

FINAL REPORT

Passive Reactive Berm (PRBerm) to Provide Low Maintenance Lead Containment at Active Small Arms Firing Ranges

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LIST OF ACRONYMS

AEC	Army Environmental Command
AFB	Air Force Base
ASTM	American Society for Testing and Materials
ATC	Aberdeen Test Center
BB	Buffer Block
BAT	Best Available Technology
C	Carbon
cm	Centimeter
CoC	Chain of Custody
COD	Chemical Oxygen Demand
DDI	Dissolved De-Ionized Water
DDI S&S	Dissolved De-Ionized Water Suspend and Settle
DO	Dissolved oxygen
DoD	Department of Defense
DOE	Department of Energy
Eh	Redox potential
EPA	Environmental Protection Agency
ERDC	Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
ETL	Engineering Technical Letter
ft	Linear foot
GAC	Granular Activated Carbon
gpm	Gallons per minute
GW	Groundwater
ha	Hectare
HA	Health Advisory
HASP	Health and Safety Plan
hr	Hour
HQ-AFCESA	Headquarters Air Force Civil Engineer Support Agency
IC	Ion Chromatograph
K _d	Soil / Water Distribution Coefficient

kg	kilogram
km	Kilometers
lb	Pound
L	Liter
LW	Leachate Water Sample when applied with a sample number (e.g. LW##)
m	Meter
mg	Milligram
min	Minute
ORP	Oxidation-reduction potential
OSHA	Occupational Health and Safety Administration
Pb	Lead
PI	Principal Investigator
PM	Project Manager
ppb	Parts per billion
PPE	Personal Protective Equipment
ppm	Parts per million
PRBerm	Passive Reactive Berm
PVC	Polyvinyl Chloride
QA	Quality assurance
QC	Quality control
RO	Reverse Osmosis Water
RO	Runoff Water Sample when applied with a sample number (e.g. RO##)
SACON [®]	Shock Absorbing Concrete
SAFR	Small Arms Firing Range
SDZ	Surface Danger Zone
SOP	Standard Operating Procedure
SW	Surface Water Sample when applied with a sample number (e.g. SW##)
TCLP	Toxicity Characteristic Leaching Procedure
TOC	Total Organic Carbon
TSS	Total Suspended Solids
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency

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EXECUTIVE SUMMARY

Heavy metals are released into the environment as a result of critical military live-fire training. Preventing heavy-metal release and contamination into the local environment is crucial because cleaning contaminated soils is technically resource intensive, difficult, and costly. Previous studies have demonstrated that phosphate amendments have been successfully used as a best management practice to immobilize metal contaminants. The Passive Reactive Berm (PRBerm™) technology incorporates phosphate amendments with ballistic sand to immobilize soluble metals (e.g., lead) during the inevitable bullet corrosion process. Treatability studies conducted at ERDC Vicksburg determined that an amendment ratio of 5% (weight/weight) to sand was sufficient to contain > 90% of soluble lead within the berm material. The technology was field tested on the small arms firing range (SAFR - M-60 range) at Charleston Air Force Base (CAFB) in Charleston, SC. The CAFB PRBerm™ tested a 5% TRAPPS™ amendment (a granular, apatite-based material), alone and in combination with, 5% thermally treated fish bone Apatite™.

For CAFB PRBerm™, storm water runoff and leachate water samples were collected and analyzed for metals, total suspended solids, and pH. Results indicated that the pH of the runoff waters from the amended berms remained acidic. The total suspended solids in the leachate and runoff waters from the amended berms increased over the control berm. Phosphate concentrations were highest in the leachate from the lysimeter with the 5% TRAPPS™ amendment and lowest in the runoff water from the un-amended lysimeter.

The benefits of the PRBerm™ when compared to the traditional earthen berm, or a fully-contained bullet trap, include reduced metals migration in soil leachate and surface water runoff, as well as reduced construction and operation costs. The PRBerm™ has the potential to provide a useful, low-cost tool for defense forces to maintain active firing ranges while managing the inevitable effects of small arms residue corrosion in a low-cost and effective manner.

1. INTRODUCTION

1.1 BACKGROUND

The Department of Defense (DoD) operates more than 3,000 small arms firing ranges (SAFR's). Live-fire training exercises are necessary to maintain mission readiness for our nations' war fighters. Compliance with existing state and federal environmental regulations is an important factor in training range availability. Traditional small-arms rounds consist of copper-jacketed lead-alloy projectiles. Training exercises result in the deposition of lead alloys in berm soils as particles ranging in size from microscopic dust to whole projectiles. Metals present in SAFR soils can migrate off-site into sensitive environmental receptors (e.g., wetlands, surface-water bodies, groundwater supplies) through surface-water transport (runoff) or by vertical migration (leaching) of metals into groundwater. The resulting environmental contamination can result in state or federal regulatory action, which may ultimately impose constraints on critical training activities at SAFRs (**Figure 1**).

The use of earthen backstops (berms) composed of native soil can present environmental and regulatory challenges for installations that contain SAFR's, depending on the physical and chemical properties of the soil, and the proximity of the berm to sensitive environmental receptors. All of the lead entering a berm on a firing range initially is present as metallic lead. As the metallic lead ages within the SAFR berm it undergoes corrosion processes that can result in the release of dissolved lead cations. Depending on the environment within the berm, the fate of dissolved lead can range from transport to groundwater as soluble lead, transport to surface water as soluble lead, sorption onto electronegative particle surfaces (e.g., clays, organic matter, iron or manganese oxide), precipitation of lead salts (e.g., carbonates, sulfates, sulfides, and phosphates).

Generally, the mobility of dissolved lead is controlled by pH conditions, adsorption/desorption of lead with soil particles, and advective processes such as groundwater or surface-water flow. When conditions aren't optimal, the range may face regulatory issues, with lead or other heavy metals, being transported off-range (**Figure 1**). Low pH soil (acidic soils) generally enhances lead solubility, while neutral to basic pH conditions tend to favor the precipitation of lead salts. Soils rich in clay and (or) organic matter typically exhibit high soil/water distribution coefficients (K_d values) for lead, and may thus be effective in retarding the lead migration to the surrounding environment. However, the erosion and transport of lead contaminated soils by surface runoff (especially those soils containing a high proportion of silt and clay) can result in the redistribution of lead over relatively large distances.

Soils that are characterized by either high acidity (low pH), high alkalinity (high pH), high permeability, and (or) low soil/water K_d values for lead may be ineffective in retarding the migration of soluble lead into nearby groundwater or surface water bodies (**Figure 1**). Conversely, soils characterized by neutral to slightly basic pH conditions, relatively low permeability, and (or) which exhibit a high K_d value for lead may be effective in limiting the mobility of soluble lead to the surrounding environment. However, mechanical erosion and transport of such soils (especially clay-rich soils) can lead to offsite transport of lead in surface water runoff (**Table 1**). Conversely, soils characterized by neutral to slightly basic pH conditions, relatively low permeability, and (or) which exhibit a high K_d value for lead may be effective in limiting the mobility of soluble lead to the surrounding environment(**Figure 2**).

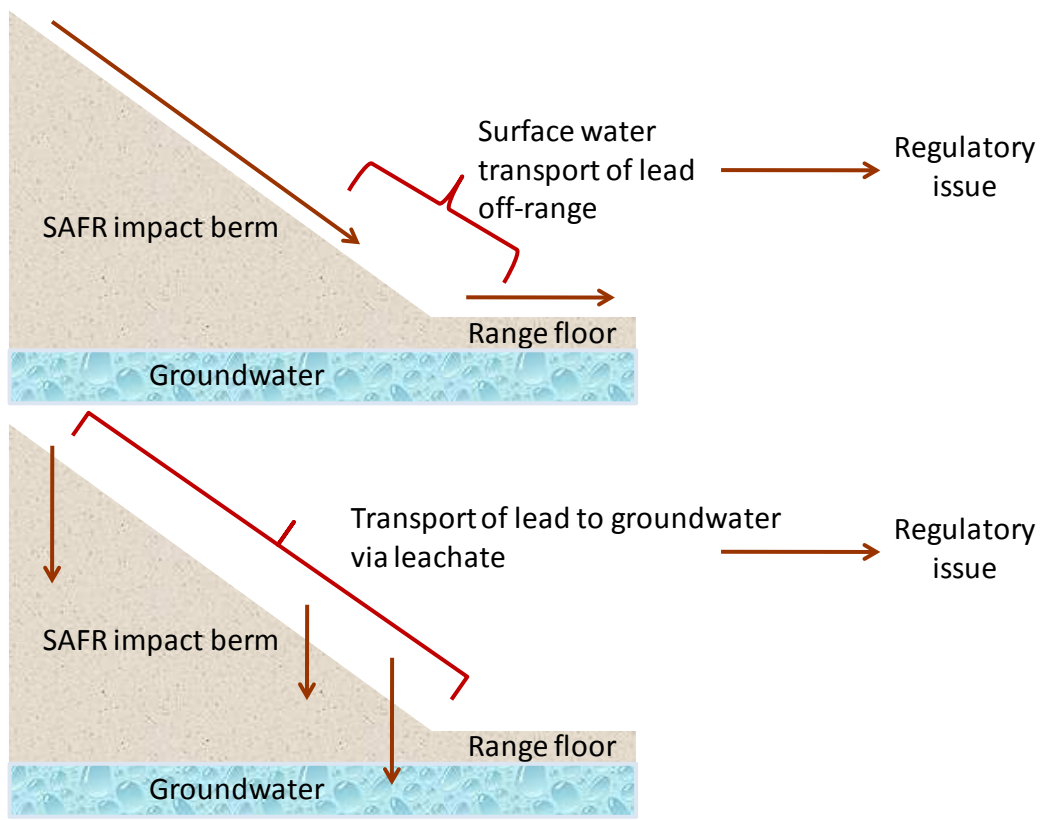


Figure 1. Potential Compliance Issues on Small Arms Firing Ranges

Table 1. Soil chemistry that promotes transport of lead off-range in surface water and to groundwater via leachate.

Surface water transport	Leachate transport
High CEC	Low CEC
High percentage of fines (small particle size)	Lower percentage of fines
Extreme pH (acid or alkaline)	Extreme pH (acid or alkaline)
Low permeability	High permeability
High sorption capacity (high K_d)	Low sorption capacity (low K_d)
Potential problem soil types: Silt, clay soils	Potential problem soil types: Sandy soils
Regulatory Issue	Regulatory Issue

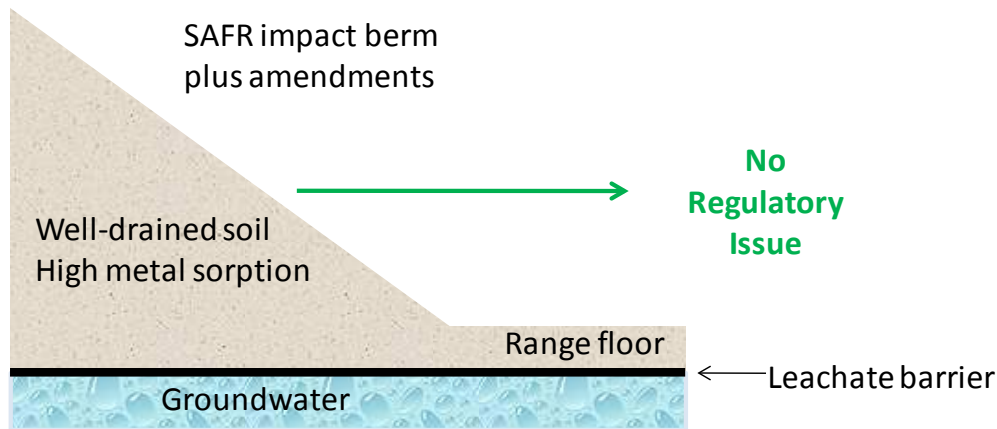


Figure 2. Effect of PRBerm technology on regulatory compliance issues

1.1.1 Impact Berm Deceleration Media

The design and construction of new ranges and rehabilitation of older ranges should include consideration of pollution prevention opportunities. Moreover, operators of existing ranges may wish to consider implementing design changes that will reduce or eliminate migration of lead into the surrounding environment. One critical design factor is the choice of material for impact berms. In many cases, the physical and chemical characteristics of the native soil will be adequate to retard the migration of lead, and thus prevent the contamination of nearby surface water or groundwater. In cases where the native soils have undesirable chemical properties for range purposes (e.g., high acidity or low pH, low K_d for lead), or are easily eroded from berm surfaces, an alternative berm material may be utilized to minimize the risk of off-site transport, while still providing an economical alternative to enclosed steel bullet traps.

Washed, construction sands that consist principally of silicate minerals (e.g., quartz), such as those commonly used in masonry and concrete manufacture may provide a suitable medium for the construction or replacement of SAFR impact berms. Commercially available masonry or concrete sands are relatively low cost materials and are widely available due to their extensive use in construction. From an operational standpoint, sand has numerous beneficial properties as a deceleration medium at firing ranges, and is generally the material of choice for this purpose. Impact berms made from sand are effective in decelerating fired projectiles safely, with minimal fragmentation, a low risk of ricochet, and relatively little dust generation. The chemical inertness of silicate sands minimizes berm cementation and hardening, thus ensuring proper deceleration of projectiles. Further, the granularity, low bulk density, and non-cohesive nature of sand facilitate the separation of spent bullet fragments during range maintenance or clearance activities (e.g., by soil screening). Finally, the refractory and non-flammable nature of sand provides additional benefits in ranges where tracer rounds may be used.

From an environmental perspective, the use of silicate mineral sand offers three principal benefits: 1) Washed sand typically contains a low proportion of silt and clay-sized particles, which reduces the potential for lead transport by storm water runoff, 2) The relatively high hydraulic conductivity of sand minimizes the amount surface runoff down the berm face, and 3) The drainage characteristics (combination of the high permeability and low specific retention) of

sand tend to limit the contact time between water and lead particles, thus inhibiting the *in-situ* corrosion (weathering) of lead.

However, from an environmental standpoint, there are a number of disadvantages associated with the use of sand in SAFR berms: 1) Most silicate mineral sands have a negligible pH buffering capacity. The lack of an adequate buffering capacity could lead to a reduction of soil pH to levels where both the rate of lead corrosion and extent of lead solubility in water are significantly increased. For this reason, lead present in an un-amended sand berm would be susceptible to leaching by acid precipitation (acid rain). 2) Commercially available washed construction sands typically contain relatively low proportions of clay, silt, and organic (humic) material, and are thus characterized by relatively low K_d values. 3) Further, un-amended silicate sands generally contain minimal amounts of carbonates, iron and manganese oxides, sulfides, organic matter, and phosphate compounds, and are generally ineffective in retarding lead mobility through precipitation reactions and are also difficult to vegetate. Thus, SAFR berms constructed entirely of un-amended silicate sand may be more likely to release soluble lead into the environment than berms that are constructed using other soil types. This shortcoming can be addressed by amending construction sand with materials that will buffer soil pH, enhance lead adsorption, and (or) promote the precipitation of stable lead salts.

1.1.2 Phosphate Amendments

The bioavailability and environmental risk of a contaminant are directly related to its accessibility to the biota in the soil medium, which is generally controlled by its solubility and mobility (Traina and Laperche 1999, Brown et al. 2004). Linking lead bioavailability to its solubility rather than to its total concentration makes possible the consideration of remediation strategies based on in situ reduction of contaminant solubility, rather than its complete removal or physical isolation (solidification). Due to the high costs of soil excavation and off-site remediation, in situ chemical stabilization with phosphorus (P-) based amendments has been investigated as a more efficient and cost-effective method of site remediation (Wilson et al 2006; Hettiarachchi and Pierzynski 2004; Traina and Laperche 1999; Berti and Cunningham 1997; Ma and Rao 1999; Kumpiene et al. 2008; Mench et al. 2007; Vassilev et al. 2004, Nriagu 1984, Ma et al. 1993). P-based amendments reduce the Pb bioavailability to allowable levels through the conversion of relatively soluble/bioavailable forms of Pb to relatively insoluble/less bioavailable pyromorphites ($Pb_5(PO_4)_3X$ (s), where $X = Cl^-, F^-, OH^-$), the most stable forms of Pb in oxic surface soils under a wide range of environmental conditions (Traina and Laperche 1999). Although P amendments have mainly been applied to remediate Pb-contaminated soil, they may also be applicable to other metals in firing-range soils such as Cd and Zn (Hamon et al. 2002). Spuller et al. (2007) reported that the addition of phosphate to soil increased Cu mobility.

Several laboratory and bench-scale remediation studies have demonstrated the effectiveness of the addition of phosphate-based soil amendments in producing highly insoluble lead phosphate minerals such as pyromorphite and hydroxypyromorphite (Berti and Cunningham 1997; Lambert et al. 1997; Ma and Rao 1997; Lower et al. 1998; Traina and Laperche 1999). When sequestered within these phosphate minerals, lead has been shown to be far less soluble, as indicated by the results of acid leaching tests (Tardy et al. 2003), and its bioavailability to soil organisms has been demonstrated to be sharply reduced (Berti and Cunningham 1997; Pearson et al. 2000; Traina and Laperche 1999). The USEPA has recognized that bioavailability of lead in contaminated

soils varies greatly depending upon its form in the soil, and had suggested that phosphate treatment has potential for in-situ remediation of contaminated soils and sediments (USEPA 2001c).

Lead compounds show the greatest aqueous solubility at the acidic ($\text{pH} < 4$) and alkaline ($\text{pH} > 11$) ranges. Under acidic conditions, elemental lead will dissolve, releasing a hydrated cation Pb^{2+} . Under alkaline conditions, elemental lead will dissolve, theoretically forming the dissolved hydroxide complex $\text{Pb}(\text{OH})_3^-$ and ion-pair $\text{Pb}(\text{OH})_2(\text{aqueous})$ (ITRC, 2003a).

Several factors affect the amount of lead that is dissolved in water. In a typical water body, dissolved lead forms precipitates of lead hydroxide [$\text{Pb}(\text{OH})_2$], lead carbonate [PbCO_3 , cerussite], or basic lead carbonate [$\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$, hydrocerussite]. Overall lead solubility in a natural system is fundamentally determined by the concentrations of the anions in solution (e.g., the hydroxide and carbonate ions) and by the ionic strength of the solution, which affects the activity coefficients of the ions. These factors can be related to more directly measured parameters such as pH, alkalinity, and total dissolved solids (TDS) (Vaccari 1992).

In any system having water in equilibrium with a solid phase, the metal precipitate that has the lowest solubility will be the only stable solid phase and will increase in its relative concentration at the expense of the more soluble forms. Thus, the presence of Pb compounds with extremely low solubilities, such as lead phosphates, influences the solubility and availability of the Pb in the environment.

The metalloid, antimony (Sb), has also been detected in shooting range soil at high concentrations (Ackermann et al. 2009, Dermatas et al. 2006, Johnson et al. 2005, Kilgour et al. 2008, Klitzke and Lang 2009). The Sb is added to lead alloy as a hardening agent and it is released, along with Pb, during the bullet corrosion process. However, unlike the cation, Pb, Sb is an oxyanion and the geochemistry is different from that of Pb. The geochemistry has been reviewed by Wilson et al. (2010). Antimony is reported to be associated with ferrihydrates, carbonates and oxides in soil. High pH (alkaline conditions) and anoxic conditions increases the dissolution of these complexes and leads to the release of Sb in to the soil pore water and surface water (Chen et al. 2003, Johnson et al. 2005). Therefore, in conditions of well-drained soil, with high concentrations of free carbonate and iron, a low percentage of clays and fines, and a low pH, Sb transport should not be a concern. However, when soil is amended with P for immobilization of Pb, the Sb may inadvertently be mobilized through competitive reactions with the P (Kilgour et al. 2008).

1.1.2.1 Thermally Treated Fishbones (TTF)

Fishbone is a form of biogenic apatite produced, mechanically or enzymatically, from fish industry by-products. This results in a composition of clean and dried fish bone and fish hard parts. The major elements of bones are calcium (Ca), phosphorus (P), sulfur (S), and magnesium (Mg) as well as several minor elements (Shinomiya et al. 1998). A study conducted by Shinomiya et al. (1998) investigated the eventual demineralization of mammal bones buried underground for 2 years and determined that phosphorous concentrations initially decreased within the bone and then increased, potentially due to nucleation sites (Wright et al. 2004) provided by the bone material. As a soil amendment, fishbone Apatite II has several advantages over other forms of natural apatite and terrestrial bone sources (e.g., cow bone). Apatite II has low trace metals concentrations and exhibits poor crystallinity compared to other naturally

occurring forms of apatite (Conca et al. 2000). Unlike cow bones, Apatite II is highly microporous (Wright et al. 2004; Lu et al. 2001), and thus provides a readily available and reactive source of soluble phosphates along with a potential seed crystal for heterogeneous nucleation of lead-pyromorphites (Wright et al. 2004). Depending on the presence of certain metals in solution, a lead removal efficiency of 37 to 100 percent can be achieved through the process of hydroxyapatite dissolution and hydroxypyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2]$ precipitation (Ma et al. 1994; Wright et al. 2004).

Apatite II was used at the Camp Stanley Storage Activity in Boerne, TX to remediate lead-contaminated soils. First, the large bullet fragments were separated from the soil by screening, after which Apatite II was mixed into the screened, metal-contaminated soil. A vegetative cap was established over the untreated soil and the Apatite II treated area. The average lead leachate concentration of the untreated area at Camp Stanley was 0.373 mg/L, whereas the average lead leachate concentration of the Apatite II treated area was 0.003 mg/L (Wright et al. 2004). The TCLP results for both the treated and untreated soils were well below the EPA's regulatory level of 5 mg/L. However, the TCLP lead concentrations for the Apatite II treated soil were, on average, 78% less than the untreated soil (Wright et al. 2004).

Fishbones used in the study at CAFB were thermally treated in a muffle furnace at 450 degrees C to remove organic matter (Martin et al 2008).

1.1.2.2 TRAPPS

TRAPPS™ is a COTS product, a formulation of apatite and other insoluble phosphate mineral, in which lead is precipitated as stable pyromorphite. According to the manufacturer, TRAPPS™ also does not cause increased mobilization of copper, arsenic and antimony or release excessive amounts of phosphate (http://www.slateruklimited.co.uk/us/trapps_firing_range.html).

1.1.3 Metal Oxide Amendments

Hydrous oxides of aluminum, iron and manganese are ubiquitous in soils and strongly implicated in the sorption of metals and a reduction in metal mobility in soil systems (Bradl 2004, Covelo et al. 2007, Ford et al. 1997, Han et al. 2006, Martinez and McBride 1998, Martinez et al. 1999, Ndiba et al. 2008, Orsetti et al. 2006, Trivedi and Ax 2000). The highest adsorption is found from Pb and Cu; the least adsorption from Cd, Ni, and Zn (Covelo et al 2007, Ford et al. 1997, Martinez and McBride 1998). Cadmium and Zn were not affected by changes in soil pH but Cu solubility increased (desorption) as the soil pH decreased. The iron hydroxides are generally determined to be more effective at immobilizing Pb and less effective at immobilizing Cd and Cu. However, as the metal oxides aged, the Pb was reported to undergo desorption. Unlike Pb which had rapid initial sorption into ferrihydrite, the metals with lower initial sorption (Mn and Ni) became incorporated into the more stable iron minerals goethite and hematite and remained immobilized (Ford et al. 1997, Martinez and McBride 1998).

Copper, Pb, Ni and Zn have also been reported to adsorb to Mn-oxide. Manganese oxide is a surface acidic oxide with a pH_{pzc} (point of zero charge) of approximately 1.5 to 4.5 (Han et al.

2006). Soil amendment with phosphate reduced the leachability of these complexes by 89% compared to controls (Ndiba et al. 2008).

1.2 OBJECTIVE OF THE DEMONSTRATION

The objectives of this technology demonstration are to assess the environmental benefits, feasibility, and cost of using sand as a deceleration medium in SAFR berms in conjunction with amendments designed to retard the migration of lead into the surrounding environment. The amendments provide for reduction of lead solubility through pH buffering of pore fluids within the SAFR berm, as well as the sequestration of lead through surface adsorption and the precipitation of insoluble lead salts. This technology application is known as a passive reactive berm (PRBerm™). The purpose of the technology demonstration is to provide range operators with an economical means of controlling the off-site migration of lead, while maintaining the benefits of sand as a deceleration medium. The PRBerm technology is applicable to new and existing ranges. In particular, this technology is designed to address sites where the native soils available for SAFR berm construction either lack the characteristics necessary to retard the migration of soluble lead (e.g. acidic soils) or are susceptible to erosion and off-site transport of lead as a result of their high clay content.

1.3 REGULATORY DRIVERS

The regulatory drivers at the Charleston Air Force base M-60 range were derived from the regulatory permitting requirements of the initial demonstration site, Barksdale Air Force Base, LA. The LPDES permit LA0007293 issued to Barksdale AFB on 1 Apr 1997 and reissued 1 Nov 2002, established the SAFR complex daily maximum:

- total lead discharge limit to 0.15 mg/L (150 µg/L),
- copper limit of 0.5 mg/L,
- Total Organic Carbon (TOC) of 50 mg/L,
- Discharge pH between 6.0 and 9.0.

Total Suspended Solids (TSS) is not a required measurement under the Barksdale AFB discharge permit, but since it is an important indicator of the potential metals leaving the range, TSS analysis was requested by the CAFB range personnel and was an additional parameter tested. Research performed by the Engineer Research and Development Center - Environmental Laboratory (ERDC-EL) has shown that the majority of the lead in the runoff water occurs as insoluble lead associated with suspended (colloidal) soil particles (Larson et al. 2007).

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

Figure 3 shows a typical PRBerm cross-section with the PRBerm technology application. A non-woven geo-membrane / fabric is a barrier between native soils and the ballistic impact media. Amended sand is placed on top of the newly contoured earthen berm. A SACON[®] or timber toe support was placed at the base of the PRBerm to prevent excessive sand erosion from the berm.

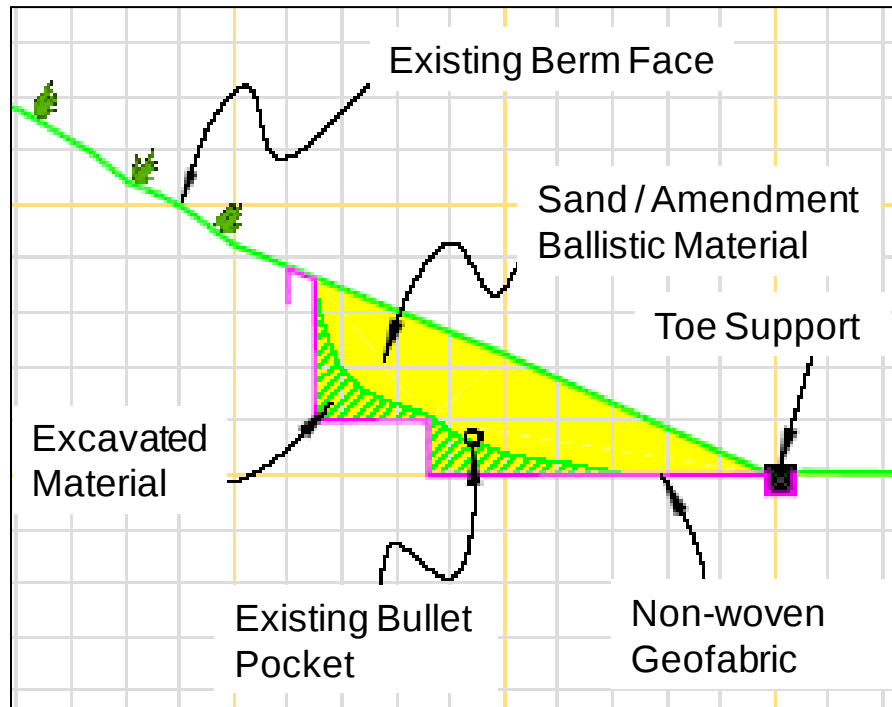


Figure 3. Schematic Cross Section of Typical Range Berm with the PRBerm Technology Application

Pre-construction views of the CAFB M-60 range are provided in **Figures 4 and 5**. A construction diagram detailing changes in the berm at the CAFB M-60 range for the installation of the PRBerm is shown in **Figure 6**.



Figure 4. Pre-construction view of the firing points and impact berm area at the CAFB M-60 range. View is through the individual firing positions towards the impact berm



Figure 5. Pre-construction close up view through the pipe that forms the firing line and looking towards the berm

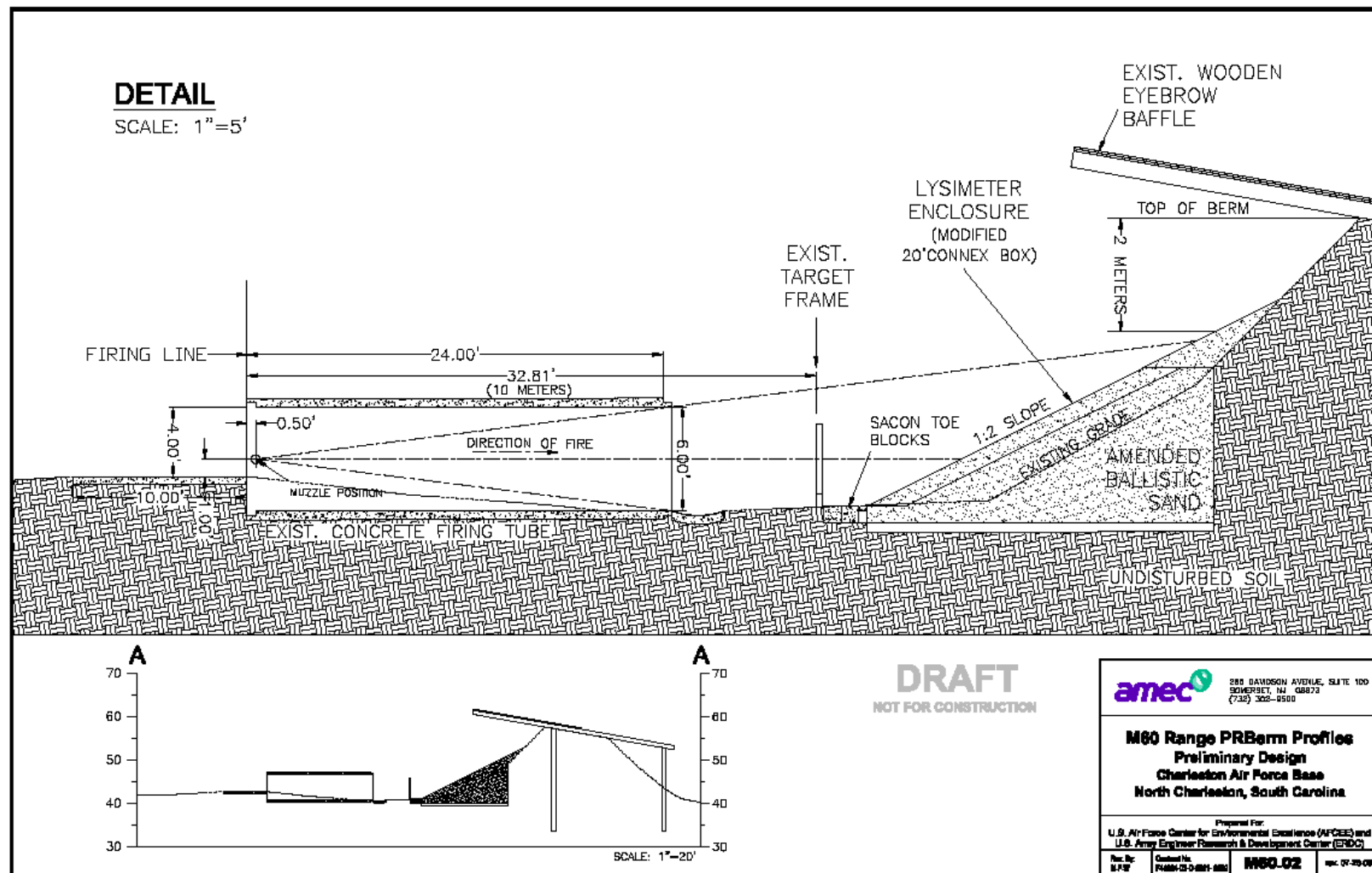


Figure 6. Designs for the implementation of the PRBerm technology at the CAFB, M-60 range

Replacement of easily suspended, clay-rich soil in the primary impact area with a material that has high hydraulic conductivity and a low potential for producing suspended solids is expected to drastically reduce the amount of the lead currently leaving the site. By amending the berms with buffer and lead immobilization amendments such as the TRAPPS™ amendment and the thermally-treated fishbones (TTF), the amount of soluble and colloidal lead in the surface water and the leachate water leaving the new berm will also be reduced (Larson et al. 2007). Both TRAPPS™ and the TTF have been used for lead stabilization in analogous systems. Lead enters the impact area at SAFRs primarily as intact bullets that break into pieces ranging from microscopic dust to large chunks of metal upon impact or smear onto soil particles. Due to weathering events, lead will eventually corrode and this results in soluble lead in rain water that percolates through the soil as leachate or becomes a surface water runoff problem. As the water that contains soluble lead passes over soils that have a high affinity for the charged lead metal the soil can provide a location for the lead to attach to. If the soil particles are small, such as clay, then there is a tendency that these particles can be washed off of the range and thus provide an increase total concentration of lead leaving the range. The PRBerm is designed to use sand as a non-reactive material thus limiting the reaction with soluble lead, but provides the amendment to bind with the soluble lead potentially creating an insoluble lead species such as plumbogumite or scotlandite that is less likely to leave the range. In addition there is potentially the transport problem of sand particles that have lead smeared onto them, but the sand used in the PRBerm matrix will consist of a ballistic sand that has an even particle size distribution, with limited fines and limited large sand particles. The limited fines will reduce the potential of suspended particles from leaving the range while the limited large particles will reduce the potential incident of bullet fragmentation upon impact.

2.2 TECHNOLOGY DEVELOPMENT

Development and pilot-scale testing of the PRBerm technology has been published in Larson et al. (2007), “Amended Ballistic Sand Studies to Provide Low Maintenance Lead Containment at Active Small Arms Firing Range Systems”. In this report, treatability studies determined that a sand to amendment ratio of 5 percent (w/w) was sufficient to contain greater than 90 percent of soluble lead within the berm material. Lysimeter studies used regulated artificial rain events to evaluate the metals concentrations, total suspended solids, dissolved organic carbon, and runoff and leachate pH over time for the amended and sand-only (control) berms. Several amendments were evaluated including four different types of Buffer Block, SulfiTech A/T, and Whole Bone and Crushed Bone Apatite II. The Buffer Block and the SulfiTech A/T maintained average leachate lead and copper concentrations below the selected study limit of 0.150 mg/L and 0.500 mg/L, respectively, maintained a pH between 6 and 9, and maintained a dissolved organic carbon level at less than 50 mg/L for the leachate and runoff waters. However, the Apatite II achieved the TCLP lead permit level. The PRBerm, when compared to the traditional earthen berm, or a fully-contained bullet trap, reduced metals migration, and reduced construction and operation costs.

Apatite II was further investigated for its ability to sequester Pb from solution (Martin et al. 2008). The treatability study reported that organic compounds were formed in the apatite-amended lysimeters during aging and this hindered Pb immobilization. Because Apatite II is known to contain up to 40% residual organics (Conca and Wright 2006), the fish bones were

treated using several different methods to remove the residual organics. Laboratory and column studies established that thermally treated Apatite II consistently removed >90% of soluble lead from solution and reduced the biological oxygen demand (BOD) of the solutions to non-detect levels. For this reason, it was chosen as one of the soil amendments in the PRBerm field demonstration.

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The most commonly used technologies for metals containment at SAFRs range from using native earthen berms to installing steel bullet traps. The cost of the PRBerm technology will be compared against using a native earthen berm to installing a steel bullet trap. The cost basis for comparison will be \$ per running foot of PRBerm as compared to \$ per running foot of earthen berm and purchase and installation of a single steel bullet trap.

The sand or dirt berm is the oldest and most basic type of bullet trap. It uses the mass of the berm itself to stop and store bullets. Earthen backstops require immediate care to re-vegetate, to prevent potential on-going erosion problems. Use of fiber mulch, filter fabric or other material is almost certainly needed for a facility constructing a new earthen backstop. Proper seed mix recommendations, matching soil conditions, moisture and sun light conditions must be met for successful re-vegetation. Concentrations of lead called hot spots can form behind the targets. Bullet deflection and splatter causing subsequent shots to ricochet and bounce back towards the shooter may begin to take place on an older, existing backstop if periodic removal is not included as a part of the maintenance plan of the range. In order to recover spent bullets, the berm must be mined and the lead separated out. A certain amount of the sand will be contaminated and must be replenished each time the berm is re-built. Sand and dirt berms are coming under increasingly harsh environmental scrutiny due to high lead levels in the ground around the impact areas, and the tendency of the lead to seep into surrounding groundwater and surface receiving waters.

The benefits of a sand berm include low installation cost and the speed with which they can be constructed using a bulldozer or some other piece of earth moving equipment. Earthen berms also require relatively low maintenance, and the ability to use any kind of ammunition. Weaknesses include potential environmental hazard, constant, expensive maintenance, and the possibility of hot spot ricochet, mentioned above.

The benefits of a bullet trap include lower initial cost and simple installation. Some variations don't involve sand or granules. Most variations make it easier to collect the spent lead bullets for recycling and/or disposal. Other benefits are the durability of steel and the smaller training space requirement. Weaknesses include bullet fragmentation on impact, lead build-up and bullet ricochet, no close-range shooting and high maintenance. The act of firing into a steel bullet trap is also a significantly different training experience from firing into a berm.

Advantages of the PRBerm technology include:

- Ease of procuring the amendments. The PRBerm™ is designed to minimize procurement problems by incorporating commonly available (*i.e.*, off-the-shelf) construction materials such as masonry sand and landscaping fabric. Both of the Buffer/Lead Immobilization Systems (Buffer Block and SulfiTech A/T) are available through authorized commercial suppliers. These are both proprietary technologies for use in remediation and management systems but with significant differences from the PRBerm approach. The associated transportation costs for these materials may vary by location.

- The technology can be installed using conventional construction machinery (e.g., frontloader with track excavator).
- Selection of amendments to address immobilization of both cationic and anionic metal species
- Impact media plus amendments passed the TCLP for waste disposal in a non-hazardous waste landfill, a considerable cost savings when considering removal of the training range berms.

Potential limitations of the PRBerm™ technology include:

- Possible solubilization of phosphate and transport of phosphate off the range in storm water runoff, depending on the type of amendment selected. High phosphate concentrations have been observed to result in algal blooms.
- Variation in the amount and type of rounds fired into berms has an effect on the Pb concentrations contained in leachate and runoff. Heavy use of the PRBerm™ with lead ammunition will eventually fill all adsorption sites and increase the concentration of lead released into the leachate and runoff water. Sampling should be continued in order to monitor the life cycle of the PRBerm™.

3.0 PERFORMANCE OBJECTIVES

The Performance Objectives of the CAFB PRBerm field demonstration are summarized in Table 2.

Table 2. Performance Objectives

Type of performance objective	Primary Performance Criteria	Expected performance (metric)	Actual performance (Objective met?)
Quantitative	Objective goals based on the treatability study and Barksdale AFB permit limits (carried through field demonstration for continuity purposes)	Bi-monthly soluble Pb runoff ≤ 150 ppb	Success
		Bi-monthly maintain pH 6 to 9	Success
		Bi-monthly TOC ≤ 50 ppm ^a	Success
		Bi-monthly soluble Cu runoff ≤ 500 ppb	Success
Qualitative	Capture metals prior to off-range migration	Reduced soluble Pb and other metals concentration results as compared to the control with no amendment	Successful for the TTF amendment.
	Reduce range operational costs	Provide comparable long term cost savings as compared to steel bullet traps	Success
	Increase use of training availability	Provide a functional range for airmen to conduct regular small arms training	Success
	Provide Best Available Technology (BAT) for range operations	Low cost, ease of use, and minimal maintenance required by range personnel	Success
	Reduce the potential for leaching to groundwater	Compare metals leaching results (TCLP) to state/federal requirements	Successful for the thermally treated fish bone (TTF) amendment.
^a At the request of CAFB, TOC analysis was changed to TSS as the suspended solids were a greater concern to them.			

4.0 SITE DESCRIPTION

The Charleston AFB ranges that will be used during this demonstration is the M-60 range. There is an underground drain that allows the range runoff water to flow under a nearby road and into storm water drainage nearby. This is a suitable means to collect and store rainwater for use in artificial raining on of the PRBerm if needed. The drainage system located at the range will assist with collection of storm water samples leaving the range complex and prevents potential cross contamination of leachate water collection systems (i.e. on-site pooling of water).

4.1 SITE LOCATION AND HISTORY

Charleston Air Force Base, also known as Joint Base Charleston, is a United States Air Force base located in North Charleston, South Carolina (**Figure 7**). Charleston Air Force Base originated when the city of Charleston purchased land in 1931 to build Charleston Municipal Airport. On 11 December 1941, the Army Air Corps took control of the field and anti-submarine missions were being flown out of Charleston Army Air Field by August 1942. Returned to civilian control after World War II, the United States Air Force began joint use of the facility on 11 July 1952 and the military part of the airfield was renamed Charleston Air Force Base on 1 June 1953.



Figure 7. Location of Charleston AFB, SC.

CAFB is assigned to Air Mobility Command (AMC). A joint civil-military airport, Charleston AFB shares runways with Charleston International Airport for commercial airline aircraft operations on the south side of the airfield and general aviation aircraft operations on the east side (**Figure 8**). Charleston Air Force Base is home to Joint Base Charleston 628th Air Base Wing (628 ABW), the "host wing for installation support". The 437th Airlift Wing (437 AW) focuses on operating the C-17 Globemaster III strategic airlift aircraft. The base has four operational groups consisting of 21 squadrons and two wing staff directorate. It is augmented by

a parallel, collocated Air Force Reserve Command (AFRC) "associate" wing, the 315th Airlift Wing (315 AW), which shares the same C-17 aircraft with the 437 AW.

The 628th Air Base Wing's primary duties are to provide installation support to 53 DoD and Federal agencies, servicing a total force of over 79,000 Airmen, Sailors, Soldiers, Marines, Coast Guardsmen, civilians, dependents and retirees on Charleston AFB and Naval Weapons Station Charleston. Additionally, they also provide mission-ready expeditionary Airmen to combatant commanders in support of joint and combined operations.

The 437th Airlift Wing's mission is to fly C-17s and provide airlift of troops and passengers, military equipment, cargo, and aeromedical equipment and supplies worldwide in support of tasking by Air Mobility Command and unified combatant commanders.

Location of the
M-60 range

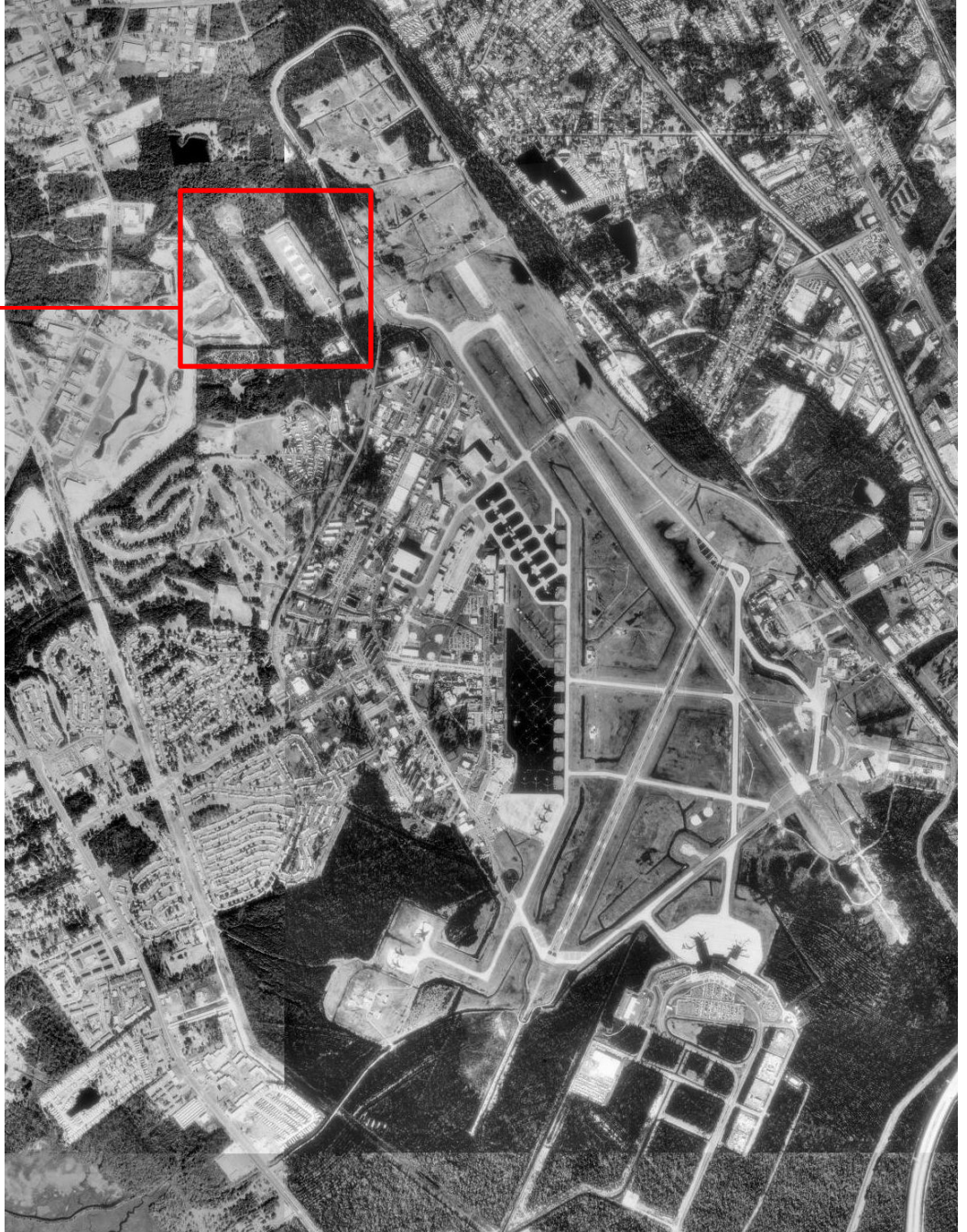


Figure 8. Aerial view of the Charleston Air Force Base with the location of the M-60 range indicated within the red box.

The Charleston AFB M-60 range contains three firing positions that are used for the qualification/familiarization of the 5.56mm (M249) and 7.62mm (M240) weapons systems. The range has an adequate drainage system. Typically the Charleston AFB personnel fire more than 100,000 rounds of 5.56mm and/or 7.62mm ammunition per year for qualification/familiarization purposes (**Figure 9**).



Figure 9. Aerial view of the M-60 range at Charleston AFB indicating possible bullet firing distances.

Prior to installation of the PRBerm technology installation range safety management determined the need for a new eyebrow over the firing line to limit the ricochet potential and possible harm to human dwellings and aircraft maintenance areas. The ricochet safety design is illustrated in **Figure 10**.

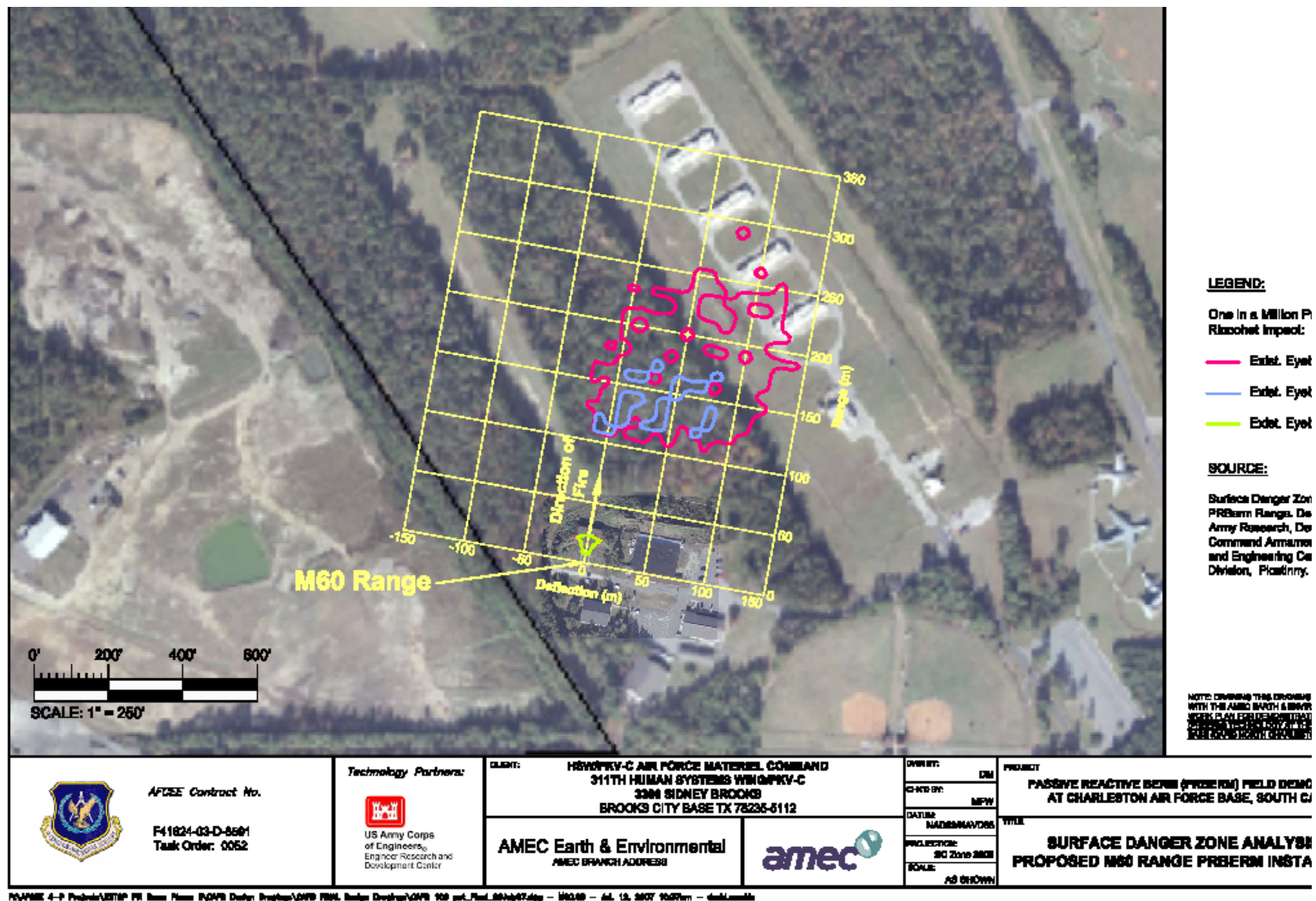


Figure 10. Surface danger zone analysis of proposed M60 range PRBerm installation.

4.2 SITE GEOLOGY/HYDROGEOLOGY

The native soil at the CAFB is characterized as fifteen different soil types; primarily consisting of fine sands and fine sandy loams that provide the potential for suspended solids transport of lead associated particulates from the SAFR berm.

4.3 CONTAMINANT DISTRIBUTION

Charleston AFB has two SAFRs that are configured for M-9 and M-60 training. The SAFR's are located on the base that uses the same runway as the local Charleston Airport. The Charleston AFB range that will be used during this demonstration is the M-60 range. The current M-60 range has been in operation for over 20 years.

There is an underground drain that allows the range runoff water to flow under a nearby road and into stormwater drainage nearby. This is a suitable means to collect and store rainwater for use in artificial raining on of the PRBerm if needed. The drainage system located at the range will assist with collection of storm water samples leaving the range complex and prevents potential cross contamination of leachate water collection systems (i.e. on-site pooling of water).

As this was new construction, and the construction designs themselves were part of the experimental design, there was no baseline sampling prior to the field demonstration.

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

This technology demonstration assessed the environmental benefits, feasibility, and cost of using sand as a deceleration medium in SAFR berms in conjunction with amendments designed to retard the migration of lead into the surrounding environment. The amendments provided for reduction of lead solubility through pH buffering of pore fluids within the SAFR berm, as well as the sequestration of lead through surface adsorption and the precipitation of insoluble lead salts. This technology application is known as a passive reactive berm (PRBerm™).

The PRBerm™ can provide range operators with an economical means of controlling the off-site migration of lead, while maintaining the benefits of sand as a deceleration medium. In particular, this technology is designed to address sites where the native soils available for SAFR berm construction either lack the characteristics necessary to retard the migration of soluble lead (e.g. acidic soils) or are susceptible to erosion and off-site transport of lead as a result of their high clay content.

The amendments incorporated into the ballistic sand were TRAPPS™ and TTF, both phosphate-based amendments.

5.2 BASELINE CHARACTERIZATION

Baseline characterization was performed on soils from the initial demonstration site at Barksdale AFB, LA. Due to range construction at the Barksdale site, the field demonstration was moved to CAFB where an unused range was selected for the lysimeter construction. No baseline characterization studies were performed on the CAFB M60 range site. The study design required that the previous impact berm, composed of native soil, be completely dismantled and replaced with the three test lysimeters of the PRBerm™.

5.3 TREATABILITY STUDY RESULTS

A treatability study (Larson et al. 2007) evaluated the use of ballistic sand with amendments in the construction of impact berms. Laboratory and mesoscale studies using both static and live-fire lysimeters determined optimum sand/amendment combinations to immobilize soluble metals, such as lead, in situ. Bench-scale studies determined that the incorporation of nonreactive ballistic sand with amendment(s) will contain metals within an impact berm. A sand to amendment ratio of 5% (w/w) was sufficient to contain greater than 90% of soluble lead within the berm material.

Lysimeter studies then used regulated artificial rain events to evaluate the metals concentrations, total suspended solids, dissolved organic carbon, and runoff and leachate pH over time for both the amended and sand-only (control) berms. Several phosphate-based amendments were evaluated including Apatite II. The results of static lysimeter studies I and III are presented in **Table 3 and Table 4**. These studies amended ballistic sand with 3%, 5%, or 8% Apatite II (w:w) or 5% Buffer Block #4 (w:w) or 5% TRAPPS or 5% TRAPPS plus 7% Baked Apatite II (TTF).

Two points were immediately apparent. First, the bench-scale studies did not adequately predict the results of the lysimeter studies. The effect of aging on the sand and amendments was more pronounced than expected. Second, the leachate from the combination of TRAPPS and TTF were the only amendment that met the experimental parameters in all areas. However, static lysimeter study II observed high concentrations of DOC and TSS in the leachate from the Apatite II-amended lysimeters.

The results of the post-LFL TCLP of the berm sand amendments is presented in **Table 5**. By comparing the metals concentrations remaining in solution after 18 hours of tumbling in the TCLP extraction solution against control soils with no amendments, the amended soils decreased the leaching of lead from 45 to 99 percent. The ballistic sand combined with TRAPPS and the baked apatite was most effective at reducing the Pb TCLP concentration at the lowest amendment loading rate.

Apatite II™ was further investigated for its ability to sequester Pb from solution (Martin et al. 2008). The treatability study reported that organic compounds were formed in the apatite-amended lysimeters during aging and this hindered Pb immobilization. Because Apatite II™ is known to contain up to 40% residual organics (Conca and Wright 2006), the fish bones were treated using several different methods to remove the residual organics. Laboratory and column studies established that thermally treated Apatite II™ consistently removed >90% of soluble lead from solution and reduced the biological oxygen demand (BOD) of the solutions to non-detect levels. For this reason it was chosen as one of the soil amendments in the PRBerm field demonstration.

Table 3. Static lysimeter leachate parameters from different ballistic sand and amendments*

Lysimeter study and amendments		Lead ^b (µg/L)		DOC (mg/L)	pH	TSS (mg/L)
		Filtered	Total			
Study Goals		≤150		≤50	6 to 9	
Lysimeter Study I ^a	Ballistic sand (Control - no amendments)	<50	387	2	6.91	1.9
	3% Apatite II	646	2,031	347	6.88	ND
	5% Apatite II	1,008	3,143	934	6.74	17.2
	8% Apatite II	488	2,050	1,739	6.55	ND
	5% Buffer Block #4	825	3,231	8	10.67	1.4
Lysimeter Study III	5% TRAPPS	<50	529	ND ^c	ND	ND
	5% TRAPPS and 7% Baked Apatite II (TTF)	<58	119	ND	ND	ND
*Shaded values are those that met the goals ^a Collected data from only 4 rain events on all samples due to high Pb concentrations ^b ICP reporting limit = 50 µg/L ^c ND = not determined						

Table 4. Live-fire lysimeter (LFL) leachate parameters from different ballistic sand and amendments*

Lysimeter study and amendments		Lead ^b (µg/L, avg. n=10)		DOC (mg/L, avg., n=10)	pH (n=10)
		Filtered	Total		
Study Goals		≤150		≤50	6 to 9
LFL Study I ^a	Ballistic sand (Control - no amendments)	<62	1,944	8	7.08
	Sand and 5% Buffer Block #5	<90	1,667	9	7.55
LFL Study II	Sand and 5% TRAPPS 2	<50	<66	57	6.38
	Sand and 5% TRAPPS 1	<50	<52	47	6.44
*Shaded values are those that met the goals ^a Collected data from 10 rain events ^b ICP reporting limit = 50 µg/L					

Table 5. Results of TCLP analysis of post-live-fire lysimeter berm sand and amendments (n=3)

Sample	TCLP Pb Concentration (mg/L)
Control (no amendment)	64.6
Ballistic sand with 5% TRAPPS 2	210.07
Ballistic sand with 5% TRAPPS 1	395.87
Ballistic sand with 5% TRAPPS 1 and 7% Baked Apatite II (TTF)	0.48

5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

5.4.1 Sand Amendments

Two amendments were selected for field testing at the CAFB M60 range: TRAPPS™ (Slater, UK) and thermally treated fish bones (TTF). The TRAPPS™ would be tested alone and with the addition of the TTF. TRAPPS™ is a COTS product, a formulation of apatite and other insoluble phosphate mineral, in which lead is precipitated as stable pyromorphite. According to the manufacturer, TRAPPS™ also does not cause increased mobilization of copper, arsenic and antimony or release excessive amounts of phosphate (http://www.slateruklimited.co.uk/us/trapps_firing_range.html).

The second amendment is thermally-treated fishbones (TTF). Fishbone is a source of biogenic apatite known to sequester lead from solution (Martin et al. 2008). Although the fish bone amendment did not perform as well as the other amendments initially in the treatability study, the problem was identified and solved (Martin et al. 2008). Thermal treatment removes organic carbon that interferes with lead sorption sites. This increases the treatment effectiveness over the long-term versus increased product cost in the short-term. The TTF was also found, in bench-scale studies, to achieve the regulatory TCLP discharge limit for lead. This affected the decision to use a limited amount of the TTF in a concentrated area of the lysimeter and observe the benefit to heavy metal immobilization.

5.4.2 Lysimeter Construction

The three lysimeters placed inside the impact berm of the M60 range were constructed from ISO Standard 20-foot by 8-foot insulated containers by Sea Box, Inc., located in East Riverton New Jersey (**Figure 11**). The lysimeters were designed for the collection of surface runoff water and soil leachate. Construction details of the leachate collection system are shown in **Figures 12 and 13**. For the lysimeter that contained both TRAPPS™ and thermally treated fish bones, a high-

density polyethylene lysimeter measuring 0.787 m (31 in.) by 0.787 m by 0.609 m (24 in.) (inside length x width x height) was placed inside of the stainless steel lysimeter. The polyethylene lysimeter contained 5% TTF. Separate leachate collection piping was attached to the stainless steel lysimeter and the polyethylene lysimeter insert.



Figure 11. Completed field lysimeter prior to transport to the CAFB M60 range.



Figure 12. Interior view of the completed lysimeter demonstrating the ridged bottom to facilitate flow of the leachate from the amended ballistic sand.



Figure 13. Interior view of the completed field lysimeter demonstrating the leachate collection system.

5.4.3 Lysimeter Assembly at the CAFB M60 Range

The amendments used in the three lysimeters placed inside the impact berm of the M60 range are illustrated in **Table 5**. Detailed diagrams of the lysimeters and the leachate and surface water collection systems are provided in **Figures 14, 15, and 16**.

Table 6. Amendment composition in the three field demonstration lysimeters.

Lysimeter Location and Amendment Composition		
Left Lysimeter	Center Lysimeter	Right Lysimeter
Clean ballistic sand mixed with 5% TRAPPS	Clean ballistic sand mixed with 5% TRAPPS	Clean ballistic sand
5% TTF in a separate container inset within the Sand/TRAPPS		

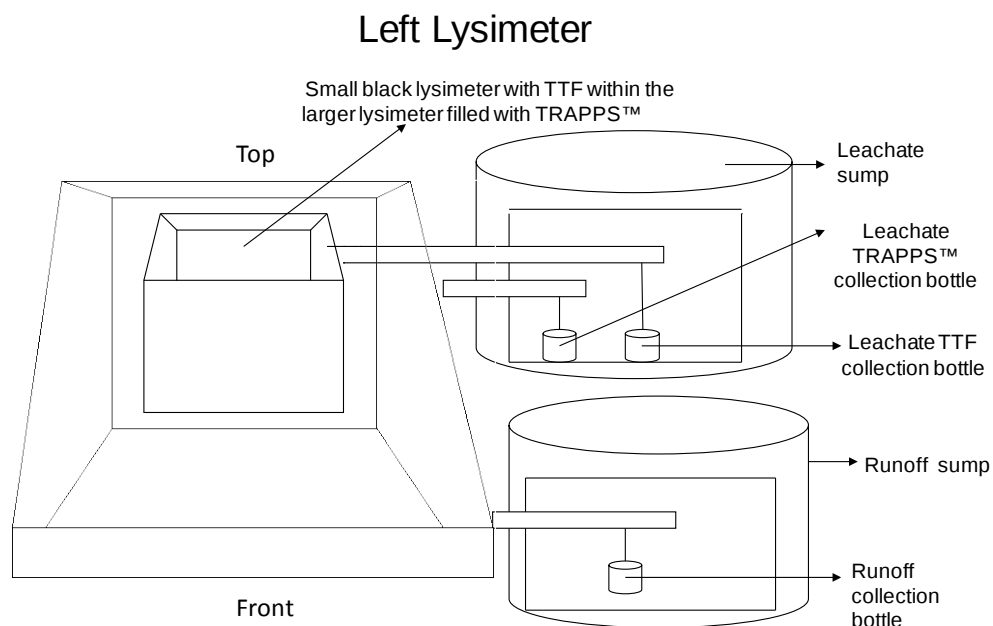


Figure 14. Assembly diagram of the left lysimeter showing arrangement of the leachate and runoff water collection systems for both the outer TRAPPS material and the inset lysimeter with the TTF.

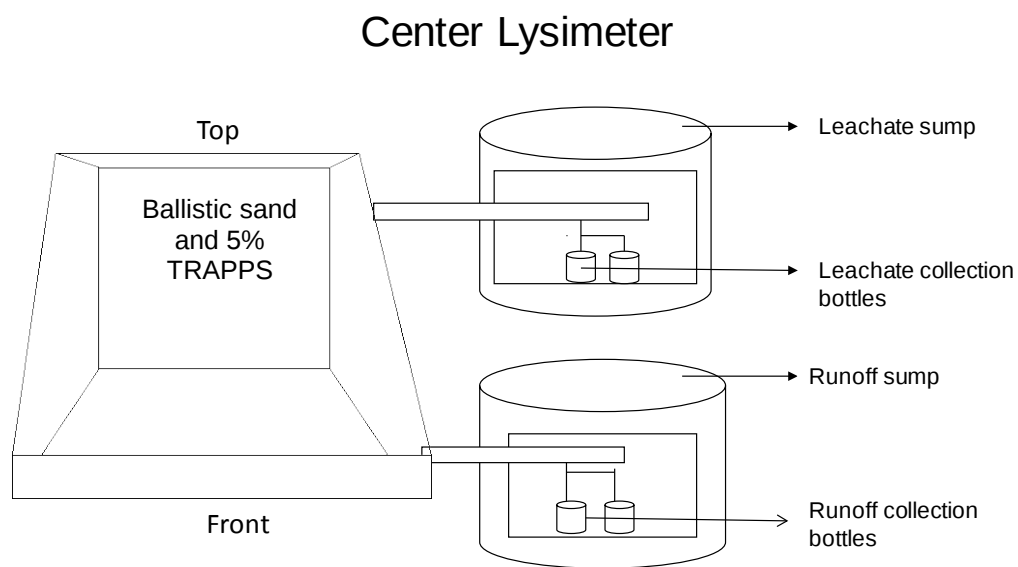


Figure 15. Assembly diagram of the center lysimeter showing arrangement of the leachate and runoff water collection systems.

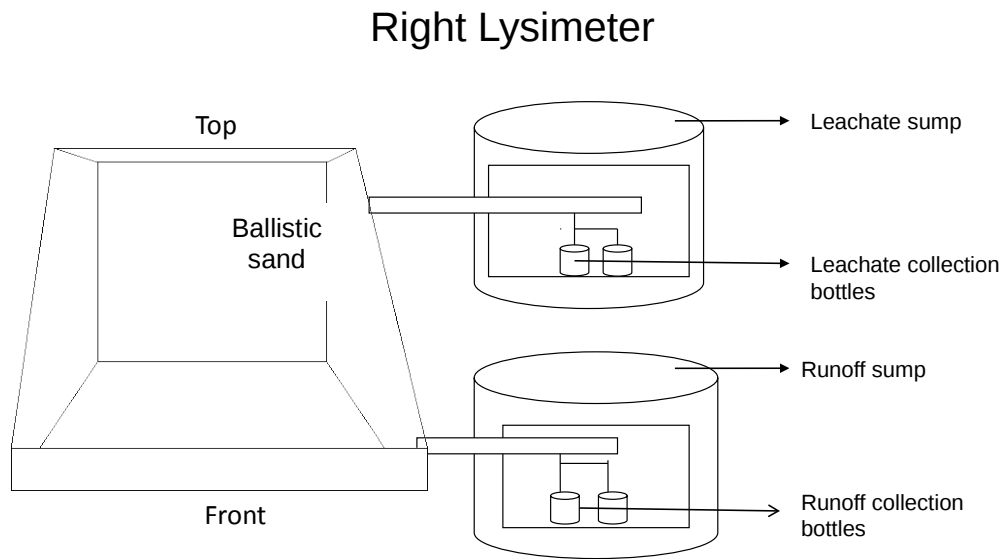


Figure 16. Assembly diagram of the right lysimeter showing arrangement of the leachate and runoff water collection systems.

A series of photographs (**Figures 17, 18, 19 and 20**) shows the sequence of construction steps to install the three lysimeters in the impact berm in front of the firing positions of the M60 range.



Figure 17. Removal of the old impact berm composed of local soil from under the newly constructed protective eyebrow.



Figure 18. Placement of the three lysimeters in the impact berm in line with the three fixed firing positions.

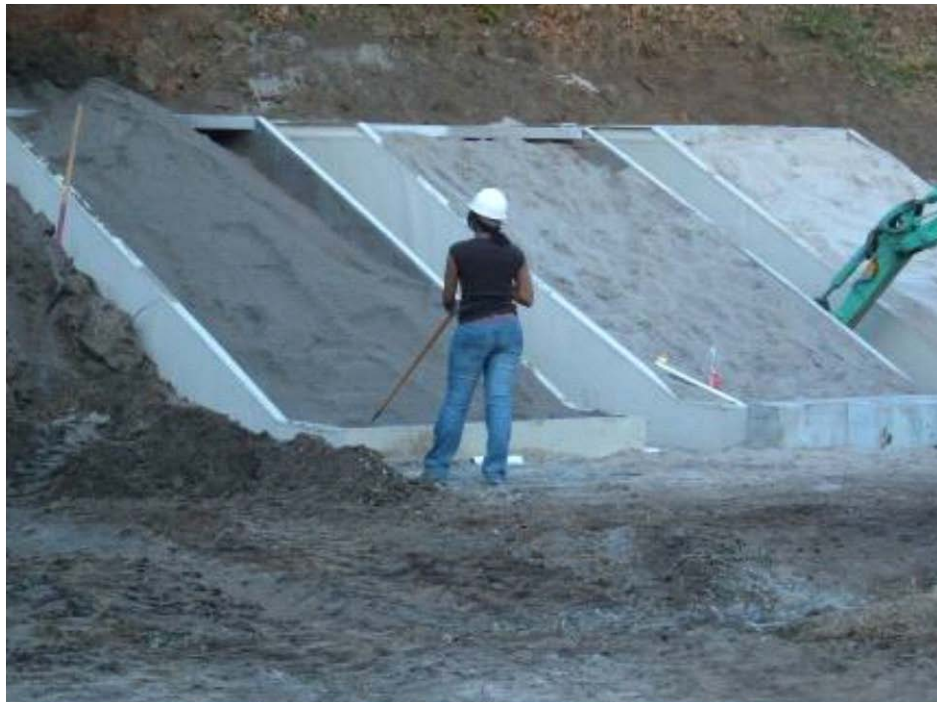


Figure 19. Placement of the amended ballistic sand in the lysimeters.



Figure 20. The completed impact berm enclosing the three experimental treatment lysimeters on the M60 range, CAFB.

5.5 FIELD TESTING

5.5.1 Metal Contamination Based on Rounds Fired

Records were kept of the bullet type and number of rounds fired into the PRBerm to obtain an accurate account of the total lead loading on the range. Background metals (lead) concentration in the native ballistic sand was determined. The lead loading on the three lysimeters is detailed in **Table 7**. The 7.62 mm round, used in the M60 machine gun, and the 5.56 mm round, used in the M-16 rifle, were both fired on the CAFB range. The lysimeter amended with 5% TRAPPS™ had the most 7.62 mm rounds fired and no 5.56 mm rounds fired. The smallest number of 7.62 mm rounds fired was 5,100, into both the control and 5% TRAPPS™+ 5% TTF lysimeters. The control lysimeter had 2,400 total 5.56 mm rounds fired and the 5% TRAPPS™+ 5% TTF had almost twice that number.

Table 7. Type and number of rounds fired into each lysimeter on the CAFB M60 range during the 2009 field demonstration.

Date	7.62-mm rounds			5.56-mm rounds		
	Control	5% TRAPPS	5% TRAPPS + 5% TTF	Control	5% TRAPPS	5% TRAPPS + 5% TTF
March 27	200	200	200	0	0	0
June 28	100	100	100	0	0	0
July 31	100	3,400	0	2,400	0	2,400
August 18	0	0	0	0	0	1,200

September 10	0	600	600	0	0	600
October 22	0	4,200	4,200	0	0	0
December 4	4,800	0	0	0	0	0
Total	5,100	8,500	5,100	2,400	0	4,200

Based on the number of rounds fired and the metal available in each type of round, the potential metal contamination was calculated (**Tables 8, 9 and 10**). The mass of the soil was the same in each of the lysimeters. The number of rounds varied per lysimeter. The control and the 5% TRAPPS™ + 5% TTF both had the same amount of 7.62 mm rounds fired so the Pb, Cu, Zn, Fe, Mg, and Sb masses were the same. The 5%TRAPPS lysimeter had the most metal mass present for all metals for the 7.62 mm rounds. No 5.56 mm rounds were fired in the 5%TRAPPS lysimeter. The 5% TRAPPS™ + 5% TTF had the most metal mass content for the 5.56 mm round. **Table 10** shows the total metal concentrations in each lysimeter for both the 7.62 mm and 5.56 mm rounds. The highest Pb concentration was present in the 5% TRAPPS™ lysimeter. The untreated lysimeter (Control) had the least amount of Pb present in the sand.

Table 8. Calculations of lysimeter metal concentration based on 7.62 mm round.

Metal	Metal Mass per Round, g	Mass of Sand, kg	Control			5% TRAPPS™			5% TRAPPS™ + 5% TTF		
			Number of Bullets Fired	Mass per Total Rounds Fired, g	Conc. in Sand, mg/kg	Number of Bullets Fired	Mass per Total Rounds Fired, g	Conc. in Sand, mg/kg	Number of Bullets Fired	Mass per Total Rounds Fired, g	Conc. in Sand, mg/kg
Pb	4.9982	19583	5100	25490.61	1301.63	8500	42484.35	2169.38	5100	25490.61	1301.63
Cu	2.8105			14333.58	731.92		23889.30	1219.86		14333.58	731.92
Zn	0.3091			1576.48	80.50		2627.47	13417		1576.48	80.50
Fe	1.5473			7891.10	402.94		13151.84	671.57		7891.10	402.94
Mg	0.0019			9.69	0.49		16.15	0.82		9.69	0.49
Sb	0.0504			257.04	13.13		428.40	21.88		257.04	13.13
Other metals	0.0326			166.26	8.49		277.10	14.15		166.26	8.49

Table 9. Calculations of lysimeter metal concentration based on 5.56 mm round.

Metal	Metal Mass per Round, g	Mass of Sand, kg	Control			5% TRAPPS™			5% TRAPPS™ + 5% TTF		
			Number of Bullets Fired	Mass per Total Rounds Fired, g	Conc. in Sand, mg/kg	Number of Bullets Fired	Mass per Total Rounds Fired, g	Conc. in Sand, mg/kg	Number of Bullets Fired	Mass per Total Rounds Fired, g	Conc. in Sand, mg/kg
Pb	4.9982	19583	2400	4928.40	251.66	0	0.00	0.00	4200	8624.70	440.40
Cu	2.8105			2771.28	141.51		0.00	0.00		4849.74	247.64
Zn	0.3091			304.80	15.56		0.00	0.00		533.40	27.24
Fe	1.5473			1525.68	77.91		0.00	0.00		2669.94	136.34
Mg	0.0019			11.76	0.60		0.00	0.00		20.58	1.05
Sb	0.0504			49.68	2.54		0.00	0.00		86.94	4.44
Other metals	0.0326			22.32	1.14		0.00	0.00		39.06	1.99

Table 10. Total metal concentration in soil for both rounds.

Metals	Control (mg/kg)	5% TRAPPS™ (mg/kg)	5% TRAPPS™ + 5% TTF(mg/kg)
Pb	1553.29	2169.38	1742.03
Cu	873.43	1219.86	979.56
Zn	96.06	134.17	107.74
Fe	480.85	671.57	539.28
Mg	1.10	0.82	1.55
Sb	15.66	21.88	17.56
Other metals	9.63	14.15	10.48

5.5.2 Demonstration Phase

5.5.2.1 Demonstration Schedule

The original field demonstration schedule is shown in **Figure 21**. This schedule was changed several times due to changes in the demonstration site, delays in design and construction of a safety eyebrow over the fixed firing positions, and delays in use of the site for training purposes.

Milestones	FY 2004				FY 2005				FY 2006			
	Qtr				Qtr				Qtr			
	1	2	3	4	1	2	3	4	1	2	3	4
Field Sampling												
Treatability Study												
Field Demonstration												
Complete Reports												

Figure 21. Original PRBerm field demonstration schedule

5.5.3 System Shutdown and Demobilization

5.5.3.1 Residuals Handling

Amended sand samples were analyzed by TCLP and DDI leaching techniques to determine the safety of handling. The lead bullets inside the berm material can be collected by a conventional recycling technology, such as soil sieving, and sent to an approved lead recycling facility. This issue is addressed in the Demonstration Plan Appendix F: Health and Safety Plan for PRBerm Demonstration.

5.6 FIELD SAMPLING

5.6.1 Berm Soil Samples

Initial and final soil samples were taken to determine metal concentrations, TCLP and SPLP leaching concentrations, DDI suspend and settle leaching concentrations, partition coefficient (K_d), and pH of the amended ballistic sand. For the final soil sampling, bulk and dimensional samples were taken from each of the lysimeters. The lysimeter dimensional samples were based on the following measurements:

1. 0-4 feet x 0-5 feet (length x height)
2. 0-4 feet x 5-10 feet (length x height)
3. 4-8 feet x 0-5 feet (length x height)
4. 0-4 feet x 5-10 feet (length x height).

These samples were taken with plastic cores 1 in. in diameter and 8 in. in length. Nine subsamples were taken from each of the different dimensions. Triplicate analysis was performed on each of the nine subsamples.

5.6.1.1 Soil Leaching Tests

The TCLP was performed on both bulk soil and the dimensional core samples using a 1:20 soil:solution ratio. The SPLP was performed only on the bulk soil samples using Extraction Fluid #1 and a 1:20 soil:solution ratio. TCLP and SPLP samples were allowed to mix on the tumbler for 18±2 hours. After removal from the tumbler, samples were allowed to settle for about 30 minutes and filtrates were obtained using 0.45 micron filters attached to 10 mL syringes. The DDI Suspend and Settle Leaching Procedure (DDI S&S) is a variation of the TCLP replacing the acid solution with DDI water. The DDI S&S test consisted of a one (1) hour shake test and 18 hours settling time. After settling, samples were filtered using a 10 mL syringe with a 0.45 micron filter attached to 10 mL syringes. The pH was tested from the filtrates.

5.6.1.2 Determination of Partition Coefficient, K_d

A 24-hour partition coefficient was performed on the pre-fired soils following procedures established in Appendix 6 of USEPA (1999b). The metals of interest for these soils were Pb, Cu, and Fe. Stock solutions were prepared using Pb nitrate (CAS#10099-74-8, Fisher Scientific), copper II sulfate pentahydrate (CAS#7758-99-8, Sigma Aldrich) and ferrous sulfate (CAS#7782-63-0, Sigma Aldrich).

A 1:10 soil to solution ratio was used for the 24-hour test. Triplicate samples with 10 grams of soil per sample were weighed into each 125 mL nalgene bottle and 100 mL of each solution was added. Sample bottles were placed on the shaker for 24 hours, removed from shaker, and allowed to settle for 10 minutes. Liquid samples were filtered using a 0.45 micron syringe filter attached to a 10 mL syringe and stored in the dark at 4 °C until analysis was conducted.

5.6.2 Surface Water Runoff and Leachate

During the PRBerm field demonstration, stormwater runoff samples were collected biweekly using natural rain events. Samples were collected by the CAFB Bioenvironmental Engineering personnel under the general supervision of the ERDC-EL Principal Investigator (PI) or a Co-PI.

While flow-or time-averaged sampling may provide a better profile of runoff water quality over the storm event duration, there were logistical problems associated with collecting these samples. The proposed collection locations on the range could not use automated samplers because the equipment could not be located in areas that are out of the line-of-fire. The equipment could not be protected from being shot unless limits were placed on range use, which was not an option. As a result, manual grab samples were collected from sumps installed in the runoff flow path from each test cell on the berms.

Water samples were collected in 1-L plastic bottles. The sampling collection point was then drained. As part of the QA/QC plan (ERDC 2005, Appendix E), replicate samples were taken periodically in order to ensure that sampling was not biased. Samples were preserved in accordance with EPA and ASTM preservation guidelines. Samples were properly labeled and tightly sealed to avoid cross-contamination during storage and/or shipment. Samples were packaged for shipment in rigid, insulated plastic ice chests. These samples were sent to ERDC-EL for analysis via overnight delivery.

5.6.3 Analysis Methods

The methods and procedures detailed in **Table 11** were used for chemical and physical analysis of the PRBerm samples. Both liquid and soil samples were analyzed for heavy metals using an Inductively Coupled Plasma (ICP) Atomic Emission Spectroscopy (AES), with a reporting limit of 0.025 mg L⁻¹ for liquids and 5 mg/kg for soils (Perkin-Elmer Optima 4300 dual view, Perkin-Elmer, USA). Analyses for total metals in soils were performed using USEPA SW846 Method 3051 (1999a). Aqueous samples were analyzed in the laboratory for metals (total and dissolved) and TSS. Samples were field filtered using 0.45 micron filters prior to shipping for dissolved metals analysis in the laboratory.

Table 11. Summary of Analysis Methods and Frequency.

Contaminant/Parameter	Analytical Method	Analytical Frequency
Aqueous Samples		
Metals –total and dissolved	SW846-3015 ^a	Bi-weekly
Total suspended solids (TSS)	SM 2540D ^b	Bi-weekly
pH	Electrode	Bi-weekly
Soil Samples		
Metals– total and dissolved	SW846-3051 ^a	Initial and final
pH	Electrode	Initial and final
TCLP	SW846-1311	Final
SPLP	SW846-1312	Final
DDI S&S	Modified SW846-1311	Final
K _d	24-hr partition coefficient test ^c	Final
^a USEPA (1999a) ^b American Public Health Association (1998) ^c USEPA (1999b)		

5.7 SAMPLING RESULTS

5.7.1 Aqueous Samples

5.7.1.1 Volumes Collected

Volumes were taken biweekly. The total volume results are shown in **Table 12**. The control lysimeter had the greatest total effluent. The volume of leachate from the experimental lysimeters ranged from 51% to 63% of the total for the 5% TRAPPS and the 5% TRAPPS + 5%TTF, respectively. The volume of runoff water from the experimental lysimeters ranged from 37% to 49% of the total volume for the 5% TRAPPS + 5%TTF and the 5% TRAPPS, respectively. The most runoff was generated from the control lysimeter whereas the 5% TRAPPS™+ 5% TTF generated the most leachate.

Table 12. Volume of effluent (L) collected from the PRBerm lysimeters during the field demonstration.

Lysimeter	Total leachate	Total runoff	Total effluent	Leachate (% of total)	Runoff (% of total)	Ratio of Leachate to Runoff
Control	23.02	36.11	59.12	39	61	0.64
5% TRAPPS™	21.94	20.68	42.62	51	49	1.04
5% TRAPPS™ + 5% TTF	27.87 ^a	16.60	44.47	63	37	1.70
^a Total leachate for 5% TRAPPS + 5% TTF includes leachate from both the main lysimeter and the inset lysimeter (TRAPPS and the TTF)						

5.7.1.2 Aqueous pH

The average pH of the leachate and runoff water collected from the three PRBerm lysimeters ranged from 6.44 to 7.01 (**Table 13**). The unamended lysimeter had the lowest pH in both leachate and runoff water samples. The TTF leachate sample had the highest pH and the 5% TRAPPS™ + 5% TTF sample had the lowest runoff pH. Both amended and unamended lysimeters had acidic pH readings, except for the TTF leachate sample. It has been reported that inducing acidic conditions will promote the solubility of Pb compounds leading to effective Pb immobilization via formation of Pb pyromorphite (Yang et al. 2001).

Table 13 gives the pH readings collected for the pre- and post-firing demonstration soils. There was a slight increase in the pH readings of the post-firing soils when compared to the pre-firing soils for all of the lysimeters. The pre- and post-firing soils yielded pH values that were slightly basic except for the 5% TRAPPS™+ 5% TTF whose pH before firing was slightly below 7.

Table 13. Soil pH from control and experimental lysimeters pre- and post firing (n=3).

Lysimeter		pH values		
		Avg	Stdev	%Stdev
Control	Pre-firing	7.73	0.15	1.88
	Post-firing	8.06	0.03	0.33
5% TRAPPS™	Pre-firing	7.29	0.03	0.42
	Post-firing	7.48	0.14	1.90
5% TRAPPS™ + 5% TTF	Pre-firing	6.95	0.10	1.42
	Post-firing	7.37	0.03	0.34
Inset box (5% TTF)	Post-firing	7.09	0.06	0.78

5.7.1.3 Total Suspended Solids (TSS)

Suspended solids provide adsorption surfaces and a route of transmission for many organic contaminants, heavy metals, and some soil nutrients. High TSS has been correlated to higher concentrations of metals in the water (Larson et al. 2007). The TSS concentrations from the lysimeters varied depending on the amendment. **Table 14** shows the average TSS concentration for both leachate and runoff from each of the three lysimeters and the inset of the left lysimeter. The left lysimeter had leachate from the main lysimeter (TRAPPS) and the inset (TTF) combines. No runoff water was collected from the TTF inset. The control lysimeter showed higher TSS concentrations in the leachate than either of the amended sands. The TSS values in the runoff water from the control were lower than from the amended sands. The TRAPPS and fishbone amendments appear to require longer contact time with rainfall to reduce the loss of suspended solids.

Table 14. Comparison of total suspended solids (TSS) concentrations (mg) in leachate and runoff water collected during the PRBerm demonstration at the CAFB M60 range.

Lysimeter	Total suspended solids (TSS)			
	Leachate (mg/L)		Runoff Water (mg/L)	
	AVG	STEDV	AVG	STEDV
Right - Control	13.6	10.1	5.6	7.5
Center - 5% TRAPPS	2.1	1.1	17.0	17.3
Left - 5% TRAPPS + 5% TTF	5.5	5.4	60.3	76.2
Left - Inset (5% TTF)	3.2	3.2	NA	NA
NA = not applicable				

5.7.1.4 Total Metals

Total (digested) metals occurred over a wide range of concentrations in runoff water and leachate from the lysimeters. **Table 15** shows the average concentration of total metals in the leachate. The leachate concentration for all metals was high from the 5% TRAPPS™ lysimeter when compared to the other experimental lysimeters. The Pb leachate concentrations ranged from 0.08 (control lysimeter) to 50 mg/L (5% TRAPPS™ lysimeter).

Table 15. Average concentration of total (digested) metals in lysimeter leachate (mg/L, n=3).

Metal	Lysimeter					
	Control		5% TRAPPS™		5% TTF	
	AVG*	STDEV	AVG	STDEV	AVG	STDEV
Pb	0.08	0.16	50.13	178.40	6.35	13.25
Cr	0.03	0.00	0.09	0.16	0.03	0.01
Cu	0.13	0.22	32.74	100.07	1.31	2.58
Ni	0.02	0.00	0.08	0.13	0.03	0.01
Zn	0.05	0.05	11.03	31.05	0.22	0.35
Fe	0.51	0.52	30.51	89.46	4.20	6.38
Mn	0.03	0.01	0.32	0.82	0.06	0.07
Sb	0.21	0.31	2.26	5.66	0.16	0.27
P**	5.00	0.00	70.90	40.01	38.55	17.45
*Averages and standard deviations are calculated based on a detection limit of 0.025 mg/L for all metals except for P. **The detection limit for P is 5.00 mg/L.						

The concentrations of total (digested) metals in the runoff water (**Table 16**) were less in the Left TRAPPS™ compared to the 5% TRAPPS™ for all metals. The Left Lysimeter runoff water also received runoff water from the TTF inset. The Center 5% TRAPPS™ lysimeter had the highest concentration of total metals in the runoff water of all the experimental lysimeters.

Table 16. Average concentration of total (digested) metals in lysimeter runoff water (mg/L, n=3).

Metal	Lysimeter					
	Control		Center -5% TRAPPS™		Left - 5% TRAPPS + 5% TTF	
	AVG*	STDEV	AVG	STDEV	AVG	STDEV
Pb	0.62	1.07	9.78	19.48	2.34	5.20

Cr	0.04	0.01	0.05	0.02	0.03	0.00
Cu	0.42	0.55	2.09	3.67	0.54	0.92
Ni	0.04	0.02	0.05	0.01	0.03	0.00
Zn	0.04	0.02	0.05	0.01	0.03	0.00
Fe	0.83	0.99	7.82	14.77	2.46	4.08
Mn	0.04	0.01	0.10	0.12	0.10	0.23
Sb	0.44	1.03	0.50	0.96	0.30	0.41
P**	8.23	3.04	15.81	15.23	7.62	8.80
*Averages and standard deviations are calculated based on a detection limit of 0.025 mg/L for all metals except for P. **The detection limit for P is 5.00 mg/L.						

5.7.1.5 Soluble Metals

The average concentrations of soluble metals in the lysimeter leachate are shown in **Table 17**. Leachate was collected separately from the left lysimeter containing the inset with 5% TTF. The 5% TRAPPS™ lysimeter had 74.09 mg/L of P compared to the unamended control lysimeter which had 5.00 mg/L of P. The metal with the highest leachate concentration in all the lysimeters, except for P, was Sb.

The soluble Pb, Cr, Cu, Zn, and Fe concentrations in the runoff water decreased in both amended lysimeters when compared to the control (**Table 18**). Runoff water from the TTF inset in the left lysimeter was not collected separately. Runoff water from the left lysimeter is both the 5% TRAPPS and the 5% TTF inset. The soluble Pb concentration in the control runoff water was 3.91 mg/L, 5% TRAPPS™ (center lysimeter) was 1.85 mg/L, and the 5% TRAPPS™+ 5%TTF (left lysimeter) was 0.95 mg/L. When compared to the 5% TRAPPS™ lysimeter, the Left TRAPPS™ lysimeter showed the greatest reduction for the soluble Pb, Cu, Ni, and Sb. The Fe concentration in the 5% TRAPPS™ lysimeter runoff water was decreased compared to the Left TRAPPS™.

Table 17. Average concentration of soluble metals in lysimeter leachate (mg/L, n=3).

Metal	Lysimeter							
	Control		Center - 5% TRAPPS™		Left- 5% TRAPPS		Left - 5% TTF Inset	
	AVG*	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Pb	0.03	0.01	0.11	0.28	0.03	0.02	0.03	0.01
Cr	0.03	0.00	0.04	0.01	0.03	0.00	0.03	0.00
Cu	0.03	0.02	0.09	0.08	0.03	0.00	0.03	0.00
Ni	0.03	0.00	0.04	0.01	0.03	0.00	0.03	0.00
Zn	0.03	0.01	0.03	0.00	0.03	0.02	0.06	0.13

Fe	0.04	0.03	0.06	0.05	0.03	0.00	0.03	0.07
Mn	0.03	0.00	0.05	0.01	0.03	0.00	0.03	0.00
Sb	0.30	0.39	0.65	1.51	0.13	0.18	0.09	0.12
P**	5.00	0.00	74.09	48.32	40.13	31.06	38.85	20.00
*Averages and standard deviations are calculated based on a detection limit of 0.025 mg/L for all metals except for P. **The detection limit for P is 5.00 mg/L.								

Table 18. Average concentration of soluble metals in lysimeter runoff water (mg/L, n=3).

Metal	Lysimeter					
	Control		Center - 5% TRAPPS™		Left -5% TRAPPS + 5% TTF	
	AVG*	STDEV	AVG	STDEV	AVG	STDEV
Pb	0.18	0.29	0.15	0.32	0.06	0.08
Cr	0.04	0.01	0.03	0.01	0.03	0.00
Cu	0.24	0.38	0.23	0.30	0.08	0.10
Ni	0.04	0.01	0.05	0.01	0.03	0.00
Zn	0.04	0.01	0.03	0.01	0.03	0.00
Fe	0.30	0.36	0.15	0.17	0.25	0.51
Mn	0.04	0.01	0.04	0.01	0.04	0.07
Sb	0.38	0.71	0.53	0.92	0.37	0.50
P**	8.33	2.71	9.83	3.92	5.32	1.05
*Averages and standard deviations are calculated based on a detection limit of 0.025 mg/L for all metals except for P. **The detection limit for P is 5.00 mg/L.						

Based on the total mass of Pb and other metals added to the amended impact media, the control lysimeter had the highest Pb concentration in the soluble runoff (**Table 19**). The 5% TRAPPS™ lysimeter (center) had the highest soil Pb concentration. Surface runoff transports soil particles containing adsorbed Pb, which assists in the migration and subsequent desorption of Pb from contaminated soils. The mobility of dissolved Pb in the runoff may be due in part to the enhanced solubilization of organo-Pb when organic matter is present in the soil. Zhou and Wong (2001) state that DOC may enhance metal transport, especially in calcareous soil by acting as a carrier through the formation of soluble organo-metal complexes. It is estimated that these mobile, organically complexed forms of Pb could account for large cumulative losses of Pb from the soil (McBride et al, 1997). The high content of P in the 5% TRAPPS + 5% TTF (left) lysimeter soil reduced the filtered Pb in the runoff samples through the formation of Pb phosphates. Santillan-Medrano and Juntiak (1975) suggested that Pb

pyromorphite is the primary mineral controlling Pb solubility in soils amended with various forms of phosphates.

Table 19. Calculated Pb concentration in lysimeters

Lysimeter	Pb in soil (mg/kg)	Soluble leachate (mg/L)		Soluble runoff (mg/L)		Total leachate(mg/L)		Total runoff (mg/L)	
		Avg.	St. Dev	Avg.	St. Dev	Avg.	St. Dev	Avg.	St. Dev
Control - Right	1553.29	0.0265	0.01	0.1745	0.30	0.0809	0.16	2.3350	5.20
5% TRAPPS™ - Center	2169.38	0.1137	0.28	0.1398	0.32	50.1319	178.40	9.7802	19.48
5% TRAPPS™ + 5% TTF - left	1742.03	0.0365	0.15	0.0637	0.08	11.1417	28.56	0.6163	1.07
5% TRAPPS™ - left	NA	0.0334	0.02	NA	NA	7.8897	18.82	NA	NA
5% TTF - left	NA	0.0303	0.01	NA	NA	6.3549	13.25	NA	NA
NA – not applicable									

5.7.2 Soil Samples

5.7.2.1 Soil pH

For the pre- and post-demonstration soils (initial and final, respectively), pH readings were taken. **Table 20** shows that there was an increase in the pH readings of the post-demonstration soils when compared to the pre-demonstration soils for all of the lysimeters. The pre-and post-demonstration soils yielded pH values that were in the neutral to alkaline range except for the 5% TRAPPS™+ 5% TTF whose pH before firing was slightly below 7.

Table 20. Comparison of pre- and post-demonstration soil pH from the PRBerm lysimeters (n=3).

pH	Control		5% TRAPPS		5% TRAPPS + 5% TTF		5% TTF (inset lysimeter)
	Initial	Final	Initial	Final	Initial	Final	Final

Average	7.73	8.06	7.29	7.48	6.95	7.37	7.09
STDEV	0.15	0.03	0.03	0.14	0.10	0.03	0.06
% STDEV	1.88	0.33	0.42	1.90	1.42	0.34	0.78

5.7.2.2 Total Metals

Table 21 shows the average total (digested) metal concentrations in the post-firing bulk soil samples taken at the conclusion of the field demonstration. The unamended control lysimeter had the highest concentrations of Pb, Cu, Zn, Sb, and As when compared to the amended lysimeters. The lysimeter amended with TRAPPS™ only had lower Pb, Cu, Zn, and Sb concentrations than the other amended lysimeters.

Table 21. Average concentration of total (digested) metals in bulk lysimeter soil post-firing (mg/Kg, n=3).

Metal	Lysimeter							
	Control		5% TRAPPS™		Left 5% TRAPPS™		5% TTF	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Pb	10,215	1,842	2,477	894	6,566	546	186	15
Cr	ND	*	13	0.5	ND	*	24	5
Cu	905	249	354	12	628	12	95	22
Ni	ND	*	8	0.5	ND	*	16	4
Zn	92	24	37	3	62	1	13	2
Fe	656	63	6,742	386	2,078	497	15,537	4,754
Mn	ND	*	39	1	10	2	87	29
Sb	115	16	28	15	74	16	ND	*
Ca	372	26	3,761	92	1,098	7	4,273	213
As	7	2	ND	*	ND	*	ND	*
P**	ND	*	2,942	143	2,098	96	3,729	218
ND = non-detect. The detection limit is 0.025 mg/Kg for all metals except P								
*Not applicable								
**The detection limit for P is 5.00 mg/Kg.								

5.7.2.3 Soil Leaching Potential

The Pb TCLP concentration (**Table 22**) was higher than the US EPA regulatory concentration level of 5-mg/L for all lysimeters except for the inset lysimeter which contained 5% TTF+5%TRAPPS™. The amended lysimeters had lower TCLP metal concentrations of Pb, Cu, Zn, Sb, and As compared to the control lysimeter.

Table 22. Average TCLP metal concentration of post-firing bulk lysimeter soils (mg/Kg, n=3).

Metal	Lysimeter							
	Control		5% TRAPPS™		Left 5% TRAPPS™		5% TTF	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Pb	473	9	147	3	64	0.4	2	1
Cr	ND	*	0.1	0	0.1	0	ND	*
Cu	28	0	6	0.1	7	0	ND	*
Ni	<1	0	0.1	0	0.2	0	0.2	0
Zn	3	0	1	0	1	0	0.1	0
Fe	7	0.3	71	2	45	1	6	1
Mn	<1	0	2	0	1	0	1	0
Mo	ND	*	ND	*	ND	*	<1	0
V	ND	*	ND	*	ND	*	ND	*
Sb	5	0.1	<1	0	<1	0	<1	0
ND = non-detect. The detection limit is 0.025 mg/Kg for all metals.								
*Not applicable								

The control lysimeter which has the higher total Pb concentration also has the highest TCLP Pb concentration. In order to compare the Pb leachability ratios, the TCLP Pb was divided by the Total Pb. The TCLP Pb was first multiplied by 20 (the ratio of liquid to solid in the TCLP procedure). The highest leachability ratio was in the 5% TRAPPS™ lysimeter (119.00%) > control lysimeter (92.68%) > Left 5% TRAPPS™ lysimeter (19.55%), > inset lysimeter (18.15%) (**Table 23**). The control lysimeter had a leachability ratio smaller than the amended lysimeters.

Table 23. TCLP Pb, Total Pb and the Pb leachability ratios (TCLP to total Pb) in lysimeters.

Lysimeter	TCLP Pb (mg/L)	Total Pb (mg/Kg)	Leachability ratio (%)
Control	473	10,215	93
5% TRAPPS™	147	2,477	119
Left 5% TRAPPS™	64	6,566	20
5% TTF	2	186	18

Table 24 compares the TCLP metals concentrations in pre-firing soil with those in post-firing soil. TCLP concentrations in the post-firing soil increased for all metals except Ca and P which decreased in the amended lysimeters. There was an increase in post-firing soil Ca concentration for the control lysimeter.

Table 25 shows the concentration of metals after TCLP extraction in the post-firing soil sampled at different dimensions. For the unamended and amended lysimeters, the highest concentrations of Pb, Cu, and Zn were observed in soils closest to the surface. The soil samples taken from the control lysimeter at all four dimensions had lower concentrations of all metals listed. The metal concentrations for each dimension varied with the amendments.

The average concentration of metals in solution determined by the DDI S&S procedure is shown for the bulk soil samples in **Table 26**. The Pb concentrations ranged from 0.04-0.56 mg/L. The Left 5% TRAPPS™ lysimeter had the lowest Pb concentration and the 5% TRAPPS™ lysimeter had the highest Pb concentration.

Table 27 compares the pre- and post-samples taken at the site after a DDI suspend and settle (S&S) test. The inset lysimeter contains results for post samples taken after firing on the range. For all three lysimeters tested, the Pb, Cu, and Sb concentrations was higher in the post soils than in the pre-soils. There was an increase in the Fe and Ca present for the pre- soils in all lysimeters. The other metals were below machine detection limits.

Table 28 shows the concentration of metals after DDI S&S in the post-firing soil sampled at different dimensions. No phosphorus was detected in either the unamended or the amended lysimeters. For the Pb concentration in the control lysimeter, the 0-4'L:0-5'H sample was greater than the 0-4'L:5-10'H. For Cu, Zn, Fe, Sb, and Ca, the control lysimeter samples taken farthest away from the bottom were greater. For the control samples taken at 4-8'L:5-10'H, the Pb, Cu, Zn, Sb, and As were all greater than the samples taken closer to the bottom. The amended lysimeter had greater Pb, Cu, Sb, and As concentrations for samples taken closer to the top of the lysimeter.

Table 24. Comparison of average TCLP metal concentrations from pre-firing and post-firing soil (mg/L, n=3).

Metal	Lysimeter treatment													
	Control				5% TRAPPS™				Left 5% TRAPPS™				5% TFF	
	Pre		Post		Pre		Post		Pre		Post		Post	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Pb	ND	*	473.37	8.52	ND	*	147.40	3.13	ND	*	64.19	0.38	1.69	0.78
Cr	ND	*	ND	*	ND	*	0.05	0.00	ND	*	0.05	0.00	ND	*
Cu	ND	*	28.11	0.12	0.06	0.03	4.62	0.08	ND	*	6.55	0.01	0.20	0.01
Ni	0.03	0.00	0.03	0.00	0.08	0.01	0.28	0.00	0.07	0.01	0.23	0.00	0.16	0.00
Zn	ND	*	2.98	0.04	0.13	0.01	1.19	0.01	0.11	0.00	1.23	0.02	0.09	0.00
Fe	0.42	0.59	6.87	0.32	0.40	0.23	71.02	2.18	0.67	0.31	44.87	0.58	6.39	0.76
Mn	ND	*	0.10	0.01	0.48	0.02	1.51	0.01	0.37	0.04	0.92	0.01	0.60	0.01
Mo	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*	0.03	0.01
V	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*
Sb	ND	*	5.32	0.09	ND	*	0.43	0.01	ND	*	0.08	0.00	0.03	0.01
Ca	14.17	3.74	13.22	0.41	169.47	12.56	48.97	0.20	69.21	3.89	34.89	0.16	122.30	2.02
As	ND	*	0.05	0.01	ND	*	ND	*	ND	*	ND	*	ND	*
P**	ND	*	ND	*	12.52	5.06	ND	*	8.20	1.75	ND	*	18.79	0.34
ND = non-detect. The detection limit is 0.025 mg/L except for P. *not applicable **The detection limit for P is 5.0 mg/L.														

Table 25. Average post-firing TCLP metal concentrations in lysimeters at different dimensions (mg/L, n=3).

Metal	Lysimeter and sampling depth							
	Control				5% TRAPPS™			
	0-4'L:0-5'H	4-8'L:0-5'H	0-4'L:5-10H	4-8'L:5-10'H	0-4'L:0-5'H	4-8'L:0-5'H	0-4'L:5-10H	4-8'L:5-10'H
Pb	153± 38	158 ±50	277 ±78	216 ±43	47± 48	53 ±41	144 ±97	53 ±26
Cr	ND	ND	ND	ND	0.04 ±0.01	0.15± 0.09	0.05 ±0.01	ND
Cu	5±2	8± 2	11± 3	11± 2	3± 2	3 ±2	7±4	4 ±2
Ni	ND	ND	ND	ND	0.21 ±0.08	0.37± 0.09	0.37± 0.08	0.12± 0.06
Zn	0.73± 0.23	0.82± 0.18	1.58± 0.38	1.39± 0.15	0.77± 0.60	0.62± 0.40	1.83± 0.62	0.94± 0.47
Fe	0.91 ±0.73	1.18± 0.49	0.64 ±0.39	0.36±0.24	73± 23	99± 55	63± 21	23 ±11
Mn	0.03± 0.00	0.04± 0.01	0.04 ±0.01	0.04± 0.00	0.86± 0.29	1.28 ±0.30	1.46± 0.36	0.50 ±0.18
Mo	ND	ND	ND	ND	ND	0.07± 0.04	ND	ND
V	ND	ND	ND	ND	ND	0.05 ±0.00	ND	ND
Sb	1.22±0.32	1.43± 0.27	1.52± 0.44	1.23± 0.21	0.50 ±0.29	0.95± 0.85	0.10± 0.05	0.51± 0.24
Ca	5± 1	8± 1	6± 2	7±1	87 ±34	28± 6	52± 22	22±7
As	ND	ND	ND	ND	ND	ND	ND	ND
P*	0.04±0.01	ND	0.07±0.01	0.03 ±0.01	ND	ND	ND	ND
ND=non-detect. The detection limit is 0.025 mg/L except for P. *the detection limit for P is 5.0 mg/L.								

Table 26. Average metal concentrations (mg/L) for bulk lysimeter soil samples post-DDI suspend and settle (n=3).

Metal	Lysimeter							
	Control		5% TRAPPS™		Left 5% TRAPPS™		5% TFF	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Pb	0.37	0.01	0.44	0.01	0.04	0.00	0.36	0.05
Cr	ND	*	ND	*	ND	*	ND	*
Cu	0.04	0.00	0.06	0.00	ND	*	0.56	0.02
Ni	ND	*	ND	*	ND	*	ND	*
Zn	ND	*	ND	*	ND	*	0.10	0.00
Fe	0.04	0.00	0.35	0.00	ND	*	ND	*
Mn	ND	*	ND	*	ND	*	ND	*
Mo	ND	*	ND	*	ND	*	ND	*
V	ND	*	ND	*	ND	*	ND	*
Sb	0.15	0.00	0.17	0.00	0.29	0.01	0.20	0.00
ND = non-detect. The detection limit is 0.025 mg/Kg for all metals.								
*Not applicable								

Table 27. Comparison of average DDI S&S metal concentrations from pre-firing and post-firing soil (mg/L, n=3).

Metal	Lysimeter treatment													
	Control				5% TRAPPS™				Left 5% TRAPPS™				5% TFF	
	Pre		Post		Pre		Post		Pre		Post		Post	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Pb	ND	*	0.37	0.01	ND	*	0.44	0.01	ND	*	0.04	0.00	0.36	0.05
Cr	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*
Cu	ND	*	0.04	0.00	ND	*	0.06	0.00	ND	*	ND	*	0.56	0.02
Ni	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*
Zn	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*	0.10	0.00
Fe	0.40	0.04	0.04	0.00	1.94	0.32	0.35	0.00	2.13	0.16	ND	*	ND	*
Mn	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*
Mo	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*
V	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*
Sb	ND	*	0.15	0.00	ND	*	0.17	0.00	ND	*	0.29	0.01	0.20	0.00
Ca	7.29	0.87	1.98	0.03	18.06	0.94	3.71	0.07	12.77	1.48	6.03	0.06	11.94	0.06
As	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*
P**	ND	*	ND	*	ND	*	ND	*	ND	*	ND	*	18.79	0.20
ND = non-detect. The detection limit is 0.025 mg/L except for P. *not applicable **The detection limit for P is 5.0 mg/L.														

Table 28. Average post-firing DDI S&S metal concentrations in lysimeters at different dimensions (mg/L, n=3).

Metal	Lysimeter and sampling depth							
	Control				5% TRAPPS™			
	0-4'L:0-5'H	4-8'L:0-5'H	0-4'L:5-10H	4-8'L:5-10'H	0-4'L:0-5'H	4-8'L:0-5'H	0-4'L:5-10H	4-8'L:5-10'H
Pb	1.18±1.91	0.46±0.29	0.90±0.43	0.97±0.48	0.44±0.27	1.43±1.26	1.23±1.80	5.47±7.68
Cr	ND	ND	ND	ND	ND	ND	ND	ND
Cu	0.13±0.12	0.10±0.05	0.15±0.05	0.25±0.24	0.12±0.08	0.16±0.12	0.22±0.16	0.77±1.05
Ni	ND	ND	ND	ND	ND	ND	ND	ND
Zn	0.02±0.02	ND	0.03±0.00	0.03±0.00	ND	ND	0.05±0.04	ND
Fe	0.12±0.07	0.09±0.02	0.15±0.08	0.09±0.05	0.77±0.88	0.45±0.31	0.60±0.21	17.64±24.43
Mn	ND	ND	ND	ND	ND	ND	ND	0.20±0.22
Mo	ND	ND	ND	ND	ND	ND	ND	ND
V	ND	ND	ND	ND	ND	ND	ND	ND
Sb	0.17±0.06	0.13±0.05	0.27±0.12	0.21±0.06	0.12±0.09	0.22±0.07	0.32±0.11	0.13±0.10
Ca	1.16±0.41	1.32±0.42	1.49±0.69	ND	6.39±1.14	ND	ND	ND
As	ND	ND	ND	1.36±0.65	ND	4.94±0.86	4.72±0.68	12.16±8.11
P*	ND	ND	ND	ND	ND	ND	ND	ND
ND=non-detect. The detection limit is 0.025 mg/L except for P. *the detection limit for P is 5.0 mg/L.								

As can be seen in **Table 29**, the pre-SPLP Fe concentration for the control lysimeter was 0.20 ppm and 0.06 ppm for the post soil SPLP concentration. The Left 5% TRAPPS™ also showed a decrease in the post soil Fe concentration. For the post samples, the inset lysimeter had 0.12 ppm Pb and the control had 2.46 ppm Pb. The post Pb and Cu concentrations for the 5% TRAPPS™ and Left 5% TRAPPS™ lysimeters were also less the control lysimeter. **Table 30** shows the SPLP leaching concentrations for the post soils. Most Pb was leached from the control lysimeter, followed by the 5% TRAPPS™ lysimeter, Left 5% TRAPPS™, and the 5% TTF. The control lysimeter had more Cu and Zn than the other three samples. More Sb was leached from the Left 5% TRAPPS™ and more Fe from the % TRAPPS™ lysimeter when compared to the other lysimeters.

Table 29. Comparison of average SPLP metal concentrations from pre-firing and post-firing soil (mg/L, n=3).

Metal	Lysimeter treatment													
	Control				5% TRAPPS™				Left 5% TRAPPS				5% TFF	
	Pre-firing		Post-firing		Pre-firing		Post-firing		Pre-firing		Post-firing		Post-firing	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Pb	0.03	0.00	2.46	2.65	0.03	0.00	0.53	0.41	0.03	0.00	0.13	0.01	0.12	0.04
Cr	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00
Cu	0.03	0.00	0.62	0.59	0.03	0.00	0.13	0.08	0.03	0.00	0.09	0.00	0.03	0.01
Ni	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00
Zn	0.03	0.00	0.15	0.11	0.03	0.00	0.03	0.00	0.03	0.00	0.05	0.00	0.03	0.00
Fe	0.20	0.03	0.06	0.06	0.03	0.00	0.40	0.29	0.24	0.05	0.07	0.01	0.18	0.02
Mn	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.05	0.00	0.03	0.00
Mo	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00
V	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00
Sb	0.03	0.00	0.21	0.06	0.03	0.00	0.12	0.01	0.03	0.00	0.38	0.01	0.03	0.00
Ca	4.72	0.13	2.71	1.05	17.50	0.42	4.67	2.25	10.21	5.50	21.73	0.55	8.68	0.62
As	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00
ND = non-detect. The detection limit is 0.025 mg/L except for P. *not applicable														

Table 30. Average metal concentrations (mg/L) for bulk lysimeter soil samples post-SPLP (n=3).

Metal	Lysimeter							
	Control		5% TRAPPS™		Left 5% TRAPPS		5% TFF	
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
Pb	2.46	2.65	0.53	0.41	0.13	0.01	0.12	0.04
Cr	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00
Cu	0.62	0.59	0.13	0.08	0.09	0.00	0.03	0.01
Ni	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00
Zn	0.15	0.11	0.03	0.00	0.05	0.00	0.03	0.00
Fe	0.06	0.06	0.40	0.29	0.07	0.01	0.18	0.02
Mn	0.03	0.00	0.03	0.00	0.05	0.00	0.03	0.00
Mo	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00
V	0.03	0.00	0.03	0.00	0.03	0.00	0.03	0.00
Sb	0.21	0.06	0.12	0.01	0.38	0.01	0.03	0.00
ND = non-detect. The detection limit is 0.025 mg/Kg for all metals.								
*Not applicable								

5.7.2.4 Partition Coefficient (K_d)

The data generated from the Pb and Sb sorption K_d experiments yielded adsorption isotherms for each soil type in the three lysimeters. Metal soil concentrations were obtained by subtracting the concentration of the given metal from the total mass of metal added to the system. While filtering is a possible source of metal loss, standard procedure for K_d determination using the batch method involves analysis of a filtered solution. The material retained on the filter is defined as insoluble material (USEPA 1999a). Complete data on the triplicate metal analyses (including average and standard deviation) for each lysimeter soil is reported in Wynter et al. (2011, in review). A representative example is given here for linear isotherms obtained from the experimental soils.

Results of a linear fit determination of sorption K_d for Sb using a section of the curve in the linear region (USEPA 1999b) is provided in Table 32. A least squares fit was performed using selected points in the linear portion of the isotherm to produce a K_d value that is valid for entire concentration range.

The Sb(III) K_d values ranged from a high of 15.77 (Left 5% TRAPPS™) to a low of 0.75 (Control) (**Table 31**). The Sb(V) K_d values ranged from a high of 1.51 (Left 5% TRAPPS™) to a low of 0.49 (Control). All three lysimeter soils had low K_{d100} values (<10).

Table 31. Summary of Sb(III) and Sb(V) linear K_d data.

Lysimeter	Sb(III)		Sb(V)	
	K	R ²	K	R ²
Control	0.75	1.00	0.49	0.91
5% TRAPPS™	8.81	0.91	0.64	0.98
Left 5% TRAPPS™+ 5% TTF	15.77	0.96	1.51	0.96

6.0 PERFORMANCE ASSESSMENT

The objectives of this technology demonstration were to:

- assess the environmental benefits, feasibility, and cost of using sand as a deceleration medium in SAFR berms,
- assess sand amendments to retard the migration of Pb and Sb into the surrounding environment through reduction of lead solubility through pH buffering of pore fluids within the SAFR berm, as well as the sequestration of lead through surface adsorption and the precipitation of insoluble lead salts, and
- provide range operators with an economical means of controlling the off-site migration of munitions metals, while maintaining the benefits of sand as a deceleration medium.

The PRBerm™ technology is applicable to new and existing ranges. In particular, this technology is designed to address sites where the native soils available for SAFR berm construction either lack the characteristics necessary to retard the migration of soluble lead (e.g. acidic soils) or are susceptible to erosion and off-site transport of lead as a result of their high clay content.

6.1 Quantitative Performance Objectives

The results of the Quantitative Performance Objectives are outlined in Section 3, Table 2 and discussed below.

6.1.1 Meet State Release Permit requirements for release of munitions metals in runoff water

The success criterion for this objective was to observe monthly soluble Pb concentrations in runoff water that were ≤ 150 ppb and monthly soluble Cu concentrations ≤ 500 ppb. This criterion is addressed by results presented in Sections 5.7.1.4 and 5.7.1.5, for total and soluble metals, respectively. Cationic metals, such as Pb and Cu, were increased in the amended lysimeters over the control lysimeter with the unamended ballistic sand. Thermally-treated fishbones produced the best performance of the amendments.

6.1.2 Meet State Release Permit requirements for pH of discharge water

As discussed in Section 5.7.1.2, the pH of the discharge water (runoff water) was maintained between 6-9 and required no further treatment.

6.2 Qualitative Performance Objectives

The Qualitative Performance Objectives are outlined in Section 3, Table 2 and discussed below.

6.2.1 Reduce transport of munitions metals from the range

As discussed in Sections 5.7.1.4 and 5.7.1.5 for total and soluble metals, respectively, in the leachate and runoff water, and in Section 6.1.2, concentrations of munitions metals in the discharge water met State regulatory permits. The concentrations of metals in amended soils were lowest with the 5% TRAPPS (Section 5.7.2.2). As stated in Section 5.7.2.3, the soil

leaching potential of the munitions metals was established by TCLP analysis. The Pb concentration from TCLP was higher than the US EPA regulatory concentration level of 5-mg/L for all lysimeters except for the inset lysimeter which contained 5% TTF+5%TRAPPS™. The amended lysimeters had lower TCLP metal concentrations of Pb, Cu, Zn, Sb, and As when compared to the unamended control lysimeter, but did not meet the TCLP criterion. The low K_d values for Sb (Section 5.7.2.4) from the amendment containing the TTF confirmed the efficacy of the biogenic apatite in reducing transport of metals from the range.

6.2.2 Reduce range operational costs

Elimination of fines for non-compliance with discharge regulations reduced operational costs. Installation and maintenance costs, compared to a steel bullet trap are also reduced.

6.2.3 Provide Best Available Technology (BAT) for range operations

Anecdotal evidence from range personnel indicates the ease of use and maintenance.

7.0 COST ASSESSMENT

The cost of using sand and amendments as a ballistic media to prevent transport of munitions metals off-range is dependent on the number of impact berms being replaced and the amendment used. In the treatability study (Larson et al. 2007), five sands and five amendments were evaluated to determine the proper amendment ratio for immobilization of metals. The field demonstration looked at the best performing of these sands/amendments that were available at the time as well as an alternative amendment selected to perform well in the new field demonstration location.

7.1 COST MODEL

The cost elements that influence the installation of a PRBerm™ to immobilize metals in a SAFR impact berm include initial treatability testing required to determine the appropriate sand/amendment for the metals of concern, and cost of construction and installation. Labor for sampling and analysis costs will be incurred for long-term monitoring of the runoff water and leachate to determine when amendment replenishment will be required. No permitting or environmental reporting costs were incurred other than the initial filing of the appropriate NEPA documentation prior to the berm installation.

In the field demonstration, three PRBerms were installed, one to be used as an untreated control, one filled completely with a sand/amendment mixture, and the third with the same sand/amendment mixture and a small added test area of a second amendment. This is not a situation that would be encountered on a range. In the assessment, the costs will be calculated as (1) sand with 5% TRAPPS amendment and (2) sand with 5% TTF amendment, compared to an untreated control. These PRBerms will be compared to the cost of installation of a fully contained bullet trap system. The relevant costs, documented in **Table 32**, reflect a “per berm” cost to construct, and install a PRBerm™. Generally, these costs will not scale linearly with increasing numbers, unless cost breaks are given by the manufacturer for a large number of berms, since the cost of sand and amendments is relatively small.

The majority of the costs associated with the PRBerm™ field study are material cost and labor. Baseline characterization should not be needed because these areas generally have already been characterized to support ongoing monitoring of range activities. Minor treatability costs are incurred prior to the construction and installation to determine metal leaching to establish the appropriate sand/amendment concentrations. No waste disposal costs were incurred. Some monitoring of the runoff water will be required to confirm the installation continues to meet State permits for discharge.

Table 32. Cost Model for a Permeable Reactive Berm (PRBerm)

Cost Element	Data Tracked During the Demonstration	Costs	
Treatability study	- Personnel required and associated labor - Materials - Analytical laboratory costs	Program manager	\$20,000
		Student	\$10,000
		Materials ¹	\$4,000
		Analytical laboratory ¹	\$5,000
Material cost	Unit: \$ per pound for reactive material Data requirements: - Initial amount of sand and amendment material required based on size of the PRBerm - Reapplication necessary – assessed via laboratory testing	Amendments	\$20,000
		Excavation	\$15,000
Installation	Unit: \$ per berm Data requirements: - Recommended installation method - Mobilization cost - Time required	Installation	\$22,145
Waste disposal	Standard soil disposal, no cost tracking	NA	
Operation and maintenance costs	No unique requirements recorded	NA	
Long-term monitoring	Standard discharge or runoff water monitoring, no cost tracking	NA	

¹ Detailed list of materials and analytical costs provided in Final Report

7.2 COST DRIVERS

Cost drivers that should be considered when implementing the technology include the cost of metal fabrication, materials and labor. Additional cost drivers are installation labor and down-time of the range. Management goals and regulatory permit monitoring requirements may require more frequent monitoring to verify that source zone contaminant levels are controlled in source or transport media.

7.3 COST ANALYSIS

It is intended that the PRBerm™ technology be installed on SAFRs with fixed firing positions. Key cost elements to consider in a Life Cycle Cost (LCC) analysis associated with the containment berm units are material costs and labor. In the case of the PRBerm, an engineering cost approach was the most applicable method, where a direct estimate is made at the component level leading to a detailed engineering build of the system (Farr 2011). The PRBerm technology has been migrated to the end-user, leveraging funds provided by Army Environmental Command (AEC) in a project initiated by Dr. Robert Kirgan. The engineering cost validation was performed on the Fort Knox, KY, Heins Qualification Test Range (QTR), a multipurpose range. Detailed costs are presented in **Table 33** (adapted from Kirgan et al. 2012). Kirgan et al. (2012) reported that the cost of construction and installation of a single unit can run from \$7,000.00 to \$18,500.00 depending on the available assets and resources of a given installation (Table 31). Generally, material costs will not scale linearly with increasing numbers, unless cost breaks are given by the manufacturer for a large number of connexes, since the cost of sand and amendments is relatively small. However, the cost can be offset by the installation of multiple containment berm units at the same time which reduces equipment mobilization fees.

Table 33. Cost breakdown for installation of one containment berm unit

Element	Quantity	Fort Knox		Potential	
		Cost (\$)	Total (\$)	Cost (\$)	Total (\$)
20 ft Connex	1			1500	1500
Fabrication / Handling	1	5000	5000	5000	5000
Painting	1	2000	2000	2000	2000
Drainage tile (10-ft sections)	2	6	12	6	12
Equipment operator labor (man-hr)	12			50	600
Supervisor	6			75	450
Bobcat	1			2000	2000
Backhoe	1			2000	2000
Fork lift	1			1500	1500
Dump truck	1			2000	2000
Grass seed	1			25	25
Straw	12			20	240
Sand (per 10 ton)	3			400	1200
TOTAL		7,012		18,527	

The cost and maintenance of a PRBerm is compared to a traditional earthen berm and a steel bullet trap in **Table 34**. In general the cost of a PRBerm™ is slightly more than a traditional earthen berm due to the addition of the amendment, but significantly less than the cost of a steel bullet trap system. Maintenance of the PRBerm is minimal, little more than what is required for an earthen berm. Life cycle cost analysis should note that the PRBerm reduces metal migration, therefore the potential of permit problems and regulatory fines, range shutdown issues and a reduced training capability. In addition, lead recycling from the PRBerm could offset yearly maintenance costs.

Table 34. Comparative Cost and Maintenance of the PRBerm™

Technology	Construction cost	Yearly O&M	Overhaul at 10 years	Cleanup cost at 40 year lifespan	40 year Total Cost (\$K)
Earthen berm	100	0	50	350**	350
PRBerm™	1,000	30*	100	0	2,600
Steel bullet trap	3,000	350	2,500	0***	7,000

8.0 IMPLEMENTATION ISSUES

8.1 ENVIRONMENTAL CHECKLIST

The PRBerm™ technology does not involve the use of any toxic or hazardous chemicals. The TRAPPS™ amendment is not regulated and is approved for addition to soils. The thermally treated fishbones are also non-regulated.

8.2 REGULATORY ISSUES

The potential for off-range migration of munitions metals should be investigated prior to implementing any management strategy. If migration potential is present and threatens nearby open water or groundwater resources, then Clean Water Act and/or Safe Drinking Water Act regulations may be of concern to ongoing range operations.

8.3 END-USER ISSUES

The primary end-user for this innovative in situ technology will be managers of active small arms ranges. The technology is expected to stabilize munitions metals within the impact berm before they can migrate to surface water or storm water discharge areas.

Several factors determine the constituent management costs.

1. Analytical Cost: Periodic sampling to monitor metals concentrations in runoff water.
2. Capital Cost: Capital costs will include PRBerm™ construction and installation, preparation of the impact media with amendments, and filling the berm; and if planned into regular berm maintenance should run similar to scheduled maintenance procedures.
3. Operation and Monitoring Cost: O&M costs will mainly encompass the costs associated with labor, water sampling and analysis.
4. Management Goal: More stringent management goals may require additional monitoring to verify that regulatory levels of discharge are maintained.

8.4 LESSONS LEARNED

The PRBerm™ is not suitable for all range backstops. Range operations and range soil conditions dictate what type of application, if any, is needed in order to reduce metals migration off the SAFRs. An alternative to the PRBerm™, for example, is the fully contained bullet trap system. Although the bullet trap will reduce the potential migration of metals into the environment, significant cost, O&M, and loss of training value is associated with such a system.

Depending on the PRBerm™ soil amendment type, one potential limitation is the solubilization of phosphate and transport of phosphate off the range in storm water runoff. High phosphate concentrations have been observed to result in algal blooms. Phosphate concentrations in leachate water and surface water from simulated berms were measured during both the treatability study and field demonstration phases of the project.

Another potential limitation is the occurrence of ricochets or rounds skipping over the berm, impacting the Surface Danger Zone (SDZ). Ricochet modeling was conducted in order to mitigate the risk of ricochets leaving the range through improper design of the PRBerm™.

Lessons learned from this demonstration include:

1. Flexibility in site selection. At the conclusion of the Treatability Phase of the Demonstration, the Barksdale AFB, LA range was transitioned into a steel bullet trap so it would not be available for use as the field demonstration site as originally planned.
2. Flexibility in personnel. With personnel shifts the core team must remember to “cross-train” in order to provide project continuity.
3. Find a suitable means to collect and store rainwater for use in artificial raining on the PRBerm™, if needed.
4. The need for a drainage system located at the range that will assist with collection of storm water samples leaving the range complex and prevent potential cross contamination of leachate water collection systems.
5. Determination that there are no known environmental drivers that limit the technology use at the selected site.

9.0 REFERENCES

- Ackermann, S., Gieré, R., Newville, M., and Majzlan, J. 2009. Antimony sinks in the weathering crust of bullets from Swiss shooting ranges. *Science of the Total Environment*, 407, 1669-1682.
- American Public Health Association. 1998. *Standard methods for the examination of water and wastewater*. Method 3010. Andrew D. Eaton, Lenore S. Clesceri, Arnold E. Greenberg, Mary Ann H. Franson, ed., 20th ed., prepared and published jointly by American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC.
- American Society for Testing and Materials. 2001. ASTM D422, D854, and D2487. West Conshohocken, PA.
- American Society for Testing and Materials. 2001. *Standard test method for leaching solid material in column apparatus*. ASTM D4874-95. West Conshohocken, PA.
- Anderson, P.R. and Christensen, T.H. (1988). Distribution coefficients of Cd, Co, Ni, and Zn in soils”, *Journal of Soil Science* 39: 15-22.
- Berti, W. R., and S. D. Cunningham. 1997. In-place inactivation of Pb in Pb-contaminated soils. *Environmental Science and Technology* 31, 1359-1364.
- Bradl, H. 2004. Adsorption of heavy metal ions on soils and soil constituents. *J. Colloid Interf. Sci.*, 277, 1-18.
- Cao, X., L. O. Ma, M. Chen, D. W. Hardison, Jr., and W. G. Harris. 2003. Weathering of lead bullets and their environmental effects at outdoor shooting ranges. *J. Environ. Qual.*, 32, 526-534.
- Carlson, C., Valle, M. Dalla, and Marcomini, A. (2004). “Regression models to predict water – soil heavy metals partition coefficients in risk assessment studies”, *Environmental Pollution* 127(1): 109-115.
- Chemical Rubber Company (CRC). 2004. *Handbook of Chemistry and Physics*, 84th Edition
- Chen, Y-W., Deng, T-L., Filella, M., and Belzile, N. 2003. Distribution and early diagenesis of antimony species in sediments and porewaters of freshwater lakes. *Environ. Sci. Technol.*, 37, 1163-1168.
- Chen, Z., Cai, Y., Solo-Gabriele, H., Snyder, G.H., and Cisar, J.L. (2006). Interactions of arsenic and the dissolved substances derived from turf soils, *Environmental Science & Technology* 40(15): 4659-4665.
- Chrysochoou, M., Dermatas, D., and Grubb, D.G. 2007. Phosphate application to firing range soils for Pb immobilization: the unclear role of phosphate. *J. Haz. Mats.*, 144, 1-14.
- Conca, J.L. and Wright, J. 2006. An Apatite II permeable reactive barrier to remediate groundwater containing Zn, Pb and Cd. *Appl. Geochem.*, 21, 1288-1300.
- Conca, J. L., N. Lu, G. Parker, B. Moore, A. Adams, J. Wright, and P. Heller. 2000. PIMSremediation of metal contaminated waters and soils. *Remediation of Chlorinated Recalcitrant Compounds* 7, 319-326.

Covelo, E.F., Vega, F.A., and Andrade, M.L. (2007). “Competitive sorption and desorption of heavy metals by individual soil components”, *Journal of Hazardous Materials* 140(1-2): 308-315.

Dermatas, D., Cao, X., Tsaneva, V., Shen, G. and Grubb, D.G. 2006. Fate and behavior of metal(loid) contaminants in an organic matter-rich shooting range soil: Implications for remediation. *Water, Air and Soil Pollution: Focus*, 6, 143-155.

Engineering Technical Letter (ETL) 02-11: Small Arms Range Design and Construction. (2002). Department of the Air Force, Tyndall AFB, FL.

Fabian, G. L. and Watts, K. 2005. *Army small arms training range environmental best management practices (BMP) manual*. U.S. Army Environmental Center.

Farr, J.V. 2011. *Systems Life Cycle Costing. Economic Analysis, Estimation, and Management*. CRC Press, Boca Raton:FL.

Ford, R.G., Bertsch, P.M. and Farley, K.J. 1997. Changes in transition and heavy metal partitioning during hydrous iron oxide aging. *Environ. Sci. Technol.*, 31, 2028-2033.

Hamon, R.E., McLaughlin, M.J. & Cozens, G. 2002. Mechanisms of attenuation of metal availability in in situ remediation treatments. *Environmental Science & Technology*, 36, 3991–3996.

Han, R., Lu, Z., Zou, W., Daotong, W., Shi, J., and Jiujun, Y. 2006. Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand. II. Equilibrium study and competitive adsorption. *J. Haz. Mats.*, 137, 480-488.

Headquarters, Department of the Army (HQDA). 1996. *Army ammunition data sheets small caliber ammunition FSC 1305*. Technical Manual (TM) 43-0001-27. Washington, DC.

Holmgren, G. G., M. W. Meyer, R. L. Chaney, and R. B. Daniels. 1993. Cadmium, lead, copper, and nickel in agricultural soils of the United States of America. *J. Environ. Qual.* 22:335-348.

Hooda, P.S. and Alloway, B.J. (1998). “Cadmium and lead sorption behaviour of selected English and Indian soils”, *Geoderma* 84(1-3): 121-134.

Houlihan, J., and R. Wiles. 2002. *Lead pollution at outdoor firing ranges*. Washington, DC: Environmental Working Group. Available at: www.ewg.org/reports/poisonouspastime/leadpoll.pdf

Impelliteri, C.A., Lu, Y., Saxe, J.K., Allen, H.E., and Peijnenburg, W.J.G.M. 2002. Correlation of the partitioning of dissolved organic matter fractions with the desorption of Cd, Cu, Ni, Pb and Zn from 18 Dutch soils. *Environ. Intl.*, 28, 401-410.

Interstate Technology and Regulatory Council (ITRC). 2003. Characterization and remediation of soils at closed small arms firing ranges.

Interstate Technology and Regulatory Council (ITRC). 2005. Environmental management at operating outdoor small arms firing ranges.

Janssen, R.P.T., Peijnenburg, W.J.G.M., Posthuma, L., and van den Hoop, M.A.G.T. (1997). “Equilibrium partitioning of heavy metals in Dutch field soils. 1. Relationship between metal partition coefficients and soil characteristics”, *Environmental Toxicology & Chemistry* 16(12): 2470-2478.

Johnson, C.A., Moench, H., Wersin, P., Kugler, P., and Wnger, C. 2005. Solubility of antimony and other elements in samples taken from shooting ranges. *J. Environ. Qual.*, 34, 248-254.

Kilgour, D.W., Moseley, R. B., Barnett, M.O., Savage, K.S., and Jardine, P.M. 2008. Potential negative consequences of adding phosphorus-base fertilizers to immobilize lead in soil. *J. Environ. Qual.*, 37, 1733-1740.

Kirgan, R., Martin, W.A., Larson, S.L., Felt, D.R., and Nestler, C.C. 2012. *Fort Knox, KY Containment berm Unit Installation*. AEC Report

Klitzke, S. and Lang, F. 2009. Mobilization of soluble and dispersible lead, arsenic, and antimony in a polluted, organic-rich soil – Effects of pH increase and counterion valency. *J. Environ. Qual.*, 38, 933-939.

Lambert, M., G. Pierzynski, L. Erickson, and J. Schnoor. 1997. Remediation of lead-, zinc and cadmium-contaminated soils. *Issues in environmental science and technology*; No. 7, Contaminated land and its reclamation, R. E. Hester and R. M.Harrison, ed., 91-102. Herts, United Kingdom: The Royal Society of Chemistry.

Larson, S. L., Malone, P. G., Weiss, C. A., Martin, W. A., Trest, C. Fabian, G., Warminsky, M. F., Mackie, D., Tasca, J. J., Wildey, J., Wright, J. 2007. Amended Ballistic Sand Studies to Provide Low Maintenance Lead Containment at Active Small Arms Firing Range Systems. ERDC TR-07-14. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Lin, Z., B. Comet, U. Ovarfort, and R. Herbert. 1995. The chemical and mineralogical behavior of Pb in shooting range soils from central Sweden. *Environmental Pollution* 89, 303-309.

Lower, S. K., P. A. Maurice, and S. J. Traina. 1998. Simultaneous dissolution of hydroxylapatite and precipitation of hydroxypyromorphite: Direct evidence of homogeneous nucleation. *Geoch. Cosmoch. Acta* 62, 1773-1780.

Lu, N., J. Xu, J. Wright, and J. L. Conca. 2001. PIMS-remediation of metal-contaminated groundwater and soil using a special reactive form of the mineral apatite. *Appl. Miner. Res. Econ. Technol., Ecol. Culture* 2, 603-606.

Ma, Q. Y., and G. N. Rao. 1997. Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils. *J. of Environmental Quality* 26:788-794.

Ma, Q. Y., S. J. Traina, T. J. Logan, and J. A. Ryan. 1994. Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite. *Environmental Science and Technology* 28, 1219-1228.

Manninen, S., and N. Tanskanen. 1993. Transfer of lead from shotgun pellets to humus and three plant species in a Finnish shooting range. *Archives of Environmental Contamination and Toxicology* 24:410-414.

Martin, W.A., Larson, S.L., Felt, D.R., Wright, J., Griggs, C.S., Thompson, M., Conca, J.L. and Nestler, C.C. 2008. The effect of organics on lead sorption onto Apatite II. *Appl. Geochem.*, 23, 34-43.

Martinez, C.E. and McBride, M.B. 1998. Solubility of Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} in aged coprecipitates with amorphous iron hydroxides. *Environ. Sci. Technol.*, 32, 743-748.

- Martínez, C.E.; Sauvé, S.; Jacobson, A.; McBride, M.B. 1999. Thermally induced release of adsorbed Pb upon aging ferrihydrite and soil oxides. *Environ. Sci. Technol.*, 33, 2016–2020.
- Martinez, C. E., A. R. Jacobson, and M. B. McBride. 2004. Lead phosphate minerals: Solubility and dissolution by models and natural ligands. *Environ. Sci. Technol.*, 38, 5584-5590.
- McBride, MB., Richards, B., Steenhuis, T., Russo, JJ., Sauve, S. 1997. Mobility and solubility of toxic metals and nutrients in soils fifteen years after sludge application. *Soil Science*, 162:487-496.
- Moreno, A.M., Quintana, J.R., Pérez, L., and Parra, J.G. (2006). Factors influencing lead sorption–desorption at variable added metal concentrations in Rhodoxeralfs, *Chemosphere* 64(5): 758-763.
- Murray, K., A. Babzzi, C. Carter, A. Ehlert, and M. Kopec. 1997. Distribution and mobility of lead in soils at an outdoor shooting range. *Journal of Soil Contaminations* 6, 79-63.
- Ndiba, P., Axe, L., and Boonfueng, T. 2008. Heavy metal immobilization through phosphate and thermal treatment of dredged sediments. *Environ. Sci. Technol.*, 42, 920-926.
- Orsetti, S., de las Mercedes Quiroga, M., and Andrade, E.M. 2006. Binding of Pb(II) in the system humic acid/goethite at acidic pH. *Chemosphere*, 65, 2313-2321.
- Pearson, M. S., K. Maenpaa, and G. M. Pierzynski. 2000. Effects of soil amendments on the bioavailability of lead, zinc and cadmium to earthworms. *Journal of Environmental Quality* 29, 1611-17.
- Santillan-Medrano, J. and Jutinak, J.J., 1975. The chemistry of lead and cadmium in soil: solid phase formation. *Soil Sci Soc Am Proc*, 39: 851-856.
- Shinomiya, T., K. Shinomiya, C. Orimoto, T. Minami, Y. Tohno, and M. Yamada. 1998. In- and out-flows of elements in bones embedded in reference soils. *Forensic Sci. Int.* 98, 109-118.
- Spuller, C., Weigand, H. and Marb, C. 2007. Trace metal stabilization in a shooting range soil: Mobility and phytotoxicity. *J. Hazard. Mats.*, 141, 378-387.
- Stack, A. G., R. Erni, N. D. Browning, and W. H. Casey. 2004. Pyromorphite growth on lead-sulfide surfaces. *Environ. Sci. Technol.* 38, 5529-5534.
- Tardy, B. A., R. M. Bricka, and S. L. Larson. 2003. *Chemical stabilization of lead in small arms firing range soils*. ERDC/EL TR-03-20. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Traina, S. J., and V. Laperche. 1999. Contaminant bioavailability in soils, sediments, and aquatic environments. *Proc. Natl. Acad. Sci. USA* 96, 3365-3371.
- Trivedi, P. and Axe, L. 2000. Modeling Cd and Zn sorption to hydrous metal oxides. *Environ. Sci. Technol.*, 34, 2215-2223.
- U.S. Environmental Protection Agency (USEPA). 1999. *Test methods for evaluating solid waste, physical/chemical methods*. SW-846. Washington, DC.
- _____. 2001a. *Indoor Environment Division: Lead fact sheet*. Office of Emergency and Remedial Response. www.epa.gov/iaq/lead.html

_____. 2001b. *Best management practices for lead at outdoor shooting ranges*. EPA/902-B-01-001. New York: RCRA Compliance Branch.

_____. 2001c. *Providing solutions for a better tomorrow: Reducing the risks associated with lead in soil*. EPA/600-F-01/014. Washington, DC: Office of Research and Development.

_____. 2002. *Lead in drinking water regulation: Public education guidance*. EPA 816-R-02-010. Washington, DC. Available on line at: <http://www.epa.gov/safewater/lcrmr/implement.html>

_____. 2003. *America's children and the environment: Measures of contaminants, body burdens, and illnesses* (2nd ed.). EPA/240-R-03001. Washington, DC: Office of Children's Health Protection.

United States Patent and Trademark Office (USPTO). 2001. *Low-lead leaching foamed concrete bullet barrier*. U.S. Patent No. 6,264,735, Washington, DC.

_____. 2002. *Sulfite treatment of spent industrial wastes*. U.S. Patent No. 6,476,287. Washington, DC.

_____. 2003. *Material, and method of producing it, for immobilizing heavy metals later entrained therein*. U.S. Patent No. 6,620,236. Washington, DC.

_____. 2004. *Sulfite treatment of spent industrial wastes*. U.S. Patent No. 6,680,039. Washington, DC.

_____. 2005. *Self-dispensing bullet trap buffer block*. U.S. Patent Application No. 20050006849. Washington, DC.

Vaccari, D. A. 1992. *Computation of aqueous metal solubilities using spreadsheet programs*. Hoboken, NJ: Stevens Institute of Tech. Available at: <http://www.attila.stevens-tech.edu>

Weiss, C. A., P. G. Malone, J.R. Tom, E. J. Fransen, and J. Peiten. 2005. Modeling physical and chemical changes during bullet trapping and recovery. *6th Annual Environmental Technology Symposium and Workshop, Portland, OR*.

Wilson, S.C., Lockwood, P.V., Ashley, P.M., and Tighe, M. 2010. The chemistry and behavior of antimony in the soil environment with comparisons to arsenic: A critical review. *Environ. Pollut.*, 158, 1169-1181.

Wright, J., K. R. Rice, B. Murphy, and J. L. Conca. 2004. Pims using Apatite II: Remediation of Pb-contaminated range soil at Camp Stanley storage activity, TX. *Proceedings of the Conference on Sustainable Range Management. New Orleans, LA*.

Yang, J., Mosby, D., Casteel, S.W., and Blanchard, R.W. 2001. Lead immobilization using phosphoric acid in a smelter-contaminated urban soil. *Environmental Science and Technology*, 35, 3553-3559.

Zhou, L.X., and Wong J.W.C. 2001. Effect of dissolved organic matter from sludge and sludge compost on soil copper sorption. *J Environ Qual*; 30:878-883.

APPENDICES

Appendix A: Points of Contact

POINT OF CONTACT Name	ORGANIZATION Name Address	Phone Fax E-mail	Role in Project
Steven L. Larson	USACE ERDC-Environmental Lab 3909 Halls Ferry Road Vicksburg, MS 39180	601- 634-3431 (601- 634-3518 Steven.L.Larson@usace.army.mil	PI
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Appendix B. Sampling Methods

B1. Sample Handling and Labelling

Samples were properly labeled and tightly sealed to avoid cross-contamination during storage and/or shipment. A sample identification system was followed to ensure tracking of a sample through collection, analysis, data validation and data reduction. Each identification label was unique within this demonstration project. A typical sample label is shown in **Figure 22**. In the sample label “L” represents a lysimeter sample, “SW” indicates a surface water sample, and “S” indicates soil sample. The number sign (##) is the number of the lysimeter or the surface water sampling point.

All samples were kept cool after collection. Samples were packaged for shipment in rigid, insulated coolers. Samples were shipped to the ERDC-EL laboratory, Vicksburg, MS via overnight delivery.

Environmental Laboratory, ERDC, Vicksburg, MS
CAFB PRBerm™ Demonstration
Sample ID: L##/SW## (circle one)
Sampling Location: 1 / 2 / 3 / 4 / 5 / 6 / 7 (circle one)
Sample Type: Surface/Composite/Lysimeter (circle)
Analysis Requested: Metals/TSS/pH
Date: MM/DD/YY Time: HH:MM hr
Sampler's Initials: ABC

Figure 22. Example of a sample label used for sample containers

The chain of custody (COC) is a record of the sampling information and requested laboratory analysis. The COC also documents the release of the samples at the site by authorized personnel and acceptance of the samples at the laboratory by authorized personnel. An example of a COC used during the lime demonstration is presented in **Figure 23**.

U.S. Army Corps of Engineers

Proj. No.		Project Name		
Sampler 1 (Signature)				
Date	Time	Pres.	Grab Cont.	Site Code/Sample Num

Figure 23. Example of a Chain of Custody (COC) document used during the lime application field demonstration at APG OD site

B2 Data Quality Control and Quality Assurance

The types of samples that were utilized during the field demonstration included various authentic samples and Quality Control (QC) samples (**Table 33**). The QC samples used included blanks, splits, composites, duplicates and spikes (fortified with an analyte or surrogate of interest). The general use of these sample types is discussed below.

Laboratory blank samples were used to detect systematic analytical problems during analysis. A laboratory blank is a “clean” sample, which is produced in the laboratory. Typically, laboratory blanks are composed of de-ionized water or uncontaminated soils.

A split sample is one sample that is divided equally into two or more sample containers and then analyzed separately. Split samples are used to measure analytical precision. Often the sample preparation process or the method of analysis for one analyte is destructive or modifies the sample with respect to a different analyte. Sample splits were used to conduct different analyses on the same representative sample. Additionally, a split sample may be handled as a blind sample for analysis by the laboratory.

A composite sample is a single sample combined from a number of smaller samples. Composite samples are useful for cases in which the sample preparation or analysis requires large sample amounts.

Duplicate samples are differentiated from split samples in that duplicate samples are obtained when two samples are taken from the same site, at the same time, using the same method, and independently analyzed in the same manner. These types of samples are representative of the

same environmental condition. Duplicates can be used to detect the variability in the treatment, testing, and analysis.

Matrix spike (MS) samples are environmental samples to which known concentrations of compounds are added. The added compounds are chemically similar to the analyte group but not expected to occur in the environmental samples (typical for organic compounds and known as surrogates), or are known components of target analytes (typical for metals analyses). The spiked samples are then processed through the entire analytical procedure, and percent recovery of the spike is calculated. Recovery of the matrix spike analytes is used to monitor for unusual matrix effects or gross sample processing errors.

Matrix spike duplicate (MSD) samples are a second aliquot of an environmental MS sample. The samples are spiked with identical concentrations of target analytes and then processed through normal sample preparation and analysis procedures. MSD samples are used to document the precision and bias of a method in the sample matrix.

These QC samples were used throughout the field demonstration. The following control samples were collected:

- Duplicate (10% of each matrix type or one per day per matrix type);
- Laboratory blank (one per batch);
- MS (one per batch [approximately 5% of each matrix type]); and
- MSD (one per batch [approximately 5% of samples]).

The quality control checks incorporated in the analysis of samples included such quality control samples as blanks, reagent blanks; duplicate samples, matrix spike and matrix spike duplicate samples. These quality control checks are cited in Appendix B of the Demonstration Plan. The QAPP prescribes the specific quality control measures to be used and frequency of those quality control samples for all analytical methods to be used. Descriptive statistics such as the mean, variance, and standard deviation were used to describe and evaluate the results of sample analysis. Analytical precision was evaluated using the concentrations of duplicate samples and/or MS/MSD to calculate the RPD between replicate analyses.

Well-accepted and commonly used indicators of data quality were used to describe the results obtained from laboratory and field analysis. These indicators included descriptive statistics, measures of precision and interpretive tests.

General descriptive statistics that were used in data analysis included the calculation of the *Mean* ($\bar{X}$), *Variance* (σ^2), and *Standard Deviation* (σ). The precision of analyses will be determined by calculating the *Relative Percent Difference (RPD)* and *Relative Standard Deviation (RSD)* of quality control samples included for analysis. Calibrations and correlation in the results were analyzed using *Least Squares Analysis* with measures of the “goodness of fit” determined through the calculation of the *Correlation Coefficient* (r) and *Coefficient of Determination* (r^2). Interpretive tests such as the Student's *t*-test and Analysis of Variance (ANOVA) were used to evaluate the differences between treatments groups.

Table 30. Data Quality Objectives

Variable	QC Sample Type or Measurement Procedure	Frequency of Use	Data Quality Objective
Analytical Chemistry			
Metals by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)	Method Blank Duplicate Sample Matrix Spike Matrix Spike Duplicate Calibration (Target Compounds)	1 per analytical batch 1 per analytical batch 1 per analytical batch 1 per analytical batch 1 per analytical batch	< PQL ⁽¹⁾ RPD ⁽²⁾ <30% Recovery 50 - 150% RPD <30% $r^{2(3)} \geq 0.995$
Total Organic Carbon (TOC)	Method Blank Duplicate Sample SRM ⁽⁴⁾ LRM ⁽⁵⁾	1 per analytical batch 1 per analytical batch 1 per analytical batch 1 per analytical batch	< PQL RPD <30% RPD <30% RPD <30%
Explosives	Method Blank Duplicate Sample Surrogate Spike	1 per analytical batch 1 per analytical batch 1 per analytical batch	< PQL ⁽¹⁾ RPD ⁽²⁾ <30% Recovery 70 - 130%
Perchlorate	Method Blank Duplicate Sample Matrix Spike	1 per analytical batch 1 per analytical batch 1 per analytical batch	< PQL ⁽¹⁾ RPD ⁽²⁾ $\pm 15\%$ Recovery 80 - 120%

⁽¹⁾Practical Quantitation Limit - 5 times the minimum detection limit (MDL) listed in SW846 method.

⁽²⁾RPD - Relative percent difference.

⁽³⁾ r^2 - Coefficient of determination.

⁽⁴⁾SRM - Standard reference material.

⁽⁵⁾LRM - Laboratory reference material.

B3 Calibration of Analytical Equipment

The calibration procedures followed during the execution of the field demonstration are method specific. Some analytical methods are straightforward and require only ASTM or NIST traceable equipment. Other methods require more sophisticated calibration procedures. For example, Method 9056, Determination of Inorganic Anions by Ion Chromatography, requires evaluation of calibration standards at multiple levels. Each level of calibration standard is further evaluated for deviations from expected values with respect to both retention time and response factor.