



Defence Research and  
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# Characterization of atmospheric emissions produced by live gun firing:

*Test on the M777 155 mm Howitzer*

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**Defence R&D Canada**  
Technical Report  
DRDC Toronto TR 2007-102  
October 2007

Canada



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## Abstract

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Atmospheric emissions produced by live gun firing of the 155 mm howitzer were characterized during a live firing training exercise in Canadian Forces Base (CFB) Valcartier in January 2007. Sampling was performed continuously for three hours during the exercise during which particles and chemicals accumulated on sampling media. Sixty-nine rounds were fired, each round using four bags of propellant, and an additional 3 rounds were fired, each round using 5 bags of propellant. Established occupational health methods were used to collect and analyze samples for particulate matter, hydrogen cyanide, polycyclic aromatic hydrocarbons (PAHs), dinitrotoluene compounds, benzene, toluene, ethylbenzene and xylene, metals, aldehydes, nitric acid (HNO<sub>3</sub>), nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), hydrogen sulphide (H<sub>2</sub>S) and sulphur dioxide (SO<sub>2</sub>). Two sets of samples were collected, one at approximately 8 m at the left of the gun, and the second one at approximately 22 m in front of the gun muzzle, in the line of fire. Most of the chemicals were not detected during the trial. For both sets of samples, particles were found at concentrations much higher than the recommended environmental standards. The size distribution showed that at least 60 % of the particles were below 10 µm. These findings suggest that there is a potential risk to health associated with exposure to particles for artillery soldiers. Formaldehyde was also detected at concentrations of 7.1 and 3.6 µg/m<sup>3</sup> for the left and the front locations, respectively. These findings suggest that there is a need to conduct personal sampling to assess the health risk, if any, to artillery soldiers. For all substances, it is recommended that further investigations of air concentrations be made to properly assess personal exposure. It is also recommended to use more sensitive environmental methods to collect and analyse the samples.

## Résumé

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Les composés gazeux et particulaires émis lors des tirs d'obusier de 155 mm ont été caractérisés lors d'un exercice d'entraînement à la Base des Forces Canadiennes (BFC) de Valcartier en janvier 2007. L'échantillonnage a été effectué en continu pendant trois heures lors de l'exercice, les particules et émissions gazeuses s'accumulant sur les media d'échantillonnage. Soixante neuf tirs ont été effectués, en utilisant quatre sacs de charge propulsive et trois tirs additionnels en utilisant une charge de cinq sacs de charge propulsive. Des méthodes reconnues en hygiène du travail ont été utilisées pour collecter et analyser les échantillons pour les particules en suspension, le cyanure d'hydrogène, les hydrocarbures aromatiques polycycliques (HAP), les composés dinitrotoluène, le benzène, le toluène, l'éthylbenzène et le xylène, les métaux, les aldéhydes, l'acide nitrique (HNO<sub>3</sub>), le monoxyde d'azote (NO), le dioxyde d'azote (NO<sub>2</sub>), le sulfure d'hydrogène (H<sub>2</sub>S) et le dioxyde de soufre (SO<sub>2</sub>). Deux lots d'échantillons ont été collectés, le premier à environ 8 m à gauche du canon, et le deuxième à environ 22 m en avant du canon, dans la ligne de tir. La plupart des composés n'ont pas été détectés lors de l'exercice. Pour les deux lots d'échantillons, les particules en suspension ont été observées à des concentrations beaucoup plus élevées que les standards environnementaux. De plus, plus de 60 % des particules avaient une taille inférieure à 10 µm. Ces résultats suggèrent que l'exposition aux particules en suspension pose un risque potentiel pour la santé des artilleurs. Le formaldéhyde a été détecté à des concentrations de 7.1 et 3.6 µg/m<sup>3</sup> respectivement à gauche et en avant du canon. Ces résultats suggèrent qu'il est nécessaire de mesurer l'exposition individuelle au formaldéhyde afin d'évaluer le risque, s'il y a lieu, pour la santé des artilleurs. Pour toutes les substances il est recommandé de déterminer l'exposition individuelle. Il est également recommandé d'utiliser des méthodes environnementales, plus sensibles, pour collecter et analyser les échantillons.

## Executive summary

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### Characterization of Atmospheric Emission Produced by Live Gun Firing: Test on the M777 155 mm Howitzer

Quémerais, B., Diaz, E., Poulin, I., Marois, A.; DRDC Toronto TR 2007-102;  
Defence R&D Canada – Toronto; October 2007.

**Introduction or background:** For many years, Defence Research and Development Canada (DRDC) Valcartier has performed environmental site assessments on the live ranges of the major Canadian Forces training bases to evaluate the contamination by explosives and metals at target and firing points. It was found that most of the fixed firing positions are contaminated with propellant residues. In 2003, DRDC Valcartier began to assess the dispersion of residues at firing points during 105 mm howitzer live firing exercises. Residues of nitrocellulose fibres collected in front of the muzzle showed measurable amount of 2,4-Dinitrotoluene (2,4-DNT). After discussion with the soldiers, it was determined that the gunners may be affected by the gaseous emissions. In Spring 2006, researchers from DRDC Valcartier contacted researchers at DRDC Toronto to do further investigations on airborne substances emitted during live gun firing. Preliminary tests were conducted at the muffler installation of the Munitions Experimental Testing Centre (METC) in Nicolet (Quebec) both inside the muffler and outdoors on the C3 105 mm howitzer. Samples were analyzed for particulate matter, hydrogen cyanide, nitroaromatic compounds, dinitrotoluene compounds, benzene, toluene, ethylbenzene and xylene. Direct reading instruments were used to determine levels of nitrous oxide (NO), nitrogen dioxide (NO<sub>2</sub>) and sulphur dioxide (SO<sub>2</sub>). In January 2007, DRDC Toronto and DRDC Valcartier collected air samples during a live training exercise on the M777 155 mm howitzer. Metals, polycyclic aromatic hydrocarbons (PAHs), aldehydes, hydrogen sulphide (H<sub>2</sub>S), and nitric acid (HNO<sub>3</sub>) were added to the previous list of compounds. Two sets of samples were collected at two different locations around the gun. In total, 72 rounds were fired, 69 rounds using 4 bags of propellant each and 3 rounds using 5 bags of propellant each.

**Results:** Most of the chemicals were not detected during the trial. Suspended particles were detected and their size distribution determined. Formaldehyde was the only chemical detected. Particle concentrations were 3.42 and 4.62 mg/m<sup>3</sup>, respectively. More than 60 % of the detected particles had a size distribution under 10 µm. Concentration of fine particles (< 3.5 µm) was approximately 1.2 mg/m<sup>3</sup>, which is much higher than the recommended environmental standards and suggests that particles pose a potential risk to soldiers' health. Formaldehyde concentrations were 7.1 and 3.6 µg/m<sup>3</sup>, respectively. These findings suggest that there is a need to conduct personal sampling to assess the health risk, if any, to artillery soldiers.

**Future plans:** It is recommended to further investigate soldiers' exposure to howitzer chemicals emitted by properly assessing personal exposure. As few contaminants were detected, it is recommended to use methods that are more sensitive for sample collection and analysis. It is recommended to collect both environmental and personal exposure samples as it was observed that there are also many soldiers located further away from the gun.

## Sommaire

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### Caractérisation des émissions atmosphériques produites par les tirs d'artillerie: Tests sur l'obusier de 155 mm M777

Quémerais, B., Diaz, E., Poulin, I., Marois, A.; DRDC Toronto TR 2007-102;  
R & D pour la défense Canada – Toronto; Octobre 2007.

**Introduction ou contexte :** Depuis plusieurs années, Recherche et Développement Défense Canada (RDDC) Valcartier étudie l'aspect environnemental des secteurs d'entraînement des principales bases des Forces Canadiennes afin d'évaluer la contamination par les matériaux énergétiques et les métaux aux positions de tirs et aux cibles. Les résultats ont montrés que la plupart des positions de tir sont contaminées par des résidus de poudre propulsive. En 2003, RDDC Valcartier a commencé à étudier la dispersion des résidus aux positions de tir lors d'un exercice d'entraînement avec l'obusier de 105 mm. Les résidus de fibres de nitrocellulose prélevés devant la bouche du canon ont montré des concentrations non négligeables en 2,4-dinitrotoluène. Après discussion avec les soldats, les chercheurs se sont aperçus que les artilleurs pouvaient être affectés par les émissions gazeuses. Au printemps 2006, les chercheurs de RDDC Valcartier ont contacté les chercheurs de RDDC Toronto afin d'étudier les substances gazeuses émises lors des tirs d'artillerie. Des tests préliminaires ont été effectués au silencieux du Centre Expérimental de Test des Munitions à Nicolet (Québec), à l'intérieur du silencieux et à l'extérieur sur l'obusier C3 105 mm. Les échantillons ont été analysés pour les particules en suspension, le cyanure d'hydrogène (CN), les composés nitroaromatiques, les composés de dinitrotoluène, le benzène, le toluène, l'éthylbenzène et le xylène. Des instruments à lecture directe ont été utilisés pour déterminer les niveaux de monoxyde d'azote (NO), de dioxyde d'azote (NO<sub>2</sub>) et de dioxyde de soufre (SO<sub>2</sub>). En janvier 2007, RDDC Toronto et RDDC Valcartier ont collecté des échantillons d'air lors d'un tir d'entraînement sur l'obusier M777 155 mm. Les métaux, les hydrocarbures aromatiques polycycliques, les aldéhydes, le sulfure d'hydrogène et l'acide nitrique ont été ajouté à la liste précédente. Deux lots d'échantillons ont été collectés à deux sites différents autour du canon. Au total, 72 munitions ont été tirées, 69 en utilisant 4 sacs de charge propulsive et 3 en utilisant 5 sacs de charge propulsive.

**Résultats :** La plupart des composés chimiques n'ont pas été détectés. Les particules en suspensions ont été détectées et la distribution de la taille des particules a été déterminée. Le formaldéhyde a été le seul composé à être détecté. Les concentrations de particules étaient respectivement de 3.42 et 4.62 mg/m<sup>3</sup>. Plus de 60 % des particules détectées avait une taille inférieure à 10 µm. La concentration des particules fines (< 3.5 µm) était d'environ 1.2 mg/m<sup>3</sup>, ce qui est beaucoup plus élevés que les normes environnementales et qui suggère que les particules posent un risque pour la santé des soldats. Les niveaux en formaldéhydes étaient respectivement de 7.1 et de 3.6 mg/m<sup>3</sup>. Ces valeurs suggèrent qu'il est important de mesurer l'exposition individuelle pour évaluer si le formaldéhyde cause un risque pour la santé des artilleurs.

**Perspectives :** Il est recommandé d'examiner de plus près l'exposition des soldats aux composés chimiques en évaluant l'exposition personnelle. Puisque peu de contaminants ont été détectés, il est recommandé d'utiliser des méthodes plus sensibles pour la collection et l'analyse des échantillons environnementaux. Il est également recommandé de collecter à la fois des

échantillons environnementaux et des échantillons pour l'exposition personnelle puisque de nombreux soldats étaient localisés plus loin du canon.

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# 1 Introduction

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For many years Defence Research and Development Canada (DRDC) Valcartier has been involved in the study of environmental impacts due to gun firing activities on live firing training ranges ([1] to [8]). Environmental site assessments were performed on the major training bases to evaluate the contamination by energetic materials and metals at target and firing points ([5]). It was found that most of the fixed firing positions are contaminated with propellant residues such as nitroglycerine (NG) and 2,4-dinitrotoluene (2,4-DNT) embedded in nitrocellulose fibres deposited in front and around the gun muzzle after artillery or tank firing exercises ([7]).

In 2003, DRDC Valcartier began to assess the dispersion of gun residues at firing points during a 105 mm howitzer live firing exercise ([8]). Residues of nitrocellulose fibres collected in front of the gun muzzle showed measurable amounts of 2,4-DNT ([8]).

After discussions with the gunners, DRDC Valcartier researchers felt that the gunners may be affected by the gaseous emissions produced by gun firings. In addition, the researchers were concerned about the size of the particles emitted during gun firing. It was then decided to characterize the gaseous emissions, as well as the particle size distribution and composition during live artillery gun firings.

Since researchers in DRDC Valcartier did not have the capability to perform gas sampling and analysis, they initiated a joint project with DRDC Toronto researchers, who are specializing in Occupational Health. The Deployable Health Hazards Assessment Team (DHHAT) at DRDC Toronto has the capacity to performing airborne measurements for a variety of substances using sorbent tubes, filters or direct reading instruments.

In September 2006, a first test was performed at the Munitions Experimental Testing Centre (METC) in Nicolet, Québec, on the C3 105 mm howitzer ([9]). Samples were analyzed for hydrogen cyanide, nitroaromatic compounds, dinitrotoluene compounds, benzene, ethyl benzene, toluene and xylene, nitrogen oxides (NO and NO<sub>2</sub>) and sulphur dioxide (SO<sub>2</sub>), and particulate matter, including size distribution ([9]). Results showed that the atmospheric emissions contain toxic compounds that can induce a potential health risk for the soldiers. Therefore, it was decided to further investigate atmospheric emissions emanating from live gun firing ([9]).

In January 2007, DRDC Toronto and DRDC Valcartier collected another set of air samples during a live training exercise in Valcartier on the new M777 155 mm gun. This report describes the results on the gaseous emissions produced during the M777 155 mm training exercise. It is important to note that personal exposure was not assessed during the exercise.

## 2 Experimental design

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The exercise was conducted at Canadian Forces Base (CFB) Valcartier on January 12<sup>th</sup> 2007 in the Training Sector #14. The artillery setup included only one M777 155 mm howitzer. It was planned to fire a total of 72 rounds of M107, 155 mm ammunition, using green bag propellant charge. DRDC Valcartier was in charge of coordinating with the artillery unit, of the particulate matter sampling and analysis, and of the 2,4-DNT analysis. DRDC Toronto was in charge of airborne contaminant sampling and analysis (except for 2,4-DNT).

### 2.1 Equipment and munitions

Tests were performed on a M777 155 mm howitzer. This gun is a light-weight (10,000 lbs) towed system adopted by the Canadian Forces in November 2005, replacing the former self-propelled, tracked M109 series medium howitzer (Figure 1). It is United States (US) built, has optimized, digitalized fire control, is highly mobile and air transportable. The 39-calibre 155 mm barrel has a 19 L chamber, which can accept all US and North Atlantic Treaty Organization (NATO) standard 155 mm projectiles and charges (including Modular Artillery Charge System (MACS)) as well as new families of precision munitions. This type of gun has a minimal range of 2.6 km and a maximal range of 30 km ([10]).

The 155 mm ammunition consists of the projectile, fuse, propellant charge and primer. All components are stored and issued separately. Depending on the application or training, different projectiles may be used. The propellant charges for 155 mm howitzer are designed in various size increments to provide overlaps in range coverage. Charges are available according to modular or regular charges. Regular charges are presented in bags, and the range of firing is dictated by the number of bags used. Contrary to the 105 mm ammunition, the 155 mm does not have a lead foil inside any bag. The propellant charge composition is M1 and the projectile is filled with Composition B.

The full green bag charge consists of approximately 2.5 kg of granular propellant (M1 composition). The propellant is contained in bolt shaped cartridge cloth bags, dyed green and divided in 5 sections (Figure 2 and Figure 3). The composition of the propellant charge is given in Table 1. The increment charges are held together with four cloth straps sewn to the base and tied on top of Charge 5. An igniter charge, consisting of 99 g of Clean Burning Igniter (CBI) powder in a red cloth bag is sewn to the rear of the base charge. A flash reducer pad containing 57 g of potassium nitrate or potassium sulphate (in this study it was sulphate) is assembled forward on the base of the charge. Similar 28.4 g pads are assembled forward of increments 4 and 5 (Figure 2 and Figure 3). The flash reducer pads limit breech flare-back as well as muzzle flash and blast overpressure.

Table 1. Composition of the M1 propellant charge

Charge	Mass of propellant (kg)
1	0.864
2	0.227
3	0.298
4	0.425
5	0.709

## 2.2 Parameters and sampling methods

Based on the previous trial in Nicolet ([9]) and on a study done in the US on ordnance detonation ([11]), it was decided to sample for the following parameters: particulate matter and size distribution of the particles, hydrogen cyanide, 2,4-DNT, benzene, toluene, ethyl benzene and xylene, nitrogen dioxide (NO<sub>2</sub>), nitric oxide (NO), SO<sub>2</sub>, nitric acid (HNO<sub>3</sub>), hydrogen sulphide, polycyclic aromatic hydrocarbons (PAHs), metals and aldehydes. Nitroaromatic compounds were not analyzed as they were never detected in the previous trial ([9]).

### 2.2.1 Particulate matter and size distribution of the particles

Total particulates were collected using National Institute of Occupational Safety and Health (NIOSH) Method 0500 ([12]). The method was slightly modified as a filter was used with a smaller porosity than is normally required. Briefly, the air is pumped through a 37 mm 0.8 µm GN-4 Metrice membrane (PALL Life Science). The filter is weighed prior to and after sampling to determine the amount of particles retained. Pumps were GilAir5 personal sampling pumps from Sensidyne or 224-PCXR7 and 224-PCXR4 personal sampling pumps from SKC<sup>®</sup>. Pumps were calibrated prior to and after sampling. The average flow rate was used to calculate particles concentrations. The flow rate was set at 4 L/min.

Particle size distribution was performed with a cascade impactor Maple Personal Cascade Impactor (Series 290) from Thermo Electron Corporation. It is a multi-orifice, multi-stage cascade impactor (Figure 4). The impactor was connected to a GilAir5 pump from Sensidyne which was calibrated prior to and after sampling. The pump flow was set at 2 L/min. The cut-off points at this flow for the impactor are shown in Table 2. Note that these values are calculated as aerodynamic diameters (spherical particles of unity mass in air at 25°C).

Analysis of the filters to determine particle size distribution, morphology and chemical composition were performed by scanning electron microscopy (SEM). The microscope is a JEOL LSM-840A equipped with a NORAN energy dispersive X-ray (EDX) spectrometer. These

analyses were performed by DRDC Valcartier scientific team and details are given in reference [13].

*Table 2 . Cut-off points for the personal cascade impactor*

Impactor stage	Cut-off point ( $\mu\text{m}$ )
1	21.3
2	14.8
3	9.8
4	6.0
5	3.5
6	1.55
7	0.93
8	0.52
F	0 (plain filter)

### **2.2.2 Hydrogen cyanide**

Particulate and gaseous hydrogen cyanide samples were collected and analyzed according to NIOSH Method 7904 ([12]). Particulate samples were collected on a 0.8  $\mu\text{m}$  polyvinylchloride (PVC) membrane and gaseous samples were collected using a bubbler filled with 15 mL of a 0.1 N potassium hydroxide (KOH) solution. Immediately after sampling, the KOH solution was transferred into a glass vial to be sent for analysis. Analysis was performed using an ion-specific electrode. A GilAir5 sampling pump was used with a flow rate of 1 L/min. The pump was calibrated prior to and after sampling.

### **2.2.3 Dinitrotoluene compounds**

Samples were collected and analyzed using Occupational Safety and Health Administration (OSHA) Method 44 ([14] and [15]). Briefly, samples were collected using Tenax<sup>®</sup> sorbent tubes. After extraction with acetonitrile, samples were analyzed by high pressure liquid chromatography with an ultraviolet detector (HPLC/UV). The sampling pump was a GilAir5 set at a flow rate of 1 L/min. The pump was calibrated prior to and after sampling.

### **2.2.4 Benzene, toluene, ethyl benzene and xylene**

Samples were collected and analysed using OSHA Method 7 ([14]). Samples were collected on a charcoal sorbent tube. After extraction, samples were analyzed using a gas chromatography/flame ionization detector (GC/FID). Samples were analyzed for benzene, toluene, ethyl benzene and

total xylene. The sampling pump was a LFS-113 low flow sampling pump from Sensidyne operating at a flow rate of 0.2 L/min. The pump was calibrated prior to and after sampling.

### **2.2.5 Nitric oxide and nitrogen dioxide**

NO and NO<sub>2</sub> were collected and analyzed using OSHA Method ID-190 ([14]). The collection apparatus consists of two glass tubes filled with a triethanolamine impregnated sieve separated by a tube containing an oxidizer. NO<sub>2</sub> is retained on the first triethanolamine tube while NO passes through the oxidizer, is oxidized to NO<sub>2</sub> and is then retained on the second triethanolamine tube. After extraction, the sample is analyzed using ion chromatography (IC). Samples were collected using LFS-113 low flow sampling pumps from Sensidyne. The pumps were calibrated prior to and after sampling with a sampling flow of 0.025 L/min.

### **2.2.6 Sulphur dioxide**

Samples were collected and analyzed according to OSHA Method ID-200 ([14]). SO<sub>2</sub> is retained on a glass tube filled with impregnated activated beaded carbon. The sample is desorbed using a sodium hydroxide solution, which contains approximately 1 % of hydrogen peroxide. The sample is analyzed by IC. Samples were collected using LFS-113 sampling pumps calibrated prior to and after sampling. Pumps flows were set at 0.1 L/min.

### **2.2.7 Hydrogen sulphide**

Samples were collected and analyzed using NIOSH Method 6013 ([12]). Hydrogen sulphide is collected on a tube filled with coconut shell charcoal. After extraction, the sample is analyzed by IC. Samples were collected using GilAir5 sampling pumps. Pumps were calibrated prior to and after sampling and the flow was set at 1.5 L/min.

### **2.2.8 Nitric acid**

Samples were collected and analyzed using NIOSH Method 7903 ([12]). HNO<sub>3</sub> is collected on a tube filled with washed silica gel. After extraction, the sample is analyzed by ion chromatography. Samples were collected using GilAir5 sampling pumps. Pumps were calibrated prior to and after sampling and the flow was set at 0.5 L/min.

### **2.2.9 Polycyclic aromatic hydrocarbons**

Samples were collected and analyzed using NIOSH Method 5506 ([12]). Briefly, particulate PAHs are collected on a 37 mm 2 µm polytetrafluoroethylene (PTFE) filter while gaseous PAHs are collected on a tube filled with Amberlite XAD-2 resin. After extraction, both particulate and gaseous samples are analyzed by HPLC equipped with a fluorescence/ultraviolet detector (fluorescence/UV). Samples were collected using GilAir5 sampling pumps. Pumps were calibrated prior to and after sampling and the flow was set at 2 L/min. List of PAHs analyzed by this method is given in Table 3.

Table 3 . List of polycyclic aromatic hydrocarbons analyzed

Gaseous and particulate PAHs
Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(e)pyrene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

### 2.2.10 Metals

Samples were collected and analyzed using NIOSH Method 7300 ([12]). Metals are collected on a 5 µm PVC membrane. After extraction, the sample is analyzed by inductively coupled argon plasma atomic emission spectroscopy (ICP/AES). Samples were collected using GilAir5 sampling pumps. Pumps were calibrated prior to and after sampling and the flow was set at 4 L/min. This method allows for the determination of approximately 30 metals. However, some of them such as calcium or sodium are not of interest as they would not be toxic at airborne concentrations. The list of metals was chosen according to a US Environmental Protection Agency (US EPA) report on ordnance emissions ([11]) and is given in Table 4.

*Table 4. List of metals of interest analyzed*

<b>Metals</b>
Aluminium
Antimony
Arsenic
Barium
Cadmium
Chromium
Cobalt
Copper
Iron
Lead
Manganese
Nickel
Selenium
Silver
Vanadium
Zinc

### **2.2.11 Aldehydes**

Samples were collected and analyzed using US EPA Method TO-11A ([16]). Aldehydes are collected on a tube filled with silica gel impregnated with 2,4-dinitrophenylhydrazine (2,4-DNPH). After extraction, the sample is analyzed by HPLC equipped with a UV detector. Samples were collected using LFS-113 sampling pumps. Pumps were calibrated prior to and after sampling and the flow was set at 0.5 L/min. The list of aldehydes analyzed by this method is given in Table 5.

Table 5. List of aldehydes analyzed

Aldehydes
2-Butanone (MEK)
Acetaldehyde
Acetone
Benzaldehyde
Butyraldehyde
Crotonaldehyde
Formaldehyde
Hexaldehyde
Methacrolein
O,m,p-Tolualdehyde
Pentanal (Valeraldehyde)
Propionaldehyde (Propanal)

### 2.3 Sampling strategy

Military personnel were tasked to install the gun and provide the ammunition for the firing. A minimal number of 7 to 10 gunners are necessary to operate the M777 155 mm howitzer. The positions of the gunners are given in Figure 5. Gunner #1 makes the firing adjustments, Gunner #2 fires the gun, Gunner #5 supervises and Gunners #6 and #7 load the gun (Figure 5).

To collect the plume (Figure 6), two tables were setup with the sampling equipment. As shown in Figure 7, one table was located on the left side of the gun at approximately 8 m (identified as Table #1), and the second one was located in the firing direction at approximately 22 m (identified as Table #2). To avoid any damage caused by the blast effect, it was imperative to set up the tables at a certain distance from the gun. In addition, the tables could not be in the way of the gunners operating the gun.

Sampling was carried on January 12, 2007 from 10:30 am to 13:20 pm. Weather data were obtained from the meteorological station at Quebec City International Airport ([17]) and are shown in Annex B. The temperature for the sampling day varied from  $-2.7$  °C to  $0.6$  °C during the sampling period. Wind speed was low and varied from 6 to 19 km/hr while the wind was coming from the West-South-West. However, on the range the wind speed seemed to be lower, maybe because the range is located further away from the St. Lawrence River and is protected by surrounding forests. Although data do not give humidity values after 6:00 am, it is supposed that it was 100% humidity as it was slightly snowing. Average atmospheric pressure was 100.8 kPa.

Each table was equipped with sampling pumps and the media necessary to collect for all of the parameters. As only one cascade impactor was available, it was put on the nearest position from the gun on Table #1. As it was snowing, all the pumps were protected from the snow by putting them in a Ziploc bag with the media outside of the bag and pointing toward the gun. The total sampling time for both tables was 170 min. During the trial, 72 rounds were fired, 69 rounds at charge 4 plus 3 rounds at charge 5.

Two blanks were brought to the field and sent for analysis along with the samples. Samples were not taken in duplicates. All the pumps were calibrated the day before the trial in a cold room (3 °C) to account for the expected cool temperature. They were calibrated again as soon as possible after sampling in the same cold room. Samples were kept refrigerated and sent to the laboratory for analysis. Size distribution and 2,4-DNT analyses were performed in the laboratory at DRDC Valcartier (Quebec City). All other analyses were done by Clayton Group Services Inc. (Novi, Michigan and Atlanta, Georgia).

## **3 Results and discussion**

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For data interpretation, environmental standards and toxicology reports from the US EPA, Health Canada, and the Canadian Council of the Ministry of Environment (CCME) were used. (Threshold Limit Values (TLV) from the American Conference of Governmental Industrial Hygienists (ACGIH) were not considered applicable as there was no evaluation of personal exposure over an 8-hour period as required by the ACGIH. Data interpretation is mainly based on possible rather than actual health risks due to exposure to emissions compounds.)

Contrary to the previous trial in Nicolet, most of the chemicals were not detected. This is probably the result of different atmospheric conditions. Formaldehyde was the only chemical detected during the exercise at both tables. Particles were also detected at each table.

### **3.1 Pump calibration**

Results for the pumps calibration are shown in Table 6 for each type of substances. The last column shows the difference between pre and post sampling.

For all parameters the difference between pre and post sampling is always less than 10 %, which is considered as acceptable. Average pump flow was used for further calculations.

Table 6 . Pump calibration for each type of substances

Parameter	Table #	Pre-flow (L/min)	Post-flow (L/min)	Average (L/min)	Difference %
PAHs	1	1.978	1.955	1.967	0.58
PAHs	2	2.080	2.105	2.093	0.6
Cyanide	1	1.086	1.079	1.083	0.32
Cyanide	2	1.039	1.058	1.049	0.91
Metals	1	4.072	4.073	4.073	0.01
Metals	2	3.984	4.003	3.994	0.24
Particles	1	3.969	3.936	3.953	0.42
Particles	2	3.965	3.932	3948.5	0.42
2,4-DNT	1	1.075	1.096	1.086	0.97
2,4-DNT	2	1.047	1.062	1.055	0.71
Benzene/toluene	1	0.2116	0.2078	0.2097	0.91
Benzene/toluene	2	0.2105	0.2061	0.2083	1.06
Aldehydes	1	0.4998	0.4834	0.4916	1.67
Aldehydes	2	0.5113	0.4816	0.4965	2.99
HNO <sub>3</sub>	1	0.5016	0.4779	0.4898	2.42
HNO <sub>3</sub>	2	0.5023	0.4757	0.4890	2.72
H <sub>2</sub> S	1	1.532	1.477	1.505	1.83
H <sub>2</sub> S	2	1.509	1.603	1.556	3.02
SO <sub>2</sub>	1	0.1059	0.1293	0.1176	9.95
SO <sub>2</sub>	2	0.1001	0.1154	0.1078	7.1
NO/NO <sub>2</sub>	1	0.0268	0.0265	0.0267	0.56
NO/NO <sub>2</sub>	2	0.0276	0.0263	0.0270	2.41
Impactor	1	1.994	1.925	1.960	1.76

### 3.2 Particle concentration and size distribution

Particle concentrations at Tables #1 and #2 (Figure 7) were 3.42 and 4.62 mg/m<sup>3</sup>, respectively. The higher concentration found at Table #2 is likely due to the fact that this table was located directly in the line of fire in front of the muzzle while Table #1 was on the left side of the gun. During the trial, gaseous emissions were observed at the muzzle immediately after firing and each time Gunner #1 (Figure 6) opened the bridge to insert a new round. The emissions observed at the

opening of the bridge were in a smaller amount than the emissions at the muzzle, which could explain the lower concentration at the left side of the gun for particles. In addition, wind was low and gaseous emissions did not show high dispersion that day (Figure 6).

The size distribution of particles is given in Table 7 and recommendations from Health Canada, the US EPA and the CCME are given in Table 8. Approximately a third of the particles on Table #1 have a size lower than 3.5  $\mu\text{m}$ , and approximately 63 % are smaller than 10  $\mu\text{m}$ . These results are similar to the ones observed in the previous study ([9]).

The complete description of the particulate matter analyses is described in another report by Poulin et al. ([13]).

*Table 7. Size distribution of particles*

	< 3.5 $\mu\text{m}$	3.5 to 10 $\mu\text{m}$	> 10 $\mu\text{m}$
	%	%	%
Table #1	37.3	25.4	37.3

*Table 8. Recommendations for particulate matter concentration in ambient air*

Particle size	CCME ( $\text{mg}/\text{m}^3$ ) ([18])	US EPA ( $\text{mg}/\text{m}^3$ ) ([19])	Health Canada ( $\text{mg}/\text{m}^3$ ) ([20])
PM10 <sup>1</sup>		0.15	
PM2.5 <sup>2</sup>		0.015	
PM2.5 <sup>3</sup>	0.03	0.035	
TSP <sup>4</sup>			0.07
TSP <sup>5</sup>			0.12
TSP <sup>6</sup>			0.40

<sup>1</sup> Particulate Matter  $\leq 10 \mu\text{m}$ , 24-hour standard

<sup>2</sup> Particulate Matter  $\leq 2.5 \mu\text{m}$ , annual standard

<sup>3</sup> Particulate Matter  $\leq 2.5 \mu\text{m}$ , 24-hour standard

<sup>4</sup> Total Suspended Particulate, annual standard, maximum acceptable level

<sup>5</sup> Total Suspended Particulate, 24-hour standard, maximum acceptable level

<sup>6</sup> Total Suspended Particulate, 24-hour standard, maximum tolerable level

Fine particles are considered to be the most hazardous ([18]). Particles under 4  $\mu\text{m}$  are known to be deposited in the gas-exchange region of the lungs ([21]). Health effects related to chronic exposure to fine particles include cardiac-related and respiratory effects ([22]).

In this study, the concentration of particles under 3.5  $\mu\text{m}$  at Table #1 is approximately 1.2  $\text{mg}/\text{m}^3$ . This is about thirty times higher than the recommended 24-h standard for PM<sub>2.5</sub> from the US EPA (Table 8). In addition, it is probable, although not measured, that particles concentration closer to the gun, where the gunners are located, was significantly higher than at Table #1, as heavy smoke was observed when opening the bridge. Therefore, gunners are exposed to concentrations of fine particles that are potentially harmful.

It is recommended to perform personal sampling to further investigate on PM<sub>2.5</sub> exposure by assessing personal exposure as the environmental standard is set for particles less than 2.5  $\mu\text{m}$ .

### 3.3 Formaldehyde

The only aldehyde detected during this study was formaldehyde. Results are shown in Table 9.

Formaldehyde is known to cause irritation of the mucosa of the eyes and upper airways ([23]). Formaldehyde is also considered as a probable carcinogenic by the US EPA ([24]). Excess of nasopharyngeal cancers and lung cancers have been observed in workers exposed to formaldehyde ([25]). Formaldehyde can be found in combustion products such as diesel exhaust and cigarette smoke ([26]).

*Table 9. Concentrations of formaldehyde for each sampling location*

	<b>Formaldehyde</b> <b>(<math>\mu\text{g}/\text{m}^3</math>)</b>
Table #1	7.1
Table #2	3.6

Contrary to the particle concentration (Section 3.2), formaldehyde concentration at Table #1 was twice as high as the concentration at Table #2 (Table 9). Table #1 was closer to the gun than Table #2, which could explain this result. It is possible than dispersion of gases is different than dispersion of particles. On the other hand, Table #1 was located in between the gun and the trucks. However it was noticed that the truck drivers left their truck running during the exercise. It is possible therefore that part of the formaldehyde detected at Table #1 was coming from diesel exhausts from the trucks.

The US EPA does not have any Reference Concentration (RfC) for chronic inhalation exposure ([24]). The RfC is “an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is

likely to be without an appreciable risk of deleterious effects during a lifetime” ([25]). However, the EPA has calculated carcinogenic risk using very conservative models, based on lifetime exposure day after day.

According to the US EPA, a formaldehyde concentration of  $8 \mu\text{g}/\text{m}^3$  gives a carcinogenic risk level of 1 in 10,000 ([25]). This level is similar to formaldehyde concentration observed at Table #1 and in the same order of magnitude than formaldehyde concentration observed at Table #2. Since the soldiers are not exposed on a daily basis for a lifetime their risk is likely far lower than the EPA estimates and likely to be no more than the risk of the general population. However, some soldiers are working quite close to the gun and it would be prudent to conduct personal sampling to compare their exposure to occupational standards. It is recommended that further investigation on formaldehyde exposure be performed.

## 4 Conclusion

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This study was performed following a preliminary study on the howitzer 105 mm done at Nicolet Québec. In the first study, it was recommended to add metals, PAHs, aldehydes, nitric acid and H<sub>2</sub>S to the list of substances evaluated. Contrary to the first study, the samples were collected during a live firing exercise on the M777 155 mm howitzer. In total, 72 rounds were fired and samples were collected continuously during 3 hours.

Samples collected during this study showed significant concentrations for particles and formaldehyde. However, no other contaminants were detected, including those measured during the preliminary study.

Results for the particles were in agreement with results found in the previous study, that live gun firing produces mainly particles under 10 µm and that artillery soldiers are exposed to high concentrations of fine particles ([9]). Overall particle concentrations ranged from 3.42 to 4.62 mg/m<sup>3</sup> with 63 % of the particles being under 10 µm. It suggests that particles emitted during live firing may cause a potential health risk for the artillery soldiers.

Formaldehyde concentrations (7.1 and 3.6 µg/m<sup>3</sup>, respectively) observed during this study give a risk level for cancer of 1 in 10,000 for a lifetime exposure ([25]). The higher concentration at Table #1 (located in between the gun and the trucks) can be explained by the fact that trucks were running during the entire experiment as formaldehyde is a component of diesel exhaust.

Considering that soldiers are actually a lot closer to the gun than the Tables, it is likely that they are exposed to higher levels than the ones observed in this study. It is therefore recommended to properly assess personal exposure to all of the contaminants analyzed during this study.

Since few contaminants were detected, it is recommended that methods that are more appropriate for environmental sample collection and analysis such as US EPA TO Compendium methods ([16]) be used. It is also recommended that a background sample further away from the gun be collected to have the requisite background concentration of each chemical.

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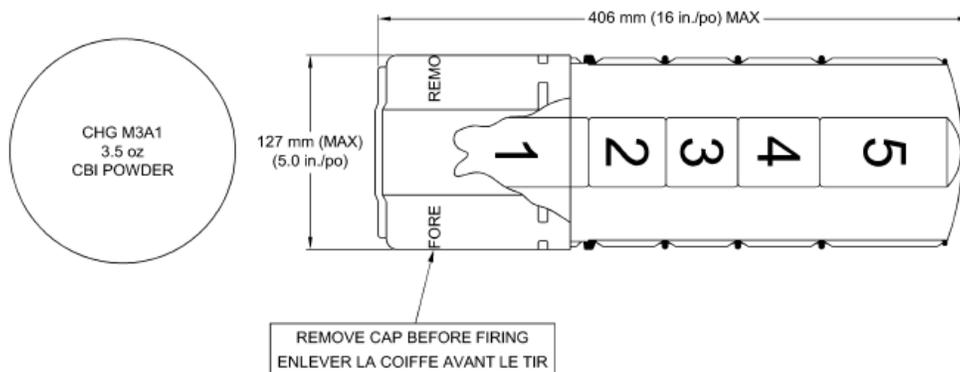
# Annex A Sampling installation

## A.1 Equipment and munitions



Photo: Cpl Marc-André Gaudreault, Imaging Section, CFB Valcartier

*Figure 1. The M777 155 mm howitzer*



*Figure 2. M1 propellant charge for the 155 mm*

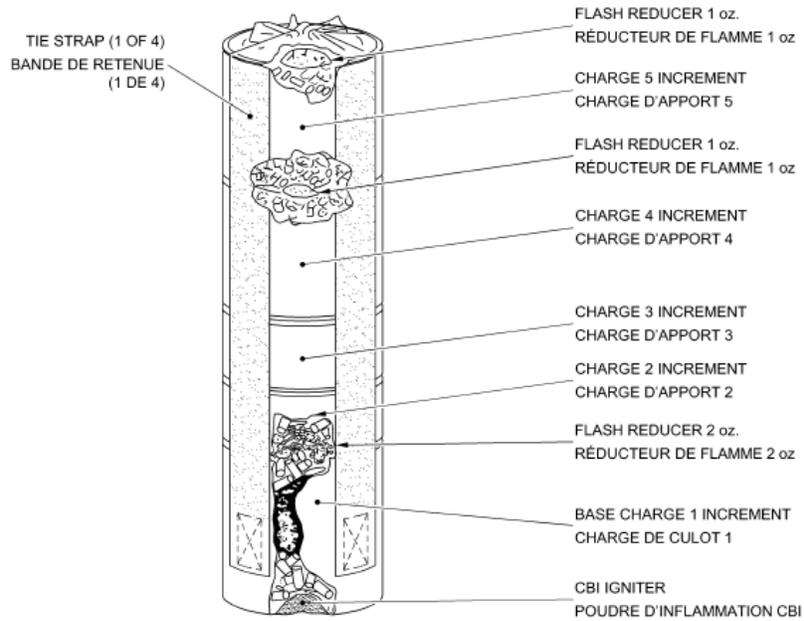


Figure 3. Propellant bags within the M1 charge

## A.2 Sampling equipment



Figure 4. Marple Personal Cascade Impactor

### A.3 Sampling strategy

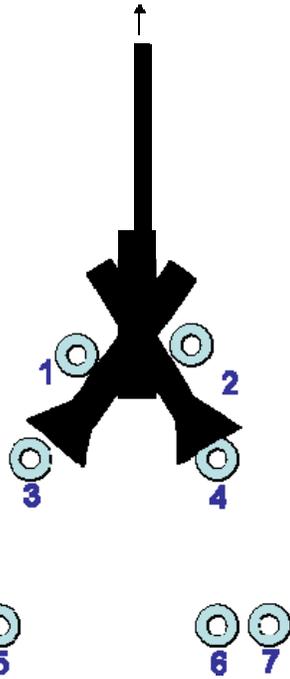
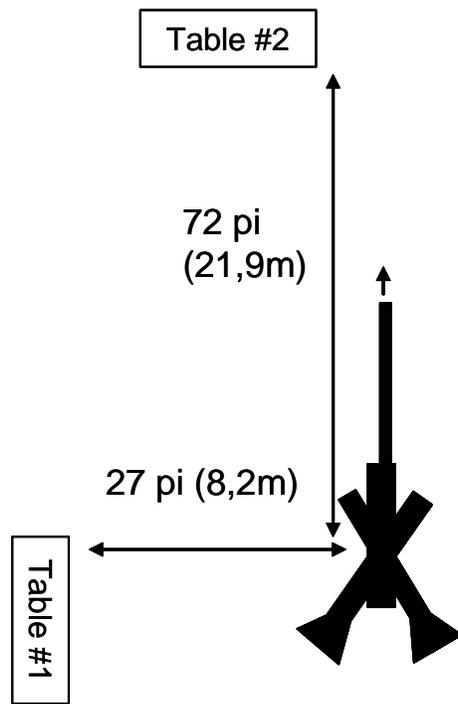


Figure 5. Positions of the gunners (blue circles) around the M777 105 mm howitzer



Figure 6. Emission at the muzzle end of the M777 155 mm howitzer



*Figure 7. Location of the tables around the gun*

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## Annex B Climate data

Hourly Data Report for January 12, 2007										
<u>T i m e</u>	<u>Temp</u> °C	<u>Dew Point Temp</u> °C	<u>Rel Hum</u> %	<u>Wind Dir</u> 10's deg	<u>Wind Spd</u> km/h	<u>Visibility</u> km	<u>Stn Press</u> kPa	<u>Hmdx</u>	<u>Wind Chill</u>	<u>Weather</u>
00:00	-8.0	-10.3	83	36	6	M	101.22			NA
01:00	-7.7	-10.0	84	36	4	M	101.18			NA
02:00	-6.8	-9.2	83	1	4	M	101.12			NA
03:00	-6.8	-8.7	86	26	4	M	101.09			NA
04:00	-6.7	-8.3	88	26	4	M	101.03			NA
05:00	-6.2	-8.5	84	22	4	M	101.00			NA
06:00	-6.3	-6.3	100	28	6	M	101.00			NA
07:00	-5.5	M	M		0	M	100.98			NA
08:00	-5.2	M	M	16	2	M	100.94			NA
09:00	-4.0	M	M	21	4	M	100.92			NA
10:00	-2.7	M	M	26	6	M	100.93			NA
11:00	-1.7	M	M	26	6	M	100.85			NA
12:00	-0.2	M	M	24	17	M	100.79		-5	NA
13:00	0.0	M	M	25	15	M	100.72		-4	NA
14:00	0.6	M	M	25	19	M	100.70			NA
15:00	0.7	M	M	25	22	M	100.77			NA
16:00	0.9	M	M	25	17	M	100.80			NA
17:00	1.0	M	M	25	15	M	100.83			NA
18:00	1.1	M	M	24	19	M	100.80			NA
19:00	1.3	M	M	24	17	M	100.77			NA
20:00	1.3	M	M	24	15	M	100.69			NA
21:00	1.4	M	M	25	17	M	100.70			NA
22:00	1.3	M	M	25	17	M	100.64			NA
23:00	1.4	M	M	25	19	M	100.61			NA

Meteorological station – Quebec City International Airport

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## List of symbols/abbreviations/acronyms/initialisms

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2,4-DNPH	2,4-Dinitrophenylhydrazine
2,4-DNT	2,4-Dinitrotoluene
ACGIH	American Conference of Governmental Industrial Hygienists
AES	Atomic Emission Spectroscopy
BFC	Base des Forces Canadiennes
CBI	Clean Burning Igniter
CCME	Canadian Council of Ministers of the Environment
CFB	Canadian Forces Base
D FHP	Directorate of Force Health Protection
DHHAT	Deployable Health Hazards Assessment Team
DRDC	Defence Research and Development Canada
EDX	Energy Dispersive X-ray
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
GC	Gas Chromatography
H <sub>2</sub> S	Hydrogen Sulphide
HAP	Hydrocarbures aromatiques polycycliques
HNO <sub>3</sub>	Nitric Acid
HPLC	High Pressure Liquid Chromatography
IC	Ionization Chromatography
ICP	Inductively Coupled Plasma
KOH	Potassium Hydroxide
MACS	Modular Artillery Charge System
METC	Munitions Experimental Testing Centre
NATO	North Atlantic Treaty Organization
NG	Nitroglycerine
NIOSH	National Institute of Occupational Safety and Health
NO	Nitric Oxide
NO <sub>2</sub>	Nitrogen Dioxide
OSHA	Occupational Safety and Health Administration

PAHs	Polycyclic Aromatic Hydrocarbons
PM	Particulate Matter
PTFE	Polytetrafluoroethylene
PVC	Polyvinylchloride
RALC	Régiment d'Artillerie Légère du Canada
RfC	Reference Concentration
SEM	Scanning Electron Microscopy
SO <sub>2</sub>	Sulphur Dioxide
TLV	Threshold Limit Value
US	United States
UV	Ultraviolet

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Atmospheric emissions produced by live gun firing of the 155 mm howitzer were characterized during a live firing training exercise in Canadian Forces Base (CFB) Valcartier in January 2007. Sampling was performed continuously for three hours during the exercise during which particles and chemicals accumulated on sampling media. Sixty-nine rounds were fired, each round using four bags of propellant, and an additional 3 rounds were fired, each round using 5 bags of propellant. Established occupational health methods were used to collect and analyze samples for particulate matter, hydrogen cyanide, polycyclic aromatic hydrocarbons (PAHs), dinitrotoluene compounds, benzene, toluene, ethylbenzene and xylene, metals, aldehydes, nitric acid (HNO<sub>3</sub>), nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), hydrogen sulphide (H<sub>2</sub>S) and sulphur dioxide (SO<sub>2</sub>). Two sets of samples were collected, one at approximately 8 m at the left of the gun, and the second one at approximately 22 m in front of the gun muzzle, in the line of fire. Most of the chemicals were not detected during the trial. For both sets of samples, particles were found at concentrations much higher than the recommended environmental standards. The size distribution showed that at least 60 % of the particles were below 10 µm. These findings suggest that there is a potential risk to health associated with exposure to particles for artillery soldiers. Formaldehyde was also detected at concentrations of 7.1 and 3.6 µg/m<sup>3</sup> for the left and the front locations, respectively. These findings suggest that there is a need to conduct personal sampling to assess the health risk, if any, to artillery soldiers. For all substances, it is recommended that further investigations of air concentrations be made to properly assess personal exposure. It is also recommended to use more sensitive environmental methods to collect and analyse the samples.

Les composés gazeux et particulaires émis lors des tirs d'obusier de 155 mm ont été caractérisés lors d'un exercice d'entraînement à la Base des Forces Canadiennes (BFC) de Valcartier en janvier 2007. L'échantillonnage a été effectué en continu pendant trois heures lors de l'exercice, les particules et émissions gazeuses s'accumulant sur les media d'échantillonnage. Soixante neuf tirs ont été effectués, en utilisant quatre sacs de charge propulsive et trois tirs additionnels en utilisant une charge de cinq sacs de charge propulsive. Des méthodes reconnues en hygiène du travail ont été utilisées pour collecter et analyser les échantillons pour les particules en suspension, le cyanure d'hydrogène, les hydrocarbures aromatiques polycycliques (HAP), les composés dinitrotoluène, le benzène, le toluène, l'éthylbenzène et le xylène, les métaux, les aldéhydes, l'acide nitrique (HNO<sub>3</sub>), le monoxyde d'azote (NO), le dioxyde d'azote (NO<sub>2</sub>), le sulfure d'hydrogène (H<sub>2</sub>S) et le dioxyde de soufre (SO<sub>2</sub>). Deux lots d'échantillons ont été collectés, le premier à environ 8 m à gauche du canon, et le deuxième à environ 22 m en avant du canon, dans la ligne de tir. La plupart des composés n'ont pas été détectés lors de l'exercice. Pour les deux lots d'échantillons, les particules en suspension ont été observées à des concentrations beaucoup plus élevées que les standards environnementaux. De plus, plus de 60 % des particules avaient une taille inférieure à 10 µm. Ces résultats suggèrent que l'exposition aux particules en suspension pose un risque potentiel pour la santé des artilleurs. Le formaldéhyde a été détecté à des concentrations de 7.1 et 3.6 µg/m<sup>3</sup> respectivement à gauche et en avant du canon. Ces résultats suggèrent qu'il est nécessaire de mesurer l'exposition individuelle au formaldéhyde afin d'évaluer le risque, s'il y a lieu, pour la santé des artilleurs. Pour toutes les substances il est recommandé de déterminer l'exposition individuelle. Il est

également recommandé d'utiliser des méthodes environnementales, plus sensibles, pour collecter et analyser les échantillons.

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Atmospheric emissions, health effects, artillery gun firing, M777 howitzer, 155 mm

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