ENVIRONMENTAL EXPLOSIVE CONTAMINATION RESULTING FROM MUNITIONS USE

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ABSTRACT.
Local, State and Federal authorities are concerned about the potential environmental contamination resulting from the intended and unintended detonations of Unexploded Ordnance (UXO) at sites where active firing of munitions occurs, and where investigations and removal activities are conducted for former ranges or open burning/open detonation activities.

This paper discusses the results of studies conducted by the Corps of Engineers at Formerly Used Defense Sites (FUDS), Base Realignment and Closure Sites (BRAC), active ranges, and for sites where others have conducted studies. Sampling procedures and analysis used for studies will be presented.

BACKGROUND.
Along with being a potential imminent safety hazard to the public, nitroaromatic compounds, specifically explosives, are compounds of concern to local State and Federal authorities. These explosive compounds generally include, but are not limited to: 2,4,6-trinitrotoluene (TNT); Hexahydro-1,3,5-trinnitro-1,3,5-triazine (RDX: **R**esearch **D**epartment E**x**plosive; **R**oyal **D**emolition E**x**plosive; or **R**oyal **D**utch E**x**plosive); octahydro-1,3,5,7-tetranitro-1,3,5-tetrazocine (HMX); N-methyl-N,2,4,6-tetranitroaniline (tetryl); and associated byproducts and degradation products. These "nitroaromatics" are also potentially toxic to indigenous species and present a significant concern for site remediation. (9) This paper presents the results of studies that attempted to quantify these compounds in the environment under a variety of field conditions, as well as the sampling procedures, and analytical methods used for the studies. The studies and reports referenced are a compilation of information collected by the Ordnance and Explosives (OE) Center of Expertise (CX) for soil testing at OE sites suspected to contain contamination of explosives, including the results from performing field screening on inert OE scrap. Since air emissions, and non-explosive constituents are not considered thoroughly here, this paper should not be construed to be a comprehensive listing of all U.S. Army or Corps of Engineers sampling efforts for potential explosive contaminants, but as a presentation of common sampling and analysis techniques, and a collection of several project studies as examples.

Explosives can be transported to a project site through a variety of pathways, such as from ammunition plant operations, as "firing point residue" (casings or shells) or from munitions on a firing range that have not functioned properly. On firing ranges, the resultant "range residue" may not have gone "high order" or may have broken open upon impact rather than exploding as designed. A high order detonation is a very efficient process, where the majority, if not all, of the explosives are expended as designed. There is a concern regarding those items that do not function properly, thus potentially depositing residual explosives on the surface or subsurface.

Explosives are generally solids at ambient temperatures, have low water solubilities, meaning they don't usually dissolve in water, but do cling to soil particles. They are relatively non-volatile, are generally located at or near the surface of the soil (2 to 6 inches) and may persist on the surface for long periods of times (50 to 100 years). (7)

The product constituents for the detonation of explosives are generally limited to “environmentally benign” compounds, such as carbon dioxide, nitrogen, and water, with miniscule yet “varying amounts of carbon monoxide, mixed nitrogen oxides (NOX), volatile organic compounds (VOCs),” and some unconsumed explosives. “The amounts are dependent on the efficiency of the detonation and elemental makeup of the [munition].” (1) While studies are available for more detailed evaluations, this paper does not focus on air emissions of explosives. (14)

As safety should be the first and last consideration for sampling in any areas suspected of containing explosives, visual observation of a sampling location is important when a sample is collected from a site expected to contain explosives. Lumps of material that have a crystalline appearance should be suspect and great care should be taken during blending, or homogenizing, of the soil. Explosives are generally a very finely ground grayish-white material. (11). Soils containing greater than 10% of explosives (dry weight) have been determined to pose an explosive hazard (Engineering Regulation (ER) 1110-1-8153, and 40 CFR 261.23(a)(6)). Therefore, reasonable precautions should be taken when sampling soils or sediments that may contain explosives.

SAMPLING METHODS. Regardless of the media being sampled, to have confidence in contaminant concentration data, care must be exercised in the collection, and handling of all samples. Sampling error can be a major factor in total characterization error. (7)

Soils.
Sampling protocols that meet the minimum requirements for a particular analysis method must be followed. The quantity and location of samples are project-specific decisions. Each site has its own needs that the project team must determine in order to meet project objectives. For sites where potential UXO restricts access, with proper training, collection of soil samples by Ordnance and Explosives (OE) personnel have worked very well at some sites. (7).

Distribution of Samples. One study attempted to characterize the distribution of soil and residual compounds after a planned detonation on newly fallen snow. As a result analysis showed that, while still very small amounts, residues of TNT and RDX were distributed heterogeneously over a large area of the snow, emphasizing the need to collect a significant quantity of surface area samples to achieve representativeness. (5) Another study found that the use of “composite sampling”, or combining same-depth samples at a variety of sampling points, obtained more representative samples. This same study showed that by taking six-inch deep samples at the center, and along the edges of a four-foot diameter circle around a crater, or detonation, results varied by an order of magnitude (HMX from 16 Mg/Kg to 328 Mg/KG). These sample locations were within a separation of 4 ft. This results in many more samples being collected than might seem necessary, yet may be required to achieve an accurate characterization of a detonation site. (7) Past studies also supported the large quantities of samples required to fully characterize a detonation site. (2)

Homogeneity of Soil. The soil collected from a sampling location should be well blended to ensure homogeneity of the sample. Same-depth samples taken mere inches apart have resulted in substantial differences in analysis results (3). “Blending” the soil sample, prior to packaging for shipment to the laboratory, or prior to field screening, is needed to ensure the sample is homogeneous.

Depth of Samples. Samples should be taken at consistent depths in order for profiles to be established for a sampling location, but care should be taken to collect discrete samples at shallow depths to verify if any residual explosives remain that are near the soil surface. “Vertical composites” should not be used, as the concentration of explosives usually drops off with depth. Again, sources of explosives are generally at or near the surface, and a vertical composite will not give a representative sample. (3)

ANALYSIS METHODS
Field Analysis.

Field analysis is useful in increasing the likelihood that 1) samples for expensive laboratory samples are taken at locations containing the contaminant of concern, and 2) the area, or footprint, of the area of concern is better defined when only a rough estimate of contamination, not laboratory quality results, are needed. There are numerous commercial field-screening kits available as a field method for screening for concentrations of TNT in soil or sediment. There are also field-screening kits for water samples. For all field methods used, it is crucial that personnel have proper training on sampling protocols so the results will be accurate. Laboratory analysis of split samples may be needed to confirm that the field screening kit results are within a reasonable range in order to verify the accuracy of the field analysis.

Soil. Method 8515 can be used to screen soil samples for the presence of TNT and other chemically related nitroaromatic compounds (e.g., dinitrotoluenes (DNT) and 1,3,5-trinitrobenzene (TNB)) at concentrations above 1 parts-per-million (ppm), but this method does not measure RDX or HMX. (12) While it may not provide the accuracy or results of proven field sampling methods for other explosive contaminants, Method 8510 is a field method that might be considered for screening for concentrations of RDX in soil or sediment, but HMX may interfere with the detection of RDX. Some colorimetric methods have been very effective for site characterization of HMX and TNT Concentrations. (7) Field screening techniques have also been useful in determining whether residual explosives are found on “inert” range residue, or OE scrap. (8)

Water. Studies have been conducted for a variety of commercially available field test kits (i.e., colorimetric, or immunoassay analytical methods) for explosives in water, but field screening water samples has not been performed as often as for soil screening. Over a range of field conditions, the colorimetric methods for TNT and RDX showed the highest accuracy of the commercially available methods. (13)

Range Residue. Wipe samples and “Webster Reagent “drop tests have been utilized to determine whether residual explosives remain on range residue, or inert OE scrap. (8) There are very likely other proven commercial tests that provide similar or better results.

Laboratory Analysis.
Regardless of the analysis method selected, the laboratory and analyst must demonstrate the ability to generate acceptable results for the required analysis. Method 8330 provides high performance liquid chromatographic (HPLC) conditions for the detection of parts-per-billion (ppb) levels of certain explosives residues in water, soil and sediment matrix. It is very important to ensure that in addition to receiving quality analysis results for the “parent” nitroaromatic (e.g. TNT, RDX) that secondary nitroaromatics (i.e., 2-amino-4,6-dinitrotoluene (2ADNT), produced from naturally occurring processes, such as transformation, or biotransformation, are also analyzed at similar detection limits. Again, prior to use of any method of analysis, appropriate sample preparation techniques must be followed. (11)

While analysis methods for metals indicative of OE may be useful to meet project objectives, the imminent hazard of explosives in the environment is the focus of this paper, and is usually the driving force for field investigations. Sampling and analysis protocols for metals and other subsidiary contaminants generally contained in OE items are well established and can be performed by the appropriate environmental professionals.

Soil. Standard precautionary measures used for handling other organic compounds should be sufficient for the safe handling of the analytes targeted by Method 8330. Extra precaution should be taken when handling soil samples that are highly contaminated with explosives. It is advisable to ensure that the laboratory is screening soil samples using Method 8515 to determine whether high concentrations of explosives are present. While Method 8515 is for 2,4,6-TNT, the analyte most often detected in high concentrations in soil samples, other nitroaromatics will also cause a color change that would provide a rough estimate of their concentrations. (11)

Water. While safety precautions should be taken for water sampling, the standard sampling protocols and Method 8330 for target analytes should be used, whether for surface or ground water samples.

EXAMPLE PROJECT FINDINGS.

Camp Bonneville, WA: "All OE related scrap with at least two dimensions greater than 3 inches in size" was inspected and tested by a variety of field screening tests to confirm that no residual explosives remained on the inert items. Websters Reagent and Diaphenylamine Reagent were used as field screening tests for nitroaromatics (TNT) and nitroamines (RDX), respectively, in order to eliminate reactive or ignitable waste. This was coordinated with the local and Federal Regulators. No reactive or ignitable wastes were reported as a result of the field screening reagent "drop" tests. (8)

Open Burning/Open Detonation at Camp Claiborne, LA and Camp Grant, IL: The oldest study considered (1996) was one of the most extensive in nature, in that it evaluated the results at two study sites using similar sampling protocols and analysis. Method 8330 was used for laboratory analysis of soils and for the few water samples collected. Soil samples were taken in the center of the detonation as well as "two samples or more in each of the cardinal compass directions at set radial distances" from the detonation point. The sampling and analysis resulted in "no notable contamination involving explosives or their by-products [being] found in any samples." While concluding the results after extensive soil and limited water samples that the concentration of explosives residuals after a detonation are negligible, the study did recommend that emissions and emission fractions be determined in future studies. (2)

Camp Ethan Allen Firing Range, VT and Fort Drum NY: The distribution of sampling locations is discussed earlier in the paper, but there are noteworthy results from this study that need to be highlighted here. While analysis results are negligible for explosive constituents, the study found "that a higher percentage of TNT is consumed in detonations than RDX when the main charge [of the munitions] is Composition B. This appears to be true whether C4 explosives are used to detonate the [UXO] or not. Thus, residues of RDX are present at much higher surface concentrations than TNT. HMX was also observed in residues with approximate surface concentrations about 20% of RDX." These results are also likely influenced by the types of UXO detonated (81-mm mortar round and 64-mm mortar round), but are noteworthy for future studies. The key points of this study are the minimal residual contaminants, and that residues of TNT and RDX were distributed heterogeneously on the surface snow, emphasizing the need to collect a large quantity of surface area samples to achieve representativeness. (6)

Four Installations—Canadian Force Base, Valcartier, Quebec; Fort Ord, CA; Canadian Force Western Training Center Wainwright; and Canadian Forces Ammunition Depot Dundurn: The results of the study at four separate ranges found that "in general, low levels of multi-contamination by explosives were found on firing ranges, demonstrating that the detonation of ammunition is a relatively clean process which lead to minimal impact on the environment. The exception was high levels of HMX in surface soils at a Canadian antitank range." Also, the study noted that "the concentration of HMX was almost always several orders of magnitude higher than TNT in soil at all four installations. The study also states that the lower concentrations of TNT may be a result of "an attenuation process", since "TNT dissolves more rapidly in water and leaches into the soil profile, where it can be transformed." As would be expected, the ranges with the lowest usage as a firing range had lower levels of residual explosives contamination. (15)

CONCLUSIONS.

The studies and reports reviewed showed that there are proven sampling techniques and analysis that may be used to characterize the potential for residual explosives at detonation locations. The studies also showed that for munitions that function as designed, the likelihood of residual explosives being released at a point of detonations is very low, if not negligible.

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