Comprehensive List of Chemicals Likely to be Found at Military Ranges - A Case Study of Camp Edwards, Massachusetts

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Abstract

Camp Edwards located within the Massachusetts Military Reservation (MMR) is one of only a few ranges in the world that has been exhaustively studied. Camp Edwards has been used for military training since 1911. Activities include small arms, machine gun, artillery, mortar, ground to ground rocket, air to ground rocket, open burning/open (OB/OD), detonation of explosive ordinance and pyrotechnics training. The Camp Edwards experience provides a depth of analysis allowing one to make recommendations on what compounds should be contaminants of concern at military ranges throughout the U. S. and elsewhere. To date, over 7,800 surface soil samples, 1,500 deep soil, 3,900 monitoring well, 1,400 groundwater profile, 60 surface water and sediment, and 5 storm water runoff samples have been collected. Data on over 200 analytes is being collected including explosives, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), metals, pesticides/herbicides, polychlorinated biphenyls (PCBs), dioxins, perchlorate, and polychlorinated napthalenes (PCNs). The typical analyte list for several analyte suites, including explosives, was expanded to include likely target compounds. In addition, an exhaustive review of tentatively identified compounds (TICs) was conducted. Based on the studies at Camp Edwards the likely contaminants are based on the particular site activity for that range. This poster will identify and discuss which contaminants are of concern for military ranges.

Introduction

MMR is a 21,000-acre facility located on Cape Cod, Massachusetts (Figure 1). The Massachusetts Army National Guard conducts training operations at Camp Edwards located on the northern portion of the MMR facility under the direction of the National Guard Bureau (NGB). Approximately 14,000-acres of Camp Edwards constitute the Training Ranges and Impact Area. The Impact Area covers approximately 2,200 acres and contains targets at which artillery and mortars were fired at during training activities. Mortar and artillery training have been conducted since 1908. The level of activity at MMR has varied over its operational history. The most intensive U.S. Army activity occurred during World War II and during demobilization after the war. The firing of high explosive (HE) artillery rounds was discontinued in 1989. Low intensity training rounds (LITR) were fired up until the U. S. Environmental Protection Agency (USEPA) moratorium on live artillery and mortar firing at Camp Edwards in 1997. Both inert and HE mortar rounds were fired at Camp Edwards until 1997. Numerous firing ranges, artillery and mortar positions, and training areas surround the Impact Area. (Figure 2).

Studies have been conducted at several different types of firing ranges, OB/OD, and firing positions. Areas discussed include the Impact Area, Gun and Mortar Firing Positions (G&M), KD Rocket Range, Demolition Area 1 (Demo 1) and Subcontractor Munition Testing Area - J Ranges (Figure 3).

This evaluation is based on:

- 7,833 shallow surface soil samples representing 1,989 individual locations from 182 areas of investigation;
- 1,533 soil boring profile samples from 146 soil borings;
- 69 sediment samples from 19 water bodies;
- 64 surface water samples from 19 water bodies;
- 5 storm water samples from the perimeter of the Impact Area;
- 3,959 groundwater profiling samples from 256 borings; and
- 1,467 groundwater samples from 651 monitoring wells at 256 locations.

The primary explosive mixture used in post-WWII munitions fired into the Impact Area is Composition B, which is a 60:39 mixture of RDX and TNT. HMX, which is an impurity in RDX introduced during the manufacturing process, is also typically present in Composition B. HMX may account for up to ten percent of the total RDX mass in Composition B. Perchlorate is a component of rocket propellant, pyrotechnics, fuzes, spotting charges, and some explosive munitions.

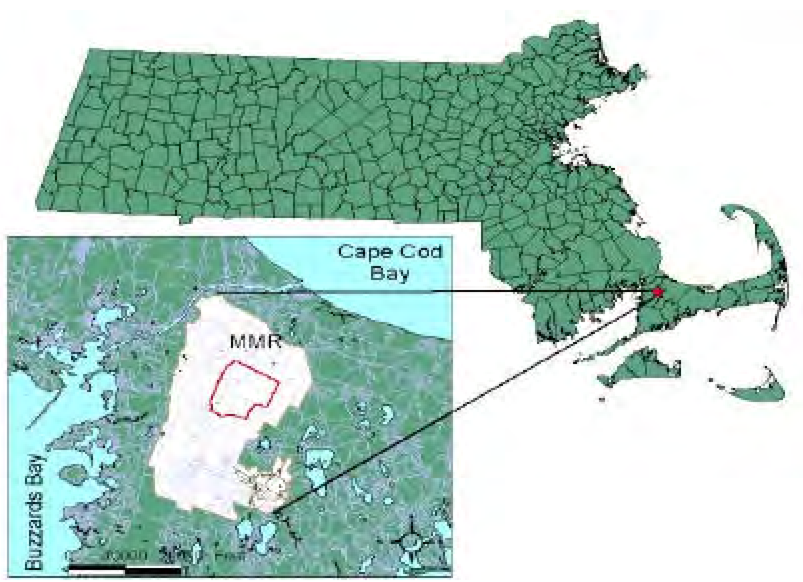

Figure 1. Location of Camp Edwards.

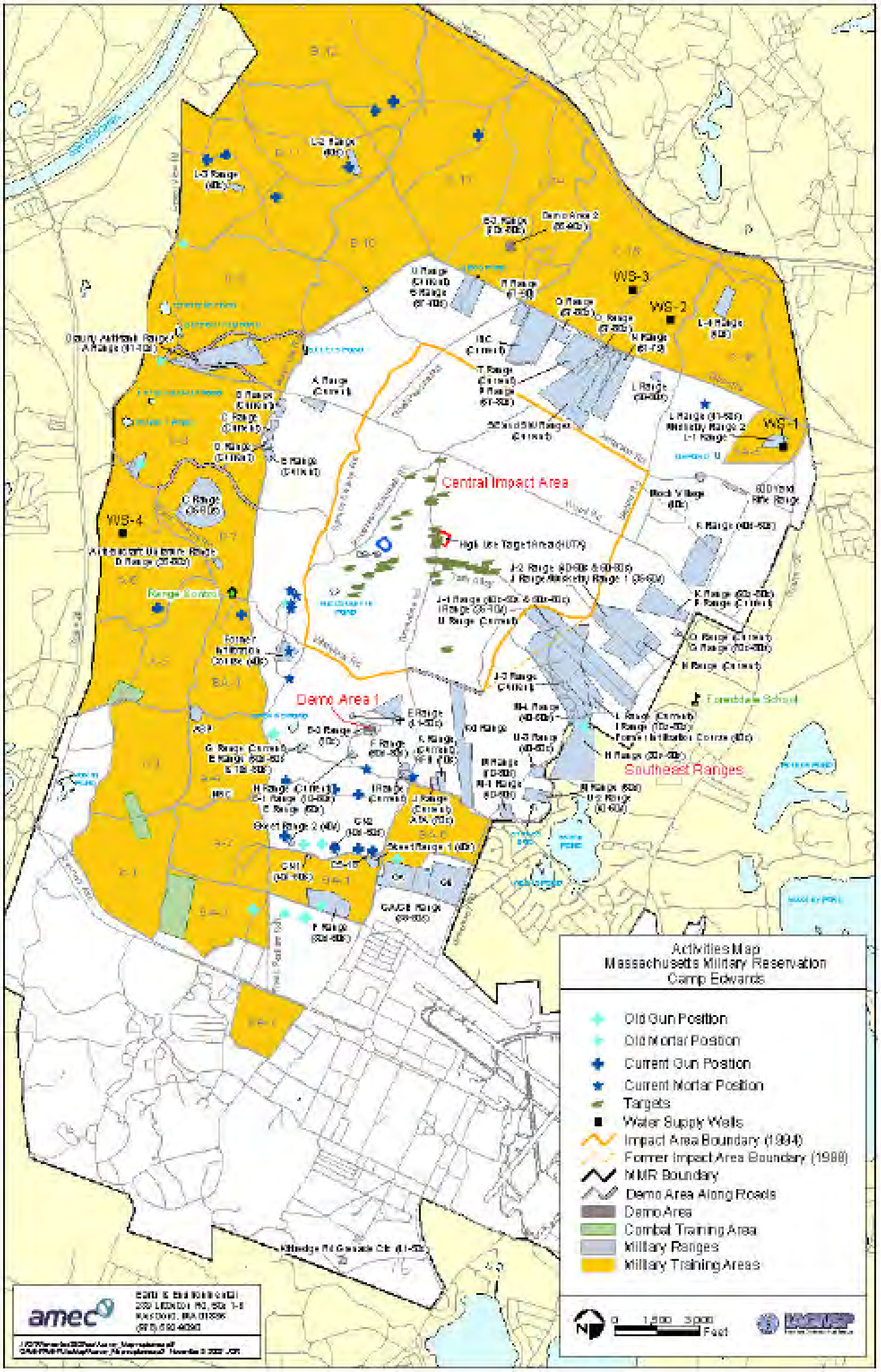

Figure 2. Training Areas at Camp Edwards.

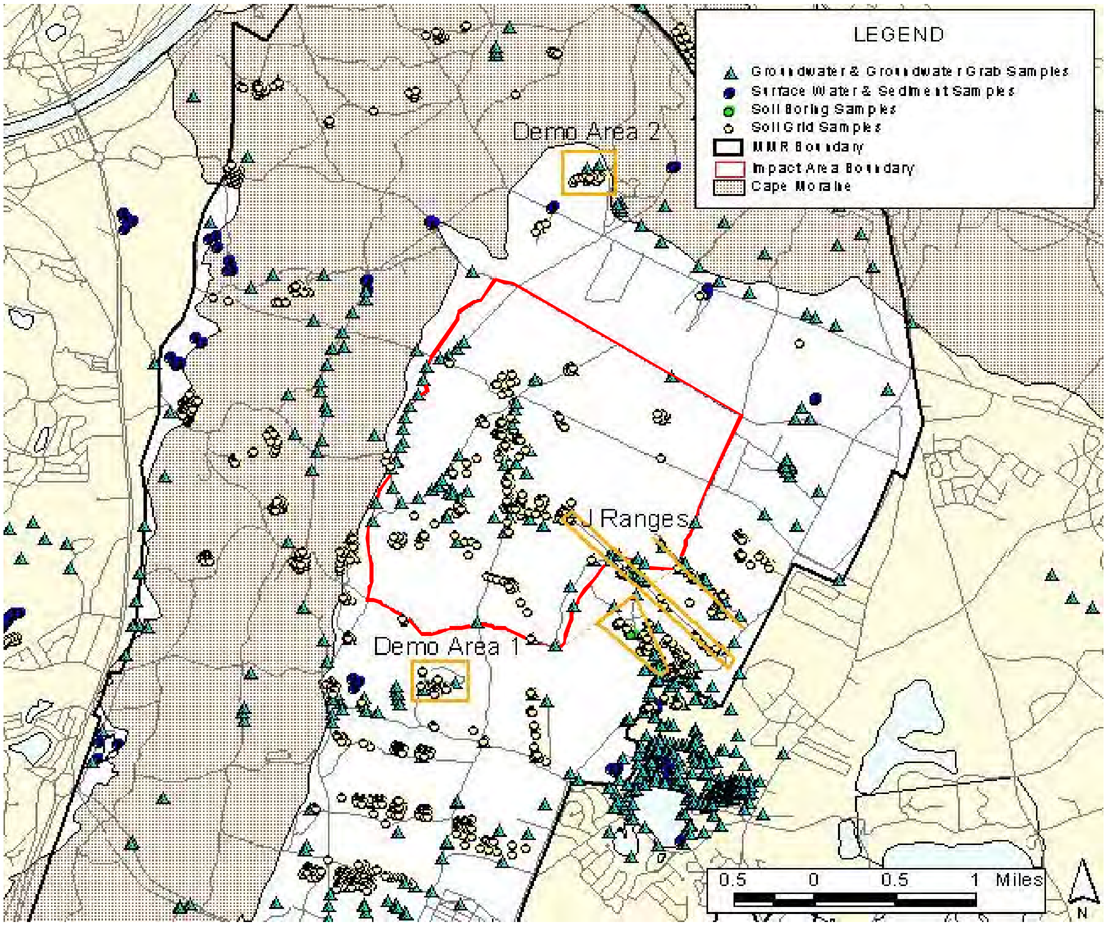

Figure 3. Sample Locations at Camp Edwards.

Geology

Fine to coarse-grained sands forming a broad outwash plain, lie between the two moraines which form hummocky ridges to the west and north of the Impact Area. The lithologic material varies from very coarse sand and gravel at the top of the saturated zone to silt and clay at the bottom. A layer of till is present on top of bedrock. Bedrock is present at a depth of 285 to 365 ft below ground surface and can be considered impermeable. A generalized lithologic sequence for the Impact Area is shown in Figure 4.

Hydrogeology

The Training Ranges and Impact Area lie directly over the Sagamore Lens, a major groundwater recharge area and the most productive part of the Cape Cod Aquifer. Groundwater flows radially in all directions from the apex of the

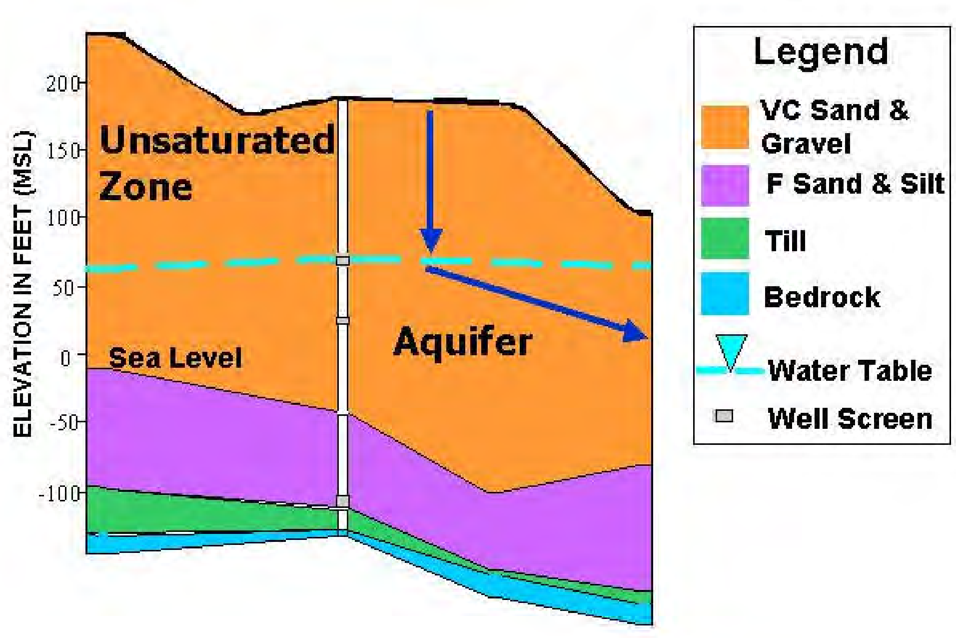

Figure 4. Generalized Lithologic Cross-Section for Camp Edwards.

Sagamore Lens located at the southeast corner of the Impact Area. Except on extreme slopes, surface water runoff at Camp Edwards is virtually nonexistent due to the highly permeable nature of the sand and gravel underlying the area (Figure 5). The ocean bounds the aquifer on three sides.

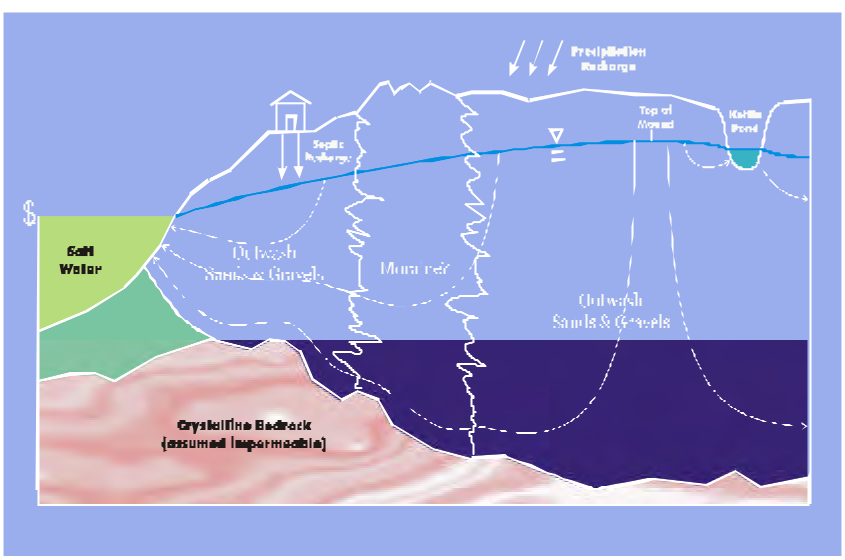

Figure 5. Hydrogeological Conceptual Model for Camp Edwards.

METHODS

The standard analyte suite used for each area of study at Camp Edwards for both soil and groundwater included (218 analytes): SVOCs, VOCs, methyl tert-butyl ether (MTBE), ethylene dibromide (EDB), PCBs, herbicides, pesticides, metals, cyanide, phosphate-phosphorous, nitrate/nitrite-nitrogen, ammonia-nitrogen, total organic carbon, and explosives (Tables 1 & 2).

VOC (except background locations)	OLC 02.1
Explosives (except background locations)	8330
Metals	6010
Cyanide	ILM04
Pesticides/PCBs	OLC02.1
SVOC (Note: changed to modified 8270 in 2000)	OLC02.1
Herbicides	8151
Phosphate-phosphorous	365.2
Nitrate/Nitrite-nitrogen	353.2
Ammonia-nitrogen	350.2
MTBE	8021
EDB	504.1
VOCs	OLM 03.01

Table 1. Soil Analytical Methods.

VOC (except background locations)	OLC 02.1
Explosives (except background locations)	8330
Metals	6010
Cyanide	ILM04
Pesticides/PCBs	OLC02.1
SVOC (Note: changed to modified 8270 in 2000)	OLC02.1
Herbicides	8151
Hardness as Calcium Carbonate	130.1
Phosphate-phosphorous	365.2
Nitrate/Nitrite-nitrogen	353.2
Ammonia-nitrogen	350.2
MTBE (except background locations)	8021
EDB (except background locations)	504.1

Table 2. Groundwater Analytical Methods

Later in the study perchlorate, antimony and molybdenum were added as standard groundwater analytes. In selected areas dioxin/furans, smoke dyes

(Disperse Red 9 (methylaminoanthraquinone), Disperse Violet 1 (1.4-diaminodihydroanthraquinone), Yellow Dye (benzanthrone), Vat Yellow 4 (dibenzochrysenedione) and Solvent Green 3 (1,4-di-o-toluidine-9,10-anthraquinone), perchlorate, PCNs, titanium, and white phosphorous have been analyzed in soil samples.

In addition, TICs were intensively scrutinized for all areas. Many of these compounds are present in the filler material of the munitions or are secondary degradation products of explosive compounds. The TIC compounds in Table 3 are in the reference library for the SVOC and VOC analysis and are specifically evaluated for their presence and semi-quantification.

The reporting limit for the majority of the explosive compounds in soil is 250 ug/kg with the 8330 analytical method. Current sampling activities are utilizing a modified 8330 method, which includes 22 analytes (see Table 4) and have a reporting limit of 10 to 20 ug/kg for soil. The method was optimized to include PA, PETN, 2,4-DANT, 2,6-DANT, DNX, MNX, TNX, and NG as target compounds. The explosive reporting limit for water samples is 0.2 ug/L. In some instances the explosive Methods 8095 and 8321 were also utilized.

2- chlorobenzaldehyde 3,5-dinitroaniline 2,4,6-trinitrobenzaldehyde 2-amino-4-nitrotoluene 2-nitrodiphenylamine di-n-propyl adipate ethylcentralite (diethyldiphenyl urea) methylcentralite (dimethyldiphenylurea) 1,3-dinitroglycerol 1-nitroglycerol aryl amines oxalic acid amide phloroglucinal (1,3,5 trihydroxybenzene) pyrogallol (1,2,3-trihydroxybenzene) 4-acetamide-2-nitrotoluene 2-amino-6-nitrotoluene formamide 4-nitroaniline Disperse Red Dye 9 (methylaminoanthraquinnone, MAA) Anthraquinone Aminoanthraquinone Benzanthrone o-anisidine chloroacetophenone	dichlorodifluoromethane 2,3-dihydro-1-methyl-1H-indene iso-propylbenzene n-propylbenzene trichlorofluoromethane 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene/sec-butylbenzene 2,2,4-trimethylhexane 2,2,4-trimethylpentane 2,3,4-trimethylpentane acetophenone benzothiophene phenylactealdehyde 2,3-dihydro-4-ethyl-1H-indene 2,2-dimethylbutane 2,3-dimethylbutane 2,3-dimethylhexane 2,5-dimethylhexane 2,3-dimethylpentane 2,4-dimethylpentane m-ethyltoluene o-ethyltoluene p-ethyltoluene 2-furaldehyde heptanal n-heptane n-hexane 1-hydroxy-2-propanone

camphor ethyl acetate n-hexane stearic acid sulfur tetracene (2,3-benzanthracene) triacetin (1,2,3-propanetriol triacetate) acrolein carbon disulfide carbonyl sulfide chloromethylbenzene cyclohexane cyclopentane cyclopentanone decanal n-decane	indane 2-methyl-1-butene methylcyclohexane methylcyclopentane 2-methylheptane 2-methylhexane 3-methylhexane methylnitrate (nitromethane) methylpentane nitromethane nonanal n-nonane octanal n-octane n-pentane

Table 3. Tentatively Identified Compounds (TICs) Evaluated at Camp Edwards.

1,3-dinitrobenzene 1,3,5-trinitrobenzene (TNB) 2-amino-4,6-dinitrotolurne (2A-DNT) 4-amino-2,6-dinitrotoluene (4A-DNT) 2,4-diamino-6-nitrotoluene (2,4-DANT) 2,6-diamino-4-nitrotoluene (2,6-DANT) 2,4-dinitrotoluene (2,4-DNT) 2,6-dinitrotoluene (2,6-DNT) 2-nitrotoluene (2-NT) 3-nitrotoluene 4-nitrotoluene	dinitroso-hexahydro-1,3,5-triazine (DNX) nitroso-dinitro-hexahydro-1,3,5-triazine (MNX) tri-nitroso-hexahydro-1,3,5-triazine (TNX) octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) nitrobenzene Nitroglycerine (NG) pentaerythritol tetranitrate (PETN) Picric acid (PA) hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) 2,4,6-trinitrotoluene (TNT) tetryl

Table 4. Explosive Analyte List for Camp Edwards.

Impact Area

The Impact Area was principally used for training with 75, 105, and 155 mm and 8-inch artillery rounds, and 60 and 81 mm, 3 and 4.2-in HE mortars, illumination, smoke, and white phosphorous mortars. As a consequence, unexploded ordnance (UXO) as well as low order detonations can be found.

Soil

A total of 58 targets have been sampled within the Impact Area with over 2000 soil samples collected to date. Soil results indicate the explosives RDX, HMX, TNT and TNT's degradation products 2A-DNT, and 4A-DNT are the primary contaminants present (Figure 6). 2,6-DNT has not been detected in any soil samples and 2,4-DNT was only detected four times. PETN was detected seven times and PA three times. TNB was detected once and 2-NT seven times.

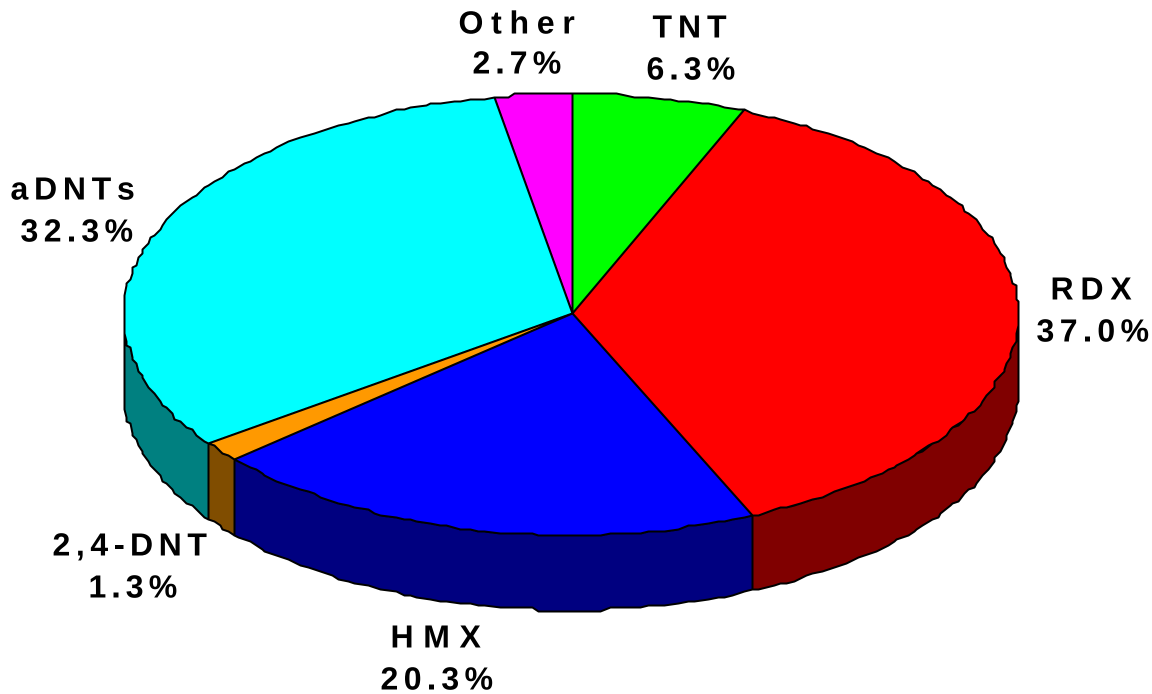

Figure 6- Impact Area Explosive Distribution in Soil.

Detections of TNB, 2-NT, PETN, and PA are believed to have been false positives. The distribution of explosives in soil is heterogeneous (Figure 7). In general, explosives levels decrease with depth and distance from the targets.

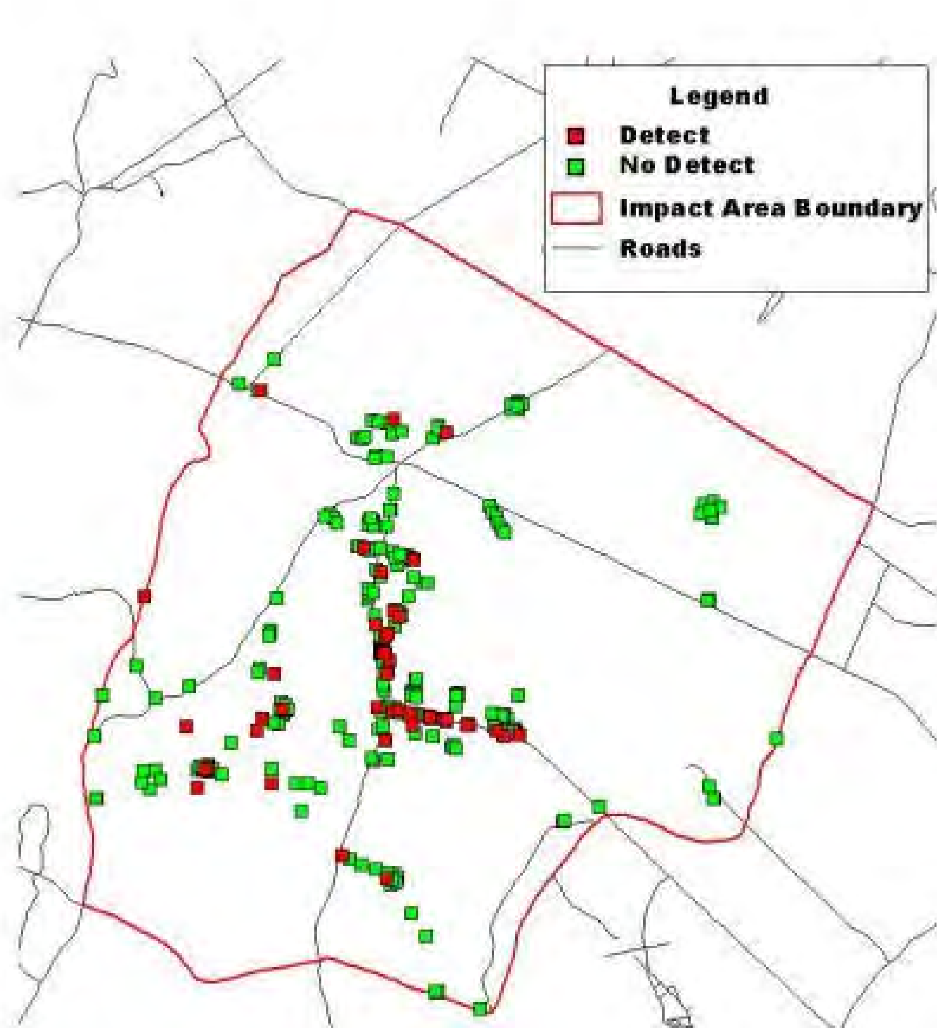

Figure 7. Impact Area Distribution of Explosives in Soil at Camp Edwards.

The conceptual model for movement of explosive contaminants from the soil surface to groundwater is presented in Figure 8. The metals aluminum (Al), iron (Fe) and manganese (Mn) appear elevated over background conditions. Perchlorate and several SVOCs have also been detected.

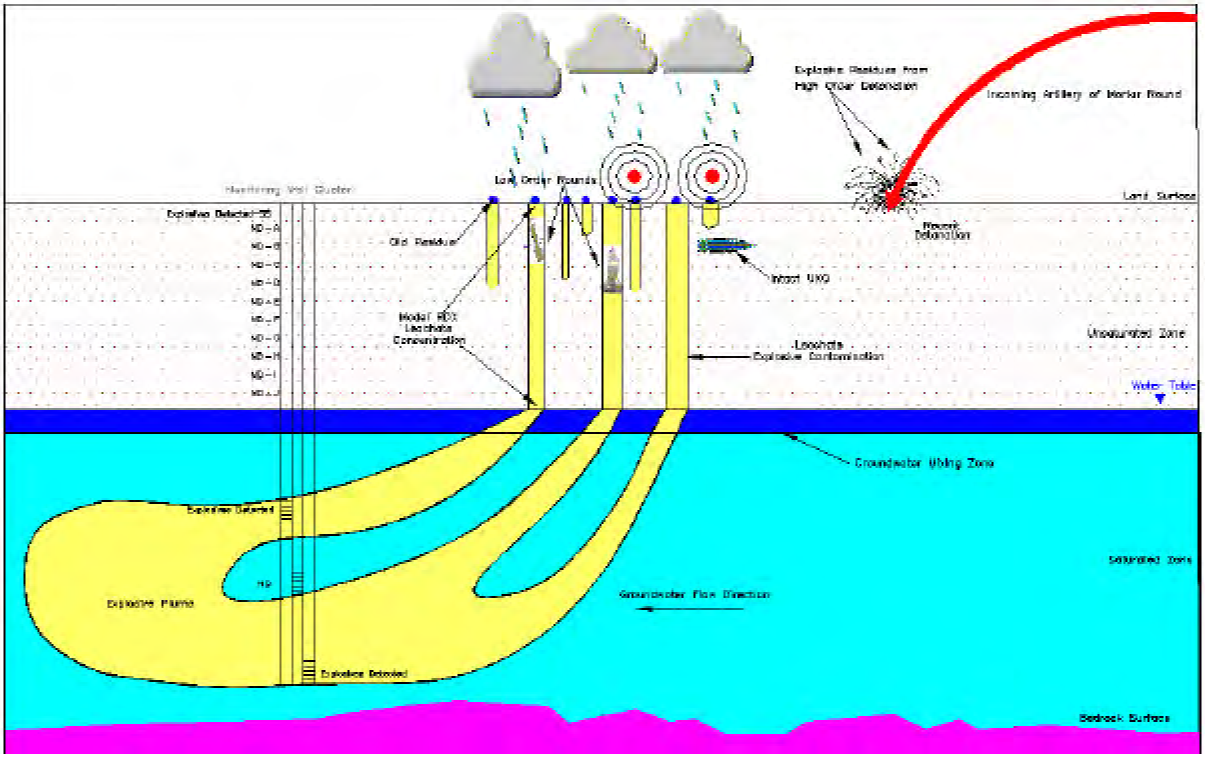

Figure 8. Contaminant Transport Conceptual Model for Camp Edwards.

Groundwater

Over 300 individual monitoring wells have been installed at over 100 separate locations within the Impact Area and areas downgradient. In excess of 1,000 groundwater profile samples have been collected and analyzed for explosives and VOCs. Profile samples are collected from the water table down to the terminus depth of the well boring. RDX, HMX, and 4A-DNT have been identified as groundwater contaminants of concern (COCs) (Figure 9). RDX contamination is principally focused on an area immediately downgradient of targets. Other explosive compounds, such as TNT, 2A-DNT and 4A-DNT have been identified at several locations close to the targets but have not been detected further downgradient (Figure 10). Preliminary data suggest perchlorate may become a COC.

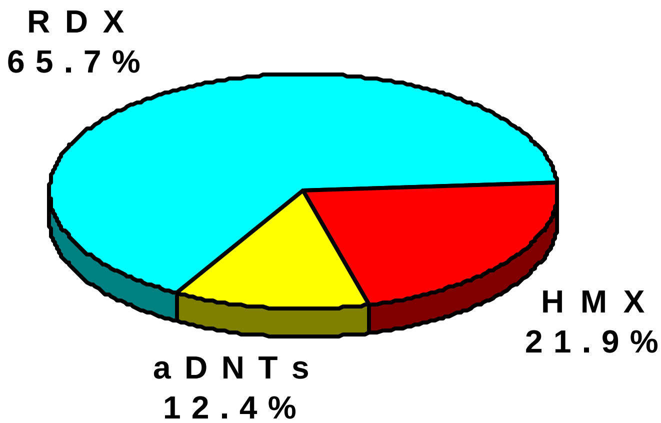

Figure 9. Impact Area Explosive Distribution in Groundwater.

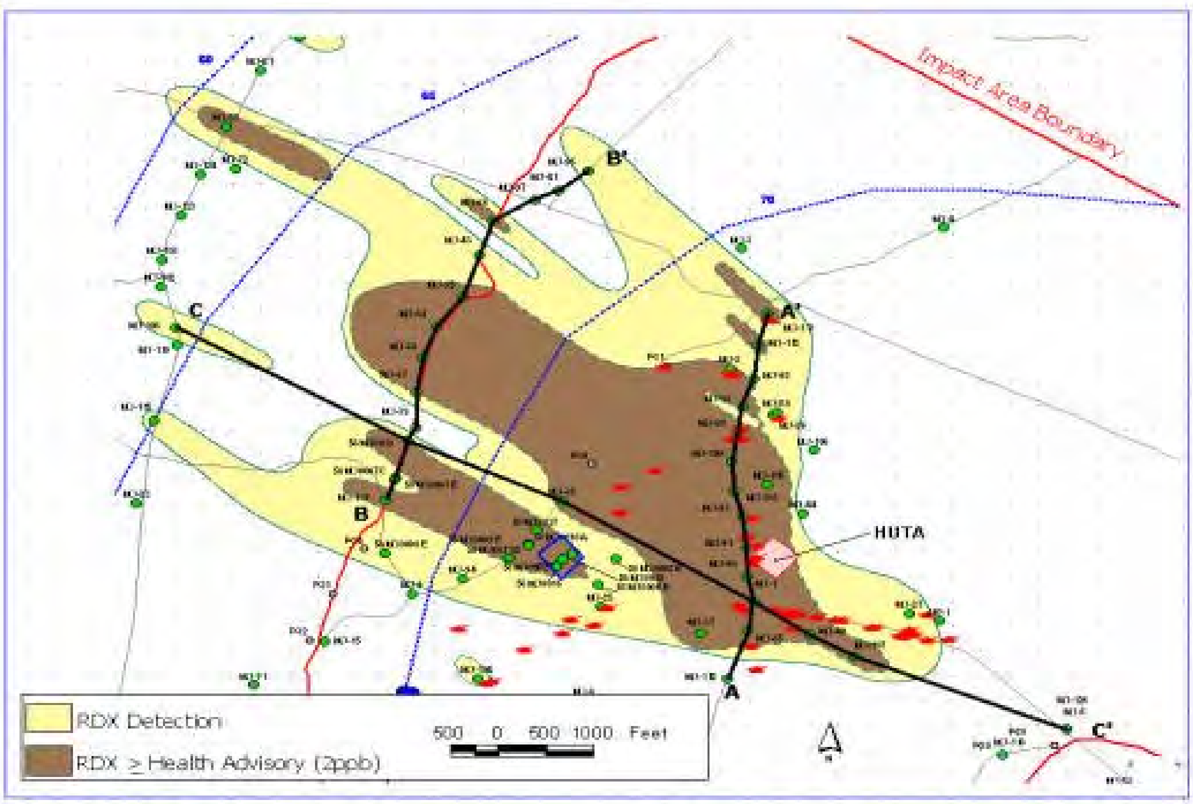

Figure 10. Distribution of RDX in groundwater from the Impact Area.

Gun and Mortar Firing Positions

The 37 identified G&M firing positions are located outside of the Impact Area in the Training Ranges and were used to fire artillery and mortars at targets (Figure 2). Excess propellant bag burning and cleaning of artillery were reported to have been conducted. The average size of the firing positions is 2.2 acres. The type of propellant (M1, M2, M3, etc.) used is dependent on the type of munition. These mixtures contain nitrocellulose (0-43% by weight) as the primary constituent. There is no evidence triple-based propellants were ever used at Camp Edwards. Secondary compounds used in propellants include DNT, di-n-butylphthalate, diphenylamine, and NG, each ranging from 0-10% depending on the mixture specifications. Diphenylamine is not persistent in the environment and during combustion is transformed to N-nitrosodiphenylamine. Barium nitrate, potassium nitrate, potassium sulfate, and graphite are also present in the propellant mixture from 0-1.5% of the overall mixture. The compound 2,4-DNT (<1%) is used as a plasticizer in single-based propellants used for some mortars and artillery munitions. 2,6-DNT is an impurity associated with the manufacture of 2,4-DNT.

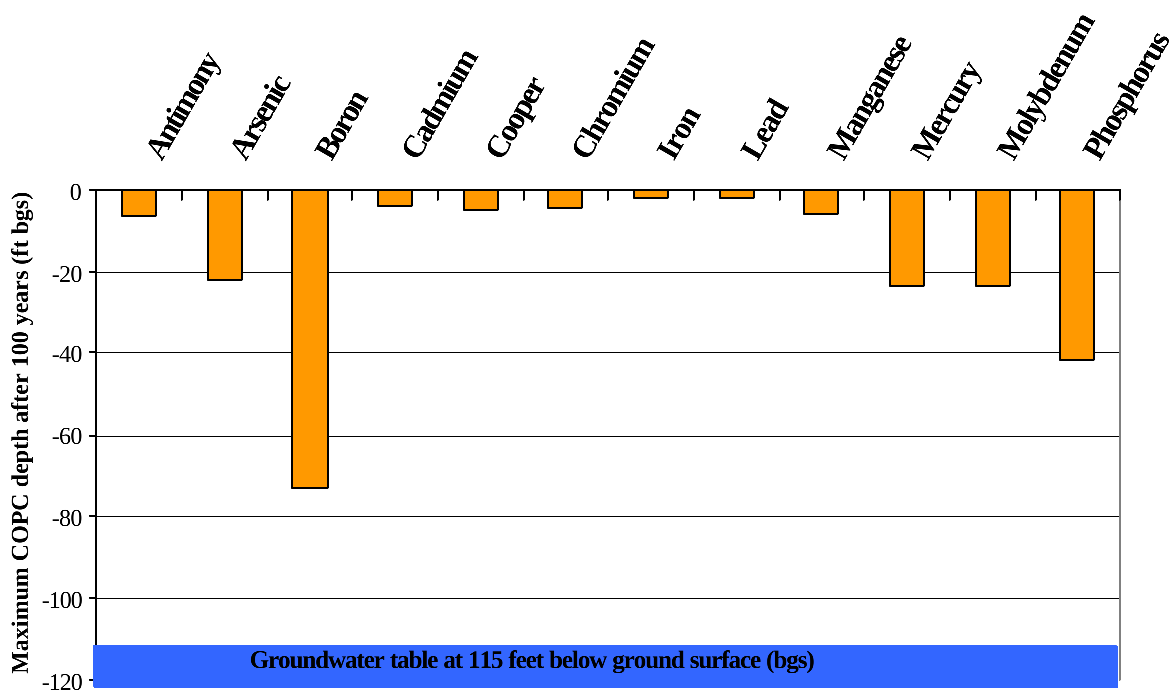

Figure 11. Metals at Gun and Mortar Firing Positions Identified as Contaminants of Potential Concern (COPC) and Results from Vadose Zone Modeling.

Soil

Over 1,200 soil samples were collected and analyzed for DNT with over 500 samples analyzed for the standard analyte list. Analytical results and initial risk screening identified 39 contaminants of potential concern (COPCs) (Figures 11-13). Overall, 2,4-DNT was detected in four percent of samples, approximately four times more often than 2,6-DNT. The majority (29) of the detections were in samples collected above one foot in depth. There were infrequent detections of NG and PETN. The two detections of PETN are likely false positives. Diethyl phthalate and N-nitrosodiphenylamine were detected at low frequencies. Di-n-butyl phthalate was detected at a higher frequency. Lead (Pb) was the only metal where the mean concentration exceeded the background concentration.

Groundwater

Twenty monitoring wells at eight locations were installed downgradient of four gun positions and four mortar positions. The groundwater data indicates military training activities at the G&M positions have not adversely impacted groundwater and no COCs are identified. Perchlorate was recently detected at one monitoring well.

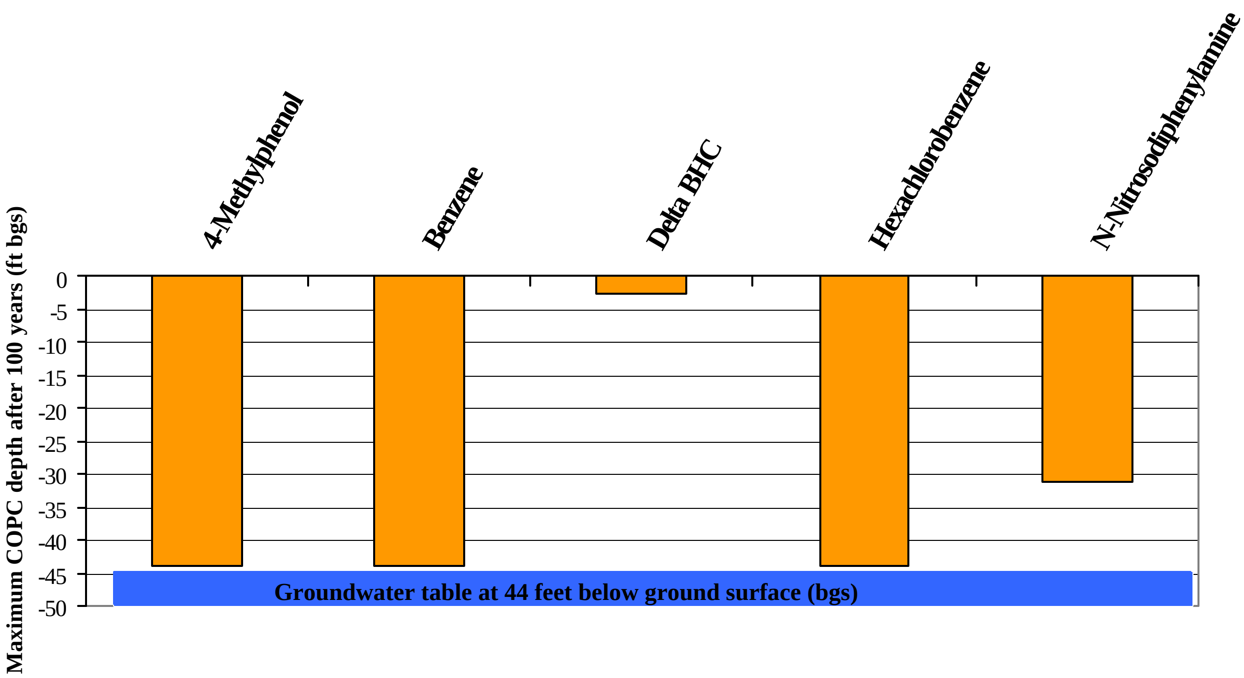

Figure 12. Volatile Organic Compounds (VOCs) and Semi-Volatile Organic Compounds (SVOCs) at Gun and Mortar Firing Positions Identified as Contaminants of Potential Concern (COPC) and Results from Vadose Zone Modeling.

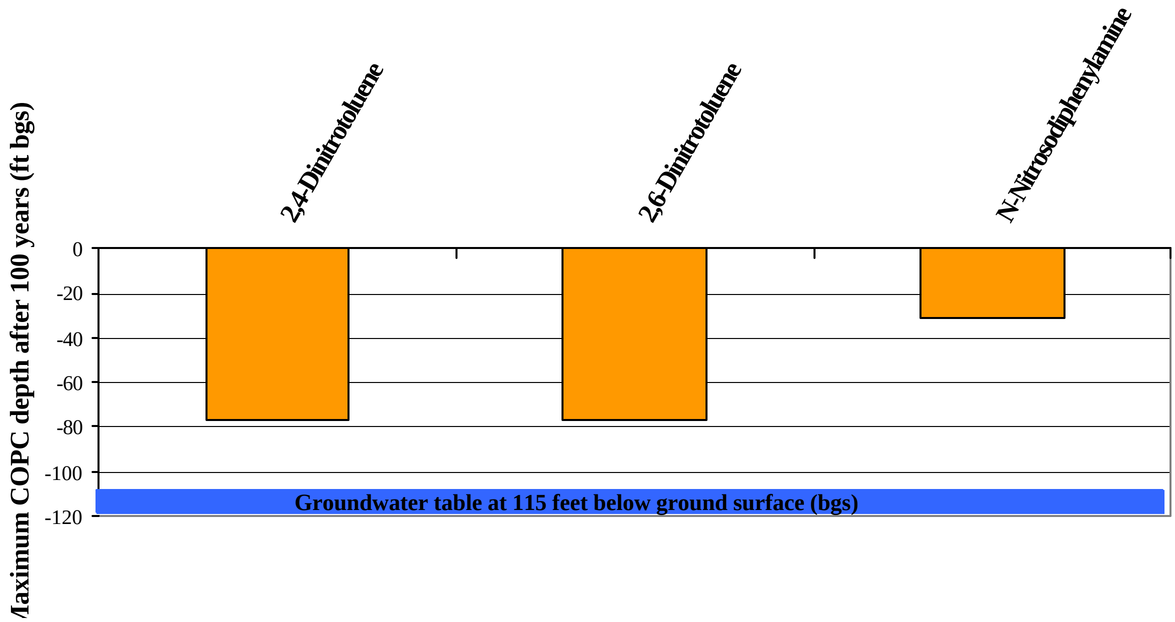

Figure 13. Propellants at Gun and Mortar Firing Positions Identified as Contaminants of Potential Concern (COPC) and Results from Vadose Zone Modeling.

KD Rocket Range

The KD Range is comprised of approximately 98 acres with two firing points for Dragon missiles and 90mm recoilless rifle training, and one firing point for TOW missiles. A portion of the range has also been used for helicopter gunship, machine gun, and grenade launcher training. Live tank gunnery may also have been conducted. Camp Edwards Range Safety Regulations indicate that the following anti-tank munitions were authorized for use: M371 HEAT (90mm cartridge, recoilless rifle), M371E1; M183 PD, 40mm practice grenade; Dragon, M222 HEAT, M223 practice inert warhead (Anti-Tank); 90 mm recoilless rifle and HEAT practice; M31 FA trainer (rifle grenade) with M183 (smoke); TOW, inert warhead (Anti-Tank).

An armored personnel carrier target is located approximately midway downrange (Figure 14). Based on damage to the target and the amount of ordnance debris in the immediate vicinity, it is presumed to be the primary range target due to the presence of rockets, housings, fins and electronic circuitry debris. Surface clearance of the range discovered numerous ordnance remnants including M747 22mm Sabot rounds, 35mm LAW subcaliber rounds, Dragon and TOW missile motors, and 40mm practice grenade debris.

Figure 14. Location of Firing Points and Targets at the KD Rocket Range.

Soil

Over 300 total soil samples were collected and analyzed with the standard analyte list. NG was the most widespread explosive/propellant compound detected. NG was likely deposited on the surface as residue along with other propellant compounds from the ejected gases produced during rocket and missile launching. Other explosive compounds such as HMX, RDX, and TNT were discovered only in the primary target (Figure 15). Lead and copper levels appeared elevated and dieldrin, an herbicide was present. The dieldrin is not likely related to the use of munitions at this range. There is no indication of other contaminants present.

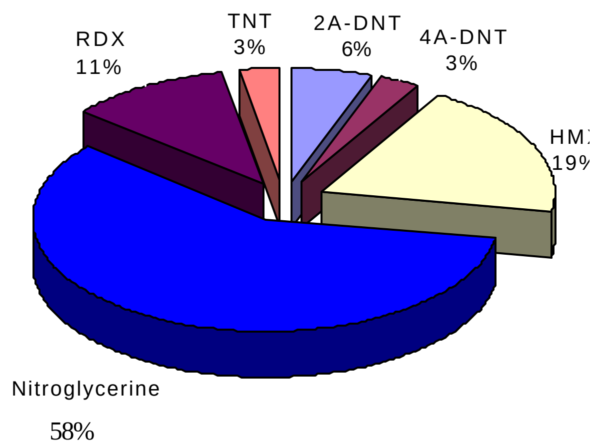

Figure 15. Distribution of Explosives and Propellants in Soil at the KD Rocket Range.

Groundwater

Monitoring wells placed immediately downgradient of the primary and secondary targets and TOW firing position do not indicate any contaminants are present in groundwater. Each well was analyzed following the standard analyte list.

Demolition Area 1 (Demo 1)

Demo 1 is located south of the Impact Area in a one-acre kettle hole, with the bottom 45 feet below the surrounding grade (Figure 16). OB/OD began sometime in the mid-1970s and included the destruction of various types of ordnance using explosive charges of C4, TNT, and detonation-cord. As part of a comprehensive site reconnaissance, chunks of C4 and other residual munitions were found on the ground surface. Pits identified by a geophysical survey contained metal debris including; razor wire, railroad rails, metallic mesh, and scrap, concertina wire, steel I-beams and plates, and miscellaneous metal items. Ash, burnt-out small arms cartridge casings (5.56mm, 7.62mm, 50 caliber), pyrotechnics, fuzes, thermal batteries, rocket bodies, spent 20 mm and 30 mm practice rounds, smoke flares, and one 20 mm round with full ballistic tip were also identified and recovered.

Figure 16. Photograph of Demolition Area 1 at Camp Edwards.

Soil

Over 500 soil samples have been collected from the Demo 1 area following the standard analyte list. In addition, samples have been collected and analyzed for perchlorate, dyes, and dioxin/furans. The following explosive and propellant compounds have been repeatedly detected in soil: perchlorate, RDX, HMX, 2A-DNT, 4A-DNT, TNT, and 2,4-DNT. Detections of these explosives and propellants are heterogeneous with the highest concentrations generally being detected at the surface. RDX and HMX were the most frequently detected explosive compounds. The highest RDX and HMX concentrations were detected in discrete surface soil samples, collected beneath C4 residuals. Deep soil sampling indicated sporadic detections of explosives within the unsaturated zone. The low frequency of TNT in soil is most likely due to the rapid degradation of TNT to the daughter products 2A-DNT and 4A-DNT, which were detected more frequently than TNT. Di-n-butyl phthalate and N-nitrosodiphenylamine are associated with the DNT detections. SVOCs were frequently detected in surface soils and are most likely attributable to the burning of fireworks or other wood/paper materials. The mean concentration of antimony, barium, calcium, Cu, Pb, Mn, silver and zinc exceeds the shallow soil background concentration. A dye, perchlorate, and dioxin were detected in soil at low-levels.

Groundwater

A total of six explosive compounds have been detected in groundwater sampled from 19 of the 62 monitoring wells including; perchlorate, RDX, HMX, 4A-DNT, 2A-DNT, TNT and 2,4-DNT. The highest observed concentrations were of RDX at 370 ug/L (Figure 17) and perchlorate at 174 ug/L. Di-n-butyl phthalate, N-nitrosodiphenylamine, and SVOCs have not been detected in groundwater. Metals, a dye, and dioxin were detected but metals were below background levels. The dye and dioxin detections are likely false-positive results, since these detections have not been present in repeated sampling.

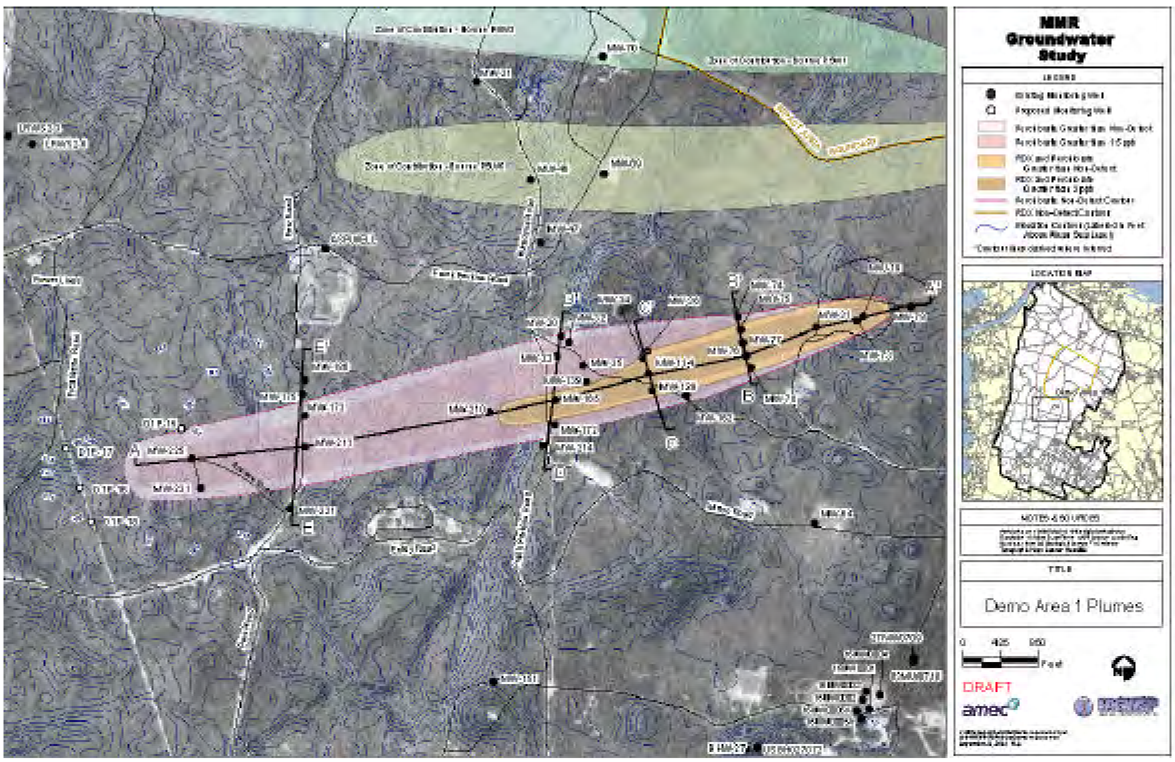

Figure 17. Extent of RDX and perchlorate in groundwater from Demo 1.

J Ranges (Subcontractor Munition Testing Ranges)

The J Ranges consist of 4 ranges used by defense contractors for munitions testing, which included research and development activities. The J-1 Range was used primarily as an estimation, anti-tank, and transition range from the mid-1930s through the 1950s and by a variety of military contractors thereafter for weapons testing. The J-2 Range was used historically as a musketry range (1935 - 1940s), transition range (1940's - 1950's), rifle range (1960's - 1980's), and a contractor test range (1953 - 1980). Examples of activities conducted by various contractors included testing of: propellant and fuze, penetration for various munitions, fragmentation, obscuration, infrared tank heat signatures, as well as propellant and waste burning, munitions disposal, and loading of munitions with explosives. The J-3 Range was used as a mortar and machine gun range from 1935 through the 1950s. Subcontractors, under various military contracts, used the range from 1968 to the 1990s for the loading and testing of various munitions and fuses, and a wide variety of other munitions-related tests. The L Range was used variously as an infiltration course and a grenade launcher range from the 1940s to the present.

Soil

Over 800 surface soil samples have been collected from the J-Ranges. Soil results have indicated the presence of HMX at various locations throughout the study area. At the J-1 Range, RDX was detected in ash samples collected from a former burn kettle and from mixed soil and debris from a steel-lined pit which contained discarded munitions. Explosive residues are present in the Ammunition Storage Magazine and the Melt Pour building on the J-2 Range. PCNs were also detected in many of the soil samples, as were low levels of dioxin and furans.

Groundwater

To date 61 monitoring wells have been installed with over 800 groundwater samples collected. Groundwater contaminants identified include RDX, HMX, TNT, and perchlorate. There are various activities known or reported to have occurred in this area that could have provided a source for the detected contaminants. These include firing and detonation of munitions, cook-off tests, burning of excess munitions in a steel-lined pit and popper kettle, disposal by burning of lead azide on the range road, disposal of J-3 Range Melt/Pour wastewater, and burial of vehicles and pails of various waste materials.

CONCLUSIONS

If ranges are proposed for closure, it is evident from the exhaustive study at Camp Edwards a limited analyte list of potential contaminants would be appropriate. A variety of explosive compounds in soil were found on the firing ranges. Method 8330 would be sufficient for evaluation of these ranges with the inclusion of PDA confirmation. Due to the low concentrations observed at Camp Edwards, the method would need to be modified to accommodate the lower concentrations expected. Analysis for perchlorate, metals, and PCNs may be appropriate if a surface risk pathway is being evaluated. In addition, at G&M firing positions it would be appropriate to conduct an SVOC analysis. If rocket ranges are being evaluated the explosive method 8330 should be modified to increase the sensitivity to NG. At OB/OD sites the same method used for ranges would be appropriate with the possible addition of SVOCs and dioxins.

There is no evidence from Camp Edwards warranting the collection of VOCs, SVOCs, herbicides/pesticides, PCBs, dioxins, or evaluating TICs for ranges. In terms of groundwater, perchlorate and explosives analysis are the only two warranted analyte suites needing analysis. This analysis is warranted for ranges and OB/OD sites being considered for closure and active ranges and OB/OD sites located in humid environments. The installation of monitoring wells and collection of groundwater samples is not likely needed for artillery and mortar firing positions unless they are located in a humid environment with a shallow depth to groundwater.