Bureau of Land Management

Arizona Magma Mine Site Waste Evaluation

Background Research Document

CENE 476: Capstone Prep

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List of Abbreviations

AAS	Atomic absorption spectrometry
ADEQ	Arizona Department of Environmental Quality
ASRS	Arizona Soil Remediation Standards
BLM	Bureau of Land Management
BMD	Benchmark dose
BMDL	Benchmark dose lower-confidence limit
CDI	Chronic daily intake
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	Contaminant of concern
EPA	Environmental Protection Agency
FLAA	Flame atomic absorption
GFAA	Graphite furnace atomic absorption
GPS	Global positioning system
HRS	Hazard Ranking System
ICP	Inductively coupled plasma
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ICS	Incremental composite sample
IDW	Investigation derived waste
IEUBK	Integrated Exposure Uptake Biokinetic
LOAEL	Lowest Observed Adverse Effect Level
NOAEL	No observed adverse effect level
NPL	National Priorities List
NRC	National Response Center
PA	Preliminary assessment
PPE	Personal protective equipment
PRP	Potentially responsible party
RfC	Reference concentration
RfD	Reference dose
ROD	Record of Decision
SI	Site inspection
TCCR	Transparency, clarity, consistency, reasonableness
QA	Quality assurance
QC	Quality control
XRF	X-ray fluorescence

1.0 Description of Technical Aspects

This report will provide the background information necessary to develop and execute a mine site waste evaluation. This includes sampling techniques, equipment considerations, safety considerations, environmental regulations and standards, risk assessment techniques, and lab analysis techniques. Sampling techniques include grid sampling, hotspot sampling, background sampling, grab sampling, composite sampling, and soil sampling. It is also important to consider statistical significance, quality assurance (QA), and quality control (QC). Equipment considerations include x-ray fluorescence (XRF) devices, global positioning systems (GPS), measuring equipment, sample collection materials, and chain of custody materials. Safety considerations include personal protective equipment (PPE), investigation derived wastes (IDW), and a site health and safety plan. Environmental regulations and standards include the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Arizona Soil Remediation Standards (ASRS). Risk assessment techniques include the Environmental Protection Agency's (EPA) techniques and the Bureau of Land Management's (BLM) techniques. It is also important to consider models such as the Integrated Exposure Uptake Biokinetic (IEUBK) model for lead in children and the adult lead model for lead in adults. Lab analysis techniques include acid digestion, atomic absorption spectrometry (AAS), and various techniques that use inductively coupled plasma (ICP).

2.0 Sampling Techniques

2.1 Grid Sampling

Grid sampling involves sampling at fixed spatial intervals. Grid sampling is often preferred because it is easy to implement and more easily identifies contamination patterns (Innis 24). There are two ways to go about grid sampling, centrally aligned and unaligned (EPA A 75). Figure 2.1 illustrates a centrally aligned grid sample approach.

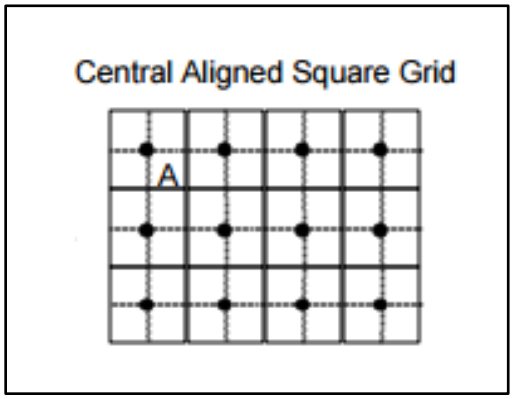

Figure 2.1 Centrally Aligned Grid (EPA A 75)

Based on where point A in Figure 2.1 is chosen, the rest of the points are known once a grid is laid down. The drawback of a centrally aligned grid is that all points are separated at equal lengths from each other. This is an issue if the contamination of concern occurs in a fixed pattern (EPA A 75). Counter to a central grid, unaligned grid sampling is still dependent on where point A is placed, but is more random. Figure 2.2 illustrates an unaligned grid sample approach.

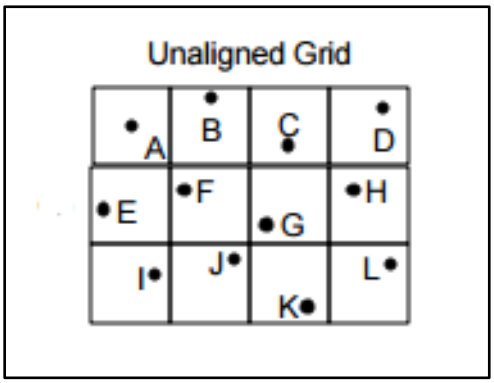

Figure 2.2 Unaligned Grid (EPA A 75)

The grid in Figure 2.2 is still based on point A's location, but all other points are *only* located within the squares the grid establishes and are not centrally aligned. The benefits to an unaligned grid sampling approach is randomness combined with good coverage (EPA A 76). Grids can typically be developed in the field by selecting a point or designating boundaries using a GPS (section 3.2). Materials necessary for laying out a grid include measuring tape, protractors, stake flags, and compasses.

2.2 Hotspot Sampling

Hotspot sampling involves the sampling of specific locations based on knowledge of a contaminant's distribution pattern. Hotspot sampling is used when there are locations with obviously high concentrations of a contaminant (Innis 23). As such, this sampling is used to determine the highest levels of concentration in an area. It is important to understand that hotspot samples are not acceptable in demonstrating environmental compliance (Innis 23). Justification for taking a hotspot sample falls on a site investigator's better judgement, and the decision must be well-documented and defensible (Innis 23).

2.3 Background Sampling

Background sampling is performed "at or near the waste site in areas not influenced by site contamination" (Innis 24). Background samples demonstrate what the naturally occurring concentrations of a contaminant of concern (COC) are in the site investigator's medium of choice (soil, surface water, groundwater, etc.) (Innis 24). The number of background samples necessary for an investigation is dependent on sample media type, contaminant type, and other site-specific factors (Innis 24). A difference in concentration between background samples and

site samples should not immediately trigger a cleanup action, but instead encourage further data evaluation (Innis 25).

2.4 Grab Samples

Grab samples are “samples taken from a particular location at a distinct point in time” (Innis 23). These samples are necessary for hotspot and background sampling. Grab samples can be collected in jars, plastic bags, polyethylene bottles, or any other viable collection device.

2.5 Composite Samples

Composite samples are gathered by taking multiple grab samples over a spatial range, physically combining them, and then drawing one or more subsamples for lab analysis (Innis 23). The benefits of composite sampling are potentially improved precision and a reduction in cumulative sample volume (Innis 23). Composite samples are relevant when there is no need to identify peak concentrations at a site.

2.6 Sampling Soil

When collecting soil samples, it is important to consider the COC’s properties. For example, a COC with volatile organic compounds may release volatiles into the air when the sample is collected (Innis 27). Ideally, field personnel will use soil sample collection devices that allow them to collect minimally disturbed samples (Innis 27). Additionally, the collection devices should allow personnel to easily log and later identify their samples. Plastic bags are an example of a collection device that can be used for soil sampling.

It is important to consider the homogeneity or heterogeneity of soil at a site investigation. A site with large variances in soil type may also have large variances in COC concentrations, due to the COC’s chemical properties (Innis 27).

2.7 Soil Sample Preservation

Sample preservation helps minimize chemical and physical changes in a sample from sampling location to lab analysis (Innis 37). Preservation techniques largely depend on the COC of the site, but typically include sample cooling and/or the addition of a chemical preservative (RMB Environmental Laboratories, Inc. 18-20).

2.8 Statistical Significance

Statistical significance deals with relationships between variables being due to chance or being real. Testing for statistical significance includes 1) stating a research hypothesis, 2) stating a null hypothesis, 3) selecting a probability of error level, 4) computing for statistical significance, and 5) interpretation.

2.9 Sampling Quality Assurance and Quality Control

For QA/QC in soil sampling, the use of blanks and replicates can be beneficial. Equipment rinsate blanks are samples of analyte-free water poured through decontaminated sampling equipment prior to the collection of samples. Equipment rinsate blanks provide an analytical check for sources of contamination due to inadequate equipment decontamination techniques (Stroh and Weber 22). Field blanks are samples of analyte-free water poured into a typical sampling container. Field blanks provide an analytical check for sources of contamination due to field sampling conditions. Trip blanks are empty sample cells that are taken from the laboratory to the field site and back to the laboratory. Trip blanks provide an analytical check for sources of contamination due to improper transportation and field handling techniques.

An example of a replicate sample is a replicate incremental composite sample (ICS) (Stroh and Weber 22). Replicate ICS help measure precision for overall soil sampling and analysis processes (Stroh and Weber 22). Replicate ICS can be gathered by extracting portions from all sample units.

3.0 Equipment Considerations

3.1 XRF Devices

Portable XRF devices can be used as screening devices in site waste evaluations for chemicals such as lead (EPA B). Additional analyses, such as AAS (section 7.2) must be done to confirm the presence of such chemicals in a soil sample (EPA B). XRF technology can work either by using sealed radioisotope sources or x-ray tubes to irradiate soil samples with x-rays (EPA B). The irradiated sample will either scatter or absorb the source x-rays, a process called photoelectric effect (EPA B). Figure 3.1 illustrates how the source x-rays either scatter or absorb.

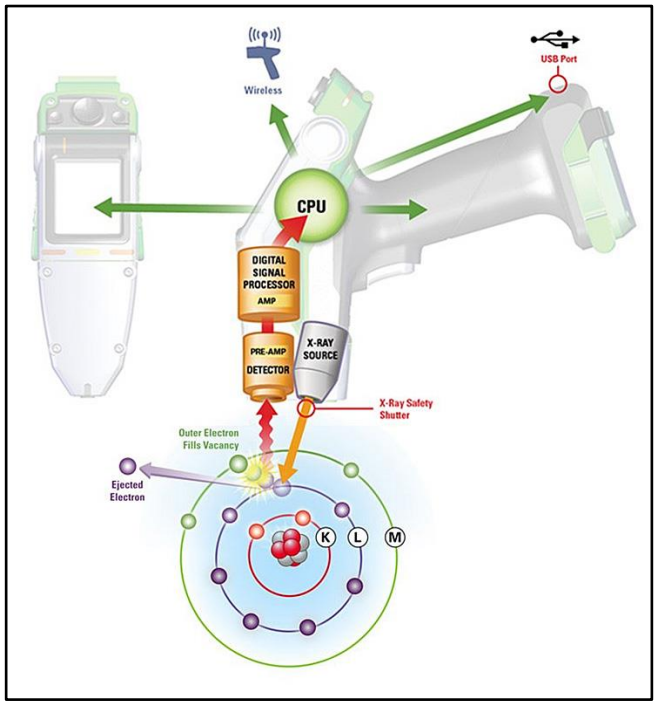

Figure 3.1 Photoelectric Effect (Thermo Fisher)

When the source x-rays are absorbed by the sample, electrons are dislodged from the inner K-shell of the atom creating vacancies (EPA B). As electrons fall from a higher electron shell (M or L) to a vacancy on a lower shell, energy is emitted (EPA B). The re-arrangement of electrons in the soil sample provides characteristic feedback signatures of specific atoms that are present (EPA B). The energy emission from the sample is termed the x-ray fluorescence.

Data quality for an XRF device is limited by sample preparation error, spectral interference, chemical matrix interference, and a soil's moisture content. Preparation error comes from the degree of homogeneous samples (EPA B). More homogeneous soil samples will have more accurate XRF data results (EPA B). However, if the XRF device is used in-situ, the preparation error can not be controlled (EPA B). Spectral interference occurs when the detector's resolution capacity and software can not discern x-rays of similar energy (EPA B). Some elements naturally produce x-rays that are similar to others. Chemical matrix effects result from "differences in the concentrations of interfering elements" (EPA B). These effects occur as "either spectral interferences or as x-ray absorption and enhancement phenomena" (EPA B). For soils contaminated with heavy metals, both phenomena are common (EPA B). To minimize errors due to high soil moisture content, sample drying is recommended.

3.2 Global Positioning System

GPS is a satellite-based navigation system that uses trilateration to pinpoint a person's location within three to five meters (Garmin). Portable GPS units can be used to identify relatively exact locations by latitude and longitude, and are necessary in site waste investigations. Most importantly, GPS units can be used to identify site boundaries and/or an individual sample point. This is essential when laying out a sampling grid. A sample grid can be developed by identifying a single point by GPS, then using measuring equipment (section 3.3) to map-out the rest of the grid in the field.

3.3 Measuring Equipment

Measuring equipment that can be used to map-out a sample grid include measuring tape, protractors, stake flags, and compasses. Measuring tape can be used to ensure precise distances between samples points. A protractor and compass can be used to ensure distances are being paced-out at precise directions. Finally, stake flags can be used to pinpoint sample locations.

3.4 Sample Collection Materials

Materials for sample collection can include jars, plastic bags, and/or polyethylene bottles (American Society of Testing and Materials). To ensure samples are properly preserved (section 2.6.1), ice bags, coolers, and/or chemical preservatives may be necessary (RMB Environmental Laboratories, Inc. 18-20).

3.5 Chain of Custody Materials

Chain of custody documents serve as legal tracking of a sample that is transferred from person to person, place to place, etc. A proper sample should have a sample type, sample number, date, time, collector initials and possibly a grid number on it for chain of custody purposes (Stroh and Weber 21). Additionally, a sample log form should be maintained to keep track of all samples (Stroh and Weber 38). For samples designated for lab analysis, a chain of custody form should be filled-out (Stroh and Weber 21). Chain of custody forms identify who has relinquished and received a sample at various points in time, among other things. Additionally, it is sometimes necessary to use chain of custody seals on samples, to indicate instances of tampering and/or sample invalidation.

4.0 Safety Considerations

4.1 Personal Protective Equipment

PPE includes various forms of clothing that protect an individual from injury or illness. For site waste evaluations, relevant PPE can include the following items:

- nitrile gloves
- disposable industrial respirators
- large white Tyvek coveralls
- safety glasses
- portable eyewash
- disposable shoe covers

4.2 Investigation Derived Wastes

For site waste evaluations, IDW can include soil, sediment, decontamination fluids, disposable sampling equipment, and disposable PPE (Stroh and Weber 24). It is important to minimize IDW when possible. Disposable sampling equipment and disposable PPE are solid wastes and should be disposed of properly.

4.3 Site Health and Safety Plan

A site safety and health plan is helpful in categorizing various hazards of the site evaluation process. A proper safety and health plan identifies possible chemical hazards, possible physical hazards, and task-specific risks (Stroh and Weber 30).

5.0 Environmental Regulations and Standards

5.1 CERCLA

For a site to have a funded investigation and remediation, it must first go through a process to determine its toxicity and danger to human health. Described below is the process both the EPA and BLM use.

CERCLA, also known as Superfund, was established in 1980 by the EPA (EPA C). CERCLA was established in response to several toxic waste dumps discovered in the 1970's, most notably Love Canal (EPA D). Its main purpose is to provide liability, compensation, cleanup, and emergency response to hazardous waste disposal sites (EPA C). Although the EPA acts as the lead agency for these Superfund sites, the BLM (alongside the Department of Interior) acts as lead agency for their sites. The process and guidelines of assessing and investigating a site is

similar for the EPA and BLM. For CERCLA, in order for a site to receive funding for a cleanup it must first be placed on the National Priorities List (NPL).

To start this process, a site is reported to the EPA as potentially hazardous. This can be done by residents, local, state, or federal agencies, or businesses through the National Response Center (NRC) (EPA D). After the EPA knows about the site, a preliminary assessment and site inspection (PA/SI) is completed. The preliminary investigation usually involves interviews with local residents and tests of the surrounding soil, water, and air for contamination. The PA also includes research of online documentation on the site. Depending on the toxicity of the site and its dangers to human health, early action may need to be taken on the site to remove the contaminants or provide resources to surrounding communities (EPA D). The information learned in the PA/SI assists in scoring a site in terms of the Hazard Ranking System (HRS).

The HRS is determined by considering four different pathways: ground water migration, surface water migration (drinking water, human food chain, environmental), soil exposure (resident and nearby population), and air migration (EPA E). These pathways are reviewed under their likelihood of release/exposure, waste characteristics, targets and input into an equation. If the site receives a high enough score, it is eligible for the NPL (EPA E). Once a site is eligible for the NPL, it is put in the Federal Register and can be voted on by the public. Finally, if the public recommends it, the site is put onto the NPL.

The HRS is where the EPA and BLM process differ. The EPA uses this score to determine if the site is eligible for funds and remediation. However, for BLM, the site is usually already determined to have toxic waste and be in need of remediation, so the score is not necessary.

Once a site is established for both EPA and BLM processes, a remedial investigation is completed on the site. Similarly to the PA/SI, the RI includes gathering and analyzing soil, water, and waste throughout the site and assessing risks. Next, a feasibility study is completed to analyze the advantages and disadvantages of potential treatment and cleanup methods. The two actions that may be taken are either a removal action or remedial actions (EPA D). Removal actions are short-term and usually completed due to an emergency or immediate threat to human health. Remedial actions are long-term solutions that aim for permanent removal of contaminants. A site must be on the NPL to be considered for remedial actions in CERCLA.

As soon as the site is discovered, the EPA tries to identify the generators, operators, and owners of the site. These potentially responsible parties (PRPs) are responsible for paying for all investigation, remediation, and removal on the site. If the parties do not comply, EPA may continue with the cleanup and sue them later for the cost (EPA D). If the parties cannot be found, the EPA will use the money allocated for projects in the Superfund.

After the treatment methods are developed and compared, the EPA recommends a Proposed Plan to the community to be implemented. Once the plan is accepted, remediation or removal

begins and is documented in the Record of Decision (ROD). The EPA keeps the public updated on all remedial design and action with Five-Year Reviews detailing the site's status and new sample analysis. With time, the EPA may remove a site from the NPL if the goals have been met and no further cleanup is required (EPA D).

5.2 Arizona Soil Remediation Standards

After a site is determined by CERCLA and BLM processes, it must be investigated and remediated according to ASRS. The standards include both residential and non-residential standards. Residential standards are for remediation completed on properties owned and lived on by people, while non-residential standards are for public land with access available to anyone (ADEQ). The non-residential site-specific remediation level is a level of contaminant after remediation that results in a excess lifetime cancer risk between 1×10^{-6} and 1×10^{-4} and a Hazard Index less than or equal to 1 (ADEQ). These risks are based on exposure assumptions for non-residents. For example, recreation on the site can be considered an exposure scenario for a non-residential site.

The contaminant levels required to meet the standards vary depending on the chemical. For a non-residential standard, arsenic must be removed to a concentration of 10 milligrams per liter while lead must be removed to a concentration of 2000 milligrams per liter (ADEQ). The Soil Remediation Levels (SRLs) for these contaminants, as well as hundreds more, can be seen in Appendix A or B of the Arizona Department of Environmental Quality's (ADEQ) Title 18 document on Environmental Quality. The SRLs used for a site are dependent upon the person(s) completing the remediation and the possible future exposure scenarios. The most dangerous COCs pertaining to mining sites may include lead, arsenic, mercury and cyanide. The residential and non-residential SRLs can be seen below in Table 5.1.

Table 5.1 SRLs for COCs

Contaminant	Residential (milligrams/kilograms)			Non-residential (milligrams/ kilograms)
	Carcinogen		Non-carcinogen	
	10^{-6}	10^{-5}		
Arsenic*	10	10	10	10
Cyanide (free)**			1200	1200
Cyanide (hydrogen)***			11	35
Lead			400	800
Mercury and compounds			23	310
Mercury (methyl)			6.1	62
*Arsenic standards are not risk-based standards, but based on background. Cyanide from other cyanide metal complexes is required.				
**Free cyanide is a subset of total cyanides. If any approved method for total cyanide reports a concentration exceeding this standard, further analyses to differentiate cyanide subsets are required.				
***If cyanide concentrations exceed the hydrogen cyanide standard, then hydrogen cyanide vapor samples must be collected at the site.				

6.0 Risk Assessment Techniques

6.1 EPA's Risk Assessment Techniques

The EPA has standard approaches for both human and ecological risk assessment. The subsections below describe the process for both risk assessment techniques.

6.1.1 Human Health Risk Assessment

The EPA has a four-step process to determine human health risk assessment. The process includes the following items (EPA F):

- Planning
- Step 1: Hazard Identification
- Step 2: Dose-Response Assessment
- Step 3: Exposure Assessment
- Step 4: Risk Characterization

6.1.1.1 Planning

The planning phase starts by identifying the population(s) at risk. This includes people such as children, teenagers, adults, pregnant/nursing women, the elderly, susceptible people (such as people with asthma), and exposed groups of people (geographic area, gender, socioeconomic status). This step is followed up by determining the environmental hazards of concern. Potential hazards include, but are not limited to, radiation, particulate matter, biological, and chemical. Environmental hazards come from point sources, non-point sources, and natural sources. Exposure pathways and routes for the given hazards must be determined. Multiple pathways are possible for a given hazard, such as air, water, soil, food, and solid waste. Exposure routes include ingestion (food and water), dermal contact, inhalation, and non-dietary ingestion. Factors such as race, gender, and age are considered to determine adsorption, bodily distribution, metabolism, and excretion of the hazard. Health effects and the timing of such impairments are considered. Potential health effects include, cancer, heart disease, nerve damage, and death. These health effects may be acute, chronic, subchronic, or intermittent (EPA F).

6.1.1.2 Hazard Identification

This step involves identifying adverse health effects that may be caused by exposure to given contaminants. Exposure to contaminants may cause birth defects, cancer, disease, and death. This information may or may not be taken from epidemiological studies. Animal testing may be conducted to infer potential human health effects of exposure to given contaminants. However, there is a degree of uncertainty associated with extrapolating animal studies to determine potential human health effects (EPA F).

6.1.1.3 Dose-Response Assessment

This step involves identifying the relationship between a given dose of an agent and the potential/severity of health effects. As dose increases, the response will typically increase as well. Dose-response relationships could include multiple responses for one given agent. There is a lack of data establishing the relationship between dose and response for human subjects. As a result, data is primarily taken from animal studies and extrapolated as needed, because the dosage given to animals is higher than what humans are expected to encounter. Mode of action refers to the interaction between an agent with a cell. This interaction results in operation and anatomical changes that for example, may cause cancer (EPA F).

Equation 6-1 and Equation 6-2 are used to assess the toxicity of non-carcinogens and carcinogens (LaGrega, Buckingham, and Evans):

Equation 6-1: *Toxicity for non-carcinogens*

$$TS = C_{max}/RfD$$

TS = toxicity score
C_{max} = maximum concentration
RfD = reference dose

Equation 6-2: *Toxicity for carcinogens*

$$TS = SF * C_{max}$$

SF = slope factor (carcinogen potency factor)

6.1.1.3.1 Non-linear dose response Assessment

If the mode of action suggests that there is a toxicity threshold (threshold at which toxic effects are observed), then it is appropriate to conduct a non-linear dose response assessment. Because there is a certain tolerance for a given dose of an agent, dose-response assessments focus on the most susceptible members of the population. (EPA F).

No Observed Adverse Effect Level (NOAEL) refers to the highest dose possible for an agent that does not result in a statistically significant increase in observed health effects. On the other hand, Lowest Observed Adverse Effect Level (LOAEL) refers to the lowest dose that is known to cause adverse health effects. The Benchmark Dose (BMD) or Benchmark Dose Lower-confidence Limit (BMDL) is used as an alternative to the NOAEL. The reference dose (RfD) is derived from the NOAEL, LOAEL, or BDML. It is an oral or dermal dose that generally uses an uncertainty factor of 100. RfD is calculated using the Equation 6-3 (LaGrega, Buckingham, and Evans):

Equation 6-3: *Reference dose*

$$RfD = LOAEL\ (NOAEL\ or\ BMDL)/UF$$

UF = uncertainty factor

The RfD estimates the daily oral dose of an agent that will likely not result in adverse health effects during a lifetime. Generally, the RfD is expressed in units of milligrams per kilogram of body weight per day. The reference concentration (RfC) is similar to the RfD, where it is used to calculate inhalation risk in units of milligrams of agent per cubic meter (EPA F).

6.1.1.3.2 Linear Dose-Response Assessment

If the mode of action suggests that there is no toxicity threshold for the given agent, then this is referred to as a linear dose-response assessment. In the case of carcinogens, a slope factor is developed. Cancer risk is calculated using Equation 6-4 (LaGrega, Buckingham, and Evans):

Equation 6-4: *Cancer risk*

$$Cancer\ Risk = Exposure * Slope\ Factor$$

6.1.1.4 Exposure Assessment

The exposure assessment consists of measuring or estimating exposure or future exposure to a given agent in the environment. Exposure is typically measured indirectly by considering the environmental fate and transport of a given agent. Exposure assessments must consider exposure pathways and exposure routes (dermal contact, ingestion, inhalation). Three basic methods for quantifying exposure can be used. They are: point of contact measurement (measuring exposure, concentration, and duration while contact occurs), scenario evaluation (estimating exposure concentration and duration), and reconstruction (estimating exposure dosage after it occurs by using biomarkers) (EPA F).

Any given individual will experience different exposure levels depending on a variety of factors. Individuals at a high risk of exposure include workers on a contaminated site. People who occasionally use a contaminated site or are downwind of it are at a lower risk of contact and for a shorter period of time. The EPA defines two common exposure frequencies: central tendency (average exposure for a given population), and high end (highest dose approximately equal to the 90th percentile of exposure) (EPA F). Equation 6-5 is used to calculate chronic daily intake (CDI) (LaGrega, Buckingham, and Evans):

Equation 6-5: *Chronic daily intake*

$$I = \frac{C * CR * EF * ED}{BW * AT}$$

I = intake (milligram/kilogram of bodyweight per day)
C = concentration at exposure point
CR = contact rate
EF = exposure frequency
ED = exposure duration
BW = bodyweight
AT = averaging time

This equation is typically modified to account for specific exposure routes. Table 6.1 shows the average contact rate and body weight of adults, children aged 6 - 12, and children aged 2 - 6 for water, air, and soil:

Table 6.1 Average Body Weight and Ingestion Rates for Adults and Children (LaGrega, Buckingham, and Evans).

Parameter	Adults	Children aged 6 -12	Children aged 2 - 6
Body weight (kilograms)	70	29	16
Water ingestion rate (Liters/day)	2	2	1
Inhalation rate (cubic meters/hour)	0.83	0.46	0.25
Soil ingestion rate (milligrams/day)	100	100	200

Averaging time for non-carcinogens is taken as the exposure duration, while averaging time for carcinogens is 70 years (LaGrega, Buckingham, and Evans).

6.1.1.5 Risk Characterization

This step involves integrating the previous steps to compute risk. A risk characterization includes the possible risk, how the risk was assessed, assumptions that were made, and potential uncertainties. The EPA's Risk Characterization Policy requires: transparency (full and explicit disclosure of the risk assessment methodology), clarity (the risk assessment must be easily understood by all readers), consistency (the risk assessment must be conducted in a manner consistent with the EPA's method), and reasonableness (the risk assessment must be consistent with current practice and science). The four principles are referred to as TCCR (EPA F). Equation 6-6 is used to calculate carcinogenic risk (LaGrega, Buckingham, and Evans):

Equation 6-6: *Carcinogenic risk*

$$Risk = I * SF$$

Equation 6-6 shows the risk of excess lifetime cancer due to exposure to the specified chemical. This methodology assumes that the carcinogenic risk can be calculated by adding the risk of each contaminant for a specified exposure route. The regulatory goal for excess cancer risk is 1 in a million (10^{-6}) (LaGrega, Buckingham, and Evans). Equation 6-7 is used to calculate noncarcinogenic risk (LaGrega, Buckingham, and Evans):

Equation 6-7: *Noncarcinogenic risk*

$$HI = I/RfD$$

HI = hazard index

Hazard indices cannot simply be added together to calculate cumulative hazard index. If possible, they should be summed up by an organ specific basis. A hazard index below 1.0 is deemed acceptable (LaGrega, Buckingham, and Evans).

6.1.2 Adult Lead Model

The adult lead model is used by the EPA to calculate risk for adults. This is because lead has harmful neurological effects even at low exposures. As as result, there is no established RfD for lead. EPA and the Center for Disease Control and Prevention have determined that a blood lead level of 10 micrograms per deciliter compromises children's health. The most susceptible receptor is a fetus because of lead's ability to impair neurological development (EPA G).

The adult lead methodology is recommended for long term exposure scenarios and should not be used for acute exposure. The EPA recommends exposure durations of at least 90 days and an exposure frequency of at least once per week. This model defaults to an exposure frequency of 219 days per year. For onsite, full-time workers, the exposure frequency is expected to increase. This model can evaluate dermal exposure of lead. However, it is not recommended to do so because the uncertainty of dermal adsorption for the various forms of lead. A soil ingestion rate of 50 milligrams per day for non-residential exposure involving non-contact intensive activities should be used. A soil ingestion rate of 200 milligrams per day is recommended for contact-intensive activities (EPA H).

6.1.3 IEUBK Model

The IEUBK model for lead in children is a stand-alone, computer-compatible software package. It allows the user to estimate, for a hypothetical child or population of children, a plausible distribution of blood lead concentrations centered on the geometric mean blood lead concentration predicted by the model from available information about children's exposure to lead (EPA I). From this distribution, the model calculates the probability that children's blood lead concentrations will exceed the user-selected level of concern (EPA I). The user can then explore an array of possible changes in the exposure media that would reduce the probability that blood lead concentrations would be above this level of concern (EPA I). The model should be viewed as a tool for making rapid calculations and recalculations of an extremely complex set of equation that includes scores of exposure uptake, and biokinetic parameters (EPA I).

The IEUBK model is designed to evaluate relatively stable exposure situations, rather than rapidly varying exposures. The model does not report each iterative calculation, instead it reports one-year average lead blood level concentrations (EPA I). The IEUBK model provides reasonable accuracy for blood lead concentration predictions as long as the changes in environmental lead concentrations can be approximated by annual average values (EPA I).

6.1.4 Ecological Risk Assessment

An ecological risk assessment evaluates potential environmental impacts resulting from exposure to environmental stressors (EPA J). The EPA outlines the steps of an ecological risk assessment as the following items (EPA J):

- Step 1: Planning and Scoping
- Step 2: Problem Formation (Phase I)
- Step 3: Analysis (Phase II)
- Step 4: Risk Characterization (Phase III)

6.1.4.1 Planning and Scoping

The first step of the ecological risk assessment focuses on making early judgments and outlining the purpose, scope and necessary technical approaches (EPA K). This step will assess what plants, animals and people at risk. The hazards of concern and their sources will be determined. A focus will be put on how the hazards impact the body with respect to life-stage, genetics and how it varies based on species and potential ecological impacts (EPA K). Potential exposure pathways and routes will be assessed. This step will determine how long it takes for the COC to cause a toxic effect and how the toxic effect varies by stage of life (EPA K).

6.1.4.2 Problem Formation

The focus of the second step of the ecological risk assessment determines what entity requires protection (EPA K). This entity could potentially be a species, group of species, community, ecosystem or habitat (EPA K). After the entity at risk has been chosen, the different attributes will be determined and ranked by importance to protect (EPA K). Determining ecological relevance is not always clear and may requirement professional judgement. When an assessment endpoint has been chosen a conceptual model is developed accompanied with a written description to show relationships between entities and hazards (EPA K).

6.1.4.3 Analysis

The third step involves the use of calculations to predict or determine the ecological responses to hazards under different exposure conditions (EPA K). An important part of this step is to determine the hazard quotient for each hazard of concern found. During this step different parameters will be established such as area use, food ingestion rate, bioaccumulation rates, bioavailability, and life stage (EPA K).

6.1.4.4 Risk Characterization

The final step uses the results of the analysis to determine the risk the COCs pose to the entities of importance (EPA K). This step provides a summary of results, an interpretation of results, and addresses any major assumptions and uncertainties encountered throughout the assessment (EPA K).

6.2 BLM's Risk Assessment Techniques

The BLM's approaches to human health and ecological risk assessments are largely similar to those of the EPA. However, the BLM does not use HRS in its risk assessment techniques.

7.0 Lab Analysis Techniques

7.1 Acid Digestion

Acid digestion helps determine elements in solids after sampling by transferring the analytes into solution so that they can be used in the determination step (e.g. atomic absorption and inductively coupled plasma) in liquid form. The goal of a digestion process is to create a complete solution of the analytes (Berghof).

EPA method 3050B is an acceptable approach to acid digestion (EPA L). A summary of the method is presented below:

1. For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid and hydrogen peroxide.
2. For graphite furnace atomic absorption (GFAA) or ICP mass spectrometry (ICP-MS) analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 milliliters.
3. For ICP atomic emission spectrometry (ICP-AES) or flame atomic absorption (FLAA) analyses, hydrochloric acid is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals, this digestate is filtered and the filter paper and residues are rinsed, first with hot hydrochloric acid and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional hydrochloric acid and then filtered again. The digestate is then diluted to a final volume of 100 milliliters.
4. If required, a separate sample aliquot shall be dried for a total percent solids determination.

7.2 Atomic Absorption

AAS is an analytical technique that measures the concentrations of elements. AAS is sensitive and can measure down to parts per billion in a sample (Royal Society of Chemistry). The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level (Royal Society of Chemistry).

Atoms of different elements absorb characteristic wavelengths of light (Royal Society of Chemistry). Analyzing a sample to see if it contains a particular element means using light from that element. For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the sample (Royal Society of Chemistry). In AAS, the sample is atomized and a beam of electromagnetic radiation emitted from excited lead atoms is passed through the vaporized sample (Royal Society of Chemistry). Some of the radiation is absorbed by the lead atoms in the sample. The greater number of atoms there are in the vapor, the more radiation is absorbed. The amount of light absorbed is proportional to the number of lead atoms. A calibration curve is constructed by running several samples of known lead concentration under the same conditions as the unknown.

The amount the standard absorbs is compared with the calibration curve and this enables the calculation of the lead concentration in the unknown sample (Royal Society of Chemistry).

7.3 Inductively Coupled Plasma

ICP-AES, also known as ICP, is a multi-element analysis technique that uses an inductively coupled plasma source to dissociate samples into their constituent atoms or ions, exciting them to a level where they emit light of a characteristic wavelength (Thermo Elemental). ICP-MS is different from ICP because the atoms of the cell are actually detected (Thermal Elemental). ICP-MS offers some of the best detection limits around because of the number of ions it produces (Thermal Elemental).

7.4 Statistical Analyses

Statistical analyses are conducted to determine if the results of a study are reliable. Statistical analyses begin by computing the average using Equation 7-1 (Artiola, Brusseau, and Pepper):

Equation 7-1: *Average*

$$\bar{x} = \frac{\sum x_i}{n}$$

$\bar{x}$ is the average
n is the sample size

The standard deviation can be calculated from the average by using Equation 7-2 (Artiola, Brusseau, and Pepper):

Equation 7-2: *Standard deviation*

$$\sigma = \sqrt{\frac{\sum(\bar{x} - x_i)^2}{n - 1}}$$

σ is the standard deviation

Confidence intervals are used to identify the likelihood that a sample mean will be close to the true mean. Typically, confidence intervals use a z-score of 1.96 for 95% confidence. Confidence intervals are calculated using Equation 7-3 (Artiola, Brusseau, and Pepper):

Equation 7-3: *Confidence intervals*

$$\bar{x} \pm \frac{z * \sigma}{\sqrt{n}}$$

Addition yields the upper confidence interval
Subtraction yields the lower interval

The required sample size can be determined for a given confidence level *(1 – α)100%* and a tolerance *d* using Equation 7-4 (Artiola, Brusseau, and Pepper):

Equation 7-4: *Sample size*

$$n = \left(\frac{z\alpha/_2 * \sigma}{d}\right)^2$$

A linear regression can be conducted to understand the correlation between measured values. Equation 7-5 is the linear regression equation (Artiola, Brusseau, and Pepper):

Equation 7-5: *Linear regression*

$$y = a + bx$$

a is the y-intercept
b is the slope of the function

Sample data is plotted on a graph and fitted to the linear regression equation in order to obtain the coefficient of correlation r^2. The coefficient of correlation is used to measure the relation between data points, where r^2 values close to 1 have a strong relation. At times, the data will necessitate a polynomial regression (Artiola, Brusseau, and Pepper).

8.0 References

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