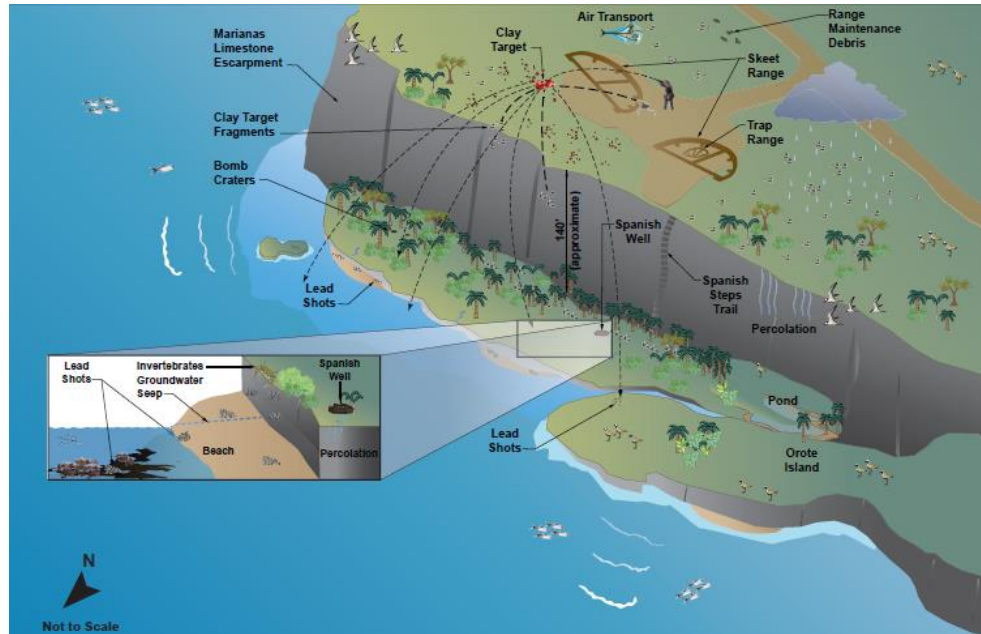


**TECHNICAL REPORT
TR-NAVFAC EXWC-SH-2306**

**BEST PRACTICES AND RISK
MANAGEMENT OPTIONS FOR METAL-
IMPACTED SITES**



Prepared for NAVFAC EXWC under Contract No. N39430-16-D-1802

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ACRONYMS AND ABBREVIATIONS

ARAR	applicable and relevant and appropriate requirements
BMP	best management practice
BTV	background threshold value
CalEPA	California Environmental Protection Agency
CEC	Cation Exchange Capacity
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COPC	contaminant of potential concern
COC	contaminant of concern
CPS	calcium polysulfide
CSM	conceptual site model
CW	chemical waste
DoD	Department of Defense
DON	Department of the Navy
DU	Decision Unit
DQO	data quality objective
EA	enhanced attenuation
EE/CA	Engineering Evaluation/Cost Analysis
ERP	Environmental Restoration Program
FBL	fixed-base laboratory
FEC	Field Engineering Command
FS	Feasibility Study
GWRTAC	Groundwater Remediation Technologies Analysis Center
HHRA	human health risk assessment
IRZ	in situ reactive zone
ISM	incremental sampling methodology
ITRC	Interstate Technology and Regulatory Council
MCL	maximum contaminant level
MNA	monitored natural attenuation
NAVFAC	Naval Facilities Engineering Systems Command
NIRIS	Navy Installation Restoration Information Solution
NSF	Naval Support Facility
ORP	oxidation-reduction potential
OSWER	Office of Solid Waste and Emergency Response

PAH	polycyclic aromatic hydrocarbon
PAL	project action limit
PbB	blood lead
PCB	polychlorinated biphenyl
QA/QC	quality assurance/quality control
RI	Remedial Investigation
REST	Range Evaluation Software Tool
RBA	relative bioavailability
RCRA	Resource Conservation and Recovery Act
RPM	Remedial Project Manager
RSL	regional screening level
SAFR	Small Arms Firing Range
SAR-QAPP	Small Arms Range Quality Assurance Project Plan
SMCL	secondary maximum contaminant level
SPLP	synthetic precipitation leaching procedure
SRB	sulfate reducing bacteria
SRNL	Savannah River National Laboratory
TAL	Target Analyte List
TCLP	toxicity characteristic leaching procedure
TOC	total organic carbon
UFP-QAPP	Uniform Federal Policy Quality Assurance Project Plan
US EPA	U.S. Environmental Protection Agency
USGS	United States Geological Survey
XRF	X-ray fluorescence

1.0 INTRODUCTION

Metals are a focus of site investigations, remediation, and ongoing monitoring at a significant proportion of Naval Facilities Engineering Systems Command (NAVFAC) Environmental Restoration Program (ERP) sites. For example, Figure 1 shows metal-impacted sites representing 20% of NAVFAC Southeast ERP sites. Even at sites where petroleum hydrocarbons or chlorinated solvents are the primary drivers for risk, metals are frequently evaluated as co-occurring contaminants and may be detected at concentrations that exceed risk-based screening criteria in both soil and groundwater. Metals are distinguished from other classes of contaminants in that they are naturally occurring and indefinitely persistent in the environment.

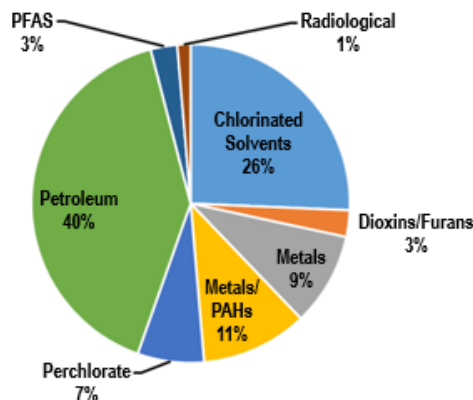


Figure 1. Contaminants at NAVFAC Southeast Restoration Sites (Courtesy of NAVFAC Southeast, 2020)

This report will also provide best practices for the development and refinement of an optimized conceptual site model, important considerations for metals in background, information on how transport of metals can be influenced by biological, chemical, and physical processes, and considerations for improving risk to receptor estimations. Further, this report presents guidance on appropriate sampling methodologies for metals given site specific considerations and the goals of the sampling program. The report highlights technical challenges and solutions for two primary site types, small arms ranges and groundwater sites. Case studies are included throughout the document to illustrate best practices during site investigations.

1.1 KEY PRINCIPLES OF METALS BEHAVIOR

Metals and metalloids are elements that form positive ions, or cations, by losing electrons during chemical reactions. Arsenic, antimony, and selenium are all considered metalloids and have properties of both metals and non-metals (forming anions). For simplicity, metals and metalloids are collectively referred to as metals in this report. The types of metals and metalloids of primary interest at cleanup sites are highlighted here.

Metals releases and/or mobilization at NAVFAC ERP sites are associated with industrial processes, small arms firing ranges (SAFRs), waste disposal, pesticide and herbicide applications, and other base support operations. Metals can also be mobilized from

Key Principles of Metals Behavior in Soil and Groundwater Media at Metal-Impacted Sites

- Metals are naturally occurring and therefore exist in background concentrations that vary geographically.
- Metals occur in the environment as mixtures and are introduced into the environment as mixtures.
- The environmental chemistry of metals strongly influences their fate and transport, along with their effects on human and ecological receptors.
- Changing environmental conditions impact metals behavior in the environment.
- The toxicity of a particular metal depends on its chemical form, and an organism's ability to regulate and/or store the metal.

Reference: US EPA, 2007

soil into groundwater during attenuation of organic plumes. While metals are naturally occurring in the environment, federal and state risk-based screening criteria and standards are established to protect human and ecosystem health. These criteria are established to protect from potential acute or chronic exposure to metals that have been released to the environment and/or mobilized as a result of geochemical changes from waste disposal and other contaminant releases (e.g., petroleum hydrocarbons).

Metals and Metalloids of Primary Interest at Cleanup Sites*	
Aluminum	Manganese
Antimony	Mercury (inorganic) ¹
Arsenic ^{1,2}	Molybdenum
Barium ¹	Nickel ²
Beryllium	Selenium ^{1,2}
Boron	Silver ¹
Cadmium ^{1,2}	Strontium
Chromium ^{1,2}	Tin
Cobalt	Thallium
Copper ²	Vanadium
Iron	Zinc
Lead ^{1,2}	

*Primary metals of toxicological concern as identified by US EPA, 2007.
¹RCRA 8 metals, which are regulated as hazardous waste.
²Focus of EPA's Monitored Natural Attenuation guidance (2007a, 2007b)

1.2 BY THE NUMBERS: METALS IN SOIL AND GROUNDWATER AT NAVFAC ERP SITES

Trends in metal detections were characterized from site-specific data compiled in the Naval Installation Restoration Information Solution (NIRIS) database. This trend evaluation included the analysis, detection, and relative impact of individual metals in soil and groundwater at NAVFAC ERP sites. The analyses compiled data for sites sampled for metals within each of the NAVFAC Regions, along with the number of samples collected for individual metals within a given region.

1.2.1 Trends Across All NAVFAC Regions

Trends across all NAVFAC Regions are summarized in Figure 2 as follows:

- Lead is the most frequently sampled metal in both soil and groundwater, followed by arsenic, chromium, cadmium, and mercury.
- In soil, lead, arsenic, and chromium are detected in greater than 90% of samples, illustrating that these metals are part of background at nearly all sites. In contrast, cadmium and mercury are detected less than 50% of the time.
- In groundwater, the most frequently sampled metals (e.g., lead and arsenic) are detected in less than 50% of samples. Instead, barium, iron, and manganese are the most frequently detected metals, with detected concentrations in greater than 75% of collected samples.
- Overall, metals are less frequently detected in groundwater than soil, reflecting the influence of geochemical and aquifer conditions on solubility.

1.2.2 Trends within NAVFAC Regions

When data are compiled for each NAVFAC Field Engineering Command (FEC), region-specific trends emerge for metals detected in soil and groundwater (see Figures 3 to 5).

Trends in soil sampling results include:

- Arsenic, antimony, copper, zinc, and selenium are also among the most frequently sampled metals in some regions.
- In the NAVFAC Southeast Region, the sample collection number and overall detection frequency for metals are highest.
- In the NAVFAC Northwest Region, the sample collection number and overall detection frequency for metals are lowest.
- Selenium is a frequently sampled metal in the NAVFAC Mid-Atlantic Region and is detected at the majority of sites, but in less than 50% of samples.
- Copper is a frequently sampled metal in NAVFAC Hawaii, NAVFAC Marianas, NAVFAC Southwest, and NAVFAC Southeast Regions, but its detection frequency in samples varies from 82% to 97%.

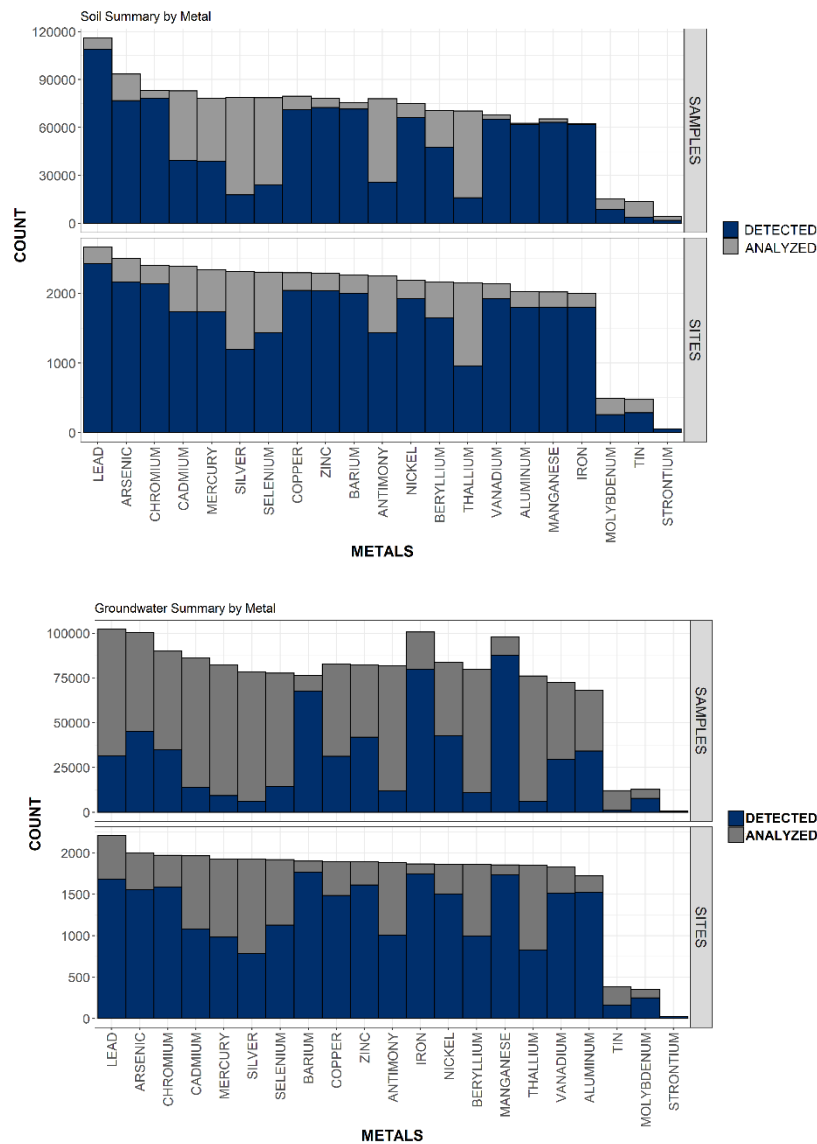


Figure 2. Metals Analyses in Soil and Groundwater across all NAVFAC Regions (Courtesy of Battelle) Panels for “Samples” depict the total number of samples analyzed for a particular metal versus the total number of samples in which a detected concentration was reported. Panels for “Sites” depict the total number of sites at which analyses for the metal were performed versus the total number of sites in which a detected concentration was reported.

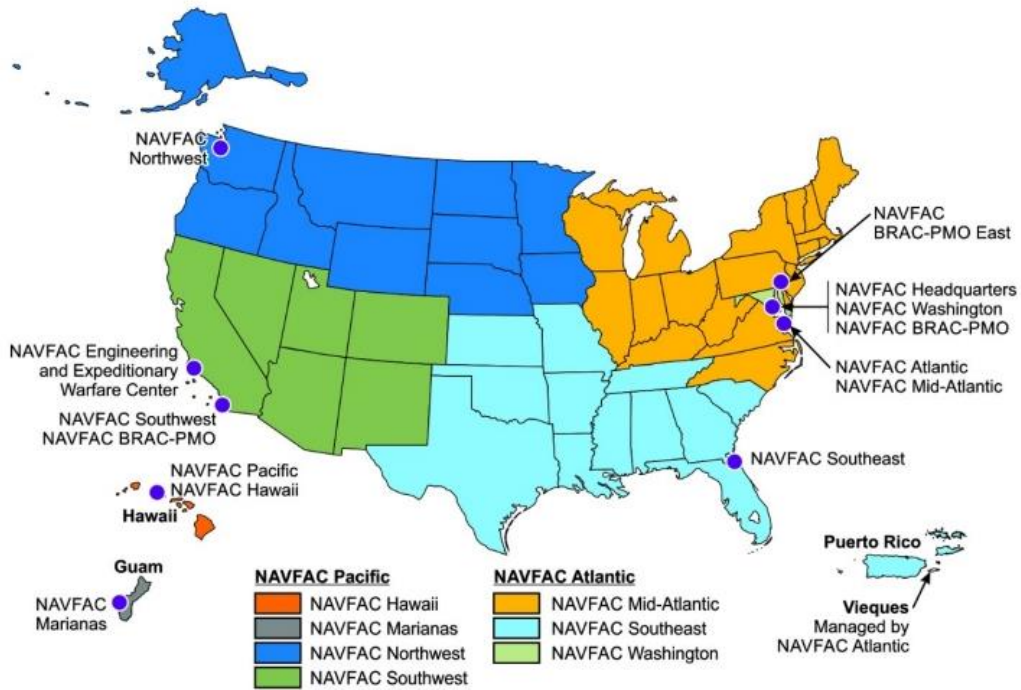


Figure 3. NAVFAC FEC Regions (Courtesy of NAVFAC)

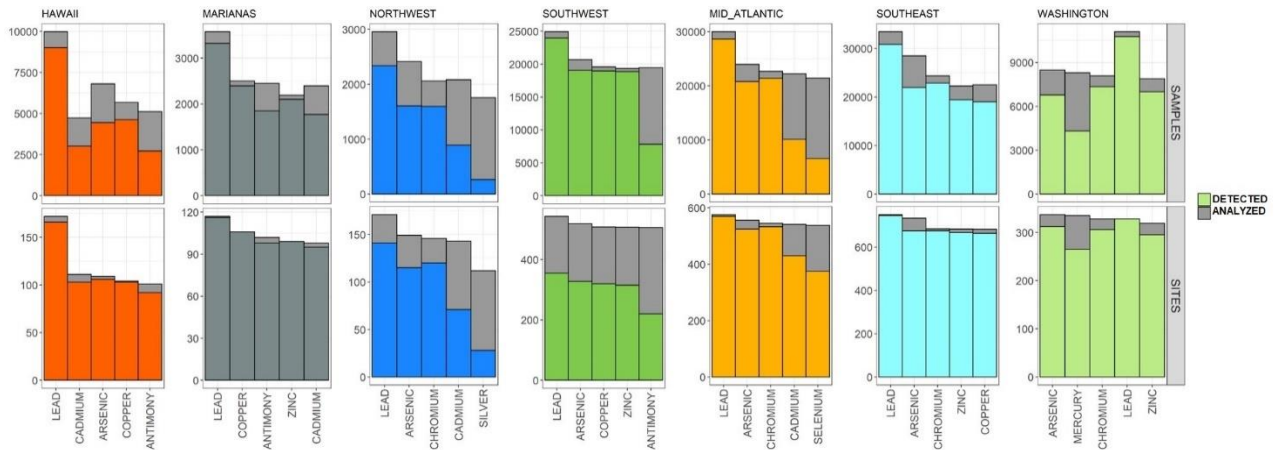


Figure 4. Top Five Metals Sampled in Soil across the NAVFAC Regions and Relative Frequency of Detection (Courtesy of Battelle)

Trends in groundwater sampling results include:

- The most frequently sampled metal within NAVFAC Regions varies between lead, arsenic, and copper. Arsenic is generally the most frequently detected metal, although it is not a “top five metal” for NAVFAC Marianas and barium is the most frequently detected metal for NAVFAC Washington.
- Beryllium, silver, iron, and barium are regionally specific and are among the top five metals sampled in a single region only.

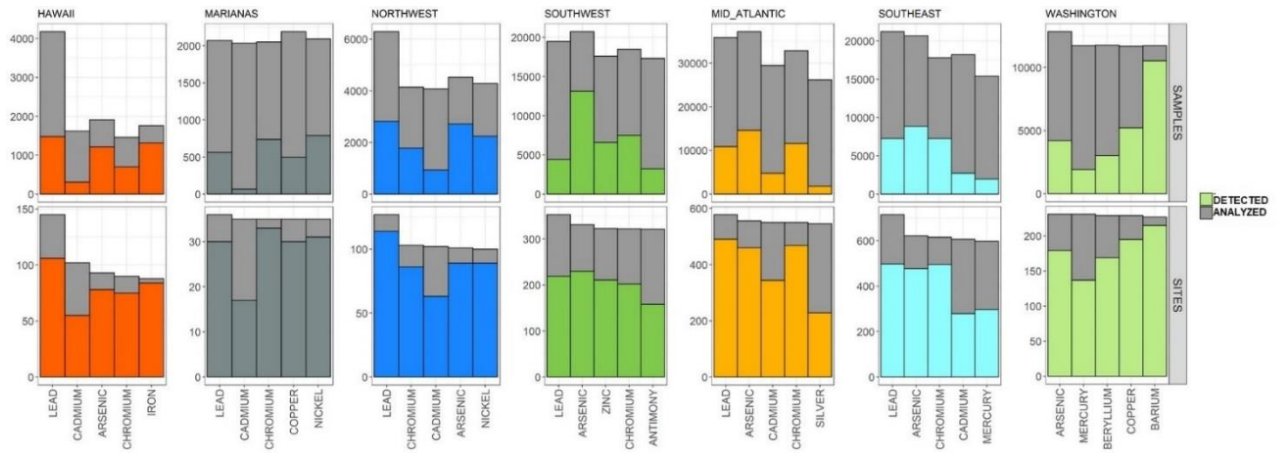


Figure 5. Top Five Metals Sampled in Groundwater within NAVFAC Regions and Relative Frequency of Detection (Courtesy of Battelle)

1.3 OVERALL CONCLUSIONS

Overall, the sampling trends for metals at NAVFAC ERP sites, particularly for soils, are consistent with trends observed for the United States Environmental Protection Agency (US EPA) Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Program as a whole, also known as the Superfund Program. The most commonly occurring metals at Superfund sites are lead, chromium, arsenic, zinc, copper, and mercury (GWRTAC, 1997; US EPA, 1999).

The Department of Defense (DoD) oversees more than 3,000 active SAFRs, which are some of the primary NAVFAC ERP sites for metals characterization and remediation. SAFRs include rifle, pistol, trap, skeet, and sporting clay ranges, which accept 50 caliber or smaller ammunition (ITRC, 2005). SAFRs may contain lead, antimony, copper, zinc, and arsenic from non-exploding (non-energetic) bullets and fragments, bullet jackets, and related sporting material (e.g., clay targets) (NAVFAC, 2020; USACE, 2015).

The case studies presented at the end of this report illustrate site characterization and remedial actions that focus on chromium, lead, and other metals, particularly at closed SAFR sites.

2.0 METALS IN THE ENVIRONMENT

The objective of most environmental sampling programs is to characterize the nature and extent of contamination and to estimate chemical concentrations to which receptors may be exposed at a site. This information is captured in a conceptual site model (CSM) that is developed as part of the site investigation process. The development of a CSM for metal-impacted sites requires special consideration of biological, physical, and chemical processes taking place at the site. This section reviews elements of an optimized CSM including a careful evaluation of metals background, metals fate and transport processes, and metals bioavailability.

2.1 BUILDING AN OPTIMIZED CONCEPTUAL SITE MODEL

A CSM is an integrated representation of the physical and environmental context of a site that includes the fate and transport of contaminants of potential concern (COPCs) and the complete exposure pathways associated with each potential receptor at a site that is being evaluated (ITRC, 2020). CSMs will evolve through the site investigation process as data gaps are identified and resolved through sampling (US EPA, 2007). Special considerations for building a CSM at metal-impacted sites are highlighted here including key CSM components and fate and transport.

Key CSM Components for Metal-Impacted Sites

- Physical factors of a site
- Sources of contamination
- Potentially contaminated media and the vertical and horizontal extent
- Contaminant transport or migration pathways
- Exposure units and pathways applicable to receptors

CSMs should be utilized as follows:

- During the investigative phase of a site, the CSM is used as a tool to assist in the development of data quality objectives (DQOs) and is applied to decisions about the sampling design and the analytical methods to be used to characterize the nature and extent of contamination and potential risk to human or ecological receptors.
- During later stages of investigation, it can be used to evaluate the feasibility of specific remedial activities and institutional controls.
- CSMs are important communication tools to community and regulatory stakeholders.

Figure 6 is an example of a CSM that focuses on a broader understanding of a site and the source, transport, and fate of COPCs in a pictorial format for a skeet range. Figure 7 focuses on potentially impacted media as exposure points to metals, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) for the diverse ecological receptors that might inhabit a site.

Questions for Metals CSMs: Fate and Transport Mechanisms

- What are site background concentrations?
- What are the geochemical mechanisms that will influence fate and transport?
- What is the bioavailability of metals within the soil matrix?
- What are the metal sources and species that may be present now and in the future?
- What are the key physical transport processes?

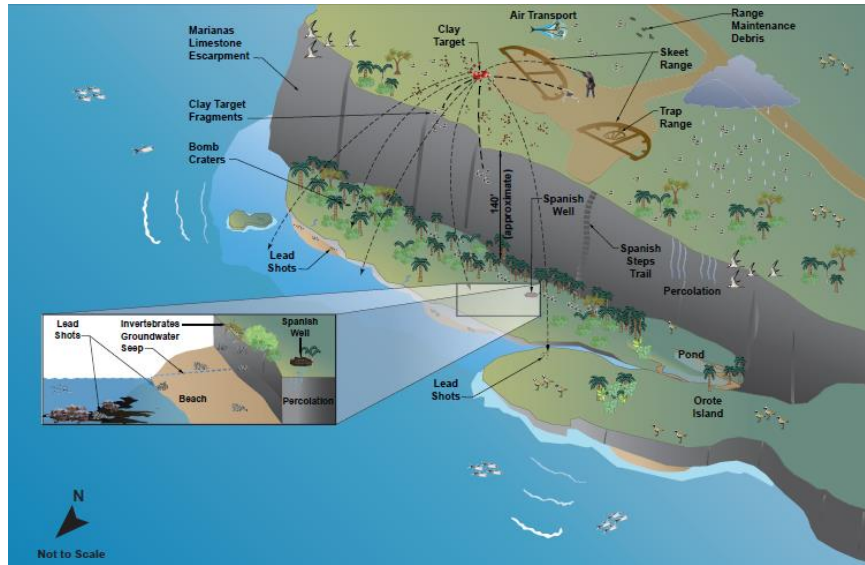


Figure 6. Pictorial CSM for a Skeet Range that Characterizes Key Mechanisms for Contaminant Sources and Fate and Transport (Courtesy of NAVFAC)

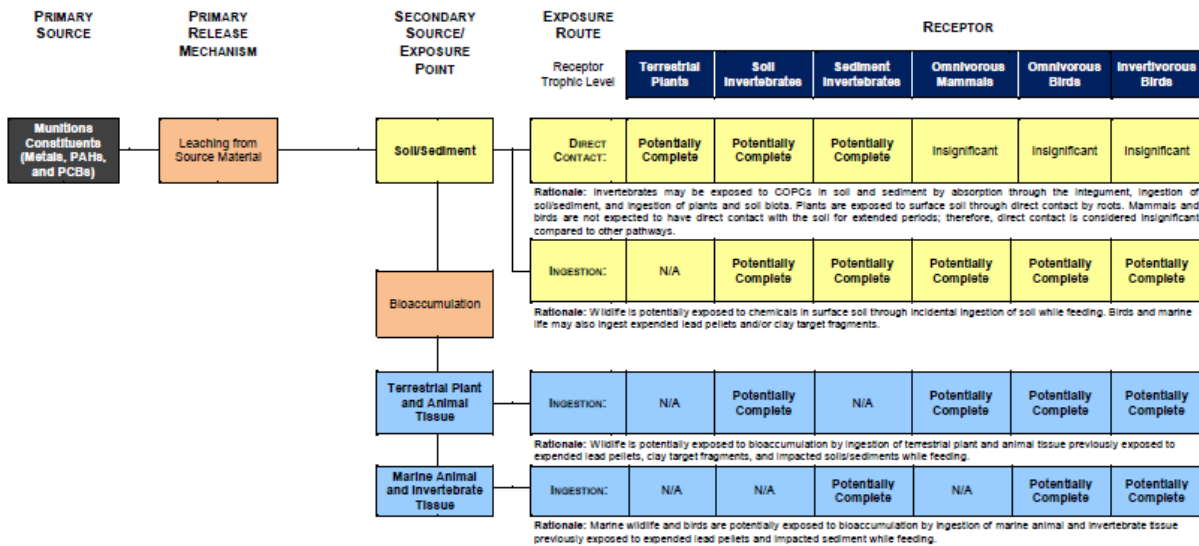


Figure 7. Risk Assessment CSM that Depicts Contaminant Sources, Exposure Media and Potentially Complete Exposure Pathways for Ecological Receptors (Courtesy of NAVFAC)

During CSM development, the sampling approach is aligned with the data end use (such as risk assessment or regulatory screening criteria) and designed to characterize the site and subunits (exposure units or decision units) to inform decisions. As described later in this report, discrete, composite, or incremental sampling can be used to delineate hot spots, establish average values across homogeneous areas for risk assessment and remedial alternatives scoping, determine complete and incomplete exposure pathways, and bioavailability of metals.

2.2 METALS BACKGROUND CONSIDERATIONS

A key step in CSM development is identifying the types of metals that may be present due to Navy activities and potential release sites. Metals concentrations at ERP sites may originate from releases attributable to Navy site operations, as well as other sources including natural sources and anthropogenic ambient sources (Department of the Navy [DON], 2004). Cleanup efforts at Navy sites should address only those risks associated with chemical concentrations that are elevated due to a site-related release and not background chemicals (DON, 2004; NAVFAC, 2002). This can be difficult in practice, and specific planning and statistical strategies to reduce uncertainty in background analyses through scientifically defensible and verifiable approaches are described in several Navy guidance documents (e.g., NAVFAC, 1998, 1999).

What is Background?

Natural Background: Substances present in the environment in forms that have not been influenced by human activity (US EPA, 1989, 2002).

Anthropogenic Background: Substances present in the environment as a result of human activities, not specifically related to the site release in question (US EPA, 1989, 2002), including nonpoint sources. An example of a nonpoint source is the long-distance transport of mercury from fossil fuel emissions. Another example is lead in soil from the historic use of leaded gasoline, where accumulation may have occurred over the long term in areas along roadways.

Additional information can be found within the Interstate Technology and Regulatory Council (ITRC) Guidance on Soil Background and Risk Assessment (ITRC, 2022).

Reminder: For practical purposes, soil background concentrations are often presented as a specific value, but they are more accurately described as a range that explicitly recognizes the variability inherent in soils.

Background can be evaluated using the following approaches:

- Identifying and collecting samples from a project-specific reference site. The data should be collected in a statistically defensible manner in accordance with Navy and US EPA guidance;
- State-specific studies and established values (e.g., Natural Background Groundwater Concentrations in Washington State, Washington State Department of Ecology, 2022); and
- Available databases (e.g., United States Geological Survey [USGS] National Water Quality Assessment).

Key concepts and best practices for characterizing background include:

- Soil background concentrations should be completed as early as possible in the site characterization process and follow appropriate Navy policies and guidance (DON, 2004).
- The CSM and problem formulation of a risk assessment should identify chemicals that may be present due to potential releases and their expected locations.
- During risk assessment, naturally occurring and anthropogenic chemicals that are below background levels should be eliminated from further consideration, even if they exceed screening levels.

- Remedial action levels should explicitly account for site-specific background and not be set below site-specific background concentrations.
- Development of site-specific background requires selection of a reference site, development of a sampling plan, and determination of a statistical approach for comparing background data to site data (US EPA, 1994; NAVFAC, 2002). Tools are available for the statistical methods used to determine background such as US EPA ProUCL as highlighted here.
- Geochemical analyses can be used for soils background.

US EPA ProUCL

US EPA's ProUCL statistical software can support comparative methods that use hypothesis testing to compare site datasets to background datasets, in addition to supporting the identification of background threshold values (BTVs).

Available at:

<https://www.epa.gov/land-research/proucl-software>

Special Considerations for Arsenic-Impacted Sites

Arsenic background is frequently above risk-based thresholds in soil and groundwater at many sites (NAVFAC, 2004). Visual comparisons of site and background datasets can be used along with statistical tests to demonstrate similarity between data distributions and/or to identify outliers that may represent "hot spots." In Figure 8, the site data and background data from a reference site are similar, with the exception of a single sample that may represent a release with an elevated arsenic concentration.

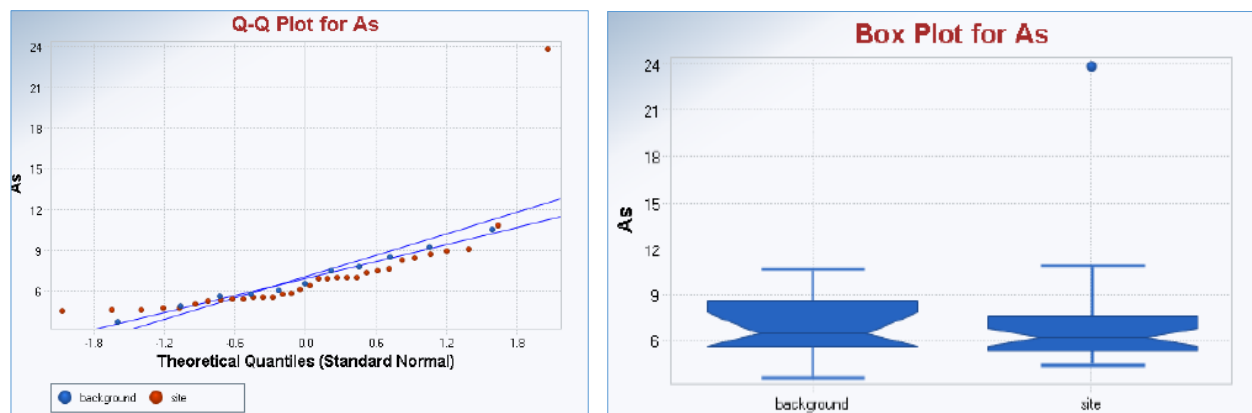


Figure 8. Data Plots (Q-Q plot and Box Plot) Used to Compare Background and Site Datasets (Courtesy of Battelle)

2.3 METALS FATE AND TRANSPORT CONSIDERATIONS

2.3.1 Metal Species

The chemical form or species of a particular metal (US EPA, 2004):

- Depends on the source of the metal and the soil and groundwater chemistry at the site;
- Profoundly affects its behavior in the environment and its effects on receptors; and
- Influences its solubility, mobility, availability, and toxicity.

Chemical analyses for metals are generally presented as total metals (for soils) or total and dissolved metals (for groundwater) (US EPA, 2004). Analytical results that present sums of all species present in a sample may initially be adequate for developing CSMs, characterizing

potential risk, and scoping a remedy. However, for metals that have been identified as driving risk and subsequently remedial actions, analyses to quantify individual metal species may be important. In a CSM, it is important to understand and capture how a particular metal may be: 1) stabilized in place at the location of the source or 2) transported from a source (or site of release) to other media and locations. Mobility of metals in the unsaturated zone or groundwater is dependent on speciation.

2.3.2 Key Fate and Transport Processes for Metals

Fate and transport of metals is influenced by several biological, chemical, and physical processes as described below:

- Sorption is the attachment of chemical species to minerals or other surfaces. Metal COPCs have a high affinity for adsorption under soils with high organic or clay content, alkaline pH, and high cation exchange capacity. In contrast, sandy soils typically have a low cation exchange capacity (CEC) and higher infiltration, which may transport dissolved metal ions to groundwater. Soil samples can be collected from site soils to evaluate the fate and transport potential of COPCs.
- Solubility is a measure of the degree to which a constituent will dissolve in water and is highly dependent on the oxidation state of the metal. Solubility decreases as pH increases, and solubility influences the mobility of a metal through the soil and between the soil and groundwater.
- Most dissolved metals do not occur as solitary ions in solution. In addition, they exist in an equilibrium of different dissolved forms, which is called aqueous speciation. Naturally-occurring anions that tend to form aqueous complexes with metals include hydroxyl (OH^-), carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), and chloride (Cl^-).
- Metals may combine with oxygen and hydroxides to form insoluble oxyhydroxides (aerobic environments);
- Metals may combine with phosphate, sulfate, and carbonate to form insoluble mineral precipitates;
- Metal sulfide complexes, which form in reducing environments, are extremely insoluble; and
- Precipitation involves chemical reactions that cause aqueous phase inorganic chemicals to become solid phase mineral components of soil.

Role of Microbial Processes

Microbes are ubiquitous in the subsurface and can catalyze redox reactions. An increase in iron and manganese is a simple indicator of enhanced microbial activity in an area with an organic contaminant plume. Therefore, redox conditions and microbial processes play an important role in the presence of metals in groundwater.

2.3.3 Metals Reduction-Oxidation (Redox) Sensitivity

Metals are considered redox sensitive if they can exist in soil and/or groundwater in different oxidation states under different conditions. Mobility can vary widely, depending on oxidation state, and so can relative toxicity. For example, in anaerobic environments where oxygen is limiting, trivalent chromium [or Cr(III)] is reduced to hexavalent chromium [Cr(VI)]. As shown in Table 1, samples for chromium species are collected at approximately 14% of sites for groundwater and 8% of sites for soil. Hexavalent chromium is detected at less than 10% of sites and in less than 5% of samples. For the sites sampled, these data indicate trivalent chromium to be the more abundant chromium species. Trivalent chromium is less mobile and less toxic than hexavalent chromium, so this distinction can be critical in remedial investigations and identifying remedial actions. Where chromium is a contaminant of concern (COC), it is of critical importance that speciation data be collected to determine the hexavalent chromium concentration.

Metals Speciation Example: Chromium Risk and Remediation in Soil and Groundwater

- In nature, chromium exists primarily as trivalent chromium ([Cr(III)]) and to a lesser extent as hexavalent chromium, or Cr(VI).
- Cr(VI) in the environment is frequently a contaminant.
- Toxicity: Cr(VI) is very toxic to human and ecological receptors. Cr(III) has low toxicity.
- Mobility: Cr(VI) dissolves and can be transported within groundwater at PH=7.
- Chemical mechanism of remediation: Redox change – conversion of Cr(VI) to Cr(III) halts mobility and minimizes toxic effects that may result from exposure. Cr(III) is insoluble and becomes sorbed to soil particles.

See Case Study 1: Excavation and In Situ Treatment of Hexavalent Chromium in Groundwater for details.

Table 1. Sites and Samples for Chromium Species Analyses across NAVFAC Regions

Media	Cr Species	Measured Sites	Detected Sites	Measured Samples	Detected Samples
Groundwater	Cr, Total	1620	1359	70720	27158
	Cr(VI)	225	102	2991	843
	Percent	13.89%	7.51%	4.23%	3.10%
Soil	Cr, Total	1898	1828	64053	59993
	Cr(VI)	159	87	3580	1286
	Percent	8.38%	4.76%	5.59%	2.14%

Redox conditions can change over time. Design of effective remediation must consider speciation under current conditions and how conditions may change after the remedy is implemented. In some cases, implementing a change in redox conditions is the focus of the remedy (see Case Study 1). Metals with redox sensitivity include arsenic, chromium, mercury, manganese, and selenium (Suthersan and Horst, 2008). See Table 2 for a summary of metal species geochemistry and relative toxicity.

Table 2. Redox Sensitivity, Oxidation States, Mobility, and Toxicity for Target Metals at NAVFAC ERP Sites

Metal	Redox Sensitivity	Most Common Oxidation States	Mobility/Solubility	Complicated Aqueous Speciation	Relative Toxicity
Antimony	No	III V	Low Moderate	No	High
Arsenic	Yes	III V	Moderate Low	Yes	High
Cadmium	No	II	Low to Moderate	No	High
Chromium	Yes	III VI	Low Moderate to High	Yes	Low High
Copper	No	II	Low	No	Low
Lead	No	II	Low	No	High
Mercury	Yes	II	Low	Yes	High
Zinc	No	II	High	No	Low

Notes:

Table developed from data from Envirowiki; DoD, 2005; USAEC, 2005; US EPA, 2005
Lead and copper are found in the highest concentrations on SAFRs (USAEC, 2005)

2.4 METALS BIOAVAILABILITY AND BIOACCUMULATION CONSIDERATIONS

The concentration of a particular metal in a bulk soil or groundwater sample does not necessarily reflect the fraction to which an organism is exposed. This concept becomes important for metals in soils or groundwater that exceed screening levels or other risk-based thresholds.

2.4.1 Bioavailability Concepts

Bioavailability is the extent to which a substance can be absorbed by a living organism or is “available” to have an effect on an organism (DoD, 2003).

Why is this important? Site-specific chemical and physical conditions (as described above) greatly influence the form in which metals occur in the environment and the degree to which they are sorbed to soils (NRC, 2002). Characterizing and understanding bioavailability at a site can improve risk estimation, which can impact decisions on how to manage risk.

How to quantify? Quantify the total and individual species concentrations for select metal species.

Bioavailability Example

Physiologically-based extraction procedures can be used to estimate the approximate site-specific bioavailable fraction of metals. At a former SAFR site, lead was determined to be the most bioavailable metal under digestive conditions for site receptors, but ranged from 38% to 100%, with highest bioavailable fractions detected in sandy soils (NAVFAC, 2019).

Case Study 1: Excavation and In Situ Treatment of Hexavalent Chromium in Groundwater

Background: Site 14 Former Chemical Waste (CW) Evaporation Pond is located at the Naval Support Facility (NSF) Dahlgren, in Dahlgren, Virginia. The pond received historical discharges of waste chemicals from a variety of activities, including chemical warfare waste decontamination and gun barrel rinsing. The areal extent of the CW pond was 120 ft x 60 ft.

Contaminant of Concern: Concentrations of total chromium (Cr) and hexavalent Cr [Cr(VI)] in soils and groundwater at the site posed a potential human health risk.

Selected Remedial Action: Source removal, including soil excavation and off-site removal, was combined with in situ chemical reduction treatment of groundwater using calcium polysulfide (CPS). The CPS treatment facilitates a redox change and a series of reactions that convert Cr(VI) to trivalent chromium ([Cr(III)]). The remedy was selected to mitigate the potential transport of Cr(VI) from subsurface soil into the groundwater and to reduce concentrations of Cr(VI) in groundwater. As shown in Figure C1-1, soil was excavated and removed to a depth of 7 ft based on remedial action objectives for Cr in soil. Further excavation from 7 to 10 ft was conducted, so that CPS could be applied at the water table. After CPS application, the additional excavation material was placed back in the excavated area before backfilling with clean soil (NAVFAC Washington, 2006).

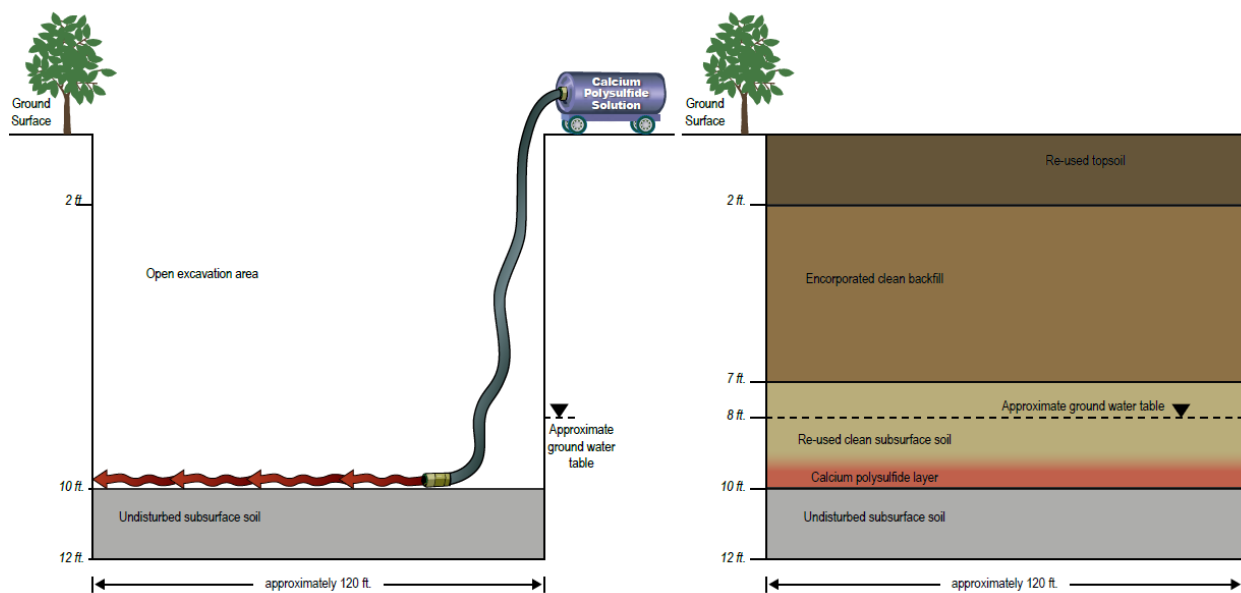


Figure C1-1. CPS Application and Soil Backfilling
(Courtesy of NAVFAC Washington)

Results: Pre-remedy concentrations of total and hexavalent chromium in soil ranged 12 to 120 mg/kg and 1.8 to 330 mg/kg, respectively. The removal action was successful in eliminating a continuing source of total Cr and Cr(VI) contamination to groundwater.

Total Cr and Cr(VI) concentrations in groundwater were reduced from greater than 300 µg/L to trace amounts after the remedy was implemented in 2008 (NAVFAC Washington, 2009). See Figure C1-2 showing the pre- and post-treatment Cr concentrations in groundwater.

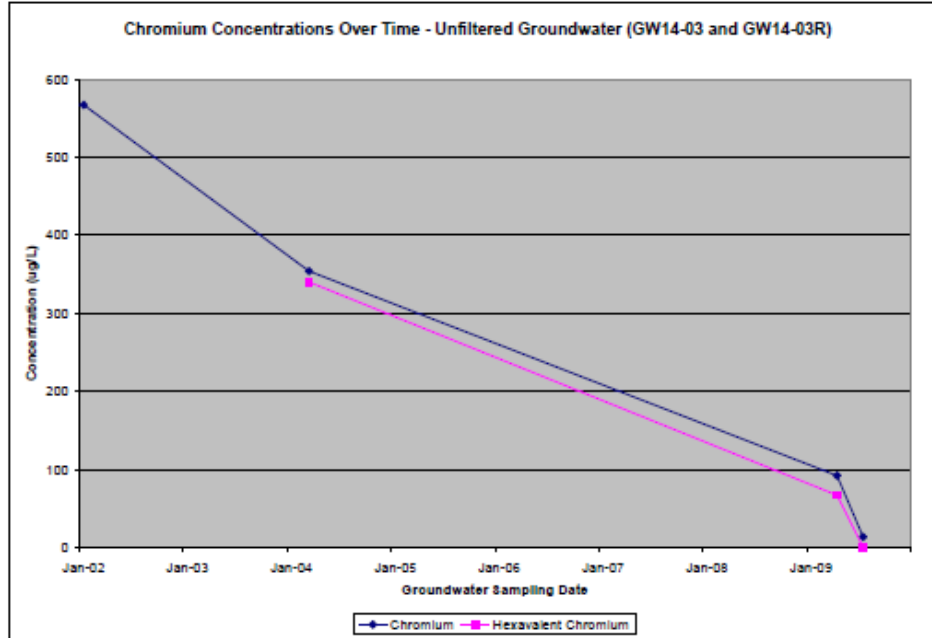


Figure C1-2. Pre- and Post-Cr Concentrations in Groundwater (Courtesy of NAVFAC Washington)

Best Practices:

- A well-developed CSM was critical to understanding Cr exposure, fate and transport within soil and groundwater.
- A pre-Engineering Evaluation/Cost Analysis (EE/CA) investigation was completed to delineate the horizontal and vertical boundaries of the excavation and included extensive soil sampling.
- The remedy included removing the source and reducing the concentration of Cr(VI), which is the more mobile and more toxic Cr species, in groundwater.
- Quarterly groundwater monitoring was conducted post-remedy (2009-2010) to measure and track concentrations of Cr(VI) and target analyte list (TAL) metals.

Lessons Learned:

- Groundwater remediation is a complex process that may involve ongoing treatment and further evaluation of risk to ensure protection of human health and the environment. The remedy significantly reduced total chromium and Cr(VI) concentrations in groundwater; however, Cr(VI) and several other metals concentrations remained above maximum contaminant levels (MCLs). Further evaluation of human health and ecological risk at the site was completed within a Remedial Investigation (RI), which was followed by a Feasibility Study (FS). In the FS, in situ chemical reduction was selected as a groundwater treatment for arsenic, Cr(VI), cobalt, and iron, which were above risk-based thresholds (NAVFAC Washington, 2013).
- CSMs may change through time to reflect additional data collection that refines contaminant exposure pathways. During the 2016 remedy refinement investigation, porewater samples were collected from a water body adjacent to the site (Gambo Creek). Metals concentrations in the samples exceeded surface water quality criteria, and additional sampling was proposed to better characterize this potential contaminant transport pathway and associated risk to aquatic receptors (NAVFAC Washington, 2019).

Additional information about CPS for soil and groundwater remediation includes the following:

- CPS is a cost-effective and environmentally protective remedial alternative for treating some cation metals (such as As, Pb, Cd, and Cu), which precipitate as non-toxic metal sulfides in the presence of CPS.
- CPS works by establishing a reducing environment in the aquifer. These conditions are also optimal for the growth of sulfate-reducing bacteria (SRBs), which are naturally occurring in many aquifers but thrive under anaerobic, reducing conditions (low ORP). SRBs convert sulfate produced by CaS back into sulfide ions, which maximizes the benefit of the applied CaS and limits net production of sulfates, which are subject to secondary drinking water standards (DOE, 2006).

References:

Department of Energy (DOE). 2006. Treatability Test Report for Calcium Polysulfide in the 100-K Area. DOE/RL-2006-17. February.

NAVFAC Washington. 2006. Site 14 Engineering Evaluation/Cost Analysis, Former Chemical Waste Evaporation Pond. Prepared under LANTDIV CLEAN III Program Contract N62470-02-D-3052 by CH2MHill.

NAVFAC Washington. 2009. Supplemental Groundwater Investigation at Site 14 Round 2, NSF Dahlgren, Virginia. Prepared under Joint Venture III (JV III), Contract N40080-07-D-0301, Task Order 023 by CH2M HILL and AGVIQ.

NAVFAC Washington. 2013. Proposed Remedial Action Plan Site 14 Former Chemical Waste Evaporation Pond NWSC Dahlgren VA. Prepared by CH2MHILL. N00178.AR.000892.5090.3a.

NAVFAC Washington. 2019. Final Uniform Federal Policy Sampling and Analysis Plan Addendum for Site 14 Remedy Refinement NSWC Dahlgren VA. Prepared by CH2MHILL. N00178_001351. SSIC 5000-33a.

2.4.2 Bioaccumulation Concepts

Bioaccumulation is the net accumulation of a chemical by an organism as a result of uptake from all routes of exposure (DoD, 2003).

Why is this important? Site-specific conditions (including bioavailability) influence the bioaccumulation of individual metals in an organism's tissue (plant, invertebrate, or animal).

How to quantify? Site-specific measurements of tissue concentrations in receptor and prey organisms, in combination with related soil concentration data, provide a measure of bioaccumulation and an integrated measure of bioavailability across all exposure routes (US EPA, 2002).

Site-specific bioaccumulation and bioavailability can be used to model the potential for toxic or adverse impacts to organisms that are exposed to contaminants within the soil matrix.

More information on these concepts can be found in the ITRC guidance document on "Bioavailability of Contaminants in Soil: Considerations for Human Health Risk Assessment" (ITRC, 2017).

3.0 CHARACTERIZING METAL-IMPACTED SITES

Sampling design can be optimized to obtain data that are aligned with DQOs and the designated use for site characterization, risk assessment, and/or remediation goals. A Uniform Federal Policy Quality Assurance Project Plan (UFP-QAPP) should capture the justification for the sampling design and approach and end use of the data. At most metal-impacted sites, dividing the site into strata optimizes the sampling design by decreasing variability and improving the representativeness of the data within each stratum. X-ray fluorescence (XRF) analysis and incremental sampling methodology (ISM) can be incorporated into the sampling approach at metals sites. These methods are especially effective in characterizing metals concentrations at sites where the CSM indicates that metals were heterogeneously distributed due to former site activities.

3.1 PORTABLE MULTI-ELEMENT XRF ANALYSIS

Portable multi-element XRF analysis may be used to approximate lead, arsenic, and some other metals in situ (Figure 9). XRF is best used as a field screening tool and should be used in conjunction with the collection of confirmatory samples that will be submitted to a laboratory for quantitative chemical analysis. If used correctly, XRF can result in significant time and cost savings, particularly in cases where contaminant delineation is needed. The inherent trade-off is that XRF can be utilized to collect a large number of measurements, but the measurements may not be as accurate or precise as chemical analyses performed at a laboratory. XRF can be useful in identifying decision units for ISM through initial characterization and verification of homogeneity within areas. See the case studies below on how XRF can be applied for measuring lead in soil.

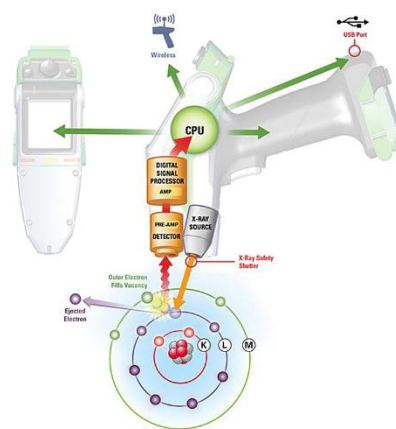


Figure 9. Schematic of a Portable XRF Unit (Courtesy of NAVFAC)

Key Benefits

- Real-time data can be used for dynamic decision-making and adaptation in the field to enhance site characterization
- Can be used to identify “hot spots” and to delineate boundaries of contamination. It is especially useful when contaminant concentrations are spatially heterogeneous (e.g., SAFRs).

Best Practices for Robust XRF Data Collection

- Develop rigorous sampling plan/design and associated quality assurance (QA)/quality control (QC) protocols
- Collect multiple scans (triplicate) on each sample and average the results
- Calibrate the instrument daily using standards
- Use statistical analyses to establish strong, predictive relationships between XRF and laboratory results
- Soil moisture can impact results, so samples should be collected to minimize soil moisture changes

Case Study 2A: Expanded Site Inspection and Removal Action at Former Skeet and Trap Ranges at Naval Support Activity Annapolis

Background: XRF for measuring lead in soil was used to optimize excavations for a non-time critical removal action (NTCRA) related to former skeet and trap ranges at Naval Support Activity Annapolis in Annapolis, Maryland. Covering 23 acres, the former skeet and trap ranges were used until the late 1940s. A housing area was subsequently built in the area in the late 1940s to 1950s.

Contaminant of Concern: The results of an Expanded Site Inspection (ESI) determined that lead concentrations were exceeded in surface and subsurface soils in comparison to the Maryland Department of Environment (MDE) lead screening value of 200 mg/kg. Twelve yards for nine housing units were designated to be addressed for lead in soil as part of the NTCRA.

XRF for Site Characterization: Prior to mobilization for the excavation work, an additional phase of lead delineation was implemented as part of the ESI for the two former range sites. All surface soil samples were analyzed for lead both by XRF field screening and by laboratory analysis. As shown in Figure C2-1, the strength of the correlation at 0.89 between the lead data from the laboratory and XRF was found to be statistically significant.

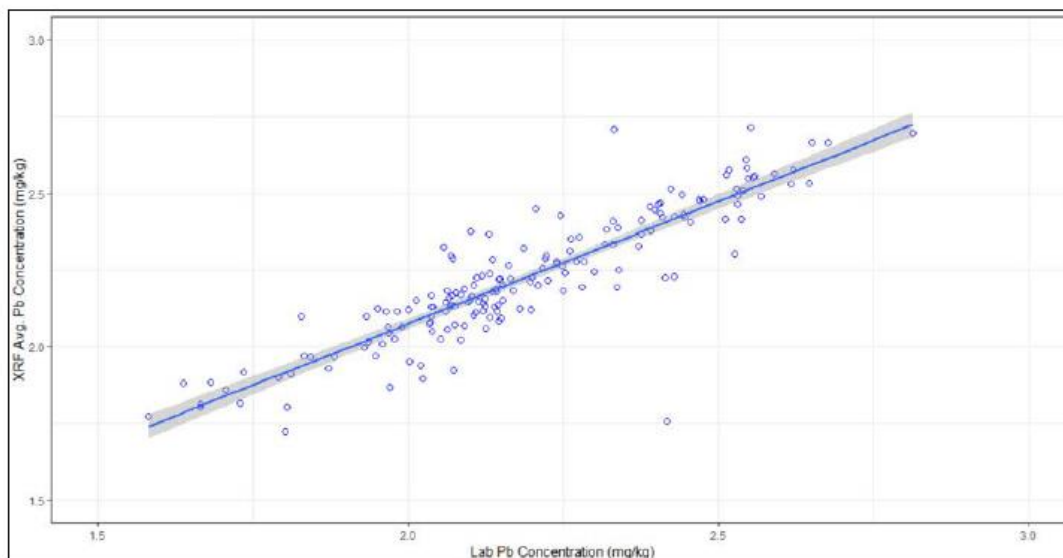


Figure C2-1. Regression Line for the Lab Pb and XRF Pb Concentrations Using Box-Cox Transformation (Courtesy of NAVFAC Washington)

Best Practices: Based on statistical analysis of data collected during the ESI, XRF was determined to be a reliable tool for estimating the concentration of lead in soil at the two sites. As part of the ongoing NTCRA, the XRF is being used to generate screening data to determine whether the lead impacts extend beyond the boundaries of the yards and the extent of excavation required in the housing areas.

Lessons Learned:

- XRF can be used to generate reliable data for field screening. It is important that the sampling and analysis plan capture all details of the approach from sample collection through statistical testing (per US EPA SW-846 Method 6200). Sufficient pairwise data on soil samples, consisting of XRF measurements and laboratory analyses, must be collected to demonstrate statistical validity of the XRF data across the range of concentrations of the metal of interest at the site.

- There is considerable time investment upfront to statistically validate the relationship between XRF measurements and laboratory analytical results. Once established, XRF can streamline decision-making in the field and is a cost-effective alternative when many samples are needed to delineate boundaries for excavation.

References:

NAVFAC Washington. 2020. Expanded Site Inspection Report Former Skeet and Trap Ranges, North Severn, Naval Support Activity Annapolis, Annapolis, Maryland. Prepared under Contract N62470-16-D9000 by CH2M. June.

Case Study 2B: Site Investigation and Removal Action for Lead in Soil and Small Arms and Skeet Ranges at Naval Support Facility Indian Head

Contaminants of Concern: Lead in surface and subsurface soil at shotfall areas posed human health and ecological risks at two sites (former rifle, skeet, and trap ranges) at Naval Support Facility Indian Head (NSFIH) in Maryland. Erosion and transport of contaminated soil was also a concern. Other metals were co-located with lead and PAHs at the firing points and target areas.

XRF for Site Characterization: During the Phase I Site Investigation, all soil and sediment samples were field-screened for lead using XRF and a subset of samples were submitted to a fixed-based laboratory (FBL) for metals analyses. The regression equations developed for the XRF and FBL data at the two sites (UXO 14 and 15) were statistically acceptable and allowed for the prediction of lead concentrations in areas where only XRF data were collected.

Selected Removal Action:

- Source removal consisted of targeted soil excavation and off-site disposal in a landfill to reduce on-site lead concentrations below the 400 mg/kg project action limit (PAL).
- For disposal of lead-contaminated soil in a Resource Conservation and Recovery Act (RCRA) Subtitle D permitted landfill, lead in soil needed to be stabilized to minimize the potential for leaching to groundwater. Chemical stabilization of lead was achieved through the addition of Blastox[®] 215.
- The removal action consisted of the following:
 - Delineation sampling to define lateral and horizontal extent of contamination at the SAFRs;
 - Excavation of impacted soils in 250 cubic yard (CY) in-place soil increments;
 - Waste characterization (toxicity characteristic leaching procedure [TCLP]) of excavated soil piles to determine the need for chemical stabilization of lead; and
 - Treatment of soil piles that exceeded the TCLP criteria (5 mg/L lead) with Blastox[®] 215 and off-site disposal of soil (both treated and untreated).

Best Practices:

- Knowledge regarding the firing and target locations, shot fall areas, and ballistics behavior was incorporated into the CSM to identify spatial patterns of COCs and their fate and transport. It was also used to guide sample collection.
- Combining XRF and FBL sampling to characterize the nature and extent of lead contamination within a site. Statistically robust relationships were established between the two datasets, resulting in improved spatial coverage at lower cost.
- Pre-excavation soil borings and step-out samples were used to further delineate horizontal and vertical boundaries for excavation.

- Excavation piles were segregated, and waste characterization samples were collected to determine treatment needs to stabilize lead.
- Iterative sampling of soil piles was conducted to reduce lead concentration below the TCLP level and promote cost-effective application of the stabilizing agent.

Lessons Learned: XRF was used in combination with pre-excavation sampling to determine the lateral extent of lead-contaminated soil requiring excavation. The lateral extent of contaminated soil increased slightly at UXO 15 based on the XRF field screening results (see Figure C2-2 for example results). Final confirmation results from the excavation walls were collected and analyzed in a fixed laboratory. All final confirmation results were below the cleanup goals/project action levels.

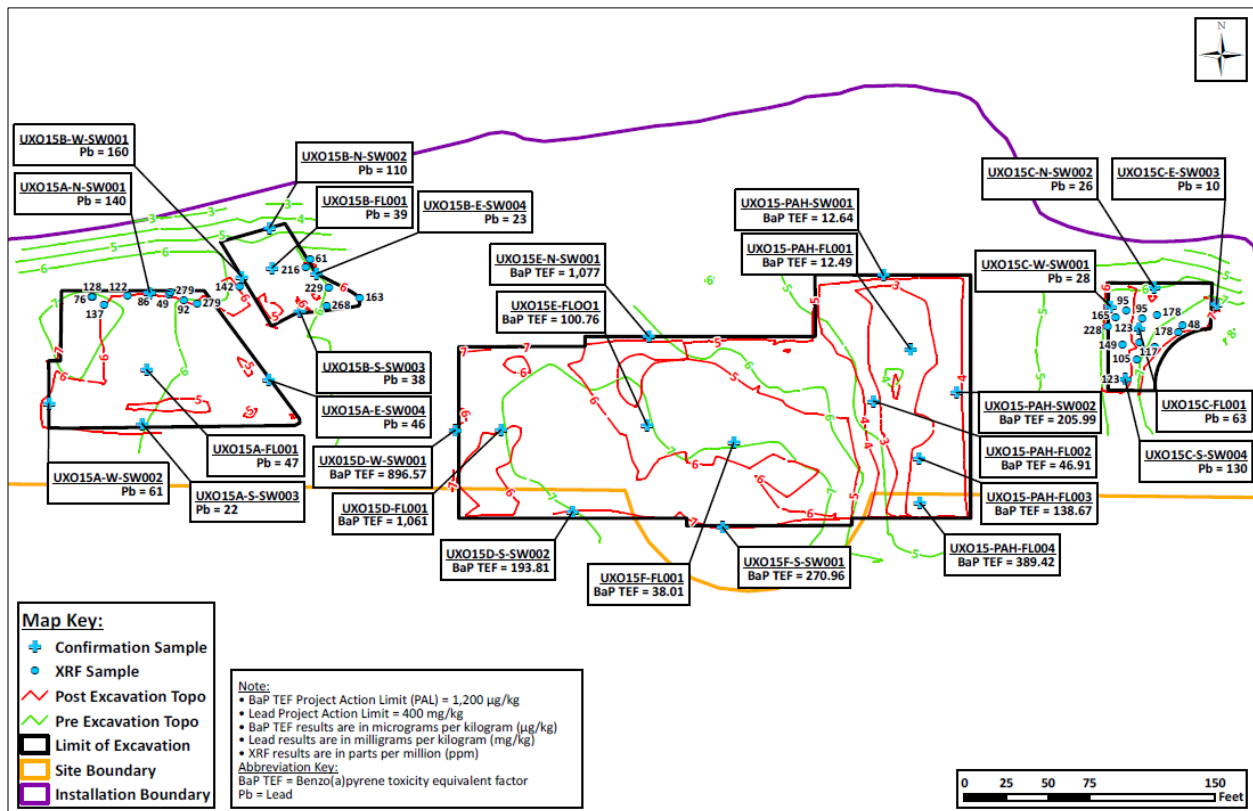


Figure C2-2. XRF Screening and Lead Confirmation Sampling Results (Courtesy of NAVFAC Washington)

References:

NAVFAC Washington. 2021. Final Removal Action Completion Report Volume I of II Text – Appendix B. Prepared under Radiological Multiple Award Contract (RADMAC) Number N62473-17-D-0005, Contract Task Order (CTO) by Gilbane Federal.

3.2 INCREMENTAL SAMPLING METHODOLOGY

ISM is a structured, composite sampling processing protocol that is designed to reduce data variability and provide a reasonably unbiased estimate of mean contaminant concentration for a given area. It is a sampling approach that focuses on the use of decision units (DUs), that are identified and scaled to areas in space in which a decision will be made. As shown in Figure 10, many increments (typically 30 to 100 samples) are systematically collected for ISM and composited to derive a single concentration value (NAVFAC, 2021).

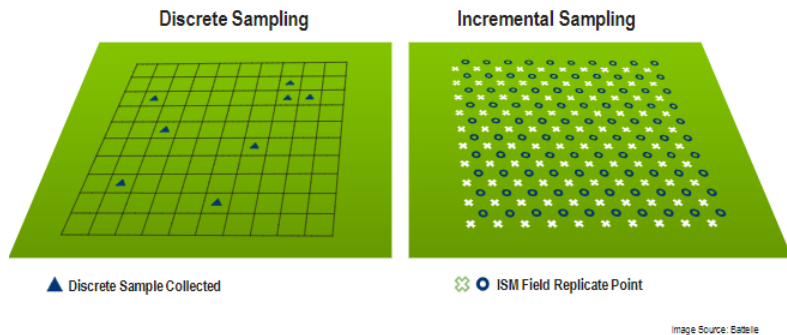


Figure 10. Comparison of Sampling Approaches for Discrete versus Incremental Sampling (Courtesy of Battelle)

Well-defined DQOs, a CSM, and DUs need to be established during

project planning to successfully implement ISM (USACE, 2013). Four components that need to be considered and will differ from discrete or composite sampling approaches include:

1. Sample design: Number and size of DUs, number of replicate ISM samples, and the number of increments for each ISM sample which are guided by problem formulation and study goals;
2. Field sample collection;
3. Laboratory sample processing and analysis; and
4. Statistical analyses for risk assessment.

ISM works well under the following site conditions:

- Contaminants are primarily limited to soil surface (0-2 feet) (NAVFAC, 2021);
- Best estimate of the mean for an area is desired over precise spatial characterization of contamination and contaminant concentrations are known to vary (e.g., SAFRs); and
- Meets a guidance requirement (e.g., Hawaii or Alaska) or is approved/endorsed by the regulatory agency.

Case Study 3 describes how ISM can be applied at an ERP site during the remedial investigation and feasibility study phase. USACE (2015) also includes a case study that can be used to guide ISM at a site.

Case Study 3: Application of ISM to Estimate Metals and PAHs in Surface Soil at a Former SAFR

Contaminants of Concern: Concentrations of metals and PAHs in soil and groundwater exceeded risk-based screening levels at the Orote Point (Spanish Steps) Trap and Skeet Range Naval Base Guam (a former SAFR). Additional data were needed to characterize the nature and extent of contamination within DUs so that remedial actions, aligned with potential future re-use scenarios, could be identified.

Site Background Information and Investigation Approach: The site is approximately 66 acres in size and includes the firing range area of three former small arms ranges (two skeet ranges and one trap range), areas of associated range maintenance, and the Fringing Reef and associated islands. As shown in Figure C3-1, the sampling approach combined ISM (25 DUs) with targeted discrete and composite sampling. In addition to lead, other target metals included antimony, arsenic, cadmium, copper, nickel, and zinc.



Figure C3-1. Twenty-five DUs Used to Characterize Risk at the Orote Point SAFR on Naval Base Guam (Courtesy of NAVFAC)

Site Sampling Approach: Samples were collected in accordance with the State of Hawaii Department of Health’s *Technical Guidance Manual for the Implementation of the Hawaii State Contingency Plan and Procedure I-B-1, Soil Sampling*. Hawaii is one of a small number of states with guidance for ISM sample collection and application of the resulting data. A summary of the sampling approach by DU is included in Table C3-1 (DON, 2015a).

Table C3-1. ISM Sampling Plan for the Site

Matrix	Sample Location	Analytical Group	Number of Samples
Surface Soil			
Incremental	DU01–DU17, DU23, SM05, DU24–DU28	Metals (antimony, arsenic, cadmium, copper, lead, nickel, zinc)	24 primary 5 field duplicates 5 field triplicates
	DU01–DU17, DU23, SM05, DU24	PAHs	20 primary 5 field duplicates 5 field triplicates
	DU01–DU11 and SM05	PCBs	12 primary 3 field duplicates 3 field triplicates
	DU05, DU09, and DU13	SPLP metals, SPLP PAHs, bioavailable metals	3 primary
	ST01–ST04	CEC, TOC, pH	4 primary
	DU08, DU09, DU13, and DU16	Quantitative Laboratory Pellet Count	4 primary
	DU01–DU17, DU23, SM05, DU24–DU28	Qualitative Field Pellet Count	24 primary

Best Practices:

- Characterizing surface and subsurface soils for TOC, CEC, and pH to assess potential transport and fate of individual metals from spent rounds.
- Two phases of sampling, with the second phase to address data gaps.
- Collection of total and dissolved concentrations of metals in groundwater to evaluate relative contributions of COPCs for each sample. Dissolved concentrations of metals contributed minimally to total metals concentrations indicating that most metals were adsorbed to particulates.
- Synthetic precipitation leaching procedure (SPLP) analyses for all metals to evaluate leaching potential of surface and subsurface soil samples.
- Metals bioavailability testing to better characterize potential exposure to human and ecological receptors that may be present on site.

Lessons Learned:

- The key to successful ISM design lies in the selection of the DUs. DUs should be based on the specific end use of the data that must be identified during the systematic planning process. DUs for human health and ecological exposure may be different.
- Systematic planning following the US EPA DQO process is a required part of any environmental investigation, but it is especially important for an investigation using ISM.
- Training of staff to collect and process samples for laboratory analysis is critical to successful implementation of an ISM sampling plan.

References:

NAVFAC. 2019. Final Remedial Investigation Orote Point Spanish Steps trap and Skeet Range Munitions Response Site Unexploded Ordnance 2 Naval Base Guam. Performed under contract number N62742-12-D-1829 task order JQ05.

4.0 TECHNICAL CHALLENGES AND SOLUTIONS FOR MANAGING METAL-IMPACTED SITES

Numerous technical challenges are unique to the management of metal-impacted sites. This section summarizes technical challenges that may be encountered at soil and groundwater sites, along with important technical considerations, best practices, and useful reference and guidance documents.

4.1 SOIL: SMALL ARMS FIRING RANGES

The DoD oversees more than 3,000 active SAFRs. Heterogeneous distribution of metallic residues in surface soils creates unique challenges for characterizing the nature and extent of metals contamination at SAFRs (USACE, 2015). In most cases, lead will be the primary COPC due to prevalence and relative toxicity (ITRC, 2003).

4.1.1 Best Practices for Small Arms Firing Ranges

In addition to those previously cited, the following documents are specifically focused on SAFR management and site investigations and can be used as guidance by RPMs:

- **Small Arms Range Quality Assurance Project Plan (SAR-QAPP) Tool (DoD, 2013):** This tool was developed to provide guidance and a systematic planning process that focuses on SAFR COPCs, their transport pathways, and bioavailability considerations. It includes information and examples to assist in completing specific UFP-QAPP worksheets.
- **Army Small Arms Training Range Environmental Best Management Practices (BMPs) Manual (USAEC, 2005):** This manual provides detailed information on the species of individual metals that are COPCs at SAFR sites, including fate and transport mechanisms.

Recommended best practices to consider include:

- **Spatial Distributions of Metal Contaminants are Heterogeneous but can be Generally Mapped Based on Historical Operations and Activities.** Range design, use (e.g., firing fan areas/distances), and maintenance operations should guide initial CSM development for SAFRs. Sites can be subdivided or stratified into units with similar characteristics. This process should be based on historical use, known or suspected impacts, and future use. For example, a rifle range could be stratified into four strata or DUs that include the impact berm, firing line, range floor, and side berms (DoD, 2013).
- **Contaminants from projectiles may migrate in the environment.** Depending on the depth of groundwater, climate, soil chemistry, or proximity to surface water at the range, contaminants can reach surface water or groundwater. This information should be considered in CSM development.
- **The primary source of metals contamination is spent bullets and lead shot (solid material), but bullets can fragment and disintegrate over time.** Metals commonly associated with range activities include lead, copper, zinc, tungsten, arsenic, antimony, and nickel (DoD, 2013). Soil concentrations and fragments (which may be used as grit by wildlife) should be quantified in estimating exposure and risk. Procedures for handling debris and

performing sieving or grinding should be captured in project DQOs. Large bullets or metal fragments > 2 mm in diameter are typically excluded from soil samples collected to support risk assessment. However, fragments may be important for characterizing ecological risk (DoD, 2013). The relative condition of the round can also influence migration from the point of impact.

4.1.2 Lead Fate, Transport, and Exposure Mechanisms

Understanding the potential for lead at SAFRs to migrate beyond the point of impact is integral to CSM development. Characterizing lead concentrations in soil is one part of site characterization. Measuring total organic carbon (TOC) in soil, pH, and CEC are critical in assessing both vertical and lateral migration of lead. Rounds that fragment into small, dust-like particles are susceptible to corrosion and leaching that may release lead and other metal ions in the dissolved phase. In soils with high CEC and organic matter, ions will bind to soil particles, but in sandy (low CEC) soils, these released ions may be transported in surface water runoff or vertically to groundwater in the soil pore fluid (USAEC, 2005).

Physical processes such as surface water flow may also be an important consideration at some NAVFAC ERP sites. A watershed approach, as described in USAEC (2005), may be helpful in characterizing the physical processes that move metal contaminants (e.g., lead) within and beyond site boundaries. The Range Evaluation Software Tool (REST) may be used in developing a preliminary analysis of lead transport. The tool uses site-specific conditions to rank the potential for transport that includes ammunition mass, corrosion, aerial transport, surface water transport, and groundwater transport.

The bioavailability of lead is an important consideration at SAFRs. In general, bioavailability of metallic lead decreases with increasing particle size (ITRC, 2003). Intact and minimally fragmented rounds present the lowest chronic exposure to human and ecological receptors. Ecological receptors, especially some bird species, may experience acute exposure when lead fragments are ingested and used as dietary grit (ITRC, 2003). Because lead bioavailability is variable, bioavailability studies can be integral to more accurately estimating potential risk to receptors. Studies conducted at SAFR sites have shown that lead from ammunition may contribute to soil as metallic lead, Pb^{2+} (dissolved from the crust of ammunition), and as a variety of oxidized compounds (largely hydroxycarbonates, carbonates, and sulfates). The relative bioavailability of these forms is shown in Table 3 below.

Table 3. Potential Bioavailability of Lead Minerals

Potentially Lower Bioavailability (RBA < 25%)	Intermediate Bioavailability (RBA = 25% to 75%)	Potentially Higher Bioavailability (RBA > 75%)
Galena (PbS) Anglesite (PbSO ₄) Pb (M) Oxides Pb Fe (M) Sulfates Native Pb	Pb Oxide Pb Fe (M) Oxides Pb Phosphate Slags	Cerussite = PbCO ₃ Pb Mn (M) Oxides

Notes:

Data from US EPA, 1999. RBA = Relative Bioavailability

4.1.3 Lead Screening Values for Human Health Risk Assessment

Lead in soil frequently drives site cleanup activities. Screening values for lead are estimated using blood-lead modeling. Exposure to lead is typically evaluated in terms of the increase in blood lead (PbB) concentrations following exposure. US EPA has adopted 10 micrograms per deciliter ($\mu\text{g}/\text{dL}$) as a PbB concentration of concern to protect sensitive populations. This PbB level of concern is the basis of US EPA Regional Screening Levels (RSLs) of 400 and 800 milligram per kilogram (mg/kg) for a typical residential and commercial/industrial exposure, respectively (MDEQ, 2021). The US EPA's stated goal for lead is that children have no more than a 5 percent probability of exceeding a PbB concentration of 10 $\mu\text{g}/\text{dL}$. The most recent OLEM Directive (OLEM Directive 9285.6-56)¹ recommends using lower blood levels lower than the 10 $\mu\text{g}/\text{dL}$ (e.g., 5 $\mu\text{g}/\text{dL}$), which would lower the residential soil RSL. The US EPA has not as yet incorporated this new recommendation for calculating residential and industrial RSL. This level is assumed to also provide protection for adults (US EPA, 1998).

The California Environmental Protection Agency (CalEPA) has also developed policies and procedures for the evaluation of lead (Table 3). CalEPA's soil lead screening values of 80 mg/kg for residential and 320 mg/kg for industrial receptors were calculated using CalEPA's lead risk assessment spreadsheet tool called LeadSpread-8 (CalEPA, 2011). The CalEPA lead soil screening values are based on a PbB level of concern of 1 $\mu\text{g}/\text{dL}$ instead of 10 $\mu\text{g}/\text{dL}$ and values represent the 90th percentile estimate of a 1 $\mu\text{g}/\text{dL}$ increase in PbB in a child (CalEPA, 2011).

Table 4. Summary of US EPA and CalEPA Soil Lead Screening Values

Land Use	US EPA (a) (mg/kg)	CalEPA (b) (mg/kg)
Residential	400	80
Industrial	800	320

(a) US EPA. 2021. Regional Screening Levels (RSLs) - Generic Tables. November.

(b) CalEPA. 2020. Human Health Risk Assessment (HHRA) Note Number 3, DTSC-modified Screening Levels (DTSC-SLs). June.

In California, project action levels for lead are typically developed to align with CalEPA screening levels; however, in other states, US EPA or CalEPA screening levels may be used.

Additional information pertaining to the US EPA lead evaluation can be found at <https://www.epa.gov/superfund/lead-superfund-sites-software-and-users-manuals>.

Additional information pertaining to the CalEPA lead evaluation can be found at <https://dtsc.ca.gov/leadspread-8/>

4.1.4 Stabilization of Lead Remedial Considerations

Depending on the form of lead present in soil and the composition of the soil, lead mobility at SAFRs may be naturally constrained or can be constrained through the addition of chemical stabilizing agents. High clay and high organic matter in surface soils reduce solubility and downward migration of lead into groundwater.

¹ <https://semspub.epa.gov/work/HQ/196766.pdf>

Case Study 2B describes how soil excavation and treatment of excavated soil to stabilize lead allowed for disposal of lead-contaminated soils in a Resource Conservation and Recovery Act (RCRA) Class D landfill.

Additional information on remedial options for lead and other metals at SAFRs can be found in:

- Environmental Management at Operating Outdoor Small Arms Firing Ranges (ITRC, 2005)
- Characterization and Remediation of Soils at Closed Small Arms Firing Ranges (ITRC, 2003)

Application: Soil Lead Stabilization to Minimize Leaching

Lead in soil has the potential to become mobile and leach into groundwater. Because lead as a soil contaminant is difficult to treat, soil excavation and transport off site to a landfill may be selected as a remedy to reduce risk to human and/or ecological receptors. RCRA subtitle D landfills can accept soil that has been contaminated with lead if the lead has been stabilized and will therefore not become soluble and potentially leach into groundwater.

Leachability of lead is affected by the chemical form of the lead and the pH of the leachate. Chemical stabilizers (consisting of silicate) can be added to soil to initially adjust pH and then stabilize lead through a change in chemical form from lead oxide, carbonate, or hydroxide to a lead silicate, which is insoluble. The reactions that form lead silicate are not reversible and the result is a cementitious mass.

Case Study 2 describes how targeted excavation, treatment of excavated soil piles with a chemical stabilizing agent (Blastox[®]), and chemical testing to ensure stability can be used to successfully remediate a former small arms range.

4.2 GROUNDWATER

Several challenges can arise at sites where metals are present in groundwater. These include metals above background levels without an attributable source and metals mobilized into groundwater by changing site redox conditions. In addition, it can be challenging to implement monitored natural attenuation (MNA) for sites with metals in groundwater.

4.2.1 Metals Above Background and Not Attributable to a Known Source

Federal law requires Navy to protect human health and the environment and comply with all applicable and relevant and appropriate requirements (ARARs) at chemical release sites. Distinguishing between contaminants associated with a release and naturally-occurring background is essential to this process. While statistical analysis of chemical data is an integral part of groundwater monitoring and background analysis, it is critical to understand and characterize the geologic, geochemical, and hydrogeologic processes that control the occurrence and concentrations of naturally-occurring chemicals in groundwater (NAVFAC, 2004).

While many state and federal guidance documents describe groundwater monitoring and statistical approaches for analyzing the resulting data, the NAVFAC guidance document below can be used as a starting and central point of reference, as it contains references to other key documents and regulations relating to groundwater data collection and compliance with regulatory standards.

- *Guidance for Environmental Background Analysis Volume III: Groundwater* (NAVFAC, 2004)

This guidance also outlines procedures for selecting the locations of background monitoring wells, evaluating chemical data, hydrogeologic characteristics, and geochemical parameters needed to estimate the upper bounds of background concentration ranges and identify relevant background datasets.

Background and baseline groundwater conditions can include the chemical characteristics of groundwater affected by both natural and anthropogenic sources and can therefore include contaminants released from off-site sources and transferred to the site. These sources can be known or unknown.

While many metals can be screened out through initial comparisons to regulatory screening criteria, metals that exceed criteria should be assessed using the following weight of evidence methodology to characterize groundwater background conditions (NAVFAC, 2004):

- **Step 1:** Evaluate Geology, Hydrogeology, and Contaminant Sources
- **Step 2:** Evaluate Geochemical Conditions
- **Step 3:** Conduct Spatial and Temporal Groundwater Data Analysis

This information should be incorporated into a CSM that is focused on groundwater for the site and includes the potential contamination sources and locations. A recent study conducted by the Washington State Department of Ecology is summarized below on background arsenic concentrations in groundwater throughout the state. In this example, background arsenic is consistently above regulatory standards due to natural processes, including geochemistry (reducing conditions) and soil organic matter, which release arsenic from iron oxides.

Washington State Investigation: Arsenic in Groundwater

The federal drinking water standard (or MCL) established by US EPA for arsenic is 10 µg/L. The Washington State Department of Ecology recently conducted a study to characterize statewide background concentrations. Groundwater arsenic levels ranged from < 1 to 150 µg/L and the range was determined to be 4.9 to 15.5 µg/L (2022).

Ambient groundwater arsenic conditions vary by climate and geology, with higher groundwater concentrations found in the Western United States (Washington State Department of Ecology, 2022). Geochemical changes in iron oxide may be the cause of elevated (> 10 µg/L) arsenic in groundwater. Arsenic may be released by reactions of iron oxide with natural or anthropogenic organic carbon (e.g., petroleum products). Alkaline aquifers are another potential cause (Washington State Department of Ecology, 2022).

4.2.2 Naturally-Occurring Metals Mobilized by Changing Redox Conditions

The in situ application of chemical and biological processes to remediate contaminants in groundwater has provided more effective options for restoring groundwater quality. Such treatments, however, are complex and interact with the solid aquifer matrix. This interaction can impact naturally-occurring metals in soil, rocks, and minerals within the treatment zone, dissolving and mobilizing them in groundwater (Suthersan and Horst, 2008).

Anaerobic and reducing conditions can result in naturally-occurring iron, manganese, and arsenic to become dissolved in groundwater. These conditions can be generated by the presence of released and degrading organic contaminants, such as hydrocarbons, or engineered as a groundwater

remedy to treat other contaminants when organic substrates are delivered or injected into the subsurface environment. Both iron and manganese are soluble in their reduced valence states.

While the health risk associated with dissolved iron and manganese in drinking water is insignificant, concentrations above 0.3 mg/L for iron and 0.05 mg/L for manganese may result in a metallic taste or nuisance effects, such as staining of plumbing fixtures. These two metals fall under US EPA’s Secondary Maximum Contaminant Level (SMCL) standards.

Arsenic is a metalloid that is soluble in all valence states, unless it is adsorbed to or incorporated with other minerals. While arsenic is not as abundant as iron and manganese, it is ubiquitous in small amounts and can be released through the dissolution of iron minerals with which it is typically associated (Smedley and Kinniburgh, 2002).

Concentrations of these three metals can be expected to remain elevated while the anaerobic environment is maintained. However, as shown in Figure 11, concentrations of these dissolved metals decrease downgradient where aerobic conditions are restored and these metals reoxidize and precipitate.

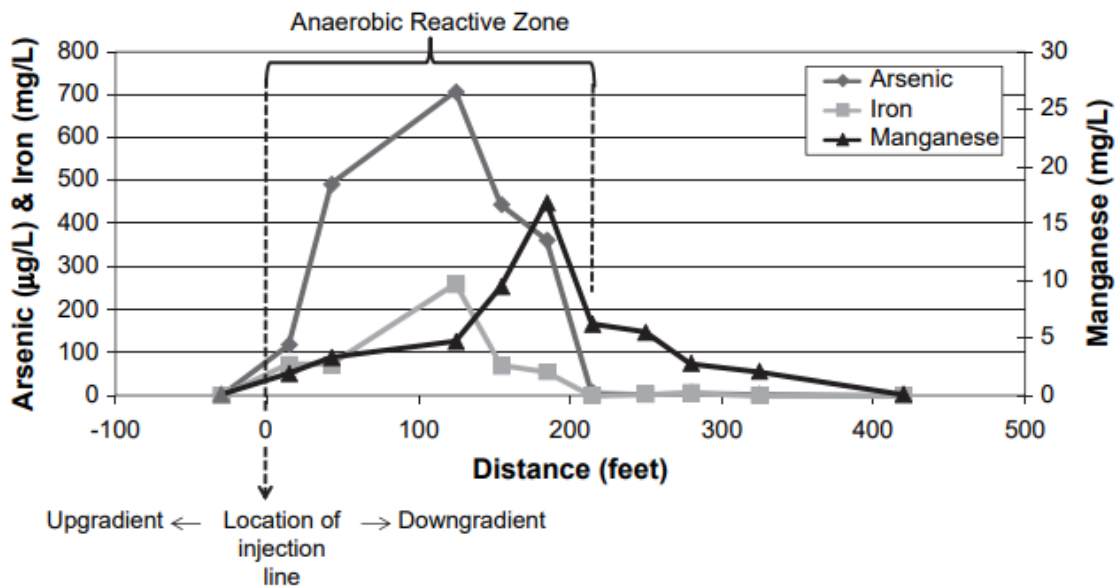


Figure 11. Dissolved Metals Concentrations through an Engineered Anaerobic In Situ Reactive Zone (IRZ) (Courtesy of Suthersan and Horst, 2008)

4.2.3 Monitored Natural Attenuation as a Remedy for Metal-Impacted Sites

At many NAVFAC ERP sites, concentrations of some metals are at low levels due to known or suspected historical releases but above regulatory standards. MNA may be an appropriate remedy in these cases. Attenuation-based remedies are typically less aggressive, less invasive, and less costly than engineered remedies, although are most often applied to organic rather than inorganic (i.e., metal) contaminants (ITRC, 2010).

What is MNA? MNA refers to “the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation

objectives within a time frame that is reasonable compared to that offered by more active methods” (Office of Solid Waste and Emergency Response [OSWER] Directive 9200.4-17P).

Conceptually, natural attenuation processes for metals are quite different than for organic constituents and result in contaminants remaining in the environment rather than being destroyed. Processes typically involve valence or oxidation state changes, which in turn affect solubility and mobility. For example, hexavalent chromium can be chemically and biologically reduced to the less soluble and less toxic trivalent chromium. Metals attenuation is predominantly the result of abiotic processes but can also be influenced by microbial processes. Metals attenuation processes are reversible and complex, so long-term monitoring is an important component of a remedy where natural processes are to be relied upon to achieve remedial action objectives (US EPA, 1999).

Dominant attenuation mechanisms for metals involve chemical reactions that cause partitioning of the contaminant to immobile forms. Oxidation reduction potential (ORP), CEC, sediment iron oxide are important geochemical parameters for assessing MNA as a groundwater remedy at a particular site (Savannah River National Laboratory [SRNL], 2011).

Components to using MNA as a remedy include the following (US EPA, 2007b):

- Demonstration of active contaminant removal from groundwater and dissolved plume stability;
- Determination of the rate and mechanism of attenuation;
- Determination of the long-term capacity for attenuation and stability of immobilized contaminants; and
- Design of a performance monitoring program, which includes defined triggers for assessing MNA failure and establishes a contingency plan.

What is the Oxidation-Reduction Potential (ORP) Condition?

HIGH ORP: oxidizing or aerobic environment ($E_h > 0$ mV)

LOW ORP: anoxic or anaerobic environment ($E_h < 0$ mV)

Which CEC Condition?

CEC influences the degree to which contaminant cations may be removed from groundwater and adsorbed to mineral surfaces, especially clay minerals.

HIGH CEC: soil with high surface charge that attracts and hold cations (> 10 meq/100 grams aquifer media)

LOW CEC: soil with low surface charge and lower adsorptive capacity (< 10 meq/100 grams aquifer media)

ITRC's *A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater* (2010) may be a useful resource for incorporating groundwater MNA or enhanced attenuation (EA) into the larger remedy evaluation for a site. EA technologies are low-energy and longer-acting, and they can act as a bridge between higher-energy remedies and MNA. EA technologies optimize aquifer conditions to provide a sustainable treatment by reducing contaminant loading and/or increasing the attenuation capacity of an aquifer.

5.0 CONCLUSIONS

This report provides an overview of how key principles of metals chemistry can be applied to risk management at NAVFAC ERP sites with releases of metals to the environment. Best practices during site investigations and to scope and implement remedial actions are also highlighted. Technical resources and the key guidance documents are provided for NAVFAC RPMs to review and consider in managing sites where metals have impacted soil and/or groundwater.

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