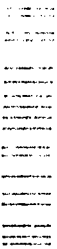
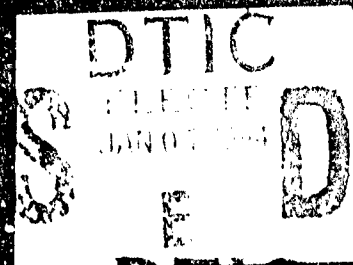


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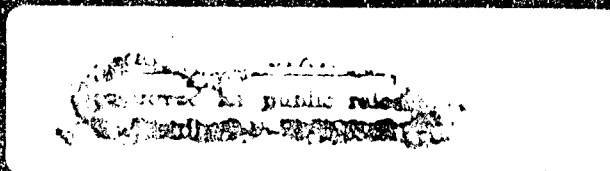


ENVIRONMENTAL CONTAMINATION
AT SMALL ARMS RANGES

1993



ANTONIO MICHAEL EDMONDS



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The Pennsylvania State University
The Graduate School
Department of Civil and Environmental Engineering

**ENVIRONMENTAL CONTAMINATION
AT SMALL ARMS RANGES**

A Report in
Environmental Engineering
by
Antonio Michael Edmonds

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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Engineering

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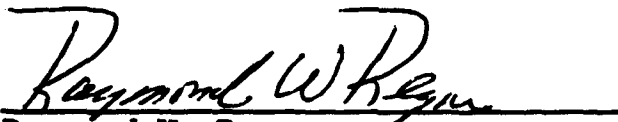
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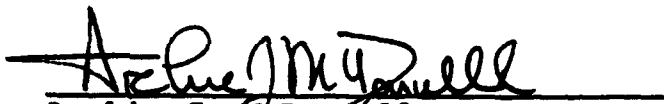
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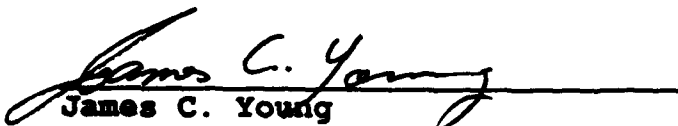
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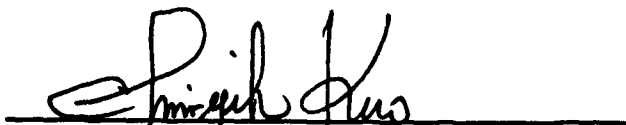
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ABSTRACT

During the normal operation of a small arms range, a substantial quantity of lead bullets is accumulated in a relatively small volume of soil. Geochemical processes result in the dissolution of these bullets and the release of lead species capable of migrating into the surrounding environment. The lead contamination emitted from small arms ranges has not been extensively studied and is not clearly regulated or understood.

In this document, the major factors influencing the speciation, partitioning, and fate of lead in the natural environment are examined. Data providing the concentrations of three metals in the soils and vegetation in the vicinity of a small arms range was obtained and analyzed. The observed lead concentrations exceeded 6000 ppm in the soil near the base of an impact berm at the range. The soil lead content was found to decline, although not uniformly, with distance from the berm. However, soil lead levels of almost 2000 ppm and greater than 100 ppm were found at distances of more than 100 feet and 200 feet from the berm, respectively.

The concentrations of the other metals, copper and zinc, were not comparable to lead and did not warrant detailed analysis.

Key technologies and management actions available to control or remediate the lead contamination at small arms ranges are discussed and evaluated.

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Chapter 1

INTRODUCTION

Small arms, including pistols, rifles, and shotguns, are routinely fired at various shooting ranges located throughout the country. Small arms ranges are commonly associated with recreational shooting facilities where the targets vary from stationary silhouettes to rapidly moving skeet. Law enforcement agencies at all levels of government are also frequent users, operators, and owners of small arms ranges. Additionally, the United States Department of Defense operates a variety of firing ranges used extensively in the training of military personnel. The Department of the Navy alone controls approximately 245 active outdoor small arms ranges and an estimated 56 abandoned ranges [1].

Outdoor small arms ranges used for rifles and pistols are often constructed with impact berms directly behind the targets as shown in Figure 1. Impact berms are usually earthen and are designed to capture and retain the fired rounds or bullets. At most skeet and trap ranges as well as at other small arms ranges lacking impact berms, the rounds continue travelling along a trajectory until ultimately coming to rest in an essentially horizontal fall area.

According to military specification MIL-L-13283B of 19 Aug 1970, the ammunition typically used by the military services contains bullets comprised of 90.0 to 99.2 percent

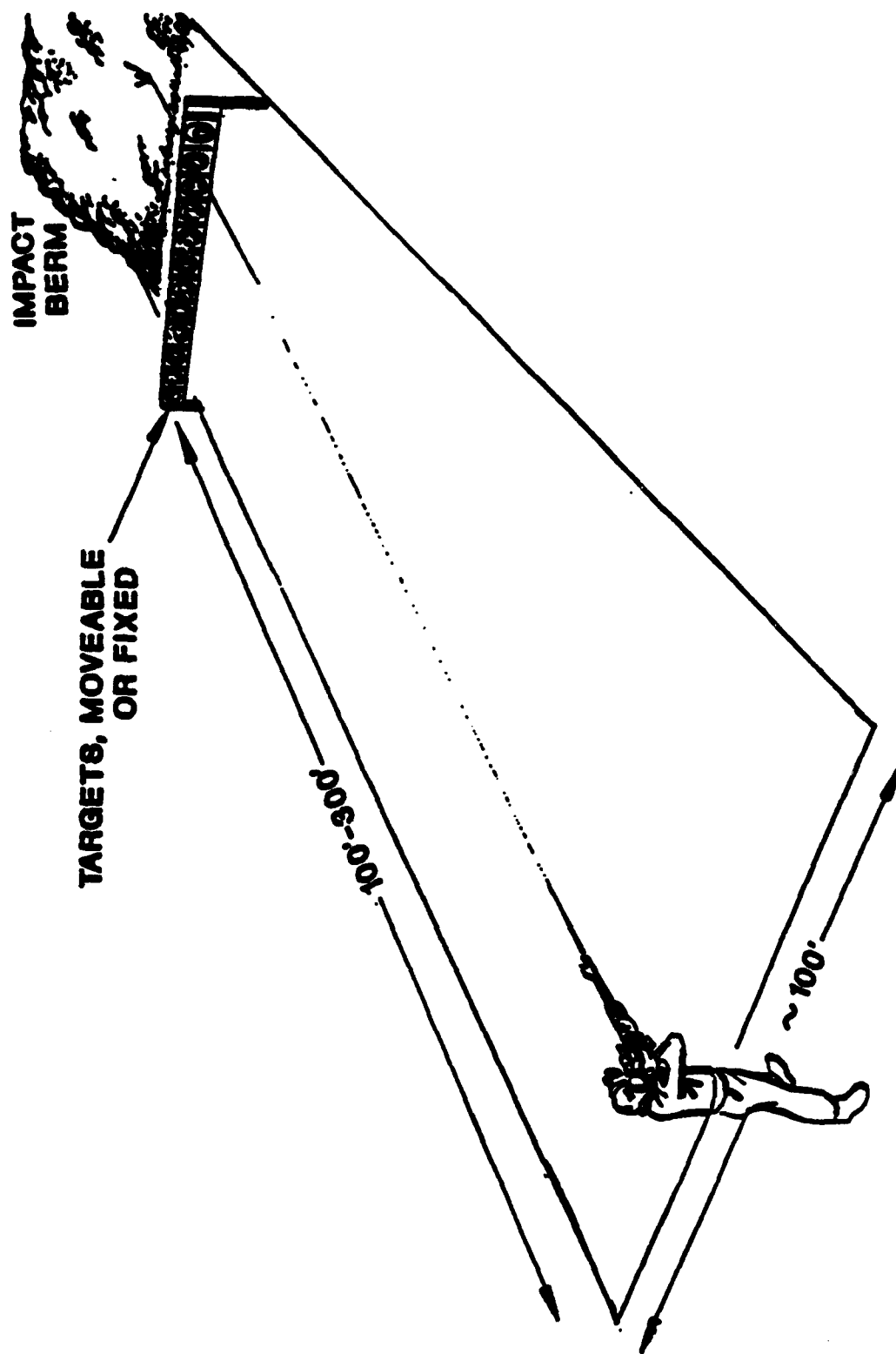


Figure 1: Configuration of a Typical Small Arms Range [1]

lead and antimony [2]. The lead content of the bullets used for non-military applications typically varies from about 85 to 98 percent [3]. Due in part to the magnitude of the lead content of bullets, lead contamination is the major concern at small arms ranges.

Lead occurs naturally in the Earth's crust, often in relatively rich ores such as galena (PbS) and cerussite ($PbCO_3$) and has a mean concentration of about 15 mg/kg [4]. Lead is a known toxin and is classified by the United States Environmental Protection Agency (EPA) as a probable human carcinogen [5]. Lead exposure is associated with numerous physiological effects in humans including interference with the heme synthesis necessary for the production of red blood cells, anemia, kidney damage, impaired reproductive functioning, delayed neurological and physical development, and elevated blood pressure [6].

Warranted by the above, the maximum contaminant level for lead in drinking water is 0.05 mg/L [7]. Additionally, the Resource Conservation and Recovery Act (RCRA) lists lead as a regulated metal that, when present in concentrations above the threshold, is subject to hazardous waste disposal restrictions [8].

The characteristic of lead that resulted in the RCRA listing is toxicity. Under RCRA, the concentration of a potentially toxic contaminant in soil is determined by an analytical extraction method known as the Toxicity

Characteristic Leaching Procedure (TCLP). If the TCLP extract of a waste contains lead in quantities greater than 5 mg/L, then that waste demonstrates toxicity and is deemed hazardous.

In the operation of a small arms range, lead rounds accumulate in the impact berm or fall area. Geochemical processes can result in the dissolution of the metallic lead into soluble and other forms that are capable of migrating through and contaminating the natural environment. The TCLP lead level of contaminated soils would be related to the extent of such dissolution and migration. TCLP lead levels exceeding the threshold could impose a requirement to either treat the soil or dispose of it in accordance with the RCRA hazardous waste disposal regulations.

On the other hand, continued lead migration could result in the contamination of natural water systems and possibly impact drinking water supplies. This too would necessitate remedial action.

It is evident that the operation of a small arms range could generate lead contamination that conflicts with existing environmental laws and regulations. The legal ramifications of any such conflicts makes it essential for the owners of range facilities to take competent management action to ensure continued, cost effective compliance with all pertinent regulations.

This document proceeds by examining the behavior of lead in the natural environment. Metal concentrations in the soils, vegetation, and natural waters in the vicinity of small arms ranges are then analyzed such that the lead contamination present can be characterized. The need to mitigate this contamination is demonstrated and several alternative approaches to site remediation and management are evaluated. Key considerations for the future design and operation of range facilities are also addressed.

While this report emphasizes issues and concerns that are of particular interest to the United States Navy, its contents can be applied to most range facilities and their respective owners.

Chapter 2

THE FATE OF LEAD IN THE ENVIRONMENT

The buildup of bullets in a capture zone, such as an impact berm or fall area, is only the beginning of the environmental contamination that can potentially result from the operation of a small arms range. Weathering of the bullets may result in the formation of mobile lead compounds capable of migrating into and through the soil profile. Lead migration could produce widespread contamination of the soil as well as of nearby surface and ground water sources. The extent of both mobilization and contamination depends upon a variety of factors as discussed below.

2.1 Speciation

Experience that the environmental behavior of an element can only be understood in terms of its actual molecular form led to the introduction of the term speciation. Identifying and modelling the speciation of various contaminants soon became the quest of many researchers. However, it was found that due to the important role of kinetically controlled processes in biogeochemistry, actual speciation is often different from what can be predicted by thermodynamic models [9]. Today, while we can comment on many of the factors impacting speciation we remain unable to quantify their effect.

Several of the more significant factors influencing the speciation of lead in the environment are evident from the Eh-pH diagrams shown in Figure 2. Among the most important is pH. Other factors constant, lead will preferentially bond with different reactants based on pH alone. The compounds that result will not only be chemically distinct but may also vary from solid phase precipitates to aqueous ions.

The oxidation-reduction potential, Eh, is another critical consideration. At its extremes, Eh can alter the oxidation state of lead. While Pb^{2+} is by far the most common oxidation state in the natural environment, Pb^0 and Pb^{4+} can and do exist under certain conditions. However, even as the divalent state of lead is maintained, the chemical interactions of Pb^{2+} will differ with modest changes in the Eh.

Figure 2 also shows that the availability of other chemical reactants can impact the speciation of lead. As shown, in a $Pb/H_2O/OH^-$ system, Pb^{2+} dominates over a wide range of pH values. However, when CO_2 is added to the system, the pH range for Pb^{2+} becomes significantly smaller. When SO_4 is also available, Pb^{2+} controls a very narrow range of extremely low pH values. In addition to the reactants mentioned above, lead is also known to commonly form compounds with iron and manganese oxides, fulvic and humic acids, and other organic substances.

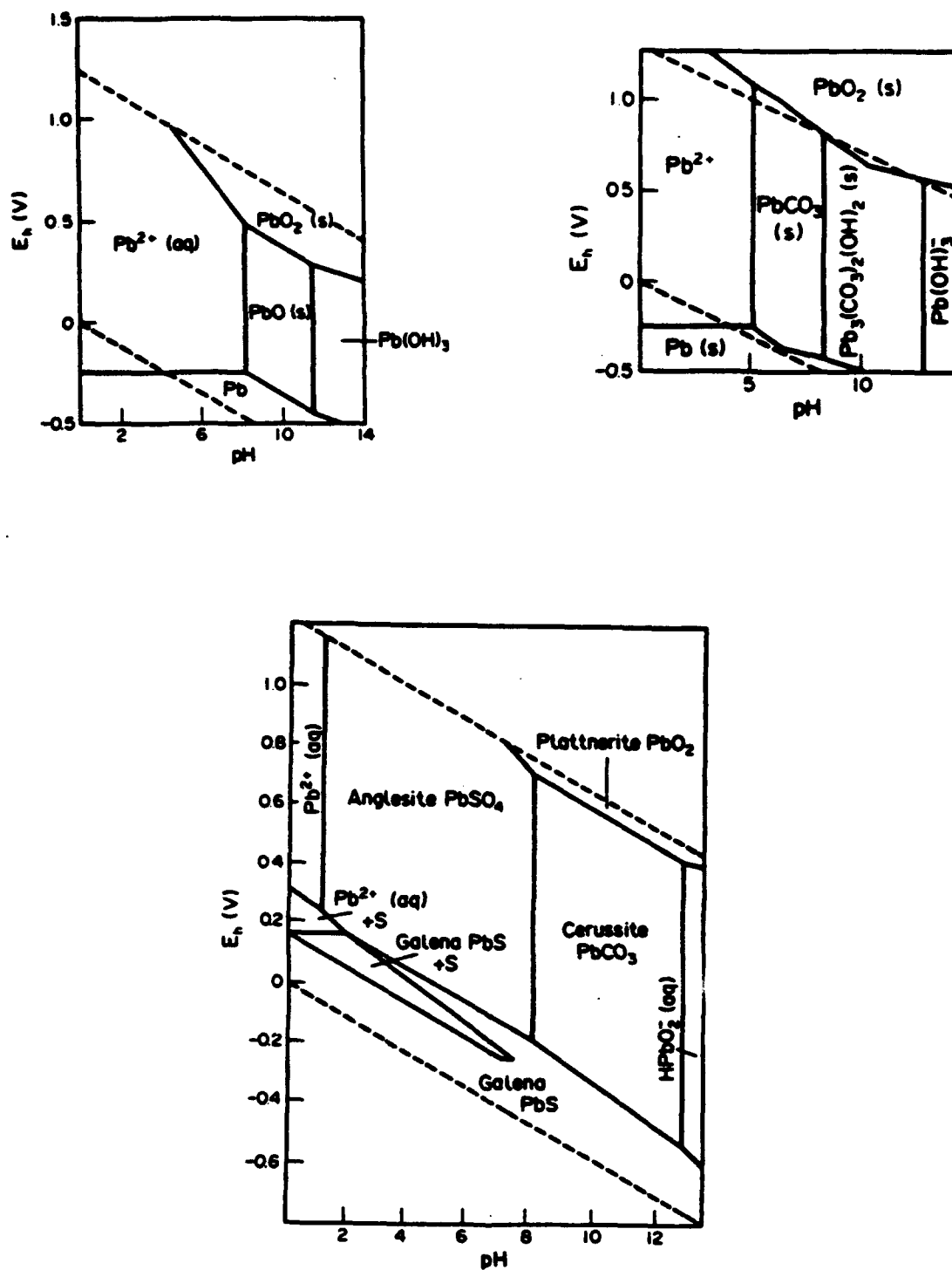


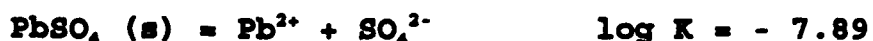
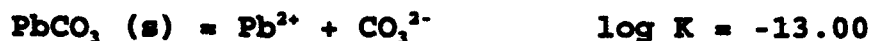
Figure 2: Eh-pH Diagrams for Various Pb Systems [10]

2.2 Partitioning

While the speciation and partitioning of lead are closely related, the former is often considered to refer to the chemical state or species while the latter is usually associated with the physical states in which the various species can be found.

2.2.1 Solubility Factors

Similar to speciation, the solubility of lead is a function of pH and re-dox potential and, in natural waters, is normally governed by the hydroxide, carbonate, or sulfate forms. The solubility equilibria responsible for the concentrations of the dominant species are as follows [11]:



However, free lead ions, Pb^{2+} , have a strong tendency to form ion pairs, including PbHCO_3^+ and PbOH^+ in natural waters. The formation of these species reduces the Pb^{2+} concentration and drives the above equilibria to the right, enhancing the solubility of lead. A similar enhancement of lead solubility occurs when organic compounds complex with the Pb^{2+} ions [12]. Solubility directly impacts mobility in the soil and thus, must be carefully considered.

2.2.2 Adsorption Phenomena

Adsorption is the term used to describe the buildup of a substance at an interface between two distinct phases as a result of physical or chemical forces. Since the adsorptive power of soils was first documented by Thompson [13], much has been learned of its nature and origins.

The relative content of the sand, silt, and clay particles, collectively known as the soil separates, plays a major role in establishing the adsorptive capacity of a soil. Unlike particles of sand and silt, most clay particles carry negatively charged exchange sites that attract cations such as Pb^{2+} . Because heavy metals have high replacing power over alkaline and alkali earth metals [14], they have a strong tendency to become and remain adsorbed to clays. If desorption were to occur, diffusion out of the relatively impermeable clay structure would be a slow process providing ample time for re-adsorption.

Exchange sites with high affinities for lead can also be found in the humus and other organic substances in soil [14]. Humic substances are also known to contain highly selective chelation sites which can exhibit a preference for lead. When formed, chelates have a high degree of stability as a result of their organometallic ring structure [15]. However, the mobility of lead will only be restricted to the extent that the organic complexes formed remain insoluble.

Iron and manganese oxides interact with heavy metals in soils in very much the same way as organics, only exhibiting an even stronger preference for lead. The occlusion of heavy metals in growing solid phases, such as the oxides of Fe and Mn has been suggested to be one of the most important mechanisms for the immobilization of heavy metals in the natural environment [16].

The overall adsorptive power of a soil can be best described in terms of its Cation Exchange Capacity (CEC), often expressed as milliequivalents of CEC per gram of soil (meq/g). While CEC does not accurately account for the selectivity of all reactive sites, it does provide a good indicator of a soil's ability to impede the migration of lead contamination.

2.2.3 Competitive Adsorption

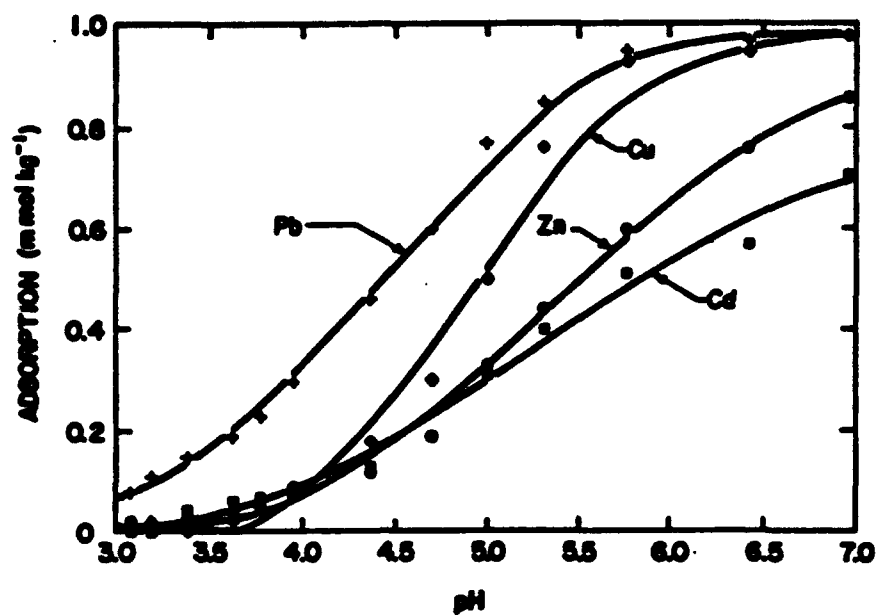
The ability of lead to effectively compete against other cations for the limited adsorptive sites found in a soil can be partially attributed to its first hydrolysis constant; that is the pH at which a lead ion's sheath of hydration loses its first hydrogen ion. Baes and Mesmer determined the following first hydrolysis constants [17]: $Pb^{2+} = 7.71$, $Cu^{2+} = 8.0$, $Zn^{2+} = 8.6$, and $Cd^{2+} = 10.08$.

Abd-Elfattah and Wada [18] found soils with differing cation exchange materials to demonstrate the following preferential adsorption sequence: $Pb > Cu > Zn > Cd$.

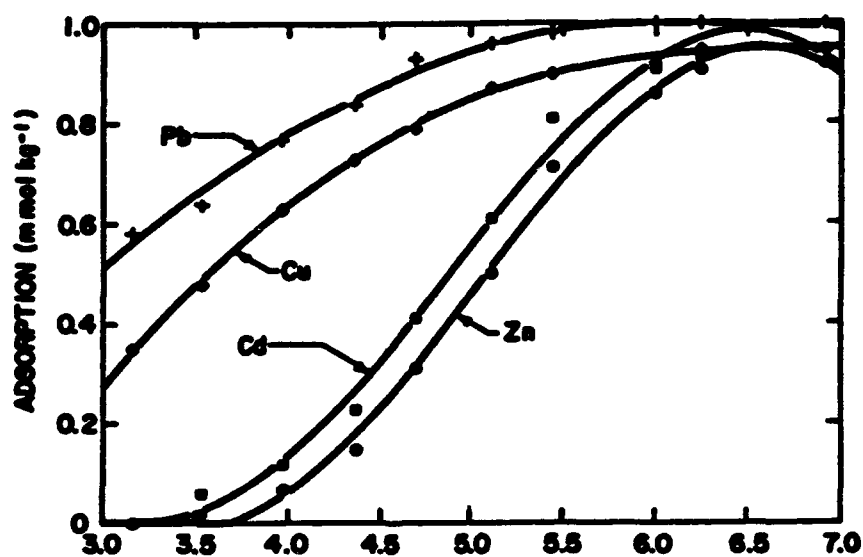
They further noted that the sequence was in the order of increasing first hydrolysis constant. This preference for lead to be adsorbed by soils has been demonstrated in other efforts with similar conclusions [19].

Caution must be exercised when using the first hydrolysis constant to predict preferential adsorption under differing environmental conditions. Deviations from the above sequence have been observed in some soils [20]. Elliott, Liberati, and Huang [21] warned that the validity of the sequence in most soils is questionable due to the selectivity of many of soil's adsorbents. Their results displayed in Figure 3 show that the predicted sequence prevailed over most of the pH range in the Christiana Soil. However, in the Pocomoke Soil, Cd was preferentially adsorbed over Zn at all pH values. Noting the higher organic content of the Pocomoke Soil, support is given to the argument that the selectivity of organics is driven by factors other than the first hydrolysis constant. It can be further reasoned that the preferential adsorption of lead may also be diminished in soils containing certain organics.

Figure 3 further demonstrates the effects of pH on the adsorption of lead. In both soils shown, the extent of adsorption increases with pH. However, in the Pocomoke Soil significant adsorption occurs at much lower pH indicating that adsorption by organics may be less dependent on pH than adsorption by clays or other exchange materials.



Christiana Soil: 284g Clay, 0.5g Organic C per kg.



Pocomoke Soil: 50g Clay, 20.5g Organic C per kg.

Figure 3: Adsorption of Heavy Metals by Soils [21]

2.3 Mobility and Transport

The mobility of lead in soils is closely related to the speciation and partitioning issues addressed above. However, mobility is only a measure of the potential for movement and thus, cannot single-handedly explain the actual migration of lead in soils. To address contaminant migration, the transport, not just the mobility, of lead must be considered.

While also a function of speciation and partitioning, transport cannot occur without the effect of at least one additional factor; some form of kinetic energy must be imparted upon the mobile lead if its potential for movement is to come to its fruition.

Under arid conditions, wind may provide the energy required and blown particulate lead may constitute the spread of contamination. Wind driven transport could be highly variable in terms of the quantities of lead, the directions, and the distances involved. Considering this variability in conjunction with the paucity of data available, wind-aided transport will not be the subject of detailed discussion or analysis in this document.

Hydrologic forces are the other major impetus to the transport of lead contaminated soils. Accordingly, the hydrologic activity of a contaminated site must also be taken into consideration when evaluating the spread of contamination. This includes, but may not be limited to,

precipitation, overland and groundwater flow, and the presence of both surface waters and aquifers.

Soluble lead species can be readily transported in either surface or ground water systems. The movement of soluble species from the soil into surface runoff has been modeled as a diffusion process [22]. In this model, raindrops impart energy to the soil, resulting in a thin, well-mixed surface layer. For a given rainfall impact energy, diffusion out of the soil increases with the hydraulic conductivity of the soil. Upon entering the surface runoff, soluble lead species will move away from the contaminated site as a result of both advection and dispersion. The direction and distance of movement will depend on the amount of runoff, the topography of the site, the rate of groundwater recharge, and the concentration gradient of the aqueous medium.

However, the rate of infiltration also increases with the hydraulic conductivity of the soil. As a result, increasing quantities of soluble lead may be carried deeper into the soil profile and thus, not be available to diffuse into the surface runoff which could be produced at some time after the start of a storm event.

Initially, with increasing soil depth the lead level should decrease, reversing the equilibrium driving force to favor adsorption of ions and precipitation of various other compounds. However, with the continued emissions expected

at active small arms ranges, this affect would diminish with time and the lead contamination could eventually impact any underlying aquifers. The quantities of lead transported into or through the soil profile would be related to the amount of infiltration.

Colloidal lead compounds would be expected to undergo similar transport mechanisms although migration through the subsurface could be somewhat reduced by the affects of straining and interception.

The transport of adsorbed and other particulate lead compounds will primarily be in association with soil losses resulting from erosion. The average rate of soil erosion can be estimated with the Universal Soil Loss Equation [23]. The equation contains factors to consider rainfall and runoff, soil erodability, slope length, slope steepness, cover and management, and support practices. The rate of erosion could then be used to predict the associated amount of lead migration.

The front faces of impact berms have relatively steep slopes and sparse vegetative cover and thus, would incur significant erosion losses. Subsequently, the spread of lead contamination via this means could be substantial.

Chapter 3

EXPERIMENTATION AT SMALL ARMS RANGES

The Naval Civil Engineering Laboratory has conducted limited sampling and analysis of the soils and vegetation at small arms ranges. Data obtained from two such efforts, hereafter referred to as Study A [24] and Study B [25], will be used in this chapter as the basis for further analysis and to characterize the environmental contamination that can result from the operation of a small arms range.

3.1 Site Characteristics

Study A focused on Range 4 at the Marine Corps Combat Development Command, Quantico, Virginia. Range 4 is located about 300 feet above sea level in the Piedmont geomorphic province. The land surface is moderately dissected, gently rolling and generally slopes to the southeast at an average rate of about 20 feet per mile. Most of the area is overlain by oak-hickory and pine woodlands. While the soils are comprised of a number of associations and series, loamy soils with clayey subsoils predominate. The regolith or decomposed bedrock acts as a reservoir that slowly feeds water into the shallow, fractured bedrock. The bedrock does not have any significant intergranular porosity. Overall, the site conditions contribute to high rates of surface runoff and a low potential for ground water migration [26].

3.2 Methodology

A sampling and analysis plan was prepared to establish a relationship between the distance from the firing range targets and the concentrations of heavy metals in the soil and the overlying vegetation.

Sampling was completed in June 1989. Samples were taken along the berm, backside, and downslope transects as shown in Figure 4. Additionally, samples were taken from a control transect located about one mile from Range 4 in an area comprised of similar soils, vegetation, and topography.

The dominant major vegetation along all of the transects was Virginia pine. Each Virginia pine located on each transect established a sample point.

Soil samples were taken adjacent to the base of the Virginia pine. Samples were taken from both Soil Horizon A, at a depth of 3 to 5 cm, and Soil Horizon B, at a depth of 10 to 15 cm. Each sample consisted of approximately 50 g of soil which was placed in a sealable plastic bag. Vegetation samples consisted of approximately 50 g of needles clipped from branch ends growing 1 to 2 m above the ground on the south side of the Virginia pine.

The vegetation samples were washed, dried, and macerated. The soil samples were screened to 80 mesh. The prepared samples underwent elemental analysis by standard Inductively Coupled Plasma (ICP) emission spectroscopy. Total concentrations of lead, copper, and zinc were reported.

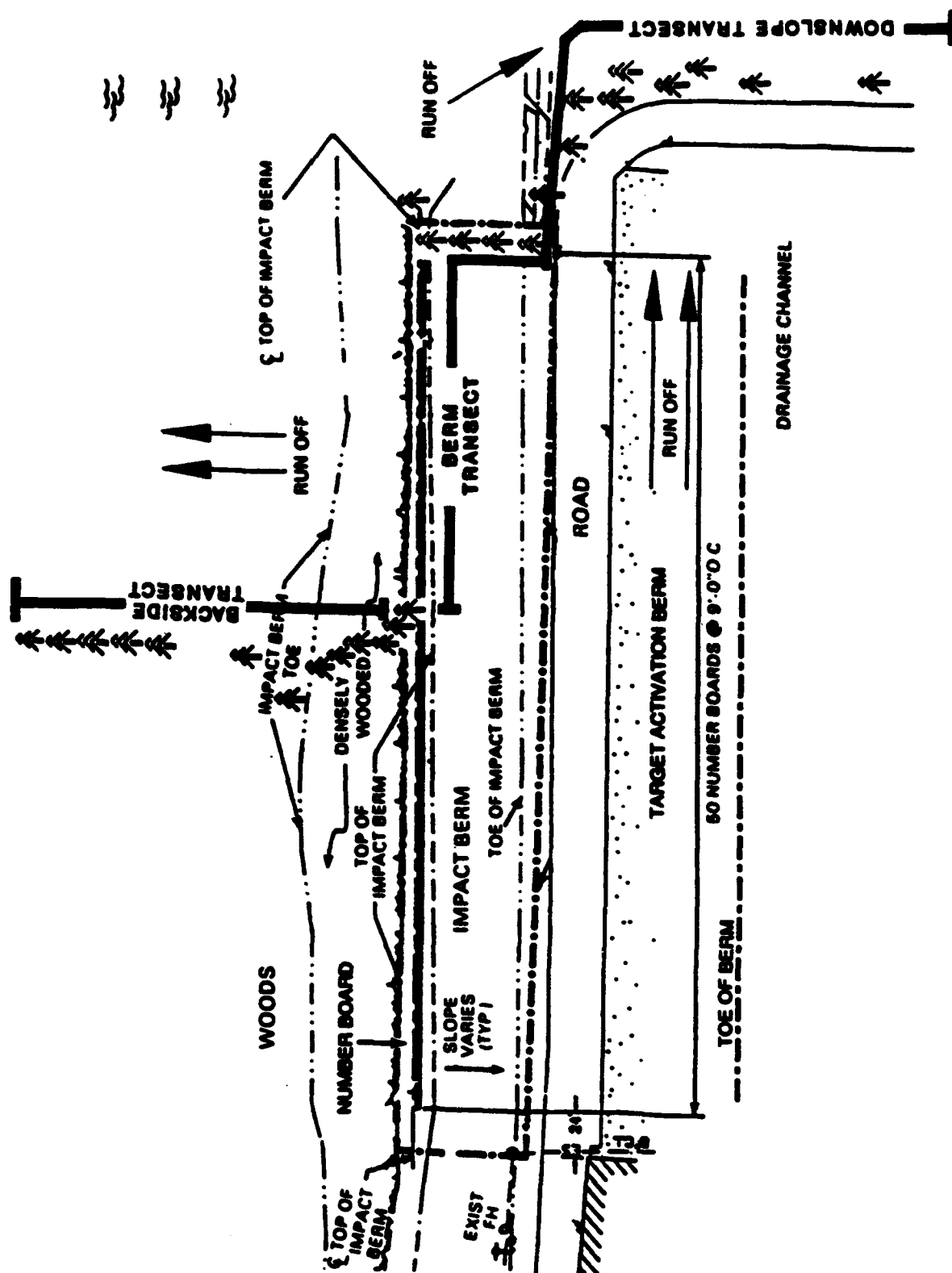


Figure 4: Study A Site and Sampling Plan [24]

3.3 Results and Discussion

The overall results are provided in Appendix A. The mean concentrations found along the berm and the control transects are presented in Table 1. As shown in Table 1, the concentrations found in the berm were significantly greater than the background levels found at the control site. However, the level of contamination in the berm may be understated by the data presented. Considering the results, the location of the berm transect, and the sample depths, there may not have been any samples taken from the extremely high concentration bullet pockets that form immediately behind the targets. This possibility is supported, if not proven, by the fact that the highest concentrations were obtained from samples taken along the backside transect rather than from the impact berm itself.

It should also be noted that the concentrations found at the control site may not represent true background levels. Based on the range of values found, particularly for lead in the B soil horizon, the presence of localized contamination must be considered a possibility. Given the location of the control site, one possible source of lead contamination would be from lead shot or other ammunition fired by hunters who frequent the area.

Accordingly, the extent to which the concentrations of heavy metals in the berm exceed background levels may be greater than indicated by the available data.

Table 1: Mean Concentrations of Heavy Metals in the Berm and Control Transects.

Notes: Concentrations in PPM

A - Soil Horizon A

B - Soil Horizon B

V - Vegetation

	L E A D		
	A	B	V
CONTROL	26.01	31.91	1.119
BERM	1818	1223	62
	C O P P E R		
	A	B	V
CONTROL	6.92	4.94	4.782
BERM	590	397	9
	Z I N C		
	A	B	V
CONTROL	19.2	13	41.63
BERM	119	130	63

3.3.1 Soil Lead Concentrations

The relationship between the soil lead concentration and the distance from the top of the impact berm along the backside transect is shown in Figure 5. The concentration of lead in the soil was not found to decrease uniformly with distance. The starting point of the transect, the top of the berm, may have contributed to the variable findings.

The maximum concentration found in both soil horizons occurred 22 feet from the top of the berm. This point may have been located near the toe of the impact berm; given that the mean width of impact berms studied on various Naval Installations was reported as 42 feet [1]. The velocity of surface runoff would be expected to decrease near the toe of the impact berm due to the dramatic reduction in slope at that point. This reduction in velocity would further promote the settling of suspended matter, including lead containing compounds, which could produce the elevated lead levels observed.

Localized concentration peaks were also observed at 56 feet in the A horizon and 37.5 feet in the B Horizon. These peaks may have coincided with groundwater discharge.

Manmade mounds, like impact berms, can disrupt natural hydrogeologic flow patterns and often create groundwater discharges at a moderate distance from the perimeter of the mound. If this were to occur, the ascending subsurface water would flow toward the surface at some undetermined

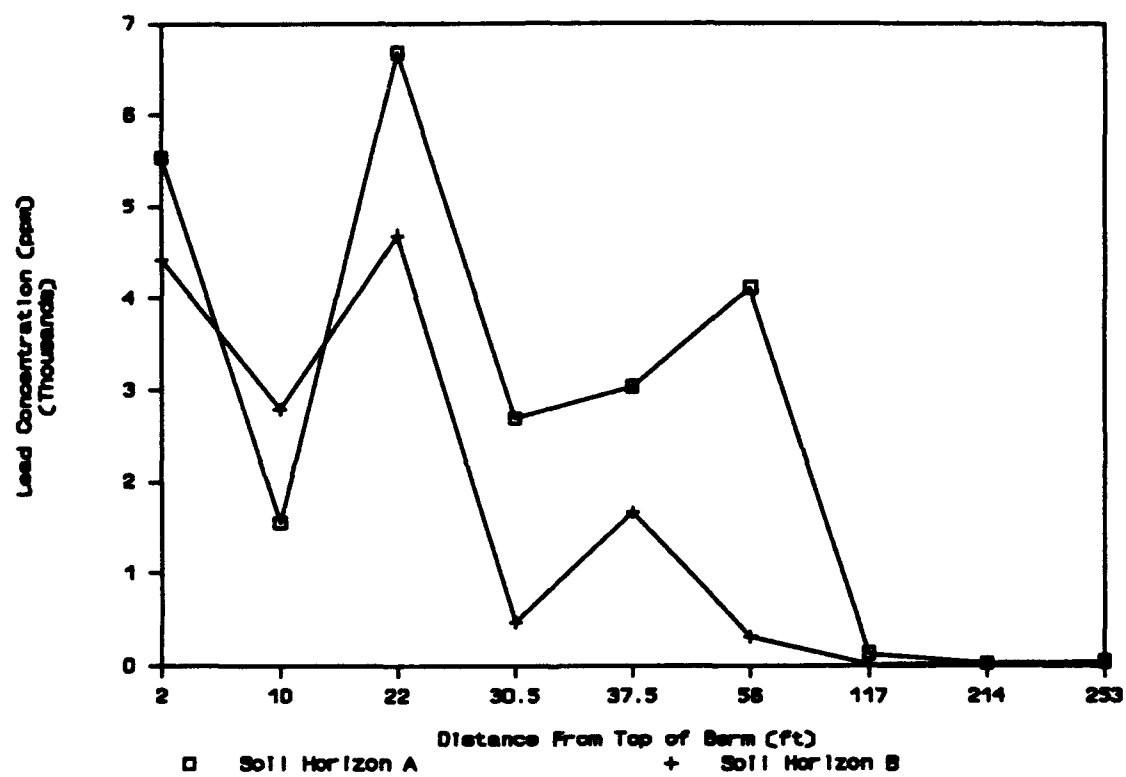


Figure 5: Lead Concentrations in Soil Horizons A and B, Backside Transect

angle as depicted by the peaks shown in Figure 5. Thus, closer to the mound, the discharge flow would be located at a greater depth while further from the mound, the flow would be at a shallower depth. If this subsurface water was carrying lead contaminants, elevated lead levels would be expected to follow the flow path. This pattern is exhibited by the referenced concentration peaks shown in Figure 5.

However, it is equally possible that the concentration peaks observed were the result of normal runoff and erosion patterns. During individual storm events, the intensity of the surface runoff would vary as would the distance that it travels. Rather than gradually declining, the velocity of the runoff and the level of saturation of the underlying soil may suddenly drop at some fixed location as a result of changing topographical or subsurface conditions. This would produce increased infiltration and the subsequent settling of suspended matter. Assuming that the suspended matter included lead containing compounds, elevated lead concentrations would be expected at such locations.

Considering the overall variability of the lead concentrations along the backside transect along with the variety of factors involved, an accurate explanation of the data obtained cannot be made. However, it should be noted that an extremely similar pattern was observed with copper and, to a lesser extent, with zinc levels in the backside transect as shown in Figure 6 and Figure 7, respectively.

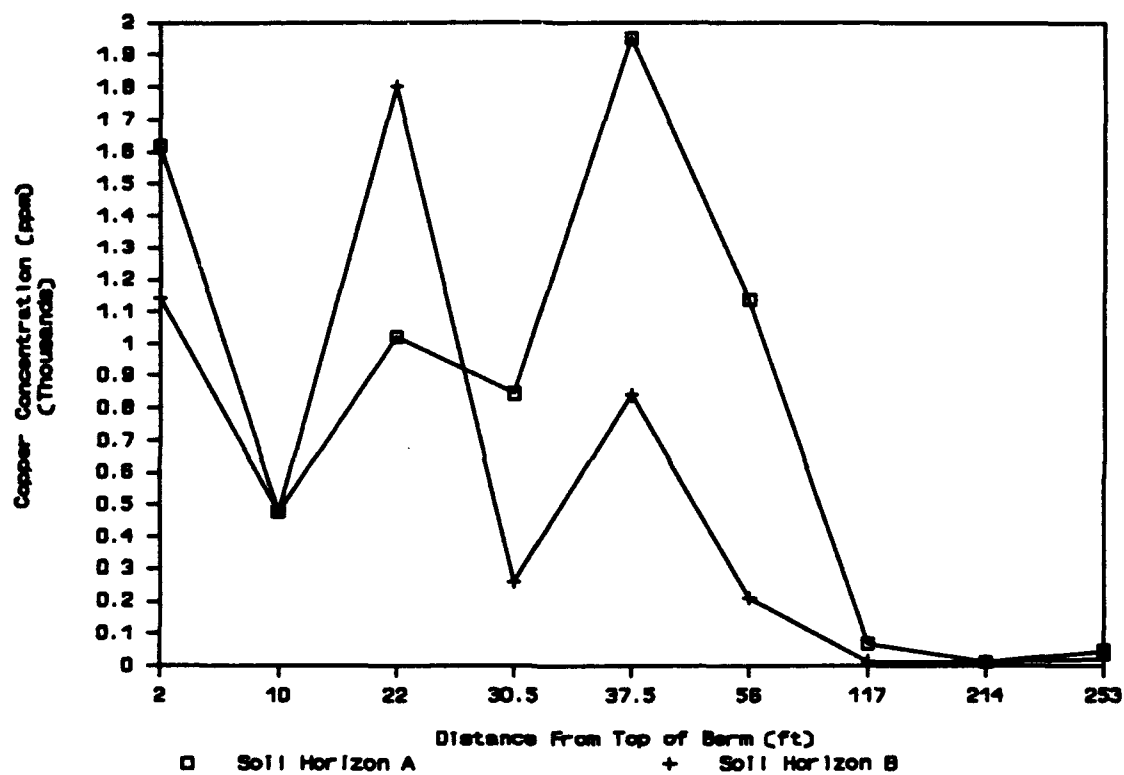


Figure 6: Copper Concentrations in Soil Horizons A and B, Backside Transect

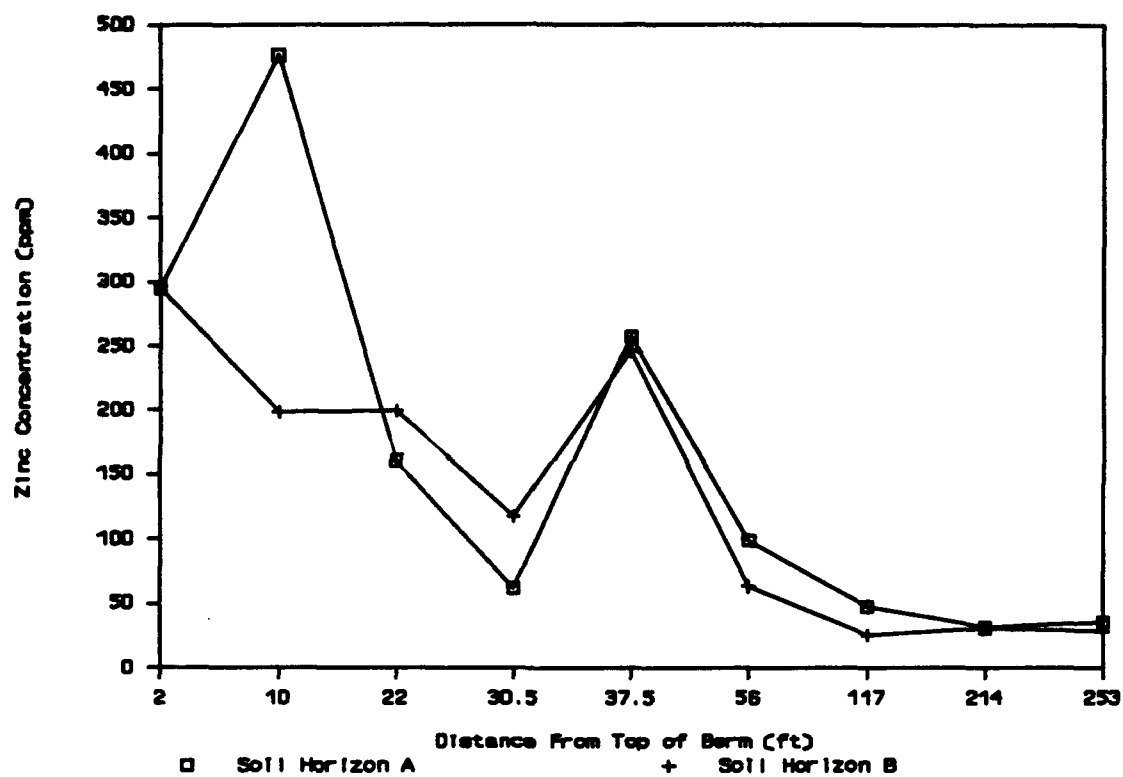


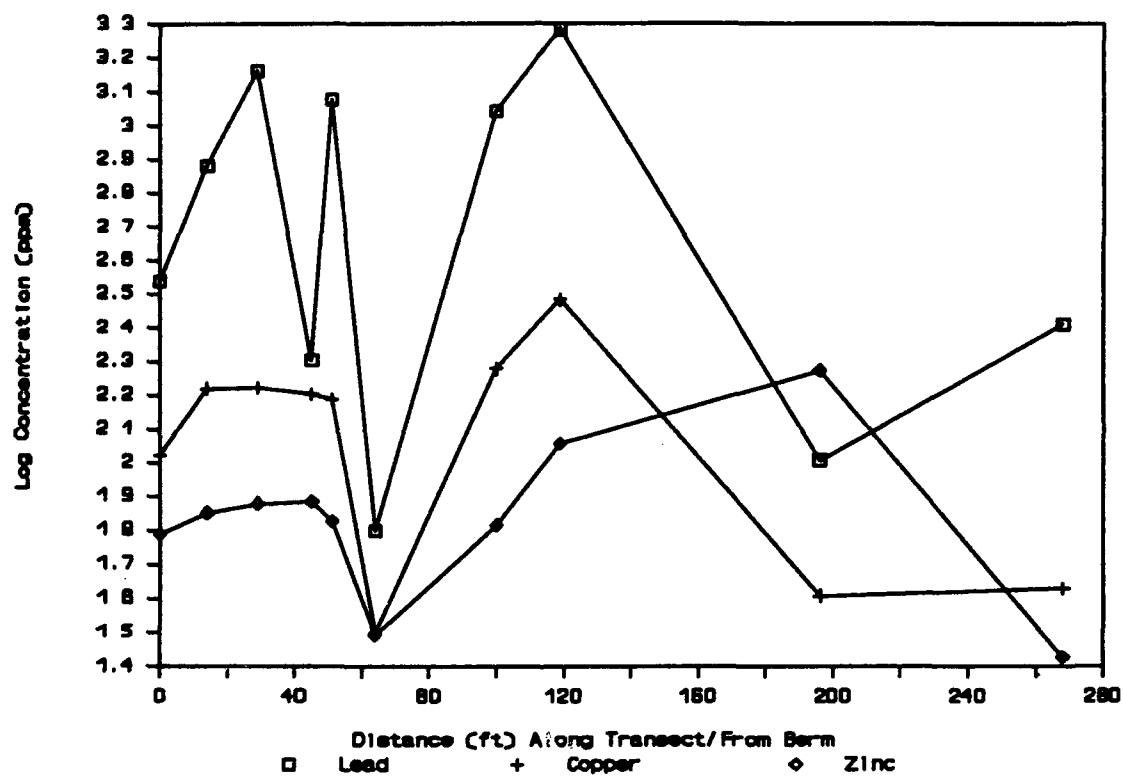
Figure 7: Zinc Concentrations in Soil Horizons A and B, Backside Transect

The soil lead concentrations along the downslope transect also failed to decrease uniformly with distance from the berm. In fact, the results from the downslope transect, as shown in Figure 8, exhibited even greater variability than did those from the backside transect.

The downslope transect received surface runoff from the front face of the impact berm. As mentioned, the front face of the berm was largely devoid of stabilizing vegetation and subsequently incurred significant erosion losses. Again, lead contamination transported by erosion would not be expected to produce a uniformly decreasing concentration gradient with distance from the source. Thus, erosion was probably the major transport mechanism for the soil contamination found along the downslope transect.

Figure 8 also shows that the relative copper and zinc levels in the soil continued to closely match the lead levels found. As with the backside transect, the similarity between the lead and copper levels was stronger than that between lead and zinc. The only major break in the correlation between lead and copper occurred at 45 feet where the lead level dropped inexplicably.

In addition to decreasing with less uniformity, all of the metal levels along the downslope transect decreased less overall. Relative to the maximum levels found along the transect, elevated levels of lead, copper, and zinc were found at greater distances from the berm.



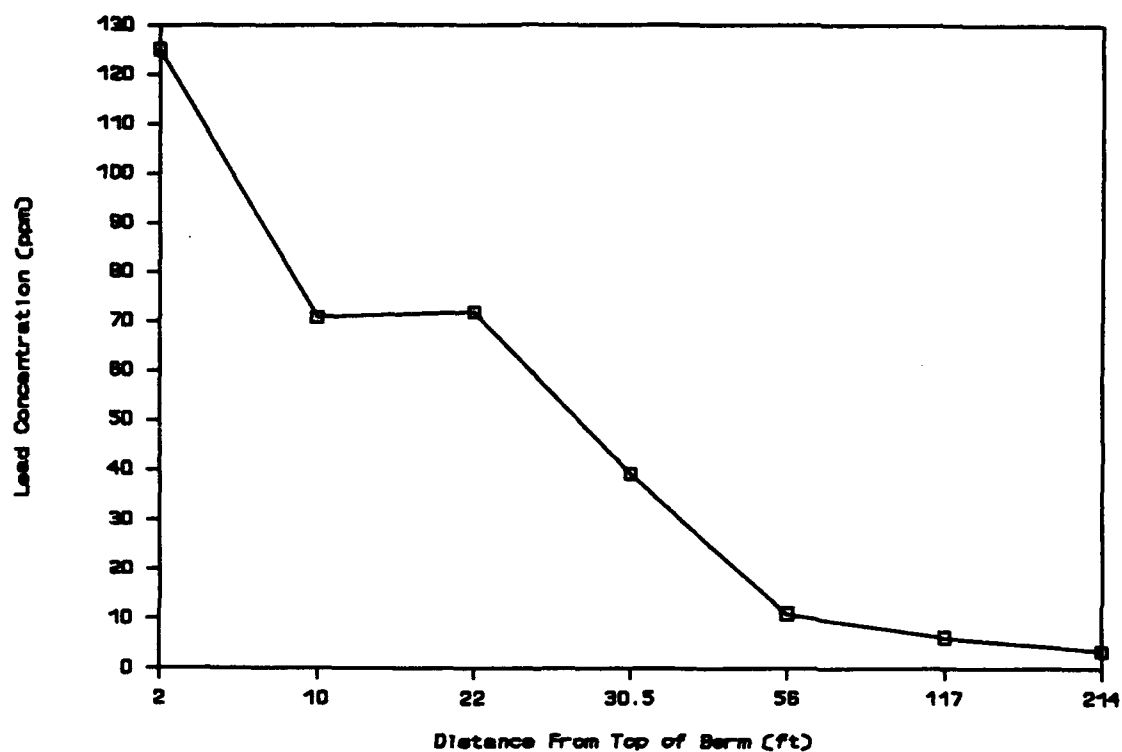
**Figure 8: Metal Concentrations in Soil Horizon A,
Downslope Transect**

3.3.2 Lead in Vegetation

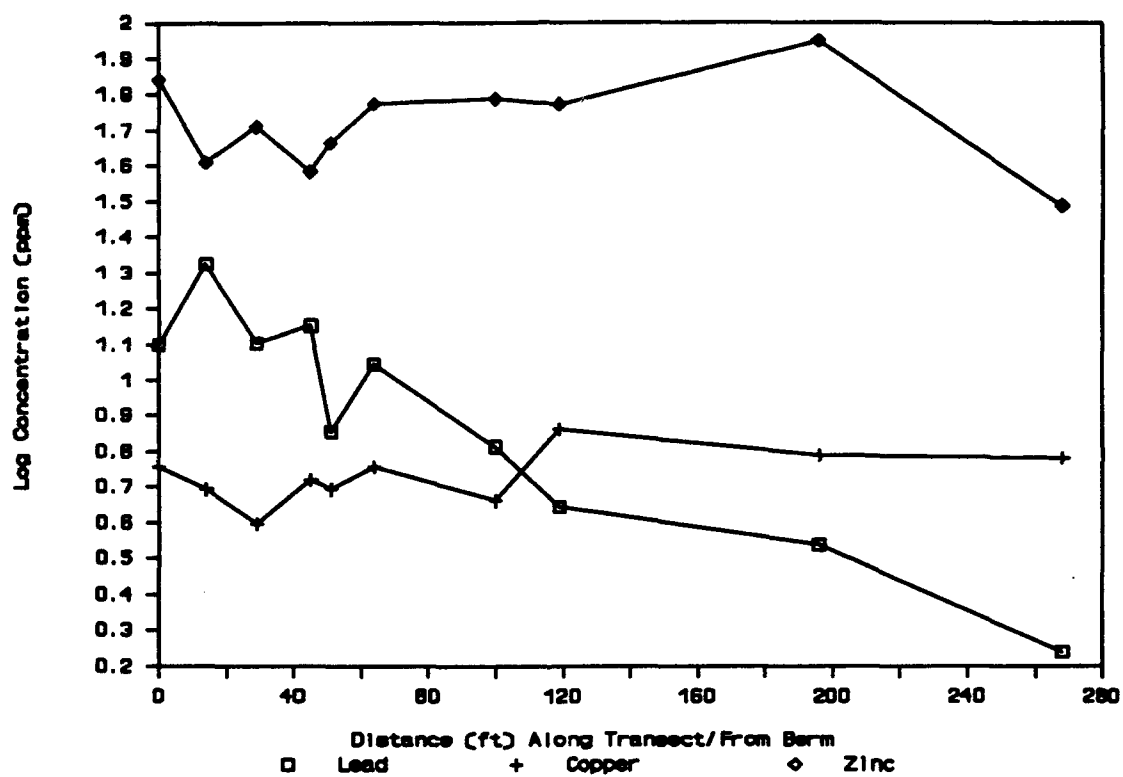
The lead concentrations found in the vegetation along the backside transect, shown in Figure 9, decreased with greater uniformity than the levels in the soil, Figure 5. Levels of heavy metals in vegetation are dependent upon the quantity of bioavailable, not total, lead in the surrounding environment. Bioavailability is closely related to the solubility and mobility of the species present [27].

Thus, while Figure 5 shows that the total lead level of the soil was highly variable, Figure 9 indicates that the level of soluble soil lead may have had a more well defined relationship with distance from the berm. Precipitated, sorbed, and other particulate forms of lead would be subject to the irregular transport resulting from erosion. Soluble lead species, on the other hand, could be more uniformly transported from the berm through the soil-water matrix, partially as a result of dispersion.

However, due to the concomitant transport of soluble species in surface runoff, an unblemished relationship between distance and concentration would still not be expected. This effect seems to be demonstrated by the vegetative lead levels found along the downslope transect as shown in Figure 10. Unfortunately, the copper and zinc levels in the vegetation along the downslope transect did not decrease much at all and therefore, tend to weaken the validity of the explanation provided above.



**Figure 9: Lead Concentrations in Vegetation,
Backside Transect**



**Figure 10: Metal Concentrations in Vegetation,
Downslope Transect**

3.3.3 TCLP Lead Levels

As stated earlier, whether or not a lead contaminated soil is classified as a hazardous waste is dependent upon the quantity of lead that can be solubilized into a TCLP extract; the threshold concentration being 5 mg/L. Thus, knowledge of the TCLP lead levels of the soils at small arms ranges would be required to thoroughly assess the magnitude of the contamination problem. While Study A did not include any analysis using the TCLP method, Study B did provide some useful information.

Study B, completed in 1991, was conducted at the small arms range at the Naval Air Station, Mayport, Florida. The impact berm and the five sample points from this range are shown in Figure 11. At each point, sample cores were drilled to a depth of six feet. Each one foot interval of soil from the core constituted a sample. Accordingly, six samples were taken at each point for a total of 30 samples.

Horizontal cores were drilled at points 1, 2, 3, and 4 on the front face of the berm. Points 1 and 4 were located in the bullet pockets of their respective range positions. A vertical core was taken from point 5, located at the top of the impact berm.

Sample numbers used in this document correspond to points and intervals as follows: Sample number 3.2 was taken at point 3 from the second one foot interval (1 foot to 2 feet). Each sample was analyzed for the total and TCLP

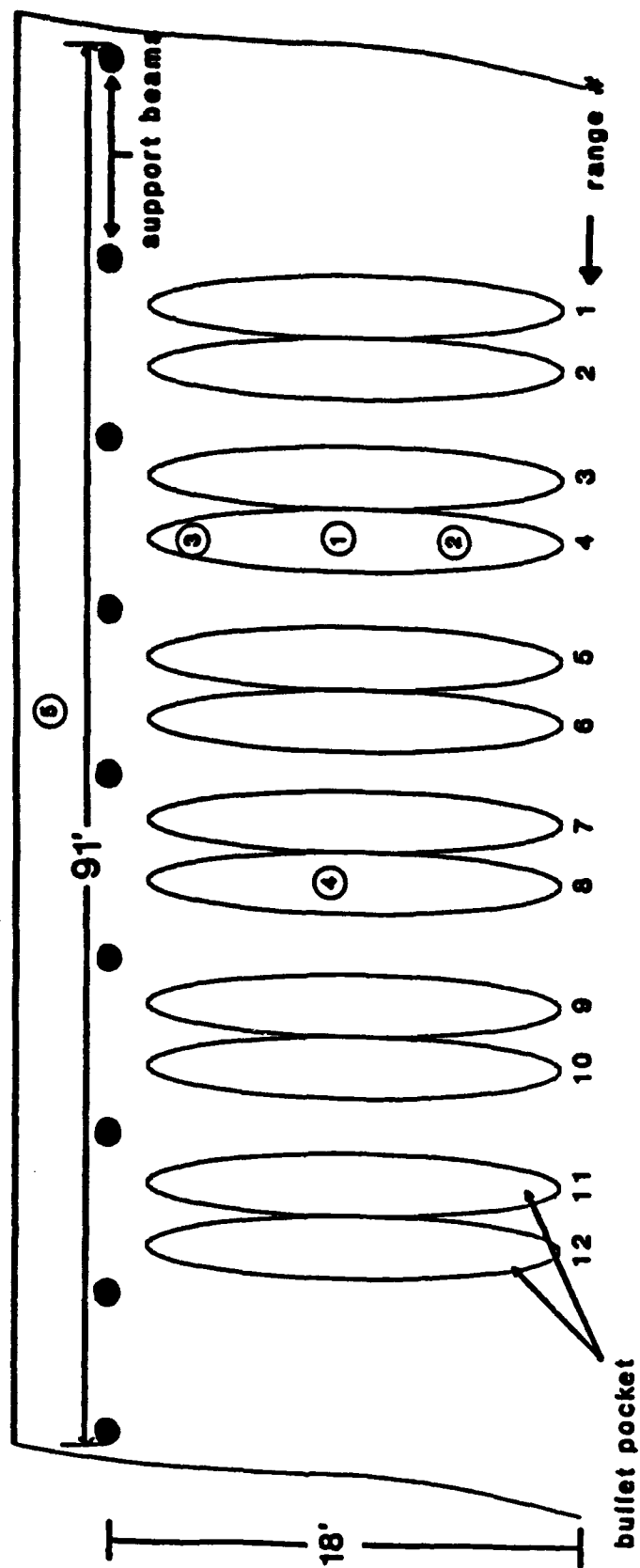


Figure 11: Study B Site and Sampling Plan [25]

levels of lead, copper, and zinc. Six of the samples were also analyzed for pH and yielded an average value of 8.4. The overall analytical results are provided in Appendix A.

Of the 30 samples analyzed, 28 produced TCLP lead levels in excess of the 5 mg/L threshold. Over half of the samples had TCLP lead concentrations of at least 100 mg/L. For comparison, the TCLP levels for both copper and zinc were all less than 5 mg/L and only 4 of the 60 values obtained were greater than 2 mg/L.

Figure 12 plots the TCLP lead levels as a function of the total lead concentration. The corresponding linear regression line is also plotted although the associated value for R-squared is only 0.39. The absence of a significant linear relationship between the TCLP and total lead levels is evident. It is further evident that TCLP lead levels in soil must be determined by direct analysis and cannot be predicted from total lead concentrations.

3.3.4 Lead in Waters

The analysis of surface or ground waters for lead contamination was not included in either Study A or Study B. Therefore, other references must be cited to document the potential for such contamination to result.

Groundwater in the vicinity of the small arms range at the Naval Amphibious Base, Little Creek, Virginia was sampled in February 1989 [1]. The groundwater sample was

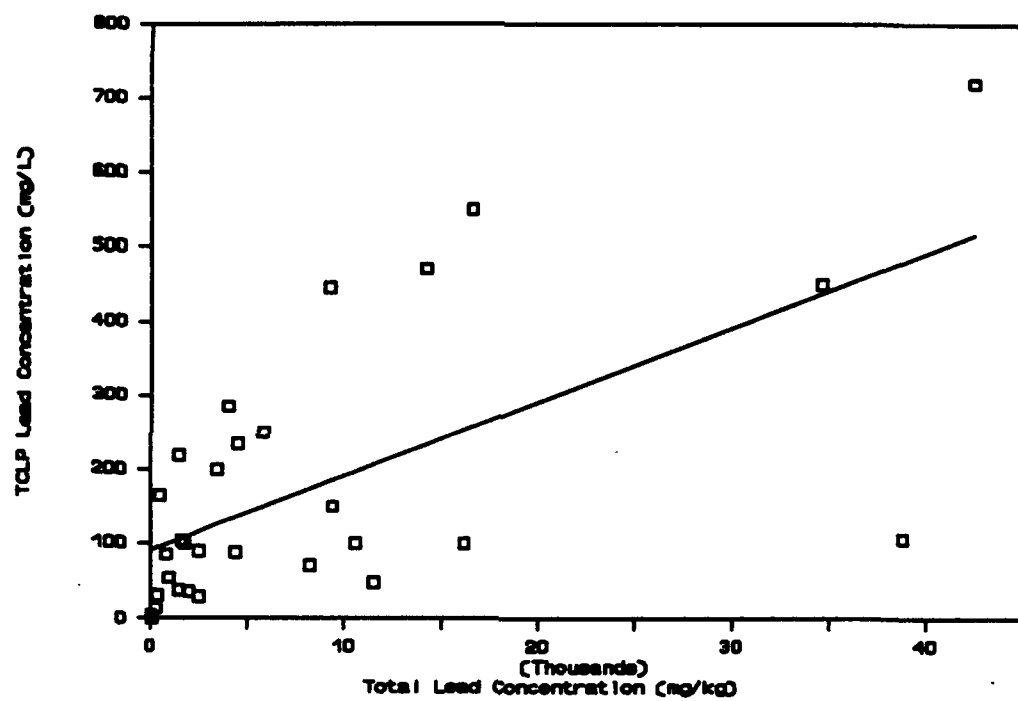


Figure 12: Relationship Between Total and TCLP Lead Content

taken at a horizontal distance of approximately 100 feet from an impact berm at a depth of 11 feet. The sample was found to have a lead content of 0.083 mg/L.

The lead concentration of a groundwater sample taken beneath a shooting range in Helsinki, Finland was found to be 0.405 mg/L [28].

A surface water sample taken from a marsh located in the fall zone of a trap and skeet range was found to have a lead concentration of 1.27 mg/L [29]. This water also had a pH of 6.3 and a total alkalinity of 20.5 mg/L as CaCO_3 . The outlet stream from this marsh had a lead content of only 0.0013 mg/L which was partially attributed to its higher pH of 7.0 and greater alkalinity of 33.9 mg/L as CaCO_3 .

Due to the paucity of data, the water contamination resulting from small arms ranges cannot be well defined. However, the data that does exist indicates that the contamination of natural waters is a realistic concern.

3.4 Findings

The operation of a small arms range can result in the release of significant levels of lead contamination into the surrounding environment. The lead is initially concentrated in the impact berms and is then spread into adjoining soils. Transport mechanisms include erosion, advection by the flow of both surface and subsurface waters, and dispersion through the soil water matrix.

The soil lead concentration does decrease, although not uniformly, with distance from the source, the impact berm. Excessive soil lead levels, greater than 1000 ppm, have been found at distances of more than 100 feet. Significant levels, greater than 100 ppm, were found more than 200 feet from the berm.

Total lead levels as low as 269 ppm have produced TCLP extracts with concentrations exceeding the 5 mg/L threshold established by RCRA. The quantity of soil at an individual range that could either require treatment or be subject to RCRA's hazardous waste disposal regulations is considerable.

The concentrations of copper and zinc in the soils at small arms ranges are not comparable to those of lead. In consideration of the relatively low levels of these metals, in addition to the fact that they are not explicitly subject to RCRA requirements, copper or zinc contamination does not appear to be a significant environmental or legal concern.

Sufficient data does not exist to evaluate the level of lead contamination in the surface or groundwater systems in the vicinity of small arms ranges. However, the potential for such contamination has been documented and should be the subject of further investigation.

The laws and regulations governing the disposition of lead contaminated soils at small arms ranges must be clearly defined. Cost effective control technologies to remediate the lead contamination need to be identified or developed.

Chapter 4

CONTROL AND TREATMENT TECHNOLOGIES

To properly manage the environmental impacts that could result from the operation of a small arms range, the alternative approaches available must be delineated and evaluated. The approaches to be addressed in this document can be broadly categorized as no action, preventive action, immobilization, separation, and disposal.

4.1 Evaluation Criteria

The EPA evaluation criteria for technologies used to remediate soil contamination at Superfund sites are as follows: Compliance with the Applicable and Relevant or Appropriate Requirements (ARARs); long-term effectiveness; reduction of toxicity, mobility, or volume; short-term effectiveness; implementability; and cost. While these criteria may not officially apply to the contamination at small arms ranges, they can be used, at least in part for that purpose.

The above criteria could result in the selection of different control technologies if applied to ranges with differing conditions. For example, a range that was resulting in the current and ongoing contamination of a nearby stream would probably not warrant the same approach as a range that was being subjected to closure. Thus, this

document will not identify a single technology to be applied to all small arms ranges. Rather, pertinent aspects of various alternatives will be presented here for future consideration with respect to distinct sites.

4.2 No Action

In many cases, the best possible course of action available may be to do nothing. Several conditions would need to be established for the no action alternative to prevail.

First, a ricochet hazard could not exist. Ricochets would never be of concern at an abandoned range. At active ranges, it would only be a matter of time before a ricochet hazard materialized. However, until that time, no action may remain a viable alternative.

If ricochets became a problem, some effort would be necessary to eliminate the hazard in order to continue range operations. A common temporary solution has been to add an additional layer of soil to the berm. The effectiveness of this approach would diminish over time, necessitating a more long-term strategy. Eventually, handling of the berm soil would be required to eliminate the ricochet problem.

Secondly, the migration of lead contamination into surface waters could not be allowed. Contamination of surface waters with lead transported by overland flow and/or through the soil water matrix could cause the range to be

deemed a nonpoint pollution source. At the same time, identifiable storm water discharges from small arms ranges could be classified as point sources of pollution and require a permit under the National Pollution Discharge Elimination System (NPDES). The transport of excessive lead levels through either point or nonpoint sources could constitute a violation of the Clean Water Act regulations and necessitate mitigating efforts.

The migration of lead into groundwater systems, as well as into surface waters, used as drinking water supplies may make it difficult or impossible for the associated treatment facility to continue to meet the drinking water standards for lead content. The continued use of the affected water supply would thus, necessitate some remedial activity at the small arms range.

Abandoned ranges meeting the above conditions may still need to be reported under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The requirement for further action would only be determined if a Remedial Investigation/Feasibility Study was completed.

The closure of an active small arms range could cause the lead contaminated soil to be considered a waste. Any range soil with a TCLP lead content greater than the 5 mg/L threshold would be further classified as a hazardous waste and, unless properly treated, would be subject to the RCRA

disposal requirements. The closure of an installation could invoke the identical sequence of events.

Although the costs associated with the no action alternative are minimized, they are not eliminated. Costs for the sampling and analysis of soils or waters would be incurred in almost all cases. Additional costs associated with physical restrictions such as fencing or signage could also be necessary.

In addition to minimal cost, the no action alternative has other advantages including the possibility of maximizing short-term effectiveness. All of the other alternatives have some potential to increase the mobility, at least initially, of the lead contamination present. Subsequently, the natural environment, public health, and especially the site workers would all experience an increased risk of exposure. With no action, the worst case scenario is that the site would continue its present course.

One final advantage of the no action alternative is that it leaves other alternatives open for future consideration. This would not be the case with, for example, an immobilization technology, which could make pump and treat technologies more difficult to implement in the future. Preserving the implementability of various alternatives could prove critical as contamination is mobilized by advanced weathering, changing environmental conditions, or other chemical transformations.

4.3 Immobilization Processes

Immobilization processes employ systems which solidify the waste mass, eliminate free liquids and stabilize the contaminants in their least soluble form [30]. The overall objective is to minimize the rate of leaching. These processes often involve chemical addition to physically solidify the soil and chemically bind the contaminants.

Immobilization processes are plagued with a number of inherent problems. One major concern is that the lead contamination would remain in the soil and could be mobilized at a future time. Additionally, the physical condition of the soil may not accommodate all otherwise potential uses of the land. Both of these problems could restrict future development and utilization of the site.

4.3.1 Soil Capping

Capping involves the installation of an impermeable barrier over the contaminated soil to restrict access and reduce infiltration of water into the soil [31]. A variety of cap designs and materials are available, although those conforming to the RCRA landfill closure requirements have been most commonly used. The capping of an impact berm and the surrounding area would not be as effective as the capping of a landfill due to the absence of a proper liner.

The cost of the capping would vary with the design and the area of the site. However, in a 1985 application for a

four acre RCRA hazardous waste landfill permit, the cost of the cap was estimated at \$6.00 per square foot [31].

One major limitation to the installation of a cap is that it would not be compatible with continued use of the small arms range. Therefore, this option could only be considered when closure of the range is intended.

4.3.2 Stabilization and Solidification

In 1986, EPA documented distinguishing definitions for stabilization and solidification processes [32].

Stabilization was to refer to techniques that reduce the hazard potential of a waste by converting the contaminants to their least soluble, mobile or toxic form; without necessarily altering the physical characteristics of the contaminated medium. Solidification was to refer to various techniques that encapsulate a waste in a monolithic solid of high structural integrity, and do not necessarily involve any chemical interactions with the contaminants. However, many of the processes employed actually include aspects of both techniques thus, they will be discussed jointly as S/S.

While in situ S/S processes are still considered innovative, two specific techniques being evaluated under the Superfund Innovative Technology Evaluation (SITE) Program hold promise for treatment of lead contaminated soils [31]. International Waste Technologies and Geo-Con, Inc. have developed a proprietary chemical and demonstrated

its application with a deep soil mixing system that can be used in almost any soil type. Seiko, Inc. has developed a technology that injects chemical agents and blends them with contaminated soils by means of multi-axis, overlapping, hollow-stem augers. This technology, which produces a monolithic block down to the treatment depth, has not yet been demonstrated.

Most ex situ S/S processes employed in the United States are based on the chemistry of lime or cement [33]. Lead contaminated soil would be excavated and mixed with portland cement or lime along with other pozzolans such as fly ash, pumice, kiln dust, and blast furnace slag. The soil mixture would be incorporated into the cement matrix and may also undergo chemical changes that further limit the mobility of lead. With the high pH of the cement mixture, above 11, lead would most likely be converted to its least soluble form, lead hydroxide, $Pb(OH)_2$. The leaching of lead would then be minimized.

The application of a S/S process to impact berm soil should probably be done on an ex situ basis. Pretreatment of the soil in the form of mechanical sieving to remove large bullet fragments would be desired. Accordingly, the cost of excavation would be incurred before the S/S efforts were initiated. To avoid the creation of a ricochet hazard, the treated material could not be excessively solidified and then returned to the impact berm for further use.

4.3.3 In Situ Vittrification

In situ vittrification is a thermal process by which contaminated soil can be converted into a glass residual. Field application requires the insertion of large electrodes into the soil and the generation of intense heat by passing a strong current through the electrodes. Volatiles emitted during the process must be captured at the surface for further treatment. After the process is terminated and the ground has cooled, the fused waste material will be dispersed into a chemically inert and stable crystalline form that has very low leachability and almost the same chemical stability of granite [34].

Several concerns have been identified with this technology, including: It is very energy intensive, specialized equipment and personnel are required, volatilized contaminants are difficult to control, and it has not been effectively demonstrated for heavy metals [31]. Accordingly, the application of an in situ vittrification process to the remediation of a contaminated small arms range would probably be premature at this time.

4.4 Separation Processes

Separation processes could also be performed on either an in situ or ex situ basis. Although in situ processes may be less expensive to implement, acceptable results may be more difficult to obtain. The in situ processes discussed

here fall under the category of soil flushing while the ex situ processes can be classified as soil washing.

Separation processes are often preferred by regulatory authorities because they physically remove the contamination from the natural environment. Also to the pleasure of the regulators, separation processes make resource recycling possible, if not convenient. The major risk associated with this technology is that at some time after completion of the remediation, contaminant leaching may be resumed.

4.4.1 Soil Washing

Soil washing is a solvent based process for scrubbing soils ex situ to remove undesirable contaminants. Removal is achieved either by dissolving or suspending contaminants in the wash solution or by concentrating them into a smaller volume of soil through particle size separation.

An acid leaching process developed by the U. S. Bureau of Mines may prove capable of effectively treating lead contaminated soils [35]. This process converts lead sulfate and lead dioxide to lead carbonate, which is solubilized in nitric acid. Lead sulfate, a potentially marketable commodity, is subsequently recovered from the solution by precipitating with sulfuric acid. Bench scale studies on lead contaminated soils from battery recycling sites have produced favorable results; Extraction Procedure Toxicity levels of less than 1 mg/L.

While showing great promise, the acid leaching process may result in the release of toxic oxides of nitrogen and does require over 70 hours of process time. Thus, an alternative process was developed to solubilize and recover lead [36]. In this process, lead sulfate is initially converted to lead carbonate. Acetic acid and oxygen are then used to convert the carbonate and elemental lead to lead acetate. Lead dioxide is also converted to lead acetate by manganese acetate. In the final step, lead acetate is precipitated and recovered as lead sulfate.

In bench scale studies of dosed soils, more than 80% of the lead content was recovered [36]. The treated soil had a TCLP lead content of 3 mg/L; less than the 5 mg/L threshold. The process required six hours if lead dioxide was present; otherwise, it took only 90 minutes.

Both the acid leaching and the acetic acid processes could seemingly be adapted to treat lead contaminated soil from impact berms at small arms ranges.

4.4.2 Soil Flushing

In soil flushing, the contaminated soil is flooded with an appropriate washing solution. The elutriate is collected in a series of shallow wellpoints or drains, treated, and recycled back to the site. Contaminants are mobilized into the solution by solubilization, formation of emulsions, or chemical reactions with the flushing solution [34].

Both acidic and basic flushing solutions have been identified for use with metals. A treatment scheme that removes metals from the elutriate by precipitation and is followed by land application could prove to be cost effective [34].

The possible mobilization of contaminants away from the site as a result of soil flushing processes must be taken into consideration. Coupled with the lack of evidence that soil flushing could effectively treat lead contaminated soils, the process cannot be recommended without further research.

4.5 Off-Site Disposal

The disposal alternative is applicable to almost all site conditions although it may be cost prohibitive for sites with more than minimal volumes of contaminated soil. If the TCLP lead content of the soil exceeds the 5 mg/L threshold, disposal would have to comply with the RCRA hazardous waste regulations which would further increase the cost.

The major inherent problem with disposal is that rather than eliminating the contamination, it simply transfers the contaminants to another location. For this reason, disposal has been severely restricted by regulators and would be negatively perceived by the community.

4.6 Preventive Measures

Efforts to mitigate lead contamination at a small arms range could be taken either before or after construction of the range facility. Before construction, proper planning and design could prevent the occurrence of contamination. After the start of operations, measures could be implemented to prevent the further spread of contamination.

4.6.1 Runoff Controls

Even if a range has been in operation for some time, it may still prove worthwhile to implement storm water runoff controls. If the soils around the impact berm have not been contaminated beyond the hazardous waste limits, runoff controls could permanently prevent those limits from being exceeded and significantly reduce future remediation requirements. Runoff controls could also prevent initial or continued discharges into natural surface waters.

Runoff controls could be installed in the form of a filter designed to remove particles from the storm water flow. Such filters would limit erosion and thus, curb the transport of lead and other particulate metals away from the site. Depending on the design of the filter, colloidal and suspended contaminants could also be removed from the flow stream. Additional research efforts would be required to identify or develop filters or other runoff control devices to be used in this capacity.

4.6.2 Design Innovations

Future initiatives to plan, design, and construct range facilities and equipment must take potential environmental impacts into consideration.

Proper planning would include selection of an appropriate site. Locations conducive to groundwater recharge should be avoided. Site selection should similarly refrain from areas which generate runoff destined for natural surface waters. Exposure pathways to humans and other biological receptors should be identified and minimized to the best extent possible.

The design innovations that could be made are too numerous to be thoroughly discussed within the scope of this document. However, the general nature of some possible design improvements are as follows: Impact berms could be replaced with structures designed to capture bullets in much the same way that indoor ranges operate. Less dramatically, impact berm materials, including soils, could be selected to maximize cation exchange and adsorptive capacities and to minimize infiltration and leaching. Leachate collection systems could be installed to prevent percolation and groundwater recharge and to facilitate treatment. Impact berms could be covered to minimize precipitation and any subsequent hydrologic activities. Finally, ammunition could be manufactured of materials that are not as hazardous as lead.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

Localized lead contamination can and, in at least some cases, does result from the operation of a small arms range. The soils in and surrounding a range's impact berms or fall areas are most susceptible to contamination. The soil lead content does decline, although not uniformly, with distance from the impact berm.

Lead migrating through the soil water matrix was found to extensively contaminate the soil in close proximity to the berm and then quickly taper off with distance. Lead contamination transported by erosion and surface runoff was found to result in more uniform soil contamination over a greater distance. Accordingly, runoff and erosion controls can effectively reduce the total volume of soil contaminated and thus, reduce potential treatment requirements and costs.

The available data pertaining to the lead content of natural waters in the vicinity of small arms ranges was inadequate and therefore, could not be used as the basis for any definitive conclusions. However, the potential for water contamination was displayed and is a suitable topic for further research.

Copper and zinc, the other metals commonly found in ammunition, were not sufficiently concentrated in the range environment to warrant additional analysis or concern.

Owners of both active and abandoned ranges should assess the hazards present at individual range facilities. The levels of contamination at and around the range should be identified along with all potential exposure pathways in order to estimate the overall risk introduced by the range. Subsequently, any required corrective actions and their criticality could be determined.

Various control technologies are available for the remediation of lead contaminated soils. Soil washing methods preceded by mechanical sieving are currently the most promising.

Several preventive measures, including runoff controls, could be implemented at new ranges to minimize subsequent contamination and the associated need for remediation.

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Appendix A
ANALYTICAL RESULTS

Table 2: Metal Concentrations, Study A, Control Site

Notes: All Concentrations in PPM

A - Soil Horizon A

B - Soil Horizon B

V - Vegetation

	L E A D			C O P P E R			Z I N C		
STAT	A	B	V	A	B	V	A	B	V
MEAN	26.0	31.9	1.12	6.92	4.94	4.78	19.2	13	41.6
MIN	12.5	11.5	0.71	4.16	2.73	3.87	13	10.7	33.3
MAX	37	103	1.55	10.3	6.62	5.45	26.8	19.2	68.6
STDV	9.5	35.6	0.31	2.2	1.4	0.58	4.8	3.1	12.2

Table 3: Metal Concentrations, Study A, Berm Transect
Notes: All Concentrations in PPM
 A - Soil Horizon A
 B - Soil Horizon B
 V - Vegetation

SAMPLE NUMBER	L E A D			C O P P E R			Z I N C		
	A	B	V	A	B	V	A	B	V
122	5534	4421	125	1619	1139	11.4	294	294	92.8
123	2587	897	117	1090	487	8.72	98.7	155	72.3
124	347	316	27.2	96.4	137	13	53.6	60.2	50
125	161	393	20.3	61.7	152	6.93	84.4	70.1	45.2
126	460	87.7	20.1	82.1	71.6	6.54	63.7	71.9	52.8
MEAN	1818	1223	61.9	590	397	9.3	119	130	62.6

Table 4: Metal Concentrations, Study A, Backside Transect

Notes: All Concentrations in PPM
FEET - From Beginning of Transect
A - Soil Horizon A
B - Soil Horizon B
V - Vegetation

FEET	L E A D			C O P P E R			Z I N C		
	A	B	V	A	B	V	A	B	V
2	5534	4421	125	1619	1139	11.4	294	294	92.8
10	1558	2787	70.8	477	478	8.48	476	198	56
22	6677	4680	71.8	1020	1799	7.7	160	199	119
30.5	2691	464	39.2	844	260	8.88	61.7	117	156
37.5	3035	1672		1952	839		257	246	
56	4112	316	10.9	1137	210	7.51	99.1	63.3	92.2
117	135	17.5	6.15	68.9	13	5.14	47.3	25.6	62.9
214	28.9	17.9	3.38	12.1	11.1	4.3	30.8	30.4	39.8
253	46.9	18.5		46.2	19.9		35.5	28.3	
MEAN	2646	1599	40.9	797	530	6.7	162	134	88.4

Table 5: Metal Concentrations, Study A, Downslope Transect

Notes: All Concentrations in PPM

FEET - From Beginning of Transect

A - Soil Horizon A

B - Soil Horizon B

V - Vegetation

FEET	L E A D			C O P P E R			Z I N C		
	A	B	V	A	B	V	A	B	V
0	344	490	12.6	105	195	5.69	61.4	58.2	69.3
14	759	2589	21.1	166	746	4.94	71.1	165	40.7
29	1450	439	12.7	167	96.9	3.96	75.5	88.4	51.2
45	201	220	14.2	160	103	5.26	76.7	70	38.2
51	1191	1107	7.19	154	149	4.94	66.9	71.1	46
64	62.8	23.6	11.1	31.6	25.4	5.72	31.2	19.8	59.4
100	1099	2298	6.5	190	398	4.58	65.2	84.8	61.2
119	1915	217	4.42	304	87.1	7.3	114	113	59.15
196	102	49.8	3.46	40.7	43.8	6.15	188	96.4	88.9
268	258	276	1.73	42.6	18.2	6.04	26.7	30.4	30.7
MEAN	738	771	9.5	136	186	5.5	77.7	79.7	54.5

Table 6: Total and TCLP Lead Concentrations, Study B**Notes: Total Concentrations in PPM****TCLP Concentrations in mg/L**

SAMPLE	LEAD		COPPER		ZINC	
	TOTAL	TCLP	TOTAL	TCLP	TOTAL	TCLP
1.1	5800	250	110	2	17	0.5
1.2	14200	470	260	1.8	40	1.2
1.3	16200	100	468	1.3	68	1.6
1.4	9200	445	125	2	26	1.1
1.5	1740	100	3740	0.6	218	0.2
1.6	1985	36	21	0.7	4	0.1
2.1	42400	720	65000	0.5	4200	3.6
2.2	34600	450	1200	0.7	180	4.1
2.3	4000	285	320	7	56	1.9
2.4	8200	70	348	4.8	59	1.6
2.5	3450	200	60	2	14	0.4
2.6	40	4	4	0.1	2	0
3.1	2500	28.9	30	0.2	2	0
3.2	50	0.9	4	0.1	0	0
3.3	269	14	8.3	0.2	7.7	0
3.4	11500	48	230	0.8	40	1.1
3.5	9400	150	72	1	19	0.5
3.6	470	165	13	0.4	5	0.2

(continued on next page)

Table 6 (continued)

4.1	16600	550	8100	1.9	900	1.3
4.2	4400	8834	140	2	18	0.5
4.3	38800	107	132	1.9	28	0.6
4.4	2490	90	126	0.9	32	0.6
4.5	10600	100	660	0.9	72	0.4
4.6	4530	235	2380	1	237	0.4
5.1	1600	104	220	1.4	26	0.6
5.2	1500	220	90	0.8	12	0.2
5.3	370	30.1	10	0.2	0	0
5.4	1460	36.7	14	0.3	0	0
5.5	790	85.4	300	0.5	27	0
5.6	940	53.9	10	0.5	0	0.4