

Appendix F

**Lead Fate and Transport Study**

(Environmental Assessment of Lead  
at Camp Edwards, Massachusetts Small Arms Range, 2007)

# Environmental Assessment of Lead at Camp Edwards, Massachusetts Small Arms Ranges

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## ABSTRACT

Environmental issues for small arms training with lead projectiles are examined in this report for Camp Edwards located at the Massachusetts Military Reservation (MMR), in order to evaluate whether past or future use of lead in small arms has or will result in lead mobilization to groundwater. A review of relevant literature and case studies demonstrates lead is toxic to humans and wildlife and, therefore, exposure must be minimized. The literature also demonstrates lead mobilization occurs chiefly by wind and surface water erosion, generally not by dissolution and leaching through soil. Environmental conditions at Camp Edwards dictate that wind and surface water are not primary avenues of transport, due to extensive vegetative cover and highly permeable soils. Highly permeable soils limit corrosion of metallic lead but also can facilitate transport for dissolved forms of lead. Because highly permeable soils favor transport, a careful analysis of the geochemical conditions with respect to lead vertical transport to groundwater was a focus for this study. It is the conclusion of this study that, lead has not contaminated the groundwater in any significant way based on the absence of lead plumes and only one groundwater monitoring well associated with the small arms ranges had a single low lead detection < 2 ppb. In addition, this conclusion is supported by a careful analysis of the geochemistry of lead and conditions under which lead is mobile as well as site-specific data. Specifically, Camp Edwards has

1. Soil conditions that are not sufficiently acidic to readily dissolve metallic lead,
2. High soil permeability, low chloride and soil resistivity of surface soils, conditions not favorable for the rapid corrosion of lead,
3. High degree of lead adsorption based on non site-specific column studies as well as site-specific soil profiles, unsaturated zone monitoring, and aquifer studies, and
4. Depth to groundwater more than 30m in those areas where training is to be resumed.

Recognizing both the lack of sufficient data to quantify the ability of Camp Edward's soils to immobilize lead, knowing the soil's ability to immobilize lead is finite, and given its toxicity, range design and maintenance programs to limit lead exposure are prudent. Although these activities are not addressed in this document, they will be addressed in the range specific pollution prevention plans. Minimizing erosion and surface water runoff is a necessary step for preventing environmental exposure. Other measures to consider, include, but are not limited to periodic removal of metallic lead particles from ranges and backstop-berms, and addition of treatment agents highly effective for immobilizing lead.

It is important to emphasize this evaluation was based upon information readily available through literature and site specific information. This study contains recommendations for additional studies which would help further refine these conclusions. However, these studies would be useful for the ongoing monitoring of range operations.

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## **PREFACE**

This report was prepared by Jay L. Clausen, Biogeochemical Sciences Branch (BSB), U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire.

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The Commander and Executive Director of the ERDC is Colonel Richard B. Jenkins. The Director is Dr. James R. Houston.



## ABBREVIATIONS

AO2	Administrative Order #2
bgs	below ground surface
Cd	cadmium
CEC	cation exchange capacity
cm	centimeter
Co	cobalt
Cu	copper
DOC	dissolved organic carbon
Demo 1	Demolition Area 1
DOM	dissolved organic matter
DPASV	Differential Pulse Anodic Stripping Voltammetry
Eh	Oxidation reduction potential
EDTA	ethylenediaminetetraacetic acid
ERDC-CRREL	US Army Corps of Engineers, Engineer Research and Development Center-Cold Regions Research and Engineering Laboratory
ER&C	Environmental and Readiness Center, Camp Edwards
$g/m^2$	grams per meter squared
$H^+$	hydrogen ion
IAGWSP	Impact Area Groundwater Study Program
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ITRC	Interstate Technology and Regulatory Council
$K_d$	partitioning coefficient
$(KFe_xPb_x)SO_4(OH)_6$	jarosite
kg	kilograms
m	meters
MAARNG	Massachusetts Army National Guard
MassDEP	Massachusetts Department of Environmental Responsibility
meq	milliequivalent
mg/g	milligrams per gram
mg/kg	milligrams per kilogram (parts per million [ppm])
mg/L	milligrams per liter
ml/g	milliliters per gram
mm	millimeter
MMR	Massachusetts Military Reservation
$Mn^{2+}$	manganese anion
Ni	Nickel
OH	Hydroxide
Pb	Lead
$Pb^{2+}$	Lead (II)
$PbAl_3(PO_4)_2(OH)_5(H_2O)$	Plumbogummite
$PbCO_3$	Lead carbonate (cerussite)
$Pb_3(CO_3)_2(OH)_2$	Hydrocerussite

Pb(OH) <sub>2</sub>	Lead oxide
Pb <sub>4</sub> O(PO <sub>4</sub> ) <sub>2</sub>	Lead oxyphosphate
Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Lead phosphate
Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	Chloropyromorphite
Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH)	Hydroxylpyromorphite
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	Hydroxypyromorphite
PbS	Lead sulphide (galena)
PbSO <sub>4</sub>	Lead sulfite (anglesite)
pH	Acidity
PAVE PAWS	Perimeter Acquisition Vehicle Entry Phased-Array Weapons System
RCS-1	Reportable Concentration Soil-1
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
SAAMI	Sporting Arms and Ammunition Manufacturing Institute
SAR	Small Arms Range
SDZ	surface danger zone
SESOIL	Seasonal Soil Compartment Model
TOC	total organic compound
TCLP	toxicity characteristic leaching procedure
µg/L	micro grams per liter (parts per billion [ppb])
µM	micro Molar
µmhos	micro ohms per centimeter squared
US	United States
USACE	U.S. Army Corps of Engineers
USAEC	U.S. Army Environmental Command
USAF	U.S. Air Force
USEPA	U.S Environmental Protection Agency
USDA	U.S. Department of Agriculture
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
µSXRF	Microfocused Synchrotron-based X-ray Fluorescence
yd <sup>3</sup>	cubic yards
Zn	zinc

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## EXECUTIVE SUMMARY

### Purpose

Military testing and training ranges are vital for preparing military troops for combat and maintaining readiness. There are increasing concerns that a reduction in United States (US) military readiness will result if training range usage is restricted. Nonetheless, range managers must balance range activities so training can proceed without the environmental consequences associated with repeated release of undesirable residues. The objectives of this study are to provide the Massachusetts Army National Guard (MAARNG) an assessment of the fate of lead on the small arms ranges (SARs) at Camp Edwards. The principal question considered is whether resumption of training with lead projectiles will have an undesirable environmental impact such as vertical migration to groundwater (> 30 m) underlying the training ranges. The approach for satisfying the objective consists of 1) general assessment of the geochemistry of lead and identification of conditions where lead migration is favorable, 2) description of the geochemical conditions at Camp Edwards and whether the environment is conducive for lead migration, and 3) evaluation of existing lead data at Camp Edwards focusing particularly on data available from the SAR.

### Small Arms Ranges

The configuration of a SAR consists of 1) a firing point where the soldier fires the weapon, 2) the range floor, down range from the firing point, 3) targets which can be located on the floor or at the end of the range, and 4) typically a primary berm backstop located behind the targets. Over the last decade, SAR design has evolved to incorporate range sustainability concepts such that berms serve both a safety and environmental function by concentrating the lead in a small area. The height of the berm can vary from a few meters up to 10 m. Sometimes a trough to collect surface water runoff is located at the base on the front side of the berm.

Once a projectile ejects from the bore of the weapon, it travels towards the target. Because of scouring of the projectile in the weapon barrel, a small amount of copper (if the bullet is copper-jacketed) and/or lead (unjacketed projectile) may be deposited near the firing point. In addition, small quantities of propellant powder and lead styphnate used in the primer may also be released. On SARs where a primary berm backstop exists, the projectile impacts the berm in a heads-on manner. The two mechanisms at work to scrub energy to stop the projectile are displacement of soil particles and fragmentation. Eventually, all of the energy is dissipated, and the projectile comes to rest.

The lead within the berm is subject to wind and water erosion and corrosion/dissolution processes. At Camp Edwards, surface water runoff or overland flow is usually unimportant because of the coarse soil texture and high soil permeability. Corrosion processes are also relatively slow at Camp Edwards because the coarse soils limit ponding and are low in chloride.

Although some shotgun training will occur; in general, the projectiles used are thought to result in mostly large fragments having a relatively small surface area thereby further limiting corrosion/dissolution. Nonetheless, all projectiles are abraded to some extent such that some small, high-surface area particles will also be present. Thus, as the lead content in the surface soil increases, removal activities may be prudent. MAARNG plans to manage the lead by performing best management practices as outlined in the Pollution Prevention Overview (Small Arms Range Supplement) which follows US Army guidelines.

Ecological receptors of concern at shooting ranges include invertebrates, fish, mammals, and birds. Although rifle ranges have been implicated in certain studies where lead toxicity has been observed, nearly all confirmed examples of harm to terrestrial species are with lead shot. The highest risks have been predicted for small mammals and birds ingesting lead shot incidentally while feeding or intentionally as grit. Research has demonstrated mortality for some small mammals and birds may result from the ingestion of a single lead pellet. Similar to shot, lead abraded from a bullet is immediately available for transport by water and wind and for bioaccumulation, but many rifle projectile fragments are too large for ingestion. For example, one investigation reported only 1.5% of a 22-caliber non-jacketed bullet was abraded when fired into a bucket of sand. In addition, research has shown large fragments are relatively stable - within 6 to 13 years, only 5 to 17% of metallic lead was corroded in lead shotgun pellets and after a period of 20 to 25 years, an average of only 5 to 16% of metallic lead in pellets had been transformed to lead carbonates ( $\text{PbCO}_3$  and  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ) and lead sulfate ( $\text{PbSO}_4$ ). The size of the particles is a function of the caliber of the projectile as well as the soil type, i.e. coarser soils result in finer lead particles and greater smearing onto soil. Finally, the distance to the target will also affect the particle size because the velocity/momentum at impact will decrease with distance.

### **Lead Geochemistry**

Lead is a relatively immobile element in the terrestrial environment. Soils may have solutions supersaturated with respect to cerussite ( $\text{PbCO}_3$ ), hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ), lead oxide  $\text{Pb}(\text{OH})_2$ , lead phosphate  $\text{Pb}_3(\text{PO}_4)_2$ , lead hydroxyapatite  $\text{Pb}_5(\text{PO}_4)_3(\text{OH})$ , and lead oxyphosphate  $\text{Pb}_4\text{O}(\text{PO}_4)_2$ . Lead phosphate minerals, in particular, are so sparingly soluble, thermodynamic data predicts these phases will control dissolved lead in soil solution under the geochemical conditions commonly found in natural systems. Under reducing conditions in which sulfate is reduced to sulfide, lead may be sequestered in galena ( $\text{PbS}$ ), which has a solubility in natural waters too low to measure by conventional technology. Consequently, under the normal range of soil pH and redox conditions, aqueous lead concentrations should generally be limited to low parts-per-billion levels, through precipitation reactions.

In addition to forming a range of stable mineral phases in both oxygen-rich and oxygen-poor environments, lead can bind to mineral surfaces directly and can form adsorption complexes on

surfaces of quartz, humus, iron oxides, aluminum oxides, manganese oxides, and virtually any mineral with oxygen or sulfur atoms at the surface.

Localized regions with potentially high lead levels will be present at firing ranges at lead accumulation areas or adjacent to corroding lead particles. Any elevated dissolved lead however, is expected to remain localized because sparingly-soluble mineral precipitates will form or the lead will be adsorbed onto the soil matrix. Consequently, in highly contaminated soils, aqueous lead levels may be elevated in or near the location where deposition occurred.

### **Camp Edwards Characteristics**

Camp Edwards surface soils are coarse-grained and typically classified as sandy loams and loamy sands. These soils permit rapid recharge of percolating water and facilitate air exchange with the atmosphere. Recent samples from several SAR impact berms were evaluated for soil pH which ranged from 6.2 to 7.4 with a median value of 6.5. Total organic carbon levels across the site range from 31 to 247,000 mg/kg, with a mean of 11,050 mg/kg. A few soil horizons have a more developed organic layer present but in most locations, an organic-rich surface soil is absent. Clay-sized particles (traces in most samples) and cation exchange capacity (8 to 10 meq/100g), factors affecting sorption processes, are low in the surface soils and lower still in deeper soils. Finally, soils have low concentrations of soluble salts (e.g. base cations such as calcium and magnesium as well as sodium and chloride) because these ions have been removed by leaching. Taken together, these characteristics yield an environment in which leaching of dissolved species can occur rapidly although the corrosion potential for metals is relatively low. Nevertheless, the most significant factors with respect to lead remain its propensity to form sparingly soluble precipitates and to adsorb to relatively inactive surfaces such as pure quartz.

The small arms training ranges lie directly over the Sagamore Lens, a major groundwater recharge area and the most productive portion of the Cape Cod Aquifer. The apex of the Sagamore Lens is located at the southeast corner of the Impact Area from which groundwater flows radially in all directions. The thickness of the unsaturated zone varies from 18 to 37 m across most of the area with 30 m being typical for the SARs. Surface water runoff is limited to a few hundreds of meters at most because of the highly permeable nature of the sand and gravel underlying the area.

### **Camp Edwards Data**

Over 9,000 soil samples have been collected and analyzed for lead across Camp Edwards to date. These data indicate an overall sporadic distribution pattern but elevated levels do coincide with the firing lines and target areas of the SARs. However, little or no migration to the subsurface is evident. The locations (firing lines, targets) where lead is highest are consistent with firing range data obtained elsewhere. The maximum concentrations at Camp Edwards

(~12,000 mg/kg), however, are lower than have been reported at many other military installations probably because larger lead fragments were physically removed, in 1999 as part of the Lead Berm Maintenance Project.

Many Camp Edwards samples with elevated lead have been subject to the Toxicity Characteristic Leaching Procedure (TCLP) - a test to determine whether the sample is hazardous under the Resource Conservation and Recovery Act. In general, TCLP-lead concentrations were greatest in the upper 1 m of the berm face, a finding consistent with the presumed penetration depth of small caliber projectiles. Based on this finding, several SARs in 1999 were selected for a treatment process consisting of the application of a liquid reagent - Maectite - a phosphate developed to chemically bond to lead within the soil matrix creating geochemically stable precipitates. Several thousand cubic meters of soil were also removed. Subsequent monitoring of soil pore water underneath these treated areas indicates no significant migration of dissolved lead.

Thirteen additional monitoring wells were installed in the fall of 2006 downgradient and near the berm face for several SARs. These wells have been sampled twice since installation and to date have had no consistent reportable lead detections. There is only one groundwater monitoring well (MW-72S) associated with the SARs with a single low detection - ppb range. These results indicate lead has not migrated to groundwater at the maintained ranges that have been monitored, including two at which training with lead ammunition began in 1935.

Finally, several modeling approaches have been used to evaluate lead mobility at Camp Edwards. Modeling of lead is problematic because of the difficulty of predicting corrosion and of including precipitation reactions. Indeed, modeling to date has conservatively assumed complete dissolution and has ignored precipitation. Nevertheless, the models predict the time for lead to migrate from the surface to the water table is several hundred centuries.

## **Conclusions**

This report has assessed the fate of lead released into the environment at Camp Edwards from firing at SARs. The principal conclusions are; corrosion and dissolution processes are sufficiently slow and mechanisms for attenuation, such as precipitation and adsorption, sufficiently robust, that lead has not migrated to groundwater. These conclusions are supported by the following facts:

1. Multiple soil profile samples collected prior and post-berm maintenance from six SARs indicated little vertical migration of lead,
2. Geochemical conditions within the surface soils, (e.g. pH, chloride, resistivity, permeability, and oxygen) are not conducive for significant corrosion, dissolution, and transport of lead,

3. Experimental results from other studies with conditions similar to Camp Edwards showed minimal lead movement,
4. Experimental results from other studies consistently demonstrate such high and variable measurements for lead partition coefficients that modeling exercises typically have uncertainties on the order of centuries in their predictions,
5. Geochemical studies found in the literature suggests the propensity to form sparingly soluble precipitates, and not sorptive capacity, may be the most important factor controlling lead migration in the subsurface,
6. The corrosion/dissolution rate, although qualitatively predicted to be slow, cannot be quantified because of several uncertainties ranging from uncertainty regarding the particle size distribution to the effects of wet/dry cycles,
7. Unsaturated zone modeling using two different software codes predicted the vertical migration of lead would take centuries to reach groundwater,
8. Water samples from most monitoring wells (except MW-72S) installed immediately downgradient of the backstop berms at a number of SARs showed no measurable lead,
9. Groundwater data collected to date from across Camp Edwards demonstrated little to no lead contamination as a result of accumulation from small arms training, despite lead being continuously released to soil for more than 60 years,
10. Tracer studies conducted by the US Geological Survey near Camp Edwards demonstrated an aqueous form of lead was rapidly adsorbed onto the soil, implying the same reactions will attenuate lead movement in the unsaturated zone, and
11. Lead introduced into the groundwater near Camp Edwards in a sewage treatment effluent was rapidly and completely attenuated.

The technical literature, however, clearly describes dangers to humans and wildlife exposed to lead. Although lead mobility is limited at Camp Edwards, the data collected to date is inadequate to quantify the amount of lead that can be safely deposited in the environment. It is important, therefore, to minimize environmental exposure through the application of best management practices.



## 1.0 Introduction

Military testing and training ranges are vital for preparing military troops for combat and maintaining readiness. There are increasing concerns that a reduction in United States (US) military readiness will result if training range usage is restricted. Nonetheless, range managers must balance range activities so training can proceed without the environmental consequences associated with repeated release of undesirable residues.

US Army/National Guard soldiers have trained with small arms ammunition containing lead on Cape Cod since 1908, and specifically at Camp Edwards since its opening in the mid 1930's until 1997. In 1997 the U.S. Environmental Protection Agency (USEPA), through Administrative Order #2 (AO2), banned training with lead projectiles at Camp Edwards due to concerns about lead mobility. Consequently, training with a tungsten/nylon projectile (5.56 millimeter [mm]) began in 1999. In February 2006, the Massachusetts Army National Guard (MAARNG) discontinued training with the tungsten/nylon projectile because of concerns about tungsten's environmental mobility and unknown toxicity. These circumstances have resulted in an inability of National Guard units to perform qualification testing as part of their training. Consequently, the MAARNG has commissioned this study to assess the environmental consequences of resuming training with lead projectiles at Camp Edwards.

Moreover, the MAARNG desired identification of engineering controls effective at eliminating migration of lead from the small arms training ranges. An example of a successful project of this type occurred in 1998 under MAARNG and the Impact Area Groundwater Study Program (IAGWSP) in response to AO2. Soil was removed from the small arms range (SAR) berms and large metallic lead fragments were separated using a soil washing technique. The soil was then treated with Maectite™, which bound up any dissolved lead into a sparingly soluble lead phosphate complex, and the treated soil was placed back on the berm.

### 1.1 Objective

The objectives of this study are to provide MAARNG an assessment of the fate of lead on the SARs at Camp Edwards, i.e. will lead have an undesirable environmental impact such as vertical migration of lead away from those SARs located over deep (> 30 meters [m]) groundwater. The methodology for meeting the objective consists of 1) general assessment of the geochemistry of lead and identification of conditions where lead migration is favorable, 2) description of the geochemical conditions at Camp Edwards and whether the environment is conducive for lead migration, and 3) evaluation of all existing lead data at Camp Edwards focusing particularly on data available from the SARs.

## 1.2 Small Arms Ranges

The purpose of a SAR is to allow training with weapons of a small caliber, i.e. handgun, rifle, shotgun, or machine gun. The distance from the firing point to the target can vary from 10 to 1,000 m. The layout of SARs consists of several different configurations depending on the training intent.

The configuration of a SAR consists of a firing point where the soldier fires the weapon. Down range from the firing point is the range floor. The targets can be located on the range floor or near the end. In some configurations, such as known distance ranges, the targets are located in a line spanning the width of the range. This layout typically has a primary berm backstop, originally installed for safety purposes, located behind the targets. Over the last decade, SAR design has evolved to incorporate range sustainability concepts such that the berm serves both a safety and environmental function by concentrating the lead in a small area. The past practice for berm construction involved material scraped from the range floor, although materials can be brought in from elsewhere. The height of the berm can vary from a few meters up to 10 m. Sometimes a trough to collect surface water runoff is located at the base of the front side of the berm. Another layout has a series of pop-up targets located at varying distances. In either configuration, the range is orientated in such a manner that the projectiles travel towards an impact area.

## 1.3 Conceptual Model

Small arms' firing introduces lead projectiles, other projectile-related metals (e.g. copper), and propellant residues into the environment. Most of the ammunition fired on military SAR consists of a steel penetrator followed by the lead/antimony slug, with a propellant cartridge and ignition cap on the end with the entire assembly jacketed with a copper alloy. The copper alloy consists of copper, lead, and zinc, which are used in the jacket as well as cup primer and case (MIDAS 2007). The ignition cap contains compounds of antimony, barium, lead (lead styphnate), and potassium.

Not all small arms projectiles have a copper jacket such as some pistol and shotgun cartridges which contain bare slugs or balls. Copper-jacketed projectiles are used in high-velocity and automatic weapon systems. Projectiles can be solid such as the lead/antimony core or filled with tracer or incendiary materials. Tracers are used to determine the direction of fire and contain barium, magnesium, potassium, strontium, and zinc compounds (MIDAS 2007). Perchlorate is also used in some tracer rounds such as the .50 cal and could be released at the firing point, range floor, and impact berm.

Once the projectile ejects from the bore of the weapon, it travels towards the target. Because of scouring of the projectile in the weapon barrel, a small amount of copper and/or lead (unjacketed projectile) may be deposited near the firing point. Small quantities of propellant and lead styphnate used in the primer (MIDAS 2007) may also be released. Propellant constituents include nitroglycerin, nitrocellulose, dibutyl phthalate, and diphenylamine (MIDAS 2007). The first three compounds may be released at the firing point. Diphenylamine is an unstable compound and upon exposure to soil will oxidize to form N-nitrosodiphenylamine. Ideally, the projectile should travel straight along the firing lane to the target, where it is deposited intact (or nearly so) into the primary berm backstop. However, projectiles can miss the target but still hit the berm. In some cases, a projectile may hit the berm face and be deflected or in rare instances, may miss the berm entirely.

On SARs where a primary berm backstop exists, the soldier faces the berm and the projectile impacts the berm in a heads-on manner. Most constructed berms, including those at Camp Edwards, are made of soil derived from the installation or of sand and gravel. The two mechanisms at work to scrub energy to stop the projectile are displacement of soil particles and fragmentation. In sandy soils, displacement of soil particles allows a lead projectile to penetrate a meter or less into the berm. Eventually, all of the energy is scrubbed, and the projectile comes to rest, buried within the soil matrix.

Consequently, the working hypothesis is elemental lead may be found as particles attached to pieces of the bullet jacket, as pieces of intact slug material, or as small particles adhered to larger soil particles. Based on field reconnaissance, both intact projectiles with intact copper jackets as well as fragments of copper jacket material, steel penetrators, and chunks of lead can be found; however, a small quantity of fragments, too small to be readily-visible, are also produced. Once introduced into the environment, metallic lead oxidizes (rusts) resulting in the formation of lead salts on the metallic lead surface (Scheetz 2004). Rainfall encountering the lead salts dissolves a small portion, which can travel with the infiltrating water into the soil. The solubility of the salts is low, which limits mobility. Any remaining dissolved lead reacts with the soil matrix resulting in the precipitation of various less-soluble lead species and sorption of lead onto soil particle surfaces. The capacity of soil for lead sorption is not infinite, but in some cases, the mass of lead introduced into the environment and subsequently dissolved is negligible compared to the sorptive capacity of the soil. The only two studies found reporting lead in deep groundwater were the result of human introduction of lead directly to the groundwater following shock chlorination (Seiler 2006) or from the use of lead counterweights in water-level recorders (Kaste et al. 1999). Thus, lead migration typically is limited to a few meters in the vertical direction. In the case of Camp Edwards, the working hypothesis is soluble lead is immobilized under natural processes within a few meters of the soil surface.

In summary, Figure 1 (modified from Morton, undated) represents the processes by which lead could be mobilized at a SAR. At Camp Edwards, however, surface water runoff or overland flow is usually limited because of the coarse soil texture and high soil permeability, see Section 3. Similarly, the projectiles used and planned to be used in the future will result in mostly large fragments (Larson *et al.* 2006, Fackler 2007). Metallic lead will build up in surface soil or berm material with time, however, and removal activities may be necessary. MAARNG plans to perform best management practices to manage the lead, which are outlined in a Pollution Prevention Plan for Camp Edwards Small Arms Ranges (URS 2006) which follows US Army guidelines (USAEC 2005).

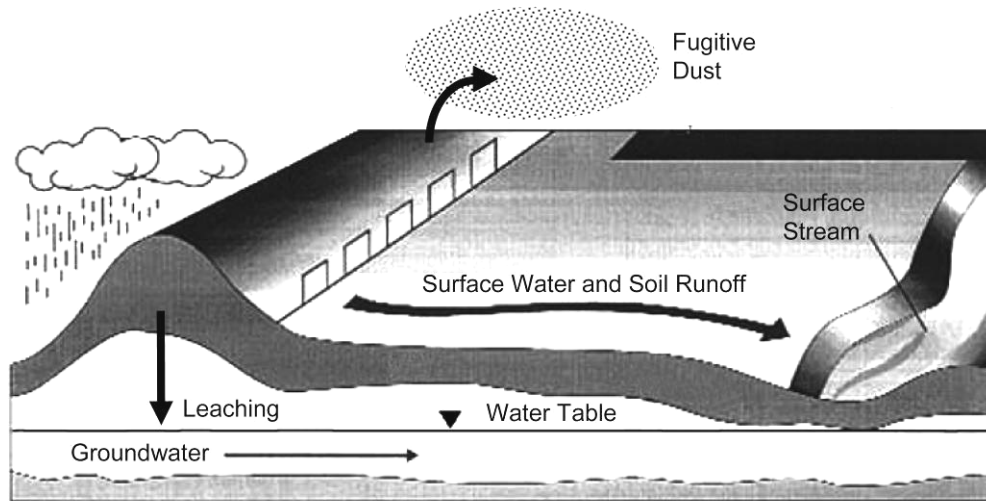


Figure 1. Conceptual site model of physical transport processes associated with a shooting range.

As will be discussed in Section 2.3.3 deposition of lead such as that introduced from firing small arms will result in immobilization within the soil through sorption processes.

## 1.4 Environmental Issues at Small Arms Ranges

Firing of projectiles at a SAR results in the introduction of metal to the environment. Typically, the primary environmental concern is with the introduction of metallic lead and the potential exposure to biota.

### 1.4.1 Lead Transport

The Sporting Arms and Ammunition Manufacturing Institute (SAAMI 1996), U.S. Air Force (USAF 1998), U.S. Army (USAEC 1998, 2005) and Interstate Technology and Regulatory

Council (ITRC 2003, 2005) have summarized the major geochemical processes affecting lead transport at shooting ranges as adsorption/desorption and precipitation/dissolution. The SAAMI report further concludes the relative influence of adsorption/desorption is approximately one order of magnitude (10 times) greater than precipitation/dissolution. Indeed, a review of these reports indicates lead transport occurs most easily by surface water and wind erosion and not by migration through soil. These processes and their relevance at Camp Edwards are discussed in detail in Sections 3 and 4. Surprisingly, very few published studies have evaluated the migration of lead in the soil profile and even fewer the migration to groundwater with the few conducted demonstrating limited lead movement. Numerous journal articles on lead research and lead reports make the statement that lead is problematic due to the potential migration of lead (Astrup *et al.* 1999, Craig *et al.* 2000, USEPA 2005a, Sorvari *et al.* 2006), however only a few studies demonstrate the limited movement of lead in the environment (Murray *et al.* 1997, Craig *et al.* 1999, Rooney *et al.* 1999, Cao *et al.* 2003a, Soeder and Miller 2003).

#### **1.4.2 Toxicity**

Lead is toxic to humans and wildlife because it affects the function and structure of a vertebrate's kidney, bone, central nervous system, and hematopoietic system and produces adverse biochemical, histopathological, neurophysical, fetotoxic, teratological, and reproductive effects (Eisler 1988, Schulz *et al.* 2006). For these reasons, the USEPA's action level for lead in water delivered to users of public drinking water systems is 15 micrograms per liter ( $\mu\text{g/L}$ ) but the goal for lead is zero. The USEPA has also established 400 milligrams per kilogram ( $\text{mg/kg}$ ) for lead in residential soils as a guidance value for protection of public health based on an analysis of the direct ingestion pathway for children. Presently, the Massachusetts Department of Environmental Protection (MassDEP), Method 1 S1/GW1 cleanup standard, applicable for sites state-wide with unrestricted use is 300  $\text{mg/kg}$ . As discussed subsequently in this report, most uncontaminated soil contains less than 50  $\text{mg/kg}$ , but soil lead levels and road and house dusts in many urban areas exceed 200  $\text{mg/kg}$  or more (Fergusson and Kim 1991). The MADEP lists several different mean background values for Massachusetts soils, which range from 15 to 100  $\text{mg/kg}$  (MassDEP, 2007).

Ecological receptors of concern at shooting ranges include invertebrates, fish, mammals, and birds. Typical risk assessments predict unacceptable levels of risk from lead for raptors, small (e.g. mice), and large (e.g. fox and deer) terrestrial mammals (Peddicord and LaKind 2000, USEPA 2003). The highest risks have been predicted for small mammals and birds ingesting lead shot incidentally while feeding or intentionally as grit (Peddicord and LaKind 2000). The predicted adverse effects on small mammals and birds are supported by the literature, which has shown mortality may result from the ingestion of a single lead pellet (Ma 1989, Roscoe *et al.* 1989, Hoffman *et al.* 2000, Vyas *et al.* 2000). Similarly, Hunt *et al.* (2006) reported that a minute

quantity of fragments dispersed in deer carcasses are highly-toxic to wildlife. Additional information is available from the USEPA ECOTOX database (USEPA 2003).

Waterfowl mortality due to the ingestion of lead shotgun pellets was documented as early as 1874. Additionally, large volumes of lead shot accumulate in terrestrial ecosystems such as shooting areas, firing ranges, and clay-pigeon shoots where they can be directly ingested by a range of terrestrial birds (Vyas *et al.* 2000, Lewis *et al.* 2001). Thus, studies that are more recent have examined terrestrial avian species. For example, of 157 doves fed 2 to 24 lead shot pellets, 104 died prior to the conclusion of the study while all 22-control doves survived (Schulz *et al.* 2006). Similarly, lead poisoning has been blamed for the loss of California Condors. A study of Condor mortality was unable to identify, with certainty, the source of lead but included military rifle ranges at Camp Roberts and Fort Hunter Liggett as possibilities (Fry 2003). In the latter instances, the proposed exposure route was through bioaccumulation. In other words, raptors feeding on rodents from lead-contaminated sites eventually consumed too much lead themselves. The study suggested other raptors are as susceptible to lead poisoning as are condors. A 1988 report by the U.S. Fish and Wildlife Service (USFWS 1988) documented lead poisoning in 31 avian species other than waterfowl while a more recent report raised the number to 59 (Fisher *et al.* 2006). The latter report notes, "While bans on the use of lead shot for hunting waterfowl will inevitably reduce the likelihood of poisoning of raptors that prey on or scavenge waterfowl, they do nothing to prevent the poisoning of raptors that feed on hunted species away from wetlands, or those that feed on a range of avian and mammalian prey." Fisher *et al.* (2006) concludes, "It is clear that the only practical way of removing the risk of lead poisoning from ammunition to avian species is to replace the use of lead with non-toxic alternatives, for all hunting and other purposes, and in all habitats. Until this happens, large numbers of birds, some of which are already of unfavorable conservation status, will continue to die from lead poisoning."

A study with respect to lead's toxicity to plants has been mixed. ITRC (2005) has proposed methods for mitigating lead impacts to closed ranges and the U.S. military has been assessing methods to manage and cleanup SARs (USAEC 1998, 2005) due to lead's toxicity to wildlife. One approach being evaluated, phytoremediation, involves the growth of plants which bioaccumulate lead (Fry 2003). Greenhouse studies indicate plants could accumulate significant lead (Behel *et al.* 1998) but field studies have been inconclusive. Apparently, sub-optimal growing conditions on most ranges and the relatively low bioavailability of particulate lead significantly inhibit bioaccumulation in plants (Fry 2003). Limiting vegetative bioaccumulation may be a viable approach for minimizing lead exposure to ecological receptors.

### **1.4.3 Environmental Exposure**

Although rifle ranges have been implicated in certain studies where toxic effects from lead have been observed, nearly all confirmed examples of harm to terrestrial species are with lead shot. Similar to shot, lead abraded from a bullet is immediately available for transport by water and wind and for bioaccumulation, but rifle projectile fragments are most likely too large for ingestion. Several studies have been conducted looking at grit uptake of birds and found that the size of grit selected is a function of the size of the bird. In general, birds prefer grit sizes less than 2 mm (Trost 1981, Pain 1990, Stafford *et al.* 1996, Peddicord and LaKind 2000). Hardison *et al.* (2004) reported only 1.5 percent of a 22-caliber non-jacketed bullet was abraded when fired into a bucket of sand. In addition, much research has shown large fragments are relatively stable. For example, within 6 to 13 years, only 5 to 17% of metallic lead was transformed in lead shotgun pellets (Jorgensen and Willems 1987) and after a period of 20 to 25 years, an average of only 5 to 16% of metallic lead in pellets had been transformed to lead carbonates ( $\text{PbCO}_3$  and  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ) and lead sulfate ( $\text{PbSO}_4$ ) (Lin *et al.* 1995). A large proportion of the fragments found on military SARs are typically larger than pellets and jacketed with copper (Clausen personal observation), however sand size particles and smaller can be found (Larson *et al.* 2006). The degree of projectile fragmentation and size of particles is likely a function of the caliber of the projectile, velocity of the fired projectile, distance to the target, as well as the soil type. Coarser soils result in finer lead particles and greater smearing onto soil particles (Larson *et al.* 2006) whereas higher projectile velocities and shorter distance to the target results in greater fragmentation (Fackler 2007).

## **2.0 Background**

### **2.1 Site Location**

The Massachusetts Military Reservation (MMR) is an approximately 22,000-acre facility located in the towns of Bourne, Falmouth, Mashpee, and Sandwich in Barnstable County, Massachusetts. The reservation is divided into two main installations: Camp Edwards, which is controlled by MAARNG, and Otis Air National Guard Base which is controlled by the Massachusetts Air National Guard and USAF. Other, smaller installations at MMR include the U.S. Coast Guard Air Station Cape Cod, Cape Cod Air Force Station (PAVE PAWS radar), and the Massachusetts National Cemetery.

Camp Edwards encompasses approximately 15,000 acres of land. The training areas include numerous active and inactive ranges, training sites, and a centrally-located artillery, mortar, and rocket impact area. Soldiers currently practice maneuvering exercises, bivouacking, and SAR training with the southern cantonment area comprised of a complex of administrative offices, maintenance and training facilities, troop housing, and other support facilities.

### **2.2 Massachusetts Military Reservation Range Use History**

The National Guard has been training since approximately 1908 on the Cape. In the 1940s, the installation was created and activated by the U.S. Army and used to train and deploy troops during World War II. The reservation was transferred to the Department of the Air Force after the Korean War and in the 1970s, the Army National Guard assumed operational control of Camp Edwards.

Historical use of ranges at Camp Edwards has been dictated by readiness needs for military forces and law enforcement agencies. The functions and use patterns of the training ranges over the years have varied to satisfy those needs. Many ranges have consequently been used for more than one type of training. Through a detailed search of archival information on historical range use, 34 sites at Camp Edwards were identified as having been used at one time or another for small arms training (USACE 1999a, 1999b, 2000). Subsequent reviews of range control records and site inspections revealed 17 of these ranges are still available for small arms training. In general, the modern, currently available SARs are positioned around the perimeter of the Impact Area with range fire directed inward towards the Impact Area (Figure 2). Each SAR has an associated surface danger zone (SDZ) which is an exclusion area identified to protect personnel from weapons firing during training. The SDZs on Figure 2 represents an area where a bullet, a bullet fragment or a ricochet could travel once fired. The SDZ represents a worse case scenario used for primarily for safety purposes in planning simultaneous operations



or activities in the range and training area. The SDZ represents the highly unlikely, however still possible, area which a bullet could travel once fired from a range. The SDZs do not account for containment systems that may be on a small arms range. Figure 3 shows the location of the small arms training ranges at Camp Edwards. The focus of this document is on those SAR available for training and does not include the Otis Fish and Game Ranges.

In response to changes in small caliber weapon systems use, SAR design at Camp Edwards has varied considerably over the decades. Modern range components, in general, include a level cleared range floor bordered by an up-range firing point and a downrange target line and earthen berm backstop constructed as a collection point for spent munitions. The number of firing positions along the firing point (which can be slightly elevated above the range floor) varies depending on the overall size of the range. Most of the available ranges also include a range control tower and target construction and repair facility. Many of the early SAR designs took advantage of natural topography and used hillsides as backstops rather than constructed berms.

Records indicate weapons used in small arms training at Camp Edwards have included pistols, rifles, machine guns, and shotguns with a variety of ammunition types fired. Rounds used in current outdoor training exercises are limited to plastic and blank ammunition. Future use of lead ball ammunition will likely include firing of 5.56, 7.62, and 9 mm, and .50 caliber projectiles as well as 00 Buckshot. Physical descriptions and use histories for each of the current and former SARs at Camp Edwards are presented in Table 1.

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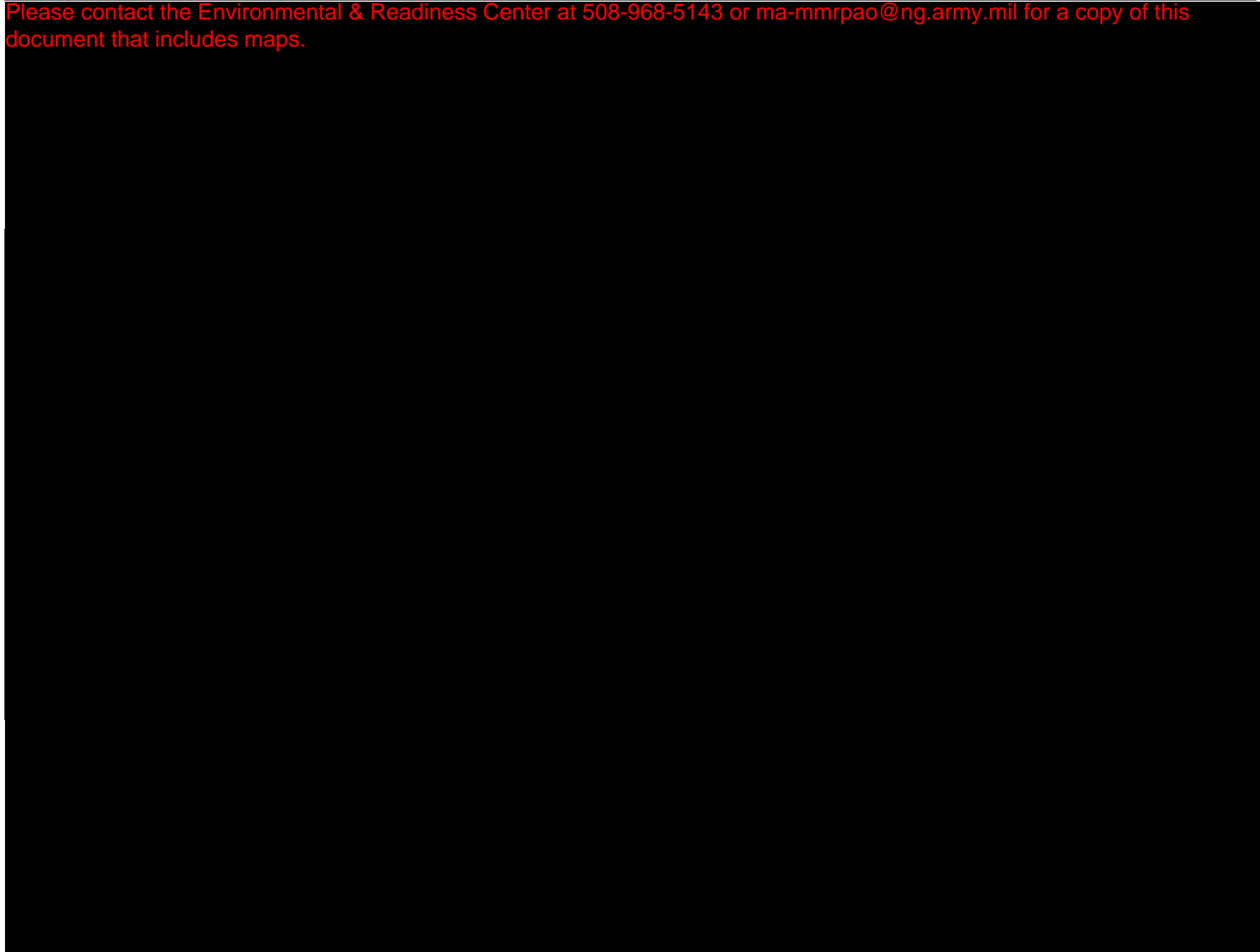


Figure 2. Small arms training range surface danger zones at Camp Edwards.

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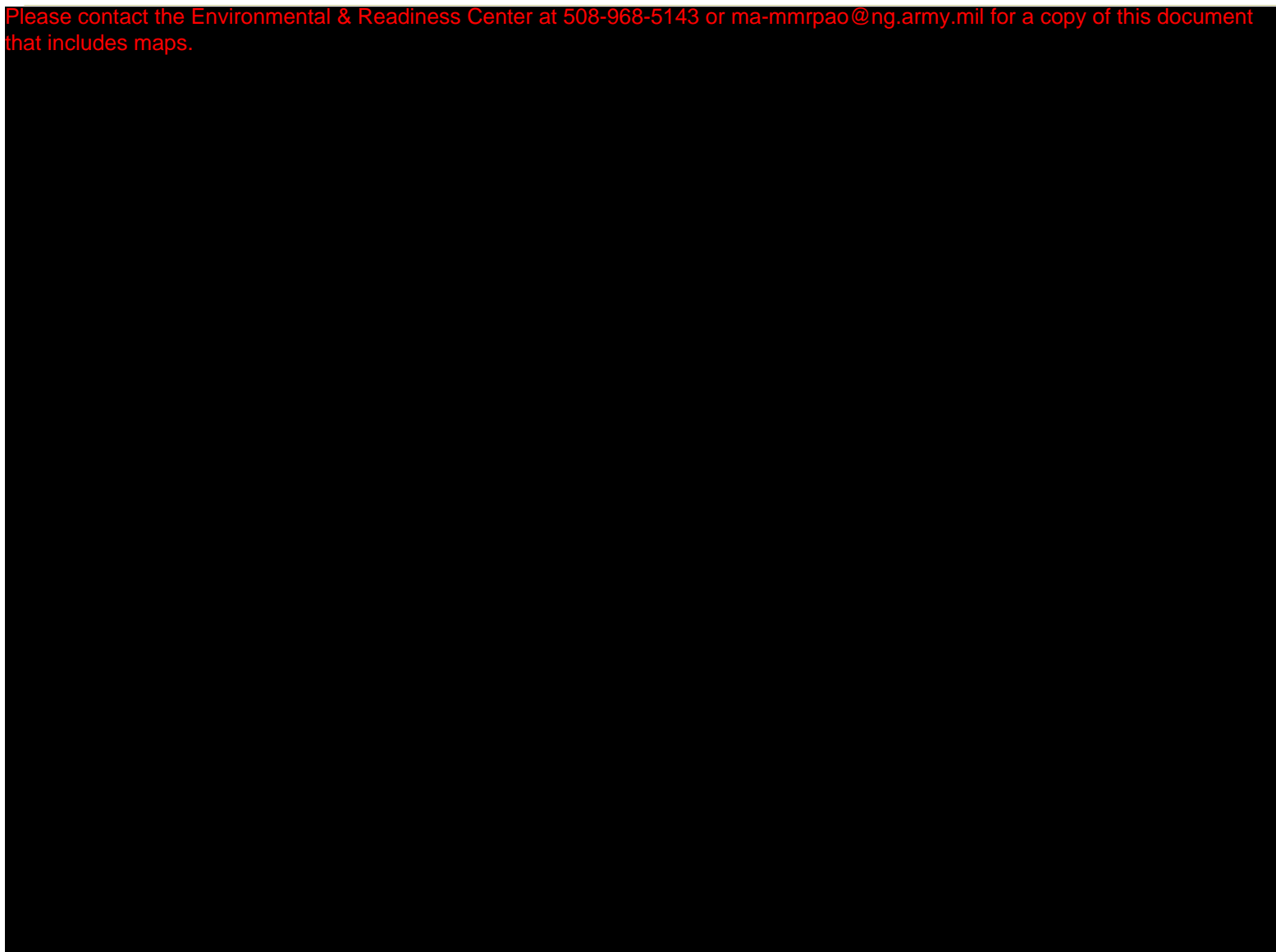


Figure 3. Small arms training ranges at Camp Edwards.

Table 1. Camp Edwards small arms ranges.

Range Name	Location	Period of Use	Training Activity	Authorized Ammunition	Inspection Observations
Current A	Burgoyne and Wood Road	Mid-1970s to present	M2 Machine Gun	.50 caliber plastic	2 fixed firing positions accommodating vehicle-mounted guns , numerous .50 caliber plastic projectiles downrange, natural embankment backstop
Current B	Burgoyne and Wood Road	1991 to present	M16 Rifle and Pistols	5.56 mm ball and tracer, .45 caliber and 9 mm ball	55 firing positions, targets at 25 m, numerous plastic projectiles on berm backstop
Current C	Burgoyne Road	1986/1989 to present	M16 Rifle and Pistols	5.56 mm ball and tracer, all pistol calibers	Identical to Current B Range except incomplete berm backstop
Current D	Burgoyne Road	1986/1989 to present	M60 Machine Gun	7.62 mm ball and tracer	8 firing positions, targets at 10 m, natural embankment backstop
Current E	Burgoyne Road	1986/1989 to present	Pistols	All pistol calibers	15 firing positions, pop-up targets, partial natural embankment backstop
Current G	Pocasset-Forestdale Road	Late 1980s to present	M16 Rifle, M249 SAW, Submachine Gun, Pistols, Shotgun	5.56 rifle and SAW ball and tracer, 7.62 mm ball and tracer, .45 caliber, 9mm, all pistol calibers	27 firing positions, targets at 25 m, numerous plastic rounds on berm backstop, metallic projectiles on downrange side of berm
Current H	Pocasset-Forestdale Road	Late 1980s to present	Identical to Current G Range	Identical to Current G Range	Identical to Current G Range

Range Name	Location	Period of Use	Training Activity	Authorized Ammunition	Inspection Observations
Current I	Pocasset-Forestdale Road	Late 1980s to 1991	Identical to Current G Range	5.56 mm ball and tracer, .45 caliber, 9 mm, All pistol calibers, shotgun	Identical to Current G Range
		1960 to Late 1980s (Old F Range)	Tank-mounted machine gun and rifle	.30 caliber, 5.56 and 7.62 mm ball	10 firing positions, moving target on rails, metallic projectiles on downrange side of berm
IBC	Gibbs Road		Rifle, Submachine Gun, Smoke Pyro	.22, 5.56 and 7.62 mm ball and blank, 40 mm smoke, 22 mm sub-caliber	5 maneuver lanes
Current J	Pocasset-Forestdale Road	Late 1980s to present	M16 Rifle and SAW, Submachine gun, Pistols, Shotgun	5.56 mm rifle and SAW, Submachine gun, .45 caliber, 9 mm, shotgun, all pistol calibers	8 firing positions, targets at 25 m, metallic .30, .40, .50 caliber, and 5.56 mm projectiles on downrange side of berm
		(Old Air Force A Range)	Pistols	.38 caliber	
Current K	Pocasset-Forestdale Road	Late 1980s to present	Identical to Current J	Identical to Current J	18 firing positions, targets at 25 m
		(Old Air Force B Range)	Pistols	.38 caliber	Approximately 30 firing positions
KD Small Arms Range	Pocasset-Forestdale Road	Mid-1980s to present	M16 Rifle and SAW, 7.62 mm Machine Gun and Rifle, Pistols, Shotgun	5.56 and 7.62 mm ball and tracer, .45 caliber, 9mm, all Pistol calibers, shotgun	35 firing positions on western side, targets at 25 m, 20 firing positions on eastern side with firing points positioned at 100 m, and 100, 200, 300, 400, and 500 ft from targets (mechanical)

Range Name	Location	Period of Use	Training Activity	Authorized Ammunition	Inspection Observations
		Mid-1970s (Old Aerial Gunnery Range)	CRT-1 and CRT-2		
Current N	Greenway Road	1986/1989 to present	Rifle, Pistols, Shotgun	5.56 mm ball and tracer, all Pistol calibers, Shotgun	55 firing positions, targets at 25 m, numerous plastic projectiles on backstop berm
Current O	Greenway Road	1986/1989 to present	Shotgun Familiarization, Pistols	Shotgun, all Pistol calibers	Bermed on four sides, firing points at 3, 5, 7, 10, 15, 25, and 50 yds from targets
Current P	Greenway Road	1986/1989 to present	Rifle, Pistol, Shotgun	5.56 mm ball and tracer, all pistol calibers, Shotgun	26 firing positions, targets at 25 m
S East	Gibbs Road	1986/1989 to present	Rifle and Machine gun	5.56 and 7.62 mm ball and tracer	Mounded firing point with 5 firing positions, targets at 100 through 800 m, no berm backstop
S West	Gibbs Road	1986/1989 to present	Rifle and Machine gun	5.56 mm and 7.62 mm ball and tracer	Mounded firing point with 5 firing positions, targets at 100 through 800 m, no berm backstop
Current T	Gibbs Road	2006-present	Rifle	5.56 mm	15 lane 25 bermed range with 1 STAPP installed, 6 dismantled firing positions and 4 mounted firing positions, targets up to 300 m downrange, numerous plastic projectiles, no berm backstop
		1990/1991 to 2006	Machine gun	.50 caliber	
		1967 to 1990/1991 (Old P Range)	Night defense/squad and platoon attack course	Blank only	
Former B	Monument Beach Road	1967 to early 1980s	1000-inch rifle	0.30 caliber, 5.56 and 7.62 mm	25 to 27 firing positions, combination hillside and constructed berm backstop, metallic projectiles and pockmarked boulders

Range Name	Location	Period of Use	Training Activity	Authorized Ammunition	Inspection Observations
		1955 to 1967	Pistol	0.38 and 0.45 caliber	Targets at 15 and 25 yds from firing point
		1935/1941 to 1955 (Former Machine Gun A Range)	1,000-inch machine gun and pistol	.30, .38, .45, and .50 caliber ball	
Former C	Frank Perkins Road	1950s to 1986/1989	1,000-inch Machine Gun	.30 caliber and 5.56 and 7.62 mm	55 firing positions, natural hillside backstop, numerous metallic projectile fragments and pockmarked boulders at top of slope
		1935/1941 to 1950s (Former Machine Gun B Range)	Machine Gun	.30 and .50 caliber ball and tracer	

Range Name	Location	Period of Use	Training Activity	Authorized Ammunition	Inspection Observations
Former D	Frank Perkins Road	Late 1980s to present	Pistol	All pistol calibers	Berm backstop in former parking area
		Early 1960s to late 1980s	Rifle	.30 caliber and 7.62 mm ball	44 firing positions
		1950s to early 1960s	1,000-inch machine gun	.50 caliber ball	20 firing positions
		1935/1941 to 1950s	Anti-Aircraft Miniature	.22 caliber ball	No constructed berm, numerous metallic projectiles found on surface downrange
GA/GB	Dolan Road	1935/1941 to 1950s	Rifle	.30 caliber ball	GA: 150 firing positions at 100 and 200 yds from target area, soil berm remnant with metallic projectiles. GB: 70 firing positions, targets at 100, 200, and 300 yds from target area
Former R	Gibbs Road	1967 to early 1980s	Squad battle assault course	.30 caliber and 7.62 mm	No discernable range remnants
Skeet 1	Howe and Turpentine Road (BA-1)	1940s	Shot gun skeet		Single fragment of clay skeet, no discernable range remnants
Succonsette Pond	Impact Area	Unknown	Machine gun	.50 caliber	No evidence of firing point, targets, or backstop found
M-1	Greenway and Pocasset-Forestdale Road	1940s	Submachine gun	.45 caliber	Remnants of 5 target frames, no evidence of firing point, no berm backstop
M-2	Original Greenway Road	1940s	Submachine gun	.45 caliber	Remnants of a former backstop berm and 30 target frames, numerous metallic projectiles on berm



## 2.3 General Lead Chemistry

Lead is the heaviest stable element on Earth and as a Group (IV) element has four valence electrons, but unlike carbon, germanium, and other members of this group, is mostly present in the oxidation state of (+2) in the environment. In surface waters, soils, and in the earth's crust, across the natural range of Eh (redox potential) and pH (measure of the acidity of a solution in terms of activity of hydrogen ( $H^+$ )) lead (II) is usually found as a hydrated  $Pb^{2+}$  cation, or as dissolved or solid compounds where it bonds directly to other inorganic species. There are also organo-lead compounds: where lead is most commonly in the tetravalent (lead (IV)) state. Organo-lead compounds have been synthesized for a variety of applications. Most notably, tetraethyl lead and tetramethyl lead compounds were used during the middle of the 20<sup>th</sup> century as antiknock additives in gasoline's and other fuels but their use has been discontinued. Tetravalent lead compounds are not very stable, and are found in very low abundance today, even in soils that were substantially impacted by gasoline containing lead-additive and other types of fossil fuel combustion (Shotyk *et al.* 2002).

Lead (II) or  $Pb^{2+}$  is a relatively immobile element in the terrestrial environment. In addition to forming a range of stable mineral phases in both oxygen-rich and oxygen-poor environments (Nriagu 1974, DeVolder *et al.* 2003, Jackson *et al.* 2005), lead (II) can form strong inner-sphere (lead binds to surface directly with no intervening water molecule) and outer-sphere (lead binding to surface within hydration shell) adsorption complexes on surfaces of quartz, humus, iron oxides, aluminum oxides, manganese oxides, and virtually any mineral with oxygen or sulfur atoms at the surface (Bargar *et al.* 1997a, 1997b, 1998, 1999, Xia *et al.* 1997, Sauvé *et al.* 2000a.). Dissolved lead phases can be some combination of  $Pb^{2+}$  and its hydrolysis species, lead bound to dissolved organic matter (DOM), and lead complexes with inorganic ligands such as chloride and sulfate anions. Eh and pH are two of the more important variables governing mobility, speciation, and potential toxicity of lead in the environment. Presence of ligands or organic matter in solution that can form complexes with lead can inhibit the precipitation of lead minerals and adsorption, thus allowing more lead to remain more soluble (Sauvé *et al.* 1998, Lang and Kaupenjohann 2003). Redox potential can be considered an indirect assessment of the amount of oxygen present. The presence of oxygen in soil and groundwater creates an oxidizing (aerobic) environment, whereas an absence of oxygen results in a reducing (anaerobic) environment. The concentration of dissolved lead species in soil solution, surface water, or groundwater is thus controlled by some combination of 1) lead mineral solubility equilibria, 2) adsorption reactions of dissolved lead phases on inorganic surfaces (e.g. crystalline or amorphous oxides of aluminum, iron, silica, manganese, clay minerals etc.), and 3) adsorption reactions of dissolved lead phases on soil organic matter (e.g. humus).

Anthropogenic activities have dispersed lead into the environment, causing the lead content of soils, vegetation, surface water, and many organisms to be elevated relative to natural (pre-

industrial) levels (Nriagu and Pacyna 1988, Nriagu 1990, Candelone *et al.* 1995). Ancient and recent atmospheric pollution associated with smelting, iron and steel foundries, the combustion of fossil fuels in automobiles, trucks, airplanes, and ships, the manufacturing of cement, and other industrial processes has dispersed lead to even the most remote environments on earth (Erel and Patterson 1994, Candelone *et al.* 1995, Kaste *et al.* 2003, Yanai *et al.* 2004, Van de Velde *et al.* 2005, Meena *et al.* 2006, Wang and Guo 2006). Furthermore, point sources of lead to the environment, such as building paint with lead additive, shooting ranges, pesticide applications, and mine tailings can result in lead loadings to the environment several orders of magnitude higher than normal (Adgate *et al.* 1998, DeVolder *et al.* 2003, Vantelon *et al.* 2005). Unfortunately, lead can be toxic to many soil fauna, vascular plants, small mammals, birds, and even humans as mentioned in Section 1 (Needleman *et al.* 1990, Nriagu *et al.* 1996, Bongers *et al.* 2004). Laboratory evidence suggests concentrations as low as 200 mg/kg can disrupt organic matter decomposition and associated nitrogen and phosphorous mineralization processes necessary for effective recycling of essential nutrients in ecosystems (Rühling and Tyler 1973, Ekenler and Tabatabai 2002).

### **2.3.1 Lead Immobilization in the Terrestrial Environment: Lead Minerals**

Given  $Pb^{2+}$  concentrations  $> 200 \mu\text{g/L}$ , a number of stable and sparingly-soluble minerals may precipitate (Figure 3). Neutral and alkaline soils may have solutions supersaturated with respect to cerussite ( $PbCO_3$ ), hydrocerussite ( $Pb_3(CO_3)_2(OH)_2$ ), lead oxide ( $Pb(OH)_2$ ), lead phosphate ( $Pb_3(PO_4)_2$ ), hydroxylpyromorphite ( $Pb_5(PO_4)_3(OH)$ ), and hydroxopyromorphite ( $Pb_4O(PO_4)_2$ ) (Badawy *et al.* 2002). Lead phosphate minerals in particular, are so sparingly soluble, thermodynamic data predicts these phases will control dissolved lead in soil solution under the Eh and pH conditions commonly found in natural systems (Figure 3, Nriagu 1974, Ma *et al.* 1993, Ruby *et al.* 1994). In other environments, poorly soluble lead carbonates such as ( $PbCO_3$ ) or ( $Pb_3(CO_3)_2(OH)_2$ ) (Rimstidt and Craig 2000), and lead sulfates such as anglesite ( $PbSO_4$ ) also may form. Under reducing conditions in which sulfate is reduced to sulfide, lead may be sequestered in galena ( $PbS$ ) a lead sulfide, which has a solubility in natural waters too low to be measured by current technology. Consequently, under the normal range of soil pH and redox conditions, aqueous lead concentrations should generally be limited to low values through precipitation reactions.

Despite the potential formation of poorly soluble lead minerals (e.g. chloropyromorphite ( $Pb_5(PO_4)_3Cl$ )) in soil, very few studies have directly shown these lead minerals actually buffer lead concentrations in natural aqueous environments. For example, Kaste *et al.* (2006) used microfocused synchrotron-based X-ray diffraction ( $\mu\text{SXRF}$ ) to analyze lead-enriched soil grains sampled from the northeastern US. They reported no evidence of any crystalline lead phases in their samples. Manceau *et al.* (1996) also used synchrotron-based x-ray studies on soils collected from contaminated sites in France, and concluded lead was bound with organic matter

and silicate minerals. Efforts to speciate soil lead using selective chemical extractions typically conclude lead is bound to organic matter, and secondary iron, aluminum, and manganese phases (Johnson and Petras 1998, Erel *et al.* 2001, Emmanuel and Erel 2002, Kaste *et al.* 2005) rather than to discrete lead minerals. At Camp Edwards, the low organic matter levels indicate the primary binding mechanism is the result of lead precipitate formation with aluminum, iron, and manganese. As a result, considerable care is necessary when evaluating environmental fate of metals based on phase diagrams alone. In particular, appropriate phase diagrams need to include a complete and accurate description of composition and other associated mineral phases. Nonetheless, several researchers have found phase diagrams to be an effective means of evaluating lead mobility (Hermann and Neumann-Mahikau 1985, Reddy *et al.* 1995, Vasquez *et al.* 2006).

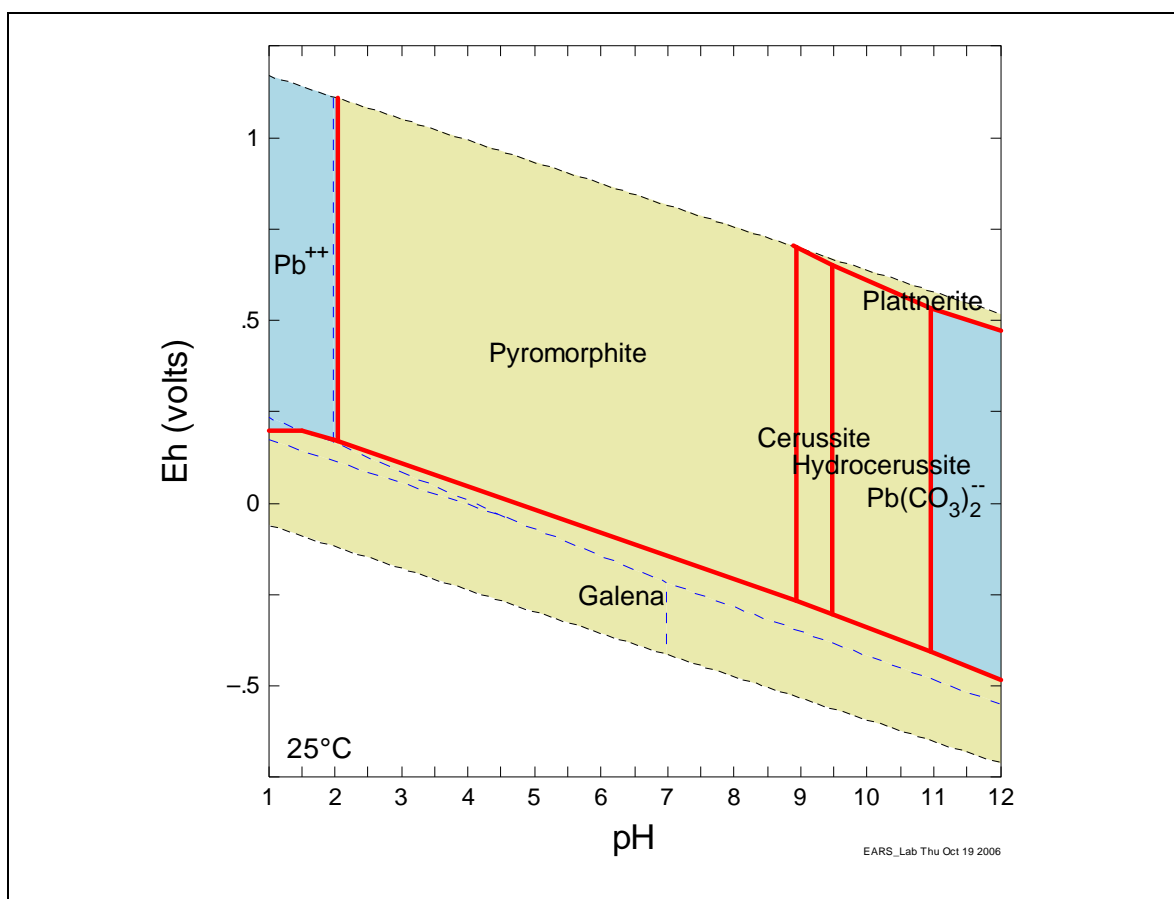


Figure 4. The formation of stable lead minerals as a function of Eh and pH given  $[Pb] = 10^{-6}$  M,  $[SO_4] = 10^{-3}$  M,  $[HCO_3^-] = 10^{-2}$  M,  $[Cl^-] = 10^{-6}$  M,  $[HPO_4^{2-}] = 10^{-6}$  M. More concentrated lead solutions would result in slightly larger stability fields for solids.

Recent studies have begun to shed light on the potential importance of biomineralization in regulating lead in the environment (Templeton *et al.* 2003). Jackson *et al.* (2005) used  $\mu$ SXRF to detail the distribution of lead and copper in the nematode *Caenorhabditis elegans*. They found that while copper was evenly distributed throughout the bodies of exposed *Caenorhabditis elegans*, lead was concentrated in the anterior pharynx region. Microfocused X-ray diffraction indicated the highly concentrated lead regions in the pharynx were actually the crystalline lead minerals pyromorphite. The authors concluded *Caenorhabditis elegans* precipitated pyromorphite in the pharynx as a defense mechanism to prevent spreading the toxic metal to the rest of the organism's body. Jackson *et al.* (2005) further suggest that because of the high turnover rate of nematodes, biomineralization could play an important role in the speciation of lead in certain soils.

A number of factors can inhibit the precipitation of lead minerals from solution. The pH and Eh of the solution are two direct controls on mineralization (Figure 4). However, certain chelating agents such as DOM may increase lead mobility (Jordan *et al.* 1997). Thus, DOM, and, in some cases, the availability of reactive surfaces can keep the  $Pb^{2+}$  below the saturation threshold. Jackson *et al.* (2005) suggested DOM could significantly inhibit pyromorphite precipitation by lowering dissolved lead activities. Alternatively, in certain natural environments, organic matter turnover may immobilize phosphate and thereby maintain a geochemical environment undersaturated with respect to pyromorphite. While dissolved lead complexes may buffer the activity of  $Pb^{2+}$  in solution and prevent precipitation of mineral phases, reactive surfaces on soil minerals can also sequester  $Pb^{2+}$  and can have a similar effect of inhibiting mineral formation (Figure 5). This may be the case for most environments at the earth's surface.

### **2.3.2 Lead Immobilization in the Terrestrial Environment: Lead Adsorption to Surfaces**

Many studies have directly demonstrated  $Pb^{2+}$  can form strong complexes with the surfaces of soil particles, including pure quartz (Schindler *et al.* 1976, Chen *et al.* 2006), iron phases (Bargar *et al.* 1997b, Ostergren *et al.* 2000a, 2000b, Sauvé *et al.* 2000a, Trivedi *et al.* 2003), manganese phases (Drits *et al.* 2002, Lanson *et al.* 2002, Manceau *et al.* 2002), aluminum phases (Bargar *et al.* 1997a, 1997b), and organic matter (Xia *et al.* 1997, Sauvé *et al.* 1998, 2000a, Strawn and Sparks 2000). The adsorption of lead to mineral and organic matter surfaces can be explained in terms of surface complex formation involving deprotonated hydroxide-[OH] groups and is thus strongly dependent on pH (Figure 6).

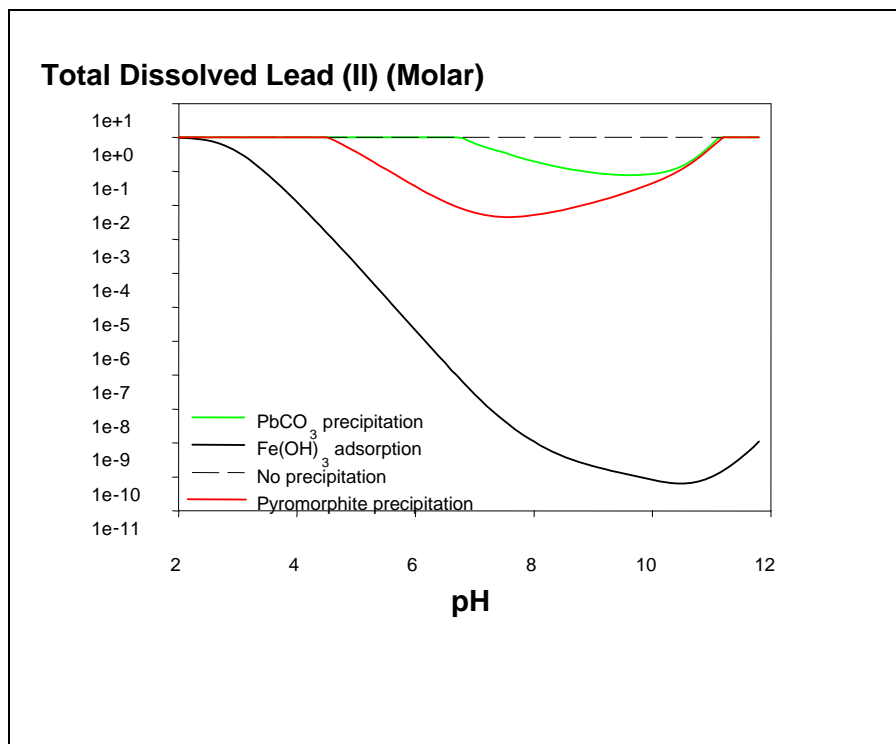


Figure 5. Buffering mechanisms of lead in aqueous environments, given:  $[Pb] = 10^{-6}$  M,  $[SO_4] = 10^{-3}$  M,  $[HCO_3^-] = 10^{-3}$  M,  $[Cl^-] = 10^{-4}$  M,  $[HPO_4^{2-}] = 10^{-6}$  M. Adsorption conditions: 1.4 g/cm<sup>3</sup> bulk density, 2% Fe(OH)<sub>3</sub> by weight in soil. The hatched area delineates the range of typical soil conditions. Thus, adsorption in most cases appears to effectively moderate lead levels to lower concentrations than the precipitation processes.

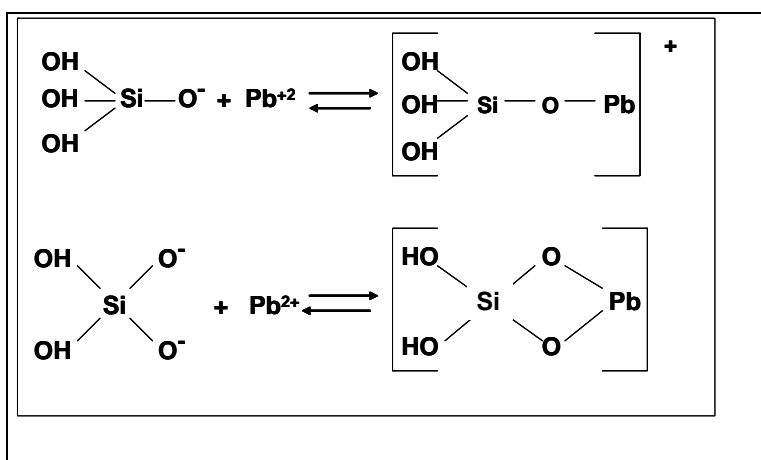


Figure 6. Conceptual framework for the adsorption of Pb<sup>2+</sup> to surface silanol groups on quartz. Adsorption can be both monodentate (upper) and bidentate (lower). Similar reactions could be given for acidic surface groups on organic matter, iron, aluminum, or manganese. (Modified from Schindler et al. 1976.)

Lead is often more strongly retained by surfaces than other divalent trace metals such as cadmium ( $\text{Cd}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), cobalt ( $\text{Co}^{2+}$ ), manganese ( $\text{Mn}^{2+}$ ), nickel ( $\text{Ni}^{2+}$ ), and zinc ( $\text{Zn}^{2+}$ ). This is attributed to lead's larger hydrolysis constant ( $\log K = -7.71$ ) compared to the previously mentioned metals ( $\log K = -8$  to  $-11$ ) (Abd-Elfattah and Wada 1981, Stumm and Morgan 1996).

Lead typically will form inner-sphere complexes with mineral surfaces and organic matter, which is a stronger and less reversible adsorption mechanism than general electrostatic adsorption by ion exchange. Even though lead tends to hydrolyze significantly only above pH 7, experimental data often show a sharp adsorption edge (i.e. the pH where lead switches rapidly from  $\text{Pb}^{2+}$  in solution to a surface bound species) near pH 4 (McKenzie 1980, Dzombak and Morel 1990, Glover *et al.* 2002). Strong binding of lead to soil even in relatively acidic pH ranges is a result of its high electro negativity, which causes it to form strong covalent bonds with oxygen atoms on mineral surfaces and organic matter functional groups (McBride 1994). Partition coefficients ( $K_d$ ) are generally  $>100$  milliliter per gram [mL/g] for lead in the normal soil pH range (see Section 3.10), where

$$1) \quad (K_d = [\text{Mass}]_{\text{adsorbed}}/[\text{Mass}]_{\text{solution}})$$

where

$\text{Mass}_{\text{adsorbed}}$  = mass of solute on solid phase per unit mass of solid phase milligram per gram (mg/g) at equilibrium.

$\text{Mass}_{\text{solution}}$  = mass of solute in solution per unit volume milligram per milliliter (mg/ml) of the liquid phase at equilibrium.

Sauvé *et al.* (2000b) demonstrated the quantity of free  $\text{Pb}^{2+}$  in equilibrium with leaf compost at pH 4 was lower than the amount adsorbed by a factor of approximately 100 ( $\log K_d = 2$  ml/g).

While the exact  $K_d$  value is a function of pH, organic matter content, substrate type, total metal burden, and concentrations of competing ligands, these studies typically show lead has very strong solid-phase partitioning. Partitioning coefficients determined by differential pulse anodic stripping voltammetry (DPASV) generally range from  $10^3$  to  $10^6$  in soils in the typical pH range (Sauvé *et al.* 2000b). Aualittia and Pickering (1987) used thin film anodic stripping voltammetry to compare the relative affinity of lead for different inorganic particulates and reported manganese (IV) oxides completely adsorbed the lead, regardless of pH in the range of 3 to 9, and had the highest affinity for lead in their study. The adsorption of lead to pedogenic iron oxides, aluminum hydroxides, clay minerals, and iron ores was reported to be pH dependent. Sauvé *et al.* (1998) used DPASV to study the effects of organic matter and pH on lead adsorption to an orchard soil and demonstrated lead complexation to DOM increased lead

solubility, and 30 to 50% of the dissolved lead was bound to DOM at pH 3 to 4, while >80% of the dissolved lead was bound to DOM at neutral pH. They concluded in most soils lead in solution would not be  $Pb^{2+}$  but bound to DOM. Sauv   *et al.* (2000a) compared the relative affinity of  $Pb^{2+}$  for synthetic ferrihydrite, leaf compost, and secondary oxide minerals collected from soils. They reported the inorganic mineral phases were more efficient at lowering the amount of  $Pb^{2+}$  available in solution than the leaf compost. Glover *et al.* (2002) used DPSAV to study the effects of time and organic acids on lead adsorption to goethite and found lead adsorption to goethite was very rapid, and remained unchanged after a period of about 4 hours. Lead desorption was found to be much slower however, and adsorption was not reversible on a timescale of 8 hours.

In the case of adsorption phenomena, total metal loading also controls the partitioning of  $Pb^{2+}$  to the solid phase: high lead loadings will result in a lower fraction partitioned to the solid phase. Sauv   *et al.* (1997, 1998) demonstrated only a fraction of the total lead in solution was actually  $Pb^{2+}$  in soils treated with leaf compost. The fraction of  $Pb^{2+}$  to total dissolved lead ranged from <1 to 60%, depending on pH and the availability of lead-binding ligands. In acidic soils, aluminum species can compete for sites on natural organic matter and inhibit lead binding to surfaces (Gustafsson *et al.* 2003). Interestingly, for a given pH, the total loading of the metal does not appear to affect the type or geometry of the adsorption complex. Trivedi *et al.* (2003) found that a mixture of monodentate and bidentate adsorption complexes formed on the ferrihydrite surface, and that their relative proportions were not related to loading.

The presence of chloride, sulfate, ligands, etc. and other complexing agents (DOM) in solutions can have a range of effects on the type and amount of adsorption of lead to surfaces. Ligands can increase or decrease the total amount of lead adsorption, change the geometry of the interaction, and affect the rate of the reaction (Strawn and Sparks 2000). The precise effect carbonate concentrations have on lead adsorption to mineral surfaces is a function of pH. At neutral to high pH, dissolved lead-carbonate complexes can inhibit adsorption, but at pH < 6.5 lead adsorption increases (Ostergren *et al.* 2000b). Ostergren *et al.* (2000b) obtained spectroscopic evidence that carbonate groups bond to lead as monodentate ligands. Increased uptake of lead onto the solid phase may result if surfaces have a higher affinity for these lead-carbonate ternary complexes that are stable in slightly acidic waters. Other evidence exists showing low-molecular weight organic acids can also form ternary complexes with lead and enhance surface adsorption (Schroth and Sposito 1998, Lenhart *et al.* 2001). The presence of sulfate in solution will enhance uptake of lead onto goethite across the pH range of 5 to 7, and will change the geometry of the lead complexes. While  $Pb^{2+}$  either will form inner-sphere complexes with corners or edges of Fe (O, OH) 6 octahedra, the relative fraction of corner sharing complexes increases in the presence of sulfate (Ostergren *et al.* 2000a).

### **2.3.3 Lead Fate and Transport in Environments with Relatively Low Levels of Lead (Concentrations < 0.1% or 1,000 mg/kg)**

Surface soils across the US have higher lead concentrations relative to levels expected from solely natural geogenic inputs (Friedland *et al.* 1984, Francek 1992, Erel and Patterson 1994, Marsh and Siccama 1997, Murray *et al.* 2004, Yanai *et al.* 2004). While some of this lead is attributed to paint, salvage yards, and the use of lead arsenate as a pesticide in localized areas (Francek 1997), lead contamination of surface soils is essentially ubiquitous because of atmospheric pollution associated with the metal and cement production industries and the combustion of fossil fuels. Surface soils in Michigan, for example, typically range from eight to several hundred-mg/kg lead (Francek 1992, Murray *et al.* 2004). Soils collected and analyzed beneath 50 centimeters (cm) in Michigan, however, range only from 4 to 60 mg/kg lead (Murray *et al.* 2004). In remote surface soils from the Sierra Nevada Mountains, litter and upper soil horizons are 20 to 40 mg/kg lead approximately 75% of which is attributed to atmospheric deposition during the 20<sup>th</sup> century (Erel and Patterson 1994). Repeated sampling of the forest floor (O horizon) in the northeastern US demonstrates the organic layer has retained much of the lead load deposited during the 20<sup>th</sup> century at 1 to 3 grams per square meters (g/m<sup>2</sup>), depending on elevation and proximity to urban areas (Miller and Friedland 1994, Johnson *et al.* 1995). Forest floors sampled during the 1980s, 1990s, and early 2000 had between 0.7 and 2 g/m<sup>2</sup> (Friedland *et al.* 1992, Miller and Friedland 1994, Johnson *et al.* 1995, Kaste *et al.* 2003, Yanai *et al.* 2004, Evans *et al.* 2005). The direct uptake of anthropogenically-derived lead by vegetation in boreal forests appears to be low (Klaminder *et al.* 2005), although one study suggested the presence of pine seedlings significantly reduced the amount of bioavailable lead (Turpeinen *et al.* 2000). An example of low uptake in boreal forests is provided by data from the Hubbard Brook Experimental Forest in New Hampshire where the pool of lead in above and below-ground biomass is approximately 0.13 g/m<sup>2</sup> (Johnson *et al.* 1995).

In the majority of cases of lead pollution from atmospheric deposition, concentrations in soil are typically in trace amounts. There has been a considerable amount of effort directed to assess the speciation, transport, and fate of atmospherically delivered lead in the terrestrial environment. Soils are effective at immobilizing lead from the atmosphere, and minimizing surface and groundwater contamination, and the residence time in soils is typically estimated to be on the order of >100 years (Wang *et al.* 1995, Wang and Benoit 1996, 1997, Kaste *et al.* 2003, Klaminder *et al.* 2006a, 2006b.). Overall, there is very little evidence lead mobility and solubility in these cases is controlled directly by the precipitation of lead minerals. Sequestration of relatively small amounts of lead is attributed to adsorption processes, although different soil types appear to sequester lead via different mechanisms. Teutsch *et al.* (2001) found most of the anthropogenic lead in soils from their study in Israel was associated with carbonates and iron oxides. Emmanuel and Erel (2002) reported organic matter was largely responsible for lead retention in soils from the Czech forest. Within O soil horizons, extractions targeting organic



matter and reducible oxides can liberate a significant quantity of lead (Johnson and Petras 1998, Ho and Evans 2000, Kaste *et al.* 2005). Manceau *et al.* (1996) used X-ray absorption spectroscopy on soil samples collected from areas contaminated by alkyl lead, and concluded lead in these samples lead was bound to salicylate and catechol-like functional groups. Other data suggests lead may bind directly to iron surfaces in addition to organic matter functional groups in organic-rich samples (Tessier *et al.* 1996, Kaste *et al.* 2006).

#### **2.3.4 Lead Fate and Transport in Environments with Relatively High Levels of Lead (Concentrations > 0.1% or 1,000 mg/kg)**

In addition to the ubiquitous lead residue resulting from atmospheric deposition, which has elevated soil levels an order of magnitude or two above natural (pre-industrial) levels, a number of anthropogenic activities have resulted in extremely high loadings to soils on a more localized scale. Soil contamination by leaded paint, projectiles, mine tailings, and short-range transport of smelter emissions has resulted in soils containing thousands of parts per million to percent level lead (Morin *et al.* 1999, DeVolder *et al.* 2003, Vantelon *et al.* 2005, Clark *et al.* 2006). In these cases, the dissolved concentration in soil pore-water is controlled by a combination of lead mineral precipitation and surface adsorption processes (Morin *et al.* 1999, 2001, Cao *et al.* 2003a, 2003b, Vantelon *et al.* 2005). Direct uptake of lead by vegetation, soil organisms, birds, and mammals has been observed at many of these sites, in addition to elevated levels in nearby surface waters (Clark *et al.* 2006). Cao *et al.* (2003b) analyzed soils, waters, and vegetation at several firing ranges in Florida. They reported lead concentrations in grasses up to 800 mg/kg, and surface water concentrations up to 289 µg/L at these sites. Several other studies have documented significant lead uptake by vegetation and earthworms from soils at shooting ranges (Darling and Thomas 2005, Levonmaki *et al.* 2006).

Soils with high lead concentrations may exhibit different geochemical behavior. Some of the difference in geochemical behavior is attributed to differences in adsorption in highly contaminated sites. Adsorption of lead to minerals controls the fate of lead in sites with low lead concentrations, but is nonlinear and limited by mineral surface area. In some contaminated environments, the lead concentration may be sufficiently high that adsorption is less effective at moderating lead levels. This effect on adsorption is most pronounced when the mineral grains are saturated and have no other available surface area for lead retention; however, partial saturation may decrease the effective partition coefficient for lead retention sufficiently to affect dissolved lead levels. In such cases, the lead concentration may be elevated somewhat from background levels, and other lead-bearing phases (such as the formation of discrete lead minerals) may form. Two such minerals, cerussite or hydrocerussite are frequently found in highly contaminated soils because soils often contain appreciable bicarbonate (Lin 1996, Cao *et al.* 2003a, 2003b, Vantelon *et al.* 2005). These minerals do not commonly form in less contaminated environments because lead concentrations are buffered to lower levels by

adsorption, consequently, the solutions remain undersaturated with respect to each mineral. These minerals, although still not highly soluble, are considerably more soluble than adsorption complexes. More importantly, the precipitation of these minerals may not proceed until the solution is considerably supersaturated, allowing dissolved lead to persist in concentrations in excess of predicted solubility. As a result, lead concentrations may not agree (and may exceed) the concentrations predicted based on thermodynamic properties such as solubility (Badawy *et al.* 2002). Once the mineral precipitates form, however, their relative insolubility may decrease dissolved lead levels considerably. Munitions containing lead are high concentration “nuggets” in soil that will corrode in place; resulting in localized regions of elevated  $Pb^{2+}$  levels. These elevated dissolved lead levels will, however, be relatively short-lived in that the mineral precipitates, once formed, bring lead into essentially insoluble phases; thus, corrosion processes will not likely result in the mobilization of lead from the range. Consequently, even in highly contaminated soils, aqueous lead levels may be elevated in or near soil embankments used as bullet stops, but usually remain at or near background levels deeper in the soil profile (Bricka 1996a, 1996b, Bricka *et al.* 1998, Astrup *et al.* 1999).

The mineralogy of lead in weathering crusts around the projectiles, which will control dissolved  $Pb^{2+}$ , is typically a mixture of litharge, hydrocerussite, cerussite, and massicot (Rimstidt and Craig 2000, Cao *et al.* 2003b, Vantelon *et al.* 2005). Vantelon *et al.* (2005) used  $\mu$ SXRF and x-ray diffraction to study the sequence of mineralogy surrounding corroding projectiles, from the core of the projectile to the surrounding soil. They concluded that as lead oxidized from  $Pb^0$  to  $Pb^{2+}$  during corrosion, the weathering sequence was from litharge to hydrocerussite to cerussite. In firing range soils with adequate phosphorous concentrations (>3,000 mg/kg), pyromorphite has been observed, which would theoretically maintain the lowest solution  $Pb^{2+}$  concentrations (Figure 7).

Soils developed on mine tailings and on lead ore-deposits can also provide a useful setting for understanding retention mechanisms that develop during pedogenesis (Merrington and Alloway 1992). It appears both mineral precipitation and adsorption reactions can control lead solubility (Morin *et al.* 1999, 2001). Ostergren *et al.* (1999) examined the speciation of lead in chemically distinct mine tailings from Leadville, Colorado. In mine tailings dominated by carbonates having near-neutral pH, adsorbed lead (inner-sphere) on iron (hydr) oxides accounted for approximately 50% of the total lead in the solid phase, with galena and lead carbonates making up most of the remainder. However, on more acidic tailings, lead phases were dominated by lead-bearing jarosites ( $KFe_xPb_x(SO_4)_2(OH)_6$ ). Adsorbed phases appear to be favored by high pH conditions, but at low pH, discrete mineralized lead-bearing phases control the dissolved  $Pb^{2+}$  (Morin *et al.* 1999). In other soils developed on a mineralized bedrock parent material, lead phases can be dominated by plumbogummite ( $PbAl_3(PO_4)_2(OH)_5 \cdot (H_2O)$ ), pyromorphite, and adsorbed lead (Morin *et al.* 2001).

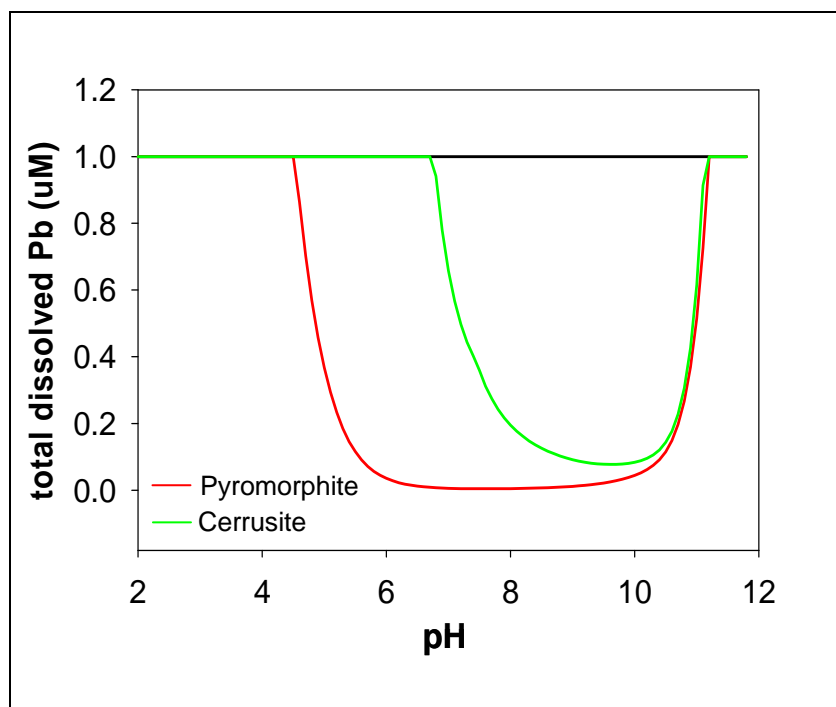


Figure 7. Impact of mineral precipitation on total dissolved lead levels. Conditions are based on the average soil chemical conditions at Camp Edwards: 1  $\mu\text{M}$  total P, 0.2  $\mu\text{M}$  Cl, 1  $\mu\text{M}$  carbonate and sulfate. Pyromorphite (red) maintains the lower equilibrium dissolved lead concentrations than cerussite (green). The black line represents zero mineral precipitation. Calculated using Visual Minteq 2.42 using the USEPA Minteq thermodynamic database.

In summary, lead migration is minimal in most environments due to adsorption or the formation of sparingly soluble mineral phases (Nriagu 1974, DeVolder *et al.* 2003, Jackson *et al.* 2005). Attenuation of lead in soil at SARs has been confirmed (Bricka 1996a, 1996b, Bricka *et al.* 1998, Scheetz 2004). Therefore, lead is usually immobile and not bioavailable even when, in contrast to Camp Edwards, the organic matter content of the soil is high (see Sections 2.4.1, 2.4.3, and 3.6 for additional discussion of organic matter and lead). Proper evaluation of the fate of lead in the environment requires an understanding of the dissolved and mineral bound chemical form. Accurate assessment of migration and bioavailability risks requires identification of the potential problematic areas in which lead concentrations may be elevated relative to other regions. Specialized environments exist in which contaminant lead may be more soluble and susceptible to transport. Although none of these are applicable to Camp Edwards, they are described below for completeness.

### 2.3.5 Transitional Redox Environments

Transitional redox environments are those of intermediate redox status that are undergoing dynamic change, becoming either more oxidic or more anoxic. Under these conditions, adsorbed

lead is actively being released from iron oxides by reductive dissolution but sequestration processes, though still occurring, are not able to remove lead at the same rate and the result is a transient rise in aqueous lead levels. Continued reduction will remove lead from solution. Since reducing conditions may arise due to persistent soil saturation (e.g. flooding), lead levels may be elevated temporarily resulting from the onset of reducing conditions.” Thus, iron-rich soil environments in which lead is adsorbed on mineral surfaces may experience elevated lead levels during periods of active geochemical reduction. Transitional redox conditions, however, are not typical of Camp Edwards.

The effect of transitional redox environments is easily observed in anaerobic incubation experiments in the presence of organic matter (Figure 8). Dissolved lead levels increase rapidly and reach a reasonably high level in response to the stimulation of iron (III) reduction (indicated by the release of soluble iron (II) into solution). This effect is kinetic—the system has available sorption sites and is precipitating practically insoluble minerals such as lead carbonate but those processes are unable to occur at a sufficient rate to remove all of the lead released during iron (III) reduction from solution. In fact, other active processes, such as sulfate reduction (which forms sulfide) may result in lead sequestration because dissolved lead may form the essentially insoluble (galena) PbS.

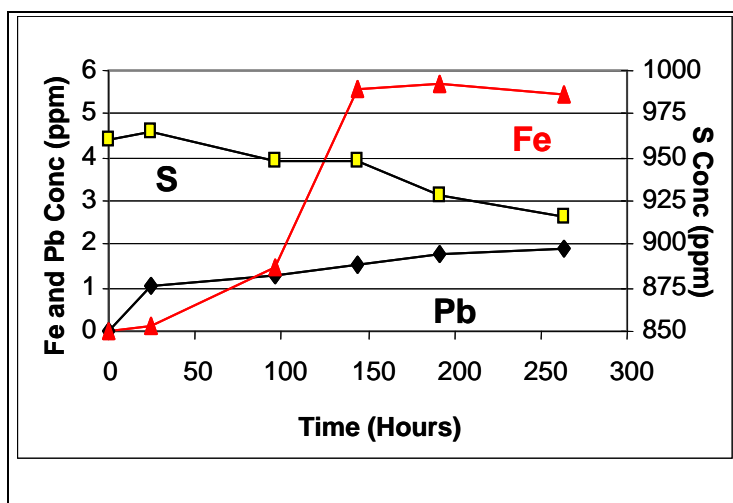


Figure 8. Anaerobic incubations of lead-contaminated soils from the Coeur d’Alene River region of Idaho. Total lead: about 4,000 mg/kg. *Data from Quicksall et al. (2005).*

Iron (III) reducing conditions are usually associated with soil flooding and/or redox processes below the water table. In the environment where these processes occur, pore-water lead levels can increase considerably due to active reduction during spring runoff. In fact, the near surface pore-water concentrations of lead are generally low (a few hundredths of milligram per liter

[mg/L]) due to scavenging by iron oxides and organic matter, but increase to nearly 0.250 mg/L in response to winter flooding events (Quicksall *et al.* 2005).

Emplacement of firing ranges on these unstable environments is generally undesirable to prevent lead-contaminated soils and materials encountering groundwater systems. Furthermore, monitoring groundwater concentration is prudent to evaluate the potential migration of lead towards groundwater in these systems.

### **2.3.6 Specific Solution Compositions**

Metallic lead solubility is low and usually effectively limits transport from surface soils to the subsurface. However, the solubility of lead minerals (or adsorption complexes) may be considerably enhanced by the formation of solution complexes such as DOM (Weng *et al.* 2002, Lang and Kaupenjohann 2003). The effect of these complexes on lead solubility can be predicted using the parameterized lead-dissolved organic carbon (DOC) binding constants in the Visual MINTEQ thermodynamic database. The solubility of cerussite at pH 7 is about 124 µg/L (assuming a typical soil  $P_{CO_2}$  of 0.0035 atmospheres. In the presence of 5,000 µg/L DOC; however, nearly all (approximately 98% of the  $Pb^{2+}$ ) is bound to DOC and the cerussite solubility increases to about 5,175 µg/L. The increased solubility of lead in organic-rich systems has been observed in natural systems. In firing range soils, Cao *et al.* (2003a) observed measurable lead migration to depth in a near neutral soil and suggested this migration was a result of complexation with organic matter under those neutral to alkaline conditions.

Given the ubiquity of DOC in the environment, lead-DOC complexes may play an important role in increasing the solubility of lead minerals, although DOC levels at Camp Edwards are believed to be minimal based on soil TOC measurements, see Sections 2.4.1, 2.4.3, and 3.6 (AMEC, 2004). DOC measurements of the soil pore-water and groundwater have not been made although TOC has been measured. TOC in soil pore-water at B, C, and I Ranges varied from 2 to 39 mg/L with groundwater values typically reported as less than 1 mg/L. Moreover, other ions, e.g., carbonate, sulfate) may also form a number of important solution complexes that need to be considered to assess the potential of lead migration in soils.

## **2.4 Summary of Camp Edwards Site Conditions**

The following discussion is focused on the conditions in the context of Camp Edwards as a whole. Where site-specific information is available for the SAR this data is presented

### **2.4.1 Surface Soil Characteristics**

Surface soils at Camp Edwards are coarse-grained and typically classified as sandy loams and loamy sands (Figure 9). These soils permit rapid recharge of percolating water and facilitate air

exchange with the atmosphere. Measurements of 61 surface soil samples collected from within the Impact Area showed low average values for organic matter (1.8% or 18,000 mg/kg as compared to typical agricultural soils which range from 1 to 6%) and pH (4.6) (Chendarian and Stewart, 2004). The low pH values for the Impact Area samples may be related to collection adjacent to corroding unexploded ordnance. In a more recent study on tungsten mobility at Camp Edwards thirty-two samples from SAR impact berms were measured for soil pH with two field duplicates collected. The pH ranged from 6.2 to 7.4 with a median value of 6.5. There was no indication of pH difference according to the area under investigation or with the four background samples, areas not treated with Maectite™, where pH ranged from 6.4 to 7.0. At two locations, pH was measured with depth and no changes were evident. These pH measurements are consistent with the median pH of the soil pore-water (6.7). The difference in pH between the Impact Area and SARs may also be related to vegetation. The small arms berms have scarcely any vegetation and what is there consists of grasses. In contrast, the impact area is mostly pitch pine and scrub oak.

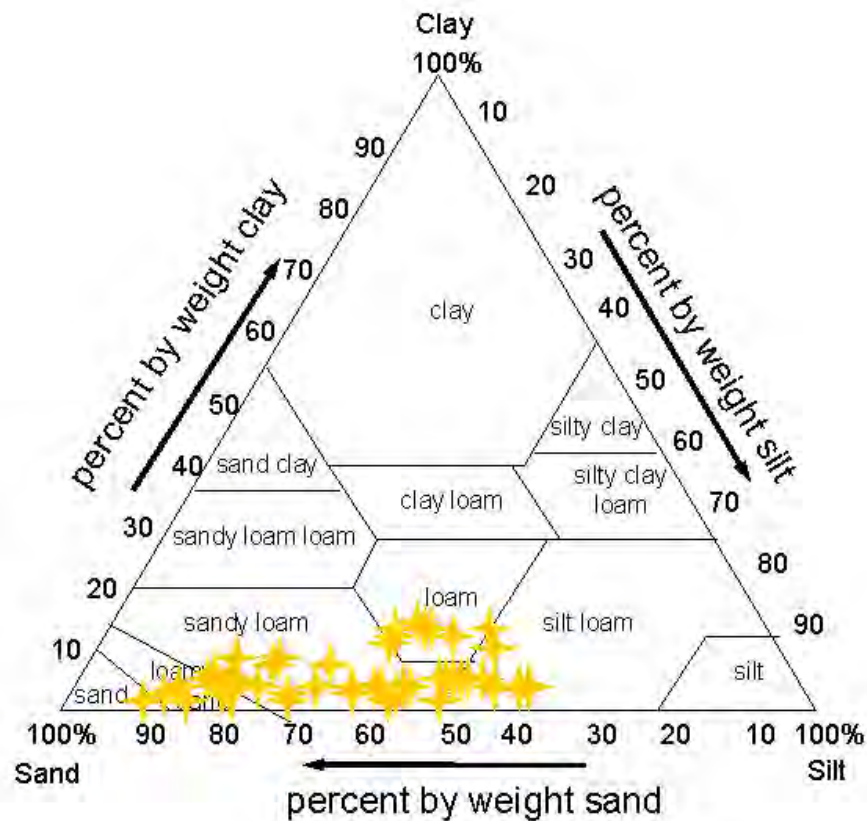


Figure 9. Classification of surface soil samples from Camp Edwards.

Total organic carbon (TOC) soil levels across Camp Edwards range from 31 to 247,000 mg/kg, with a mean of 11,050 mg/kg. A few soil horizons have a more developed organic layer present

but in most locations, an organic rich surface soil is absent. The quantity of organic matter and the moisture content decrease significantly with depth. Clay-sized particles (traces in most samples) and cation exchange capacity (CEC) (8 to 10 millequivalents (meq)/100 g), factors affecting sorption processes, are low in the surface soils and lower still in deeper soils. These soils have low concentrations of soluble salts (e.g. base cations such as calcium and magnesium as well as sodium and chloride) because these ions have been removed by leaching.

#### **2.4.2 Hydrogeologic Setting**

The geology of Western Cape Cod is comprised of glacial sediments deposited during the retreat of the Wisconsin stage of Holocene glaciation. Three extensive sedimentary units dominate the regional geology: the Buzzards Bay and Sandwich Moraines, and the Mashpee Pitted Plain. The Buzzards Bay and Sandwich Moraines lie along the western and northern edges of Camp Edwards, respectively. The Mashpee Pitted Plain consists of fine to coarse-grained sands forming a broad outwash plain and lies between the two moraines. The land surface is generally flat with topographic highs in the area of the firing ranges, which are located on or near the moraines. Bedrock is encountered at depths of 87 to 111 m below ground surface (bgs) and is considered an impermeable layer (AMEC 2003a). Therefore, regional groundwater flow is transmitted through the upper outwash units. Unconsolidated deposits within the saturated zone exhibit a coarsening upward sequence (lacustrine, bottomset, foreset, and topset sedimentary facies) consistent with a glacial depositional environment (Masterson *et al.* 1997). Lithologic material varies from very coarse sand and gravel at the top of the saturated zone to silt and clay at the bottom immediately above the bedrock impermeable layer. The aquifer system is unconfined (i.e. it is in equilibrium with atmospheric pressure and is recharged by infiltration from precipitation) and is bounded on three sides by the ocean, with groundwater discharging into Nantucket Sound on the south, Buzzards Bay on the west, and Cape Cod Bay on the north. The Bass River in Yarmouth forms the eastern lateral aquifer boundary.

The SARs and Impact Area lie directly over the Sagamore Lens, a major groundwater recharge area and the most productive portion of the Cape Cod Aquifer. The apex of the Sagamore Lens is located at the southeast corner of the Impact Area from which groundwater flows radially in all directions. The thickness of the unsaturated zone varies from 18 to 37 m across most of the saturated zone. The average hydraulic gradient in the Impact Area is 0.003 m/m (AMEC 2004). Hydraulic conductivity is estimated to range from 38 to 107 m/day based on grain size analysis and aquifer tests (Masterson *et al.* 1996, AMEC 2003b) with an effective porosity of 0.39 (AMEC 2003b). Groundwater flow velocities across the Impact Area are estimated to vary from 17 to 61 m/yr (AMEC 2004).

The unconsolidated deposits in the unsaturated zone consist of very coarse sand and gravel associated with topset and foreset sedimentary facies. Surface water runoff is limited to a few hundreds of feet at most because of the highly permeable nature of the sand and gravel underlying the area.

### 2.4.3 Geochemistry of the Soil and Groundwater

Geochemical conditions are critically important with respect to assessing the fate-and-transport of lead and the potential corrosion of spent projectiles. Geochemical conditions can be broadly assessed by considering redox potential or Eh, pH, the identity and concentration of soluble salts, the organic carbon content of soil and groundwater, and the CEC of the soils.

Evidence examined to date indicates soil and groundwater conditions are aerobic (Table 2), although anaerobic niches or seasonally reducing locations certainly occur within such a large study area.

Table 2. Evidence for aerobic geochemical conditions of soil and groundwater at Camp Edwards.

Parameter	Premise	Test	N <sup>1</sup>	Result	Evaluation
Soil Texture	Coarse texture suggests aerobic conditions	Grain Size	64	Sands/Silt Loams	Relatively Coarse, Aerobic
Moisture Content	Low moisture content suggests aerobic conditions	Moisture by weight	64	Mean value 20% +/- 5.5	Moderate moisture content, Aerobic
Oxidation Reduction Potential	Highly positive measurements suggest aerobic conditions.	Measurement with platinum electrode	64	Median value ~300 mv	Slightly oxidizing
Concentration of Dissolved Oxygen in Groundwater	Presence indicates aerobic conditions, but several mg/L and higher indicates oxidizing conditions.	Field titration or electrode measurement.	>2,000	Values near saturation in shallow wells and several mg/L in deep wells.	Oxidizing
Resistivity	High resistivity indicates low soil moisture and aerobic conditions	Field measurements	64	Median value for initial resistivity ~ 70,000 ohms	High resistivity, Aerobic

<sup>1</sup>N = number of samples.



The pH may also govern the identity and mobility of the chemical species present. Most metal contaminants (e.g. copper, lead, and zinc) become increasingly mobile as the pH decreases. Soil pH at Maectite™ treated SAR impact berms ranged from 6.2 to 7.4 with a median value of 6.5. The ability of soil minerals to sorb contaminants from water is affected by competing ions either in solution or already sorbed. Soluble salts are low as shown by the relative low specific conductance of the groundwater, typically 70 micro mhos per centimeter squared ( $\mu\text{mhos}/\text{cm}^2$ ).

Organic matter, whether from natural or anthropogenic sources may chelate with metals and enhance their mobility. However, organic matter content at Camp Edwards is low, and as shown by Cao *et al.* (2003a, 2003b), organo-lead complexes are most favored at alkaline, not acidic pH. As discussed in Appendix B, aluminum, iron, and manganese minerals present in soil and the aquifer are sufficiently present to limit lead mobility. Summaries of the metal content of soils in various areas of Camp Edwards can be found in AMEC (2001a, 2001b, 2001c, 2001d, 2001e, 2002a, 2003c) with typical soil concentrations of aluminum, iron and manganese ranging from several 1,000 ppm up to several 10,000 ppm (Ogden 1998a, 1999a, AMEC 2001a, 2001b, 2001c, 2003).

Cation exchange capacity (CEC) is an empirical measurement of the capacity of a soil to hold cations and exchange species of these ions in reversible chemical reactions. The low CEC (8-10 meq/100 g) indicates a low potential for sorption, but with respect to metal migration, the content of clay and hydrous oxides of iron and manganese are more important (Jenne 1968, Korte *et al.* 1976). Indeed, a study of aquifer material adjacent to Camp Edwards indicated strong correlation of lead adsorption with crystalline and amorphous iron and aluminum oxides (Fuller *et al.* 1996).

Aquifer geochemical conditions are an extension of those of the overlying soil. The coarse-grained unsaturated zone and coarse-grained aquifer material, in conjunction with the high precipitation rate (110 cm/yr), and relatively rapid groundwater flow rate cause conditions to be aerobic with a relatively low pH (~ 5.9) and a low concentration of soluble salts (AMEC 2004, 2001a).

## 3.0 Lead at Camp Edwards

### 3.1 Non-Military Training Sources of Lead

Studies at Camp Edwards demonstrate surface soils (0 to 0.3 m) samples collected from background locations range from 1 to 19 mg/kg (Table 3). The MassDEP lists several different mean background values which range from 15 to 100 mg/kg (MassDEP 2007). The two most reliable background studies for metals in Massachusetts are likely to be a MassDEP (1995) study which determined a mean background value of 20 mg/kg based on 141 non-urban soil samples and a study of Massachusetts Licensed Site Professional subsurface soil data samples, which yielded a mean lead value of 15 mg/kg for 583 soil samples (Haley and Aldrich, 2001). The background values determined for Camp Edwards, therefore, are similar to the MADEP studies.

It is important to place lead in context with its principal sources and usual exposure pathways in order to understand its transport in the environment. Lead has a relatively high natural abundance (usually >10 mg/kg) with common soils ranging from 2 to 200 mg/kg (Lindsay 1979). Lead has become concentrated in the surface environment because of coal and oil burning and its use in paints and gasoline.

Table 3. Comparison of lead soil concentrations (mg/kg).

	All Camp Edwards	All SAR <sup>1</sup>	Treated SAR	Non-Treated SAR	IAGWSP Background (0-0.3 m)	IAGWSP Background (0.3-0.6 m)	Tungsten Study Background <sup>3</sup>	Crustal Average <sup>2</sup>
Number of Samples	9,071	1,920	860	1,107	21	20	4	
Minimum	ND	ND	1	ND	6	4	1	2
Maximum	148,000	11,600	5,800	11,600	19	10	15	200
Median	10	13	10	16	12	6	4	
Mean	75	95	57	120	12	6	6	10
Standard Deviation	1,760	480	270	590	4	2	6	

ND – non-detect, <sup>1</sup>SAR=Small Arms Range, <sup>2</sup>Lindsay 1979, <sup>3</sup>Clausen et al. 2007

## **3.2 Military Training Sources of Lead**

### **3.2.1 Soil Distribution at Camp Edwards**

Several reports document the distribution of lead at Camp Edwards (Bricka *et al.* 1998, Ogden 1998a, 1998b, 1999a, 1999b, 1999c, AMEC 2001a, 2001c, 2001d, 2002b, 2003c). Over 9,000 soil samples have been collected and analyzed for lead across Camp Edwards to date (Figure 10) and when plotted indicate a sporadic distribution pattern with detections and elevated levels coinciding with the SARs (Figure 11). For the most part the reported lead levels in surface soils (0 to 0.3 m) are within the range of measured background levels for the site, although isolated areas of elevated lead are present. Elevated lead is somewhat related to target areas and firing lines (See also Tables 3, 4, and 5, Figure 11, and Section 2), but little or no migration to the subsurface is apparent, i.e. the frequency of lead detections and the concentration of lead decreases with increasing soil depth (Figures 12 and 13). Bricka *et al.* (1998) studied G, H, and K Ranges and found lead was generally attenuated within the top 100 cm of soil with a few higher detections at depth. These studies were conducted prior to soil remediation activities. As part of the Lead Berm Maintenance Project, soils were treated in-situ and ex-situ with Maectite™ (Table 4). Lead accumulation had occurred over several decades of range firing.

Certain locations have total lead concentrations exceeding action levels and guidance provided by both MassDEP and the USEPA. The locations (firing lines, berms) where lead is highest are consistent with firing range data obtained elsewhere. The maximum concentrations at Camp Edwards SAR (~12,000 mg/kg), however, are less than have been reported at other firing ranges (Zellmer and Schneider 1993, Cao *et al.* 2005), probably because most of the training at Camp Edwards has been conducted with bullets rather than lead shot. In addition, the active ranges were underwent berm maintenance in 1998 and training with lead projectiles has not resumed since, except for unapproved firing with lead on the J Range in October 2005.

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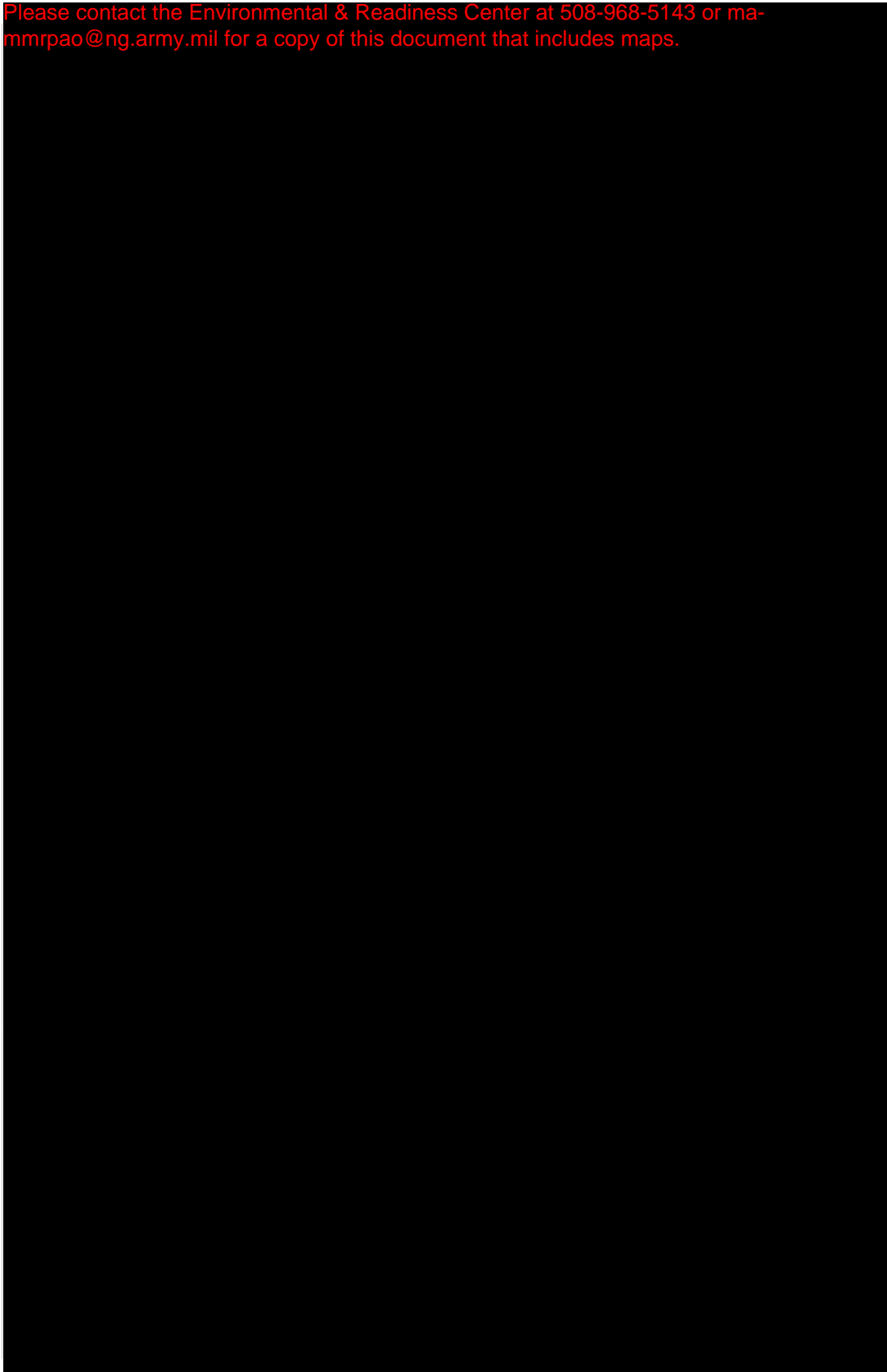


Figure 10. Location of soil samples collected and analyzed for lead.

Table 4. Impact Area Groundwater Study Program berm maintenance project.

Range Name	Soil Samples Collected	TCLP <sup>1</sup> Lead Maximum Concentration (mg/L)	Total Lead Maximum Concentration (mg/kg)	Soils Treated In-situ Total Volume (cubic yards)	Soils Treated Ex-situ Total Volume (cubic yards)	Leachability Ratio (%) <sup>2</sup> (Dermatas <i>et al.</i> 2006)
Current A	86	84	2,120	57	3,328	80
Current B	183	734	11,500	1,974	1,869	127
Current C	123	91	1,340	334	1,360	136
Current D	24	250	5,000	113	207	100
Current E	114	6.2	291	0	1,694	43
Current G	43	525	12,200	313	955	87
Current H	73	181	3,670	546	692	99
Current I	118	325	2,700	962	527	240
Current J	56	251	5,090	206	697	99
Current K	56	315	4,450	263	2,699	141
KD	39	5.7	130	0	380	88
Current N	96	44	1,670	93	540	53
Current O	53	126	2,390	408	410	105
Current P	61	33	1,190	111	904	56
S East	0	--	--	0	693	
S West	0	--	--	0	832	

<sup>1</sup>TCLP = Toxicity Characteristic Leaching Procedure, a test procedure determining if sufficient contaminant is soluble for the waste to be considered hazardous under the Resource Conservation and Recovery Act.

<sup>2</sup>Leachability ratio is discussed and defined in Section 3.8.

Table 5. Impact Area Groundwater Study Program Phase IIb investigation (2002) and small arms range investigation (2003).

Range Name	Soil Samples Analyzed	Firing Line Total Lead Maximum Concentration (mg/kg)		Backstop Total Lead Maximum Concentration (mg/kg)		Backstop TCLP <sup>1</sup> Lead Maximum Concentration (mg/L)		Leachability Ratio (%) <sup>2</sup> (Dermatas <i>et al.</i> 2006)
		0-1 feet	1-2 feet	0-1 feet	1-2 feet	0-1 feet	1-2 feet	
Current A	18	29						
Current B	30	23						
Current C	31	20						
Current D	12	1,030						
Current E	32	261						
Current G	12	497	4.8					
	3			5,170				
	4				212			
Current H	18	2,600						
Current I	13	48	71.3					
	3			35				
	3				4.5			
Current J	18	190						
	3			400				
	4				38			
Current K	36	53						
KD	64	147						
Current N	33	31						
Current O	57	201						
Current P	32	17						
S East	13	28						
S West	20	24	10					

Range Name	Soil Samples Analyzed	Firing Line Total Lead Maximum Concentration (mg/kg)		Backstop Total Lead Maximum Concentration (mg/kg)		Backstop TCLP <sup>1</sup> Lead Maximum Concentration (mg/L)		Leachability Ratio (%) <sup>2</sup> (Dermatas et al. 2006)
		0-1 feet	1-2 feet	0-1 feet	1-2 feet	0-1 feet	1-2 feet	
Current T	37	5,800						
Former B	22			2,410		0.3		0.2
	26				2,810		0.8	0.5
Former C	13	54	45.3					
	24			1,560		32		41
	27				446		2.1	92
Former D	17	58						
	23			4,200		593		282
	25				10,100		162	32
GA/GB	44	33	12.5					
	3			114		4.08		72
	4				126		2.1	34
Former R	6	28						
Skeet 1	8	56						
Succonsette Pond	3	7.2						
M-1	13	13						
M-2	4	50	7.9					
	11			1,710				
	11				856			

<sup>1</sup>TCLP = Toxicity Characteristic Leaching Procedure, a test procedure determining if sufficient contaminant is soluble for the waste to be considered hazardous under the Resource Conservation and Recovery Act.

<sup>2</sup>Leachability ratio is discussed and defined in Section 3.8.

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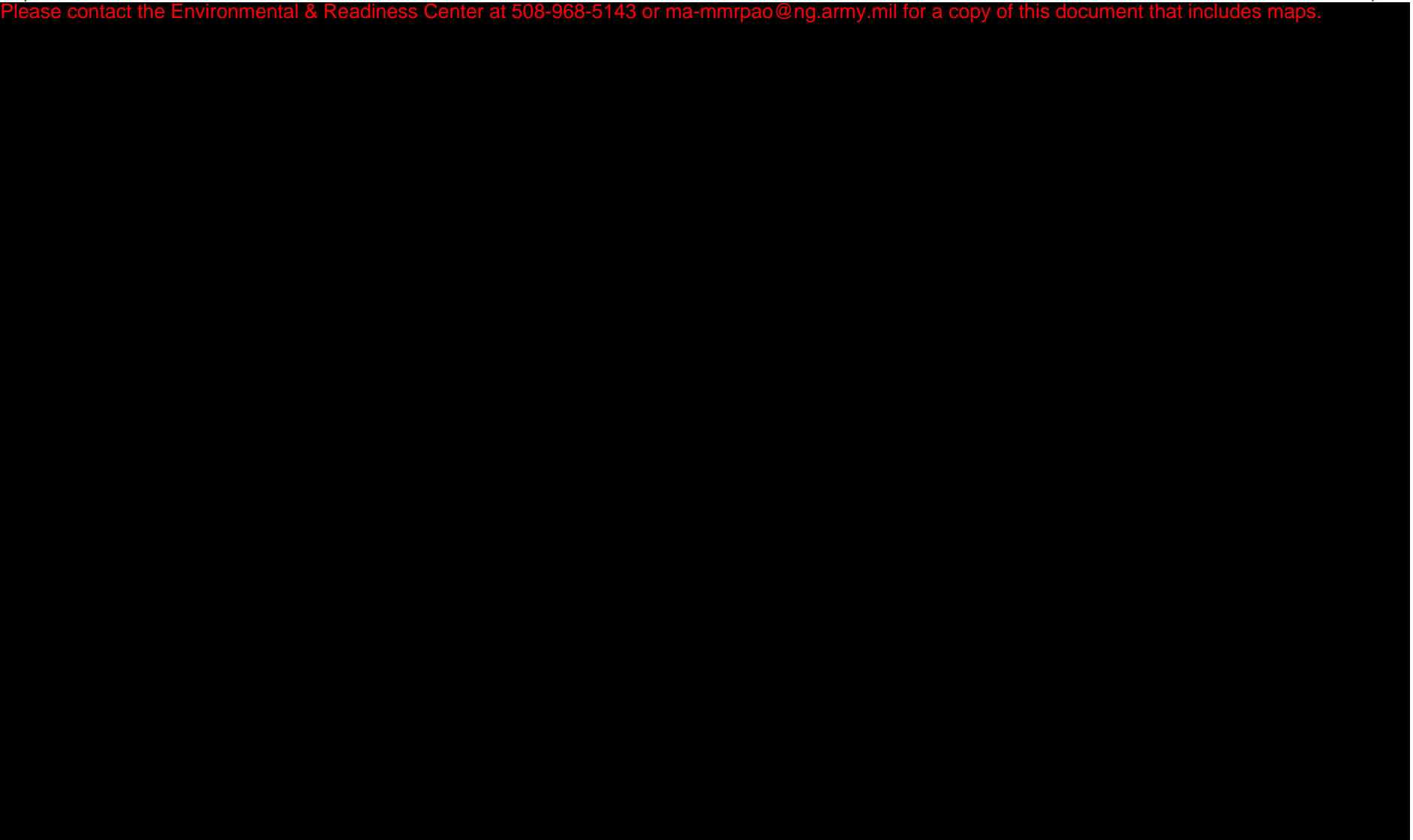


Figure 11. Detections of lead in surface soils (0 to 0.3 m).



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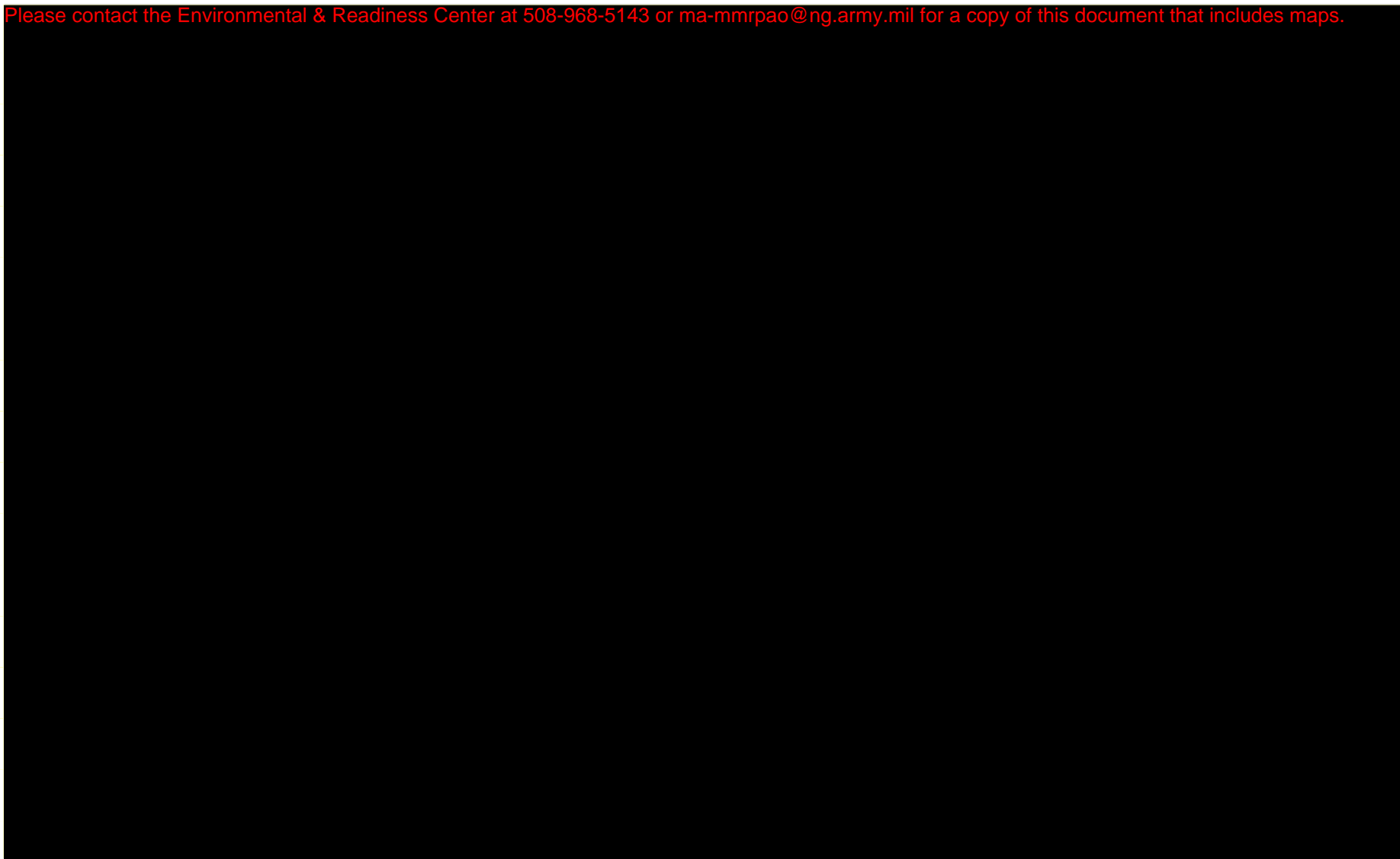


Figure 12. Detections of lead in surface soils (0.3 to 0.6 m).

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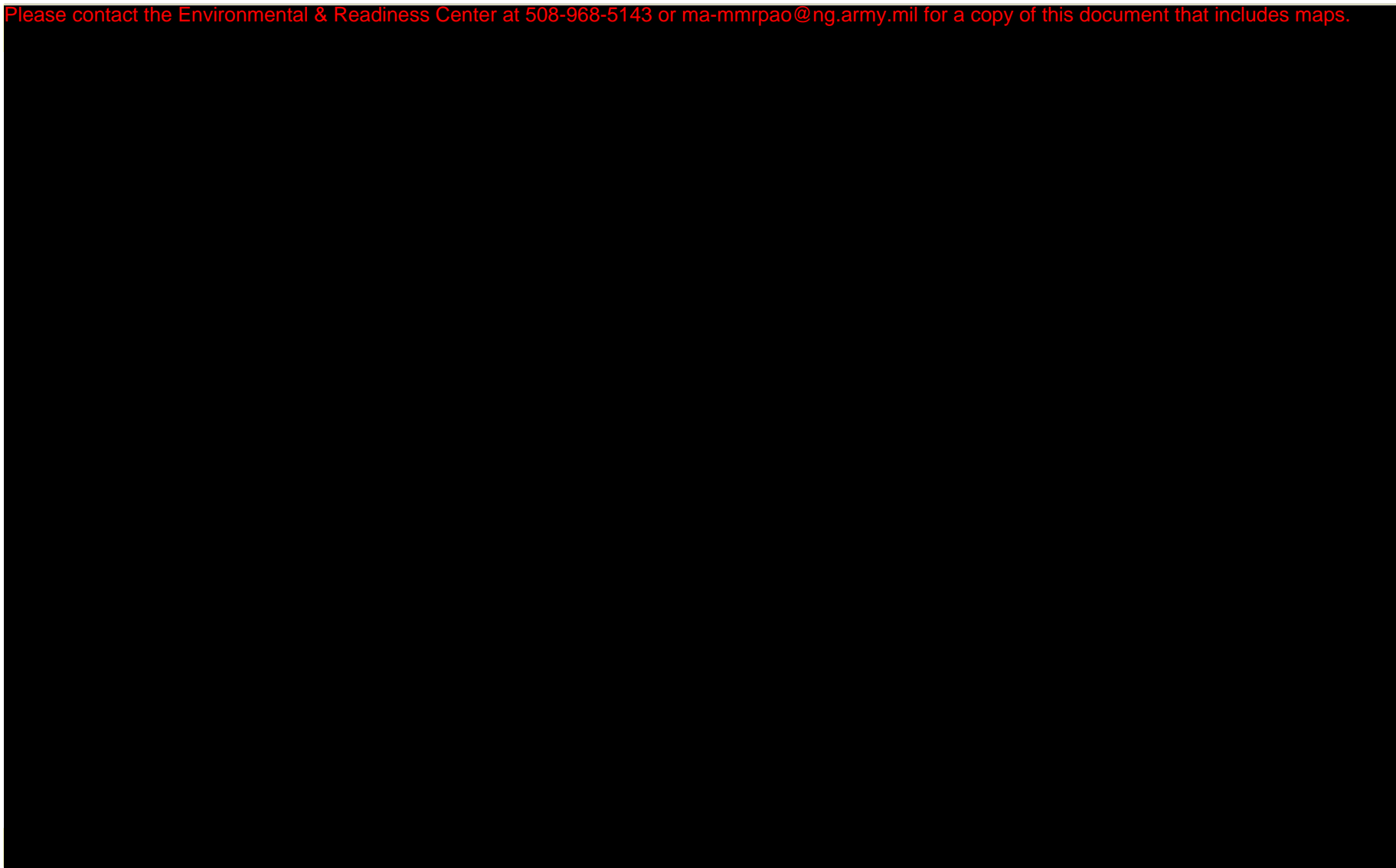


Figure 13. Detections of lead in surface soils (0.6 m and greater).

### **3.3 Projects Specific to Camp Edwards Small Arms Ranges**

#### **3.3.1 Early Small Arms Range Studies**

Prior to the Berm Maintenance Project, several SARs were studied by Bricka *et al.* (1998). Soil borings were collected from the G, H, and K Ranges. In general, all of the borings indicated relatively high levels of lead in the 1,000's ppm at the soil surface. The concentration of lead rapidly declined in all borings with background levels reached generally within 9 m. These borings did have elevated lead levels at greater depths. However, it is not apparent if these results represent lead migration from the surface or possible cross-contamination issues during sampling since these lead detections are sandwiched between samples with background levels of lead.

#### **3.3.2 Berm Maintenance Project**

In accordance with AO2, a SAR berm maintenance project was undertaken at Camp Edwards in 1998 by the MAARNG as a pollution prevention measure (Ogden 1999a). The objective of this innovative technology project was to protect groundwater by removing bulk metallic lead in the form of spent munitions from berm soils and immobilizing any remaining lead (Table 4).

To characterize the nature and extent of lead in the SAR soils, samples were collected from the up-range berm face and range floor (within 3 m of the toe of the berm slope) at active ranges. Sampling locations were established at 25-m spacing along the face of each berm and samples were collected in 0.6-m intervals to a depth of 2 or more meters. The samples were analyzed for total lead and leachable lead using toxicity characteristic leaching procedure (TCLP). A subset of these samples was also analyzed for total copper, iron, nickel, and antimony. A cumulative 1,125 samples were ultimately collected from the ranges (Ogden 1999a). Table 4 lists the number of berm samples collected by range.

In accordance with the screening criteria, soils exhibiting TCLP lead concentrations exceeding 5.0 mg/L would ultimately require treatment. The highest reported concentrations are listed by range in Table 4. In general, TCLP lead concentrations were greatest in the upper 1 m of the berm face (Ogden 1999a), which is consistent with the presumed penetration depth of small caliber projectiles. Elevated concentrations at depth were attributed to past reworking of berm materials during range maintenance and reconstruction activities. Based on the TCLP results, Current A, B, C, D, E, G, H, I, J, K, KD, N, O, and P Ranges were selected for treatment. Despite the absence of a berm backstop soil, soil treatment at the Southeast and Southwest Ranges was deemed necessary due to the presence of projectile fragments in soil mounds protecting pop-up target mechanisms there.

The treatment process consisted of an application of liquid reagent designed to permeate soil and immediately react with lead present. The reagent, Maectite™ - a phosphate, was developed to chemically bond to lead within the soil matrix creating geochemically stable (i.e. less leachable) synthetic mineral crystals. For range soils with TCLP lead concentrations exceeding the 5.0 mg/L criterion, but exhibiting no visual evidence of metallic projectile fragments (e.g. on the range floor), treatment was performed in place. Approximately 5,380 cubic yards (yd<sup>3</sup>) of soil was treated (Table 4) in this manner (Ogden 1999a).

Soils exceeding the TCLP lead criterion and exhibiting visual evidence of projectile fragments/jacketing were excavated from the berm faces and transported to central processing site. A total of 17,788 yd<sup>3</sup> of soil were ultimately excavated (Ogden 1998a); volumes treated from each range are presented in Table 4. At the central processing site, metallic munitions fragments were mechanically removed from the soils and stockpiled for off-site recycling. Processed soils were treated with the same lead-fixing reagent.

Post-treatment confirmatory samples were collected from both in-situ and ex-situ treated soils and tested again for TCLP lead. None of the post-processed soils exceeded the 5.0 mg/L performance value and 96% of these were less than one order of magnitude below that threshold, i.e. less than 0.5 mg/L (Ogden 1999a). After treatment, excavated soils were returned to the individual ranges for reconstruction of the berms.

### **3.3.3 IAGWSP Phase IIb Investigations**

In 2002, investigation of environmental impacts associated with SAR training and other types of training at Camp Edwards continued in accordance with AO1 under Phase IIb of the IAGWSP (AMEC 2000, 2003c). Preliminary efforts under this investigation included a detailed review of archived range control log entries, examination of range layout maps and aerial photographs, and conducting additional reconnaissance site inspections at known SAR sites. Sampling plans were prepared for each range to provide a screening level assessment of residual soil contaminants associated with past training activities. The study focused on both up-range propellant-related contaminants and downrange projectile-related residuals.

Sampling began at the Former B, C, D, and the GA/GB Ranges. These currently inactive ranges are some of the earliest established SARs and each was used for a variety of different weapons types over several decades of training. Soil samples were collected from the firing points (when identifiable) and range backstops. At the Former B, C, and D Ranges, samples were collected from downrange hillsides that appear to have functioned as backstops. A small soil berm, presumably a remnant of the former range backstop, was discovered at the GA/GB Ranges. Discrete soil grab samples were collected at two depth intervals (0 to 15 and 20 to 61 cm bgs) at locations where projectile fragments were abundant at each of the four berm backstops.

Samples were analyzed for total metals and TCLP lead. At the firing point, five-point multi-increment soil samples were collected at three depth intervals (0 to 5, 5 to 15, and 15 to 30 cm bgs). Each sample was analyzed for total metals and semi-volatile organic compounds.

A similar sampling approach was used under a supplemental Phase IIb investigation of the 22 remaining SARs. Currently active ranges that were addressed during the berm maintenance project were included in the list of ranges tested (Tables 4 and 5). Downrange sampling at ranges treated during the Berm Maintenance Program was limited to regions beyond the treated backstop faces, and only where evidence of metallic projectiles was observed during pre-sampling site inspections. Sampling locations downrange at Former B, C, and D Ranges were selected to complement earlier Phase IIb sampling efforts. The total number of soil samples collected and analyzed under both Phase IIb investigations is presented by range in Table 5.

Analytical results for total lead in soil reveal that firing point concentrations at these ranges are generally not significantly elevated from the background range of values for Camp Edwards; however, there are some isolated elevated detections from discrete samples (Table 5). For downrange samples, total lead concentrations are highly variable, ranging from background to as much as four orders of magnitude higher. The highest concentrations of total lead were found in soil collected from Former D Range where projectile fragments were abundant. TCLP lead concentrations for samples collected from this range were similarly the highest observed (Table 5).

### **3.3.4 Tungsten Fate and Transport Study**

Data for lead in Camp Edwards soil was also collected as part of a US Army Environmental Center (USAEC) funded tungsten study. The US Army Corps of Engineers, Environmental Research and Development Center, Cold Regions Research Engineering Laboratory (ERDC-CRREL) collected surface and subsurface soil samples from the B, C, and I Ranges. All of the surface soils were collected using a multi-increment, systematic random approach consisting of 100-increments collected over a 0 to 5 cm interval in the area of interest. The sample mass varied from 1 to 3 kilograms (kg). In surface soils, the highest lead concentrations were found on the berm face and the trough and declined towards the firing point. The lead levels at all three ranges are similar ranging from approximately 200 to 1,200 mg/kg. At B Range, lead levels in surface soils ranged from 24 mg/kg at the firing point to 1,200 mg/kg at the berm in the center firing lanes. At C Range, lead levels in surface soils ranged from 122 mg/kg for an integrated sample spanning the firing point, range floor, and targets to 1,090 mg/kg on the berm face. At I Range, lead levels in surface soils ranged from 91 mg/kg on the berm face to 815 mg/kg on the backside of the berm. The lower lead levels likely reflect soil berm maintenance activities which occurred in 1999, i.e. lead was physically removed from the soil and the soil was

treated with Maectite™. After the soils were treated training resumed with the tungsten/nylon round. Consequently, lead has not been introduced into the range soils post-treatment.

Soil profiles were prepared by collecting increments from four different soil cores. The soils from the same sample depth were combined to form a single sample. The sampling depth interval was 25 cm with one core collected using 5 cm intervals from B Range. The maximum sample depth varied from 75 to 150 cm. The termination depth was above the base of the berm except for those soil profiles collected in the trough. The sample mass varied from 5 to 20 kg for the subsurface soil. Subsurface soil data collected from the berm generally reflect a decline in lead concentrations with increasing depth for all three ranges studied. Lead concentrations at the termination depth were typically above the background range established for this study. An example from C Range is provided (Figure 14). Berm samples do not always show an obvious trend probably because the soil was reworked during remediation. A clear declining trend is evident for the trough sample which was not disturbed during excavation. .

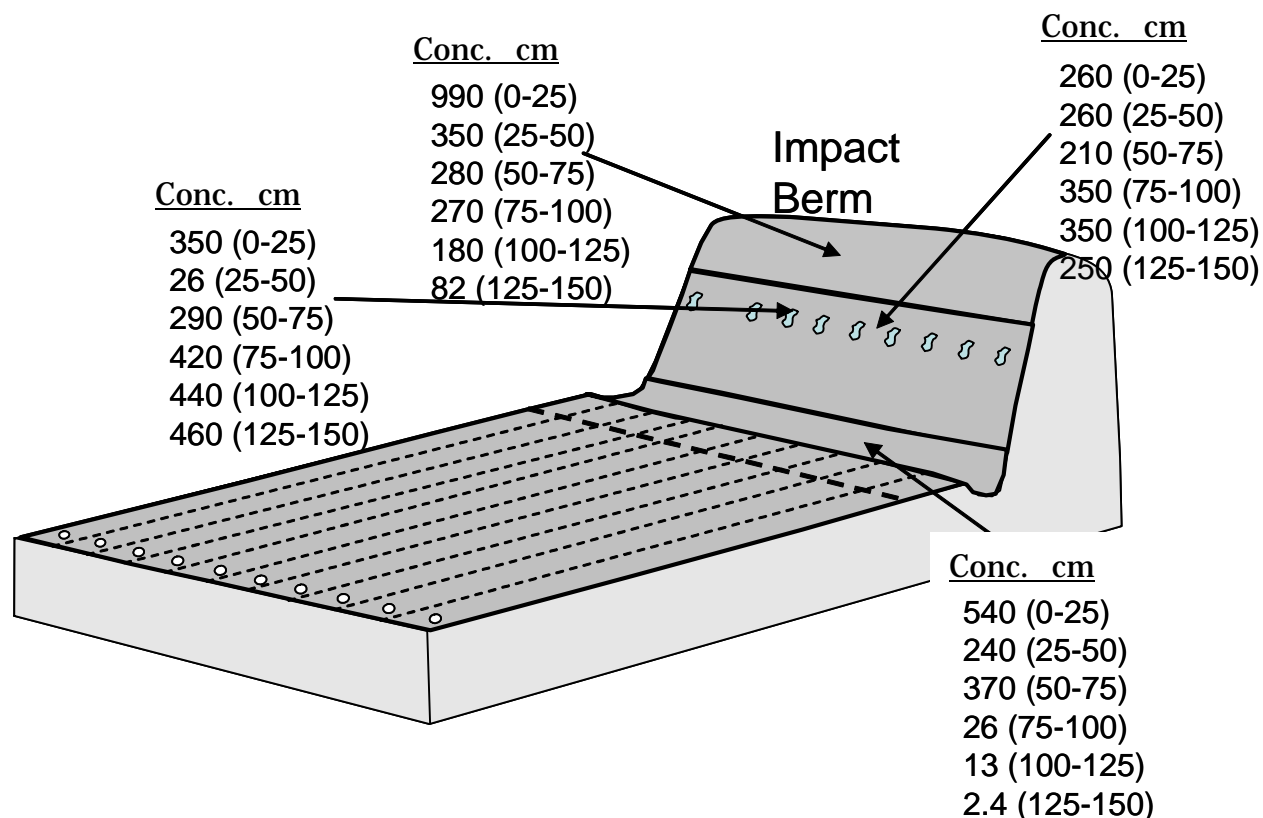


Figure 14. Lead soil concentrations (mg/kg) by depth (cm) at Charlie Range.

Four background samples were collected from a 50 x 50 m area, using the same sampling methodology as used on the SARs, away from the B, C, I, and M firing lanes. The background lead level for surface soil varied from 1.02 to 14.8 mg/kg with a mean of 5.9 mg/kg for this study, which is below the MassDEP defined state-wide mean of 20 mg/kg (MassDEP 1995), (see also Section 3.1).

### **3.3.5 Recent Small Arms Range Studies**

More recently, multi-increment surface soil samples have been collected from E, SE, SW, and T Ranges. Lead levels ranged from 13 to 560, 10 to 180, 10 to 710, and 41 to 460 mg/kg at E, SE, SW, and T Ranges, respectively.

## **3.4 Corrosion of Spent Projectiles**

Primary sources of lead at training ranges are spent projectiles and shot pellets. Thus, particle size and subsequent corrosion have a significant role in any ensuing lead migration. Small caliber military bullets (5.56mm [M16] and 7.62mm) leave residues that include chunks of metal, composed of antimony-hardened lead which can either be in a copper jacket or as a slug with masses ranging from 32 to 86 g per projectile, of which 96.4% by weight is lead (MIDAS 2007). These are relatively large chunks of metal and their low surface area inhibits both dissolution and biological availability. Moreover, soils at Camp Edwards do not significantly promote corrosion of metals despite the slightly acidic pH of 6.7 for the SAR soil, see Section 2.4.1.

There are two principal reasons corrosion processes are inhibited at Camp Edwards: lack of chloride and coarse soil texture. Chloride is the most important naturally occurring anion with regard to metal-corrosion and its content in Camp Edwards' soils and water is low. The mean chloride content of 61 soil samples collected from the Impact Area and evaluated in a corrosion investigation was 30 mg/kg (Chendarain and Stewart 2004). Six additional soil samples from Camp Edwards, collected and analyzed from the SE Range, had chloride concentrations ranging from 0.8 to 3.8 mg/kg. In contrast, various sources report approximately 130 mg/kg as the average chlorine concentration in the earth's crust (Korte 1999), with an average of 100 mg/kg for common soils (Lindsay 1979). Groundwater chloride concentrations at Camp Edwards are also low, approximately 10 mg/L. The latter value has been independently corroborated by a study reported for the shallow aquifer near Falmouth, MA where the ionic strength was reported as 28 mg/L (Fuller *et al.* 1996). Assuming approximately half of the ionic strength was contributed by chloride; the concentration at Falmouth also is approximately 10 mg/L. Savioe and LeBlanc (1998) report chloride levels of 15 to 20 mg/L for the tracer research site located south of MMR.

Pore-water chloride concentrations have not been measured to date, but are likely similar to the groundwater. The Camp Edwards chloride concentration in groundwater of 10 mg/L is less than the concentration required for pitting of stainless-steel (reported as 11 to 110 mg/L at pH 5 (Szkarska-Smialowska 1986), although one report said pitting might initiate at 4 mg/L at an unspecified pH (Bossia and Cragnolino 2000). Mendoza and Corvo (2000) identified chloride as the primary agent of aluminum corrosion. Chendarain and Stewart (2004) studied eleven aluminum fuses collected from Camp Edwards that exhibited little evidence of corrosion. Thus, while chloride may not be the primary agent reacting with lead itself, its scarcity in the Camp Edwards environment indicates a high resistivity in the soils which limits the corrosion of casings and metal alloys which may protect lead projectiles. Where the lead projectile is still encased in its copper jacket it is further protected from corrosion processes.

The second reason corrosion is limited is the effect of coarse soil texture on moisture content. This coarse texture influences the moisture content of soils, which is directly related to the corrosion rate of metal (Chendarain and Stewart 2004) including the increased galvanic corrosion that occurs when lead is jacketed by copper (Dermatas *et al.* 2004). The coarseness of the soil is demonstrated by comparing a triangular plot of sand, silt, and clay to the US Department of Agriculture (USDA) textural classification chart (Figure 8). One sample from each of the aforementioned 61 surface soil locations was used to assess soil texture. The majority of the samples classify as sandy loam, and, in decreasing order of prevalence, silt loam, loam, loamy sand, and sand. Such soils are very well-drained, therefore, despite a humid climate; surface soils have low moisture content thereby limiting corrosion and dissolution processes for spent projectiles on the soil surface.

### **3.5 Lead Solubility**

The USAF issued a fact sheet nearly a decade ago, which described lead as relatively insoluble at neutral pH but also stating, "*as water becomes more acidic (decreasing pH), lead solubility tends to increase. When storm water (normally slightly acidic) comes in contact with lead contaminated soil, the lead can be dissolved into the water and transported to nearby groundwater or surface water. If sufficient lead is mobilized, environmental receptors can be affected and risk to human health could occur if these sources are used for drinking water. When groundwater is more than 10 feet below ground surface, it is generally not affected by leaching of lead from soil*" (USAF 1998). Although, the fact sheet is an oversimplification based on a few site-specific studies, it suggests acidic conditions at Camp Edwards could promote lead mobility. However, as discussed previously, several mitigating factors such as the lack of chloride and coarse soil texture limit corrosion of metallic lead and subsequent dissolution of lead oxides at Camp Edwards. The fact sheet also suggests ground and surface water would not be affected, i.e. surface water bodies are not located near the Camp Edwards SARs and depth to water is greater than 30 m. Although a generalization, the USAF fact sheet is



consistent with a recent, more detailed review by the ITRC (ITRC 2005) which listed the major reaction classes governing lead transport and fate as follows:

- Dissolution-precipitation as a function of pH,
- Dissolution-precipitation as a function of redox environment, and
- Sorption-desorption reactions.

The extent to which these reactions occur depends on site conditions such as soil composition, extent of soil saturation, and soil organic content. The Eh/pH stability diagram (phase diagram) and other figures presented in Section 2 demonstrate how the dissolution and mobility of lead derived from lead projectiles and shot are strongly influenced by pH, precipitating agents (e.g., carbonates, sulfates, phosphates, sulfides), and sorbents (e.g. iron and manganese oxides and hydroxides, organic carbon, clays) (Figures 4, 5, and 7). Common lead minerals which form in most soils decrease in the order of solubility as follows:  $\text{PbO} > \text{PbCO}_3 > \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 > \text{PbSO}_4 > \text{PbHPO}_4 > \text{Pb}_5(\text{PO}_4)_3\text{OH} > \text{Pb}_5(\text{PO}_4)_3\text{Cl}$  (Lindsay 1979). Phosphate exerts strong control on lead mobility, perhaps, explaining why lead has never been detected above 21  $\mu\text{g/L}$  in lysimeters sampled in 2005 and 2006 located below lead-contaminated soil at the Bravo, Charlie, and India Ranges where Maectite™ treatment occurred (see Section 3.9 below).

Phosphate is not naturally present in sufficient concentrations to control lead mobility at Camp Edwards. Moreover, site data from TCLP indicate high lead solubility from some samples (see Section 3.8 below). Despite this fact, the latter test is unrealistic with respect to reproducing natural conditions; some amount of lead will dissolve in rainfall.

Thus, the low propensity for corrosion at Camp Edwards only means dissolution processes are relatively slow but not non-existent. Field and laboratory investigations have consistently reported elemental lead in shooting range soils becomes coated with cerussite and hydrocerussite (Lin *et al.* 1995, Astrup *et al.* 1999, Bruell *et al.* 1999, Lanndsberger *et al.* 1999, Hardison *et al.* 2004, Scheetz 2004, Vantelon *et al.* 2005). The latter mineral is also known as a common encrustation on native lead (AGI 1974) and both minerals commonly formed on lead fragments when subjected to alternate wetting and drying (Dermatas *et al.* 2003). For those shooting ranges with acidic soil pH similar to Camp Edwards, hydrocerussite (Scheetz 2004), cerussite, and small amounts of massicot (PbO) were predominantly present in the weathered crusts (Cao *et al.* 2003a). Massicot, the most soluble of the typical lead minerals, was not present at all ranges studied (Cao *et al.* 2003a, 2003b). These investigators calculated  $\text{Pb}^{2+}$  activities as supersaturated with regard to cerussite and hydrocerussite for both surface soil and berm soil at most locations. At one range, however, acidic soils rich in phosphorus contained hydroxypyromorphite [ $(\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2)$ ]—a very stable mineral again suggesting the addition of

phosphorus would provide an additional safety factor limiting lead mobility if added to soils at Camp Edwards.

### 3.6 Lead Sorption

When lead exists in a dissolved state, it can sorb onto iron and manganese oxides (Scheetz 2004) and to charged clay particle surfaces. On Cape Cod sediments, lead adsorbs strongly onto iron and aluminum oxides and poorly ordered allophonic (aluminosilicates) material, which occur as coatings on quartz grains (Appendix A, Coston *et al.* 1995, Fuller *et al.* 1996). Lead adsorbs extensively onto iron and aluminum oxides over pH ranges where these mineral have positive surface charge/potentials. In most natural soil environments, clays carry a net negative surface charge. In a solution having neutral pH, dissolved cations are sorbed preferentially. Therefore, when dissolved lead exists as  $Pb^{2+}$  in dilute solution, transport can also be attenuated by sorption to clays. These conditions occur in subsurface environments characterized by neutral to acidic pH, low dissolved solids concentrations, and low carbonate alkalinity — conditions similar to Camp Edwards. Although, Camp Edwards soils typically have a low clay content. In contrast, when dissolved lead exists preferentially as an uncharged ion pair or negatively charged hydroxyl complex, transport can be enhanced because sorption is negligible (presence of two negatively charged surfaces). These conditions can occur over a range of redox conditions but require alkaline pH, high total dissolved solids, or high carbonate alkalinity (ITRC 2005). The latter conditions do not exist at Camp Edwards (see Section 2).

The tendency of a solute (in this case, dissolved lead) to adhere to soil as it migrates is often presented as  $K_d$ . Larger values indicate increasing tendency for the solute to be retained by the solid phase. A  $K_d$  measurement of 34 L/kg lead was obtained for soils from the Impact Area at Camp Edwards (Larson 2007). Distribution coefficients measured for lead in a pH range relevant for Camp Edwards vary from approximately 900 to 9,000 mL/g (USEPA 1999) or for a sand 16,000 to 59,000 mL/g (Sheppard and Thibault 1990). Unfortunately,  $K_d$ s only describe solute partitioning between the aqueous and solid phases for a single set of environmental conditions. Such homogeneity does not exist in nature and greatly compromises the usefulness of the constant for calculation purposes. Therefore, measurements of  $K_d$  from multiple samples from a site are necessary to reflect accurately the intrinsic variability of soil properties. “For this reason, any comprehensive compilation of  $K_d$  values selected from the literature should be expected to present values that define a distribution” (USEPA 2005b). On the other hand, the range of values reported for sand and gravels with limited organic carbon demonstrates dissolved lead’s predominant propensity is to sorb to the soil. The  $K_d$  values reported above are large enough to predict sorption as a dominant process even in Camp Edwards’ soils where the quantity of clay is low. The results from a tracer test conducted at the USGS Toxic Substance Hydrology Research Site at Cape Cod, Massachusetts supports the higher  $K_d$  values rather

than the single sample measurement (Larson 2007) as demonstrated by the rapid attenuation of lead (Appendix B).

The concept described in the preceding paragraph has been demonstrated by many laboratory experiments, which also show a significant dependence on pH. For example, one study showed lead sorption was nearly 100% at pH 4 for grassland soils (mollisols) and highly-weathered soils high in iron oxides (oxisols) (Appel and Ma 2002). Sorption of lead remained greater than 60% under the same pH conditions for a soil with low base status (ultisol), analogous to soils found at Camp Edwards (Appel and Ma 2002). Similarly, work on three deep subsoils from the Nevada Test Site (Papelis and Um 2003) showed nearly 100% lead sorption even at pH 4 for two samples and >50% for the third. Finally, studies with aquifer material from near Falmouth, Massachusetts reported approximately 40 to 80% of added lead was adsorbed (Fuller *et al.* 1996) and a later field tracer experiment indicated 100% lead adsorption (Appendix A). All of these studies, except for those in Appendix A, were performed as batch reactions in test tubes representing only a single pass of liquid through a fixed volume of soil. In other words, if the supernatant liquid was removed and mixed once more with the same volume of fresh soil, the least efficient soil would remove > 50% of the remaining lead and so on with additional extractions. Thus, dissolved lead migrating through a column of even the least efficient soil would be approximately 100% sorbed after migrating only a short distance. An example of this behavior under extreme conditions was an experiment whereby more than 70 mg/L lead (a concentration far higher than is possible under any conditions possible at Camp Edwards) was passed into a sandy soil with low pH (4.2) at an infiltration rate of approximately 10 cm/day. (Camp Edwards' infiltration rate is approximately 75 cm/year (0.20 cm/day) (AMEC 2004, 2001a) which is relatively high for natural systems). Even under such severe conditions, lead was not observed in the leachate of a 10 cm column until approximately 50 cm of infiltration had occurred (Korte *et al.* 1975). The latter set of experiments compared 11 soils from seven soil orders and concluded lead was so immobile, even after 30 days of leaching, "from input-output data alone, differences due to soil properties could not be distinguished" (Korte *et al.* 1976).

Finally, an experiment specific to the Cape Cod, Massachusetts aquifer demonstrated lead's relative lack of mobility. Lead complexed to an organic chelate was injected into the aquifer. Little migration occurred and dissolved lead was virtually all adsorbed near the injection location (Appendix A). Particularly striking was how much more rapidly lead was attenuated than zinc, copper, and nickel chelates (Davis *et al.* 2001). Similarly, an analysis of sewage waste leachate on Cape Cod indicated rapid attenuation of lead (Appendix A). In summary, the combination of geochemical conditions at Camp Edwards and lead's own geochemical properties severely inhibit lead migration to groundwater. This conclusion is supported in the following subsections by considering site monitoring data.

### **3.7 Lead Bioavailability**

As described in Sections 1 and 2, exposure to avian species must be minimized and there are a number of factors limiting exposure at Camp Edwards. Foremost are the lack of permanent or semi-permanent standing water (e.g. wetlands) near the SARs being considered for renewed military training and the small area encompassed by these ranges relative to the habitat available for the raptors and mammals present at Camp Edwards. Finally, the Natural Resources Manager at Camp Edwards has observed no evidence of raptors, mammals, reptiles, or biota being affected by lead on the SARs (MAARNG 2006). Nevertheless, it is acknowledged that specific studies with biota have not been performed and that animals dying after lead ingestion are seldom found. Small mammal trapping data, however, indicates healthy populations exist within the range areas and there has been no indication that there should be a concern in regards to lead causing the death of such organisms.

### **3.8 Soil Lead Leachability**

Some selected data from SARs at Camp Edwards are presented in Tables 1, 3, and 4. Table 1 describes range history and Tables 4 and 5 show lead accumulation at firing lines, backstops and berms. Tables 4 and 5 include a “leachability ratio” as defined by Dermatas et al. (2006). This ratio is calculated by multiplying the TCLP result by 20 and then dividing by total lead. The TCLP method employs a 1/20 dilution of the sample as part of the USEPA Method 1311 (USEPA 2006). If the subsamples used for the total and TCLP analyses are identical, 100% leachability indicates all of the lead was leachable by TCLP.

High lead leachability under the TCLP is commonly found with shooting range soils. Dermatas *et al.* (2006) studied four army rifle ranges and reported lead carbonate precipitation/dissolution reactions controlled lead TCLP leachability in all soils. They also reported, as with some Camp Edwards data (Tables 4 and 5), virtually all of the lead was leachable (for a soil with pH of 4.2) under the TCLP in several soils. As the previous subsections (e.g. 3.6) and Appendix A show, sorption processes limit lead mobility no matter how much dissolves. Section 3.12 below further illustrates high leachability under the TCLP does not correlate to significant lead migration in the subsurface. This has been substantiated for Camp Edwards soils under laboratory conditions using lysimeters, which found no appreciable dissolved lead even though more than 1,000 mg/kg of lead was present in the soil and the column thickness was less than 0.6 m (Larson et al. 2007). Although, the TCLP is a standard test used for leachability as noted above it typically does not provide an accurate reflection of the behavior of constituent under site conditions. Therefore, greater confidence should be placed in the column leaching experiments conducted by Larson et al. (2007) and the field tracer tests conducted by the USGS (Appendix A) than the TCLP results.

Lead is heterogeneously distributed even at firing lines and impact areas. This fact is demonstrated by the significant variation in leachability (Tables 4 and 5) and the scattered distributional pattern in soil (Figure 11). A few leachability values exceed 100%. Such variations are probably a result of subsampling where the sample for total analysis and the sample for TCLP were not identical. For instance, a sample may have a high total lead concentration because of the presence of a single bullet fragment. Even though the sample might have been well-mixed, a subsample taken for TCLP may be absent of lead added by training, thus accounting for the large differences observed.

Data from the Former B range is unique for Camp Edwards, because there was a sediment depositional area at the base of a berm impacted by training. In this case, the highest concentrations of lead, copper, and antimony were detected in soil collected from a low-lying depositional area located at the base of a hillside backstop (AMEC 2003c). Concentrations of the same metals at locations higher in elevation on the hillside and nearer the former targets were lower by an order of magnitude. These data demonstrate localized soil erosion and surface runoff can concentrate lead and must be managed on an active range. It is not known, however, whether this lead deposition at the Former B Range was a result of particulate erosion or dissolution followed by precipitation.

### **3.9 Lead in Pore-Water**

In addition to the soil samples discussed previously for the tungsten study, which were treated with Maectite™, 24 tension lysimeters were installed within and below the berm face at the B, C, and I Ranges, as well as at three background locations. Tension lysimeters collect soil-pore water derived from precipitation events as it moves through the unsaturated zone. Lysimeters were sampled four times (10/20/05, 11/9/05, 12/17/05, and 5/10/06) and the water samples were analyzed for lead as well as other metals (USAEC 2006). The depth of the lysimeter tip varied from 38 to 165 cm bgs. The first round of samples were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) with a corresponding reporting limit of 0.050 mg/L and by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) with a corresponding reporting limit of 0.002 mg/L. Samples collected on 11/9/05 and 12/17/05 were analyzed with the ICP-AES. The final rounds of samples collected on 5/10/06 were analyzed with the ICP-MS and through some method modifications, the reporting limit was lowered to 0.001 mg/L. Also, as mentioned previously, the B, C, and I berms had been treated with Maectite™. This phosphate-based material will combine with any dissolved lead present to form a sparingly soluble lead phosphate. Without further study, it is not apparent whether natural geochemical conditions, Maectite™, or a combination is limiting lead movement. The IAGWSP is planning to install several lysimeters at the Former D Range, an untreated range, to assess further lead mobility.

Lead was detected in samples taken from the lysimeters with the highest reported concentration of 0.021 mg/L on 5/10/06 at MMR-18 located on C Range at a depth of 117 cm for an unfiltered sample (Table 6). Analysis of the data indicates no pattern of detection by range, depth, or soil concentrations.

Table 6. Lead concentration in soils and lysimeter samples collected from Bravo, Charlie, and India Ranges.

Lysimeter ID	Range	Target Location	Monitoring Location	Tip depth (inches bgs)	ICP-MS Lead (mg/L) Analysis 10/20/05	ICP-AES Lead (mg/L) Analysis 11/9/05	ICP-AES Lead (mg/L) Analysis 12/17/05	ICP-MS Lead (mg/L) Analysis 05/10/06	Mean Lead (mg/kg) Surface Soil (0-2 inches)	Mean XRF Lead Profile Results (mg/kg) 1-10 inches bgs	Mean XRF Lead Profile Results (mg/kg) 10-20 inches bgs	Mean XRF Lead Profile Results (mg/kg) 20-30 inches bgs	Mean XRF Lead Profile Results (mg/kg) 30-40 inches bgs	Mean XRF Lead Profile Results (mg/kg) 40-50 inches bgs	Mean XRF Lead Profile Results (mg/kg) 50-60 inches bgs
MMR-1	B	T29	TR	31	< 0.002	< 0.05	< 0.05	<0.001	308	394	401	204	NS	NS	NS
MMR-2	B	T33	TR	33	0.017	NW	< 0.05	0.021	308	259	401	204	NS	NS	NS
MMR-3	B	T33	TR	24	0.009	< 0.05	< 0.05	0.007	308	259	401	204	NS	NS	NS
MMR-5	B	T26	BP	27	0.007	< 0.05	NW	<0.001	550	289	342	135	69	75	NS
MMR-6	B	T26	BP	42	0.002	< 0.05	NW	<0.001	550	289	342	135	69	75	NS
MMR-7	B	T24	BP	36	NW	< 0.05	< 0.05	<0.001	NS	NS	NS	NS	NS	NS	NS
MMR-8	B	T23	BP	44	< 0.002	< 0.05	< 0.05	NW	550	289	342	135	69	75	NS
MMR-28	B	BK	BK	15	NI	NI	NI	NW	14.8	NS	NS	NS	NS	NS	NS
MMR-9	I	T6	TR	16	< 0.002	< 0.05	< 0.05	NW	341	NS	NS	NS	NS	NS	NS
MMR-10	I	T1	TR	10	< 0.002	< 0.05	< 0.05	<0.001	341	NS	NS	NS	NS	NS	NS
MMR-11	I	T10	BP	28	< 0.002	< 0.05	< 0.05	0.007	182	605	70	96	NS	NS	NS
MMR-12	I	T10	BP	43	< 0.002	< 0.05	< 0.05	<0.001	182	605	70	96	NS	NS	NS
MMR-14	I	T11	BP	14	< 0.002	< 0.05	< 0.05	<0.001	182	605	70	96	NS	NS	NS
MMR-15	I	BK	BK	21	NW	< 0.05	NW	0.002	1.02	NS	NS	NS	NS	NS	NS
MMR-17	C	T48	TR	15	< 0.002	< 0.05	< 0.05	0.001	390	540	123	341	34	13.4	2.4
MMR-18	C	T48	TR	46	< 0.002	< 0.05	< 0.05	0.016	390	540	123	341	34	13.4	2.4
MMR-19	C	T35	TR	43	< 0.002	< 0.05	< 0.05	<0.001	390	540	123	341	34	13.4	2.4
MMR-20	C	T36	TR	18	< 0.002	< 0.05	NW	<0.001	390	540	123	341	34	13.4	2.4
MMR-21	C	T34	BP	65	0.003	< 0.05	NW	0.001	556	353	530	285	421	435	462
MMR-22	C	T34	BP	47	0.003	< 0.05	< 0.05	0.003	556	353	530	285	421	435	462
MMR-24	C	T43	BP	23	0.005	< 0.05	< 0.05	<0.001	556	353	530	285	421	435	462
MMR-25	C	T43	BP	64	< 0.002	< 0.05	< 0.05	<0.001	556	353	530	285	421	435	462
MMR-26	C	T43	BP	53	< 0.002	< 0.05	< 0.05	0.003	556	353	530	285	421	435	462
MMR-27	C	BK	BK	15	NI	NI	NI	0.001	5.81	NS	NS	NS	NS	NS	NS

BK = background  
 BP = bullet pocket  
 NI = not installed  
 NS = no sample  
 NW = no water  
 TR = trough

Lead was detected in two of the background lysimeters sampled on 5/10/06 at 0.001 mg/L for MMR-27 and 0.002 mg/L for MMR-15 (USAEC 2006). The source of the lead in the background lysimeter samples is undeterminable when solely relying on the pore-water data. Therefore, lead could be the result of natural conditions or anthropogenically-derived from airborne deposition of particulates from propellants at the firing line. However, soil samples from the firing line indicate slightly elevated lead levels as compared to the background lead soil samples.

These background soil samples are located in the woods near the lysimeters. Also, one background soil sample was collected from a remote area near M Range and the lead levels were the same as those of the background samples from B, C, and I Ranges. Therefore, the soil data indirectly suggests the lead measured in the background lysimeters probably has its origin in the native soil. Background soil samples had lead present at concentrations ranging from 1.02 to 15.8 mg/kg. As discussed previously, the geochemical conditions at Camp Edwards do not favor dissolved forms of lead being present to any significant degree. This is supported by the lysimeter and soil profile data which indicates any dissolved lead species derived from corrosion and dissolution of metallic lead is rapidly removed from the soil pore-water through adsorption and precipitation processes.

### **3.9.1      *Lead in groundwater***

Consistent with the preceding discussion, lead has been reported in only 24 of more than 500 groundwater samples. Most of these samples are associated with the Impact Area. Nevertheless, as discussed in Section 3.2.1 the highest lead soil concentration observed, approximately 12,000 mg/kg was found in the Impact Area near an artillery/mortar target. However, lead has been only detected in four monitoring wells out of over 60 located within the Impact Area and downgradient of the target locations. Elevated soil lead levels are also evident at Demolition Area 1 (Demo 1) (AMEC 2001a), again with over 20 downgradient monitoring wells not exhibiting the presence of lead (AMEC 2001d).

Recently, 13 monitoring wells were installed specifically to monitor groundwater downgradient of the SARs (black dots on Figure 15) at the B, C, G, K, J, Former B, SW, and T Ranges. The first two rounds of samples collected from these wells were non-detect for lead at the 0.003 mg/L reporting limit. The berms at the Former B and D Ranges have not been remediated whereas the B, C, G, K, J, T, and SW Ranges have been remediated with metallic lead removed and the soil treated with Maectite™. These results indicate lead has not migrated to groundwater at any of the ranges. At the Former B and D Ranges, training with lead ammunition began in 1935 so these data represent the impact of decades of lead use. These findings are consistent with the previous Section on lead adsorption as well as the USGS Tracer and Sewage Effluent Studies (Appendix B) indicating limited lead mobility. The lack of lead in groundwater derived from the small arms firing ranges is supported by independent unsaturated zone modeling efforts discussed in the following section. These wells were drilled at several ranges and sampled between September 2006 and November 2006 by three separate organizations working at Camp Edwards: IAGWSP, Environmental and Readiness Center (E&RC), and USAEC. All locations were approved by the USEPA and MassDEP prior to installation. The IAGWSP installed wells to investigate the potential impacts to the groundwater from soil contaminants resulting from past use of the SARs. The IAGWSP selected locations based primarily on frequency of use so that the most heavily used ranges were investigated. The E&RC installed

wells to be included in their pollution prevention program (E&RC 2006). It is the author's judgment that these wells are adequate for assessing whether lead has migrated from the SARs to groundwater. Additional groundwater data will be forthcoming as these wells are sampled in the future.

In addition, well MW-72S was installed as part of the Berm Maintenance Project to monitor groundwater quality downgradient of a typical treated berm (Current B Range) in 2000. Groundwater samples have been collected from this well during 13 rounds of sampling and lead was reported only once, on 12/15/05 at 0.0014 mg/L in a filtered sample and at an estimated concentration of 0.0006 mg/L in the unfiltered sample. Samples previous to and subsequent to this single detection indicated no lead at present at the 0.001 to 0.003 mg/L reporting limit. This well is located approximately 10 m downgradient of the berm backstop, near the center of the B Range firing lanes, and near the location of some of the highest soil lead levels. Consequently, if lead was being transported to groundwater this is one of the monitoring wells most likely to show it. Lysimeters located near MW-72S exhibit sporadic detections of lead with the highest concentration observed being 0.021 mg/L. However, the lead levels observed in the lysimeters are too low to support the level of lead detected in MW-72S. Due to the depth of groundwater and dilution affects, a soil pore-water concentration in excess of 0.50 mg/L would be necessary. The detection of lead in MW-72S with non-detects both before and after is an example of the sporadic lead detections that are common and might be explained by the discussion later in this subsection.

Similarly, well MW-174 was installed at the end of the Phase IIb investigation in 2001 at the Former D Range to monitor groundwater quality directly beneath soil exhibiting very high concentrations of total lead. In the process of drilling the borehole for this well, soil samples were collected at 3 and 6 m bgs to examine lead concentrations at depth. In both samples, total lead concentrations were approximately one order of magnitude less than MassDEP mean background level of 19 mg/kg. A single well screen was installed at the water table. Groundwater samples were collected from the well during three sampling rounds and lead was not detected in any of them.

Background levels of metals in groundwater and pore water have not been established for Camp Edwards. However, as discussed in the proceeding section, background soil pore-water lead levels range from 0.001 to 0.002 mg/L (USAEC 2006). For comparison, the USEPA drinking water Maximum Contaminant Level for lead is 0.015 mg/L. Detections elsewhere at MMR have also been sporadic and low-level (Ogden 1998a, 1998b, 1999a, AMEC 2001f, 2004). Nonetheless, any migration of lead to Camp Edwards' groundwater would be problematic and any detection in groundwater seems to contradict lead's geochemical behavior as described in this report. The reasons for the reported detections at MMR are believed to be lead's ubiquity in the environment and interferences during analysis. For example, Figure 14



presents lead detection by date for those wells with more than two reported “hits” for lead. There is an apparent relationship with date suggesting a problem encountered with much less frequency either before or after roughly March 1999 to March 2003. Early in the IAGWSP study, monitoring wells were sampled by bailers and later dedicated bladder pumps were installed. Research by Kearl *et al.* (1992) has shown sampling with bailers typically increases turbidity of water samples, which could explain some of the detections during the period of note. Other issues may also be responsible for these sporadic detections. Well construction details are lacking for the ASP, Textron, and Cemetery wells. The BHW well is constructed of galvanized steel and MW-45S was installed within a known NAV Gas plume which apparently contains tetraethyl lead from the fuel. Finally, none of these wells is located close enough to a SAR to have been impacted by lead migrating from the range (Figure 15). Note the wells depicted with black dots on Figure 15 have been recently installed and sampled once with no detectable lead reported.

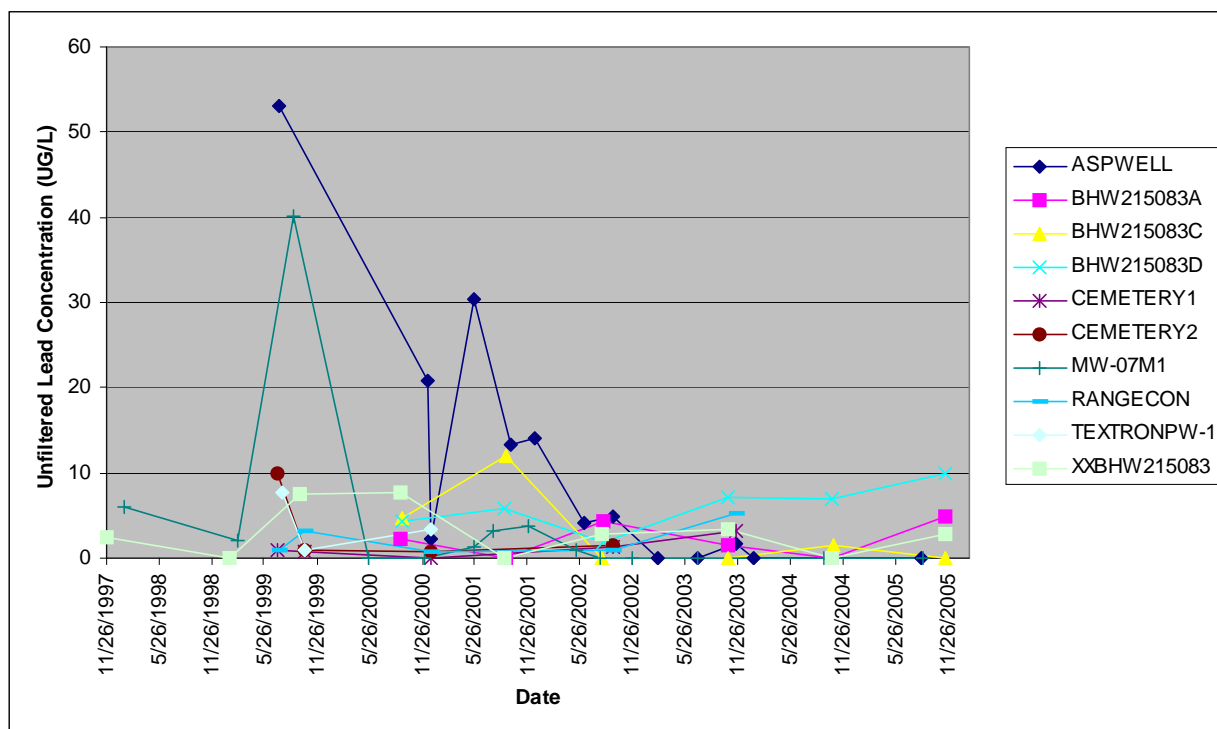


Figure 14. Unfiltered lead in groundwater where wells having more than two detections.

Please contact the Environmental & Readiness Center at 508-968-5143 or [ma-mmrapo@ng.army.mil](mailto:ma-mmrapo@ng.army.mil) for a copy of this document that includes maps.

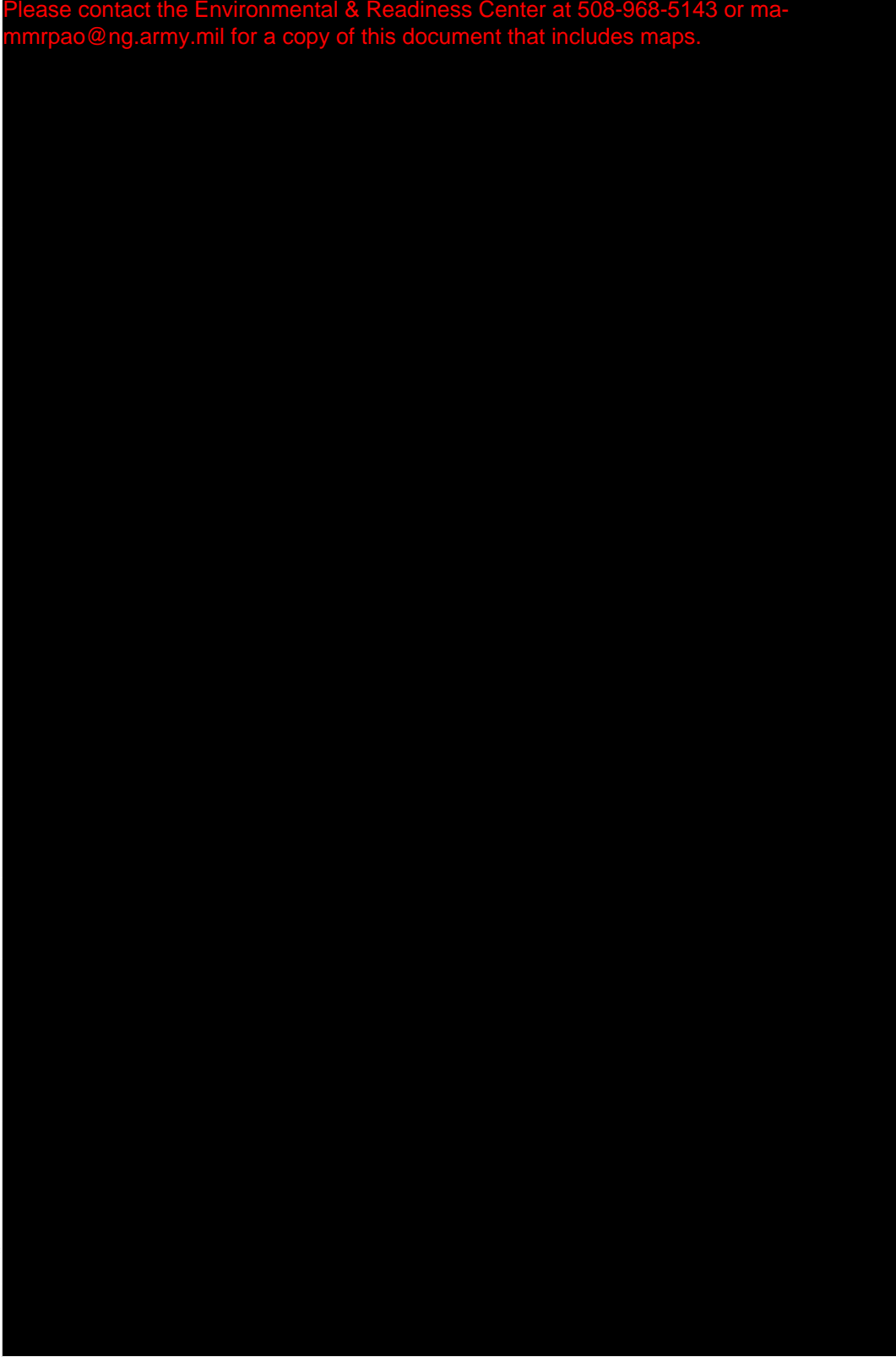


Figure 15. Shallow ground water detections of unfiltered lead.

Unlike the circumstances with synthetic organic compounds where false positive detections are rare, finding traces of lead in water samples where the lead is not indicative of groundwater conditions is relatively common. For example, USEPA Method 200.7 (USEPA 2006), "Determination of metals and trace elements by inductively coupled plasma atomic emission spectrometry" includes a discussion of spectral overlap but says only that overlap "may" require selection of an alternate wavelength. Accurate correction is left to the judgment of the analyst without further explanation. The procedure also notes that physical interferences may occur and their magnitude is related to the identity and quantity of dissolved salts in the sample. Thus, both physical interference and spectral overlap may also be responsible for some of the sporadically reported lead in MMR groundwater. This suggestion is advanced solely for those wells where lead has been reported sporadically. Figure 16 compares unfiltered lead concentrations to turbidity for MW-02S. This is a small data set and is not representative of the entire data base of turbidity versus lead detection. These results, however, show elevated unfiltered lead correlated with high turbidity. Turbidity is a measure of suspended material, which often consists of aluminosilicate clay particles having various metal species sorbed to the clay surface (e.g. iron, lead, manganese, etc.). The presence of lead could be the result of adsorption onto clay particles however, a mechanism is lacking for the introduction of dissolved lead at depth due to the sportive capacity of Camp Edwards soil and the likelihood of formation of relatively insoluble precipitates (Appendix A). Facilitated or colloidal transport has not been demonstrated in the lysimeter samples installed as part of the Tungsten-Nylon Small Arms Range Assessment based on filtration experiments (Clausen *et al.* 2007). Figure 17 shows many elevated lead values correlate to iron, which suggests the elevated metal concentrations are derived from a natural source. Due to the sample preservation technique of using nitric acid, per USEPA Methods, suspended metals present in the unfiltered sample may be dissolved and be detectable during analysis. High iron is another potential cause of analytical error because it has so many spectral lines which offer the opportunity for problems with spectral overlap. Thus, both physical interference and spectral overlap are implicated as potentially responsible for some of the sporadically reported lead in MMR groundwater.

It is also not necessary to invoke interference for sporadic lead detections. Lead is relatively abundant in soil/sediments. The fact a sample has high turbidity indicates there is a great deal of undissolved soil material in the sample. Similarly, inadvertent inclusion of microscopic dust during sampling or in the laboratory could also contribute to sporadic lead detections. As noted elsewhere in this report, natural soil contains lead and thus may account for the traces reported in wells where lead has been reported sporadically.

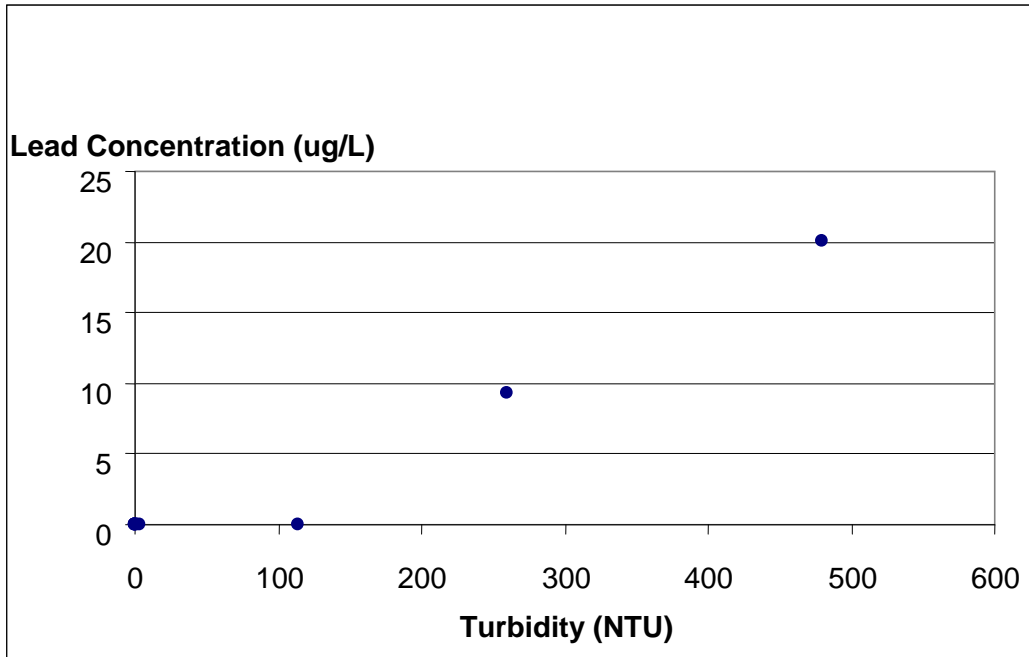


Figure 16. Unfiltered lead versus turbidity for monitoring well MW-02S.

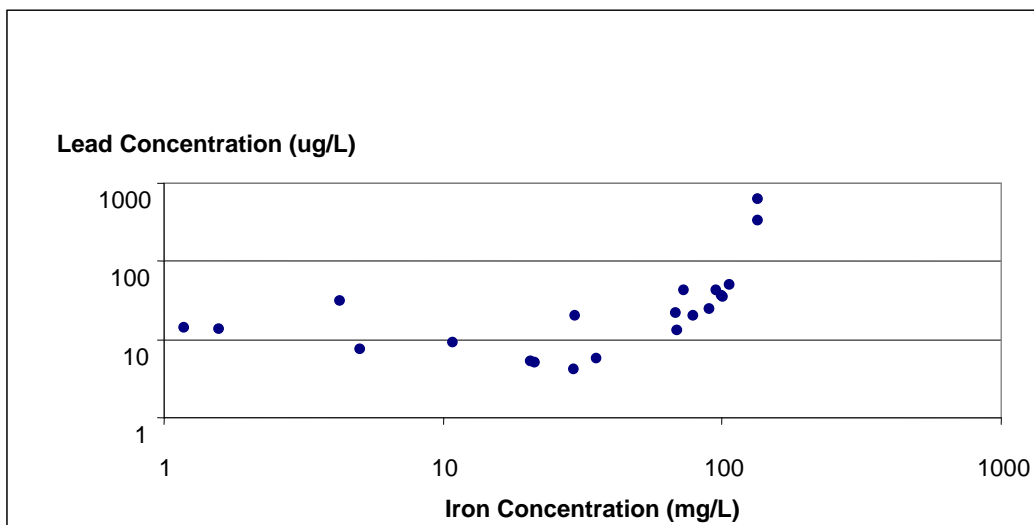


Figure 17. Unfiltered lead versus iron (log scale). Data obtained from Impact Area Ground Water Study Program, Electronic Data Management System database.

The most important rationale for discounting sporadic lead detections in groundwater, however, is the few number of detections and many are sporadic, i.e. not reproduced in multiple sampling events from the same well. Finally, the wells with the lead detections are not associated with the known primary lead sources. The few detections support the geochemical arguments advanced regarding lead's low propensity to migrate to groundwater under the geochemical conditions at Camp Edwards. This fact is supported by a review of the lead in groundwater data as presented previously in Figures 14 and 15. These data demonstrate lead is not consistently detected and when it is reported, the value is typically well below the drinking water standard. (Appendix B, Ogden 1998a, 1998b, 1999a, AMEC 2001a, 2001d, 2003c). The low percentage of lead values reported in Camp Edwards' groundwater is consistent with any large sampling program where many samples are analyzed and some are high in iron or turbidity.

### **3.10 Modeling Lead Mobility**

The potential for lead migration at Camp Edwards was modeled in 1998 (Bricka et al. 1998). This study used conservative assumptions, many of which can now be substantially refined. While this study clearly over-predicted lead mobility, it provides a useful point-of-departure for examining lead migration under more realistic conditions and for considering range maintenance measures. Although the quantity migrating was small, Bricka et al. (1998) suggested lead could migrate to groundwater in 150 to 300 years. The authors recognized their assumptions would over-predict lead migration, but recommended soil clean up every 50 to 70 years as a means of preventing groundwater contamination. To put this study in perspective, it is useful to compare some of their assumptions with facts known today:

All the lead was assumed available for transport as soon as it was deposited. In contrast, the corrosion discussion in this document shows rapid oxidation of deposited lead is not favored. Moreover, most lead-containing particles will be large and possibly jacketed with copper, which will prevent much of the lead from being available for corrosion and dissolution.

The study assumed all of the lead was in the form of a highly-soluble salt and, therefore, was all available for transport. As described previously in this report, lead salts will form following corrosion, but none of these salts is highly soluble. Moreover, if phosphate is added to the soil, the salts can be considered essentially insoluble with respect to migration in water.

Because of the difficulty of performing unsaturated zone modeling, the entire unsaturated zone was assumed to be saturated. Furthermore, alternate wet and dry cycles and the low moisture content of Camp Edwards soils was not considered, which significantly inhibit both corrosion and dissolution.

Bricka et al (1998) assumed a retardation factor for lead of 50 or a  $K_d$  of approximately 10 mL/g, which is more than a factor of three less than the value of 34 mL/g recently measured by Larson (2007) for a sample collected from the Impact Area at Camp Edwards. Both values are 1 to 2 orders of magnitude lower than the USEPA (1999)  $K_d$  recommendation of 900 to 9,000 mL/g for soils similar to Camp Edwards or the range provided by Sheppard and Thibault (1990) and Thibault et al. (1990) of 16,000 to 59,000 mL/g. Bricka et al. (1998) calculated centuries would be required until the sorptive capacity of the soil would be exhausted. The field studies of the USGS (Appendix B), soil profile, and soil pore-water data suggests the soil has a very large sorption capacity for lead. This prediction, therefore, is certainly too low based on the lowest value for  $K_d$  either as measured or as recommended by the USEPA. Finally, it should be noted this modeling is an oversimplification because pH and not  $K_d$  is probably a more important factor regarding lead transport.

As is described previously in the Soil Pore-Water subsection, one response to the predictions and assumptions of Bricka et al. (1998) is to monitor the ranges with lysimeters placed below lead accumulation areas. Should lead be detected, range maintenance can be conducted. Such practices are still conservative. Indeed, to ensure against lead migration to groundwater, the addition of phosphate (e.g. Maectite™) to the soil will result in formation of lead salts which are nearly insoluble; thus significantly enhancing the sorptive capacity of the soil.

Investigators at Camp Edwards have also employed the Seasonal Soil Compartment Model (SESOIL)—a one-dimensional finite-difference vertical transport code for simulating contaminant movement in the unsaturated soil zone (Bonazountas and Wagner 1984, Hetrick *et al.* 1993). SESOIL was designed as a screening-level tool, utilizing less soil, chemical, and meteorological input data than most similar models. The model can simulate water movement, sediment transport, and pollutant fate (i.e. degradation), and can be applied to generic environmental scenarios for purposes of evaluating the general behavior of chemicals in the unsaturated zone. SESOIL is designed to estimate contaminant concentrations in the soil following direct application at the surface and/or interaction with other media. Modeling results for lead were conducted for the Impact Area (unpublished), Gun and Mortar Firing Positions (AMEC 2001e), Demo 1 (AMEC 2001f), and for the SARs (AMEC, 2002a). The Impact Area, Gun and Mortar Firing Positions, and Demo 1 modeling indicated vertical migration of less than 1 m over 100 yrs using the maximum surface soil concentration observed. The maximum lead soil concentration used in the model for the Impact Area was 148,000 mg/kg, more than ten times higher than the maximum concentration measured at the SARs of 11,600 mg/kg. The unsaturated zone geochemical conditions at Demo 1 and Impact Area are similar to those at the SAR. Model simulations suggest travel times on the order of many centuries before lead reaches the aquifer.

More recently, SESOIL was used to simulate lead movement at the SARs (USACE 2007). Using a  $K_d$  value of 270 mL/g, as obtained from a risk assessment data base maintained by the Department of Energy, this exercise predicted lead would not reach the water table in 999 years. This simulation used a water solubility of 4,250 mg/L which, as described in Section 3 of this report, is unrealistically high.

In these simulations, the model was primarily considering sorptive reactions and did not consider precipitation reactions. In addition, the SESOIL model does not include input functions that can account for the oxidation and precipitation of metals or the dissolution kinetics going from a solid to aqueous phase. Consequently, based on the previous discussions the models over predict lead migration.. Furthermore, a sensitivity analysis included in the impact area and Demo 1 modeling found the SESOIL model predictions most sensitive to the following parameters:

**Transport Rates** - The largest area of uncertainty in unsaturated zone modeling is the relationship between the mass of the material of interest and mass flux from surface soils through the unsaturated zone to the aquifer. Sensitivity analysis with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) indicates SESOIL over-predicts RDX movement and subsequent groundwater concentrations. Similarly, SESOIL will over predict lead movement and resulting groundwater concentration since the key factors controlling transport in SESOIL are precipitation and solubility and  $K_d$  of the constituent of interest. Just as with RDX, the lead dissolution rate is a complex function of particle size, temperature, moisture, and geochemical conditions. Several of these variables such as dissolution rate and particle size of the constituent of interest and soil geochemistry are not considered in the SESOIL model.

**Concentrations In Unsaturated Zone Soil Moisture** - The concentration of lead or other constituents dissolved in soil moisture in the unsaturated zone has not been measured at untreated SAR. Thus, the concentration migrating has to be estimated. The literature review and lysimeter data presented herein suggests there may be no lead migrating more than a meter. Thus, any estimate of lead migration through the unsaturated zone almost certainly results in an over-prediction.

**Unsaturated Zone Migration Rates** - The hydraulic travel time through the unsaturated zone has not been quantified. Because it is not known how long it takes soil moisture to travel from the soil surface to the water table, it is not known how long it will take for materials to flush out of the unsaturated zone.

**Groundwater Mixing Zone** - The mixing zone thickness increases with distance from the source, but the approximate thickness in the vicinity of the source is not known.

These uncertainties coupled with reliance of existing models on  $K_d$  suggest the utility of transport models such as SESOIL to simulate lead movement is limited. Presently, there are no existing transport models that can accommodate corrosion and dissolution of a metal solid species.

In summary, a qualitative evaluation of lead migration suggests it could take centuries for lead to migrate to groundwater at Camp Edwards. A review of previously-performed modeling suggests the uncertainties in modeling lead migration are very large and the results over-predicted lead transport in one case. In the other case, modeling results suggested lead would not move appreciably from the SAR. Considering a key uncertainty is the concentration in unsaturated zone moisture, sampling with lysimeters is likely a very useful means of evaluating whether lead migration is occurring or whether the qualitative review indicating significant migration will not occur is sufficient. As discussed earlier, the lysimeter data for ranges treated with Maectite™ primarily indicates no lead is present in the soil pore-water and when present the levels did not exceed 0.021 mg/L. The planned installation of lysimeters at the untreated Former D Range should provide useful data for validating the model output.

### 3.11 Other Constituents in Lead Ammunition

There are other potential constituents (ITRC 2005) associated with use of lead at firing ranges (Table 7). A fate and transport discussion of these elements is beyond the scope of this report but Table 7 is provided for completeness. The IAGWSP plans to address the presence of metals at the SARs through a remedial investigation. Several constituents were removed from the original table (e.g. tungsten) because those are not going to be used in the forthcoming training.

Table 7. Metallic contaminants associated with outdoor shooting ranges (modified from ITRC 2005).

Constituent	Comment
Lead	Primary projectile constituent, primer constituent, and present in initiators and propellants
Arsenic	Used to increase roundness of small shot
Tin and antimony	Increases hardness, Sb used in some primer compounds
Copper and zinc	Jacket alloy metal
Cobalt and chromium	Some military rounds
Nickel	Coating improves shot performance



As noted previously, small caliber military bullets (5.56 mm [M16] and 7.62 mm) have spent projectiles composed of antimony-hardened lead in a copper jacket with masses ranging from 32 to 86 g per bullet, of which 96.4% by weight is lead (MIDAS 2007). Thus, the other constituents are relatively minor in terms of mass when compared to lead. Some in this list also may not be relevant. Arsenic and nickel are primarily used in shot, and tin, zinc, chromium, and cobalt are present mostly as impurities. Arsenic, antimony, copper, nickel, and zinc were consistently detected in the lysimeters installed at the three SARs as part of the Tungsten Fate-and-Transport study; however, the background lysimeters also had detections of these metals at similar levels. Chromium was not detected in any of the lysimeter samples, with the reporting limit at 0.001 mg/L. These minor constituents are subject to the same corrosion processes as lead but neither copper nor zinc is nearly as toxic. Copper's drinking water standard is 1.3 mg/L. Zinc has only a secondary standard (5 mg/L) meaning the primary concerns are taste and color.

### **3.12 Comparison of Camp Edwards with Other Small Arms Range Studies**

There have been several studies of sport shooting ranges world-wide but limited information is available for military SAR. Several investigations describe undesirable effects but when the data are applied to Camp Edwards, the results support conclusions previously presented, i.e. lead will not migrate significantly.

Much of the data in the technical literature is from sport ranges, where lead shot is used. Many similarities between military and sport ranges do exist with respect to both maximum lead concentrations and the use of shotguns for firing lead pellets (USACE 2006). However, many differences exist as well with the foremost being the size of the lead projectile as discussed in Section 1.4.3. An unfragmented M855, 5.56 mm projectile excluding the propellant casing is 22 mm long and 4 mm in diameter. In contrast, lead shot can range in diameter from 16 mm to less than 2 mm (Table 8). Most of the lead shot used on sport ranges is less than 2.4 mm in diameter, which is considerably smaller than the shot used on military ranges. Typically, the military uses 00 Buck shot, which has a diameter of 8.4 mm in diameter. The M-16 5.56 mm is designed not to fragment upon impact although fragmentation can occur (Fackler 2007, Larson *et al.* 2006) but the degree of fragmentation has not been quantified. Larson *et al.* (2006) work found the majority of the lead mass associated with the greater than 2 mm soil size fraction. Our own SAR work, unpublished, supports the Larson *et al.* (2006) findings in that most of the metal mass is concentrated in the > 2mm soil size fraction. Both of these studies looked at 25 m ranges. Fragmentation will be less at those ranges with greater distance to the target such as the Tango Range. Planned training at Camp Edwards is mostly with M-16 copper-jacketed bullets (some shotgun training will occur at the O Range and potentially other ranges), which is expected to result in less exposure to biota than the use of lead shot at sport ranges. The military typically uses single slugs or 00 Buck Shot and the latter has a diameter four times larger

than the lead shot used on sport ranges. Due to the greater number of lead shot pellets in sport shot, the surface area is 2 to 3 times greater than that for 00 Buckshot.

Studies from other ranges show the greatest lead concentrations near impact sources (impact and lateral berms and shotfall zones). For example, soil samples from the backstop berms at four sport shooting ranges contained lead as high as 60,600 mg/kg (Cao et al. 2005). The highest concentration reported at Camp Edwards was at the Current G Range with more than 12,000 mg/kg (Table 4). Slightly elevated lead levels have also been found at firing lines (Table 5), because common military primer formulations (FA-956 and FA-70), igniters, and propellants include organo-lead compounds (lead thiocyanate, lead styphnate, lead stearate, and lead salicylate) at approximately 0.1 to 0.2 grams per bullet (MIDAS 2007). Lead carbonate also is added to inhibit corrosion of gun barrels. Cao et al. (2003a, 2003b) examined several rifle ranges in Florida with similar characteristics to Camp Edwards—the primary difference being temperature and depth to water. The conditions for lead mobility in Florida present a relatively more favorable lead-transforming environment because of the combination of high moisture and year-round elevated temperatures (Chen et al. 2002, Cao et al. 2003a). Little movement below the surface was found for the five ranges investigated, although most surface soils failed the TCLP (Cao et al. 2003b). The soil samples indicating low leaching potential and the areas where lead movement in shallow groundwater was limited had the highest soil phosphate levels. At only one site did a “substantial amount of lead migrate to the subsurface”. However, “subsurface” referred to the concentration of lead at 1 m and the quantity of lead present was a factor of 10 less than the surface concentration. An additional factor of 10 decrease after another meter of migration and the concentration would be at background.

At only one site reviewed, the Prime Hook National Wildlife Refuge in Delaware, was “groundwater contamination” described (Soeder and Miller 2003). At the Prime Hook site lead shot, 1 to 2 mm in size, was fired into a forested wetland area with acidic soil and surface water. Depth to the water table was generally less than 1 m with groundwater discharge into a stagnant slough. The surface water and groundwater had a high TOC content and the sandy quartz aquifer material lacked iron oxide coatings. In contrast, depth to groundwater at Camp Edwards is over 30 m, the soils have a low TOC content (see Section 2.4.1), and the quartz grain aquifer material have iron oxide coatings (Appendix B). While the depth to groundwater and predominant particle size are believed to be the most important issues, sediment composition and ground-water chemistry are sufficiently similar that lead adsorption properties at the two sites are likely to be very similar. Also, the much-higher DOC concentrations observed at the Delaware site relative to Camp Edwards may not be significant.

Table 8. Shot size diameter, effective range, count, and usage.

Environmental Assessment of Lead at Camp Edwards

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Shot Name	Shot Diam (in.)	Shot Diam (mm)	Maximum Range (yd)	Maximum Effective Range (yd)	Shot Count (1 oz.) <sup>1</sup>	Comment
Round	0.645	16.38	1420		1	Typically used for military shotguns
Round	0.61	15.49	1340		1	Typically used for military shotguns
Round	0.545	13.84	1200		1	Typically used for military shotguns
Round	0.38	9.65	850		1	Typically used for military shotguns
000 Buck	0.36	9.14		40	8, 10	
00 Buck	0.33	8.38	726	40	9-18	Typically used for military shotguns
0 Buck	0.32	8.13	704		12	
1 Buck	0.3	7.62	660		12-24	
3 Buck	0.25	6.35			20,24	
4 Buck	0.24	6.10			27-41	
T	0.2	5.08			30	
BBB	0.19	4.83			44	
BB	0.18	4.57			47	
B	0.17	4.32			50	
#2	0.15	3.81			87	
#4	0.13	3.30	286		125	
#5	0.12	3.05			170	
#6	0.11	2.79	242		225	
#7½	0.095	2.41	209		350	Typically recommended for clay pigeons
#8	0.09	2.29	198		410	Typically recommended for clay pigeons
#8½	0.085	2.16			497	Typically recommended for clay pigeons
#9	0.08	2.03	176		585	Typically recommended for skeet

Landmeyer (1994) and Knechtenhofer *et al.* (2002) reported additional investigations with relevance to Camp Edwards. The former study, conducted at an Air Force Shooting range in South Carolina, once again had berm soils failing the TCLP, but lead migration to the shallow

water table (< 3 m) was not observed. Knechtenhofer *et al.* (2002) evaluated a sport shooting range much more acidic than Camp Edwards (pH 3). A contaminated soil profile was irrigated sufficiently for ponding to remain visible on the surface for twenty hours. The lead concentration was 80.9 mg/kg in the topsoil but by 40 cm in depth, the lead concentration approached background. In summary, these studies indicated:

- Lead accumulation in firing lines and target areas was common,
- Surface soil samples frequently exceeded regulatory action levels and many were hazardous based on the TCLP, and
- Subsurface migration was limited to no more than approximately 1 to 3 m.

Another relative study is the evaluation of the Lake Merced sporting range in San Francisco, California (Crosby and Overton 1990a, 1990b). This particular site shares similar soil characteristics to Camp Edwards, i.e. a sand, loamy sand, or sand loam with little organic layer development. Although later studies (SFPUC 2005) have suggested a potential leaching concern based on TCLP tests, previous and ongoing field studies show that elevated lead levels are concentrated in the top 0.6 m of the soil with no lead above background present deeper than 1.5 m.

Bricka *et al.* (1996a) studied three military SARs at Fort Benjamin Harrison in Indianapolis, Indiana and found no elevated lead beyond a depth of 0.9 m from the surface. The soil at this site had much higher clay content than Camp Edwards. Similar results were seen at two zeroing ranges located at an Army installation in Louisiana. Lead migration was limited to 1.2 m in a clay rich soil (Bricka *et al.* 1996b).

Apart from high soil concentrations, among the undesirable effects observed at sport shooting ranges (Cao *et al.* 2003a, 2003b), were elevated lead concentrations in surface water and in plants grown in shooting range soils (Murray *et al.* 1997). The highest lead concentration was found in plant roots, and it was positively correlated with soil ethylenediaminetetraacetic acid (EDTA)-extractable lead concentrations (Rooney *et al.* 1999). Mellor and McCartney (1994) reported reduced crop density of plants grown within a shot-fall zone at soil lead concentrations of approximately 1,500 to 10,500 mg/kg. Elevated lead levels in water were reported by Stansley *et al.* (1992) in an investigation of eight target shooting ranges in the US. They suggested the weathering of lead pellets resulted in elevated concentrations of water-borne lead (0.004 to 0.84 mg/L versus 0.007 mg/L at the control sites). At a trap and skeet range located in Westchester County, New York, surface water lead concentration ranged from 0.060 to 2.9 mg/L (USEPA 1994). Labare *et al.* (2004) at a trap and skeet range in Westchester, New York reported lead mobility into nearby streams and sediment. This range, however, was adjacent to

a stream. These studies emphasize the importance of preventing surface water runoff and the maintenance of sub-optimal growing conditions at Camp Edwards.

## 4.0 Recommendations

Although lead has not contaminated the groundwater in any significant way, uncertainties remain in regards to lead fate-and-transport. If there is a desire by MAARNG and others to reduce the uncertainty in regards to lead fate and transport, during the development of pollution prevention plans, specific studies could be conducted to address these issues. These recommendations are presented purely for the purpose of furthering our collective knowledge in the area of lead fate and transport behavior, and are in no way intended to undermine the conclusions which have been presented. A significant amount of resources have been invested into this project and much of the time was spent gathering and reviewing relevant studies that have been completed/published on lead behavior. Using our collective lessons learned for this study, and in an effort to more efficiently and effectively apply resources, in the future, we recommend the following:

### 4.1 Field Studies

One of the key issues to establish is whether lead is going into solution at the SARs. Although pore-water data has been collected at B, C, and I Ranges, these ranges have been treated with the Maectite™ – phosphate material. Therefore, it is unclear whether the lack of lead in the soil pore-water is a function of leads inherent fate and transport properties or the application of the Maectite™. Consequently, it would be useful to install lysimeters at untreated SARs such as the Former B and D Ranges to assess whether lead without the addition of phosphate is mobile. Our recommendation would be to install the lysimeters at the base of the berm. For each range to be studied two clusters of two lysimeters at depths of 0.6 and 1.5 m are recommended at a minimum. It is our understanding that IAGWSP intends to install several lysimeters at Former D Range to conduct such an evaluation.

Although soil profiles could be collected to ascertain the transport of lead, the concern with lead relates to its migration to groundwater. Therefore, our recommendation is to focus on the soil pore-water rather than soil. There are several concerns with the collection of soil profiles the foremost being the potential for cross-contamination during sampling in the sandy soil. Previous soil profile sampling efforts at Camp Edwards have resulted in occasional detection of lead with depth. Consequently, this makes interpretation of the transport of lead more difficult. In addition, the typical soil profile represents a point in space. Thus, the results from a single profile may not be representative of the SAR due heterogeneity issues. In contrast, a lysimeter installed at depth integrates water collected over a larger area, the area integrated being dependent on the depth of the lysimeter installation. Although profile samples could be collected using a multi-increment approach this is a time consuming process.

However, if profile samples are desired it is recommended that a slit trench approach be used to collect the samples or a coring device. With either approach, great care should be taken to prevent cross-contamination of the samples owing to the sandy nature of the soil. Our recommendation would be to collect soil samples on 25 cm intervals for the top 200 cm and then a final sample at 300 cm. Due to the heterogeneous distribution of metals in soil a multi-increment sample approach is recommended utilizing the combining of samples from at least a minimum of six different borings. Further, we recommend that the berm face be broken it three separate decision units, i.e. the area above the bullet pockets, bullet pocket and eroded area, and the trough at the base of the berm. If there are concerns about lead at the firing point then this should be included as a separate decision unit.

In addition, further work could be conducted to establish the background level of lead in surface soils, and soil pore-water. This would involve the collection of additional soil samples and the installation of additional lysimeters. Further effort could also be spent further scrutinizing the few lead detections in monitoring well samples to assess their validity.

Finally, further work could be conducted to establish the background level of lead in surface soils, and soil pore-water. This would involve the collection of additional soil samples and the installation of additional lysimeters. Further effort could also be spent further scrutinizing the few lead detections in monitoring well samples to assess their validity.

## **4.2 Laboratory Studies**

One of the key variables controlling the rate of movement of lead is the corrosion rate of metallic lead and the susceptibility of the resulting lead oxides to dissolution. Dissolution drip experiments could be conducted using unweathered and weather projectiles to assess the dissolution rate. Although, the species of lead oxides on lead shot has been studied at some sites a similar study has not been conducted for larger lead military projectiles with copper jackets. The lead oxides formed for military munitions may be different from those species found associated with lead shot since the composition of lead shot is different from that for military ammunition. Also, corrosion processes for copper jacketed lead projectiles may be different from lead shot. In addition, the site-specific geochemical environment at Camp Edwards may result in the formation of lead oxides different from other studies. Since the lead oxides are the species most likely dissolved knowing the form present would allow proper selection of the lead solubility value used in transport modeling. The current modeling approach is to select a conservative solubility value, which may lead to higher predicted lead groundwater values than warranted. In turn, this approach may lead to conservative soil action levels.

Another key unknown is the affinity of the dissolved species of lead to the soil matrix. This could be assessed through batch or column  $K_d$  experiments using site specific SAR soils. Presently,

only a single site-specific  $K_d$  value (34 mL/g) is available for Camp Edwards and this sample was obtained from the Impact Area. Many of the modeling lead assessments conducted by the USEPA have used a default  $K_d$  value of 900 mL/g with the literature suggesting even higher values. USEPA (2005) suggests that  $K_d$  values can range over several orders of magnitude for samples collected from the site. Given the importance of  $K_d$  in the transport models, i.e. it is the key controlling variable determining the depth of migration, collection of half dozen samples would seem prudent. These batch experiments should then be confirmed with several column studies since batch experiments tend to under predict sorption kinetics.



## 5.0 Conclusions

This report has assessed the fate of lead released into the environment at Camp Edwards from firing at small arms ranges. The principal conclusions are corrosion, dissolution processes are sufficiently slow, and mechanisms for attenuation, such as precipitation and adsorption, sufficiently robust, that lead has not migrated to groundwater. This review also indicates quantification of soil sorptive capacity cannot be accomplished in any meaningful way. These conclusions are supported by the following facts:

1. Multiple soil profile samples collected prior and post berm-maintenance from six small arms ranges indicated little vertical migration of lead,
2. Geochemical conditions within the surface soils, (e.g. pH, chloride, resistivity, permeability, and oxygen) are not conducive for significant corrosion, dissolution, and transport of lead,
3. Experimental results from other studies with conditions similar to Camp Edwards showed minimal lead movement,
4. Experimental results from other studies consistently demonstrate such high and variable measurements for lead partition coefficients that modeling exercises typically have uncertainties on the order of centuries in their predictions,
5. Geochemical studies found in literature suggest the propensity to form insoluble precipitates, and not sorptive capacity, may be the most important factor controlling lead migration in the subsurface,
6. The corrosion/dissolution rate, although qualitatively predicted to be slow, cannot be quantified because of several uncertainties ranging from uncertainty regarding the particle size distribution to the effects of wet/dry cycles,
7. Unsaturated zone modeling using two different software codes predicted the vertical migration of lead would take centuries to reach groundwater,
8. Water samples from most monitoring wells (except MW-72S) installed immediately downgradient of the backstop berms at a number of small arms ranges showed no measurable lead,

9. Groundwater data collected to date from across Camp Edwards demonstrated little to no lead contamination as a result of accumulation from small arms training, despite lead being continuously released to soil for more than 60 years,
10. Tracer studies conducted by the USGS near MMR demonstrated an aqueous form of lead was rapidly adsorbed onto the soil, implying the same reactions will attenuate lead movement in the unsaturated zone, and
11. Lead introduced into the groundwater at MMR in a sewage treatment effluent was quickly and completely attenuated.

The technical literature, however, clearly describes dangers to humans and wildlife exposed to lead. Although lead mobility is limited in the Camp Edwards environment, there is not adequate data to date to quantify the amount of lead that can be safely deposited in the environment. It is important, therefore, to minimize environmental exposure through the application of best management practices.

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## **Appendix A**

### **SOLUBILITY PRODUCT CONSTANTS OF LEAD MINERALS AND COMPOUNDS**



Table A-1 lists the lead compounds or minerals mentioned in the main text as well as some other minerals for which data were found. The latter are included for comparison purposes. An attempt was made to find the solubility product constants for each mineral in the table but some were not readily available.

This literature search was extensive but not exhaustive, therefore, additional data may be available. Furthermore, it is emphasized that these measurements are typically difficult to perform and are affected by pH, temperature, presence of competing ions and many other factors. In some cases, there is controversy regarding the precise mineral formula as with lead pyromorphites where 4 lead molecules and not 5 are sometimes included in the formula. Hence, direct application of these values to solubility in the field usually requires site-specific research.

Typically, the data in the Table are for room temperature (20-25°C) and deionized water. The majority of the data are from Traina et al. (1999) and from sources cited in the main text.

In considering those compounds where data are not available, note that the main text quoted the following: Common lead minerals which form in most soils decrease in the order of solubility as follows:  $\text{PbO} > \text{PbCO}_3 > \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 > \text{PbSO}_4 > \text{PbHPO}_4 > \text{Pb}_5(\text{PO}_4)_3\text{OH} > \text{Pb}_5(\text{PO}_4)_3\text{Cl}$  (Lindsay 1979).

**Table A-1.** Solubility products of selected Pb minerals.<sup>1</sup>

Mineral	Formula	Log $K_{sp}$ *
Litharge	<b>PbO</b>	<b>12.9</b>
Massicot <sup>2</sup>	<b>PbO</b>	?
Anglesite (lead sulfate)	<b>PbSO<sub>4</sub></b>	<b>-7.7</b>
Cerussite	<b>PbCO<sub>3</sub></b>	<b>-12.8</b>
Hydrocerrusite	<b>Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub></b>	?
Lead (Hydr)oxide	<b>Pb(OH)<sub>2</sub></b>	<b>-14.9</b>
Lead Hydroxyapatite	<b>Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)</b>	?
Galena	<b>PbS</b>	<b>-27.6</b>
Lead Phosphate	<b>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub></b>	<b>-54</b>
Lead Oxyphosphate	<b>Pb<sub>4</sub>O(PO<sub>4</sub>)<sub>2</sub></b>	?
Pyromorphite	<b>Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl</b>	<b>-84.4</b>
Hydroxypyromorphite	<b>Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH</b>	<b>-76.8</b>
Plumbogummite	<b>PbAl<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>5</sub>·H<sub>2</sub>O</b>	<b>-99.3</b>
Fluoropyromorphite	<b>Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F</b>	<b>-71.6</b>
Bromopyromorphite	<b>Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Br</b>	<b>-78.1</b>
Corkite	<b>PbFe<sub>3</sub>(PO<sub>4</sub>)(SO<sub>4</sub>)(OH)<sub>6</sub></b>	<b>-112.6</b>

Hindsalite  $\text{PbAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$  -99.1

**Lead-bearing Jarosites**  $\text{KFe}_x\text{Pb}_x(\text{SO}_4)_2(\text{OH})_6$  ?

<sup>1</sup>Minerals or compounds in bold print are mentioned in the report.

<sup>2</sup>Massicot and Litharge have the same formula but different crystalline structure.

## **APPENDIX B**

**Lead adsorption and lead transport studies conducted at the U. S. Geological Survey Toxic Substances Hydrology Research Site at Cape Cod, Massachusetts**



# United States Department of the Interior

U.S. GEOLOGICAL SURVEY  
Massachusetts-Rhode Island Water Science Center  
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December 5, 2006

Shawn Cody  
Director, Environmental Affairs  
Massachusetts National Guard  
50 Maple Street  
Milford, MA 01757

Dear Mr. Cody:

At your request, Dr. Douglas Kent has prepared the attached summary of research by the U.S. Geological Survey on the fate and transport of metal ions in ground water in the aquifer of western Cape Cod. The research was done under the auspices of the USGS Toxic Substances Hydrology Program. The summary focuses on findings of particular relevance to the potential for migration of lead in the subsurface.

We hope the findings of the USGS research are helpful in your assessment of the fate of lead at the small-arms ranges at Camp Edwards. Please don't hesitate to contact Dr. Kent or me if you have any questions about the summary or the USGS research program on Cape Cod.

Sincerely yours,

Denis R. LeBlanc  
Hydrologist

cc: Col. William Fitzpatrick, E&RC

Enc: Summary report

**LEAD ADSORPTION AND TRANSPORT STUDIES  
CONDUCTED AT THE U. S. GEOLOGICAL SURVEY TOXIC SUBSTANCES  
HYDROLOGY RESEARCH SITE ON CAPE COD, MASSACHUSETTS**

Prepared for the Massachusetts National Guard  
Environmental & Readiness Center  
Massachusetts Military Reservation

By Douglas B. Kent and Denis R. LeBlanc  
U. S. Geological Survey

December 5, 2006

Draft. Not for Citation

## **Introduction and Background**

Since 1983, U. S. Geological Survey (USGS) scientists and their colleagues from universities and other research institutions have conducted research on processes controlling the fate and transport of contaminants of national and global concern at a site on western Cape Cod (USGS research site). The site is located downgradient of the Massachusetts Military Reservation (MMR) wastewater-treatment facility, where a 60-year period of discharge of wastewater, which ended in 1995, resulted in a plume of wastewater-contaminated ground water. Research at the site is conducted under the auspices of the USGS Toxic Substances Hydrology Program. Multi-disciplinary research involving long-term field studies, field-scale transport experiments, laboratory experiments, and computer modeling has focused on identifying critical processes influencing the transport of pathogens, nutrients, organic, and inorganic contaminants (LeBlanc, 2006). The purpose of this report is to summarize principal findings from these studies that are relevant to understanding the potential mobility of lead(II) ( $\text{Pb}^{2+}$ ) in the aquifer on western Cape Cod.

The shallow aquifer on western Cape Cod is developed in non-calcareous sediments and, therefore, ground water is mildly acidic with low concentrations of dissolved carbonate and other dissolved salts. Under these chemical conditions, Pb-containing solids (including hydroxides, carbonates, and sulfates) are undersaturated at Pb concentrations below approximately 26 milligrams per liter (mg/L) (which equals 125 micromoles per liter,  $\mu\text{M}$ ). Thus, mineral solubility reactions will not limit Pb

concentrations until they exceed this value. Under these conditions, Pb concentrations and mobility will be controlled by adsorption. Adsorption results from reactions between aqueous species and sites at sediment surfaces. A considerable amount of work has been published by USGS researchers and their colleagues on the adsorption properties of the sediments, the transport of adsorbing metal ions and other inorganic solutes, and reactive-transport modeling of the fate and transport of adsorbing solutes in the aquifer. The best studied metal cation is zinc(II) (Zn), but adsorption of Pb has also been described, as has been the transport of Pb complexed with the strong complexing agent ethylenediaminetetraacetic acid (EDTA). Other adsorbing solutes whose adsorption and transport have been investigated include molybdate, phosphate, arsenate, arsenite, chromate, selenate, nickel(II) (Ni), and copper(II) (Cu).

### **Adsorption Properties of the Sediments**

The mineralogy and adsorption properties of the sediments collected from the USGS research site have been studied extensively. The sediments are comprised of greater than 90 percent quartz with minor quantities of feldspars and accessory ferro- and aluminosilicates and oxides (Barber 1990; LeBlanc and others, 1991; Davis and others, 1993; Coston and others, 1995). Although quartz is the most abundant mineral, adsorption properties of the sediments are dominated by coatings on quartz grains that are comprised primarily of aluminum (Al), iron (Fe), and silicon (Barber and others, 1992; Coston and others, 1995; Fuller and others, 1996; Davis and others, 1998). Hematite particles on the order of 5 nanometers in diameter have been identified in the coatings along with aluminosilicates and oxides too poorly ordered to be identified mineralogically (Banfield and Hamers 1997). Adsorption studies have shown that, on a per unit surface area basis, the sediments adsorb cations more strongly and anions more weakly than hydrous ferric oxide (Stollenwerk, 1995; Kent and others, 1995, 2002; Davis and others, 1998). Clay minerals have not been identified in bulk sediment samples but kaolinite and, possibly, smectite and chlorite have been identified in material isolated from interiors of feldspar grains, where they are likely forming as alteration products (Wood and others, 1990; Bau and others, 2004).

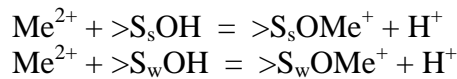
Laboratory experimental studies have shown that Pb adsorbs extensively on sediments collected at the USGS research site. The extent of Pb adsorption increases with increasing pH. At a total Pb concentration of 10  $\mu\text{M}$  (2.1 mg/L) and a surface-area-to-volume ratio of 22 square meters per liter ( $\text{m}^2/\text{L}$ ) (which corresponds to a solid-liquid ratio of 50 grams per liter), the percentage of Pb that was adsorbed onto the sediments increased from approximately 25 percent at pH 4 to 100 percent at pH 6.5. Zinc also adsorbs extensively on the sediments, but Pb adsorption is much more extensive (Coston and others, 1995; Fuller and others, 1996).

Fuller and others (1996) examined factors controlling spatial variability in Pb adsorption by sediments at the USGS research site. At constant solution conditions and solid-liquid ratio, the concentration of Pb adsorbed onto 374 different sediment samples varied by less than a factor of 4, with values for most samples falling within a factor of 2.

Lead adsorption correlated well with the crystalline Fe-plus-Al-oxide content of the sediment-coating materials when the adsorbed Pb concentration and the Fe-plus-Al-oxide content were normalized to specific surface area. The crystalline Fe-plus-Al-oxide content was determined using a citrate-dithionate extraction. No significant correlation between adsorbed Pb concentration and hydraulic conductivity of the sediments (estimated from grain-size distribution) was observed.

### **Mobility of Lead and Other Strongly Adsorbing Metal Ions**

Adsorption of Pb, Cu, and Zn on the sediments over the range of ground-water chemical conditions observed at the USGS research site can be well described by reactions of the form:



where  $\text{Me}^{2+}$  represents the metal ion (Pb, Cu, or Zn) and  $>\text{S}_s\text{OH}$  and  $>\text{S}_w\text{OH}$  represent adsorption sites with different binding strengths (Davis and others, 1993, 1998; Fuller and others, 1996). A model of this form calibrated using laboratory data for Zn adsorption on sediments from the site predicted the large impact of variable pH on the mobility of wastewater-derived Zn in the aquifer (Kent and others, 2000).

Field experiments have been conducted at the USGS research site in which Pb and other metal ions complexed with EDTA were injected into the aquifer. In one experiment, 600 liters of ground water with 100  $\mu\text{M}$  each of Pb, Ni, Cu, and Zn as EDTA complexes were injected into the aquifer (Podey and Lewandowski, 1997). A concentration of 100  $\mu\text{M}$  corresponds to 20.7 mg/L Pb, 5.9 mg/L Ni, 6.4 mg/L Cu, and 6.5 mg/L Zn. Breakthrough curves for all four metal ions, collected 2.5 meters downgradient from the injection well, are shown in figure 1. Concentrations were normalized by dividing the concentration of each metal determined at any given time by its concentration in the injectate solution. For all four metal ions, only the EDTA complexes were detected; concentrations of free metal ions (concentrations for metal ions not complexed with EDTA) could not be detected. Concentrations of Cu and Zn were below those of Ni in most samples. Concentrations of Pb were much lower than concentrations of Ni in all samples. Normalized concentrations of Ni were equal to normalized concentrations of bromide, which was the conservative, non-reactive solute added to trace the movement of the injected water. This shows that there was no loss of Ni from the tracer cloud over the 2.5-meter transport distance (Kent and others, 2002). In contrast, the fact that concentrations of Cu, Zn, and Pb were lower than the corresponding concentration of Ni is evidence of a loss of these metals to the sediments over the 2.5-meter transport distance. Integration under the breakthrough curves shows that almost 40 percent of the injected Pb was lost from the tracer cloud over the 2.5-meter transport distance. Concentrations of Fe-EDTA complexes accounted for all of the EDTA that was not complexed with Ni, Cu, Zn, or Pb.

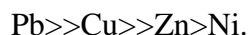
The observed loss of metal ions from EDTA complexes occurs as a result of the following reaction:



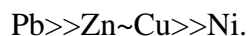
Metal ions complexed with EDTA are displaced by iron(III) (Fe(III)) leached from the sediments. The free metal ion displaced from EDTA complexes (Me) adsorbs to the sediments (Davis and others, 2000; Kent and others, 2002). The thermodynamic driving force for the reaction stems from the strength of the metal-ion-EDTA complexes and the strength of binding of the free metal ion to sediment surface-sites. Equilibrium constants for the formation of metal-EDTA complexes decrease in the order:



Equilibrium constants for adsorption of metal ions to the sediments, as determined in laboratory experiments, decrease in the order:



Overall, one predicts that the extent to which these metals would be displaced should decrease in the order (Davis and others, 2000):



This order of displacement agrees with that observed experimentally (fig. 1). The extent to which the displacement reaction occurs during transport is limited by the slow rate of dissolution of Fe(III) from the sediments (Friedly and others, 2002).

In another experiment, 10,000 liters of ground water with 250  $\mu\text{M}$  PbEDTA (which equals 52 mg/L Pb) were injected into the aquifer and transport was monitored over approximately one year (Davis and others, 2000). Concentrations of Pb decreased rapidly during the experiment. Approximately 100 days after the injection, during which time the center of mass of the tracers had moved approximately 40 meters, Pb concentrations in the tracer cloud had decreased to below detection.

### **Survey of Dissolved Lead and Other Metal-Ions Concentrations near the Abandoned MMR Wastewater-Infiltration Beds**

In order to examine further the potential for significant concentrations of Pb to occur in the aquifer, ground water in the vicinity of the abandoned infiltration beds at the MMR wastewater-treatment facility was sampled in 2006. The beds were last used in December 1995. Wastewater from the treatment facility contained low concentrations of Pb, along with other metal ions, such as Zn and Cu, that are typically associated with pipe corrosion. Concentrations of Pb in wastewater discharged to the disposal beds at the MMR were in the range of 6-29  $\mu\text{g/L}$  (0.03-0.14  $\mu\text{M}$ ) (E. C. Jordan, 1986; Vaccaro and



others, 1979). Concentrations of Cu and Zn were 40-90  $\mu\text{g/L}$  (0.6-1.4  $\mu\text{M}$ ) and 25-130  $\mu\text{g/L}$  (0.4-2.0  $\mu\text{M}$ ), respectively (E. C. Jordan, 1986; Vaccaro and others, 1979). More recent assays of the wastewater discharged to the beds found similar concentrations of Cu and Zn, but the analytical methods used were not sufficiently sensitive to determine Pb concentrations at the low levels previously observed in the wastewater (Rea and others, 1991, 1996; Savoie and LeBlanc, 1998; Kent and others, 2000).

Sampling locations were chosen at which wastewater-derived Zn and Cu had been detected consistently over the past decade (Kent and Maeder, 1999; Kent and others, 2000). The sampling locations are shown in figure 2 and the sampling-site characteristics are given in table 1. Samples were collected, filtered, and preserved by acidification as described elsewhere (Savoie and LeBlanc, 1998). Concentrations of Pb, Cu, Zn, and other inorganic solutes were determined by inductively coupled plasma mass spectrometry. The limit of quantitation for Pb was 0.08  $\mu\text{g/L}$  (0.0004  $\mu\text{M}$ ); the limit of quantitation for Cu and Zn was about 0.4  $\mu\text{g/L}$  (0.006  $\mu\text{M}$ ).

Concentrations of dissolved Pb, Cu, and Zn, along with other water-quality data are presented in tables 2-4. Concentrations of Pb were at or below the limit of quantitation in all samples. In contrast, dissolved Zn and Cu were detected in most samples. Dissolved Zn and Cu concentrations in shallow ground water under the wastewater-disposal beds (for example, samples at MA SDW 473-M01-02GNT, MA SDW 436-M01-02GNT, and MA SDW 469-M01-02GNT) were in the same range as those previously determined in the wastewater samples themselves. Concentrations of Zn and Cu were similar to those observed at these sampling points over the past several years (Kent and Maeder, 1999).

## Conclusions

Results of experimental studies and determinations of metal-ion concentrations in the wastewater-contaminated ground water at the USGS research site on Cape Cod have implications for assessing Pb concentrations and mobility in the aquifer. First, Pb adsorbs extensively on the sediments. Extensive adsorption should help maintain low concentrations and mobility of Pb in the aquifer. Assuming that Pb concentrations in the wastewater discharged to disposal beds at the MMR wastewater-treatment facility were consistently in the range 1-10  $\mu\text{g/L}$  over the 60 years during which disposal to these beds occurred, the observed absence of Pb at concentrations above 0.08  $\mu\text{g/L}$  in shallow ground water below the beds must be a result of extensive Pb adsorption onto the sediments. Second, laboratory experimental studies have shown that adsorption of Pb onto the sediments is a strong function of pH, with Pb adsorption decreasing with decreasing pH. Thus, the mobility of Pb should be greater at lower pH values, as has been previously shown for Zn (Kent and others, 2000). Third, at a pH of 5.8, which is a typical pH value in uncontaminated ground water at the USGS research site, adsorption of Pb onto the sediments should be extensive and Pb concentrations in equilibrium with the sediments should be very low. Twenty-one grams of Pb complexed with EDTA at a concentration of approximately 52 mg/L (250  $\mu\text{M}$ ) was completely removed from ground water injected into the aquifer at pH values at or near 5.8 by adsorption onto the

sediments over a transport distance on the order of 50 meters. Fourth, if a region of the aquifer were to become contaminated with Pb, a subsequent decrease in pH values in that region would be expected to result in increases in concentrations and mobility of Pb in that region. This has been observed for Zn and has been shown to result from the pH-dependence of metal-ion adsorption on the sediments (Kent and others, 2000).

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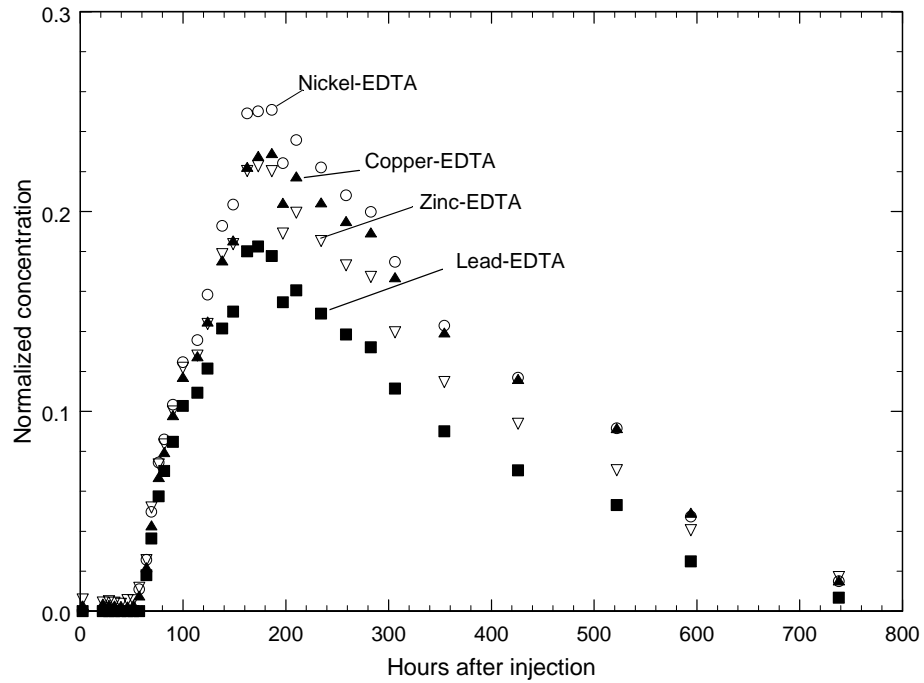
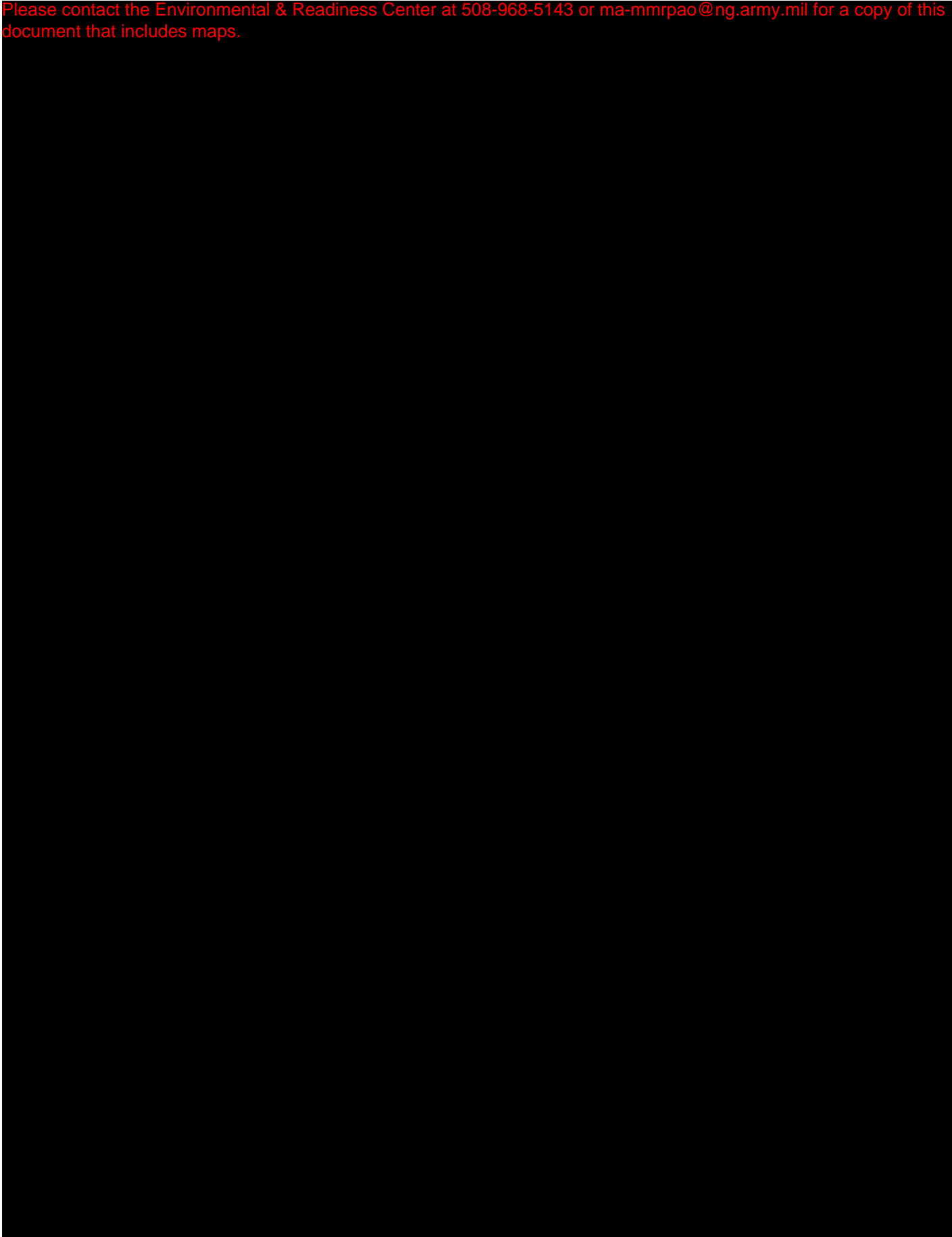


Figure 1. Concentrations of nickel, copper, zinc, and lead EDTA complexes detected 2.5 meters downgradient from the injection site plotted against time in hours after the injection. For each metal ion, its concentration has been divided by the corresponding concentration in the injected solution (“normalized concentration”). Concentrations of the free metal ions (i.e., metal ions not complexed with EDTA) were below detection for all the metal ions.

41°38'3



41°3

Figure 2. Location of study area, monitoring-well and multilevel-sampler sites, and abandoned treated-wastewater infiltration beds at the Massachusetts Military Reservation, Cape Cod, Massachusetts.

**Table 1.** Location coordinates, land-surface and screen altitudes, and water levels for monitoring wells and multilevel samplers near the treated-wastewater plume, Ashumet Valley, Cape Cod, Massachusetts.

[Locations are shown in figure 2. Latitude and longitude are given in degrees, minutes, and seconds relative to North American Datum of 1927 (NAD 27). Altitudes are in feet above or (-) below National Geodetic Vertical Datum of 1929 (NGVD 29)].

Well or multilevel-sampler port	Latitude	Longitude	Lat/Long datum	Altitude of land surface (feet)	Altitude of top of screen (feet)	Altitude of bottom of screen (feet)	Water-level date	Altitude of water level (feet)
MA-FSW 343-M03-03RT (01-19)	413814.38	703235.01	NAD27	68.65	43.68	43.58	--	--
MA-FSW 343-M03-07O (01-19)	413814.38	703235.01	NAD27	68.65	40.28	40.18	--	--
MA-FSW 343-M03-10P (01-19)	413814.38	703235.01	NAD27	68.65	37.78	37.68	--	--
MA-FSW 343-M03-14BK (01-19)	413814.38	703235.01	NAD27	68.65	34.44	34.34	--	--
MA-FSW 577-0051	413817.19	703236.82	NAD27	94.31	45.41	43.44	3/27/1996	46.21
MA-FSW 577-0061	413817.19	703236.82	NAD27	94.73	35.72	33.75	8/18/1995	45.10
MA-FSW 586-0058	413815.90	703235.93	NAD27	99.40	43.15	41.18	5/1/1996	46.68
MA-FSW 586-0068	413815.90	703235.93	NAD27	99.52	33.24	31.27	5/1/1996	46.68
MA-SDW 436-M01-02GNT	413819.52	703238.91	NAD27	68.84	43.44	43.34	--	--
MA-SDW 436-M01-04BUT	413819.52	703238.91	NAD27	68.84	37.42	37.32	--	--
MA-SDW 436-M01-08GY	413819.52	703238.91	NAD27	68.84	13.39	13.29	--	--
MA-SDW 469-M01-02GNT	413818.31	703238.09	NAD27	68.76	43.29	43.19	--	--
MA-SDW 469-M01-04BUT	413818.31	703238.09	NAD27	68.76	37.28	37.18	--	--
MA-SDW 469-M01-08GY	413818.31	703238.09	NAD27	68.76	13.23	13.13	--	--
MA-SDW 473-M01-02GNT	413821.76	703239.78	NAD27	69.09	43.63	43.53	--	--
MA-SDW 473-M01-04BUT	413821.76	703239.78	NAD27	69.09	37.59	37.49	--	--
MA-SDW 473-M01-08GY	413821.76	703239.78	NAD27	69.09	13.54	13.44	--	--
MA-SDW 521-M01-02GNT	413821.16	703239.50	NAD27	69.43	43.63	43.53	--	--
MA-SDW 521-M01-04BUT	413821.16	703239.50	NAD27	69.43	36.53	36.43	--	--
MA-SDW 521-M01-08GY	413821.16	703239.50	NAD27	69.43	13.37	13.27	--	--

**Table 2.** Field water-quality analyses for water samples from wells and multilevel samplers near the treated-wastewater plume, Ashumet Valley, Cape Cod, Massachusetts, 2006.

[Locations of wells and multilevel samplers are shown in figure 2. **Dissolved-oxygen method:** C, CHEMetrics colorimetric; M, dissolved oxygen meter and electrode.  $\mu\text{S/cm}$ , microsiemen per centimeter at 25 degrees Celsius; mg/L, milligram per liter; meq/L, milliequivalent per liter; --, no data]

Well or multilevel-sampler port	Date	Specific conductance ( $\mu\text{S/cm}$ )	pH (standard units)	Temperature (degrees Celsius)	Dissolved oxygen (mg/L)	Dissolved oxygen method	Phosphate, mg/L as orthophosphate	Alkalinity (meq/L)
FSW 343-M03-03RT (01-19)	6/20/2006	57.4	5.24	12.4	3.94	M	0.00	--
FSW 343-M03-07O (01-19)	6/20/2006	69.6	5.66	12.5	4.25	M	4.35	--
FSW 343-M03-08GY (01-19)	6/20/2006	81.5	5.79	12.8	1.61	M	4.65	--
FSW 343-M03-10P (01-19)	6/20/2006	97.3	5.99	13.0	0.085	C	5.40	--
FSW 343-M03-14BK (01-19)	6/20/2006	112	6.13	13.3	0.003	C	4.95	--
FSW 577-0051	7/17/2006	72.0	5.27	15.1	6.41	M	4.05	0.10
FSW 577-0061	7/17/2006	110	5.52	15.3	0.353	C	3.35	0.18
FSW 586-0058	7/13/2006	72.2	5.51	13.2	2.62	M	3.80	0.08
FSW 586-0068	7/13/2006	111	5.81	13.1	0.213	C	3.45	0.30
SDW 436-M01-02GNT	6/29/2006	89.4	5.49	12.7	6.66	M	4.75	0.06
SDW 436-M01-04BUT	6/29/2006	83.8	5.63	12.4	4.84	M	1.35	0.09
SDW 436-M01-08GY	6/29/2006	129	5.48	13.5	1.14	M	1.55	0.08
SDW 469-M01-02GNT	6/15/2006	71.2	5.58	12.0	5.06	M	5.10	0.07
SDW 469-M01-04BUT	6/15/2006	83.4	5.52	11.3	3.27	M	2.25	0.07
SDW 469-M01-08GY	6/15/2006	179	5.55	12.5	0.177	C	2.30	0.12
SDW 473-M01-02GNT	6/13/2006	95.9	5.27	12.4	8.59	M	0.05	0.02
SDW 473-M01-04BUT	6/13/2006	83.2	5.87	15.2	8.26	M	0.45	0.13
SDW 473-M01-08GY	6/13/2006	75.6	5.41	14.2	7.67	M	0.30	0.07
SDW 521-M01-02GNT	6/14/2006	91.2	4.86	13.3	9.28	M	0.35	--
SDW 521-M01-04BUT	6/14/2006	73.4	5.77	13.4	8.10	M	0.70	--
SDW 521-M01-08GY	6/14/2006	83.9	5.29	13.5	7.38	M	0.50	--



**Table 3a.** Concentrations of selected inorganic solutes for water samples from wells and multilevel samplers near the treated-wastewater plume, Ashumet Valley, Cape Cod, Massachusetts, 2006.

[Source of data: U.S. Geological Survey National Water Quality Laboratory, Denver, CO. Locations of wells and multilevel samplers are shown in figure 2. µg/L, microgram per liter; fltrd, filtered; <, actual value is less than value shown; E, estimated; M, presence verified but not quantified]

Well or multilevel-sampler port	Date	Aluminum, water, fltrd, µg/L	Antimony, water, fltrd, µg/L	Arsenic water, fltrd, µg/L	Barium, water, fltrd, µg/L	Beryllium, water, fltrd, µg/L	Boron, water, fltrd, µg/L	Cadmium, water, fltrd, µg/L	Chromium, water, fltrd, µg/L	Cobalt water, fltrd, µg/L	Copper water, fltrd, µg/L	Lead, water, fltrd, µg/L
MA-FSW 343-M03-03RT (01-19)	6/20/2006	23	<.20	<.12	11	<.06	E8	E.02	E.03	0.09	<.40	<.08
MA-FSW 343-M03-07O (01-19)	6/20/2006	30	0.34	2.5	5	<.06	13	0.15	0.08	1.4	9.2	<.08
MA-FSW 343-M03-10P (01-19)	6/20/2006	9	0.57	4	8	<.06	19	0.07	0.08	7.6	8.8	<.08
MA-FSW 343-M03-14BK (01-19)	6/20/2006	5	0.67	3.3	6	<.06	17	0.21	0.07	1.1	2.5	<.08
MA-FSW 577-0051	7/17/2006	122	0.32	1.2	1	<.06	13	0.51	0.88	1.3	27.8	<.08
MA-FSW 577-0061	7/17/2006	71	0.37	1.7	M	<.06	15	E.03	0.21	5.1	1.2	<.08
MA-FSW 586-0058	7/13/2006	46	0.38	1.9	2	<.06	15	0.35	0.28	2.6	14.7	<.08
MA-FSW 586-0068	7/13/2006	23	0.52	2.9	5	<.06	15	E.03	0.2	0.73	1.7	<.08
MA-SDW 436-M01-02GNT	6/29/2006	236	0.4	1.1	2	0.06	19	0.46	0.22	0.88	77	<.08
MA-SDW 436-M01-04BUT	6/29/2006	75	<.20	0.36	1	<.06	10	0.54	0.05	0.75	14.8	<.08
MA-SDW 436-M01-08GY	6/29/2006	28	<.20	0.63	3	<.06	13	0.42	0.05	2.2	4.4	<.08
MA-SDW 469-M01-02GNT	6/29/2006	213	0.43	1.2	M	<.06	12	0.29	0.22	0.62	66.5	0.08
MA-SDW 469-M01-04BUT	6/15/2006	191	<.20	0.64	M	<.06	13	0.49	0.09	1.5	40.5	<.08
MA-SDW 469-M01-08GY	6/15/2006	93	0.23	1.3	2	<.06	10	0.11	0.04	8.7	0.45	<.08
MA-SDW 473-M01-02GNT	6/13/2006	33	<.20	0.12	8	0.07	9	2.6	E.03	1.4	45.1	<.08
MA-SDW 473-M01-04BUT	6/13/2006	3	<.20	0.18	2	<.06	E8	0.17	<.04	0.08	1.1	<.08
MA-SDW 473-M01-08GY	6/13/2006	3	<.20	0.14	11	<.06	14	0.08	0.07	<.04	0.6	<.08
MA-SDW 521-M01-02GNT	6/14/2006	150	<.20	<.12	4	0.24	10	1.98	0.06	1.9	105	<.08
MA-SDW 521-M01-04BUT	6/14/2006	6	<.20	0.22	M	<.06	E6	0.24	E.02	0.12	3.4	<.08
MA-SDW 521-M01-08GY	6/14/2006	8	<.20	0.23	4	<.06	11	0.46	0.18	0.05	2.6	<.08

**Table 3b.** Concentrations of selected inorganic solutes for water samples from wells and multilevel samplers near the treated-wastewater plume, Ashumet Valley, Cape Cod, Massachusetts, 2006.

[Source of data: U.S. Geological Survey National Water Quality Laboratory, Denver, CO. Locations of wells and multilevel samplers are shown in figure 2. µg/L, microgram per liter; fltrd, filtered; <, actual value is less than value shown; E, estimated; M, presence verified but not quantified]

Well or multilevel-sampler port	Date	Lithium water, fltrd, µg/L	Manganese, water, fltrd, µg/L	Molybdenum, water, fltrd, µg/L	Nickel, water, fltrd, µg/L	Selenium, water, fltrd, µg/L	Silver, water, fltrd, µg/L	Strontium, water, fltrd, µg/L	Thallium, water, fltrd, µg/L	Tungsten, water, fltrd, µg/L	Uranium, natural water, fltrd, µg/L	Vanadium, water, fltrd, µg/L	Zinc water, fltrd, µg/L
MA-FSW 343-M03-03RT (01-19)	6/20/2006	<.6	1.8	<.4	0.53	<.08	<.2	11.1	<.04	<.06	<.04	<.10	10
MA-FSW 343-M03-07O (01-19)	6/20/2006	<.6	11.9	E.4	7	0.09	<.2	32	<.04	<.06	<.04	0.73	156
MA-FSW 343-M03-10P (01-19)	6/20/2006	<.6	64.4	1.3	7.1	0.1	<.2	35.7	<.04	<.06	<.04	1.2	6.4
MA-FSW 343-M03-14BK (01-19)	6/20/2006	<.6	95.4	1.6	4.1	<.08	<.2	31.9	<.04	<.06	<.04	1.1	2.1
MA-FSW 577-0051	7/17/2006	1.6	23.4	0.5	4.4	0.09	<.2	25.1	<.04	<.06	<.04	1.7	110
MA-FSW 577-0061	7/17/2006	0.8	48.5	E.4	5.6	<.08	<.2	28.9	<.04	<.06	<.04	6.3	E.42
MA-FSW 586-0058	7/13/2006	0.9	23.5	0.6	4.7	0.12	<.2	22.7	<.04	<.06	<.04	2.1	105
MA-FSW 586-0068	7/13/2006	<.6	68.4	0.5	2.9	<.08	<.2	22.6	<.04	<.06	<.04	1.7	1.6
MA-SDW 436-M01-02GNT	6/29/2006	1.2	32.2	0.5	3.2	0.11	<.2	33.9	<.04	<.06	<.04	2.9	87.9
MA-SDW 436-M01-04BUT	6/29/2006	0.9	11.2	<.4	1.7	<.08	<.2	39.2	<.04	<.06	<.04	2.9	155
MA-SDW 436-M01-08GY	6/29/2006	1.4	1080	<.4	1.4	0.23	<.2	19.3	<.04	<.06	<.04	2.6	51.2
MA-SDW 469-M01-02GNT	6/29/2006	1.2	10	0.7	3.5	0.28	<.2	26.2	<.04	<.06	<.04	2.3	92.5
MA-SDW 469-M01-04BUT	6/15/2006	1.5	32.5	<.4	3.5	<.08	<.2	23	<.04	<.06	<.04	3.4	99.1
MA-SDW 469-M01-08GY	6/15/2006	0.9	104	<.4	10	<.08	<.2	34.6	<.04	<.06	<.04	1.5	96.6
MA-SDW 473-M01-02GNT	6/13/2006	1.2	72.1	<.4	3.4	<.08	<.2	27.9	0.05	<.06	<.04	0.27	178
MA-SDW 473-M01-04BUT	6/13/2006	<.6	2.5	<.4	0.12	<.08	<.2	16.2	<.04	<.06	<.04	0.73	15.2
MA-SDW 473-M01-08GY	6/13/2006	<.6	24.5	<.4	0.17	<.08	<.2	13	<.04	<.06	<.04	0.2	33.8
MA-SDW 521-M01-02GNT	6/14/2006	1.6	94.8	<.4	3.5	<.08	<.2	25.5	<.04	<.06	<.04	0.26	227
MA-SDW 521-M01-04BUT	6/14/2006	<.6	2.1	<.4	0.19	<.08	<.2	19.5	<.04	<.06	<.04	1.2	7.4
MA-SDW 521-M01-08GY	6/14/2006	<.6	82	<.4	0.42	<.08	<.2	14.5	<.04	<.06	<.04	0.49	10.1

**Table 4.** Concentrations of selected inorganic solutes for equipment-rinsewater water samples, Ashumet Valley treated-wastewater plume, Cape Cod, Massachusetts, 2006.

[Source of data: U.S. Geological Survey National Water Quality Laboratory, Denver, CO. Locations of wells and multilevel samplers are shown in figure 2. µg/L, microgram per liter; fltrd, filtered; <, actual value is less than value shown; E, estimated; M, presence verified but not quantified]

Well or multilevel-sampler port	Date	Aluminum, water, fltrd, µg/L	Anti-mony, water, fltrd, µg/L	Arsenic, water, fltrd, µg/L	Barium, water, fltrd, µg/L	Beryllium, water, fltrd, µg/L	Boron, water, fltrd, µg/L	Cadmium, water, fltrd, µg/L	Chromium, water, fltrd, µg/L	Cobalt, water, fltrd, µg/L	Copper, water, fltrd, µg/L	Lead, water, fltrd, µg/L
Equipment-rinsewater sample MA-FSW 343-M03-07O (01-19)	6/20/2006	<2	<.20	<.12	<.2	<.06	<8	<.04	<.04	<.04	<.40	<.08
Equipment-rinsewater sample MA-FSW 586-0058	7/13/2006	<2	<.20	<.12	<.2	<.06	<8	<.04	0.14	<.04	<.40	<.08

Well or multilevel-sampler port	Date	Lithium water, fltrd, µg/L	Manganese, water, fltrd, µg/L	Molybdenum, water, fltrd, µg/L	Nickel, water, fltrd, µg/L	Selenium, water, fltrd, µg/L	Silver, water, fltrd, µg/L	Strontium, water, fltrd, µg/L	Thallium, water, fltrd, µg/L	Tungsten, water, fltrd, µg/L	Uranium natural water, fltrd, µg/L	Vanadium, water, fltrd, µg/L	Zinc, water, fltrd, µg/L
Equipment-rinsewater sample MA-FSW 343-M03-07O (01-19)	6/20/2006	<.6	<.2	<.4	E.04	<.08	<.2	<.40	<.04	<.06	<.04	<.10	1.3
Equipment-rinsewater sample MA-FSW 586-0058	7/13/2006	<.6	<.2	<.4	<.06	<.08	<.2	<.40	<.04	<.06	<.04	<.10	E.52