CHARACTERIZATION OF RANGES, LESSONS LEARNED

Jay Clausen, AMEC Earth and Environmental, Inc., Westford, MA. US
Joe Robb, AMEC Earth and Environmental, Inc., Westford, MA. US

ABSTRACT
Over the past several years, a number of ranges have been studied for environmental impacts. These ranges encompass activities such as training with artillery, mortars, ground-to-ground rockets, air-to-ground rockets, and pyrotechnics. A comprehensive review of these studies has identified several key issues that must be addressed for successful characterization of military ranges. The categories to be addressed in the presentation will include; analytical, soil sampling, groundwater sampling, geophysical, contaminants of concern, fate-and-transport, and modeling.

RÉSUMÉ
Au cours des dernières années, plusieurs champs d'entraînement militaires ont été étudiés en relation avec leurs impacts environnementaux. Ces champs sont utilisés pour diverses activités d'entraînement incluant l'artillerie, les mortiers, les missiles sol-sol, les missiles air-sol et les pièces pyrotechniques. Une revue exhaustive de ces études a permis d'identifier plusieurs aspects clés qui doivent être considérés pour la caractérisation efficace des champs d'entraînement militaires. Les aspects considérés dans la présentation sont les suivants : méthodes analytiques, échantillonnage des sols, échantillonnage de l'eau souterraine, la géophysique, les contaminants d'intérêt, le devenir et le transport des contaminants et la modélisation.

1. INTRODUCTION

Contamination of military ranges is a potential problem in the USA and other countries. Armstrong (1999a,b) estimated there are 50 million acres in the USA impacted by training activities. However, the scope of the problem is largely unknown since most active and inactive military ranges have not been studied. Ranges at military installations can span a few acres up to 100,000s of acres making traditional investigations expensive and time consuming. Extensive studies at a select number of military ranges has resulted in the identification of a number of lessons learned covering analytical issues, soil sample protocols, identification of contaminants of concern, groundwater sampling, geophysical applications, fate-and-transport modelling, remedial scenarios, and regulatory issues that are applicable for most range investigations. This paper will discuss the significant findings of the first four lessons learned categories.

2. BACKGROUND

The lessons learned and applied involve the study of several military ranges in the USA. However, the primary source of information involves an exhaustive study of a military installation located in the eastern USA. The 21,000-acre facility contains ranges for rocket, artillery and mortar, and small arms that have been used for training activities since 1908. Site investigations, therefore, have addressed a variety of types of firing ranges, OB/OD (open burn/open detonation) sites, firing positions, and targets.

The primary high explosive used prior to WWII was 2,4,6-trinitrotoluene (NT) while Composition B (60:39 hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)/TNT) was introduced during WWII. Another explosive compound, octahydro-1,3,5-7-tetranitro-1,3,5,7-tetrazocine (HMX) is present in Composition B as an impurity (up to 10% by weight) of RDX and is used in Octol (70:30 HMX/TNT). Perchlorate is an oxidizer found in rocket propellant, pyrotechnics, fuses, spotting charges, and some explosive munitions such as flash grenades.

2.1 Sampling Analysis Program

The scope of the sampling program for the Eastern USA site has been large and can be summarized as follows;

- > 10,000 shallow surface soil,
- > 1,600 deep soil boring,
- 69 sediment and 64 surface water,
- > 10,000 monitoring well, and
- > 6,000 groundwater profile samples.

The analytical suite has been as extensive as the scope of the sampling program consisting of 218 analytes: explosives, semi-volatile organic compounds (SVOCs), volatile organic compounds (VOCs), methyl tert-butyl ether (MTBE), ethylene dibromide (EDB), polychlorinated biphenyls (PCBs), herbicides, pesticides, metals, cyanide, phosphate-phosphorous, nitrate/nitrite-nitrogen, ammonia-nitrogen, total organic carbon, and certain explosive metabolites or byproducts. In selected areas dyes, polychlorinated napthalenes (PCNs), titanium, and white phosphorous were analyzed in soil samples. Later in the program, perchlorate, antimony, and molybdenum were added as standard groundwater analytes. An exhaustive study of tentatively identified compounds was also conducted (Clausen et al. 2004).

3. RESULTS AND DISCUSSION

During the course of investigation at various military installations and the eastern USA site it has become clear a number of standard operational procedures for environmental investigations needed to be altered to address the unique aspects of military ranges.

3.1 Analytical Lessons Learned

Early on in the study of the Eastern USA site, it became clear that a number of analytical methods needed modification. The explosive analytical methods were largely developed to address assessment of ammunition plants and their associated potential high concentration in the environment. In contrast, explosive levels in the environment associated with military ranges have been found to be much lower (Pennington et al. 2003).

3.1.1 Field Explosive Methods

Field explosive test kits utilizing colorimetric techniques were employed in the early stages of the range studies. The colorimetric methods have an analytical detection limit of approximately 1 ppm (Jenkins et al. 1995). Lack of detections with the explosive colorimetric method led to modifications of the method resulting in numerous false positives. Collection of split samples and performing USEPA Method 8330 analysis confirmed the high number of false positives indicating the method change was inappropriate (Ogden, 1998). Since the Method 8330 analysis indicated most detection of explosives were below 1 ppm it became clear the colorimetric methods were not suitable for military range studies. Consequently, our field studies have relied solely on Method 8330 with the modifications discussed below.

3.1.2 Laboratory Explosive Analysis

Our initial studies of military ranges suggested the standard explosive analytical method, Method 8330, was insensitive for a number of explosive compounds and did not include all explosive compounds of interest. In particular if the presence of nitroglycerine (NG), a primary propellant in some rockets needs to be evaluated then method modifications are necessary to improve the sensitivity of the method to this compound. Although picric acid (PA) Is also insensitive to this method our studies indicate this compound is rarely found, which is consistent with its limited usage and quantity in most munitions (AMEC, 2001a).

Method modifications, primarily mobile-phase adjustments, were also necessary to expand the analyte list. TNT and RDX intermediate transformation products are not included on the standard analyte list for Method 8330 nor is pentaerythritol tetranitrate (PETN). Therefore, method modifications were necessary to add 2,4-diamino-6-nitrotolune (2,4-DANT) and 2,6-diamino-4-nitrotoluene (2,6-DANT) to assess the presence of TNT transformation products as well as the RDX transformation products of MNX, DNX, and TNX.

Sample preparation procedures, such as increasing the sample aliquot size to 30 grams and using solid phase extraction, were also implemented to lower the analytical detection limit of the method. Finally, it was recognized that Method 8330 often provided apparent false positives given the uncertainty of chromatography curve matching when numerous interference peaks were present (AMEC, 2001a). This last issue was dealt with by utilizing the photo diode array (PDA) spectra over a brad wavelength, which can be captured with the chromatography instrument and provides a more positive identification of analytes. The PDA spectra review on all samples greatly reduced the uncertainty in the results and resulted in a much lower number of false positives.

3.1.2 Perchlorate Analytical Methods

At the request of the regulatory agencies involved in our projects, it became necessary to lower the analytical detection of perchlorate using USEPA Method 314.0 in water and soil. Method 314.0 a drinking water method was not developed for environmental investigations. Consequently, interference issues are significant factor especially when lowering method detection limit. Currently, the standard Method 314.0 procedures have been modified to lower the method detection limit from 4 to 0.34 ug/L in water. Two methods have been developed to address the potential for false positives. The first approach involves a second chemist to independently assess the chromatography results. If necessary, samples are reanalysed to confirm the first result. A second approach has been to utilize USEPA Method 8321 developed for explosives but modified for perchlorate analysis to provide confirmation of Method 314.0 results. The second approach has found a limited number of instances where a false positive result had to be reversed. In a few cases, the modified 8321 Method suggested the presence of perchlorate when Method 314.0 indicated no perchlorate present.

3.2 Soil Sampling Lesson Learned

Through the efforts of our work (AMEC, 2001b) as well as the work of Pennington et al. (2003), and Jenkins et. al. (2001) it is apparent standard surface soil sampling protocols, i.e. discrete sample collection, are not appropriate for military ranges. The distribution of energetic residues is heterogeneous and thus to capture a representative sample requires the collection of composites. Higher maximum explosive concentrations and an increased frequency of detections were observed with composite versus discrete samples (AMEC, 2001b). In addition, sample homogenization in the field and laboratory is required to reduce the intra-sample variability. Split samples from the same sample container have exhibited ppm levels and non-detects of explosives. Given the large size of many military ranges and concomitant large number of samples necessary to adequately characterize it may not be prudent to collect soil samples unless specific target locations are known prior to the start of field efforts. As discussed below, groundwater may be a more useful starting point to assess environmental impacts from range operations.

3.3 Groundwater Sampling Lessons Learned

The general concern at most military installations is whether environmental degradation of groundwater has occurred. A groundwater investigation is a good starting point since it is a useful integrator of environmental impacts over a large surface area. Thus, a few appropriately placed groundwater borings can provide information covering a large area. Our experience suggests a well fence of three to five borings placed perpendicular to groundwater flow several hundred to thousand feet downgradient of the primary target area provides the most useful information (AMEC, 2001c, d). Groundwater borings placed at the range boundary, in many cases, are located too far downgradient to adequately characterize whether munition explosive constituents (MEC) are present.

However, one observation from the collection of groundwater profiling "grab" samples is the increased risk of interferents in the water samples. Interferents from drilling greases used for lubrication of drill pipe as well as increased turbidity of water resulted in an increase in false positives for certain explosive compounds. (AMEC, 2001a). The use of the PDA spectra as discussed in Section 3.1.2 greatly reduced the number of false positives and aided in chromatography interpretation.

3.4 Munition Explosive Constituents present at Military Ranges

As discussed in (Clausen et al. 1994) an exhaustive study at the eastern USA military installation permits the development of a conceptual model to guide investigations at other training ranges. The type of training range is instrumental in determining what type of compounds can be expected and then selecting the appropriate analytical method. General observations suggest the following types of MEC can be expected in soil (Table 1).

Table 1. MEC expected by range activity.

Range Activity	MEC Anticipated
Artillery/Mortar Impact Area	RDX, HMX, TNT, 2a-DNT, 4a-DNT
Artillery/Mortar Firing Position	2,4-DNT, 2,6-DNT, N-nitrosodiphenylamine, diethyl phthalate, di-n-butyl phthalate
Rocket Impact Area	RDX, HMX, TNT, NG
Rocket Firing Point	NG, nitrocellulose, EC
Demolition Area	Explosives, metals, PAH, PCNs, perchlorate, dioxins
Weapons Test Ranges	Explosives, perchlorate, PCNs, dioxins

2a-DNT - 2-amino-4,6-dinitrotoluene
4a-DNT - 4-amino-2,6-dinitrotoluene
2,4-DNT - 2,4-dinitrotoluene
2,6-DNT - 2,6-dinitrotoluene
EC – ethyl centralite
PAH – polynuclear aromatics
PCN – polychlorinated napthalenes

Figure 1 is a summary of and frequency of detection of MEC found in soil at the eastern USA installation across all sites studied. The primary MECs evident are the explosives - principally RDX, HMX, and TNT transformation products 2a-DNT and 4a-DNT, the propellants – principally DNT, EC, and NG, and propellant additives – phthalates and N-nitrosodiphenylamine derived from the oxidation of diphenylamine. TNT's frequency was low indicating rapid aerobic transformation as suggested by more frequent detection of the 2a-DNT and 4a-DNT transformation products (AMEC, 2001b). The other category includes detection of the explosive compounds PETN, nitrobenzene (NB), nitrotoluene (NT), picric acid (PA), and tetryl. Subsequent work has indicated the PETN detections were false positives (AMEC, 2001a). The presence of detections of NB, NT PA, and tetryl remain suspect due to the limited number of munitions containing these compounds or their absence in the munitions known to have been used at the eastern USA site.

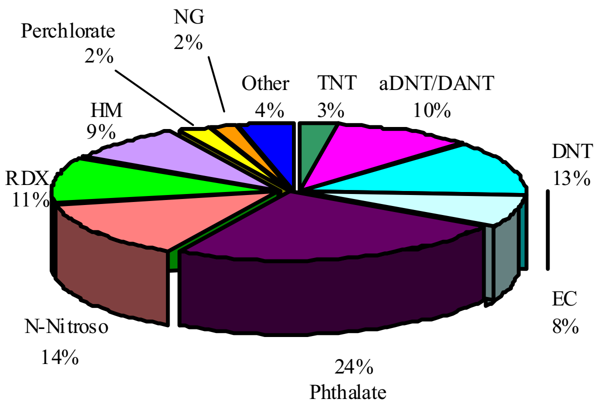

Figure 1. Distribution of munition explosive constituents in soil at the eastern USA military installation.

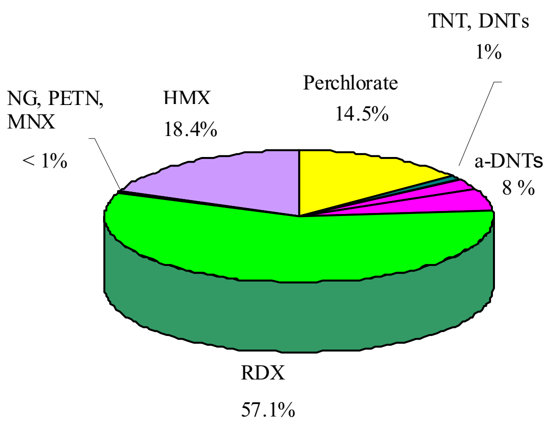

Figure 2. Distribution of munition explosive constituents in groundwater at the eastern USA military installation.

The distribution of MEC in groundwater is different than observed in soil and reflects abiotic and biological transformation as well as sorption processes. Figure 2 shows the distribution of MEC in groundwater from the eastern USA military installation.

Figure 2 indicates that the most mobile MEC are RDX, HMX, and perchlorate owing to their lack of transformation and sorption. These three compounds should be considered the primary compounds of interest for any study of military installation. Comparison of Figure 2 with Figure 1 indicates that the mobility of TNT is further limited in groundwater. Studies of two different sites; a demolition area and artillery/mortar range indicate TNT is only found near the source area and is sufficiently transformed several hundred feet downgradient to be non-detectable levels (AMEC, 2001c,d). Both of the sites had an aerobic aquifer, which is less conducive to transformation than an anaerobic aquifer. Although, the aDNTs extend slightly further downgradient, several hundred more feet, they are also undergoing transformation reactions. Therefore, TNT and aDNT are not likely to be MEC's of concern at most military installations. The other important finding is the propellant related compounds (NG, EC, DNT, phthalates, and N-nitrosodiphenylamine) are not found in groundwater owing to their likely increased sorption and transformation potentials.

4. CONCLUSIONS

Lessons learned from several military installation studies suggest modifications are necessary to the analytical methods. The modifications include;

- If rocket firing positions are investigated Method 8330 should be modified to improve the sensitivity to NG,
- Explosive field analytical methods are not suitable for low concentrations anticipated on ranges,
- Modifications to explosive analytical methods may be needed to 1) expand the analyte list, 2) change to sample preparation procedures, and 3) lower detection limits through the collection of larger soil sample aliquots, and
- Photo diode array is a necessity for Method 8330 analysis along with solid phase extraction.

Soil sampling observations suggest the following are applicable and expected conditions for most military ranges;

- Explosives on ranges and propellants at firing positions are very heterogeneously distributed
- Composite soil sampling is necessary to, determine mass of contaminants present and collection of discrete soil samples is not recommended,
- Sample homogenization in the field and lab is a necessity, and
- Soil sampling at targets or source release areas "hotspots" is useful whereas the number of samples necessary to adequately characterize the entire military range may be less useful due the large acreage associated with most ranges

In terms of groundwater, the lesson learned were that an;

- Ideal way for determining the release point of contaminants on ranges is through collection of groundwater profile samples, and
- Some drilling greases and water turbidity produce interferents with Method 8330.
- RDX, HMX, and perchlorate readily move through soil and aquifer materials and are not significantly adsorbed (Speitel et al. 2002),
- DNTs, EC, NG, and TNT undergo rapid transformation and sorption, and
- OB/OD sites are likely to poise as worse case scenarios (highest contaminant concentration and greatest mass)

Acknowledgements

The authors would like to acknowledge Don Wood with the USA Army Corps of Engineers-New England District as well as Bill Gallagher with the Impact Area Groundwater Study Program.

References

AMEC. 2001a, Final IAGS Technical Team Memorandum 99-6, Evaluation of False-Positive Explosive Detections for the Impact Area Groundwater Quality Study, February 2001, AMEC Earth and Environmental, Inc., Westford, MA.

AMEC. 2001b, Final IAGWSP Technical Team Memorandum 01-3 Tank Alley and Turpentine Road Targets Investigation for the Impact Area Groundwater Quality Study, AMEC Earth and Environmental, Inc., Westford, MA.

AMEC. 2001c, Final IAGWSP Technical Team Memorandum 01-6 Central Impact Area Groundwater Report for the Impact Area Groundwater Quality Study, AMEC Earth and Environmental, Inc., Westford, MA.

AMEC. 2001d, Final IAGWSP Technical Team Memorandum 01-2, Demo 1 Groundwater Report for the Impact Area Groundwater Quality Study, April 2001, AMEC Earth and Environmental, Inc., Westford, MA.

Armstrong, D. 1999a, More Costly Cleanup on Horizon, Boston Globe, November 14.

Armstrong, D. 1999b, US Presence on Foreign Soil is Tainted, Boston Globe, November 15.

Clausen, J., J. Robb, D. Curry, and N. Korte. 2004, A case study of contaminants on military ranges, USA, Environmental Pollution, Vol. 129, pp. 13-21.

Jenkins, T. F., J. C. Pennington, T. A. Ranney, T. E. Berry, P. H. Miyares, M. E. Walsh, A. D. Hewitt, N. M. Perron, L. V. Parker, C. A. Hayes, and E. G. Wahlgren. 2001a, Characterization of Explosives Contamination at Military Firing Ranges, ERDC TR-01-5, U. S. Army Corps of Engineers, Engineer Research and Development Center, Hanover, NH.

Jenkins, T. F., M. E. Walsh, P. W. Schumacher, and P. G. Thorne. 1995, Development of colorimetric field screening methods for munitions compounds in soil, SPIE, Vol. 254, pp. 324-332.

Ogden. 1998, Draft Completion of Work Report Volume 1-5: Impact Area Groundwater Quality Study, July 1998, Ogden Environmental and Energy Services, Westford, MA.

Pennington, J. C., T. F. Jenkins, G. Ampleman, S. Thiboutot, J. M. Brannon, J. Lewis, J. E. DeLaney, J. Clausen, A. D. Hewitt, M. A. Hollander, C. A. Hayes, J. A. Stark, A. Marois, S. Brochu, H. Q. Dinh, D. Lambert, A. Gagnon, M. Bouchard, R. Martel, P. Brousseau, N. M. Perron, R. Lefebvre, W. Davis, T. A. Ranney, C. Gauthier, S. Taylor, and J. Ballard. 2003, Distribution and Fate of Energetics on DoD Test and Training Ranges, ERDC TR-03-2, United States Army Corps of Engineers, Engineer Research and Development Center, Arlington, VA.

Speitel, G. E., H. Yamamoto, R. L. Autenrieth, T. McDonald. 2002, Laboratory Fate and Transport Studies of High Explosives, Final Report, January 2002, University of Texas at Austin and Texas A&M University.