

The document below is my interpretation of the “Lead” problem and remedies. I have read many professional documents and drawn my conclusions. NO WAY should this report be interpreted as legal or the “correct” way to handle lead, just my thoughts and conclusions.

## Lead Problems?

Lead pollution from shooting – is it as bad as reported?

The last section is a collection of ideas from the results of the following observations, examinations and studies, compiled to give a better understanding of the fate and mobility of Pb contamination in shooting range soils, with the ultimate goal of aiding the development of best management practices (BMP’s) for shooting range operators.

I have read, re-read, studied and analyzed many reports and documents covering the subject of lead pollution, lead migration, lead mitigation, lead remediation and Best Remedial Services. The information below is a collection of my understanding of these documents and their explanation of lead pollution in shooting ranges.

Start.....

The majority of all shooting, uses some form of lead projectile, be it shotgun, rifle or pistol ammunition, but what is the pollution and hazards generated from this lead.

Who reports lead contamination? -- Citizen groups have been the most active in bringing legal suits against outdoor shooting ranges.

NOTE: There is only one liability – “if the waste presents an imminent and substantial endangerment to human health or the environment”...

### First look at the controlling bodies and their functions.;

Top of the list is the **Clean Water Act (CWA)** which prohibits the pollution of any United States Waterways, whether government owned OR privately owned. Even if you own your own lake or pond, the **Clean Water Act** prohibits you from polluting it with lead. Following the CWA are the **Resource Conservation and Recovery Act (RCRA)** and the **Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)**. Then finally, the **Environmental Protection Act (EPA)**, which covers all the above, plus pollution from noise.

Breaking these down into some form of classification we can see what really affects us....

**CWA** – If you have a river, waterway, lake or pond on your property you definitely cannot fire over it or into it, but further, you have to watch where the “run-off” from your range finishes up. i.e. when it rains, does the run-off water run down the side of a hill, into a culvert, into a stream, then into a river which in turn runs into a lake?

Where’s the water-table on your land? How far down is it and what’s the soil composition? Does water easily seep through the soil and into the water table, even though the nearest river or lake is miles away?

What’s the chemical composition of the soil? What’s the ph value?

Let’s assume we’re over that one... What’s next?

The **CERCLA** concerns itself mainly with the abandonment and resale of shooting range property, especially closed, abandoned or re-classified military property.

**RCRA**’s main concern is the storage or cleanup of abandoned shooting ranges.

Which leaves **EPA**..... and the storage of toxic materials.....

Approximately 80,000 tons of lead per year is used in the production of bullets and shot (1999)

On March 29, 1993 the United States Court of Appeals for the Second Circuit ruled that Pb shot in shooting ranges met the statutory definition of solid waste, and if the Pb was not reclaimed it could be labeled hazardous waste subject to the Resource Conservation and Recovery Act. The RCRA is primarily concerned with “tracking” the hazardous waste. As the Summit is in perpetuity a BSA shooting Range, there will be no license required to store the lead.

Lead (Pb) contamination in both shotgun and rifle shooting range soils is of increasing environmental concern, due to the elevated concentrations of Pb in these soils. There are an estimated 9,000 non-military outdoor shooting ranges in the United States that collectively shoot millions of pounds of Pb on an annual basis (US Environmental Protection Agency [USEPA], 2001).

Elevated Pb concentrations have been reported in surface water samples however, these levels *decreased significantly with distance from the shooting range*

Approximately four percent (80,000 tons per year) of all Pb produced in the United States is made into bullets and shot, with an estimated 58,300 tons per year of shot and munitions being deposited into the American landscape through shooting activities.

While contamination at rifle shooting ranges is typically localized due to berm backstops, - shotgun and skeet ranges show more extensive areas of elevated concentrations of Pb in soils. In only seven years of operation, a shotgun range in Virginia accumulated 11.1 metric tons of Pb in an area of 66,000 sq.m.

**First solution to pollution is “Don’t use Lead!”** -- High quality, non toxic metal alloys that are being manufactured as alternatives to Pb shot and bullets do exist for avid shooters including bismuth/tin (Bi/Sn), steel (Fe), zinc (Zn), tungsten/iron (W/Fe), and tungsten/polymer. However, due to increased cost and/or inferior ballistic properties, these alloys are typically less popular among shooting enthusiasts. So, let’s continue with the pollution problem. (Note: At the end of this report are 4 pages on **Green Ammunition**.)

We are shooting lead projectiles and lead shot which is generally laying on the ground or embedded in earthen berms. Metallic Pb readily corrodes when exposed to the atmosphere and a protective layer of Pb minerals generally forms on the surface of metallic Pb in the environment, protecting against further corrosion. Most common weathering products of Pb typically found in the environment are (PbO) lead oxide lead in contact with CO<sub>2</sub> and H<sub>2</sub>O, anglesite (PbSO<sub>4</sub>), cerussite, and hydrocerussite; These compounds usually appear on the surface of Pb as a white crust material. Once oxidized, the Pb is protected from further leaching, although the “type” of coating varies as to if “any” leaching takes place.

10% of the Pb pellets removed from a shotgun range is composed of an encrusted outer rim of decomposed and transformed secondary minerals. These rims consisted of an outer rim that was approximately 10 to 150µm composed of hydrocerussite, and an inner rim that was

approximately 10 to 30µm composed of massicot and anglesite. The relationship between these rings suggests that Pb-oxides are being replaced by Pb-carbonates as the pellets remain in soil. If the oxidized Pb is left undisturbed there will be no more dissolving after 7 days. The lead becomes locked.

Soil pH has been shown to increase in shooting ranges due to the weathering and transformation of metallic Pb bullets to secondary minerals. It was found that in soil with metallic Pb bullets present, the soil pH was between 6 and 7, whereas the pH of the soil underneath was 5, plus there is a positive correlation between total Pb and soil pH in a shooting range soil. Of the Pb compounds typically found in shooting range soils, cerussite and hydrocerussite are more stable at high soil pH values >6. This suggests that the addition of Pb shot limits the solubility of Pb in the shooting range soils due to its natural liming ability. **i.e with the addition of more Pb shot, the chemical structure of the soil changed so that the solubility of Pb dropped as the Pb oxide changed to hydrocerussite.**

### **Lead Mobility in Shooting Range Soils**

Secondary Pb minerals may be removed from the bullet crust material by leaching as hydrated Pb ions or as soluble Pb-organic complexes. Once in solution, Pb is likely to precipitate as less soluble Pb compounds, adsorb on to mineral or organic soil components, or be taken up by plants or other organisms that inhabit the soil. Once in soil, Pb has a long residence time due to its low solubility and its strong affinity for soil.

The concentration of dissolved Pb in shooting ranges typically diminishes and downward transport is impeded due to adsorbing surfaces within the soil. Retention of Pb in shooting range soils is most likely due to a combination of soil pH, organic matter content, soil cation exchange capacity (CEC), and soil leaching rate in addition to precipitation reactions.

While mobility of Pb in soils is typically very low, downward migration of Pb has been found in several shooting range soils. It was found that the migration of Pb in a shooting range soil was greater than sorption/desorption reactions should have allowed, and attributed this translocation of Pb to factors such as grass roots, repair of soil embankment, and dissolved organic carbon in the soil solution. They concluded that Pb migration rate at the shooting range site was approximately **2mm per year**

### **Lead in Surface Water of Shooting Ranges**

Several sources have reported elevated concentrations of Pb in surface water on shooting ranges, values of total Pb (1,270 µg L) and filterable (83 µg L) in surface water within the shot fall zone of trap and skeet (shotgun) ranges compared to nearby control areas (< 1 µg L total Pb). Also, similar values of total Pb (1,300 µg L) in surface water on a clay shooting range (shotgun). Elevated Pb has also been found in surface water on rifle shooting ranges. They found elevated total Pb (289 µg L) and filterable Pb (234 µg L) near the firing line of a rifle range in Florida, also elevated levels of filterable Pb (473 µg L) in a rifle range near the berm backstop. While all of these ranges exhibited levels of Pb above the Environmental Protection Agency (EPA) action level for Pb (15 µg L) in drinking water, concentration of Pb in surface water **dropped significantly with distance** in most of the range soils. This was most likely due to the tendency for Pb-carbonates to precipitate out of surface water.

## Liming Amendments

The liming of soils has been very effective in controlling heavy metal mobility in soils, Lime amendments buffer the pH of soil in order to reduce the mobility of Pb. This is especially important in Eastern United States soils that typically have pH values lower than 6, The application of lime may also be a cost effective form of remediation since 50 pounds usually only costs between 2 and 4 dollars, and may be applied by the range owners themselves.

## Phosphate addition

Lead phosphates (in particular fluoropyromorphite [ $Pb_{10}(PO_4)_6F_2$ ] and chloropyromorphite [ $Pb_5(PO_4)_3Cl$ ]) are extremely insoluble forms of Pb compounds in soils under a wide range of environmental conditions compared to other Pb compounds, thus reducing the leachability of Pb in soils. Phosphate may be applied in several forms. The most common and easiest to find would be in the form of lawn fertilizer. Lawn fertilizers typically cost \$7.00 per 40 pound bags. This form of phosphate is extremely soluble, and care should be taken not to apply this form near bodies of water in order to prevent runoff that results in algal blooms and eutrophication of the body of water. Phosphate rock is the raw material used for phosphate fertilizer production and is relatively insoluble compared to other sources of phosphate and should reduce P losses in runoff and phosphate rock was equally or more effective than Triple Super Phosphate. It has been reported that **15-20 pounds of pure phosphate per 1,000 square feet will effectively control Pb migration.**

## Other Methods...

Lead may also be stabilized in soil by addition of cement – it is reported that Pb contaminated shooting range soil that had been bound with cement passed the **Toxicity Characterization Leaching Procedure (TCLP)** The TCLP test is used to determine the leaching capacity of the soil under landfill conditions (acidic with  $pH < 6$ ). This test is more stringent than need be for a shooting range because conditions in a landfill are totally different to a shooting range. A more accurate test is the Synthetic Precipitation Leaching Procedure (SPLP), which is almost identical to TCLP, but simulates acid rain, rather than landfill conditions. Since SPLP uses a higher pH, it is much less efficient at solubilizing lead from the soil than TCLP and results are typically 5 to 100 times lower than TCLP.

**TCLP uses acid levels around 2.8PH where SPLP uses 5.8PH plus. So, TCLP tests give worse results than SPLP tests.**

The establishment of **best management practices (BMPs)** for shooting ranges has been advocated and developed by regulatory agencies at the state and federal level. The establishment of these BMPs requires an understanding of the mechanisms by which soils are contaminated with Pb shot and bullets as well as the factors that result in the mobilization of Pb in shooting range soils. The present study was done to better understand the processes of Pb contamination and weathering and mobility of Pb in shooting range soils, in an effort to help these ranges and regulatory agencies establish BMPs that will result in better environmental stewardship of our resources.

## Summary.

Past research on soil Pb contamination has focused on the contamination and geochemical weathering reactions of Pb bullets in the soil of shooting ranges that have been operated for many years, however, contamination of soils due to **the abrasion of Pb bullets passing through soil** would result in a contamination of the soil with smaller metallic Pb particles. It was hypothesized that this material would contribute more to immediate contamination of these soils as well as environmental risk due to its quick buildup as fine particles and rapid transformation to more reactive compounds; residual Pb particles (<2 mm) in soil were completely dissolved by EDTA, This type of contamination has implications regarding the age of a shooting range for which best management practices must be implemented.

## Leaching tests

Synthetic Precipitation Leaching Procedure (SPLP) is used to determine leachable Pb concentrations in the soils collected from the field abrasion experiment as well as field sampling. The SPLP method is believed to be an appropriate test for determining the mobility of Pb in the soils of shooting ranges as opposed to TCLP.

Based on the data it can be concluded that physical abrasion of Pb is a significant contributor to soil Pb contamination in shooting ranges, and may pose a more immediate concern for shooting range owners.

Tests show that there is less leaching on the pistol range than a rifle range, this is probably due to more bullets being fired in the rifle range, and/or greater amounts of jacketed bullets being fired in the pistol range. Jacketed bullets are Pb bullets that are coated in metallic Cu. A typical Pb bullet is composed of 97% metallic Pb, while a jacketed bullet is composed of 90% metallic Pb, with a 9% outer coating of metallic Cu.

It is hypothesized that jacketed bullets will decrease the amount of physically abraded Pb, because there will be no Pb on the surface of the jacketed bullet to be physically removed. In fact, visible observation of jacketed bullets found in samples revealed that in most cases the metallic Cu outer shell was still intact after being fired and entering the berm soil. The instances when this did not occur appeared to be when the jacketed bullet struck another bullet as it entered the berm.

Based on the field abrasion experiment, it was concluded that abraded Pb consists of a fine Pb powder that is removed from the bullet as it passes through berm soil.

**Abraded Pb in shooting range is weathered at an accelerated rate and rapidly converted to Pb-minerals. The result of this experiment was a transformation of virtually all metallic Pb to hydrocerussite as well as other Pb minerals within 7 days. Previous weathering rates of Pb shotgun pellets reported were 5-17% within 6-13 years. The dramatic increase in weathering rate is most likely a result in the decrease in size of the material. When a Pb pellet weathers, the pellet is covered by a crust of the resulting weathered minerals. resulting in a protective coat that inhibits further weathering of the inner metallic Pb. In**

contrast, the Pb powder is too small for a coat to form, and it is completely converted to Pb minerals.

**This has implications when considering time periods and techniques for remedial action in shooting ranges.**

Mechanical sieving is not applicable in remediating abraded Pb, because this material would easily pass through a sieve due to its size. Washing soils with EDTA would remove abraded Pb from soil; however, time would be an important issue when using this remediation technique. Due to the rapid weathering rate of this material, washing the soil with EDTA on a regular basis would not be economically feasible. The use of phosphate rock was a cost effective way to remediate Pb-contaminated soils, which may be applied to shooting range soils. Lead phosphates are extremely insoluble compared to other Pb compounds thus reducing the leachability of Pb in soils.

This study demonstrated that physical abrasion of Pb bullets passing through soil contributes substantially to soil Pb contamination in shooting ranges. The 22-caliber bullet used in the field abrasion experiment is the smallest caliber that is typically used in shooting ranges. An increase in Pb contamination in the form of physical abrasion would probably result from an increase in the size of caliber. This would be due to an increase in surface area of the bullet that is susceptible to physical abrasion as it passes through soil, as well as the fact that higher caliber rounds travel at higher velocities resulting in an increase in friction. This fine form of metallic Pb is rapidly converted to Pb-minerals, and may pose a risk to groundwater contamination in shooting range soils. Our research has demonstrated that Pb contamination (elevation of Pb concentrations in soils) as well as Pb transformation (from inert metallic Pb to more reactive Pb compounds) in shooting range soils occurs rapidly in newly opened ranges. Therefore, it is important to develop **best management practice** to minimize the adverse impacts of Pb in all shooting ranges.

Metallic Pb is only stable under extremely reducing conditions at high pH and as a result, it undergoes atmospheric corrosion fairly readily. In stability diagrams for metals, there exists a passive zone in which the stable solid is not the metal but an oxide, hydroxide or salt. Under these conditions the metal becomes coated with these secondary minerals, which may form a non-porous film in which the metal is protected from solution, and/or a porous film in which the metal is partially protected from solution. **In the case of Pb, there are only small regions for stability for surface oxides, and as a result Pb-oxides are typically too soluble to provide any protection against further corrosion. However, Pb-carbonates, such as cerussite ( $\text{PbCO}_3$ ) and hydrocerussite [ $\text{Pb}_{33/2}(\text{OH})_2$ ] generally form a protective layer that prevents further weathering on the surface of metallic Pb.** These protective layers have been found on the surface of metallic Pb pellets and bullets in shooting range soils. White crust material found on the surface of Pb pellets and bullets were identified as secondary Pb minerals such as hydrocerussite, cerussite, anglesite ( $\text{PbSO}_4$ ), and occasionally massicot ( $\text{PbO}$ ). It was found that the crust material consisted of two layers with the inner layer being predominantly massicot, and the outer layer being predominantly hydrocerussite. This suggested that Pb-oxides were being replaced by Pb-carbonates in the shooting range soils.

Immobilization of heavy metals via soil amendments has been used extensively in remediating contaminated soils. It has been suggested that soil amendments such as phosphorus and lime may be a potential approach towards limiting Pb solubility and mobility in shooting range soils. The relationship between solubility of Pb and soil pH has been well documented. The addition of lime to soil has been shown to reduce Pb availability due to an elevation in soil pH, however it may increase Pb solubility at high pH due to the formation of organo-Pb complexes. Lead phosphates are extremely insoluble, and may be important in controlling Pb in soil environments and phosphorus in the form of rock phosphate has been used to effectively reduce the solubility of Pb in contaminated soils.

Bullet fragments (<2mm) have been found in shooting range soils, and are believed to contribute to total Pb concentration in these soils and the conclusion is that this Pb material likely comes from abrasion of Pb bullets as they pass through soil, and that this form of Pb weathers at an accelerated rate.

The role of Pb secondary minerals as natural metal ion buffers is often overlooked. Therefore, it appears that metallic Pb has a natural liming effect when soil is contaminated with Pb bullets, and it will ultimately prevent further corrosion due to this process.

Results from the Pb bullet abrasion study, showed that 1.5% of the mass of a 22-caliber bullet was physically removed as it passed through a berm soil – this 1.5% is called Pb powder. Laboratory weathering studies found that virtually all metallic Pb powder was converted to hydrocerussite [ $Pb_3(CO_3)_2(OH)_2$ ], as well as to a lesser extent cerussite ( $PbCO_3$ ) and massicot ( $PbO$ ) within one week.

The transformation of Pb was completely inhibited in the absence of soil organic matter and no secondary Pb minerals were identified. An increase in soil pH reduced the transformation of metallic Pb to Pb-carbonates. At a higher pH, only Pb-oxides were formed. Soil microorganisms did not play a direct role in the transformation of metallic Pb; however, they probably play an indirect role due to their metabolic processes that oxidize organic matter and elevate  $CO_2$  in soils.

## Conclusions...

The pollutant from lead bullets and shot falls into 2 categories; Pb powder and projectiles. The powder is formed from a bullet passing through sand or an abrasive material used as the berm or backstop. This is about 1.5% of the bullet mass. The remaining projectile can transform into various other forms of Pb compounds. These are oxides, phosphates or salt.. Pb-oxides are typically too soluble to provide any protection against further corrosion. **However, Pb-carbonates, such as cerussite ( $PbCO_3$ ) and hydrocerussite [ $Pb_3(CO_3)_2(OH)_2$ ] generally form a protective layer that prevents further weathering on the surface of metallic Pb, and the lead, shot, bullet is coated with an insoluble protective coat. Lime, and phosphorous are extremely good at achieving this.**

**The Pb powder is carried in water and is the main component of pollution. The remaining projectiles, or “lumps” of lead, if transformed into Pb hydrocerussite, can remain in the soil with no further leaching. However, the PH must be monitored to**

**ensure it does not go too high which will allow organic influences to breakdown the protective coatings.**

All Pb powder will change into Pb hydrocerussite, and will not affect ground water.

It all depends on getting the right soil conditions.

## Two “Fail-Safe” conclusions....

### Phytoremediation

Phytoremediation combines the Greek word "phyton", (plant), with the Latin word "remediare", (to remedy) to describe a system whereby certain plants, working together with soil organisms, can transform contaminants into harmless and often, valuable forms. This practice is increasingly used to remediate sites contaminated with heavy metals and toxic organic compounds. Planning, engineering and design with the ecological paradigm as our template is the work of Sustainable Strategies. For example, the ecological paradigm reveals how to safely utilize all of the polluting components and water of human and animal wastewater to ultimately grow plants that have economic value. We use the term Wastewater Garden to describe our phytoremediation and evapo-transpiration approach to effluent management problems. The objective is to drain pretreated wastewater into an appropriately engineered gardens or forests of phreatophytes: plants known for fast growth and high water usage rates. These plants and their microbially-active rhizosphere will transform pollutants, including the nutrient nitrogen, into valuable biomass and use up the remaining water via evaporation and transpiration.

Phytoremediation takes advantage of plants' nutrient utilization processes to take in water and nutrients through roots, transpire water through leaves, and act as a transformation system to metabolize organic compounds, such as oil and pesticides. Or they may absorb and bioaccumulate toxic trace elements including the heavy metals, lead, cadmium, and selenium. In some cases, plants contain 1,000 times more metal than the soil in which they grow. Heavy metals are closely related to the elements plants use for growth. "In many cases, the plants cannot tell the difference" says Ilya Raskin, professor of plant sciences in the Center for Agricultural Molecular Biology at Rutgers University.

When large plants such as willows, poplars and bamboo are used, the idea is to move as much water through them as possible so that they take up as much of the contaminants as possible. Once the heavy metals are absorbed, they are sequestered in the plants' leaves and/or roots. Any organic compounds that are absorbed are metabolized.

Phytoremediation is an in-situ approach, not reliant on the transport of contaminated material to other sites. Organic contaminants are, in many cases, completely destroyed (converted to CO<sub>2</sub> and H<sub>2</sub>O) rather than simply immobilized or stored. The establishment of vegetation on a site also reduces soil erosion by wind and water, which helps to prevent the spread of contaminants and reduces exposure of humans and animals.

Soil microorganisms can degrade organic contaminants. This is called bioremediation and has been used for many years both as an in-situ process and in land farming operations with soil removed from sites.

Dr. Raskin also demonstrated the utility of certain varieties of mustard plants in removing such metals as chromium, lead, cadmium and zinc from contaminated soil and used hydroponic plant cultures to remove toxic metals from aqueous waste streams. Plants can accelerate bioremediation in surface soils by their ability to stimulate soil microorganisms through the release of nutrients from and the transport of oxygen to their roots. The zone of soil closely associated with the plant root, the rhizosphere, has much higher numbers of metabolically active microorganisms than unplanted soil. The rhizosphere is a zone of increased microbial activity and biomass at the root-soil interface that is under the interface of the plant roots. It is this symbiotic relationship between soil microbes that is responsible for the accelerated degradation of soil contaminants. The interaction between plants and microbial communities in the rhizosphere is complex and has evolved to the mutual benefit of both organisms. Plants sustain large microbial populations in the rhizosphere by secreting substances such as carbohydrates and amino acids through root cells and by sloughing root epidermal cells. Also, root cells secrete mucigel, a gelatinous substance that is a lubricant for root penetration through the soil during growth. Using this supply of nutrients, soil microorganisms proliferate to form the plant rhizosphere. In addition to this rhizosphere effect, plants themselves are able to passively take up a wide range of organic wastes from soil through their roots. One of the more important roles of soil microorganisms is the decomposition of organic residues with the release of plant nutrient elements such as carbon, nitrogen, potassium, phosphate and sulfur. A significant amount of the CO<sub>2</sub> in the atmosphere is utilized for organic matter synthesis primarily through photosynthesis.

Some plants used for phytoremediation are: Brassica juncea (Indian mustard greens), Ordinary tomato and alpine pennycress, Poplar trees.

## Using Phytoremediation to Clean Up Sites

Phytoremediation is the direct use of green plants and their associated microorganisms to stabilize or reduce contamination in soils, sludges, sediments, surface water, or ground water. First tested actively at waste sites in the early 1990s, phytoremediation has been tested at more than 200 sites nationwide. Because it is a natural process, phytoremediation can be an effective remediation method at a variety of sites and on numerous contaminants. However, sites with low concentrations of contaminants over large cleanup areas and at shallow depths present especially favorable conditions for phytoremediation. Plant species are selected for use based on factors such as ability to extract or degrade the contaminants of concern, adaptation to local climates, high biomass, depth root structure, compatibility with soils, growth rate, ease of planting and maintenance, and ability to take up large quantities of water through the roots.

The once toxic pits of J-Field, located in the Edgewood area of Aberdeen Proving Ground, Harford County, Maryland, were used as a disposal site for chemical warfare agents, munitions, and industrial chemicals from 1940 through the 1970s. The two most prevalent contaminants of concern in the ground water at the site included Trichloroethene (TCE) and 1,1,2,2-tetrachloroethane (1122). In the Spring of 1996, a phytoremediation study was implemented to determine if the contaminants underlying J-Field could be removed through phytoremediation using various tree species.

Chosen for their rapid growth and high transpiration rates, 183 hybrid poplar trees were planted over an area of approximately one acre in 1996. VOCs and the chemicals they break down into have been detected in the leaf tissue and gas and water vapor expelled by the trees, indicating that the poplars are removing, degrading, and releasing the contaminants of concern. Sap flow rates and shallow ground water levels also indicate that the trees are intercepting and removing the contaminants from the site. Finally, it is possible that the trees may also be enhancing the soil community, although further investigation is needed to determine this. It is estimated that within 30 years, contaminants at J-Field may be reduced by up to 85 percent

## Application of Appetite II

### PIMS – Phosphate Induced Metal Stabilization (PIMS™)

Apatite II™ is a natural phosphate material produced from fish bones that incorporates metals into new stable phosphate phases that are non-leachable. Only simple mixing into the soil is required. The advantages over other technologies are that PIMS with Apatite II is inexpensive, fast, long-lasting, and does not generate any hazard or environmental problem as a result of its production. Apatite II is manufactured from fish cannery waste producing a fish bone and fish hard part material that is primarily hydroxyl calcium phosphate with residual organics of 25-35%.

In the case of Pb-contaminated range soils, Apatite II binds Pb into pyromorphite, an insoluble phase that is stable for hundreds of millions of years. Pyromorphite has an extremely low solubility product ( $K_{sp} = 10^{-80}$ ) and will not dissolve under most environmental conditions. Apatite II works to sequester metals by continuously supplying a small, but sufficient, amount of phosphate to solution to exceed the solubility limits of various metal-phosphate phases such as pyromorphite and autunite. For Pb, the mechanism is dissolution of the Apatite II (1) followed by precipitation of pyromorphite (2). The degree of protonation of the phosphate and carbonate in the reactions depends upon the pH levels. Reaction (1) does not necessarily lead to reaction (2). However, whenever  $Pb_{2+}$  is in solutions contacting the apatite, the apatite provides a constant supply of phosphate to solution to induce reaction (2). Under almost any environmental condition conceivable, Pb-pyromorphite will precipitate only by heterogeneous nucleation, i.e., a seed crystal with the apatite crystal structure is necessary for precipitation to occur. Homogeneous nucleation (precipitation directly from solution without a seed crystal) will not occur unless Pb concentrations exceed about 10 ppm), a condition rarely achieved in the environment, even for acid mine drainage. This observation is absolutely critical for successful phosphate technologies, which are more appropriately named apatite technologies because apatite is required for the long-term stability of Pb by precipitation of pyromorphite. Without apatite, other Pb-phases will form that have much higher solubilities.

The Apatite II grains serve as an optimal seed crystal as well as an optimal source

of phosphate. Therefore, with the use of Apatite II, over the course of time all migrating Pb in the system precipitates as Pb-pyromorphite. These microscopic Pb-pyromorphite mineral phases will grow and coalesce according to the processes of Ostwald ripening eventually forming larger mineral clusters. During this process, which can take many years, the concentration of Pb in solution is kept extremely low, <15 ppb, by the presence of the Apatite II-supplied phosphate, so that no leaching of Pb occurs above drinking water limits, the material is no longer hazardous according to TCLP tests, and bioavailability is reduced.

The Phosphate-Induced Metal Stabilization (PIMS™) technology is an *in situ* stabilization or sequestration technology that uses an amendment, Apatite II™, to the contaminated soil that immobilizes the metal or renders it non-toxic, but does not change the basic nature of the soil, e.g., the permeability or porosity. This technology allows the soil to function in the future as a soil to be left in place.

## Monitor...

Ground water pollution should be periodically tested at run-off collection points and from strategically placed lysimeter wells. Samples should be classified from Toxicity Characteristic Leaching Procedure (TCLP) to monitor pollution levels should be below the non-hazardous waste classification criteria of 1.5 mg/L Pb ensuring the treated soil is non-hazardous and below 0.015mg/L for drinking water.

**All tests should be carried out via the SPLP method and NOT the TCLP method.**

**If levels exceed limits then use remediation to bring levels within range.  
First use lime or phosphate, then phytoremediation, then Apatite II**

**Note: Levels are reported differently but are the same; i.e. 1.5ug/L = 0.015mg/L**

## A simple way to catch berm runoff.

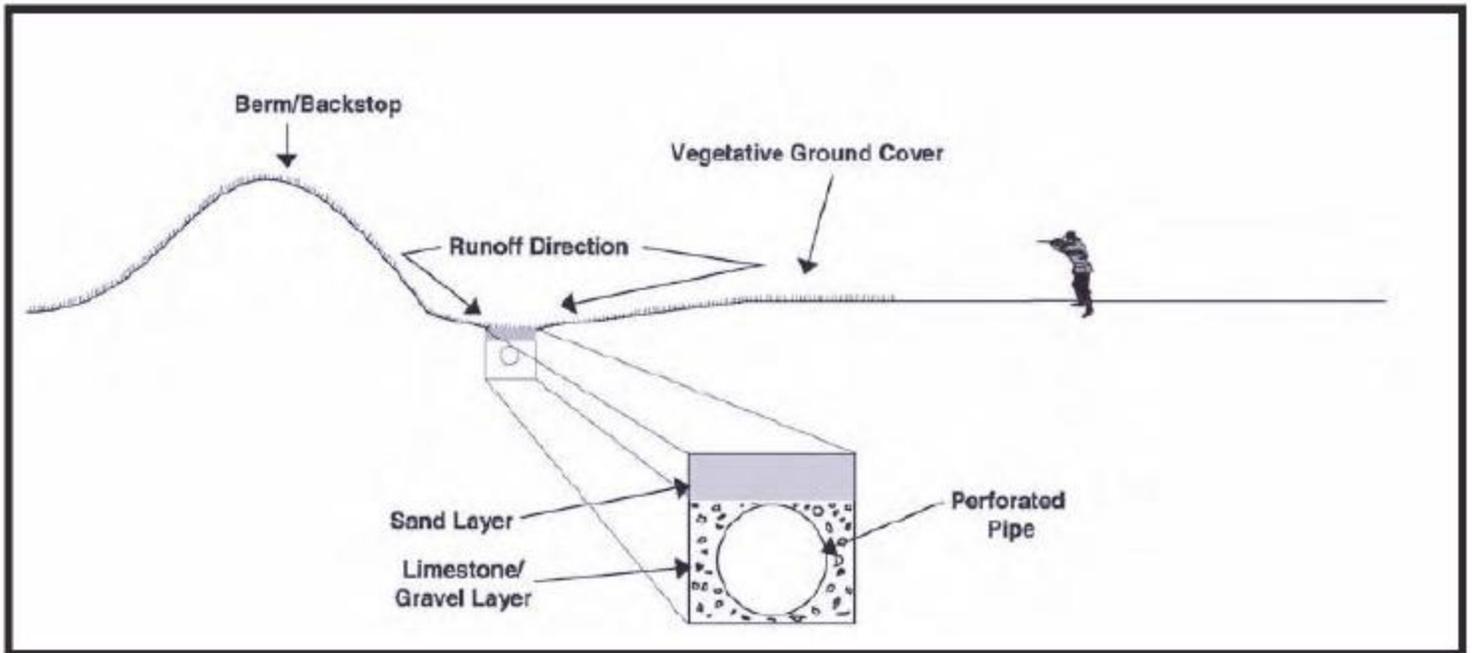
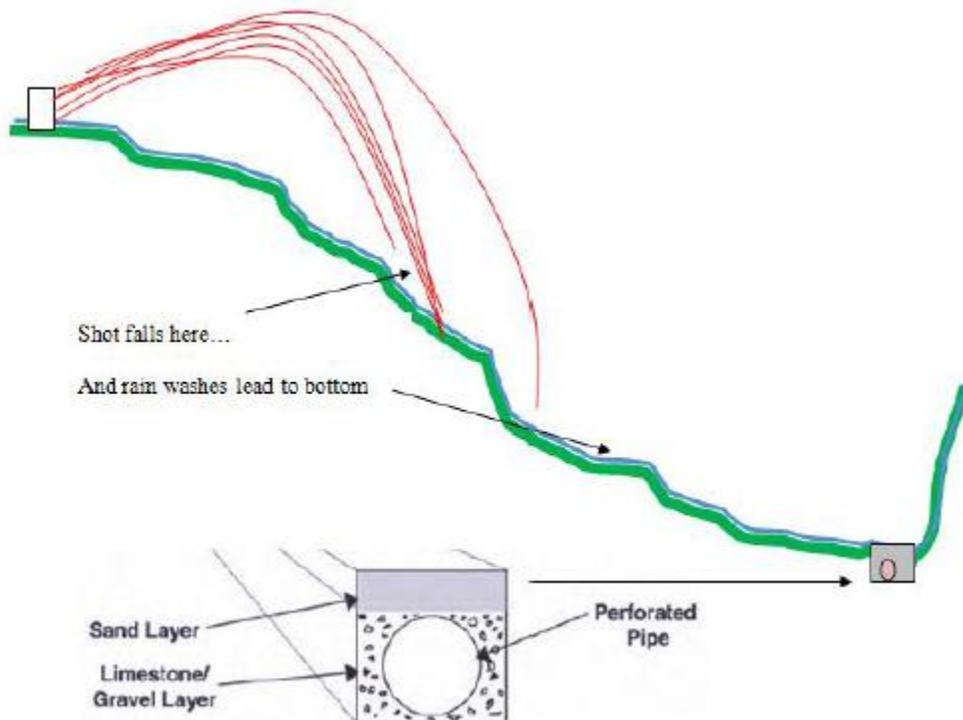


Figure 3-2 – Sample Filter Bed System (Adapted from Proceedings for National Shooting, Range Symposium, October 17-19, 1993, North American Hunting Club and Wildlife Forever)

## Same for Sporting Clays.....



## Steel Plate Shooting – 9mm and .22LR

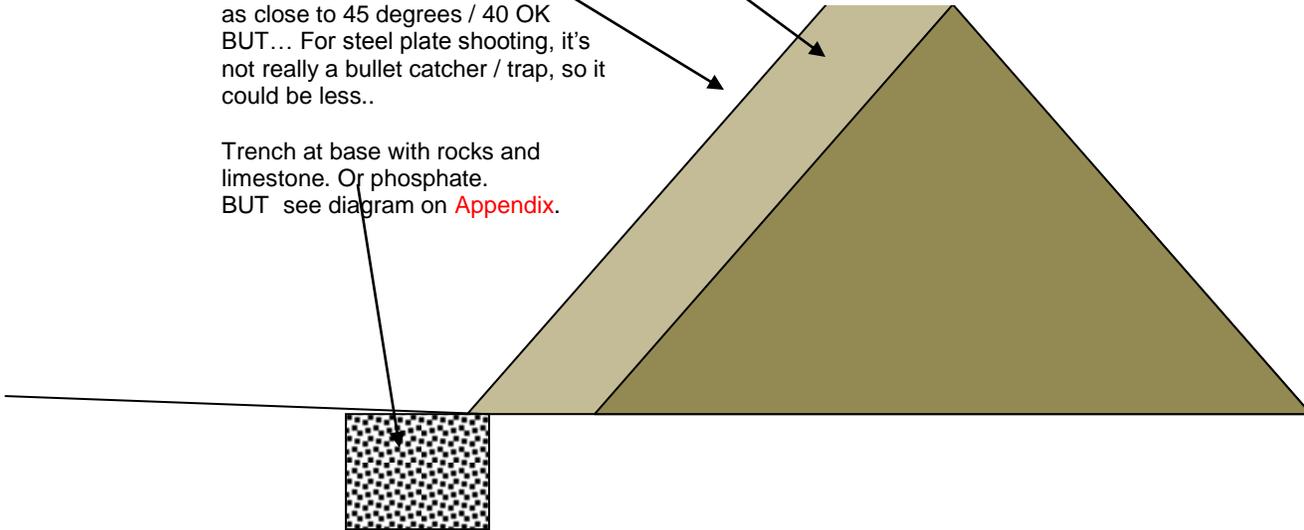
### Berm Cross Section for Pistol Range – Steel Plate

15" – 18" of sifted material, doesn't have to be sand. (95% compaction)

In Abu we used sand / clay mix. To conform, the slope needs to be as close to 45 degrees / 40 OK BUT... For steel plate shooting, it's not really a bullet catcher / trap, so it could be less..

Trench at base with rocks and limestone. Or phosphate. BUT see diagram on [Appendix](#).

Rear berm should be 15' with side berms at 10'



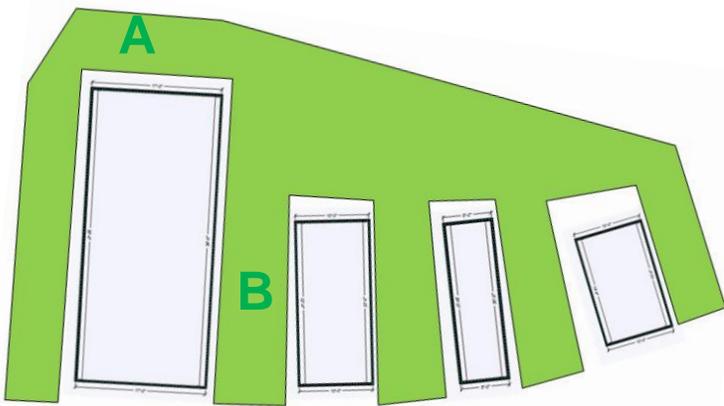
See how the "hitting area is higher than the side berms



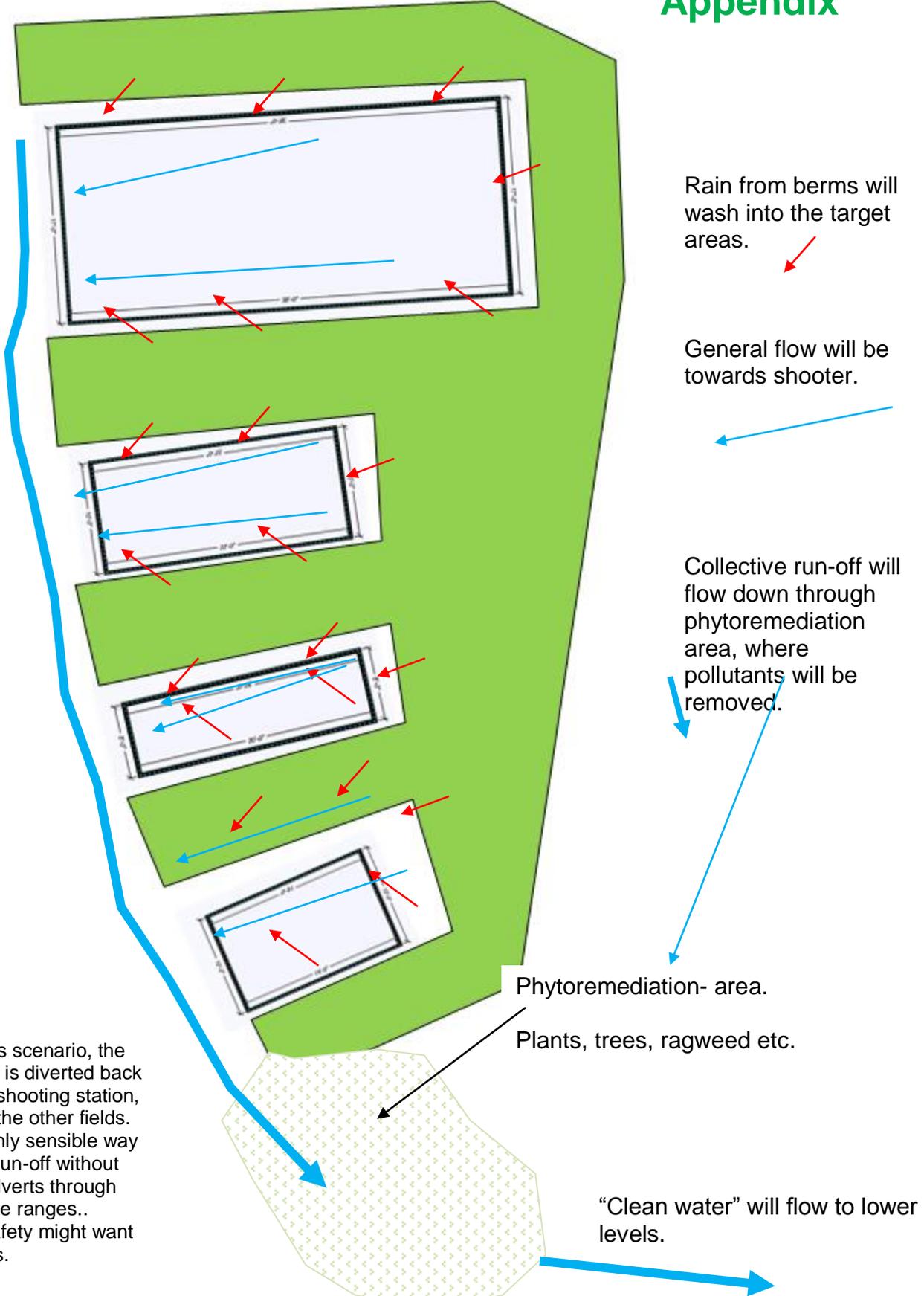
Again here, the “hitting” berm of adjoining area is higher



On this set-up, it's just into a natural hill



# Appendix



Rain from berms will wash into the target areas.

General flow will be towards shooter.

Collective run-off will flow down through phytoremediation area, where pollutants will be removed.

Phytoremediation- area.  
Plants, trees, ragweed etc.

“Clean water” will flow to lower levels.

NOTE: In this scenario, the water run-off is diverted back towards the shooting station, then across the other fields. This is the only sensible way to route the run-off without elaborate culverts through the rear of the ranges.. However, Safety might want to review this.

## Proven remediation from Aberdeen Proving Grounds...

The once toxic pits of J-Field, located in the Edgewood area of Aberdeen Proving Ground, Harford County, Maryland, were used as a disposal site for chemical warfare agents, munitions, and industrial chemicals from 1940 through the 1970s. The two most prevalent contaminants of concern in the ground water at the site included Trichloroethene (TCE) and 1,1,2,2-tetrachloroethane (1122). In the Spring of 1996, a phytoremediation study was implemented to determine if the contaminants underlying J-Field could be removed through phytoremediation using various tree species.

Chosen for their rapid growth and high transpiration rates, **183 hybrid poplar trees** were planted over an area of approximately one acre in 1996. VOCs and the chemicals they break down into have been detected in the leaf tissue and gas and water vapor expelled by the trees, indicating that the poplars are removing, degrading, and releasing the contaminants of concern. Sap flow rates and shallow ground water levels also indicate that the trees are intercepting and removing the contaminants from the site. Finally, it is possible that the trees may also be enhancing the soil community, although further investigation is needed to determine this. It is estimated that within 30 years, contaminants at J-Field may be reduced by up to 85 percent.



Earth Berms. The slope of earth berms must not exceed a 2:3 vertical-to-horizontal ratio unless materials are stabilized. If native soil characteristics will not produce a stable slope at this angle, use fabric reinforcement in the fill. The soil may require conditioning to achieve satisfactory soil pH levels to prevent lead decomposition. Typical angles of repose for natural soils in loose or least-dense state are shown in Table 5.

Use Table 5 only as a guide, since mechanical stabilization may increase the angle of repose. The width of the top of the berm must be at least 3 meters (9.8 feet). Construct the outer layer (2 meters [6.5 feet] thick) of the impact face with sands, silty sands, or clayey sands, free of rocks, and with 100 percent passing the #4 sieve, ASTM C136. Soil with more than 40 percent clay-size particles passing the #200 sieve is not acceptable for the outer 2-meter (6.5-foot) layer of the impact face. Clay may be used for the core. For erosion control, plant a vegetative cover on the faces and tops of berms. Irrigation devices may be used on the faces and tops of berms not subject to direct fire.

Soil Types	Angle of Repose/ (Internal Friction)
Silty sand/fine sand/clayey sand	30
Coarse sand	35
Silts	25
Gravel/sandy gravel/gravelly sand	34

Earth Backstops. Earth backstops are the most common backstop for outdoor ranges. As an example, for a 25-meter (82-foot) outdoor range, locate the backstop so the longitudinal centerline of the berm (backstop) is at least 50 meters (164 feet) from the firing line. The toe of the slope must be located at least 9 meters (29.5 feet) from the target line nearest the backstop. The top of the backstop must be high enough so that a line drawn from the firing line and under the last overhead baffle will intersect the backstop at least 2 meters (6.5 feet) below its top. The impact face of the earth backstop must be soil with 100 percent passing the #4 sieve, ASTM C136, for a depth of 2 meters (6.5 feet). The slopes should be stabilized with grass vegetation with access locations provided for maintenance and repair equipment. Incorporate a **steel deflector plate (eyebrow)** into the backstop if a higher degree of confidence is required to prevent direct-fired rounds from leaving the impact area of the backstop. Soil with more than 40 percent clay-size particles passing the #200 sieve is not acceptable for use in the impact area face of the backstop. If required, soil should be conditioned to achieve suitable pH levels as indicated below.

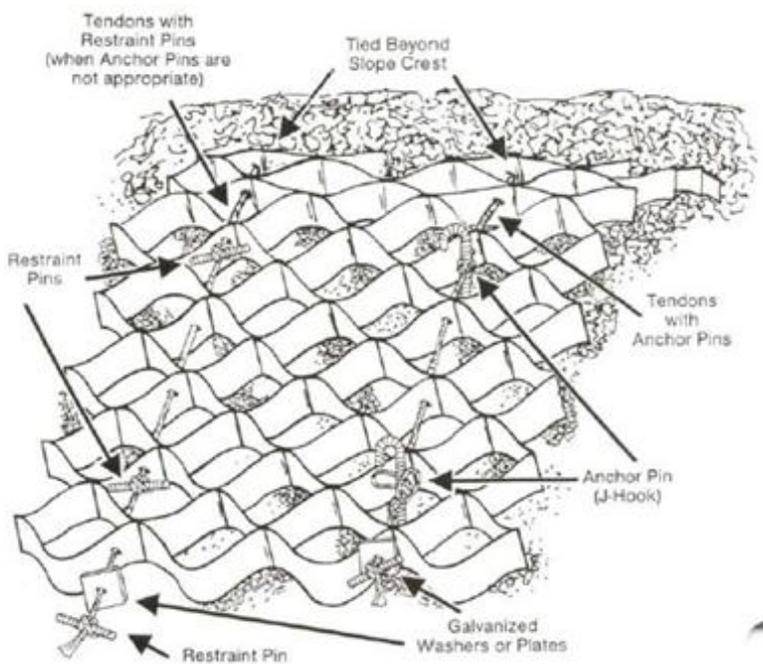
Soil Amendments. BCE environmental management must test soils within the impact areas for pH levels every two years. The desired pH ranges from 7 to 8. Test soil additives to ensure that they will not cause cementing or hardening of the soil surface. Do not use lime as an additive or soil conditioner when the natural soil gradation

includes more than 30 percent passing the #200 sieve, American Society for Testing and Materials (ASTM) C136, *Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates*, and/or the natural soil Plasticity Index is higher than 12.

**Backstop Deflector Plates (Eyebrows).** A deflector plate is not a bullet trap. A backstop deflector is typically installed on top of an earth backstop to provide added containment safety. Install the backstop deflector plate at an angle between 30 and 42 degrees from horizontal. Angles other than these are permissible if test data and calculations support the design. Set the highest edge of the deflector plate nearest the firing line. The shallow angle deflects bullets more easily and there is less metal fatigue and denting in the surface of the plate. Anchor steel plates supported by concrete or masonry with flush countersunk heads. Eliminate exposed edges which may produce erratic ricochets. Ensure edges of steel plates are milled at all joints and joints are butted flush and smooth. Plates must be free from buckle or wave. Exposed edges must be chamfered to a 45-degree angle to a fillet approximately 4 millimeters (0.16 inch) wide. Exposed structural members supporting deflector plates are not permitted. Welding must conform to American Welding Society (AWS) D1.1, *Structural Welding Code – Steel*, latest edition. Position steel plates so welds are no closer than 450 millimeters (17.7 inches) from the center of a target position. Steel plate jointed at and supported

## Berm Stability:

Teracell is a product designed to stabilize steep sloping berms (grass banks). It's formed from plastic that creates small pockets to hold material at steep angles.



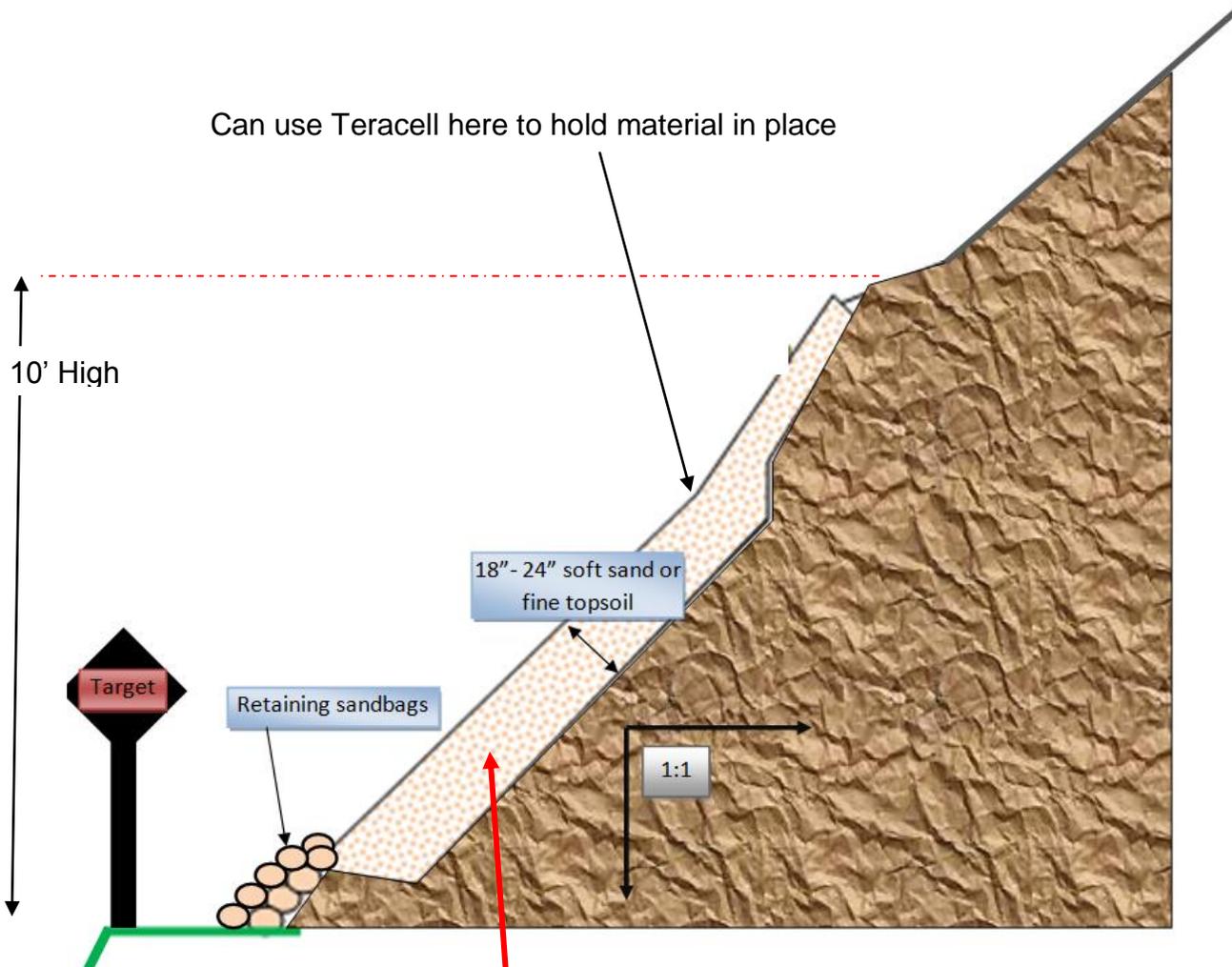


This range is another pistol range, much like Range 24. It is shaped like a long "U". The photo to the left shows the side berm just prior to planting. A bulldozer smoothed out the gullies in this berm to facilitate planting and to create dozer tracks. These tracks provide mini pockets that trap moisture. These traps give new grass plants moisture to grow. All three ranges were tracked like this. This range gets repeated use by the military.

Using Teracell as Backstop stabilization.

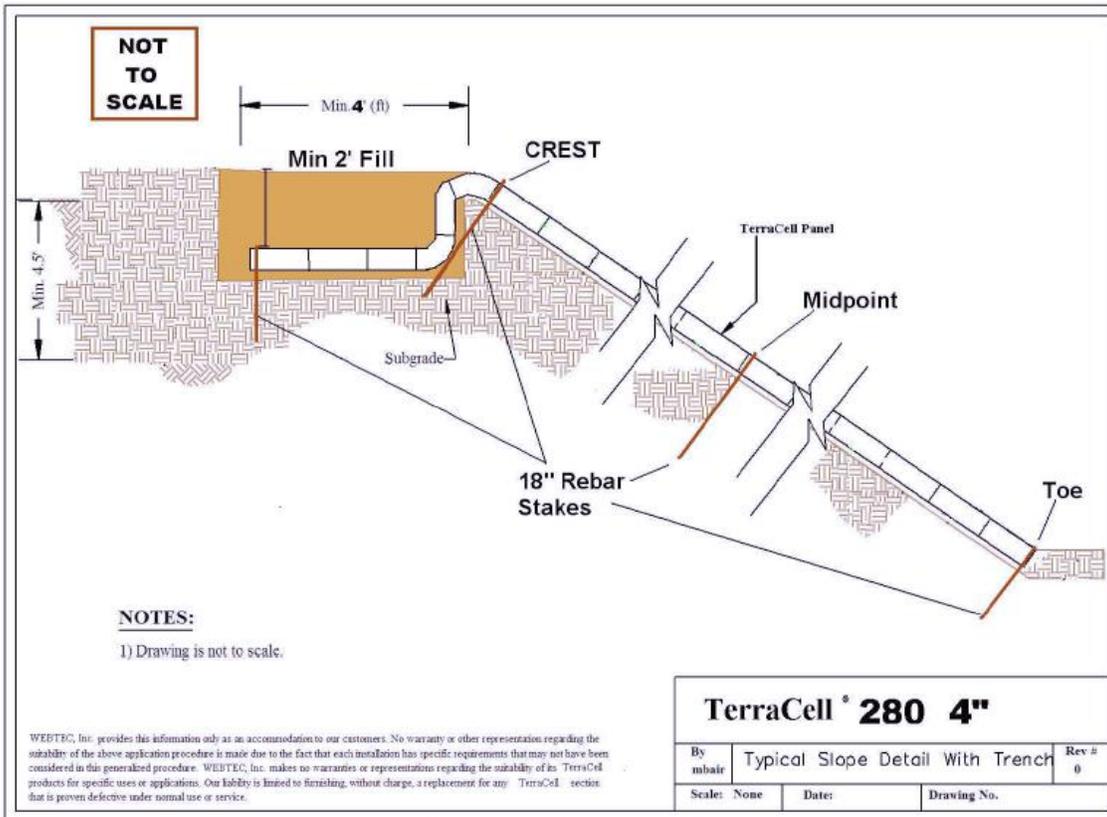


## Backstop – Bullet Catcher – 308 / 223 Range

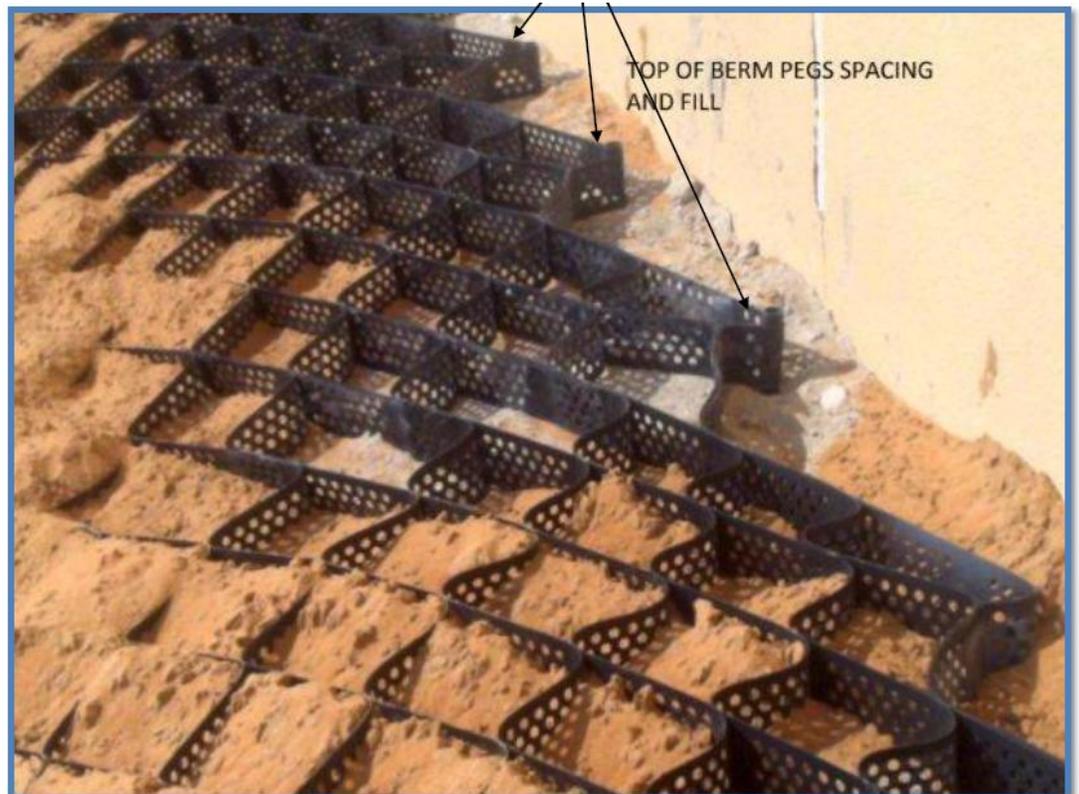


The impact face of the earth backstop must be soil with 100 percent passing the #4 sieve, ASTM C136, for a depth of 2 meters (6.5 feet). The slopes should be stabilized with grass vegetation with access locations provided for maintenance and repair equipment

**Typical installation of Teracell – note top securing method.**



**Top of berm showing Teracell anchored then running down surface**



Side berm showing layer of Teracell waiting for sand filling.



# Green Ammunition

With the advent of the Pollution Prevention Act of 1990 and the DoD response to a White House Executive Order in 1993, the DoD developed pollution prevention plans and programs for both facilities and weapons systems. In order to create an easily identifiable program that would translate to DoD employees as well as the public, the Picatinny community created the "Green Ammunition Program" for small, medium and large caliber ammunition. Acquisition documents were scanned for hazardous and toxic materials and process lines were reviewed for other materials not listed on drawings and specifications. A systematic process of elimination and/or replacement followed for "greening" ammunition.

In 1995, Picatinny established the Joint Working Group (JWG) for Non-Toxic Ammunition (green ammunition) to redesign ammunition components and manufacturing process. High visibility changes called for the removal of lead from the bullet tip (slug) and lead from the primer compound. Efforts included the elimination of other heavy metals such as barium and antimony; the elimination of Ozone Depleting Compounds (ODC) and Volatile Organic Compounds (VOC) required within the Technical Data Packages; and the elimination of other hazardous and toxic materials from the production processes. This program set the stage for "greening" more complex DoD systems and provided the DoD community with one of its first pollution prevention success stories. This program represents a benchmark in ammunition production.

## **Protecting the Environment through Science and Technology**

Through the years, Picatinny has initiated projects that will help protect the environment. Within its own community of employees and contractors using their vast knowledge and experience in science and technology, Picatinny has pursued opportunities that will result in preventing pollution, cleaning up hazardous waste and reducing further contamination. For example, a current research project focuses on degrading energetic material to innocuous products using microorganisms. When fully developed, this technology can be used for both soil and water remediation that is contaminated with energetic material, treating manufacturing waste streams and rendering safe unexploded ordinance. Using microorganisms for these tasks represents a cost effective, more environmentally friendly process compared to current methods such as incinerating contaminated soil or filtering contaminated water. With an eye to the future, Picatinny is using the lessons of the past to protect the 6,500 acres of land under its management.

## [In Search of Lethality: Green Ammo and the Development of the M855A1 Enhanced Performance Round](#)

[The full version of this essay is [available as a free download in eBook format from Smashwords.com](#). Supported formats include Amazon Kindle, Apple iBooks, Barnes & Noble Nook, Sony eReader, HTML, PDF, and other popular formats.]

The [recent public demonstration of the Army's new 5.56mm M855A1 Enhanced Performance Round \(EPR\)](#), which began fielding to units overseas in mid-2010, has put some [performance data out in open source](#) that finally enables this tale to be told. The development of EPR was not exactly a secret, but was done under a closely controlled information campaign – so much so that even a year after the ammunition has been fielded the “cover story” for the development still causes a great deal of confusion. Since I was involved with the first years of the program that ultimately became M855A1 EPR, I think it's time to shed a little more light on the subject, and perhaps try to explain how environmentally-friendly “Green Ammo” became associated with a significant upgrade in small arms capability.

M855A1 EPR. US Army photo.



If such efforts can be said to have a specific beginning, then M855A1 EPR “bronze tip” ammo – previously known as M855A1 LFS (Lead-free Slug), and before that generically as “Green Ammo” -- was born at the kickoff meeting for Phase II of the Army's Green Ammunition replacement program in 2005. That meeting, held at the [Lake City Army Ammunition Plant](#), was attended by a range of participants from the Joint Service small arms ammunition community, including representatives from the [Project Manager for Maneuver Ammunition Systems \(PM-MAS\)](#), the [Armaments Research, Development, and Engineering Center \(ARDEC\)](#), the [Army Research Lab \(ARL\)](#), the [US Army Infantry Center \(USAIC\)](#), the [US Special Operations Command \(SOCOM\)](#), and contractors supporting ammunition design and production like [Alliant Tech Systems \(ATK\)](#) and [General Dynamics – St. Mark's Powder \(GD-SMP\)](#). (The [Marine Corps Combat Development Command](#) was also a participant in this effort, though if I recall correctly not present at the initial meeting.)

Green Ammo Phase II was intended to solve problems with the Army's first attempt at environmentally friendly small arms training ammunition. The [Army had been forced to look at removing lead from its ammunition](#) to reduce the large amounts of lead that accumulate in stateside training ranges – driven in no small part by tightening state environmental regulations that would have closed range facilities at places like the Massachusetts Military Reservation. Since rifle rounds represent the bulk of ammunition produced and fired in training, the “green” effort began there, and the initial green ammo effort started by designing a lead-free drop-in replacement for M855 “green tip” 5.56mm rifle ammo by simply replacing the lead core of the round with another dense metal – tungsten. **That seemed to work fine, initially, until it was discovered that the rounds were becoming unstable in flight and “keyholing” – that is, flying sideways through targets.** Also, further environmental research was beginning to suggest that **tungsten might be even worse for the environment than lead.** So the Phase II program was initiated to fix the poor flight of the “green” training ammunition with a solution that not only **did not use lead, but also did not use tungsten.**

The program leads and contractors were laying out the scope of the effort when the Infantry Center rep spoke up, and said, basically:

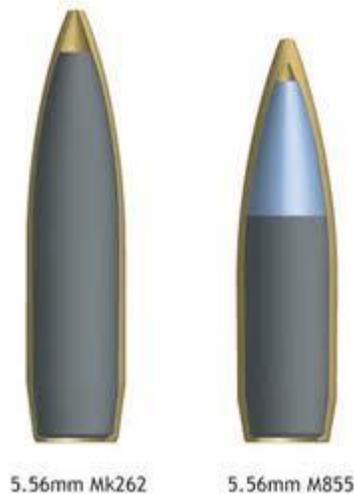
**“Look, we’re in the middle of a war. No one gives a shit about being environmentally friendly right now. Can’t you give us something better, instead?”**

The SOCOM rep echoed the same sentiment.

Complaints about the battlefield performance of the standard issue M855 had surfaced not long after our entry into Afghanistan, where troops in close quarters combat had complained that the rounds were not lethal enough – **sometimes they would hit an enemy target and have no apparent effect**, while, frustratingly, other units reported no problems with performance. The services had been looking for some time for an off-the-shelf solution that would provide better performance against “soft targets” – people – without making too many other tradeoffs.

SOCOM had started issuing the Mk262 open-tipped match round as a substitute; it was definitely a more accurate round, and anecdotally seemed to perform better against soft targets as well. The Marines were starting to use Mk262 in higher quantities, and the Army's 3<sup>rd</sup> Infantry Division was getting ready to redeploy with a stockpile of Mk262 to use in specially modified designated marksman rifles. But Mk262 was expensive – **roughly four times the cost per round of M855**, and its production process could not be scaled to meet the volumes of ammunition the Army needed, which at that point was close to a **billion rounds of 5.56mm ammo a year** for both training and war use with the bulk of the ammunition sent directly overseas. There were also a number of serious questions as to the adequacy of Mk262 as a general purpose round, or even as a dedicated soft-target round. Other alternatives, like the M995 Armor Piercing round, had advantages of high accuracy and target penetration but were also too expensive or incapable of being produced in significant quantities without major investment.

Mk262 and M855 cutaways.



The services had stood up the Joint Services Wound Ballistics Integrated Product Team (JSWBIPT) several years prior to address the battlefield performance question for M855 and see **if there was a commercially-available replacement could be found that would measurably improve soft target performance**. The JSWBIPT was beginning to wrap up its work at the time of the Green Phase II meeting, and the preliminary results indicated that there wasn't a good commercial alternative available – most of the rounds performed very similarly, and all of them had problems with **“yaw sensitivity” that caused inconsistent performance when the rounds struck targets**. In essence, all of the anecdotal evidence was correct – the M855 could be highly lethal, or highly ineffective, depending on circumstances which the user could not control.

(In the interest of brevity, I'll omit a lengthy discussion of the JSWBIPT work and findings. A couple of Army majors published an article in [Infantry Magazine](#) in 2006 that summarized the publicly releasable results to that point, and it can be found online (one source: [Alion Science WSTAIC](#)). Note that *Infantry* is written as the professional publication for the Army Infantry Branch rather than a scientific journal, so the article is written for a general audience rather than a technical one. Those looking for greater technical detail will have to go to ARDEC or ARL, as I'm not sure if there have been detailed scientific papers publicly released from the JSWBIPT's work. Much of the later JSWBIPT data and conclusions were classified, Reading between the lines of the article's conclusion, one can infer the work that was already under way for what became M855A1.)

The ARDEC and ARL members present at the meeting indicated that though there wasn't a great commercial alternative for M855, they had learned enough from the JSWBIPT work that they could design a new round to meet the Infantry Center and SOCOM request, if the requirements were sufficiently defined and someone would fund the work. After some discussion, it was clear there were three sets of competing requirements.

The Infantry Center expressed a number of performance goals compared to M855:

- Improved soft target lethality
- Improved accuracy
- General purpose capability
- Ballistic similarity
- Similar hard target performance
- Optimized for M4
- Reduced flash

I'll address these specific items, and how they ultimately related to M855A1, in a moment.

SOCOM was most interested in finding a round that would have significantly better accuracy (i.e., lower inherent dispersion) than Mk262 and be available at lower cost – best, in fact, if one of the other services adopted it, as a SOF-specific round would be purchased out of SOCOM budgets rather than provided by the big Green Army. Other concerns were secondary provided the round could be optimized for the shorter barreled weapons SOF operators were using. SOCOM could afford to have several specialty rounds available, and so was not concerned with hard target performance (though behind-barrier performance would eventually become important).

The program manager (PM-MAS) needed to find a solution that was “environmentally friendly” (defined as lead-free projectile, no tungsten) to meet the Green Ammunition mandate for which they were already funded. Any solution also needed to be scalable to the volumes of production the Army needed, and be comparable in cost at full rate production to M855 – or if it cost more, the added cost had to be reasonable relative to the added performance. Costs approaching that of Mk262, or worse, M995, could not be borne by the available budgets.

A final consideration that arose during the discussion was concern about the **public perception of the Army working on a “more lethal” rifle round**. Although given the war it was hard to imagine soldiers, the general public, or political leadership not wanting to put more capability into the hands of soldiers, there were [Hague Convention](#) – “Law of War” -- considerations. Some solutions to increased lethality like expanding or “hollow point” ammunition were known to not meet Law of War review standards. There could be a significant risk that depending on the approach, if there was a perception that the US were trying to circumvent Hague Convention restrictions the entire program could be shut down prematurely. The design agencies wanted the freedom to at least evaluate a wide range of alternatives to better understand their design trade space, rather than limit design work at the outset to only configurations which were already proven to be Hague compliant.

Ultimately, the team came up with a plan that would meet most of the requirements of most of the parties. The design effort would work to the Infantry Center's basic requirement, with the understanding that SOCOM could take or leave the solution depending on its performance. The solution would have to be "green", which would justify using the available funding and existing program to do the work, rather than having to go back and justify and fund a new ammunition development program. The PM cost targets would remain, but be applied after a range of feasible design options had been developed. The design team would also not be initially limited to Law of War-compliant designs in order to allow for a thorough exploration of the design trade space – though whatever design was proposed for the final solution would have to undergo, and pass, a legal review for Law of War compliance. The public information message would focus on the original program – environmentally friendly training ammunition – to minimize the risk that the program would get disrupted before it could demonstrate its effectiveness.