Evaluation of the Contamination by Explosives and Metals in Soils at the Älvdalen Shooting Range. Part II: Results and Discussion.

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Abstract

Previous investigations at American and Canadian shooting ranges have shown elevated levels of explosive residues in soil, water and groundwater. The distribution of explosive residues has been shown to be particularly heterogeneous, thus making the sample collection procedure vitally important. In the present study, soil samples covering three training activities; anti-tank area, hand grenade range and a crater area at Älvdalen shooting range were collected following a systematic random design. A laboratory processing method was developed for multi-increment composite samples, 0.5-1.5 kg in size, before the samples were analyzed by liquid and gas chromatography.

Trace metal analysis was only performed in the anti-tank area. In general, low levels of explosive residues were found at all the investigated sites. However, HMX (4.2 µg/g) was the dominant contaminant in the target area of the anti-tank range and nitroglycerine (262 µg/g) at the firing positions. Residues of TNT (59 µg/g) was detected around one of the target tanks at the crater area. Lead, copper and chromium were elevated in a few soil samples from the anti-tank range.

Based on the results, and when compared to similar ranges sampled either in Canada or in the USA for explosive and metals, our results tended to demonstrate that lower levels of residues were dispersed in Älvdalen. This might be explained by the lower intensity and frequency of firing events in Älvdalen.

Keywords

Explosives, HMX, RDX, TNT, soil, XRF, GC-MS, HPLC, sampling, trace metals

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Bedömning av föroreningar av explosivämnen och metaller i mark på Älvdalens skjutfält.
Del II: Resultat och diskussion.

Sammanfattning

Tidigare miljöstudier från skjutfält i Kanada och Amerika har visat på förhöjda halter av sprängämnesrester i jord, vatten och grundvatten. Spridningen har vidare visats vara synnerligen heterogen vilket ställer stora krav på att representativitet uppfylls vid provtagning och analys. Vid Älvdalens övnings- och skjutområde togs jordprover på ett antitank-område, handgranatbanan samt ett antal krevadgropar enligt ett systematisk-slumpmässigt upplägg. En laboratoriemetod för att behandla kompositprover (0.5-1.5 kg) togs fram innan proverna analyserades med vätske- och gaskromatografi. Metallanalyser genomfördes bara för prover tagna vid antitank-området. Överlag var halterna av sprängämnen låga på de tre studerade områdena.
Vid antitank-områdets målområde hittades dock HMX (4.2 µg/g) medan avfyrningsplatserna dominerades av nitroglycerin (262 µg/g). Vid krevadgropsområdet hittades förhöjda halter av TNT (59 µg/g) endast runt en av stridsvagnarna som var ditsatta som övningsmål. Av metallerna var halterna av bly, koppar och krom förhöjda i vissa prover från anti-tank området.
Baserat på resultaten, och jämfört med skjut- och övningsfält i Kanada och USA, var halterna låga på de studerade områdena på Älvdalens skjutområde. Detta kan förmodligen förklaras av både en generellt låg intensitet och frekvens av skjutövningar i Älvdalen jämfört med Kanada och USA.

Nyckelord
Explosivämnen, HMX, RDX, TNT, XRF, GC-MS, HPLC, provtagning, spårmetaller

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Foreword

This report is published under the Project Arrangement Number 2003-02 entitled Environmental Aspects of Energetic Materials to the trilateral cooperative science and technology memorandum of understanding between Canada, The Netherlands and Sweden.

The international context of demilitarization, the closure of military bases and the more stringent aspects of environmental laws have led to the establishment of new areas for research and development. Many activities of the Forces such as the firing of ammunition, demolition, and the destruction of obsolete ammunition by open burning and open detonation may lead to the dispersion of energetic compounds and other munitions-related contaminants in the environment. It is within this context that a trilateral collaborative effort has been initiated under an annex of the Memorandum of Understanding (MOU) between the Defence Research and Development Canada Valcartier (DRDC Valcartier) of the Department of national defence of Canada (DND), TNO Prins Maurits Laboratory of The Netherlands Ministry of Defence and FOI Swedish Defence Research Agency of the Swedish Ministry of Defence. The main objective of this trilateral agreement is to conduct research programs to study the environmental impact of energetic materials that are found in the respective Dutch, Canadian and Swedish ammunition stockpiles. The cooperation also deals with problems concerned with dumped ammunition and remnants from war. It was agreed under the MOU that the expertise developed for site characterization would be shared allowing the development of a unique expertise within each department to better understand the impacts of live fire training and dumped ammunition in order to be in a readiness state to answer any inquiries and take corrective actions if needed. The objectives of the cooperation are explicitly listed in the project arrangement as follows:

To exchange information related to the impacts of the live firing training on the environment and perform international site characterization.

- To understand the fates of explosives in soils and groundwater
- To understand the problems of unexploded ordnances (UXO) underwater and on land.
- To study the effects of corrosion on UXO leading to open shells and contamination of the environment.

The three points of contacts in each respective country are:

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Introduction

The sampling and subsampling errors are usually widely exceeding the analytical error in many environmental investigations (1-4). This is particularly true for investigations dealing with the characterization of the dispersion of energetic materials at shooting ranges (5-7). Similar problems were encountered while studying production and dump sites of explosives and also in the study of environmental impact of open burning/open detonation (OB/OD) ranges (8,9). The residues of energetic materials may be dispersed in the environment by either the high or low order detonations, the breaching of unexploded ordnance (UXO) casings. This often results in a widespread and heterogeneous contamination over significant areas. Most high explosives and propellants are solid at ambient temperatures (melting points 70-276 °C) and residues are found distributed in various size ranges i.e. as crystalline particles and adsorbed/dissolved within the soil matrix. This may result in a large sampling and subsampling error sometimes referred to as the nugget effect. Furthermore the different inherent properties of these compounds regarding mobility, volatility and degradability (biotic and abiotic) complicate the task on a time scale as well. For instance, TNT (trinitrotoluene) will rapidly disappear in organic rich soils and sediments due to sorption of TNT and its degradation products (10, 11). Hence, in spite its wide popularity in munitions and munition formulations, TNT should not be the sole candidate for environmental monitoring at shooting ranges. Instead, the full suite of explosives (e.g. HMX, RDX, NG, etc.) and related compounds are preferably monitored at shooting ranges to cover all types of munition residues.

Sampling and analytical strategies designed to meet the abovementioned prerequisites are of utmost importance and the theory and background for the samples collected at Älvdalen Shooting range was described previously (12). But in short, the use of multi-increment (≥30) near surface (0-5 cm depth of soil) composite samples collected in the combination of a systematic random design have been proven successful at many similar sites (13, 14). For instance, it was shown that discrete sampling and composite samples with few increments resulted in unacceptable statistical uncertainty while studying HMX and NG at an anti-tank firing range. It is however usually a good practice to combine various sampling strategies such as a completely random or a judgmental to validate the results and compare the strategies for their accuracy and suitability. Perhaps the greatest concern at military shooting ranges is the possible presence of energetic materials in the groundwater which have been the case at a few training ranges and have mandated the closure of at least one major shooting range (15). This particular situation might be explained by past extensive firing activities, highly permeable soil characteristics and/or the build-up of a high number of UXOs in a relatively small target area.

It is also important to stress that environmental aspects at shooting ranges in general not only concern residues from energetic materials. Heavy metals and petroleum residues can constitute a significant environmental contamination risk. Thus, soil samples were also collected for multielemental analysis (i.e. trace metal analysis) at the firing and impact area of the anti-tank area. However, petroleum residues and other environmental contaminants were beyond the scope of this study. Further, no biomass samples were taken and since the ground water under the shooting range was not a source for drinking water, no such samples were collected and last but not least some of the areas were not judged safe for groundwater borehole drilling. In this context, it must be recognized that this study is not comprehensive in its evaluation of all possible environmental compartments and if needed further sampling may also be required.

The present report deals with the analytical results (explosive residues and trace metals) from samples collected in Älvdalen-2003 where some of the training operations were studied. The aim of the study was also to implement sampling strategies and laboratory processing methods designed for shooting ranges at Älvdalen shooting range.

Materials and Methods

The hand grenade range was sampled according to a circular sampling strategy presuming a gradient from the likely hot spot (where most fragmentary grenades hit ground) in combination with judgmental samples (suspected hot spots). Multi-increment composite samples were collected at the anti-tank area, Karlgrav, which was divided into the target area, comprising four subareas and the seven firing positions (located in front of the target area). At the larger area of Rivsjöbrändan, where discarded tanks were set out as targets, five randomly chosen craters at the impact area were sampled at the bottom, wall and outside. Multi-increment composite sampling was also performed around one of the tanks and a container used for storage. At all the investigated areas background samples (composites) were also collected and analysed.

The samples were analyzed for explosive residues according to US-EPA Method 8330 (16) and 8095 (17) utilizing HPLC-UV and GC-ECD, respectively. Samples collected at the impact area from the anti-tank range were analysed by GC-MS in accordance to Wingfors et al (18). Due to the large size of the samples collected (0.5-1.5 kg), a pre-treatment and laboratory processing method was modified following the work by Walsh et al (5,7). These steps are laborious and time-consuming but nevertheless an absolute necessity to obtain representative subsamples for analysis. Another successful method, however not employed in this study, is the acetone slurry technique (19), where the sample is thoroughly mixed with acetone and subsequently dried before subsamples are withdrawn.

Laboratory processing method

The samples were stored in a freezer (-20°C, dark) until analysis. The samples were spread out on a laboratory tray in a dark room and let to air-dry (~24h). After visual inspection for larger crystalline objects and if any pieces found they were removed and analyzed with the EXPRAY Kit (Plexus Scientific, Maryland, USA). The EXPRAY Kit may be used as a semi quantitative detection technique in field and in this case as a safety precaution before further laboratory handling. There is also a risk that samples with very high concentrations may contaminate equipment and instruments which will result in laborious cleaning and testing before any further samples can be processed and analyzed. In short, the EXPRAY Kit works by a series of spray bottles containing reagents so that nitroaromatics can form highly coloured complexes with alkali (Meisenheimer), nitrate esters can further form nitrate ions which are detected by the Griess reaction. HMX and RDX can also be detected by essentially a similar reaction but via a reduction to form the nitrate ions. After drying, the samples were sieved to <2mm and that fraction was subjected to particle size reduction in a planetary mono mill (Fritsch GmbH, Idar-Oberstein, Germany) which was designed to both cross and grind samples. This was accomplished by rotating the bowl around its own axis and a central axis which resulted in a movement of the grinding balls both along the inner walls (grinding) and to be propelled off against the opposite wall (crossing). A grinding program was developed, consisting of 4 cycles of grinding for one minute with one minute delay between to prevent high temperatures in the bowl. High temperatures during grinding may cause analyte degradation of energetic materials (7). The different size distributions of the contaminant and the soil matrix were reduced and the resulting dry and fine powder (flour) was more appropriately subjected to representative splitting than before milling. A stationary feeder equipped with a vibrating conveyer was used to feed a sectorial splitter (a cone sample divider) into eight channels for sample size reduction. The number of increments the sectorial splitter produces is very large and thus the segregation error generated by the vibrating hopper was reduced (eliminated). The sample weight was reduced from approximately 1 kg to 30 g by the combination of the abovementioned operations.

Figure 1. Samples were dried and larger crystalline objects were removed before sieving and milling.

Figure 2. A ball mill (Planetary Mono Mill) equipped with a stainless steel bowl in which sample and grinding balls were put.

Figure 3. The samples were loaded into a stationary feeder with a vibrating conveyer connected to a sectorial splitter.

Chemical analysis

The samples were extracted with acetonitrile in an ultrasonic bath (2x30 min) and allowed to settle in a cooler before the samples were filtered with a 0.45µm PTFE syringe filter. The filtrate was analyzed by HPLC-UV (diode-array detector) according to Method 8330 (16) and by GC-ECD following Method 8095 (17). These two methods are well suited to run in conjunction since different principles of separation and detection are used and hence interferences and co-elutions are not likely to appear similarly. The need for a secondary confirmation column with respective method was thus reduced. For example, phthalate esters, sometimes used as plasticizers or gelatinizers in explosive formulations, show response on the ECD due to the effect of its conjugated carbonyl groups but not on UV. Samples collected at the impact area of the anti-tank range were also analysed by GC-MS (18). This was also done within the framework of an introductory collaborative study on the determination of explosive residues in soil organised within the MOU (memorandum of understanding) of Sweden, Canada and Holland see appendix 1. The laboratories performed well and comparably consistent data was found for the analyte solutions. However, since the concentrations of explosive residues in the soil samples were quite low and detection criteria could not be met for all the methods employed a comparison was not justified. The conclusion was that further comparisons should be performed with samples of higher concentrations. Samples collected for multi-element analysis were sent to Analytica AB for analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Results

In a few samples from the firing positions at the anti-tank range crystalline and plastic objects (>1cm) were found and removed from further laboratory processing and clean up. None of the objects showed positive response with the EXPRAY Kit.

Impact area of the anti-tank range, Karlgrav

The results from the impact area of the anti-tank range can be seen in table 1. In general, low levels of high explosives were found at this site and HMX was the high explosive that showed the highest concentration, 4.8 µg/g dw (dry weight). This was in accordance to samples taken at an anti-tank rocket range at CFB-Valcartier, Quebec (13) where the formulation Octol (70-75% HMX, 30-25% TNT) was the main composition of explosives used. The results from that study showed that the original ratio had changed since HMX is more abundant than TNT in the top soil. The relatively low levels of TNT can be a result of sorption and/or its higher biotic and abiotic degradation rate. In our study the degradation product 2-A-4,6-DNT was found at higher concentrations than 4-A-2,6-DNT, but these two products were found at similar concentrations at an artillery impact area in Fort Lewis (20). In contrast, Elovitz and Weber (21) found that the reductive degradation was regioselective both during anaerobic and aerobic conditions resulting in formation of only 4-amino-2,6-DNT. This can perhaps be explained by the two competing pathways for degradation: abiotic reduction and the bio-reductive reactions caused by micro organisms who donate electrons from NADH or NADPH. Furthermore, cytochrome P-450 enzymes are also believed to be involved in the reduction (22). The fact that we observe higher levels of 2-A-4,6-DNT when compared to 4-A-2,6-DNT in the Karlgrav range is difficult to explain and should be confirmed in further sampling studies. However, our study tends to demonstrate that adsorption to clay and humic material is significantly larger for TNT and its degradation products than for HMX and RDX as in similar cases (23). This was the main reason why the higher water solubility of TNT and its degradation products did not reflect the rate of mobility caused by percolating water in the soil matrix.

RDX was also detected in the samples but only at low levels. The source of RDX might be its presence as a production contaminant of up to 10% in commercially available HMX. It has been reported that only small amounts of RDX were adsorbed to soil organic matter and both lab and field observations were consistent in the comparably high mobility of RDX as compared to TNT (10). The mobility of HMX is on the other hand lower than RDX and HMX is also believed to be more stable under normal conditions in the natural environment which also could partly explain the altered HMX/TNT-ratio in samples from anti-tank impact areas (23). Similarly, the higher mobility of RDX versus HMX was supported in the results from Fort Lewis (20) where the ratio RDX/HMX was changed from 7.61 to 2.14 in aged surface soil and to 3.65 at deeper layers.

2,4-DNT is a common component of propellants and was also quantified in the samples, and showed increased levels in subarea C (200 µg/kg) of the impact embankment. This could be an indication of incomplete combustion of the propellants at the detonation area.

Table 1. Results from the impact area at the anti-tank firing range, analysed by GC-MS (N.B. ng/g).

ng/g dw (ppb)	*A*	*B*	*C*	*Blank*
Nitrobenzene	<0.2	<0.2	<0.2	<0.2
2-nitrotoluene	<0.2	<0.2	<0.2	<0.2
3-nitrotoluene	<0.2	<0.2	<0.2	<0. 2
4-nitrotoluene	<0.2	<0.2	<0.2	<0.2
Dinitrobenzene	<0.2	<0.2	<0.2	<0.2
2,6-DNT	<0.2	**1.8**	**69**	<0.2
2,4-DNT	**0.64**	**7.8**	**200**	<0.2
Trinitrobenzene	**1.6**	<0.76	**2.3**	<0.6
Trinitrotoluene	<0.2	**1.2**	**5.9**	<0.2
RDX	**1.5**	**6.7**	**9.8**	<0.75
4-A-2,6-DNT	<0.2	**0.50**	**0.23**	<0.2
2-A-4,6-DNT	**5.7**	**4.5**	**7.0**	<0.2
HMX *	**420**	**540**	**4800**	<4

*Analysed by HPLC-UV

Firing points of the anti-tank range, Karlgrav

The seven firing points (100-700 m from target) of the anti-tank range have been used for several types of arms over the last decades but the 15.5 cm grenade (6.8 kg of high explosive each fired by howitzers) was extensively used during 2003. Common propellants are composed of nitrocellulose (NC), nitroglycerine (NG), and/or 2,4-dinitrotoluene (2,4-DNT). Propellants have a low rate of combustion and can be designed to either be consumed at the firing point (as fired by howitzers) or also along the way to the target (rockets). In these cases sampling should be designed differently depending on the type of combustion to better capture the residues. At this site, elevated concentrations of nitroglycerine was found in some of the banks, along with detected levels of 2,4-DNT in some samples, see further table 2. Surprisingly, TNT was detected at low levels in a few samples. This might indicate that these firing lines could have been used in the past as target areas or else that duds were open detonated in the vicinity of the firing lines. The highest hit for NG was detected at the firing line 200 meters away from the target area in the bottom area located between the 200 and 300 meter firing lines, where 262 ppm of NG was detected.

Table 2. Results from the firing points at the anti-tank area.

µg/g (ppm)	*FP 100F*	*FP 100T*	*FP 100B*	*FP 100B*	*FP 200F*	*FP 200B*	*FP 300T*	*FP 300B*	*FP 400F*	*FP 400T*	*FP 400B*
NG	<0.50	<0.50	<0.50	<0.50	**18**	**262**	<0.50	**115**	<0.50	**3.1**	**31**
HMX	<0.05	<0.04	<0.08	<0.05	<0.06	<0.09	<0.05	<0.08	<0.05	<0.04	<0.06
RDX	<0.03	<0.03	<0.06	<0.03	<0.04	<0.07	<0.03	<0.06	<0.04	<0.03	<0.04
135NB	<0.02	<0.02	<0.03	<0.02	<0.02	<0.03	<0.02	<0.03	<0.02	<0.02	<0.02
1,3 DNB	<0.01	<0.01	<0.02	<0.01	<0.01	<0.02	<0.01	<0.02	<0.01	<0.01	<0.01
tetryl	<0.03	<0.02	<0.04	<0.03	<0.03	<0.05	<0.03	<0.04	<0.03	<0.02	<0.03
Trinitrotoluene	<0.02	**0.12**	<0.03	<0.02	<0.03	**0.36**	<0.02	**0.53**	**0.49**	<0.02	**0.23**
NB	<0.01	<0.01	<0.02	<0.01	<0.02	<0.03	<0.01	<0.02	<0.01	<0.01	<0.02
4ADNT	<0.03	<0.03	<0.05	<0.03	<0.04	<0.06	<0.03	<0.05	<0.03	<0.03	<0.03
2A-4,6-DNT	<0.01	<0.01	<0.02	<0.01	<0.02	0.21	<0.01	<0.02	<0.02	<0.01	<0.02
26DNT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
24DNT	<0.01	**0.08**	<0.01	<0.01	**1.3**	<0.08	<0.01	<0.01	**0.32**	<0.01	**0.42**
2NT	<0.02	<0.02	<0.04	<0.02	<0.03	<0.05	<0.02	<0.04	<0.02	<0.02	<0.03
4NT	<0.03	<0.02	<0.04	<0.03	<0.03	<0.05	<0.03	<0.05	<0.03	<0.03	<0.03
3NT	<0.02	<0.02	<0.03	<0.02	<0.03	<0.04	<0.02	<0.04	<0.02	<0.02	<0.03

µg/g (ppm)	*FP 500F*	*FP 500T*	*FP 500B*	*FP 600F*	*FP 600F*	*FP 600T*	*FP 600B*	*FP 700F*	*FP 700T*	*FP 700B*	*FP BG*
NG	<0.50	<0.50	**16**	<0.50	<0.50	<0.50	**186**	<0.50	<0.50	<0.50	<0.50
HMX	<0.04	<0.04	<0.05	<0.04	<0.04	<0.05	<0.11	<0.04	<0.04	<0.04	<0.05
RDX	<0.03	<0.03	<0.03	<0.03	<0.03	<0.04	<0.08	<0.03	<0.03	<0.03	<0.04
135NB	<0.02	<0.01	<0.02	<0.01	<0.01	<0.02	<0.04	<0.01	<0.01	<0.01	<0.02
1,3 DNB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	<0.01	<0.01	<0.01
tetryl	<0.02	<0.02	<0.03	<0.02	<0.02	<0.03	<0.06	<0.02	<0.02	<0.02	<0.03
Trinitrotoluene	0.07	<0.01	**0.15**	<0.01	<0.01	<0.02	<0.22	**0.50**	<0.03	<0.01	<0.02
NB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.03	<0.01	<0.01	<0.01	<0.02
4ADNT	<0.03	<0.02	<0.03	<0.02	<0.02	<0.03	<0.07	<0.02	<0.02	<0.02	<0.03
2A-4,6-DNT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.03	<0.01	<0.01	<0.01	<0.02
26DNT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
24DNT	<0.01	<0.01	<0.05	<0.01	<0.01	<0.01	**1.1**	**0.29**	<0.01	<0.01	<0.01
2NT	<0.02	<0.02	<0.02	<0.02	<0.02	<0.03	<0.05	<0.02	<0.02	<0.02	<0.03
4NT	<0.03	<0.02	<0.03	<0.02	<0.02	<0.03	<0.06	<0.02	<0.02	<0.02	<0.03
3NT	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.02

Hand grenade range

The number of live hand grenades used at Älvdalen in 2003 was low (~ 64 grenades, 12.2 kg of munition) and also limited over the previous years. The four hand grenade ranges at Fort Lewis, USA (20) where 6,000 to 7,000 grenades are thrown per year are more exposed to explosive residues where TNT (0.011-75 µg/g) and RDX (0.097- 28µg/g) were found in most samples. In Älvdalen grenade range TNT was only quantified in one sample, a composite sample collected by the circular sampling approach at 1-3 m (1.7 µg/g). Neither the suspected hot spots nor the samples from the circular sampling gave evidence of detectable levels of explosive residues. At the hand grenade range at the training area CFB Shilo, Canada (9) a relatively uniform contamination was found over the entire surface and this was quite consistent with the findings at Fort Lewis (20). The Älvdalen hand grenade range appears to be an exception with its low overall levels of explosive residues which might be directly attributed to its relatively limited exploitation for training.

Table 3. Results from the hand grenade range

µg/g (ppm)	*circular sampling-(0-1m)*	*circular sampling-(1-3m)*	*circular sampling-(3-5m)*	*circular sampling (5-10m)*	*circular sampling (5-10m), dupl.*	*hotspot-(0-5m) 1*	*hotspot-(5-10m) 1*
NG	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
HMX	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.04
RDX	<0.03	<0.04	<0.03	<0.04	<0.04	<0.04	<0.03
135NB	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
1,3 DNB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
tetryl	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.02
Trinitrotoluene	<0.02	**1.7**	<0.02	<0.02	<0.02	<0.02	<0.02
NB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
4ADNT	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
2A-4,6-DNT	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02	<0.01
26DNT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
24DNT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2NT	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
4NT	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
3NT	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

µg/g (ppm)	*hotspot-(0-5m) 2*	*hotspot-(5-10m) 2*	*hotspot-(10-15m) 2*	*Granate area-back*	*Granate area-left*	*Granate area-front*
NG						
HMX	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
RDX	<0.05	<0.05	<0.05	<0.05	<0.05	<0.06
135NB	<0.03	<0.08	<0.04	<0.03	<0.03	<0.04
1,3 DNB	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
tetryl	<0.01	<0.01	<0.10	<0.01	<0.01	<0.01
Trinitrotoluene	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
NB	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
4ADNT	<0.01	<0.02	<0.01	<0.01	<0.01	<0.02
2A-4,6-DNT	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
26DNT	<0.01	<0.02	<0.02	<0.01	<0.01	<0.02
24DNT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2NT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
4NT	<0.02	<0.03	<0.02	<0.02	<0.02	<0.03
3NT	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Crater areas of Rivsjöbrändan

Five craters were sampled at their bottom, wall and outside of which three were analyzed for residues of explosives. None of the samples contained levels above the limit of detection which also was supported by all field replicates. A composite sample, collected around one of the tanks contained elevated levels of RDX (6.5 µg/g) and TNT (59 µg/g) and were slightly exceeding the US-EPA Region III risk-based concentrations for residential soil. The degradation products 4A-2,6-DNT and 2A-4,6-DNT were also quantified in this sample.

Table 4. Results from crater areas and targets of Rivsjöbrändan

µg/g (ppm)	*Hotspot-around containers S-1A-HS*	*Crater composite S-1A-Cra-Com*	*Crater composite dupl. S-1A-Cra-Com*	*Target tank-comp. 1A-targtank*	*Crater1-bottom S-1A-cra-1B*	*Crater1-wall S-1A-cra-1W*	*Crater1-outside S-1A-cra-1O*
NG	**16**	<0.50	<0.50	**5.0**	<0.50	<0.50	<0.50
HMX	<0.05	<0.05	<0.05	<0.27	<0.05	<0.05	<0.05
RDX	<0.04	<0.04	<0.03	**6.5**	<0.04	<0.03	<0.04
135NB	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
1,3 DNB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
tetryl	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Trinitrotoluene	<0.03	<0.04	<0.02	**59**	<0.02	<0.02	<0.02
NB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
4-A-2,6-DNT	<0.03	<0.03	<0.03	**5.3**	<0.03	<0.03	<0.03
2-A-4,6-DNT	<0.02	<0.02	<0.01	**4.7**	<0.02	<0.01	<0.02
26DNT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
24DNT	<0.01	<0.02	<0.02	<0.07	<0.01	<0.01	<0.01
2NT	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
4NT	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
3NT	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

µg/g (ppm)	*Crater2-bottom S-1A-cra-2B*	*Crater2-wall S-1A-cra-2W*	*Crater2-outside S-1A-cra-2O*	*Crater3-bottom S-1A-cra-3B*	*Crater3-wall S-1A-cra-3W*	*Crater3-outside S-1A-cra-3O*	*U.S. EPA Region III*[a]
NG	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	**46**
HMX	<0.05	<0.05	<0.04	<0.05	<0.05	<0.05	**3900**
RDX	<0.04	<0.03	<0.03	<0.03	<0.04	<0.16	**5.8**
135NB	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	
1,3 DNB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
tetryl *	<0.03	<0.03	<0.02	<0.03	<0.03	<0.03	
Trinitrotoluene	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	**21**
NB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	
4ADNT	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	
2A-4,6-DNT	<0.01	<0.01	<0.01	<0.01	<0.02	<0.02	
26DNT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**78**
24DNT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**160**
2NT	<0.02	<0.02	<0.02	<0.02	<0.02	<0.03	
4NT	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	
3NT	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	

[a] U.S. EPA Region III, Risk-Based Concentrations in Soil, residential.
http://www.epa.gov/reg3hwmd/risk/index.htm

Multielemental analysis from the anti-tank range, Karlgrav

The introduction of field portable X-ray fluorescence (XRF) spectrometry dramatically enhanced the rapid characterisation of trace metals in the field (24). In Älvdalen, XRF was used to screen a high number of samples mainly for Pb-content which was perhaps the most obvious contaminant element to screen for. Samples were collected based on this screening together with the sampling strategy employed for the explosive residues (12) and this resulted in the collection of 16 samples. The correlation between data obtained by XRF and ICP was moderate to poor, but in our opinion sufficient for initial screening of samples (data not shown).

Most of the metals analysed are normally regarded as trace metals, but as the bullets contain lead (Pb) and the shells of most bullets (i.e. mantled bullets) and grenades contain copper (Cu) these metals were also present at elevated levels. Lead has further found use in the form of lead acetylsalicylate and lead ethylhexoate as additives in double base powder. Lead azide is known as an initiating explosive (25). Chromium was also found at higher levels and copper chromite has for instance been used as a catalyst for the burning of propellants in rockets (25).

Table 5. Multielemental analysis of the firing points and target area of the antitank area where higher levels are greyed.

	As	*Cd*	*Co*	*Cr*	*Cu*	*Hg*	*Ni*	*Pb*	*V*	*Zn*
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
target A	1.66	<0.093	1.21	18.7	26.1	<0.04	1.63	4570	<0.7	<0.8
target B	1.22	<0.073	1.87	<10	74.3	<0.04	4.53	7810	15.9	72.4
target C	<0.83	<0.075	2.1	28.3	58.1	<0.04	2.06	2640	15.2	36.8
C corner	1.49	<0.109	2.57	13.7	460	0.049	2.05	12900	15.5	117
C corner	2.09	<0.098	1.75	13.1	429	0.057	3.26	19200	13.6	105
fp 100 F	1.21	<0.084	1.64	18.2	6.42	<0.04	2.87	174	14.7	22.6
fp 100 B	2.7	<0.584	111	25.5	98.5	<0.04	6.33	2010	16.3	76
fp 400 T	1.41	<0.076	1.26	15.8	15.9	<0.04	2.48	611	12.4	25.9
fp 400 F	2.43	<0.201	1.31	<0.8	<0.4	<0.04	1.99	2520	18.2	19.7
fp 400 B	1.41	<0.082	2.28	18.1	24.7	<0.04	3.44	1360	24.5	29.6
fp 600 B	1.2	<0.076	1.26	16	15.8	<0.04	3.22	379	13.4	21.4
fp 600 T	1.2	<0.077	1.32	<0.2	9.92	<0.04	2.85	258	15.4	21.5
fp 600 F	1.15	<0.085	2.66	21.8	7.34	<0.04	3.24	756	25.2	31.6
fp 700 T	1.76	<0.074	<0.844	77.9	4.51	0.079	1.78	26.3	21.8	36.1
Fix. FP	1.26	<0.15	<0.379	17.5	5.66	0.058	1.45	33.7	<0.7	18.6
Fix. FP	<0.767	<0.094	<0.298	15.2	4.95	0.042	1.17	24.1	7.75	13.9
max	2.7	<0.584	111	77.9	460	0.079	6.33	19200	25.2	117
average	1.5	<0.13	8.8	25	82	0.057	3	3380	16	43
mod. [a]	15	<0.4	30	5.0	100	1	35	80	120	350
serious [a]	45	1.2	90	15	300	3	105	240	360	1050
very serious [a]	150	4	300	50	1000	10	350	800	1200	3500

[a] The guidelines and limits are based upon ecological endpoints and other criteria where the future use of the site is an important criterion.

The guidelines proposed by the Swedish Environmental Protection Agency (26) for sanction and possible remediation of contaminated areas were exceeded by the Pb and Cr levels in a few samples. Lead and copper were predominantly elevated in the target area (as marked by grey in table 5) whereas chromium was found at elevated levels both at the target and the firing positions. A recent report dealing with trace metals from munitions (27) states that several parameters besides the concentration were important observations related to bioavailability such as pH and amount of organic matter.

Conclusions

The three areas chosen for sampling in this study were different in many aspects mainly due to the different training activities held on each one. The hand grenade range and the anti-tank area are more spatially defined than the larger target area at Rivsjöbrändan where especially the firing positions are not equally well defined. With fixed positions for firing and targets judgmental strata can be identified. Within these strata random samples were collected to obtain representative samples based upon the sampling strategy employed. Emissions from training at moving targets were also different from fixed targets which also affected the sampling design employed in this study.
However, all the activities may give rise to emission and residues of the common secondary explosives like TNT, HMX and RDX. Rockets which propels the war-head filled with secondary explosives contain a propellant charge and howitzers are also fired assisted with propellants. Nevertheless, previous studies have shown that live fire high-order detonations leave very little of explosive residues (14). The findings from Älvdalen may not be adequate to fully support this but they are not in disagreement since only low levels of explosive residues were found. It must still be recognized that this study was not a comprehensive study where all possible residues from training and handling with energetic materials in all environmental compartments was covered (e.g. vegetation and surface or ground water). As the safety regulations did not allow any groundwater sampling, there is a lack of information about any possible leakage to the groundwater. In spite of these deficiencies in the sampling strategy and the relatively low and isolated levels of energetic materials found we still conclude that the Älvdalen range does not represent a high-risk situation from an environmental point of view. When compared to similar ranges sampled either in Canada or in the USA, our results tends to demonstrate that lower levels of munition residues were dispersed in Älvdalen. This might be explained by the lower intensity and frequency of the Älvdalen firing events.

The elevated concentrations of Pb at the target areas (Table 5) are most likely explained by the fragmentation of the lead bullet which occurs within some tens of centimetres from its intrusion in earthen berm. In a previous investigation it has been found that most of the lead is distributed within the fraction < 2mm; i.e. in the form of small particles from the demolished bullet (28). Since the soil samples in the present study concerns the < 2mm fraction, the high levels of Pb in the earthern berm of the target area is understandable. The high Cu-contents associated with the elevated Pb, probably emanate from lead bullets that are mantled by Cu. The higher Pb content in soil at some of the firing positions (Table 5) is most likely explained by the use of gun powder with some lead content (29). Also, sometimes following artillery exercises, excess propellants are burned directly on the ground and some of the bags contain lead foil that is used to replace the gun barrel during firing.

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Appendix 1

Analytical collaboration

Interlaboratory Comparison of Explosives in Soil Samples from Älvdalen, Sweden

Results - Trilateral collaboration

FOI-NBC-defence
Umeå Sweden

DRDC-Valcartier
Canada

TNO PML
The Netherlands

Introduction

Environmental impact of explosive residues at shooting ranges has been under investigation in the USA and in Canada over the past ten years. The trilateral collaboration focuses mainly on sampling and investigation strategies where information and experiences are exchanged. It has been shown that the largest source of uncertainty lies within sampling. Nevertheless, during the trilateral discussions chemical analytical issues appeared to be of significant importance to the participating laboratories. Since a chain is not stronger than its weakest link, an introductory comparison of analytical performance, based on the samples from Älvdalen shooting range in Sweden, was organised. The main scope of the study was not to designate or qualify laboratories but to address important limitations and possibilities within chemical analytical work. A consensus approach for the analytical work would also be beneficial for trustworthiness and comparisons within these studies. The internal quality work for the laboratories is also supported by international collaboration exercises and may further be used as a motive for improvements and method development.

Samples, shipment and storage

To limit the amount of work the number of samples was kept low (3 samples where one was suggested to run in triplicate). An analyte solution with known concentration was shipped along the samples to be quantified with in-house standards. Hence, precision and accuracy was covered to be able to compare performance between and within laboratories. The choice of methods was free but the laboratories were asked to specify procedures and techniques used. Soil samples were taken in Älvdalen 2003 from the antitank range (target area). Samples were sieved (2 mm) and thoroughly mixed before secondary samples (~60g for sample A and ~25 g for sample B and C) were taken. Analyte solutions (S1 and S2) were prepared from commercial standard mixtures (EPA 8330 mix A and B, Supelco, Bellafonte, USA) and diluted with acetonitrile to a target value of ~20 mg/l.

Choice of methods

The extraction and clean-up methods used were based on EPA 8330 for all laboratories but the analysis was performed with HPLC, GC and GC-MS. In short, the samples, 8-20 grams, were extracted by shaking and/or sonication with acetonitrile (10-60 ml) for a period of 1-18 hours. Thereafter followed 0.45 µm disk filter (PTFE) for the extracts and two laboratories concentrated the extract before analysis to enhance detectability. The other lab used large volume injection, 500 µl, to obtain the same effect. Internal standard was used for the GC-MS-method to compensate for losses and final volume adjustments.

Results

All laboratories reported complete results within a three month period and after introductory statistical data handling the discussion took place at the trilateral meeting at Petawawa during a sampling campaign organised by DRDC-Valcartier.

Analyte solutions

An almost complete data table was obtained for the analyte solutions S1 and S2, c.f. table 1. The target concentration was 20 mg/l for each analyte and the overall average values ranged 19-22 mg/l for all analytes except for trinitrobenzene which was lower, 13 mg/l. Individual observations might be considered as outliers but in general quite consistent data was obtained as can be verified by reasonably low coefficients of variation, < 20% in most cases. The within lab variation was a parameter not specifically asked for in this exercise, but are usually found to be much lower (< 5%).

Table 1. Results from analyte solution S1 and S2 with a target value of 20 mg/l.

	Lab1	Lab2 [1]	Lab2 [1]	Lab3 [2]		
Analyte solution	HPLC	GC	HPLC	GC-MS		
S1	mg/l	mg/l	mg/l	mg/l	Mean	CV%
Nitrobenzene	-[4]	15.9	19.2	21.3	19	14
Dinitrobenzene	22.0	15.9	19.1	23.1	20	16
2,4-DNT	23.5	16.4	19.4	22.5	20	16
Trinitrobenzene	15.5	5.1[3]	14.5	17.1	13	41
Trinitrotoluene	35.2[3]	16.8	15.9	18.7	22	42
RDX	21.8	16.4	19.4	25.7	21	19
2-A-4,6-DNT	22.1	16.2	19.4	24.3	20	17
HMX	20.2	24	19.1	-[2]	21	12
S2		mg/l	mg/l	mg/l		
2-nitrotoluene	-[4]	16.9	19.2	20.8	19	10
3-nitrotoluene	24.4	16.8	19.1	20.7	20	16
4-nitrotoluene	24.4	16.7	18	20.6	20	17
2,6-DNT	23.9	16.4	18.9	22.3	20	17
4-A-2,6-DNT	21.9	14.8	17.9	24.2	20	21

[1] Lab 2 reported results for both GC and HPLC
[2] Lab 3 used GC-MS and HMX was not analysed
[3] Observations considered as outliers
[4] not reported

Result soil samples

The results from the soil samples became difficult to interpret. The limitations of the different methods were apparent since the concentrations of explosive residues were quite low and detection criteria could not be met in most cases. Furthermore, no tests for homogeneity were executed before shipment, however the sample preparation procedure does not make non-homogeneity likely. On the other hand, sample non-homogeneity as a cause of discrepancy in the results can not be ruled out. An overall mean seems thus not applicable. The percent dry weight of the samples (sandy) were high (>90 %) resulting in that no discrepancy regarding the nature of the sample should be considerable. Lab 2 and Lab 3 show consistency for sample C for most analytes except HMX. Lab 1 has reported results for HMX in sample C which also Lab 2 supports in their results. Within lab variation can be studied in some cases and it seems that the performance regarding this parameter is far from excellent even though exceptions are present. Neither averages nor standard deviations were applicable. It is quite clear that samples with higher concentrations must be analysed in order to justify a proper interlaboratory comparison of the results.

Lab 1

SAMPLE	TNOA2-a	TNOA2-b	TNOA2-c	TNOB2-a	TNOB2-b	TNOC2-a	TNOC2-b
Nitrobenzene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-nitrotoluene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-nitrotoluene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-nitrotoluene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dinitrobenzene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-DNT	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4-DNT	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trinitrobenzene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trinitrotoluene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
RDX	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-A-2,6-DNT	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-A-4,6-DNT	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HMX	n.d.	n.d.	n.d.	230	430	2190	9840

Lab 2

	sample A1		sample A2		sample A3		sample B		sample C	
	GC	HPLC	GC	HPLC	GC	HPLC	GC	HPLC	GC	HPLC
	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
component										
Nitrobenzene	<2	<4	<2	<4	<2	<4	<2	<4	146	12.9
2-nitrotoluene	<2	<4	<2	<4	<2	<4	<2	<4	<2	<4
3-nitrotoluene	<2	<4	<2	<4	<2	<4	<2	<4	<2	<4
4-nitrotoluene	<2	<4	<2	<4	<2	<4	<2	<4	<2	<4
Dinitrobenzene	<2	<4	<2	<4	<2	<4	<2	<4	<2	<4
2,6-DNT	<2	<4	<2	<4	<2	<4	2.7	<4	38.3	51.2
2,4-DNT	<2	<4	<2	<4	<2	<4	7.6	7.4	108	135
Trinitrobenzene	<2	<4	<2	<4	<2	<4	<2	<4	<2	<4
Trinitrotoluene	<2	<4	<2	<4	<2	<4	2.2	4.0	8.5	13.4
RDX	8.0	12.0	<2	<4	<2	<4	3.0	<4	1.8	<4
4-A-2,6-DNT	<2	<4	<2	<4	<2	<4	6.6	8.8	7.0	7.0
2-A-4,6-DNT	<2	<4	<2	<4	<2	<4	3.4	4.0	2.4	3.7
HMX	2410	1230	10	15	4	17	652	544	11100	4820

Lab 3

	A1	A2	A3	B	C	Blank
sample weight	10,91	11,04	11,51	13,76	13,57	"10"
dry weight	10,1	10,3	10,7	13,2	12,3	"10"
dry weight %	93	93	93	96	91	"100"
µg/kg dw						
Nitrobenzene	<0.2	<0.1	<0.1	<0.1	<0.2	<0.1
2-nitrotoluene	<0.2	<0.2	<0.2	<0.1	<0.2	<0.2
3-nitrotoluene	<0.2	<0.2	<0.2	<0.1	<0.2	<0.2
4-nitrotoluene	<0.2	<0.2	<0.2	<0.1	<0.2	<0.2
Dinitrobenzene	0.27	<0.10	<0.10	0.10	0.11	<0.1
2,6-DNT	<0.10	<0.10	<0.10	1.8	69	<0.1
2,4-DNT	0.57	0.49	0.70	7.8	200	<0.2
Trinitrobenzene	1.6	<0.7	<0.5	0.76	2.3	<0.6
Trinitrotoluene	0.097	0.12	0.083	1.2	5.9	<0.1
RDX	2.0	1.5	1.3	6.7	9.8	<0.75
4-A-2,6-DNT	0.25	0.16	0.13	0.50	0.23	<0.1
2-A-4,6-DNT	4.1	5.4	6.1	4.5	7.0	<0.1
HMX	-	-	-	-	-	-

Discussion Samples and Analyte solutions

The main task for analysis of explosive residues at shooting ranges is to detect and quantify the distribution and the extent of contamination at these sites. The characteristics of the emission of explosives used often results in a widespread and heterogeneous contamination which for a proper description of the residue distribution generate a lot of samples. The different inherent properties of these compounds, regarding mobility, volatility and degradability complicate the task even further. Hence, the analytical methods must be of high throughput but also specific and sensitive enough to be able to generate results that can answer such questions. Below follows the summarised discussion from the meeting in Petawawa where we agreed to continue the analytical collaboration.

HPLC-methods are favourable due to their robustness and reasonably low price for operation but have drawbacks in sensitivity. This can however be compensated with higher concentration factors. However, analysing samples containing high levels of e.g. soil co-extractives might give serious problems concerning specificity when using UV-detection. The superior detectability and efficiency of the GC-MS method suffers from the inability to analyse the more ‘unstable’ compound HMX. This problem is sometimes solved for GC using EC detection and a high flow rate (15-20 ml/min) which is incompatible for MS. Practicality and the abovementioned benefits, decided for us to agree upon HPLC-UV as the common detection technique for future exercises. To combine HPLC with other techniques such as GC or MS are of course optional. Besides detection the methods were quite similar e.g. regarding sample size, extraction solvent, clean up, concentration factors etc. and all methods were essentially based on US EPA 8330. We discussed the choice of extraction technique and we agreed that it should be up to the participating labs to decide extraction technique in future exercises since we all had different experiences with different types of samples. In some cases e.g., when analytes are loosely bound to the sample matrix, the extraction technique is probably insignificant for the result.

In conclusion, the results for the first exercise were fruitful and promising. Even though the soil sample results were not proven fully satisfactory (due to low concentrations), some consensus was reached regarding: analysis of the analyte solutions, the choice of detection technique and a general approach for future laboratory exercises on explosive residues.

Action plan-Future work

We agreed that a similar approach for the next inter-laboratory comparison was adequate but with a few alterations. At least one of the analyte solutions should be of unknown concentration, but of course within reasonable ranges (e.g. 1-50 mg/l). There was further no need to separate the Mix A and B from Supelco (which was used as stock solution) in different solutions. The samples should also be checked or assured for homogeneity so that appropriate concentrations were present. DRDC-Valcartier will prepare the samples for the next exercise along with sample extracts to be able to compare the different extraction techniques employed by laboratories. FOI-NBC-Umeå will prepare analyte solutions for the next exercise. The results will further be open to all participating laboratories.