consisted of combinations of two energetics (PBXN-113 and PBXN-114) and two casing materials for the article (brass and stainless steel with tin insert). The thirteenth test article was a booster-only device. The main result of the test effort was the successful implementation of the sampling platform and the proof of its use in conjunction with the detonation test chamber (DTC). Overall, the platform performed as expected and the magnitude of the sample flowrate and ability to distribute the sample air to multiple filters and instruments made for very efficient and flexible sample collection. In all, the platform used for measurements in this SEED project is flexible enough to be used in future DTC-based testing of explosives (< 200 grams) and propellants (small arms). In-situ testing in an outdoor setting expands the list of test article to include large energetic devices, pyrotechnics, large device propellants, and rocket motors.

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OB/OD, detonation test chamber, PM10, PM2.5, Emissions Factors

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List of Acronyms

DTC: Detonation Test Chamber
EC: Elemental carbon fraction as analyzed by thermal optical reflectance (TOR)
EPA: United States Environmental Protection Agency
GC/MS: Gas chromatography/mass spectrometry
HEPA: High efficiency particulate air [filter]
HMX: Explosive compound (1,3,5,7 tetranitro 1,3,5,7 tetrazocone)
HPLC: High performance liquid chromatography
IC: Ion chromatography
LIDAR: Light detection and ranging
MFC: Mass flow controller
MOUDI: Micro-orifice uniform deposit impactor
NAWCWD: Naval Air Warfare Center, Weapons Division
Nitro-PAH: nitrous polycyclic aromatic hydrocarbon
OB/OD: Open burn / open detonation
OC: Organic carbon fraction as analyzed by thermal optical reflectance (TOR)
PAH: Polycyclic aromatic hydrocarbon
PBXN-113, PBXN-114: Explosive formulations used by the Navy based on HMX
PM: Suspended particulate matter
PM1: Particulate matter with aerodynamic diameter smaller than 1.0 micrometers
PM10: Particulate matter with aerodynamic diameter smaller than 10 micrometers
PM2.5: Particulate matter with aerodynamic diameter smaller than 2.5 micrometers
SEED: Exploratory development project funded by SERDP
SERDP: Strategic Environmental Research and Development Program (DoD)
SSI: Size-selective inlet
TD: Thermal desorption
TIGF:Teflon™ impregnated glass fiber [filter]
TOR/TOT: Thermal optical reflectance/transmittance
TSP: Total suspended particulate matter
UHMWPE: Ultra high molecular weight polyethylene
XAD: Polystyrene-divinylbenzene resin
XRF: X-ray fluorescence spectrometry

Keywords: OB/OD, Detonation Test Chamber, PM10, PM2.5, Emission Factors

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Abstract

Objectives

This SEED project sought to develop and test measurement technology that would support the characterization of airborne particulate and gas-phase emissions generated from the use of metal-based energetics and pyrotechnic formulations.

The two technical objectives were to:

-*Assemble a previously designed, but untested, measurement technology and test its operability at the Hypervelocity Laboratory facility at Naval Air Warfare Center, Weapons Division, China Lake.*

- *Characterize the practical limits of the measurement system and its potential for use in future efforts to characterize emission factors and human exposure concerns from open-burning/open-detonation (OB/OD), as well as the use of energetic materials, propellants, rocket motors, and pyrotechnics during live-fire training*.

Technical Approach

A sampling platform was designed and constructed with enough flexibility that it could be adapted to contained detonation or combustion test facility, as well as to take ground-level ambient samples of plumes from OB/OD activities or live-fire tests.

The main distinguishing features of the platform were: 1) the use of multiple mass flow controllers to precisely distribute particle laden air that has been routed from one sample port through a single PM10 (particulate matter with aerodynamic diameter smaller than 10 micrometers) selective inlet through to multiple filter collection and other measurement devices; 2) a relatively high flow rate of 113.5 liter per minute that enables collection of PM10 material on filter media in a relatively short period of time; 3) flexibility in adding or removing instrumentation with minimal impact; and 4) a rapid sample-air to clean-air port switching mechanism which provided the ability to instantly collect plume samples without any startup time or delays in achieving designed flowrates during sample platform operation.

The sampler filter ports were equipped with three types of filter media: Teflon™, quartz fiber, and Teflon-impregnated glass fiber followed by a selective resin column. A multi-stage impactor device was connected to a sampling port and used to collect size-segregated particle samples. Product gases including carbon dioxide, carbon monoxide, and oxides of nitrogen were sampled in real-time through a sample port using a gas analyzer. Particle concentration by light scattering was also measured in real-time. All real-time data were logged by a remote computer that also controlled the functions of the sampling apparatus. Filter media were analyzed with multiple techniques including gravimetric weighing to determine loading levels, X-ray fluorescence spectroscopy, ion chromatography, liquid chromatography, gas chromatography, and thermal optical reflectance/ transmittance.

Testing consisted of the detonation of thirteen test articles and one blank in a confined detonation test chamber (DTC), followed by sampling of the plume with the measurement platform. Twelve of the test articles consisted of combinations of two energetics (PBXN-113 and PBXN-114) and two casing materials for the article (brass and stainless steel with tin insert). The thirteenth test article was a booster-only device.

Results

The main result of the test effort was the successful implementation of the sampling platform and the proof of its use in conjunction with the DTC. Overall, the platform performed as expected and the magnitude of the sample flowrate and ability to distribute the sample air to multiple filters and instruments made for very efficient and flexible sample collection. This experience also provided areas where improvement can be sought and enabled assessment of the testing platform for use in other configurations and for other energetic formulations.

- The explosives tested in this study (~ 200 grams) resulted in extremely high initial concentrations of PM10, which caused overloading of filters for the first four tests. The issue was addressed by diluting the plume using the DTC active exhaust fan for five minutes before starting sample collection. In future efforts, it is recommended that a second sample line is used to monitor PM10 and gas constituent concentrations, before and after filter sample collection begins, in order to ensure optimal filter loading.
- Each gas phase compound of interest should be analyzed using an independent analyzer; the multi-gas analyzer device used in this SEED project was designed for vehicle exhaust testing and the ranges of concentrations it can accommodate were limited.
- Teflon™ filters are not ideally suited for sampling high concentrations of energetics products due to the tendency for the deposit to spall. Exploration of a different filter medium is suggested for future efforts.
- The sampling platform can accommodate either a PM10 or a PM2.5 size selective inlet, but not both at the same time. Given the labor resources required from host facilities to perform these tests, it would be more efficient to simply build another platform so that both PM10 and PM2.5 samples could be collected simultaneously.

Additional results specific to the testing conducted included:

- Compared to PBXN-113, the combustion of the carbon in PBXN-114 was less complete as indicated by a higher carbon monoxide to carbon dioxide ratio and more soot.
- The major metal constituent from PBXN-113 was aluminum and the major constituent from PBXN-114 was tin, but this was likely a result of inserting a tin disc into the PBXN-114 test articles rather than a characteristic of the detonation of PBXN-114.
- Several metals of interest were measured well above detection limits including lead, chromium, manganese, titanium, nickel, and strontium.
- The main energetic HMX was detected in the first four test samples, when the plume was highly concentrated, but not in subsequent tests. Another commonly used compound in energetics, Ethanox, was not detected in any of the samples.
- Particle size distributions indicated slightly different modes for PBXN-113 (0.3 – 0.5 micrometers) than PBXN-114 (broader mode between 0.3 and 1.8 micrometers).

Benefits

In all, the platform used for measurements in this SEED project is flexible enough to be used in future DTC-based testing of explosives (< 200 grams) and propellants (small arms). In-situ testing in an outdoor setting expands the list of test article to include large energetic devices, pyrotechnics, large device propellants, and rocket motors. One caveat is that the plume must have a portion that is at or near ground level (i.e., can be reached by elevated ground-based sample line) for at least a short period of time, so that sample materials could be channeled through an inlet line. Other than pyrotechnics all of these test articles are available at NAWCWD China Lake along with personnel and facilities to conduct both indoor and outdoor testing.

1. Objective

The objective of this SEED project was to develop and test measurement technology that would support the characterization of airborne particulate and gas-phase emissions generated from the use of metal-based energetics and pyrotechnic formulations. The technology was designed to accurately characterize the PM_{10} and $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 10 and 2.5 micrometers, respectively) emission factors, evaluate the particle size distribution following an energetic detonation or during a pyrotechnic combustion, measure the emission of metal species of interest with an emphasis on lead (as function of particle size and as aggregated within the PM_{10} and $PM_{2.5}$ umbrellas), and determine the emission of organic compounds of interest, including products of incomplete detonation and combustion. An output of the project is the documentation of technology limits in terms of safe and practical uses, detection limits for end products of interest, and the ability to provide useful information to assess human exposure to metals and other chemical constituents of interest.

The two technical objectives were to:

- *Assemble a previously designed, but untested, measurement technology and test its operability at the NAWCWD China Lake Hypervelocity Laboratory facility.* This objective was essentially pass/fail. If the system worked as designed, the objective would be considered accomplished.
- *Characterize the practical limits of the measurement system and its potential for use in future efforts to characterize emission factors and human exposure concerns from open-burning/open-detonation (OB/OD), as well as the use of energetic materials, propellants, rocket motors, and pyrotechnics during live-fire training.* This objective included characterizing the detection limits (especially for metals and other chemical constituents of interest), characterizing the practical limits (where, when, and for what energetics technology can be used?), and developing an outline of the specific test-article configurations that are amenable for testing with the instrumentation developed.

Successfully meeting these objectives would signal the successful completion of the SEED project and would provide SERDP with another measurement tool that it can use to address public concerns about emissions from Department of Defense (DoD) activities and occupational safety concerns regarding workplace exposures to toxic compounds during OB/OD and live-fire training activities.

1. Background

Gas-phase and airborne-particulate products generated from using energetic materials, propellants, rocket motors, and pyrotechnics are of interest to the DoD for two principle reasons. First, these formulations—along with a suite of others that are used for initiating and amplifying a detonation and materials associated with casings and projectiles—contribute to the air quality burden in locations where they are used and sometimes in neighboring downwind civilian communities. Contributions can occur during live-fire exercises and tests of these articles. They can also occur during a widely used set of disposal processes known collectively as “open burning/open detonation” (OB/OD), whereby items are detonated, burned, fired, or incinerated for the purpose of disposal. Emissions of OB/OD products into the atmosphere are of interest to the Department of Defense (DoD) and the US Environmental Protection Agency (EPA), as well as the state and local air quality planning agencies that are affected. These emissions have been the subject of several recent SERDP funded projects (e.g., Kim et al., [2012]; Gullett et al., [2016]; Mitchell and Suggs, [1997]).

A second area of interest for the DoD, especially as it pertains to gun propellant use, has arisen that is related to the exposure of personnel to toxic compounds and the deposition of products on soils and other surfaces. The use of lead within propellant initiator/primer formulations in addition to the small particles of lead generated from the projectile occur in quantities that are sufficient to warrant a health concern, especially for those routinely exposed to direct emissions and residues (National Research Council, 2013). This is distinct from the metallic lead that remains part of the solid projectile, which has given rise to its own set of environmental concerns (e.g., Arnemo et al., [2016]).

These two concerns have prompted interest in improving the quantitation of the amounts and characterization of the components of particulate matter (PM) smaller than 10 micrometers (PM_{10}) and smaller than 2.5 micrometers ($PM_{2.5}$) that are emitted from OB/OD activities, as well as from live-fire training exercises, including those at gun ranges and in field simulations. Some gas-phase constituents that are known to be hazardous to human health (e.g., benzene and toluene) and some semivolatile organic compounds that can be found in the gas-phase or as PM are also of interest for their potential emission into the environment and as an exposure hazard to military personnel.

1.1. Measurement technology

Broadly, OB/OD and live-fire products can be sampled either in situ where they are created under field conditions (e.g., by sampling within the plume generated) or in a controlled environment where field conditions are not as well represented but where it is easier, and usually more economical, to conduct measurements. Large OB/OD events often result in a plume that is elevated well above ground level and requires either the use of remote sensing techniques (e.g., LIDAR) or a remotely operated device that carries instrumentation and is placed in the expected path of the plume or can be directed into the plume (e.g., aerostat, drone; see Gullett et al., 2016).

Tests in controlled areas, such as a detonation test chamber (DTC), allow for these products to be collected through sampling ports that are installed in the wall of the DTC, enabling ready access to the test volume for control, measurement, and sampling. The advantages of these types of controlled tests over in situ methods are the ability to reliably obtain analyte materials above the limits of detection, the potential to repeat measurements as needed to achieve a target for uncertainty, the ability to completely remove all detonation residue from the previous test, the absence of entrained soil and material from prior detonation activity in the detonation plume, and the inherent safety and economy of personnel and equipment being located in a separate area during tests.

An alternative to collecting samples is using combustion models that have been developed specifically to represent the physics of detonation and fast combustion, which include sophisticated codes such as Cheetah. However, these specialty codes require considerable expertise to operate proficiently.

2. Materials and Methods

2.1. Sample collection instrumentation

A platform for collecting sample air from the DTC located and operated by engineering and science staff in the Naval Air Warfare Center, Weapons Division (NAWCWD) China Lake, CA was designed and constructed. It was designed with enough flexibility that it could be adapted to sample from other contained detonation or combustion test facilities, as well as to take ground-level ambient samples of plumes from either OB/OD or live-fire tests and exercises. The specifications of all instruments and devices used on the sampling platform are provided in Table 1.

One physical feature that supports this flexibility is the platform’s capability to rapidly switch between channeling clean, HEPA-filtered air through the sampling platform to channeling air influenced by detonation or combustion activity. The overall flow diagram of the sampling platform is provided in Figure 1.

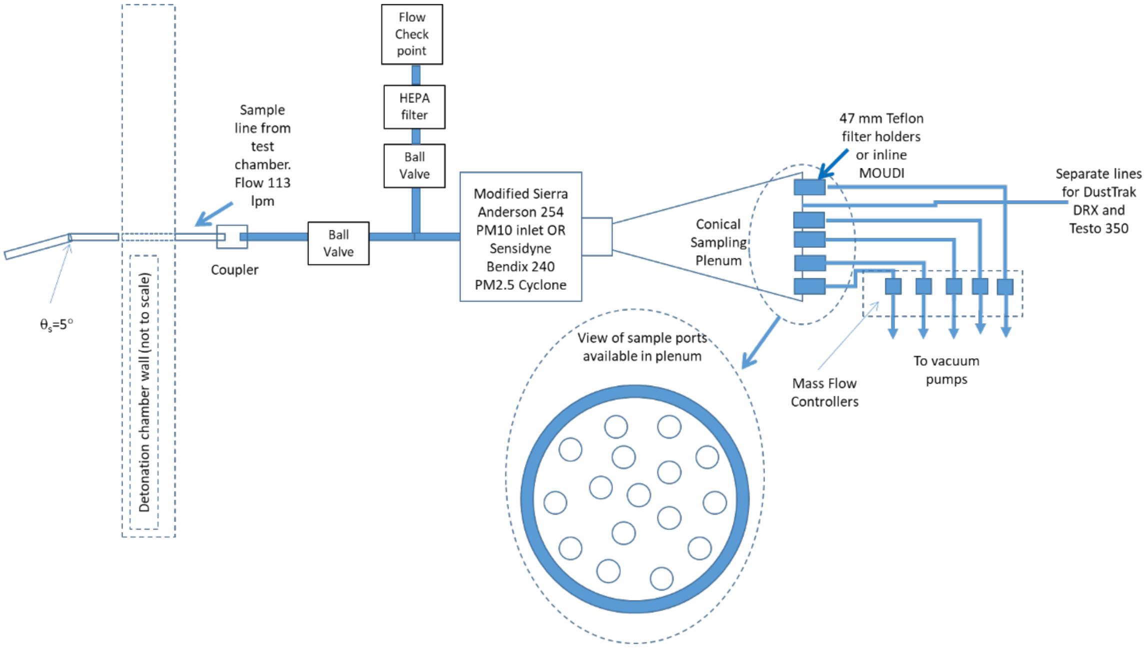


Figure 1. Flow diagram of sampling platform.

A system of two pneumatically activated ball valves (Figure 2, [1]) serves to isolate the downstream sample instrumentation from the high pressures and temperatures that result from the detonation of energetics in a relatively confined space. When sample collection is not actively occurring, the sampling line (Figure2, [2]) ball valve (the lower valve shown in Figure 2) is closed and all the instrumentation downstream of that valve is separated from whatever is occurring to the right of the valve. An important factor in sampling aerosols is that the flow of air through the instrumentation is at a constant, or nearly so, flow rate. A non-steady flow-rate complicates the emissions factors calculations that are based on aerosol measurements. Initiating sampling at the moment of initiating the air pump would result in a latency, or delay, between sample initiation and the achievement of a steady flow-rate. To avoid latency in achieving design flow rates, which are of critical importance for achieving the correct particle size selection, a second pneumatically controlled ball valve is open so that HEPA-filtered (Figure 2, [4]) air is flowing into the sample collection instrumentation at the design flow rate of 113.6 liters per minute (lpm). To initiate sample collection, the sampling line ball valve is electronically-commanded to open, and is actuated by air pressure provided by a portable compressor (Figure 2, [3]). Concurrently, the HEPA line ball valve is electronically-commanded and compressed-air-actuated to the closed position. Air is pulled through the sample train

(Figure 2, [5]) by vacuum at the left side of the trains. At the end of sample collection, this sequence—which requires less than a tenth of a second—is reversed to return to the original valve configuration that was in effect prior to sample collection (i.e., HEPA filtered air goes through the instruments).

Whether sample air stream is drawn through the HEPA filter or from the main collection line, all of the air stream is channeled through the size selective inlet (SSI) canister (Figure 2, [6]). This canister can be equipped with either a PM_{10} impactor (Sierra Andersen, model 254) or a $PM_{2.5}$ cyclone (Sensidyne, Bendix 240). The PM_{10} and $PM_{2.5}$ SSI canisters are identical on the outside and in their pneumatic connections so that they are easily swapped out as needed. They require an airflow rate of 113.5 lpm to ensure their respective design size cut. Optionally, a third canister that is not equipped with an SSI can also be swapped in the event that the characterization of total suspended particulates (TSP) is of interest.

Air exiting the SSI canister is channeled through a cone plenum for distribution to multiple sample collection and analysis devices. Up to five separate sample collection devices can be used with the system as constructed, with the ability to control the flow rate through each device independently. Each sample line is connected to a mass flow controller (MFC) (Figure 3, [10]), which in turn is connected to a vacuum pump (Figure 3, [12]). A HEPA filter capsule (not shown) is located upstream of each MFC to ensure that debris does not enter the MFC sensing chamber. The MFCs are controlled with electronic hardware (Figure 3, [9]), as well as custom software operated from a portable computer (Figure 3, [13]). Filter media can be mounted into Teflon^{TM} filter holders (Savillex, 47 mm) that are inserted into the back end of the conical sampling plenum (Figure 3, [7]). A Micro-orifice Uniform Deposit Impactor (MOUDI) with seven stages (MSP Corporation, model 100-r/7) can also be connected to the sampling plenum through an adapter and a 0.5” (Pipe size) stainless steel sample line (Figure 3, [8]). The five flow-controlled sample collection lines are used to collect filter media, MOUDI samples, and provide makeup air as needed.

In addition to housing electronic hardware for the MFC control operations, the electronics enclosure (Figure 3, [9] and Figure 4) provides the necessary hardware to send actuating signals to the pneumatic ball valves, to switch the vacuum pump on and off, and to bundle all digital and analog data so that the information can be transferred and logged in the computer in real time.

Sample collection devices were supplemented with two real-time instruments: one for measuring particle size distributions and one for measuring the components of interest in the gas phase. The DustTrak DRX (TSI, model 8534, Figure 5a) is a photometer instrument that provides the mass concentration of particles in several size fractions (PM_1, $PM_{2.5}$, PM_{10}, and Total PM) with one-second resolution. It uses the 90° light scattering from a sample particle stream to estimate the particle size distribution of particles in the 0.1 to 15 micrometer (μm) diameter range. An internal pump with flow controls provides suction at the inlet with a flow rate of 3.0 lpm. It is coupled to the sampling plenum through an adapter that converts one of the filter sampling ports in the plenum to a 0.25” barb fitting. The barb fitting is connected to the DustTrak inlet through conductive, flexible tubing (≈ 6” in length).

The Testo gas analyzer (Model 350, Figure 5b) is a self-contained gas analyzer that is used in combustion and emissions analysis applications. It has an onboard pump and flow controller (1 lpm) with up to six sensors. The Testo used in this study was equipped with sensors for carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide (NO), nitrogen dioxide (NO_2), and sulfur dioxide (SO_2). The sensors have response times that are between 10 seconds (CO_2) to 40 seconds (CO and NO_2), but data are reported once per second. The instrument cycles between reading different sensors at any one time. The Testo 350 is equipped with an insertion probe (with a nominal 0.25” diameter). One of the filter ports on the sample plenum was converted to a compression fitting that would allow the Testo 350 probe to be inserted into the cone portion of the plenum.

A panel-type computer was used to control all of the mass flow controllers, pneumatic valve operations, and the power to the pump. Additionally, the computer logged the data from these devices, as well as from the TSI DRX and Testo 350 instruments. This computer was connected through a network cable to another laptop computer that was located in the control room of the Hypervelocity Lab facility, enabling an Operator to monitor and operate the instruments and controls of the sampling platform from the safety of the Control Room.

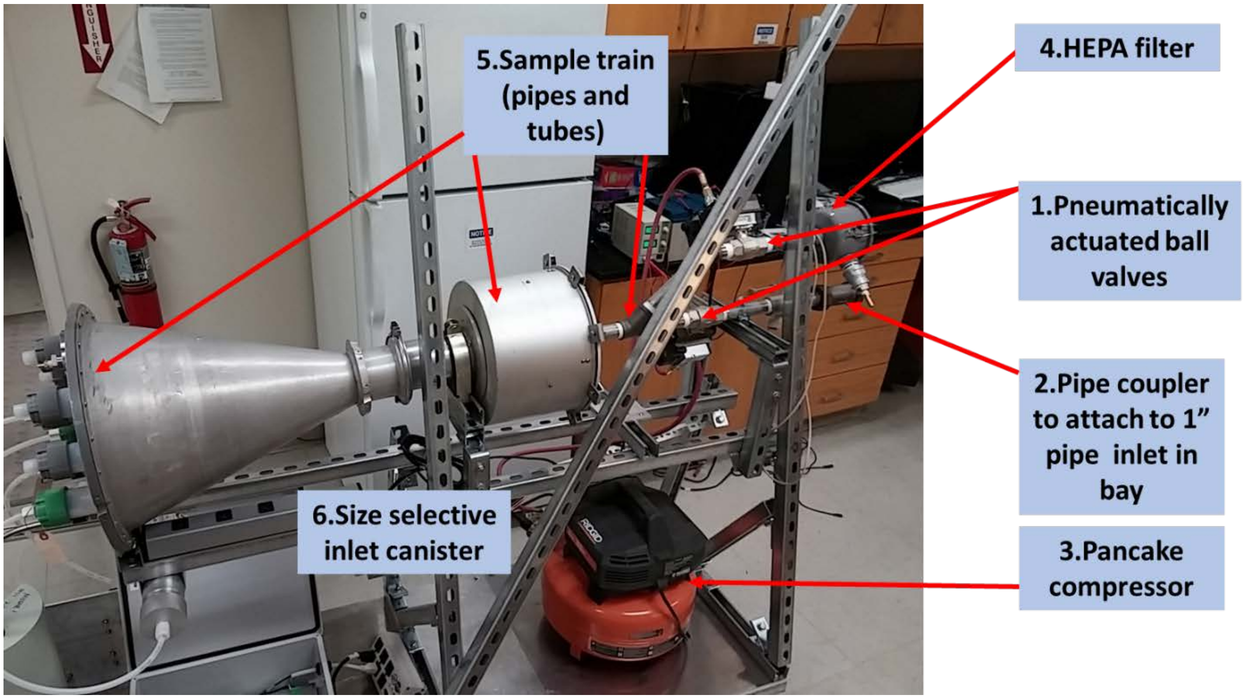


Figure 2. Overview of sample train. Air from the CCD is sampled through pipe on right and travels to the left through sample train.

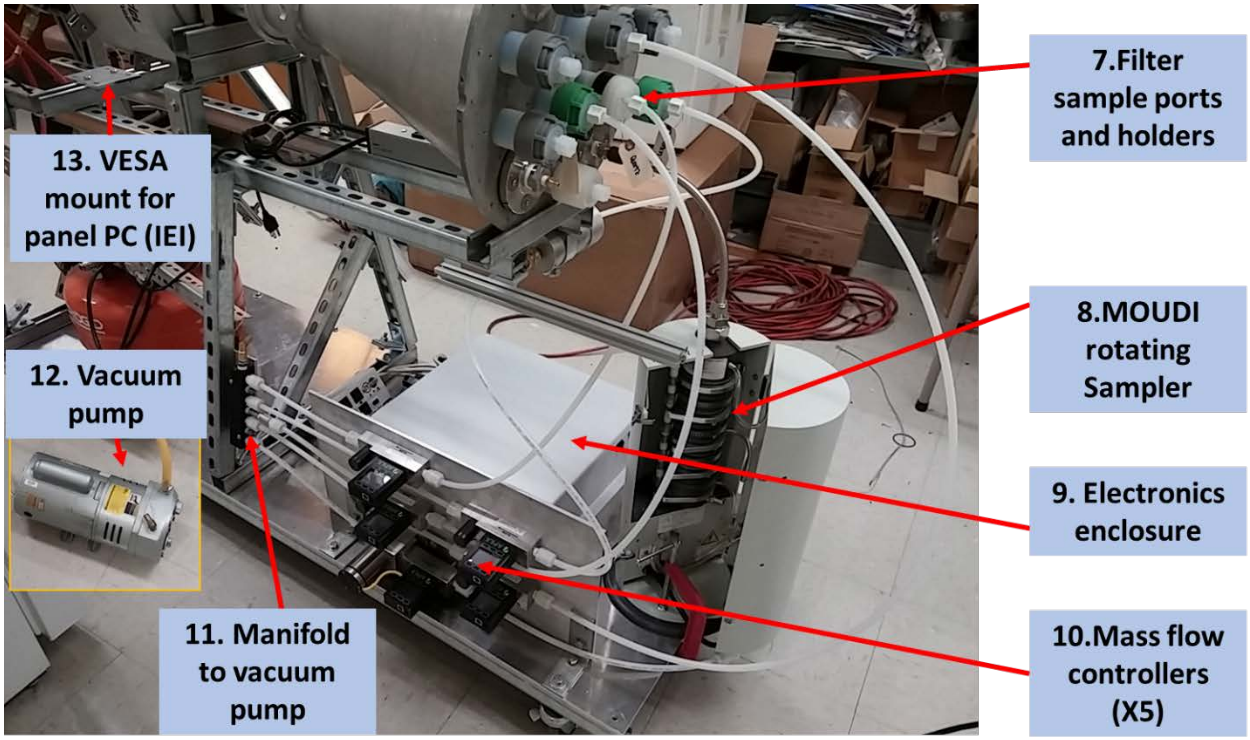


Figure 3. Back end of sample train showing sampling instrumentation and airflow control components.

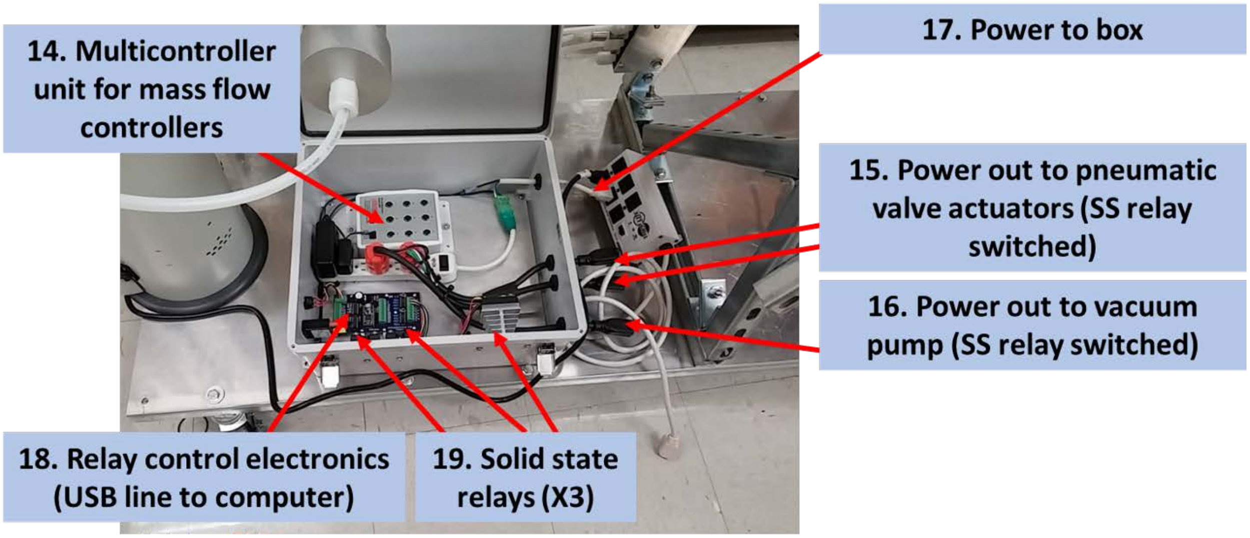


Figure 4. Contents of electronic enclosure.

a. TSI DustTrak DRX b. Testo 350 Gas Analyzer

Figure 5. Real-time instruments.

Table 1. Instrumentation used on sampling platform.

Name/Model number/ *As numbered in figures*	**Purpose**	**Computer controlled y/n**	**Electrical properties**
Pneumatic ball valves/ Durair AP0505 11 / ***1***	Direct airflow through from DTC or through HEPA filter.	Y	Solenoid actuator: 110 V input, 50 mA
Compressor/RIDGID 0F60150HA/***3***	Provide pneumatic pressure to actuate ball valves	Y	120 VAC, 12A
MOUDI Sampler/MSP Corp model 100-R / ***7***	Collect particles on different stages based on size	N	115 VAC, 3A
Mass Flow controllers /APEX AX-MCR-50SLPM-0 /***9***	Regulate the flow of air through specific sample lines	Y	24 – 30 V DC , 0.75 A, input power provided by Multi-controller
Vacuum pump/ Gast 1023-101Q-G608X/ ***11***	Provide vacuum to collect samples	Y	110 VAC, 50/60 Hz, 1 Phase, Current draw 9.2 A.
Multi-controller for Mass Flow controllers / ALICAT BB9/ ***12***	Control multiple Mass Flow Controllers and communicate by RS-232 to Panel PC	Y	Input: 110 V AC line power
Relay control electronics /NA/ ***15***	Convey commands from panel PC to actuation signals for relays	Y	5 VDC, Current draw: nominal 100 mA
Solid State relays/KYOTTO KD20C40AX /***17***	Turn pump on and off/ actuate pneumatic ball valves	Y	-Control voltage 4 – 32 V DC -Maximum output voltage: 280V -Maximum output current: 40A
Particle size spectrometer/ TSI Inc, DustTrak DRX/ **Figure 4a**	Provide particle size distribution data	Y	115 VAC, Current draw: nominal 1 A
Gas Analyzer / Testo 350/ **Figure 4b**	Provide measurement of gas concentrations (CO2, NO, CO)	Y	115 VAC, 0.45 A
Panel PC / IEI AFL-12A-N270/ **Not shown**	Control valves and record data from real-time instruments and sensors + communicate with control laptop in control room	N/A	90 – 264 VAC, 50 W power adapter
Laptop/Dell Latitude 630/ **Not shown**	Communicate from control room via cable link with Panel PC on instrument platform	N/A	90 – 264 VAC, 50 W power adapter

2.2. Sampling protocol

Measurements were conducted over a four-day period between 9/11/17 and 9/14/17 at the 1,130 cubic foot DTC located in the Hypervelocity Lab at NAWCWD China Lake, California. The laboratory and DTC are presented schematically in Figure 6 to Figure 8. The interior dimensions of the DTC are: 12’ 2” long X 12’ 2” wide and 7’ 9.5” high. The DTC has 2’ thick reinforced concrete walls, ceiling, and floor. The interior walls of the DTC are lined with 0.5" steel plate. The steel-lined DTC has explosive limits (as TNT equivalents) of 2 lbs. (910 grams) for 1.1 class energetics and 3 lbs. (1,360 grams) for 1.3 class energetics. These limits allow the detonation of shrapnel-producing items that are representative of the exterior and interior metal parts associated with ordnance. In addition, the DTC's confined volume allows for the detonation of test items containing small quantities of metals and metal coatings of interest (target metals), while still producing metal concentrations in the plume above detection limits. A set of detailed operation and safety protocols for conducting detonations in the DTC were originally developed for the Energetic Contaminated Waste (ECW) emissions characterization tests that were conducted in this facility in 2002. The safety protocols from those documents were followed for the testing reported here.

The DTC and instrumentation room at China Lake currently have the following characteristics:

- A 1" thick, airtight steel access door that is high enough and wide enough to allow easy and safe access to the DTC (Figures 6 and 7).
- A 3" diameter vent in the center of the ceiling that opens to the atmosphere, Figure 7. This vent can be equipped with a remotely activated, electrically controlled valve that allows the DTC to be pressurized or vented as desired. Additionally, a high-volume electrical vent impeller serves to expedite exhausting the DTC following a detonation test. For the tests reported here, the valve was operated manually and the exhaust impeller was operated with a manual electrical switch. Both of these tasks were completed by the NAWCWD Firing Officer.
- Two 8" and two 3" diameter ports that allow direct access to the DTC from the instrumentation room for plume sample collection equipment. Figures 7 and 8 shows the location of these sampling ports. Figure 10a shows the sampling train as installed in the instrumentation room. The entirety of these ports can be used for sample collection. However, in practice, the ports are equipped with steel 1" thick bulkhead caps that accommodate smaller, through-wall sample lines. For the tests reported here, only the large sample port on the right side of the figure was used.

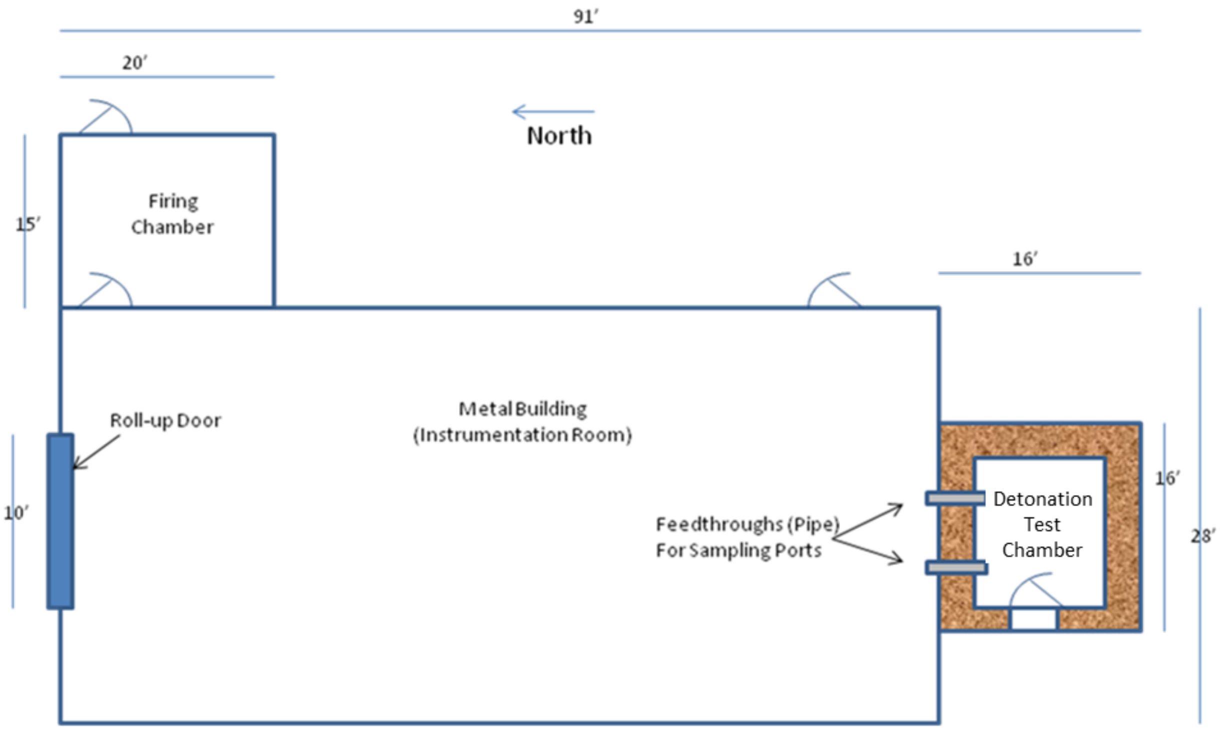


Figure 6. Overview of Hypervelocity Lab.

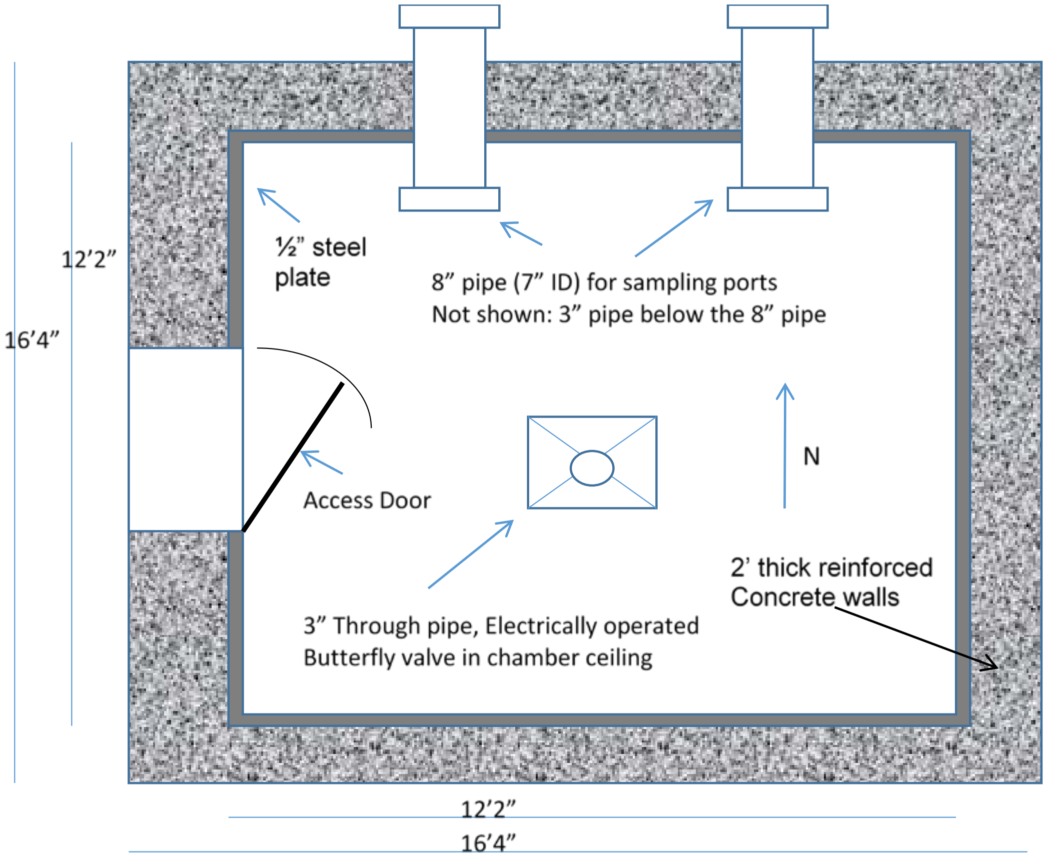


Figure 7. DTC in plan view. Sampling ports at the top of the figure connect to the work bay of the Lab.

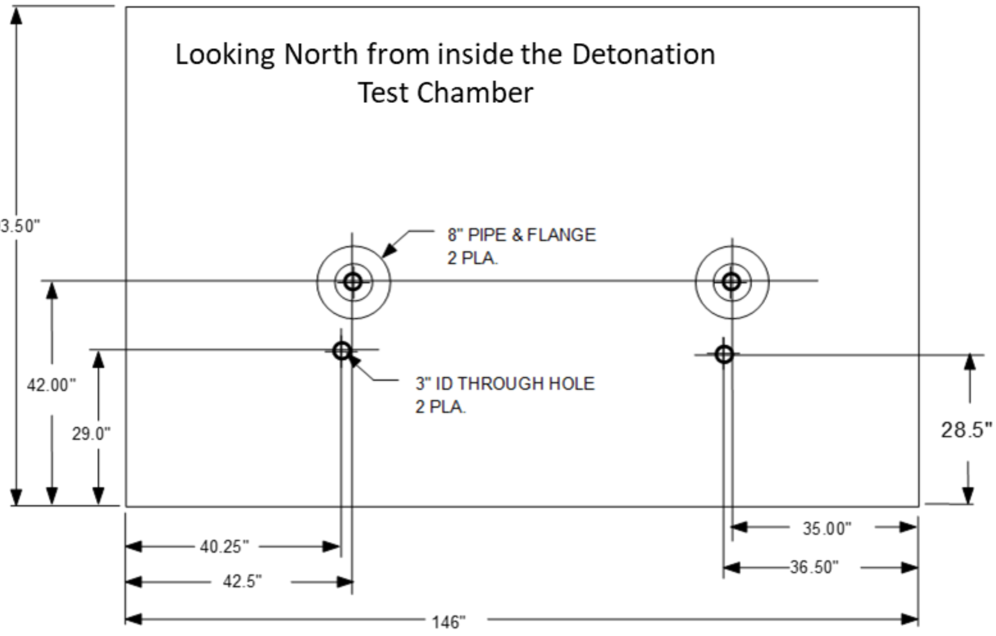


Figure 8. DTC view toward wall shared with work bay of Hypervelocity Lab.

Earlier testing (Phases I and II) not funded by SERDP that was conducted by China Lake personnel indicated that metal ordnance cases do not vaporize as the result of a detonation (Boggs et al., 2004). Instead, most of the case is ejected by the detonation as large, high-velocity fragments. During Phase I testing, it was determined that these fragments interacted with DTC walls to increase particulate levels in a manner that is not representative of OB/OD treatment operations. Because metal contaminants were considered analytes in the present tests, DTC walls were lined from top to bottom with 1 in thick Ultra High Molecular Weight Polyethylene (UHMWPE) backed by 1 in thick natural gum rubber foam. Figure 9 shows a side view of the wall liner materials. One additional layer of UHMWPE (30 cm wide) was placed along the perimeter of the DTC at a heights of approximately 1 meter (approximately at inlet height, see Figure 10b). This region was the most impacted by fragments and shrapnel. The reinforcement of the DTC at this height allowed for only the perimeter material to be replaced rather than the entire UHMWPE lining from the top of the DTC to the bottom. The perimeter material was replaced once (9/13/17) over the course of testing. Note that the sample inlet line inside the DTC was bent towards the floor at a 5° slant in order to avoid shrapnel and debris being forced into the inlet lines during the detonation event (see Figure 1).

Because of the tight clustering of the fragments on the floor, only a 3 foot by 3 foot piece was required immediately underneath where the test article was placed. As with the walls, rubber foam was compressed to maintain good contact between the UHMWPE and the steel wall. For the floor plates, two more UHMWPE plates were placed atop the plate in addition to the UHMWPE-rubber-steel sandwich. One or both of these plates was often punctured completely by fragments. These top two plates served to protect the UHMWPE-rubber-steel sandwich beneath them. They were replaced after each test article detonation. Due to the design of the charge, high velocity fragments were not directed to the ceiling of the DTC. Therefore, the ceiling did not require the addition of UHMWPE cladding.

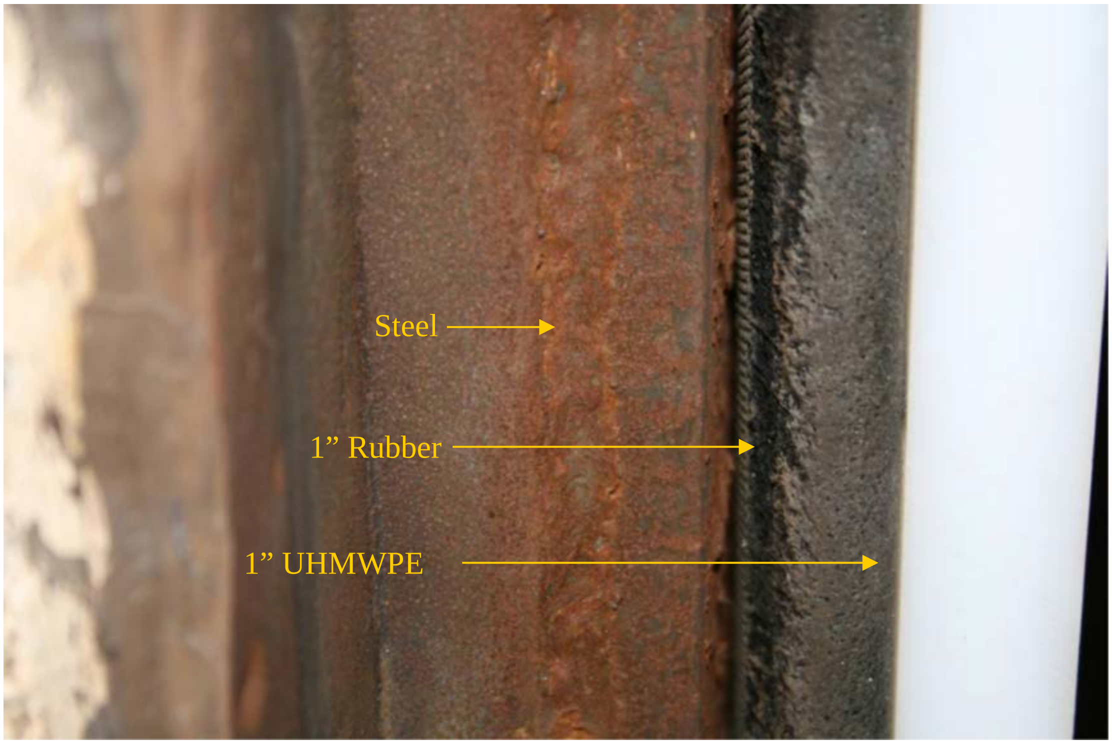


Figure 9. Side view of wall liner materials.

In between test articles, the DTC floor was swept twice to remove debris from the prior article. Sweepings were collected in a bag, but were not analyzed in this project. All wall surfaces were wiped with dry dust-removing disposable towels (Swiffer brand). Towels were discarded and replaced with fresh towels several times during each dry wiping effort, depending on soiling level. Coverage varied, but on average one towel was sufficient to clean about 50 square feet of wall area before requiring replacement. Following dry wiping, the UHMWPE surfaces were washed with cotton cloths and water. This did not completely eliminate carry over from test to test, since some debris was lodged in gouges created by testing in the UHMWPE and the gouges that existed in the DTC ceiling and floor. These gouges were difficult to clean out comprehensively. However, by the same token, the amount of debris in the gouges appeared unaffected by subsequent testing, indicating that material that had deposited in them was essentially trapped in them for all intents and purposes. Undoubtedly, some material from the previous test also remained on exposed, smooth portions of the UHMWPE. However, given the amount of material in the sweepings and the known amount of material that was in the air before the DTC was completely vented, it highly likely that the carryover amount on the smooth surfaces of the walls and ceiling was practically negligible.

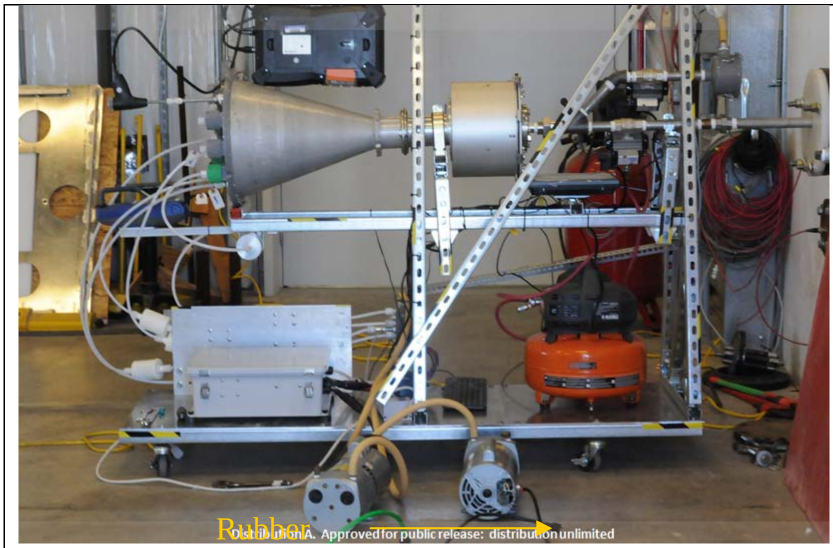
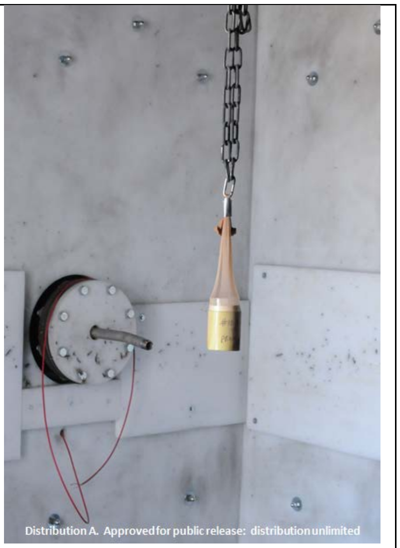
 	
a. Sampling platform connected to DTC at flange located in work bay (far right). The sample pipe goes through the DTC wall.	b. The open end of the sample pipe inside the DTC has a 5° downward bend. Also shown is a test article suspended from the DTC ceiling.

Figure 10. Sample collection apparatus as used in testing.

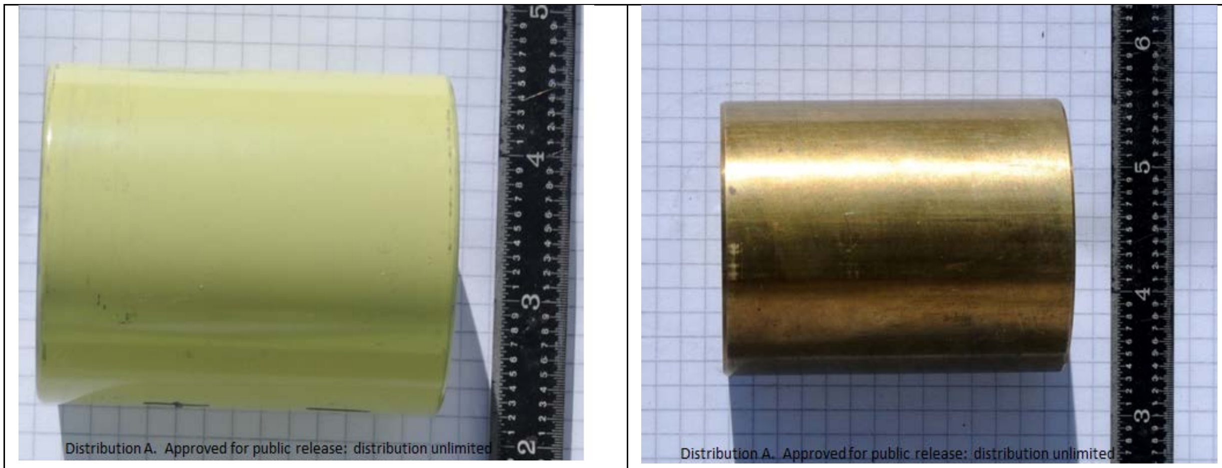
A total of 14 tests, consisting of 12 test articles, 1 booster-only-charge (pentolite), and 1 DTC blank were sampled during the measurement campaign (see Table 2). The test articles were composed of two different energetic formulations (PBXN-113 and PBXN-114) and two different types of casing (stainless steel or brass, Figure 11), resulting in four different combinations of energetic and casing. The two energetic formulations are similar and contain the commonly used HMX (1,3,5,7 tetranitro 1,3,5,7 tetrazocane) energetic along with plasticizer, binder, and catalyst agents (R45-HT [hydroxyl terminated polybutadiene], IDP [isodecyl perlargonate], IPDI [isophoron diisocynate], Lecithin, Ethanox [methylenebis tertbutylphenol], TPB [triphenal bismuth], DNSA [dinitro salicylic acid]). All test articles were prepared by the Weapons and Energetics Department, NAWCWD, China Lake, CA.

A chief difference between PBXN-113 and PBXN-114 was that the latter was aluminized through the addition of aluminum alloy powder. Additionally, test articles using the PBXN-114 energetic were modified by the addition of a thin tin disc at the bottom of the casing. The intent of the disc was to determine if any of the bulk metal would become aerosolized during the detonation. Three replicate test articles were available for each combination of energetic and casing, providing a total of 12 test articles. Pentolite is a high explosive booster (50% pentaerythritol tetranitrate [PETN] and 50% trinitrotoluene [TNT]) that was used to transfer the detonation of the “header” charge, which is activated by electrical current from the Lab Control Room to the detonation of the full test article. It was provided in the form of a 0.5 cm thick disc that was placed at the open end of the casing atop the formed energetic. Prior to detonation, the test article was encased in a suspension strap made from nylon webbing similar to hosiery material, and then hung from the center of the test DTC (See Figure 10b) at a height of 1 meter.

In each case, prior to sample collection, unexposed filters were loaded into the conical sampling plenum of the platform. The pneumatic valve controls were set to draw air through the HEPA filter capsule on the sampling platform. The vacuum pump was turned on and the mass flow controllers were allowed to reach their equilibrium set values. The total flow through the sampling platform was measured at a port located on the inlet to the HEPA filter capsule, and then compared with the total flow through all of the mass flow controllers and instruments (TSI DRX and Testo 350) to check for leaks within the system. After verification of the flow, the filter samples and other instruments were not handled again until after sample collection was complete and the airflow through the HEPA filter was maintained until sample collection was initiated. Once communication between the computer in the Control Room and the sampling platform was verified, the sampling platform was considered ready for sample collection. The Firing Officer in charge of conducting the detonation was notified of the “ready” status and the test article was prepared for detonation.

The first day of testing consisted of some “trial and error” experimentation to determine the concentration levels of product materials and optimal sampling rates. During the remaining days, airflows were set to 20 lpm each through the Teflon^{TM} and quartz-fiber filters as well as the TIGF/XAD line, 29.5 lpm through the MOUDI impactor line, and 20.5 lpm through a dummy port (no analytical filter). Combined with the 2.8 lpm airflow through the TSI DustTrak instrument and the 1 lpm flow through the Testo 350 gas analyzer, this gave a total airflow rate through the sampling plenum of approximately 113.5 lpm, which is the flow rate specified for the SSI to provide a PM_{10} size cut. Note that during tests when MOUDI impactor samples were not collected, the impactor instrument was bypassed and the same flow rate (29.5 lpm) was aspirated through a dummy sample line attached to the plenum so that the total flow through the sample plenum was the same for all tests.

On the first day of testing, sample collection was started within 30 seconds of detonation of the test article. This resulted in exceedingly high loading of filter samples, which renders the deposit on the filters prone to spalling and significantly affects measurement quality. Following some experimentation, a protocol was developed for sample collection and was used in most of the tests (see Table 2 for variations in sample collection times). The test article was detonated and the DTC was allowed to “leak out” the overpressure caused by the detonation (typically a few seconds) through imperfections in the DTC seals. Within 30 seconds of detonation, the exhaust valve was manually operated and the electrical ventilation fan was turned on. After the DTC was allowed to actively vent for 5 minutes (a total of 5.5 minutes after the detonation event), the sampling valves were switched from aspiration HEPA-filtered air to aspirating air from the test DTC. Sample collection continued for approximately 1 minute and the valves were then switched again to aspirate HEPA-filtered air. Air continued to be drawn through the sample lines for several minutes thereafter to allow all of the PM associated with the test article to clear through the sample collection train.



a. coated stainless steel

b. brass

Figure 11. Casing materials for test articles.

Table 2. Test articles and associated sample identification numbers.

Date	Detonate Time	Begin	End	Net Time (mm:ss)	Energetic	Case	Tin Disc (Y/N)	Teflon™ ID	Quartz-fiber ID	Teflon™-impregnated Glass ID	XAD ID	MOUDI Stage filters	MOUDI end filter
9/11/2017	11:35:00	11:35:29	11:37:51	02:22	PBXN-114-TJ-2	Brass	Y	CLT001	CLQ001	CLG001	I001		
9/11/2017	15:50:00	15:52:39	15:55:39	03:00	PBXN-114-TJ-2	Stainless	Y	CLT002	CLQ002	CLG002	I002		
9/12/2017	11:10:00	11:13:35	11:14:34	00:59	PBXN-113-TJ-1	Brass	N	CLT003	CLQ003	CLG003	I003		
9/12/2017	13:47:52	13:53:28	13:54:23	00:55	PBXN-113-TJ-1	Stainless	N	CLT004	CLQ004	CLG004	I004		
9/12/2017	15:14:24	15:19:56	15:20:46	00:50	PBXN-113-TJ-1	Brass	N	CLT005	CLQ005	CLG005	I005	CLI 001-009	CLTM001
9/13/2017	8:47:44	8:53:17	8:54:15	00:58	PBXN-113-TJ-1	Stainless	N	CLT006	CLQ006	CLG006	I006	CLI010-018	CLTM002
9/13/2017	10:22:21	10:27:54	10:28:49	00:55	PBXN-114-TJ-2	Brass	Y	CLT007	CLQ007	CLG007	I007	CLI019-027	CLTM003
9/13/2017	11:55:33	12:01:05	12:01:59	00:54	PBXN-114-TJ-2	Stainless	Y	CLT008	CLQ008	CLG008	I008	CLI028-036	CLTM004
9/13/2017	13:29:00	13:34:57	13:36:49	01:52	None	None	n/a	CLT009	CLQ009	CLG009	I009		
9/13/2017	14:10:30	14:16:03	14:16:57	00:54	PBXN-113-TJ-1	Brass	N	CLT010	CLQ010	CLG010	I010	CLI037-045	CLTM005
9/13/2017	15:33:25	15:38:56	15:41:07	02:11	Pentolite only	None	n/a	CLT011	CLQ011	CLG011	I011		
9/14/2017	9:28:03	9:33:35	9:34:34	00:59	PBXN-114-TJ-2	Brass	Y	CLT012	CLQ012	CLG012	I012		
9/14/2017	10:33:06	10:38:36	10:39:33	00:57	PBXN-114-TJ-2	Stainless	Y	CLT013	CLQ013	CLG013	I013		
9/14/2017	11:34:35	11:40:12	11:41:20	01:08	PBXN-113-TJ-1	Stainless	N	CLT014	CLQ014	CLG014	I014		

2.3. Chemical analyses

Prior to and following sample collection, all filter media were refrigerated to minimize the evaporation of volatile analytes. Following the experimental campaign, media were transported to the DRI laboratories in Reno, Nevada, in refrigerated coolers and stored under refrigeration while awaiting analytical procedures. Gravimetric and x-ray fluorescence analyses were completed within 3 weeks of sample collection, carbon analyses were completed within 6 weeks of collection, and the remaining analyses were completed within 10 weeks of collection.

Gravimetric analysis

Unexposed and exposed Teflon^{TM}-membrane filters were equilibrated at a temperature of 21.5 ± 2°C and a relative humidity of 35 ± 5% for a minimum of 24-hours prior to weighing. Weighing was performed on a Mettler Toledo MT5 microbalance with ±0.001 mg sensitivity. The charge on each filter was neutralized by exposure to a ^{210}Po ionizing source for 30-seconds or more prior to the filter being placed on the balance pan. Replicate weights were performed on 100% of the filters weighed before sampling (initial weights or pre-weights), and on 30% of the filters weighed after sampling (final weights or post-weights) by an independent technician.

X-ray fluorescence

The XRF analyses were performed on Teflon^{TM}-membrane filters with a PANalytical Epsilon 5, EDXRF analyzer using a side window, liquid cooled, 100 KeV, 24 milliamp dual anode (Sc/W) X-ray tube and secondary targets for: Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, W, Ir, Au, Hg, Tl, Pb, and U. The EDXRF system is calibrated using Micromatter (Vancouver, BC) thin film standards. Multi-element standards are analyzed daily to monitor for any instrument drift.

Carbon analysis (TOR/TOT)

The thermal/optical reflectance and transmittance (TOR/TOT) method measures organic (OC) and elemental (EC) carbon. The TOR/TOT method is based on the principle that different types of carbon-containing particles are converted to gases under different temperature and oxidation conditions. The different carbon fractions from TOR/TOT are useful for comparison with other methods, which are specific to a single definition for organic and elemental carbon. These specific carbon fractions are analyzed following the Interagency Monitoring Protection Visual Environment (IMPROVE_A) thermal protocol, and also help distinguish among seven carbon fractions reported by TOR/TOT:

1. The carbon evolved in a helium atmosphere at temperatures up to 140 °C (OC1).
2. The carbon evolved in a helium atmosphere at temperatures between 140 and 280 °C (OC2).
3. The carbon evolved in a helium atmosphere at temperatures between 280 and 480 °C (OC3).
4. The carbon evolved in a helium atmosphere between 480 and 580 °C (OC4).
5. The carbon evolved in an oxidizing atmosphere at 580 °C (EC1).
6. The carbon evolved in an oxidizing atmosphere between 580 and 740 °C (EC2).
7. The carbon evolved in an oxidizing atmosphere between 740 and 840 °C (EC3).

The TOR carbon analyzer consists of a thermal system and an optical system. The thermal system consists of a quartz tube placed inside a coiled heater. Current through the heater is controlled to attain and maintain preset temperatures for given time periods. A portion of a quartz filter is placed in the heating zone and heated to different temperatures under nonoxidizing and oxidizing atmospheres. The amount of carbon evolved is analyzed by optical methods. The system is calibrated by analyzing samples of known amounts of methane, carbon dioxide, and potassium hydrogen phthalate (KHP).

Ion chromatographic analysis for inorganic ions

Water-soluble nitrate, nitrite, sulfate, chloride, and ammonium were obtained by extracting a portion of the quartz-fiber particle filter (or any other filter used for sample collection) in 15 ml of deionized-distilled water (DDW). The extraction vials are capped and sonicated for 60-minutes, shaken for 60-minutes, and then aged overnight to ensure complete extraction of the deposited material in the solvent. The ultrasonic bath water is monitored to prevent temperature increases from the dissipation of ultrasonic energy in the water. After extraction, these solutions are stored under refrigeration prior to analysis.

Water-soluble chloride, nitrate, and sulfate are measured with the Dionex ICS-3000 (Sunnyvale, CA) ion chromatograph (IC). Calibration standards are prepared at least once each month by diluting the primary standard solution (Dionex Standard #57590) to concentrations covering the range of concentrations expected in the filter extracts. The calibration concentrations prepared are at 0.1, 0.2, 0.5, 1.0, and 2.0 mg/ml for each of the analysis species.

Thermal desorption (TD) and gas chromatography

The TD method was used for the qualitative and quantitative analysis of non-polar organic compounds on aerosol loaded filters. The target compounds include n-alkanes, iso/anteiso-alkanes, hopanes, steranes, other alkanes, an alkene, cyclohexanes, and polycyclic aromatic hydrocarbons (PAHs). Small strips of aerosol-laden, quartz-fiber filter material were packed into a gas chromatography (GC) split/splitless injector liner. The organic compounds on the filter were thermally desorbed in the injection port and focused onto the head of a GC column for subsequent separation and mass spectrometric detection. No instrument modification is necessary to accommodate the introduction of the aerosol organics into the GC/MS system. Compared with the traditional solvent extraction method, this injection port TD has the unique advantages of reduced labor and time by avoiding sample pretreatment and requiring less filter material for analysis (Ho and Yu, 2004).

Organic components by high performance liquid chromatography (HPLC) and gas chromatography (GC)

After sampling and prior to extraction, filters and XAD cartridges were spiked with a deuterated internal standard (acenaphthene-d10), and then extracted separately with dichloromethane followed by acetone using an Accelerated Solvent Extractor (ACE 300; Dionex). Extracts were then concentrated in a rotovap to 1 ml and filtered with Whatman™ Puradisc 25mm Syringe Filter prior to analysis.

The energetic compound known as HMX (class 5; 1,3,5,7 tetranitro 1,3,5,7 tetrazocone) was one of two analytes. HMX analyzed with HPLC (Waters 2690 Alliance System with a model 996 photodiode array detector) equipped with a Polaris column (C18-A, 3 μm, 100 mm × 2.0 mm HPLC column, Agilent). The compound known as Ethanox (methylenebis tertbutylphenol), which is used in both the PBXN-113 and PBXN-114 energetic formulations is a known toxic and was the second analyte examined from the filter/XAD sample line. Ethanox was analyzed using gas-chromatography–mass spectrometry (Varian CP-3800 gas chromatograph with Varian Saturn 4000 Ion Trap mass spectrometer system). Limits of detection (LOD) were approximately 3 Nano grams (ng) per sample for HMX and 13 ng per sample for Ethanox.

Both GC and HPLC were calibrated using standard solutions of the target compounds. The method blank was determined by spiking 20 g of Ottawa sand with 50 μL of 100 μg/mL solution of acenraphthene-d10 and 100 μL of 100 μg/mL solution of HMX, and then extracting and analyzing it using the same methods used for the field samples. The internal standard recovery was 93 ±6.5 and 91% ±6% for filter and XAD samples, respectively. Other quality assurance/quality control checks included continued calibration of the verification standard, laboratory control sample, and laboratory control sample duplicate tests. Every tenth sample was analyzed twice to check the method precision, which was better than 1%.

3. Results and Discussion

3.1. Test summaries

Summaries of the PM and gas-phase concentration measurements for each test that was conducted are provided in Table 3. Entries in the table are color coded to reflect the two different types of energetics used, as well as the blank and bare pentolite tests. The first three entries in the table correspond to tests in which the range of gas-phase and PM product concentrations were unknown a priori. During these three tests, the PM concentrations were greater than the DRX instruments upper measurement limit, most of the gaseous products were above the upper limit of the Testo 350 instrument, and many of the Teflon^{TM}, TIGF, and quartz-fiber filters were so overloaded that the deposits on them spalled off when they were removed from the testing apparatus (invalidating the data in many cases). Results from those tests are of low quality and perhaps altogether invalid.

By the fourth test, a revised protocol was established to address the filter overloading problem whereby the DTC was actively vented by an exhaust fan for 5.5 minutes following the detonation of the test article. Sample collection was then initiated and proceeded until the DRX-estimated PM loading reached 500 μg (typically approximately 55 seconds). While this change in sampling protocol did permit successful particulate sampling, it has implications for computing emissions factors. The DRI team has recognized several improvements that can be made to the DRI sampling instrumentation design to permit sampling initiation seconds after detonation, which is discussed at length in subsequent sections of this report.

After laboratory analyses were completed, it was determined that filter-based PM loadings were approximately a factor of seven or so higher than DRX-estimated loadings, so most of the filters (especially Teflon^{TM} filters) were loaded to a greater degree than is desirable to maintain the integrity of the deposit during transport and to conduct a quantitative analysis of the metals using X-ray fluorescence.

An example time series showing the DRX PM_{10} and gas-phase concentrations is provided in Figure 12. Detonation occurs at 15:14:24 (vertical dashed black line). Prior to the DTC valve opening (vertical blue dashed line before 15:20:10), CO_2 concentrations reflect the background atmospheric levels (to within the instrument error of 100 ppm). All other analytes shown are near zero. After the DTC valve opens, concentrations of analytes remain low for approximately 20 seconds as the detonation products make their way through the sample train. This is followed by a rapid rise in concentrations of PM_{10}, CO_2, CO, and NO. The two analytes, SO_2 and NO_2, remain below detection limits throughout the measurement cycle. When the valve to the DTC is closed (vertical dashed blue line after 15:20:10) and the airflow is routed through a HEPA filter, the concentrations of detonation products remain elevated for approximately 30 seconds as the clean air works its way into and replaces the detonation products within the sample train. The average concentration of the PM_{10} and gases is obtained by integrating under the entirety of the curve and dividing by the time that the sample valve is open (third column in Table 3).

A comparison of the two energetic formulations used (see Table 3, averages at bottom) indicates that there are some clear differences between the gas-phase products formed. Concentrations of CO are over an order of magnitude greater, whereas concentrations of CO_2 and NO are approximately half of what they are for PBXN-114 compared with PBXN-113. The ratio of CO to CO_2, which can be used as a gross indicator of the degree of reaction completion, is much higher for PBXN-114, indicating that less of the carbon in that energetic was totally converted to CO_2. Differences in PM_{10} concentration (whether measured by DRX or on a filter mass basis) are similar in magnitude.

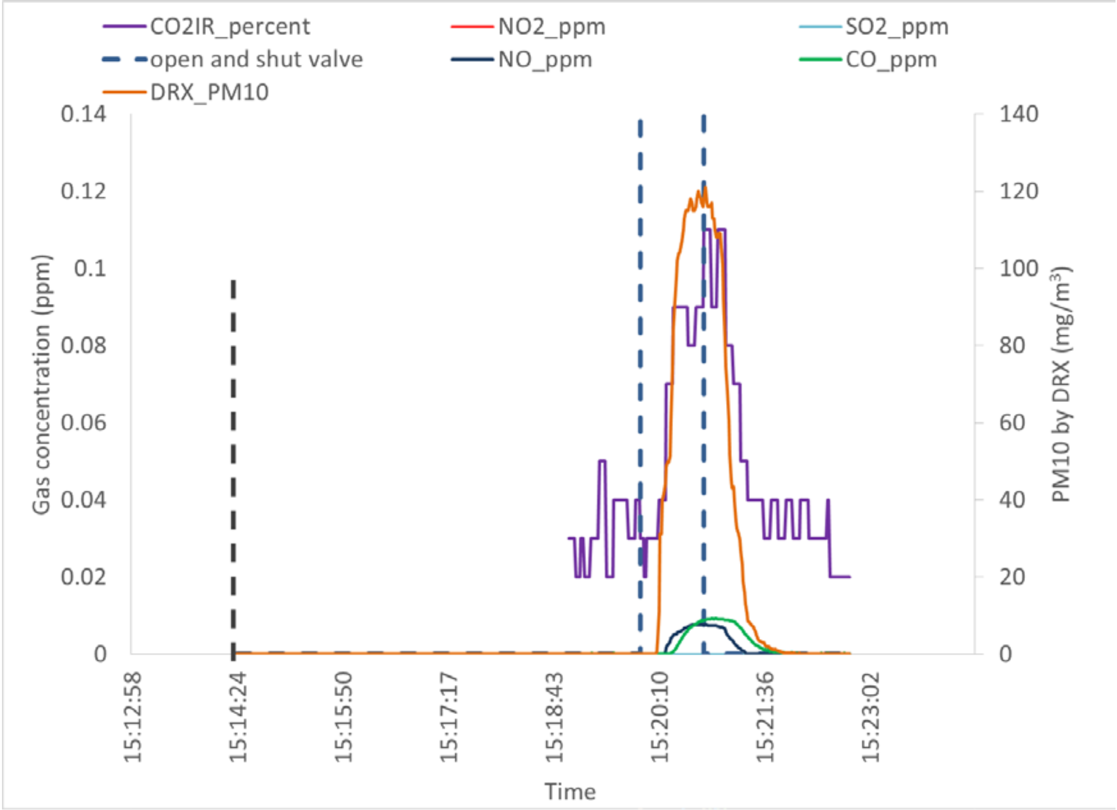


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Figure 12. Example time series of PM_{10} and gas concentrations following test article #5. Vertical, black dashed line at 15:14:24 delineates the time of the test article detonation. Sampling valve open (before 15:20:10) and close (after 15:20:10) delineated by vertical blue dashed lines.

3.2. Chemical compositions

Chemical composition data are grouped and presented by the analytical technique that was used. The X-ray fluorescence spectroscopy was limited to a subset of samples because the deposit on some of the filters collected was damaged too badly to allow analysis using this technique. Nevertheless, XRF (Figure 13 and Figure 14) revealed substantial PM_{10} concentrations of aluminum (Al), silicon (Si), iron (Fe), copper (Cu), zinc (Zn), and tin (Sn). Aluminum was the major element found in the PM_{10} associated with PBXN-113 test articles, accounting for between 27% and 32% of the total mass collected in those cases. In contrast, Sn was the dominant metal for PBXN-114 test articles, accounting for between 24% and 28% of the PM_{10} from those test articles. These large compositional differences appear to have little to do with the material used for the test article casing (i.e., stainless steel versus brass). The PBXN-114 test articles 7 (brass), 8 (stainless), 12 (brass), and 13 (stainless) all exhibit similar Sn content. It is likely that the relative enrichment of the PBXN-114 test articles with respect to Sn, is a consequence of adding a tin disc between the energetic and the casing. It appears that tin is susceptible to aerosolization under the conditions of the detonation. It is also likely that the relative enrichment of the PBXN-113 samples with respect to Al is a result of adding aluminum (H-15) particles to the energetic formulation as a detonation modifier.

Among the more trace components, PBXN-113 samples are much higher in K than PBXN-114 and much lower in Sr. Perhaps the K is associated with the aluminization powder added to the PBXN-113. It is interesting that the bare pentolite charge also resulted in a relatively high K concentration (compared with PBXN-114). Additionally, the bare pentolite charge provides levels of Fe, Ti, Cr, and Mn, which are on the same order as test articles with an energetic. The reason for this is not known. It is also unknown if the Sr is a component of the tin disc used in the PBXN-114 test articles and if this is the reason that Sr is somewhat elevated in those test articles.

Some compositional differences, associated with less abundant metals are related to the type of casing used. For example, PM_{10} samples from the brass casings used in test articles 5, 7, 10, and 12 are elevated with respect to Cu and Zn (main components of brass) compared with test articles that used stainless steel casings (8 and 13). Iron and Cr are both slightly higher in test articles with stainless steel casings. Lead was one toxic element that is of specific interest to this study because of its widespread use in some energetic and propellant primer/initiator formulations. The brass casings were approximately a factor of three higher in abundances of Pb compared with the stainless casings. It is assumed that this difference arises from constituents in the brass casing or the tin disc.

In examining the concentration of both cations (Figure 15) and anions (Figure 16), which were obtained by ion chromatography analysis of the quartz-fiber filters, the bare pentolite charge again exhibits concentration levels that are of the same order or magnitude as test articles with an energetic. It can be argued that a portion of these analytes are a consequence of particle carryover inside the DTC from the prior test (article 10) and that some of the particles from the prior test were liberated from the DTC walls and sampled on the quartz-fiber filter when the pentolite was detonated. However, given that the walls of the DTC were cleaned with both wet and dry methods between test shots, it seems unlikely that carryover from one test to the next would result in concentrations greater than 10% of the first test (it would likely be much less). Concentrations of both cations and anions in the pentolite-only sample are within approximately a factor of two of the test shot values. Overall, this suggests that pentolite is a likely major source of much of the ionic species that were detected.

Differences between the brass and stainless casings appear to be small with respect to inorganic, ionic species. PBXN-113 may result in slightly lower ammonium (NH_4^+) and sodium (Na^+) PM_{10} concentrations, but this is difficult to ascertain within experimental uncertainty.

Concentrations in the OC1–OC3 organic carbon fractions (analyzed by thermal optical reflectance of quartz-fiber filters) are comparable for PBXN-113 and PBXN-114 (Figure 17). The OC4 carbon fraction appears slightly elevated for PBXN-114 samples, but this seems to vary from shot to shot (comparing OC4 between test articles 5 and 8). Moreover, the OC4 concentration from the pentolite test shot is roughly comparable to the energetics test shots, which once again suggests that the pentolite may be a significant source of these relatively high boiling point organic compounds.

There is no ambiguity in the relative concentration of elemental carbon (EC) between the PXN-113 and PBXN-114 test articles, with the latter exhibiting concentrations of this sooty type of carbon that are an order of magnitude greater. This is consistent with observations in the field, where it was noted that the residue from PBXN-114 detonations was considerably sootier and had a slightly oily feel. Given that the two energetics are very similar in composition, it would appear that the aluminization of the PBXN-113 greatly suppresses the formation of soot that is observed in the detonation products of PBXN-114.

Analysis of the organic compounds from TIGF filters and the XAD resin was focused on two compounds that were determined to be potential health concerns. The selection of those compounds was based on the composition of the energetics used and the assumption that some portion of the organic constituents would remain unreacted after detonation, potentially posing a health risk. The main energetic compound HMX was detected on the TIGF filters from test article shots 1, 2, 3, and 4. Ethanox was not found above detection limits in any of the TIGF samples. None of the XAD samples registered either compound above detection limits.

Overall, the collection of organic samples was conducted as a proof of concept for the sampling technique. The test was successful, but the process did underscore the importance of knowing in advance which organic compounds are going to be of interest. Unlike the inorganic analyses, analytical techniques for organics are more specialized for compound classes and generally more expensive. Therefore, the target analytes or family of analytes should be well-known prior to commencing analysis. Related to this, the collection of canister samples in addition to or instead of TIGF/XAD samples may broaden the range of analytes that can be sought. Canister samples are collected by allowing sample air to be aspirated into evacuated, clean stainless steel canisters. The contents of the canister are later processed to target specific aerosol and gas compounds (e.g., BTEX).

3.3. Particle sizes

The particle size distributions as measured by MOUDI for five test shots are summarized in Figure 18. Panels a, b, and e show the particle sizes measured for the PBXN-113 shots and panels c and d show the same information for two PBXN-114 shots. The overwhelming majority (between 83% and 95%) of PM mass that was measured was associated with particles smaller than 1.8 μm in aerodynamic diameter (corresponding to MOUDI stage 4 through the after filter). This is not unexpected since aerosol products of chemical reactions, such as combustion and oxidation, are usually sub-micrometer in size. The PBXN-113 samples have a distinct, sharp peak associated with 0.3–0.5 μm particles. The PBXN-114 samples have a broader peak that spans from 0.3–1.8 μm. Given the previous observations about elemental carbon content, it is reasonable to expect that many—and perhaps the majority—of these particles are composed of compounds similar to soot.

The beginnings of a second mode are evident in the MOUDI particle size distributions, which correspond to particles that are larger than 5.6 μm but smaller than 10 μm (because the entire sample stream was subjected to a 10 μm size selection stage). These larger particles are typical of aerosols that are generated by mechanical forces. In this study, these could be portions of energetic material that were sheared off without achieving detonation, pieces of casing and other metal components, or fragments generated from the DTC walls.

For each of the five test shots with MOUDI data in Figure 18, equivalent data from the TSI DRX instrument are also shown for comparison. Overall, the DRX—which has much coarser size fractionation data (PM_1, $PM_{2.5}$, PM_4, and PM_{10})—tends to attribute much more of the aerosol mass to larger particles, with over 60% attributed to particles between 4 and 10 μm in size. It is possible that the MOUDI suffers from some particle losses in the sample line, especially in the larger size fractions because there is a 90° bend in the line between the sample plenum and the MOUDI. This could explain why the DRX measured higher concentrations for larger particles. However, because the DRX uses particle light scattering to infer mass concentrations and size distributions, it is also possible that the DRX is reporting incorrect data. Another observation is that the DRX does not provide much size resolution in the size ranges of greatest interest for human health effects (0.01 to 2.5 μm), offering only a PM_1 and a $PM_{2.5}$ measurement. Overall, this study demonstrates the utility of the DRX as a real-time particle concentration indicator and the MOUDI as a means of collecting mass-based size data (and possibly chemistry). In future iterations, the design of the sampling platform should be optimized to ensure minimal particle losses for the MOUDI or any other instrument that is designed to measure the size distribution.

Table 3. Summary of test article concentrations of PM and gas-phase constituents[a].

Article	Delay between detonation & sample (mm:ss)	Sample length (m:ss)	PM_{10} by DRX[b] (mg/m^3)	PM_{10} from filter (mg/m^3)	NO (ppm)	CO (ppm)	ΔCO2[b] (ppm)	CO:ΔCO2 X 1000	NO:ΔCO2 X 1000
1-PBXN-114-TJ-2 Brass[c]	0:29	2:22	169.4[b,c]	875[e]	24.10	421.9	2042[c]	207	11.8
2-PBXN-114-TJ-2 Stainless[c]	2:39	3:00	81.2[b,c]	510[e]					
3-PBXN-113-TJ-1 Brass[c]	3:35	0:59	88.1[b,c]	664[e]	22.69	31.8	1808	17.6	12.6
4-PBXN-113-TJ-1 Stainless	5:36	0:55	37.7	266[e]	5.95	14.2	719	19.7	8.3
5-PBXN-113-TJ-1 Brass	5:32	0:50	40.8	364[e]	7.20	9.6	721	13.4	10.0
6-PBXN-113-TJ-1 Stainless	5:33	0:58	34.2	269[e]	5.58	12.8	662	19.4	8.4
7-PBXN-114-TJ-2 Brass	5:33	0:55	38.2	236	1.76	160.1	269	595	6.6
8-PBXN-114-TJ-2 Stainless	5:32	0:54	34.0	213	2.53	171.8	500	344	5.1
9-DTC Blank	5:57	1:52	0.1	5					
10-PBXN-113-TJ-1 Brass	5:33	0:54	32.2	322	8.15	10.1	815	12.4	10.0
11-Bare Pentolite charge	5:31	2:11	5.7	34	3.87	6.9	486	14.3	8.0
12-PBXN-114-TJ-2 Brass	5:32	0:59	30.3	248	4.48	192.6	443	434	10.1
13-PBXN-114-TJ-2 Stainless	5:30	0:57	31.7	269	1.73	205.6	304	677	5.7
14-PBXN-113-TJ-1 Stainless	5:37	1:08	30.0	213	6.67	14.8	631	23.4	10.6
Average PBXN-113 (excl. article 3)[c]	5:34	0:57	35.0	286.9	**6.7**	**12.3**	**710**	**18**	9.4
Average PBXN-114 (excl article 1,2)[c]	4:25	0:56	33.6	241.3	**2.6**	**182.5**	**379**	**512**	6.8

[a] All concentrations were corrected to account for time lags in concentration measurements that result from the finite mixing volume of the sample train.

[b] PM_{10} by DRX is provided for reference purposes only. It is expected that PM_{10} by filter analysis is more accurate estimate of concentrations.

[c] Concentrations of PM and gases during the testing of first three articles were higher than the measurement ranges of the DRX and Testo 350 instrument. Additionally, filter loadings on Teflon™ filters were exceedingly high and the deposits were damaged during transport to the laboratory for weighing and analysis. Accordingly, data from these three articles are not included in the averages for PBXN-113 and PBXN-114.

[d] CO_2 concentrations measured during sample collection were background corrected by subtracting the average CO_2 concentration as measured for one minute prior to the test article detonation. Therefore, concentrations shown in the table can be considered incremental contributions from the test article detonation.

[e] Deposit on Teflon™ filter damaged. PM mass concentration values represent underestimates of actual measured concentrations.

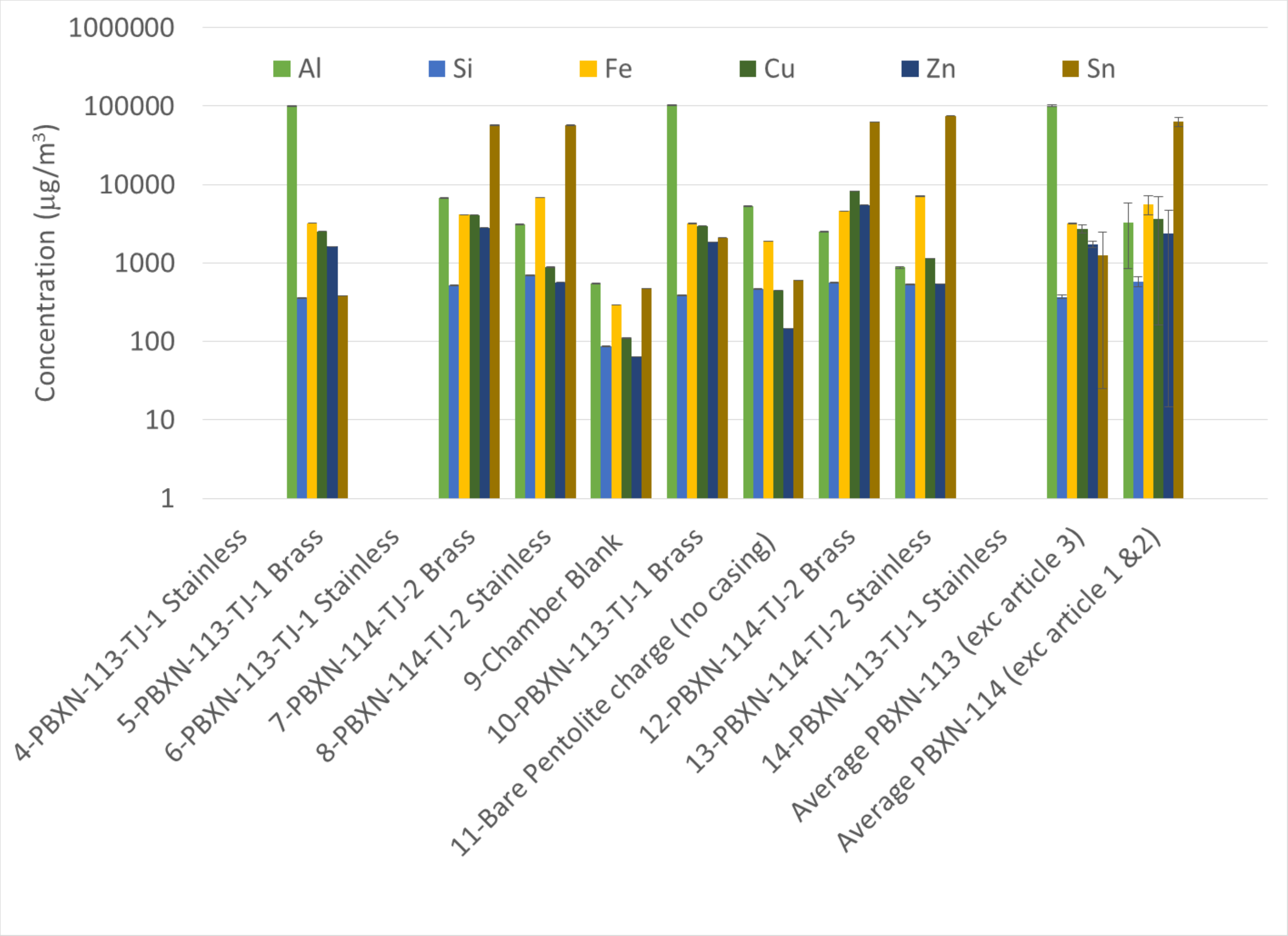


Figure 13. Major metals as measured by X-ray fluorescence (XRF) per sample and for PBXN-113 and PBXN-114 composites. Vertical bars for individual samples correspond to analytical uncertainty. Vertical bars for composites are standard deviations for all samples in the average. Test articles 1-3 not included because of heavy loading. Test articles 4, 6, and 14 could not be analyzed because of delamination of deposit from Teflon^{TM} filter during transport.

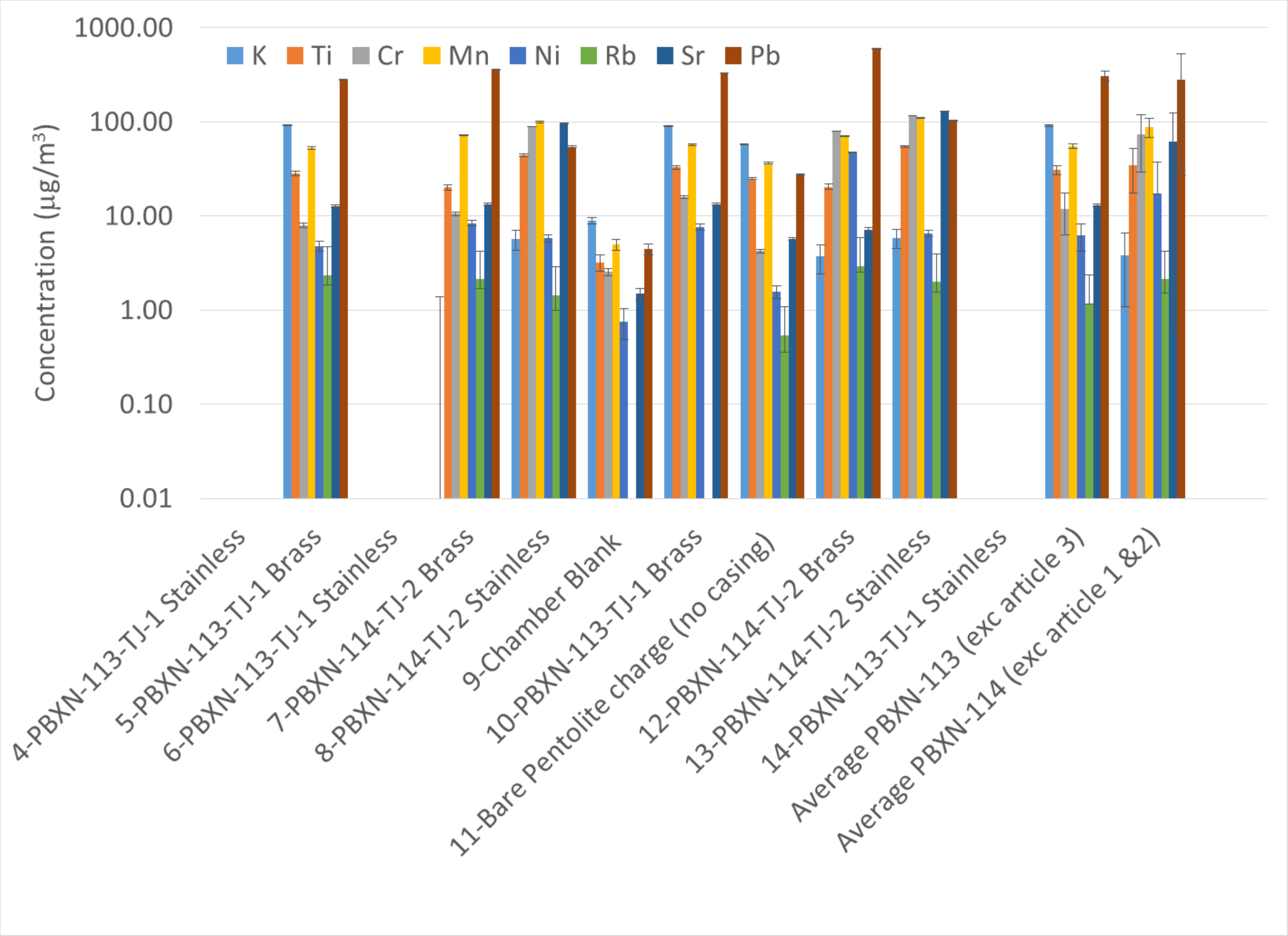


Figure 14. Minor metals by mass fraction as measured by X-ray fluorescence (XRF) per sample and for PBXN-113 and PBXN-114 composites. Vertical bars for individual samples correspond to analytical uncertainty. Vertical bars for composites are standard deviations for all samples in the average. Test articles 1-3 not included because of heavy loading. Test articles 4, 6, and 14 could not be analyzed because of delamination of deposit from Teflon^{TM} filter during transport.

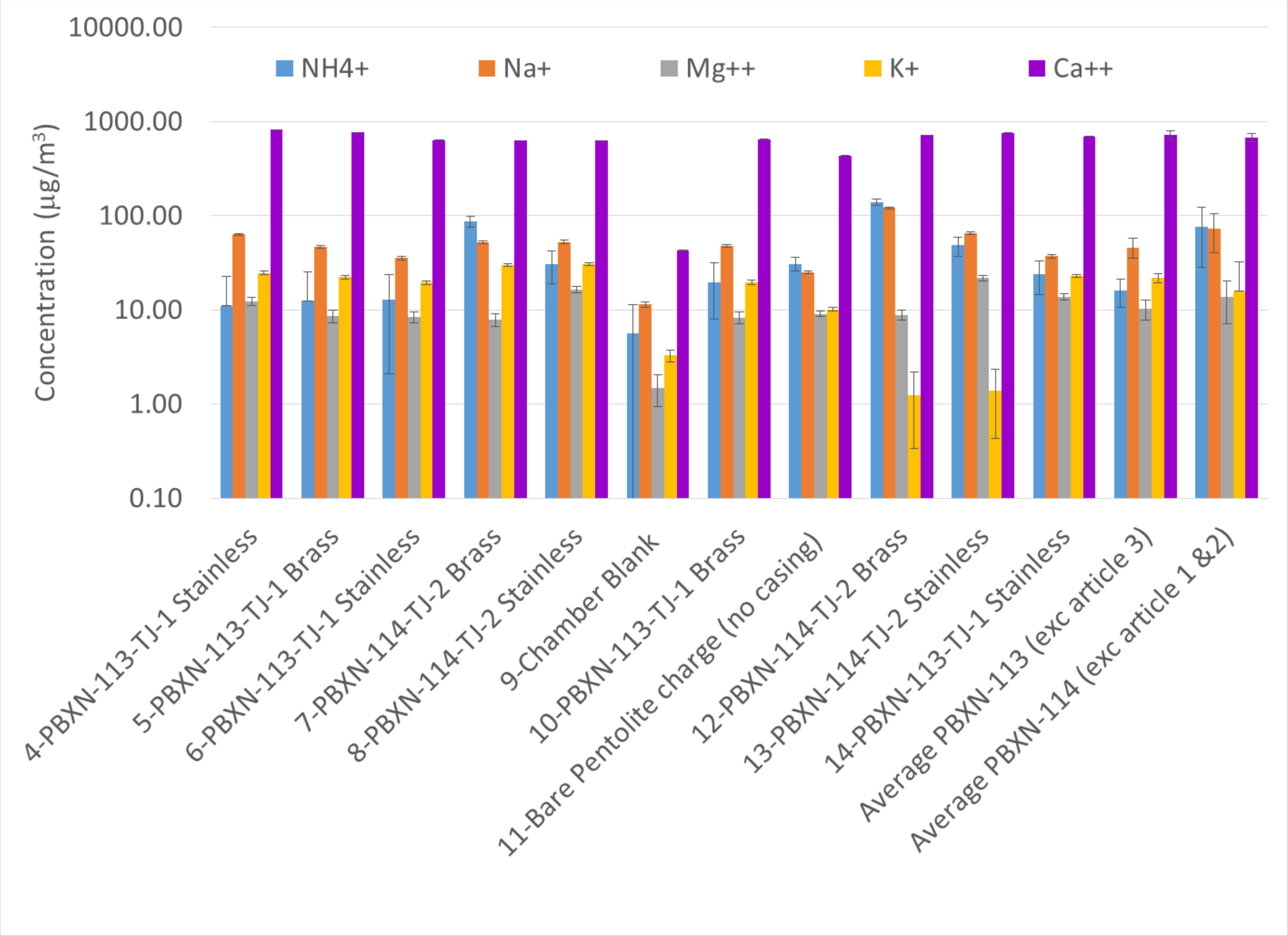


Figure 15. Cation concentrations by sample and for PBXN-113 and PBXN-114 composites. Vertical bars for individual samples correspond to analytical uncertainty. Vertical bars for composites are standard deviations for all samples in the average. Test articles 1-3 not included because of heavy loading.

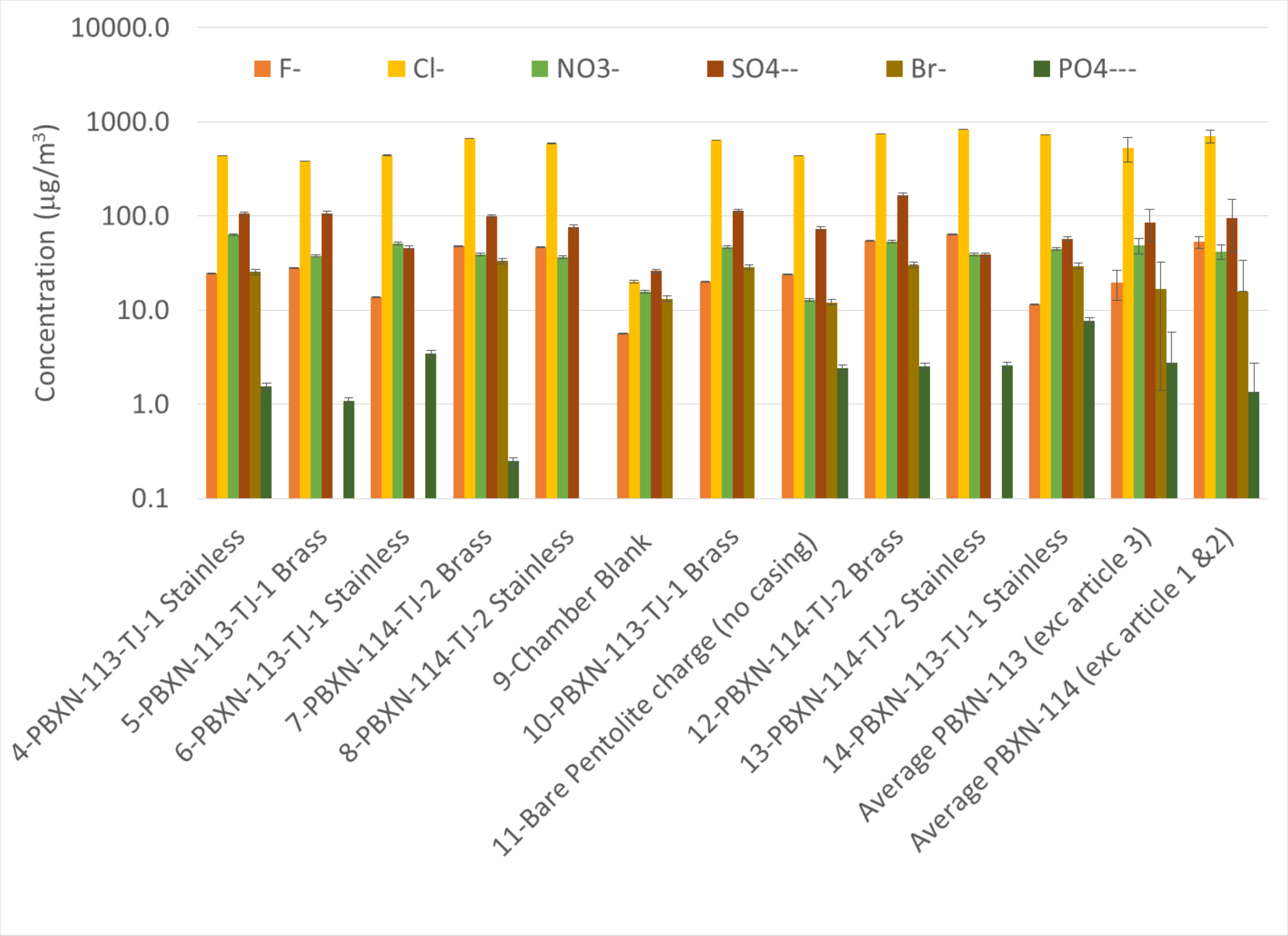


Figure 16. Anion concentrations by sample and for PBXN-113 and PBXN-114 composites. Vertical bars for individual samples correspond to analytical uncertainty. Vertical bars for composites are standard deviations for all samples in the average. Test articles 1-3 not included because of heavy loading.

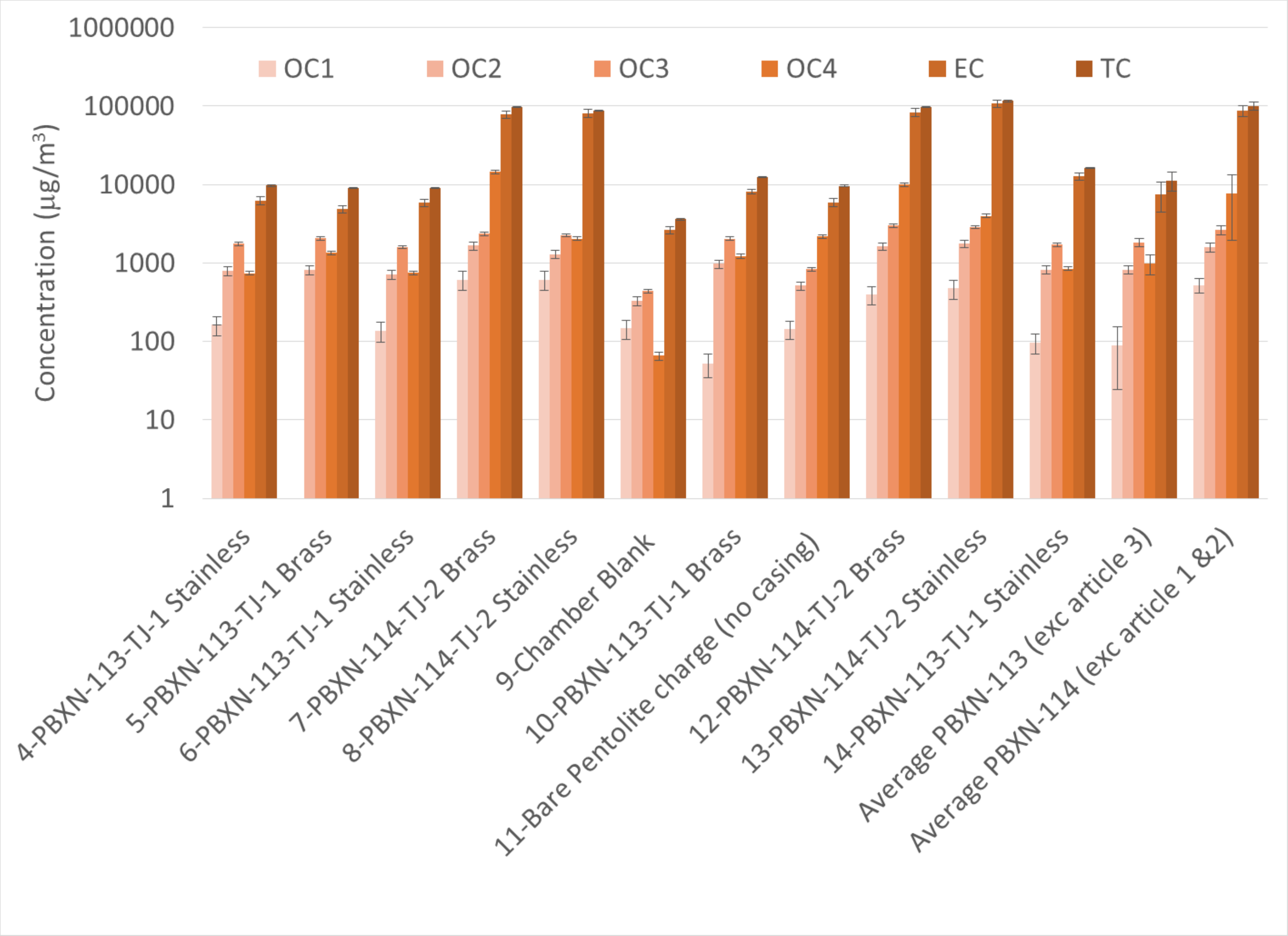
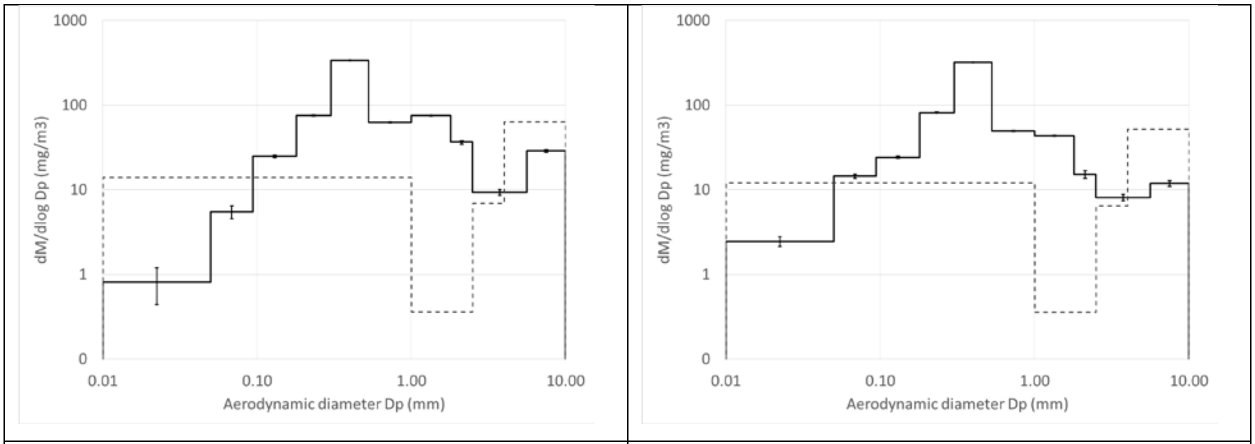
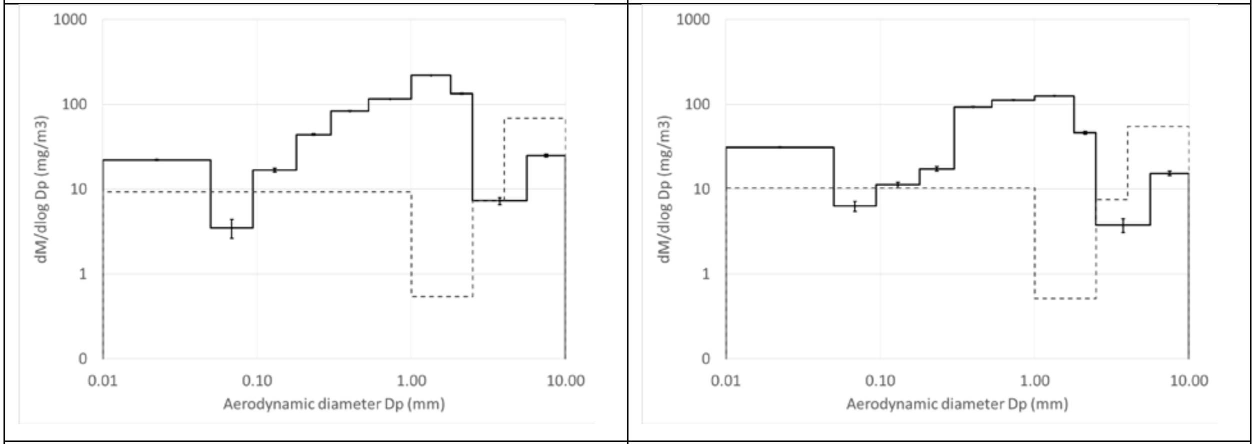


Figure 17. Organic carbon fractions (OC1-4), elemental carbon (EC), and total carbon (TC) by sample and for PBXN-113 and PBXN-114 composites. Vertical bars for individual samples correspond to analytical uncertainty. Vertical bars for composites are standard deviations for all samples in the average. Test articles 1-3 not included because of heavy loading.



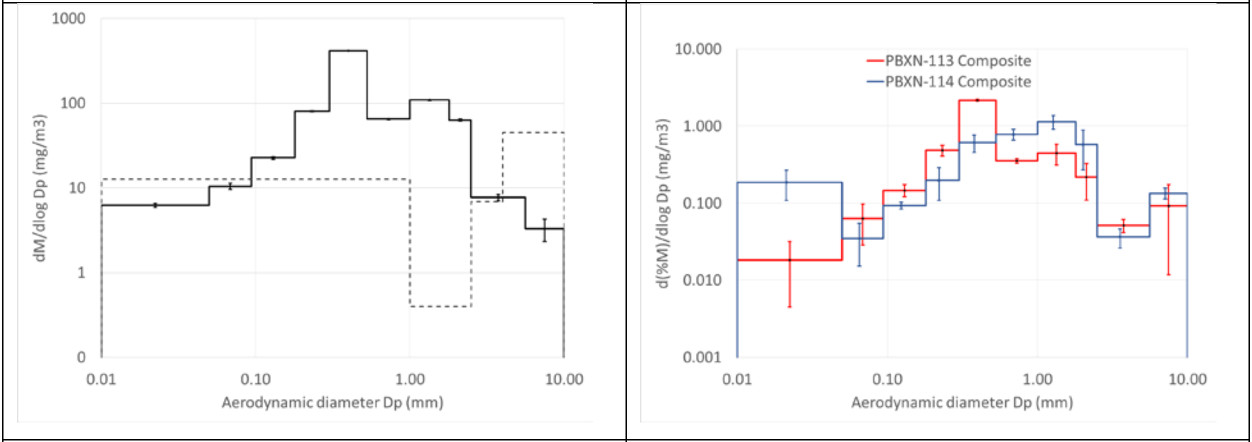
a. 5-PBXN-113-TJ-1 Brass

b. 6-PBXN-113-TJ-1 Stainless



c. 7-PBXN-114-TJ-2 Brass

d. 8-PBXN-114-TJ-2 Stainless



e. 10-PBXN-113-TJ-1 Brass

f. Composite PBXN-113 and PBXN-114

Figure 18. Particle mass size distributions for test articles 5, 6, 7, 8, and 10 (a-e) from MOUDI sampler with vertical bars representing analytical uncertainty; dashed line is equivalent data from DRX instrument. Panel f shows a composite mass fractional size distribution for PBXN-113 and PBXN-114 with vertical bars corresponding to standard deviations of fractional distribution between samples.

3.4. Discussion

The results and experience of this SEED project are instructive for implementing improvements in the sample collection protocol, as well as informing how future data collection can include a wider range of articles that use energetic, propellant, and pyrotechnic compounds in their makeup. These are addressed separately below.

Technical performance of sampling platform and areas for improvement

Overall, the sampling instrumentation that was developed for use in this SEED project performed quite well for the intended purpose. Electrically and pneumatically, the platform functioned as intended. The control software that was developed for the platform and the network communications between the platform and the remote display/control interface in the control room of the laboratory worked as designed. Electromechanical devices—such as the pneumatic valves, mass flow controllers, and pump relays—operated without any failures. Electronic data collection and storage from real-time instruments also worked well. Procedures established prior to testing and honed on the first day for loading/unloading filters, checking flow rates, assuring instrument data quality, and coordinating activities and safety with the Firing Officer for the tests were efficient and effective. Laboratory analysis techniques were established prior to the initiation of this project and have been in long-standing use at DRI's Environmental Analysis Facility and Organics Analysis Lab, so they were already known to work well. As testing proceeded, some design improvements became evident that should be incorporated in the future.

There were several notable positive attributes of the sampling platform. First, the flow rates through the sampling platform as a whole (113.5 lpm) and through the individual filter sample lines (20.5 lpm) were relatively high, compared to low-flow sampling platforms such as those used on aerial platforms (e.g., Gullett et al. [2016]). This allowed for rapid collection of PM sample material well above the detection limits in a short amount of time. In several of the early tests, filters were overloaded and unusable. However, it is straightforward to reduce the filter loading by a factor of 10 or 20 if needed, as long as the total flow through the sample line remains at the design flow rate of the PM_{10} SSI.

This leads to the second positive attribute of the system, which is that the flow rate through each of five sample lines could be independently varied (1–27 lpm for four lines, and 1–52 lpm for the fifth line). This built in flexibility in flow distribution through the five independent mass flow controllers allows for varying the loading on all or any of the filter samples by more than an order of magnitude. This is especially helpful in the event that some sample medium requires much lower or higher loading rates than other media used (e.g., samples collected for scanning electron microscopy require loadings that are much lower than is needed for bulk chemical analyses). Although not envisioned as necessary, the potential does exist for additional scalability and flexibility because additional mass flow controllers from the same manufacturer can be added to other filter ports on the sample plenum (18 ports total) and "multiplexed" into the same control electronics easily (up to 50 flow meters). Flow rate ranges can be reduced to as low as 0.001 lpm using low flow controllers if the need ever arises.

A third advantage of the system as used was that it was possible for all of the instruments and filter collection media to be operating and aspirating air at the design flow rate before and during the detonations of the test article. This was enabled by the dual pneumatic valves that direct either sample air from the DTC or HEPA-filtered air from the working bay of the facility. This feature is helpful because it ensures that all instruments are functioning properly before the detonation and because it eliminates the need for the mass flow controllers to converge on their design flow rates (as happens when the flow is first activated), which takes several seconds or longer. Related to this point, a fourth advantage is that the measurement platform was built to be a rugged field instrument that can withstand the rigors of pressure fluctuations and vibrations from exploding test articles in the DTC. Sensitive instruments are housed behind a pneumatic valve that is closed during the detonation and ensuing over-pressure period in the DTC and are, in effect, protected from potential damage.

One advantage listed previously was that the sample flow rate through the filter media was relatively high, allowing for the collection of a significant sample volume in a relatively short period of time. For example, a filter collecting at 20 lpm for 5 minutes would aspirate 100 liters of sample air. If the PM_{10} concentration is 5 mg/m^3, then the filter would collect 500 μg of particles, which would be sufficient for conducting a range of chemical analyses. However, when testing was started, it became very clear that our estimate of PM_{10} concentrations (on the order of a few mg/m^3) were grossly low and that the actual concentrations immediately after detonation were two to three (possibly more) orders of magnitude greater. Because all of the test articles had been assembled prior to the beginning of testing, it was not logistically feasible to reduce the amount of energetic placed into the test articles (say, by a factor of 10 or more). However, it was necessary to adjust filter loadings to avoid grossly overloading the filters, which would result in the deposit falling away from filters and not being available for analysis; overwhelming some of the analytical instruments such as the XRF; or loading the filter enough to choke the flow to the point that the total flow through the sampling instrument was affected. An adjustment was made in the field, whereby after the detonation of the test article, the DTC was actively vented by an exhaust fan for 5 minutes and then sample collection was initiated. This adjustment highlighted a major shortcoming that should be addressed in a future revision of the sampling protocol.

When it was assumed that sampling of the detonation products would begin essentially immediately after the detonation event (allowing a few seconds to allow for the overpressure to be relieved by leaks in the DTC), then the assumption of mass conservation could be invoked. That is, it could be assumed that the concentrations being sampled within the DTC were a result of all of the detonation products being mixed into the volume of the DTC and a simple mass closure calculation could be conducted to relate the amount of PM_{10} material found on filter samples to the total amount of PM_{10} that was suspended in the DTC. This in turn could be related back to the mass of energetic, thereby providing an emission factor (mass of PM_{10} released per mass of energetic). The reason this was considered possible is that the volume of the DTC was large enough that the extra gases produced by the detonation would result in a comparatively small amount of extra gas volume that has to be leaked for the DTC to return to atmospheric pressure. For example, consider that a 200 g test article that is composed entirely of HMX (MW = 296) would contain 0.67 moles of the compound. Based on compositions of products reported by Ornellas (1967), each mole of HMX produces 1.92 moles of CO_2 (MW =44.0), 1.06 moles of CO (28.0), 1.68 moles of N_2 (28.0), 3.18 moles of H_2O (18.0), and other solid and trace gas products. Therefore, 0.67 moles of HMX (200 g) would produce approximately 6.7 moles of gas products. At standard temperature and pressure (STP), one mole of gas occupies approximately 22.5 liters, so 6.7 moles would occupy approximately 148 liters or 0.148 m^3. Noting that this volume of gas is quite low compared with the volume of the DTC (32.6 m^3), we can be assured that the temperature of the DTC does not increase significantly (a few °C perhaps) and that the loss of detonation products that results from this small leakage of excess volume would have a negligible impact on the total mass of the detonation products. That is, one could safely assume that what is measured in the DTC immediately after the pressure equalizes with the outside ambient pressure (after a few seconds) very nearly reflects the totality of products from the detonation event.

Changing the sample collection start time to several minutes after detonation, when the exhaust fan had been operating for some time, meant that the mass closure assumption was no longer valid. Given the sampling apparatus that was in place, there was no way to monitor how much of the detonation products had left the DTC by the time sampling started. In turn, this meant that an accurate emission factor could not be calculated based on mass conservation alone.

The technique of a “fuel-based” emission factor was also not possible to use. This type of approach is used in combustion science. The premise is that the overwhelming majority of carbon in the fuel is converted to CO_2 during the combustion process. Therefore, the ratio of concentration of PM_{10} to CO_2 (above background), for example, is equivalent to the ratio of PM_{10} products to carbon in the fuel. In this way, a “fuel-based” factor can be calculated. However, this approach could not be implemented for this study because it was not clear what fraction of the carbon in the energetic ended up as CO_2 and what fraction ended up as different, unquantified constituents. For example, Table 3 and Figure 17 indicate that the concentration of PM_{10} carbon was not necessarily negligible compared with the concentration of CO_2. Moreover, it is unknown how much carbon may be associated with larger fragments of detonation products that were not sampled by the sampling apparatus, but rather fell to the DTC floors.

If it is desirable to obtain emission factors for test articles that do require that the DTC be vented for some time prior to the beginning of sample collection, there are two methods that can be implemented to accomplish this testing. The first is by introducing a tracer gas into the DTC immediately before the detonation (as suggested by Erickson et al., [2005]). An inert gas, such as helium, could be added to the DTC and the concentration of the gas immediately before detonation could be measured. Following detonation and venting, the concentration of the inert gas can be measured along with sample collection. The change in the concentration of the inert gas between the time immediately prior to detonation and when sampling is occurring can be used to calculate the amount of dilution that the detonation products had undergone. This in turn can be used to estimate the total PM_{10} and gas-phase species mass of detonation products, which can be related to the total mass of the test article.

The second method would be to have a completely separate, simplified “monitoring” sample line with in-line dilution of the sample air. This would be connected to the DTC independently of the main sampling apparatus. Immediately following detonation, a valve would allow for the aspiration of the sample air in the DTC. The aspirated air would be actively diluted by mixing with clean air (say 50:1 dilution). The diluted air would be sampled by a real-time PM monitor (e.g., DRX or equivalent) and a real-time, gas-phase monitor. This would serve two purposes. It would allow for real-time monitoring of the concentrations of PM_{10} and gases in the DTC so that the main sampling apparatus can be operated when concentrations fall into an optimal range. It would also allow for estimating the total amount of dilution that the detonation products would have undergone by the time the main sampling apparatus is used to collect PM_{10} and gas-phase products. This method is preferable over introducing an inert tracer gas into the DTC for several reasons. First, a gas such as helium is more buoyant than air and requires that it be actively mixed into the DTC to ensure uniform distribution. Second, an additional analytical instrument (with all the associated uncertainties) would be needed to quantify the tracer gas. Such an instrument can be subject to unforeseen interferences from the relatively high concentrations of other product gases in the DTC.

There were a few additional, more minor shortcomings of the sampling platform that were identified for potential improvement. The Testo 350 gas analyzer was adequate for the SEED project. However, for longer term testing, it would be desirable to have dedicated gas analyzers that are more accurate for their respective analytes and that are designed to operate more seamlessly in conjunction with serial communications. Notably, a CO_2 analyzer with 10 ppm or better accuracy would be desirable on the main sampling platform. Analyzers for CO and oxides of nitrogen could also be added as standalone instruments within the existing platform. An instrument such as the Testo 350 could be used for the extra "monitoring" sample line described above.

Similarly, the DRX instrument was useful for examining the change in PM_{10} plume over time, but the concentrations of PM_{10} estimated by the DRX were not consistent with those obtained by filter sampling. Given this, either a simpler instrument that has higher limits for PM (e.g., DustTrak 8530) or a more accurate, real-time instrument for mass characterization and particle size distributions (e.g., TSI APS) can be used as an independent check on the filter samples that are used to estimate mass concentrations.

In terms of filter media, a recurring problem was that the deposits on Teflon^{TM} filters readily spalled off, causing large uncertainty for half the mass concentration measurements and altogether prohibiting meaningful XRF analyses for those samples. This would be addressed to a large degree with the improvements in sample collection that are discussed above, which would limit the extent of the deposit on the filter. However, it may be that a more suitable medium is still needed for this type of testing. We note that the Teflon^{TM}-impregnated, glass-fiber filters were not subject to the same degree of spalling. Those filters were not pre-weighed prior to use because they are typically not used for gravimetric analyses. These types of filters should be investigated as possible replacements for the Teflon^{TM} filters (for mass concentrations only as TIGF is not compatible with XRF).

As can be seen by the very small analytical uncertainty bars in Figure 13 through Figure 18, concentrations were well above the detection limits by several orders of magnitude for many of the species that were measured including Pb, Cr, Ni, Cu, and Mn. A list of analytical detection limits by method is provided in Appendix A for some inorganic species and some organic species that are analyzed at DRI's facilities. If occupational exposure to energetic and propellant products is of concern, future analyses of XAD and TIGF filters can include polycyclic aromatic hydrocarbons (PAHs) and nitrous compounds (nitro-PAHs), which are known carcinogens. One area in which additional sample collection would be helpful would be canister sampling for organic gases and semivolatile compounds. If desirable in the future, this can be easily incorporated into the sampling platform.

In retrospect, the amount of energetic in each test article could have been much smaller than in the test articles used, at least from the perspective of providing sufficient material for analytical sampling of products. Based on these results, a factor of ten (or even twenty) reduction in the amount of energetic would still provide adequate reaction products for sampling. An added advantage of reducing the energetic is that the finite volume of the DTC is less likely to introduce artifacts, which are suspected to be associated with confined-space testing (e.g., Mitchell and Suggs, [1997]).

A final point is that the sampling platform that was built for this SEED project could accommodate either a PM_{10} or $PM_{2.5}$ SSI, but not both simultaneously. Given that the difficult work of designing the platform has been completed, it would be efficient to duplicate the sampling platform for $PM_{2.5}$ collection in future efforts so that the two types of samples could be collected simultaneously for each test article.

Potential for SEED project activities to be extended to wider range of testing

Although the SEED project has demonstrated some minor areas for improvement in the sample collection system, it has largely shown that the system works well and has some advantages over airborne measurement platforms. The DoD has a wide variety of energetic devices that are of interest from either the standpoint of requiring accurate emission factors or the potential for human exposure to harmful substances. Therefore, it is worthwhile considering which emissions characterization systems are best suited for various categories of devices. Table 4 lists the categories of devices that are well suited for testing using the DRI system either in conjunction with the Hypervelocity Lab DTC or in situ (i.e., outside) at NAWCWD China Lake.

Devices that can be tested within the Hypervelocity Lab DTC have to be small enough to meet safety standards of the DTC and be minimally affected by the confinement posed by the DTC. For example, the DTC is rated to accommodate test articles with a TNT equivalent mass of over 1 kg. However, the combustion products of energetics larger than 200 g (and probably closer to 100 g) are likely to be affected by the confinement of the DTC, which inhibits the complete combustion of the energetic, not because of a shortage of oxygen, but because of other detonation physics (e.g., Mitchell and Suggs, [1997]).

Larger energetic articles can be tested in situ provided that there is a way to sample the plume for some finite amount of time (e.g., 30 seconds) before it is either carried away by wind or is lofted well above ground level by buoyancy. Lofting (especially for smaller articles with plumes that mix and cool quickly) can be accommodated somewhat by placing the sampling inlet at an elevation with respect to the test article. In all cases, all components of the sampling platform other than the inlet would have to be located behind a blast shield of some kind. It is probably not very practical use the DRI system to measure the plume from very large energetic articles because the plume from such tests is likely to rise far above the ground very quickly. Those types of tests are more reliably sampled with a remote, airborne platform, such as a drone or aerostat (e.g., Gullett et al., [2016]).

In situ tests in an unconfined space using either an airborne platform or a ground-based system (such as the DRI system described here) allow information to be collected about carbon-based emission factors or toxic products (i.e., mass product per mass of carbon in article). This is because it is usually difficult to estimate the volume of the entire plume as well as the average concentration of the reaction products for the entire plume, which is needed for mass closure. Some remote sensing techniques can be used to obtain mass-based emissions (i.e., total mass of product per article), but these are subject to significant errors. These techniques may be useful for validating carbon-based emission measurements (Kim et al., [2012]), but in our opinion they are impractical for widespread use.

Propellants for relatively small guns can be easily accommodated in the DTC. Projectiles can be managed by either firing them into sand traps within the DTC or replacing the projectile with an equally massive object that rapidly dissipates kinetic energy. The firing of the projectile would likely be triggered remotely for safety reasons. The number of rounds to be fired can be varied to ensure adequate loading on filter samples.

At firing ranges, the sample inlet line can be placed near the exhaust of the gun barrel to collect products out of the barrel or near the personnel operating the gun to obtain representative samples of material. Given the ability to rapidly switch between routing clean air and sample air through the sampling platform, collection can be completed over multiple rounds in a short amount of time. Note that this technique is scalable to larger guns as well, although at some upper limit (e.g., M155), the buoyancy and mechanical energy of the plume may propel it well above ground level and out of reach of the sampling inlet.

Rocket motors of all sizes are tested during static fire tests at NAWCWD China Lake as part of ongoing programs. The sampling platform is well suited for static fire tests, where it is known that the plume will be directed in a certain direction, and therefore can be sampled at a location where it is cool enough not to affect instrumentation but still close to ground level. Here, the safety of each test would have to be evaluated by the Firing Officer on a case-by-case basis.

Pyrotechnic devices are not available at NAWCWD China Lake and arrangements would have to be made to conduct sampling elsewhere. This may be either in situ during training exercises or at a confined space that can accompany pyrotechnics and the sampling platform.

Table 4. List of devices of interest and potential for using the DRI system developed in this project for measuring emissions and toxic compounds.

Type of device	**NAWCWD China Lake inside Hyper-velocity Lab Detonation Test Chamber with DRI system**	**Available/appropriate for in situ testing at NAWCWD China Lake using DRI system***
Energetic ≈< 200 g	Yes - mass based, carbon based, < 100 g preferred to mitigate confinement artifacts	Yes - Carbon based
Energetic ≈> 200 g	No due to interferences from confinement	Yes - Carbon based; may require positioning in plume or elevated sampling port; highly buoyant plumes from large articles cannot be sampled
Propellant, small (e.g., small arms up to mortars)	Yes - Mass based, carbon based; DTC modified to capture projectile/disperse projectile; no confinement issues	Yes - Carbon based; firing range: inlet placed near end of barrel, near personnel nose and mouth
Propellant, large (e.g., M155 gun)	No – due to physical and certification limitations of Hypervelocity Lab	Yes - Carbon based; may require positioning in plume (behind blast shield) or elevated sampling port; highly buoyant plumes from large articles cannot be sampled; article not typically available at NAWCWD China Lake
Pyrotechnics	Not at present – pyrotechnic articles are not presently available at NAWCWD China Lake	Not at present – pyrotechnic articles are not presently available at NAWCWD China Lake
Rocket motors	No – due to physical and certification limitations of Hypervelocity Lab	Yes - Carbon based; may require positioning in plume (behind blast shield) or elevated sampling port; highly buoyant plumes from large articles cannot be sampled

* Assumes no conservative tracers are available for mass balance, either in formulation or added to article so that gas-phase carbon (CO_2, CO) must be used.

4. Conclusions and Implications for Future Work

A platform for sample collection of products of combustion of munitions used by DoD was constructed and tested at the NAWCWD China Lake Hypervelocity Lab DTC. The platform was designed to enable the collection of PM on multiple filter media, measurement of particle size distribution (and chemistry), measurement of real-time PM_{10} and $PM_{2.5}$ concentrations, and measurement of gas-phase constituents. Tests were conducted using approximately 200 g (net explosive weight) test articles of two different energetic formulations, PBXN-113 and PBXN-114, in either stainless steel or brass casings. The PBXN-114 was an aluminized formulation and the test articles with stainless steel casings contained a tin disc between the energetic and the closed end of the casing.

Overall, the platform worked as designed and the tests proved its operability and ability to collect the desired samples and data. Real-time concentrations of PM_{10} and $PM_{2.5}$ and gas-phase constituents (CO_2, CO, SO_2, NO, and NO_2) were measured. Those data indicate that although the timing of the opening of the sampling valves can be very precise, there is a lag time of approximately 30 seconds between when the sample air enters the sampling plenum and when the real-time instrument responds. This was attributed to the travel time of the sample air from the inlet valve to the instruments and no negative impact was observed on the quality of the measurement. The platform successfully collected filter samples (Teflon^{TM}, quartz-fiber, and TIGF followed by PUF) for all tests, as well as MOUDI impactor particle size distributions for a subset of tests. These were analyzed for metal content, ions, organic and elemental carbon fractions, and a toxic organic compound that are known to be constituents in the energetic formulations. Overall, this information indicated that detection limits of metals of interest from a toxics perspective (including Pb, Cr, Ni, Cu, and Mn) were two or more orders of magnitude lower than what was recovered on filter samples. Particle size distribution differences between products of PBXN-113 and PBXN-114 were resolved by the MOUDI. Substantial amounts of carbon from the energetic ended up as black carbon (soot).

The black carbon levels measured in the PM samples approached the magnitude of the concentration of gas-phase CO_2, which indicated incomplete combustion of carbon from the energetic. It was not clear if this was a feature of the energetics (especially PBXN-114) or if this was the result of artifacts introduced by the confinement of the detonation. Combined with the fact that concentrations of products of interest—such as toxic metals—were orders of magnitude greater than detection limits, the formation of large amounts of soot point to the need to reduce the net explosive weight equivalent amount of energetic tested within the DTC in future efforts.

Specific technical recommendations for the sampling platform included:

- Add a line that is totally independent of the sampling platform. The line would be diluted approximately 50:1 and would be sampled in real-time by gas-phase and PM measurement instruments to monitor the evolution of the plume concentration over time. In this way, the delay in opening the DTC isolation valves post-detonation can be minimized as much as possible (likely to a few seconds), thereby enabling mass-based emissions factors can be obtained in addition to carbon-based factors.
- Replace the Testo 350 gas analyzer with multiple, specialized analyzers to improve the dynamic range of all gases sampled. Notably, a CO_2 monitor with better than 10 ppm accuracy is needed.

- Replace the DustTrak DRX with either a more robust instrument that provides PM mass in only one size fraction (e.g., TSI DustTrak) or with a more accurate real-time size distribution measurement device (e.g., TSI Aerodynamic Particle Sizer).
- Improve the retention of deposits on filter media. Notably, Teflon™ filters used for mass and XRF analyses were subject to deposit spalling. A combination of different media, reduced deposit amounts, and improved handling protocols should address this issue.
- Replicate a sampling platform to enable the simultaneous collection of PM_{10} and $PM_{2.5}$ samples during testing. Currently, the platform can be equipped with either one or the other type of size selective device.

The sampling platform and techniques demonstrated in this project are amenable for use in future tests within the Hypervelocity Lab DTC, as well as for in situ testing of emissions from munitions in outdoor settings. DTC tests can be accommodated at NAWCWD China Lake for energetic materials (nominally < 200 g) and gun propellants where the projectile can be safely stopped within the DTC (e.g., by sand trap or other means). In situ testing can be accommodated at NAWCWD China Lake for larger energetics (> 200 g), propellants in specialized facilities such as firing ranges, larger propellants, and static rocket motor tests (any size up to a Stage 1 Trident). In situ tests with the platform provide carbon-based emissions measurements, whereas DTC tests provide those measurements as well as mass-based emissions factors. Additionally, in situ sampling of plumes from devices is limited to cases in which the plume is small enough and cool enough to be amenable to ground-based sampling or sampling from an elevated platform. In all cases, most of the instrumentation would be located behind a blast shield with only the inlet protruding into direct contact with the plume.

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Appendix A. Analytical detection limits

Table of detection limits for inorganic compounds. **Note particulate matter collected on filters for this study was in the range of several milligrams and MDLs reported here are in micrograms per filter.**

Species/Compounds	Analysis Method[a]	MDL (µg/filter[b])
Mass	GRAV	1.0000
Ammonia (NH_3) as NH_4^+	AC	1.5005
Sulfur Dioxide (SO_2)	IC	1.5005
Chloride (Cl^-)	IC	1.5005
Nitrite (NO_2^-)	IC	1.5005
Nitrate (NO_3^-)	IC	1.5005
Sulfate ($SO_4^=$)	IC	1.5005
Phosphate (PO_4^{3-})	IC	1.5005
Ammonium (NH_4^+)	AC	1.5005
Soluble Sodium (Na^+)	AAS	0.2362
Soluble Magnesium (Mg^{2+})	AAS	0.0945
Soluble Potassium (K^+)	AAS	0.1498
Soluble Calcium (Ca^{2+})	AAS	0.0945
Cesium (Cs)	ICP-MS	0.005
Barium (Ba)	ICP-MS	0.0005
Lanthanum (La)	ICP-MS	0.0001
Cerium (Ce)	ICP-MS	0.0001
Praseodymium (Pr)	ICP-MS	0.0001
Neodymium (Nd)	ICP-MS	0.0001
Samarium (Sm)	ICP-MS	0.0001
Europium (Eu)	ICP-MS	0.0001
Gadolinium (Gd)	ICP-MS	0.0001
Terbium (Tb)	ICP-MS	0.0001
Dysprosium (Dy)	ICP-MS	0.0001
Holmium (Ho)	ICP-MS	0.0001
Erbium (Er)	ICP-MS	0.0001
Thulium (Tm)	ICP-MS	0.0001
Ytterbium (Yb)	ICP-MS	0.0001
Lutetium (Lu)	ICP-MS	0.0001

Pb (Isotopes) Pb-204, Pb-206, Pb-207 and Pb-208	ICP-MS	0.0003
Sodium (Na)	XRF	3.7541
Magnesium (Mg)	XRF	1.1341
Aluminum (Al)	XRF	0.4483
Silicon (Si)	XRF	0.3613
Phosphorus (P)	XRF	0.1177
Sulfur (S)	XRF	0.0506
Chlorine (Cl)	XRF	0.0487
Potassium (K)	XRF	0.0459
Calcium (Ca)	XRF	0.0727
Scandium (Sc)	XRF	0.1938
Titanium (Ti)	XRF	0.0346
Vanadium (V)	XRF	0.0082
Chromium (Cr)	XRF	0.0382
Manganese (Mn)	XRF	0.0834
Iron (Fe)	XRF	0.0760
Cobalt (Co)	XRF	0.0041
Nickel (Ni)	XRF	0.0131
Copper (Cu)	XRF	0.0442
Zinc (Zn)	XRF	0.0391
Gallium (Ga)	XRF	0.1281
Arsenic (As)	XRF	0.0147
Selenium (Se)	XRF	0.0290
Bromine (Br)	XRF	0.0412
Rubidium (Rb)	XRF	0.0271
Strontium (Sr)	XRF	0.0633
Yttrium (Y)	XRF	0.0376
Zirconium (Zr)	XRF	0.1012
Niobium (Nb)	XRF	0.0667
Molybdenum (Mo)	XRF	0.0640
Palladium (Pd)	XRF	0.1549
Silver (Ag)	XRF	0.1473
Cadmium (Cd)	XRF	0.1152
Indium (In)	XRF	0.1271
Tin (Sn)	XRF	0.1372
Antimony (Sb)	XRF	0.2063
Cesium (Cs)	XRF	0.0585
Barium (Ba)	XRF	0.0632
Lanthanum (La)	XRF	0.0433
Cerium (Ce)	XRF	0.0417
Samarium (Sm)	XRF	0.0862
Europium (Eu)	XRF	0.1325
Terbium (Tb)	XRF	0.0976
Hafnium (Hf)	XRF	0.3950
Tantalum (Ta)	XRF	0.2579
Tungsten (W)	XRF	0.3610
Iridium (Ir)	XRF	0.1192

Gold (Au)	XRF	0.1960
Mercury (Hg)	XRF	0.0971
Thallium (Tl)	XRF	0.0654
Lead (Pb)	XRF	0.0945
Uranium (U)	XRF	0.1648

[a] GRAV=Gravimetry. OD=Optical density. AC=Automated colorimetry. IC= ion chromatography. AAS=Atomic absorption spectrophotometry. TOR=thermal/optical reflectance. XRF=x-ray fluorescence. ICP-MS = Inductively coupled plasma - Mass spectrometry.

[b] Minimum detectable limit (MDL) is the concentration at which instrument response equals three times the standard deviation of the response to a known concentration of zero.

Table of detection limits for some organic compound classes. **Note particulate matter collected on filters for this study was in the range of several milligrams and MDLs reported here are in micrograms per filter.**

Species/Compound class	Analysis Method[a]	MDL (µg/filter[b])
PAHs (multiple compounds C12 – C24)	TD-GCMS	~ 0.005 – 0.010
Alkane/Alkene - *n*-alkane (multiple compounds (nC15 – nC40)	TD-GCMS	~ 0.005 – 0.007
iso/anteiso-alkane (multiple compounds iso-C-29 – iso C33)	TD-GCMS	~ 0.004 – 0.006
methyl-alkane (C20)	TD-GCMS	0.004
branched-alkane (C19, C20, C30)	TD-GCMS	0.005
Cycloalkane (C14, C16, C19, C23, C25)	TD-GCMS	0.004
Hopane (multiple C27 – C35)	TD-GCMS	~ 0.003 – 0.004
Sterane (multiple C27 – C29)	TD-GCMS	~ 0.003 – 0.004
Sugars (multiple)	IC	~ 0.05 – 3.3
Organic Acids (formic – glutaric)	IC	~ 0.5 – 2.5

[a] Thermal Desorption Gas Chromatography - Mass Spectrometry, IC - Ion chromatography

[b] Minimum detectable limit (MDL) is the concentration at which instrument response equals three times the standard deviation of the response to a known concentration of zero.