GREDELL
ENGINEERING RESOURCES

Sikeston Power Station
Fly Ash Pond
Assessment of Corrective Measures

* * *

Prepared for:

Board of Municipal Utilities

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ACRONYMS AND ABBREVIATIONS

ACM – Assessment of Corrective Measures
ANE – ANE Engineering
ASD – Alternative Source Demonstration
BAP – Bottom Ash Pond
CBR – Closure by Relocation
CCR – Coal Combustion Residual
CIP – Closure in Place
COC – Constituent of Concern
CSM – Conceptual Site Modeling
CTP – Cooling Tower Process Well Pumping
FAP – Fly Ash Pond
GITR – Groundwater Interception, Treatment, and Reinjection
GER- GREDELL Engineering Resources, Inc.
GWPS – Groundwater Protection Standards
HELP - Hydraulic Evaluation of Landfill Performance
Loureiro - Loureiro Engineering Associates, Inc.
MDNR-WPP - Missouri Department of Natural Resources – Water Protection Program
MNA – Monitored Natural Attenuation
NOAA – National Oceanic and Atmospheric Association
NPDES – National Pollution Discharge Elimination System
RCRA - Resource Conservation and Recovery Act
RDD#4 – Richland Drainage Ditch #4
SBMU – Sikeston Board of Municipal Utilities
SPS – Sikeston Power Station
SSI – Statistically Significant Increase
SSL – Statistically Significant Levels
United States Environmental Protection Agency - USEPA
United States Geological Survey – USGS

UNITS

µg/L - Micrograms per liter
cm/s - centimeters per second
GPM – Gallons per Minute

EXECUTIVE SUMMARY

This Assessment of Corrective Measures (ACM) prepared by GREDELL Engineering Resources, Inc. (GER) was completed in accordance with requirements stated in the United States Environmental Protection Agency (USEPA) rule entitled *Hazardous and Solid Waste Management System; Disposal of Coal Combustion Residuals from Electric Utilities.* 80 Federal Register 21302 (April 17, 2015) (promulgating 40 CFR 257); 83 Federal Register 36435 (July 30, 2018) (amending 40 CFR 257) (CCR Rule). The ACM documents the evaluations performed to assess and select corrective measures to remediate groundwater contamination associated with releases from the fly ash pond (FAP) at the Sikeston Power Station (SPS) (the Site). SPS, owned and operated by the Sikeston Board of Municipal Utilities (SBMU), is an electric power producer and distributor located within the western city limits of Sikeston, in southern Scott County, Missouri (Figure 1). SBMU has operated the SPS since its construction in the 1970s. In addition to the power station, the Site has the FAP, a bottom ash pond (BAP), process waste pond, settling pond, and a coal storage area. SPS also has eight high-capacity wells (five active and three inactive) designed and installed to provide water for the purpose of power production and related activities at the SPS. Each active well can produce over 1,000 gallons per minute (GPM), but typically a well will pump approximately 600 GPM when in use.

A statistically significant increase in some of the constituents listed in Appendix III of the CCR Rule (Appendix III constituents) was noted during prescribed groundwater monitoring. It was subsequently determined that groundwater potentially impacted by the impounded fly ash exceeds the Groundwater Protection Standard (GWPS) for molybdenum and cobalt at three monitoring locations within the site.

The region has numerous drainage ditches constructed in the early 1900s to collect surface water. Groundwater in the region now flows to the nearest drainage ditch, before draining south as surface water. This drainage system resulted in draining the surface water and lowering the modern-day water table to generally 10 to 20 feet below the ground surface. Locally, groundwater flows to the drainage ditch identified as Richland Drainage Ditch #4 (RDD#4) and to the nearest SPS high-capacity well when operational.

A risk assessment concluded that there are no adverse effects on human health or the environment currently or under reasonably anticipated future uses from either surface water or groundwater due to the coal combustion residual (CCR) management practices at the SPS.

The CCR Rule has a set of criteria that must be followed for all corrective measures considered. Each set of these criteria has a minimum standard, with respect to evaluation of the remedy and ranking. A summation of the potential remedies, their ranking, and the factors considered as listed in 40 CFR 257.97(d) are presented. The overarching objectives of this corrective measure alternatives evaluation are:

- Identify and evaluate the suitability of potential corrective measures intended to prevent release of constituents listed in Appendix IV of the CCR rule (Appendix IV constituents) above their GWPS.
- Remediate releases of Appendix IV constituents exceeding their GWPS, and
- Restore groundwater in the affected area to conditions that do not exceed GWPS for those constituents.

The corrective measures presented explore three options for Closure In Place (CIP) and Closure By Relocation of CCR (CBR). Both CIP and CBR are permissible under 40 CFR 257 (the CCR Rule). The four alternatives are listed below:

- **Alternative #1:** CIP with Monitored Natural Attenuation (MNA).
- **Alternative #2**: CIP with Use of Existing SPS Cooling Tower Process Well Pumping (CTP) and MNA.
- **Alternative #3:** CIP with Groundwater Interception, Treatment, and Reinjection (GITR), and MNA.
- **Alternative #4:** CBR and MNA.

The information presented in this document along with community input provided during the public comment period, will be utilized to select the corrective measure to be implemented at SPS.

1.0 INTRODUCTION

The Sikeston Power Station (SPS), owned and operated by the Sikeston Board of Municipal Utilities (SBMU), is an electric power producer and distributor located within the western city limits of Sikeston, in southern Scott County, Missouri (Figure 1). SBMU has operated the SPS since its construction in the 1970s.

This Assessment of Corrective Measures (ACM) was completed by GREDELL Engineering Resources, Inc. (GER) to address the fly ash pond (FAP) area at the Sikeston Power Station (SPS) (the Site). This ACM was completed in accordance with requirements stated in the United States Environmental Protection Agency (USEPA) rule entitled *Hazardous and Solid Waste Management System; Disposal of Coal Combustion Residuals from Electric Utilities.* 80 Federal Register 21302 (April 17, 2015) (promulgating 40 CFR 257); 83 Federal Register 36435 (July 30, 2018) (amending 40 CFR 257) (CCR Rule). The assessment includes a summary of groundwater monitoring results and hydrogeologic site investigations at the SPS which operates under Missouri State Operating Permit MO-0095575. The permit specifies National Pollution Discharge Elimination System (NPDES) compliance requirements to include groundwater monitoring.

SBMU has conducted detailed geologic and hydrogeologic investigations to fulfill requirements of the Missouri Department of Natural Resources – Water Protection Program (MDNR-WPP) as well as the CCR Rule.

As described in this report, a statistically significant increase in some of the constituents listed in Appendix III of the CCR Rule (Appendix III constituents) was noted during the prescribed groundwater monitoring events. It was subsequently determined that groundwater potentially impacted by the impounded fly ash exceeds Groundwater Protection Standards (GWPS) for cobalt and molybdenum at three monitoring locations. The USEPA has not developed drinking water standards for either of these constituents. However, the Missouri Clean Water Commission has published a criterion for cobalt in groundwater (1,000 µg/L), but they do not provide published criterion for molybdenum. This report also discusses the proposed potential corrective measures for addressing the constituents of concern (COCs) from the FAP in groundwater.

1.1 Facility Description and Background

The design of the SPS included the construction of two facilities to store waste residuals produced during the combustion of coal (Figure 1). These by-products, fly ash, bottom ash, and scrubber sludge, were placed in designed surface impoundments called ash ponds, which are located east of the power plant and are on property owned and controlled by SBMU. The northern pond (FAP) was primarily used for fly ash disposal. It measures approximately 30 acres in size and borders the north edge of the bottom ash pond (BAP), which measures approximately 61 acres.

Notification of initiation of the FAP closure was issued to the MDNR Director on May 6, 2021 in accordance with 40 CFR 257.106. Notification was also posted in the SPS' on-site operating record in accordance with 40 CFR 257.105 and on SPS' publicly accessible internet site in accordance with 40 CFR 257.107. Initial baseline monitoring and sampling for the FAP groundwater monitoring system began in early 2018 subject to the alternate compliance schedule specified by the USEPA under 40 CFR Part 257.100(e)(5)(ii) due to its initial inactive status and the Response to Partial Vacatur (the Direct Final Rule).

Sikeston, Missouri is located in Scott County in southeastern Missouri, near the intersection of Interstate Highways 55 and 57. The SPS is located approximately one mile west of downtown Sikeston, south of West Wakefield Avenue and east of Route BB (Figure 1). Areas to the south, west, and north of the SPS are generally agricultural, while areas to the northeast, east, and southeast are mostly residential. The Sikeston area is within the Southeastern Lowland Province of Missouri (Figures 2, and 3), a vast alluvial plain representing the northernmost point of the Mississippi River Embayment. The modern course of the Mississippi River is located approximately 16 miles northeast of the site, but man-made drainage ditches convey surface water to the south with a natural gradient of about 1 foot per mile. Some drainage ditches located within the domain (limits) of the groundwater model constructed for this site, are indicated as blue lines on Figure 3.

Prior to the construction of the SPS in the late 1970s, the site was largely undeveloped. The predominant historical land use was agricultural. As summarized in previous reports, mines and karst features such as caves, springs, or sinkholes do not exist near the Site, which is underlain by several hundred feet of Holocene age sand and gravel deposits.

1.2 Hydrogeological Characterization Work Summary

GER reviewed available hydrogeologic data provided by the SPS, which includes information on the facility's high-capacity pumping wells, well drilling and installation data, testing and maintenance reports, and reports by other consultants. Publicly available literature from the scientific community was also examined. These data are presented in the report entitled Sikeston Power Station Site Characterization for Compliance with Missouri State Operating Permit #MO-0095575 and dated May 2017 (GER, 2017). Additional historical literature was reviewed to better understand the modern hydrogeology of the region and the impact that the network of man-made drainageways has made on groundwater movement in this area.

The 2017 Site Characterization Report is a comprehensive hydrogeologic evaluation of the uppermost aquifer below and down gradient of the ash ponds at the SPS. The Site Characterization investigation was conducted in accordance with a work plan approved by MDNR-WPP. Field investigation activities included:

- Drilling
- Geologic sampling and characterization
- Piezometer construction and water level monitoring
- Slug testing to assess aquifer properties
- Automated water level monitoring

Extensive data reduction was done to characterize the hydrogeology of the Site for the purposes of designing a comprehensive monitoring system that would eventually serve as a component of the monitoring systems established for state and federal environmental compliance.

In addition, a comprehensive nature and extent characterization and hydrogeologic evaluation (GER, 2023b) assessed the extent of the release from the FAP in three dimensions. Field activities mirrored those of the 2017 site characterization with the inclusion of additional surface water sampling.

1.3 Groundwater Monitoring

The CCR Rule requires groundwater monitoring with a system or systems consisting of monitoring wells in appropriate locations and depths to provide groundwater samples from the uppermost aquifer that accurately represent the quality of background groundwater and the quality of groundwater passing beneath the waste boundary of the CCR unit. These groundwater monitoring systems are routinely monitored and sampled to provide an understanding of baseline water quality, results of the detection monitoring program, and results of the assessment monitoring program as discussed below.

A summary of the construction of the wells comprising these groundwater monitoring systems for CCR Rule compliance and the NPDES/Missouri State Operating Permit compliance, is presented in Table 1. Groundwater elevations have been routinely documented in each well since installation. Historical water level measurements are summarized in Table 2. Groundwater elevation maps constructed using these data demonstrate that groundwater flows west-southwest from the FAP area toward the Richland Drainage Ditch #4 (RDD#4).

All groundwater monitoring system well design, construction, and installation techniques were completed in accordance with the Code of State Regulations (10 CSR 23-4), which is consistent with the standards summarized in 40 CFR 257.91(e).

As required by 40 CFR 257.94, a minimum of eight independent (baseline) samples from each well must be collected and analyzed for the constituents listed in Appendix III and IV (constituents for detection and assessment monitoring) of the CCR Rule. These baseline data are then subjected to exploratory data analysis to gauge the variance and validity of the data. Data are then used to calculate statistical prediction limits at levels (or ranges) that serve as an indicator of a significant change for each monitored constituent in each well, if present. If one or more for these prediction limits are exceeded during detection monitoring it represents a statistically significant increase (SSI) or change in the monitored constituent. SPS staff completed all baseline and compliance sampling in accordance with the CCR Rule and the site-specific groundwater monitoring and sampling plan (GER, 2018; 2021a).

The groundwater monitoring system for the FAP consists of six wells following the addition of MW-10 in early 2023. The historical monitoring wells are identified as MW-1R, MW-2, MW-3, MW-7, and MW-9. Well locations are depicted on Figure 1. MW-2 and MW-3 are located hydraulically upgradient of the FAP, whereas MW-1R, MW-7, MW-9, and MW-10 are located hydraulically down gradient of the FAP.

As documented in the annual FAP groundwater monitoring reports for SPS available at sikestonpower.com, monitoring well MW-1 was replaced by MW-1R in 2021, and monitoring well MW-10 was added to the monitoring system during the nature and extent characterization in 2023. The baseline monitoring and sampling for wells added to the monitoring system after the initial baseline monitoring was generally conducted within six months of well installation per 40 CFR 257.94(b).

Detection monitoring of the FAP groundwater monitoring system commenced in March 2019 under the alternate compliance schedule referenced in Section 1.1. In November 2022, SPS began conducting assessment monitoring of the FAP concurrently with detection monitoring because of SSIs relevant to boron (an Appendix III monitoring constituent) at MW-7, and pH changes at MW-1R and MW-3. The first compliance sample for MW-10, was collected in December 2023 for both detection and assessment monitoring purposes.

In April 2023, statistical analysis confirmed statistically significant levels (SSL) of Appendix IV constituents greater than the GWPS established for the FAP as specified in 40 CFR 257.95(h). As a result, the SPS is considering the most appropriate corrective action (Section 4.4) to address future releases, remediate the current release, and restore affected groundwater to a pre-release condition.

Additional groundwater evaluations have been conducted in accordance with 40 CFR 257.94(e)(2) as Alternative Source Demonstrations (ASDs) at the FAP. If warranted, ASDs allow an owner or operator to demonstrate that a source other than the CCR unit caused an apparent SSI. These ASDs are attached to the annual groundwater monitoring reports documenting the sampling event results that were affected by the alternate source (typically a naturally occurring constituent known to be present in wells upgradient of the SPS, or an error in sampling or analysis). These reports are available at sikestonpower.com.

1.4 Corrective Measures Assessment Process

The CCR Rule is prescriptive regarding the process for assessing corrective measures. The rule provides minimum requirements, set forth in 40 CFR 257.97(b), that any corrective measure must meet in order to be considered for implementation. Following demonstration that the minimum requirements have been or can be met, the CCR Rule provides three Evaluation Criteria Categories, each with sub-criteria to consider while ranking the suitability/favorability of each proposed corrective measure.

A summation of the rank from the criteria and sub-criteria is then used to select the most favorable corrective measure. Following the comparison of each corrective measure based on Evaluation Criteria Categories 1 through 3 and their associated sub-criteria, the final Evaluation Criteria will be assessed at a public meeting held for the purpose of hearing public concerns and evaluating the degree to which community concerns are addressed by a potential remedy(ies). A schedule for implementing and completing the selected corrective measure will be completed taking into consideration the factors listed in 40 CFR 257.97(d).

2.0 LOCAL AND REGIONAL CONCEPTUAL SITE GROUNDWATER MODEL

Prior to the early 1900s, most of southeast Missouri was inundated by surface water and was referred to as “The Big Swamp”. This swamp was the result of a very shallow topographic slope to the south of approximately one foot per mile and the inability of this flat topography to efficiently drain excess surface water.

Beginning in 1913, RDD#4, along with nearly 100 other drainage ditches were constructed from approximately Cape Girardeau, located approximately 20 miles north of the Site, southward toward the Mississippi River (Figures 3, 4A, & 4B). Known as the Little River Drainage District, the goal was to lower water levels in southeastern Missouri. By design, these ditches were spaced to effectively drain the region by creating numerous, roughly north-south aligned groundwater sinks (aquifer discharge areas), which resulted in a system of human-made groundwater divides paralleling these sinks. Groundwater in the region now flows to the nearest ditch, before draining south as surface water (Figure 4A and 4B). This modern system of drainage ditches that interact with groundwater flow has been in existence much longer than the SPS, and therefore is the basis for the conceptual hydrogeologic model for the entirety of the plant operation and into the future, both regionally and at the SPS. Locally, groundwater flows to RDD#4 and to the nearest SPS high-capacity well, when operational.

Initially, 85 drainage ditches (Ditch No. 1 to 85) were completed by 1920. In 1921, a western extension began by constructing Ditches No. 101 to 113. This network of drainages would eventually convey surface water out of the broad valley to the south along a very flat, one-foot per mile topographic gradient. The system’s 1,000 miles of ditches convey the surface water into Arkansas, where it flows into that state’s drainage system and eventually enters the Mississippi River at Helena, Arkansas. The result of this human-made drainage system is that approximately 2-million acres of drained land surface is now used for human development.

This drainage system resulted in draining the surface water and lowering the modern-day water table to generally 10 to 20 feet below ground. In the area of the SPS, groundwater flow is generally toward RDD#4 or to one of SPS’ nearby high-capacity pumping wells. These wells were designed and installed to provide water at high rates for the purpose of power production and related activities at the SPS (Figure 4B). Each well can produce over 1,000 gallons per minute (GPM), but typically a well will pump approximately 600 to 700 GPM when in use.

Hydrogeologic studies suggest that irrigation wells in the area have a small radius of influence, meaning the permeability of the sand and gravel is sufficient to reduce the effects (draw down) of pumping several hundred GPM to a relatively small area. Many irrigation wells within a few miles of the SPS have reported capacities over 1,000 GPM, but they typically do not operate continuously throughout the year. Therefore, overall the volume of groundwater that is discharging to one of the many drainage ditches is likely higher than that extracted via pumping.

2.1 Topography

Much of the modern-day surface expression at the SPS is a result of construction activities associated with the station and ancillary structures. The apparent, undisturbed topography surrounding the Site is relatively flat with elevations ranging between 300 and 308 feet mean sea level. However, a north-northwest trending upland termed the Sikeston Ridge that rises about 20 feet above local topography exists approximately one quarter mile east of the FAP.

2.2 Geology and Hydrogeology

As discussed in literature (e.g., Miller, 1993), the Southeastern Lowland Province or “Bootheel” region of Missouri (Figure 2) is a broad alluvial plain with low topographic relief. This is a result of the geologic history and how the geologic materials were emplaced and represents the northernmost point of the Mississippi River Embayment.

Figure 5 is a generalized geologic cross-section (Miller, 1993) showing the relationship between major stratigraphic units present within the Southeastern Lowland Province, including the Sikeston area. This figure indicates that older, Paleozoic bedrock formations, which underlie much of the remainder of the Missouri River alluvial Valley lie as much as 600 to 800 feet below ground surface in the Sikeston area. These Paleozoic strata are unconformably overlain by unconsolidated, Cretaceous age strata termed, in ascending order, the McNairy and Owl Creek Formations. The McNairy Formation, sometimes referred to as the “Ripley Sand” (Miller and Vandike, 1997), largely consists of sand, sandy clay, and clay and is distributed throughout the subsurface of the “Bootheel”. Northward, the formation crops out in the hilly terrain of Crowley’s Ridge and Benton Hills. Southward, however, the formation dips rapidly and lies an estimated 400 to 600 feet below ground surface in the vicinity of Sikeston. According to Miller (1993), the McNairy Formation is used almost exclusively for municipal supply wells in the “Bootheel”, where it sometimes produces water under artesian conditions. The overlying Owl Creek Formation largely consists of clay and sandy clay and attains a maximum thickness of 100 feet. Miller (1993) indicates that this formation and overlying, basal Tertiary strata constitute an aquitard to the underlying McNairy Formation.

Basal Tertiary strata consist of the Clayton Formation and overlying Porters Creek Formation. Both are assigned to the Midway Group of the Paleocene Series. The Clayton Formation unconformably overlies the Owl Creek Formation (Koenig, 1961). It is relatively thin (30 feet), but the formation is persistent throughout the “Bootheel” region. It is readily recognized in the subsurface by its glauconitic sand and calcareous limestone lithology, which impart a distinctive greenish hue to the unit. The overlying Porters Creek Formation is a thick, relatively homogenous unit consisting almost exclusively of dark gray to black clay. The formation is up to 650 feet thick and, based on local drilling records, lies at least 226 feet below ground surface in the vicinity of the SPS. These two formations, together with the underlying Owl Creek, are considered a regional aquitard, or confining unit, in the Southeastern Lowland Province (Miller, 1993).

The overlying Wilcox Group constitutes what is generally considered the “uppermost rock” unit in the “Bootheel” region. Strata comprising the Wilcox Group are Middle Tertiary (Eocene) in age and unconformably overlie Porters Creek Formation clays. Unlike the Porters Creek Formation, the Wilcox consists of a complex sequence of sands with some clay and thin beds of lignite and is a prominent aquifer used for municipal water supplies in the region (Miller and Vandike, 1997). From its outcrop area along Crowley’s Ridge, Wilcox Group strata thicken markedly southward to approximately 1,400 feet in extreme southeastern Missouri (Figure 5). Local drilling records obtained from the Missouri Department of Natural Resources (MDNR-Water Resources Center, 2024) and records provided by SBMU report the upper part of the formation at a depth of between 174 and 192 feet below ground surface.

Wilcox Group strata are overlain by an extensive deposit of recent (Holocene) alluvial sediment marking the youngest geological unit in the “Bootheel” region. Most, if not all, of these sediments are derived from the development of the Mississippi-Ohio River system (Luckey, 1985). They consist of a complex sequence of gravel, sand, silt, and clay and reflect a predominantly fluvial depositional setting. This alluvium has a cumulative thickness of between 100 and 200 feet in the vicinity of the Site, dependent on where the upper limit of the underlying Wilcox Group is placed. According to Miller and Vandike (1997), the alluvial deposits form an important hydrologic unit and are the most utilized aquifer in the region.

As discussed in Section 2.0, before completion of the drainage system in the “Bootheel”, groundwater movement within the unconfined alluvial aquifer was generally to the south and southwest. This drainage network successfully lowered surface and groundwater levels, which altered local flow directions in that groundwater now exits the alluvial plain by flowing toward a drain where it then flows south as surface water.

The conceptual hydrogeologic model for the FAP at the Site is schematically illustrated on Figures 4A & 4B. The water bearing units or aquifers underlying the Site are interconnected accretions of sand and gravel overlying a thick clay (Porters Creek Clay) that prevents vertical movement of water. Regionally, the Porters Creek Clay slopes toward the center of the valley flow line and along the valley flow line to the south. Two primary sources of recharge to the aquifer(s) within the model domain (Figure 3) are precipitation and percolation water from the FAP. Precipitation pools as surface water that either exits the pond through NPDES Outfall #003 (Figure 1) to RDD#4 or through percolation. Groundwater flow direction is dependent on proximity to a drainage ditch or a pumping well. These high-capacity wells have demonstrated a radius of influence of a few hundred feet under normal operation, but when Well “H” was tested at about three times the normal pumping rate (Brotcke, 2009) the radius of influence is measurable at 1,300 feet.

Surface water in the FAP seeps vertically (downward) under the influence of gravity to the water table. Groundwater upgradient of the Site flows under the base of the FAP, which was constructed above the water table and is separated from the aquifer by an unsaturated or vadose zone. Seepage from the FAP must flow through the unsaturated (vadose) zone before it enters the alluvial aquifer. Seepage eventually comingles with groundwater beneath the FAP and then flows laterally toward RDD#4 or a pumping well.

SPS’s high-capacity wells have been shown to produce drawdown within their radius of influence (Brotcke, 2009; GER, 2017). While most of these wells are considerably removed from the ash pond area, Well “C” is located approximately 200 feet west of the BAP and about 1,500 feet southwest of the FAP. Because of its proximity, a pumping test was conducted during site characterization (GER, 2017) to assess the radius of influence of Well “C.” Observation well MW-4, located approximately 300 feet away, experienced less than 1 foot of drawdown when pumping at a rate considerably higher (1,500 GPM) the typical rate for plant operation (approximately 600 GPM). This minimal drawdown suggests that Well “C” has a limited radius of influence under normal operating conditions.

Since groundwater monitoring began at the SPS in 2018, groundwater movement has consistently been from east to west-southwest with a gradient ranging from about or 2×10^{-4} to 1×10^{-3} feet per foot (ft/ft). The upper range of this gradient and predominantly westerly component of flow direction is primarily the result of RDD#4. This drainage ditch is incised below the top of the water table for most of the year. Only during periods of extreme drought conditions does the top of the water table decrease below the flowline of the ditch, but potentiometric maps still indicate westward flow from the ash ponds to monitoring points installed near RDD#4 (NE-1, NE-2, and NE-3).

2.3 Groundwater Protection Standards

In accordance with 40 CFR 257.95(d)(2), GWPS were established as specified in 40 CFR 257.95(h) for all detected 40 CFR 257 Appendix IV constituents. Table 3 summarizes the GWPS for the FAP. Additional data summaries for the FAP groundwater sampling for 40 CFR 257 are included as Appendix A.

2.4 Nature and Extent of Groundwater Impact

GER conducted a Nature and Extent Characterization (GER, 2023b) per the CCR Rule 257.95(g)(1) to determine the nature and extent of cobalt and molybdenum in the groundwater based on statistical evaluations likely due to a release from the FAP.

Additional groundwater sampling was conducted during the 2023 characterization discussed in Section 1.2. This characterization assessed shallow and deep groundwater and surface water quality. Three shallow piezometers were installed (NE-1 through NE-3, Figure 1) and sampled for the characterization. Deep groundwater quality was assessed with samples taken from high-capacity Wells “A”, “B”, “C” and “D”. Vertical profiling was conducted in high-capacity Well “B” to determine the vertical extent of constituent concentrations greater than GWPS during the initial sampling of Well “B”. Additional deep aquifer sampling and profiling was conducted with discrete groundwater samples collected at about 150 feet at DP-1 and DP-2, and at depths of about 75 and 150 feet at DP-3 (Figure 1) to assess limits of COC migration and potential vertical migration pathway near the FAP. Surface water chemistry was assessed with samples of surface water from RDD#4 at three locations (SG-N, SG-OF-50, and SG-S; see Figure 1).

Precipitation was monitored at the Site (NOAA, 2024) daily and water levels were measured regularly in the wells and surface water to assess the relationship between precipitation and interaction between the aquifer and RDD#4. The measurements were used to refine the characterization of groundwater flow dynamics/variability and other components of the conceptual site model (CSM) and to test calibration of a 3D groundwater flow and transport model used to assess potential corrective measures. Groundwater and surface water sampling as well as water level readings were also performed to characterize the transient/variable influence of RDD#4 on the groundwater movement and discharge, and to assess if discharge to the ditch has resulted in surface water impact.

The characterization involved multiple activities to assess the extent of cobalt and molybdenum in the shallower part of the aquifer, as detected by the FAP groundwater monitoring system. Sampling was also conducted to assess deeper groundwater in four high-capacity wells (Wells “A”, “B”, “C” and “D”). Note Wells “A”, “B”, and “D” had pumps removed and are no longer used for water production. The data was reduced and examined to delineate the extent of cobalt and molybdenum in the groundwater.

Molybdenum concentrations at one location (Well “B”) exceeded the GWPS of 100 ug/L. Therefore, aquifer profiling was conducted in this well by sampling at three intervals within the 40-foot screened interval (intake) of Well “B”. These data demonstrate that molybdenum concentrations above the GWPS are limited to the two shallower samples from 133 feet and 150 feet. Molybdenum above the GWPS was not demonstrated in the deeper (167 feet) sample. A second drilling and sampling effort was conducted to estimate the horizontal extent of molybdenum concentrations at deeper depths in the aquifer near the SPS property limits and to assess the vertical extent of molybdenum near the FAP.

While arsenic was detected in some of the deeper samples, the paucity of detections (at very low levels) and numerous reports of arsenic not detected in (shallow) samples from the FAP groundwater monitoring system (Appendix A) indicate that the arsenic detected in the deep aquifer is naturally occurring (GER, 2023b; USGS NGS, 2024; & MDNR, 2024b) and unrelated to the FAP.

The Nature and Extent Characterization led to the following conclusions about cobalt, boron, molybdenum, and arsenic concentrations in surface water and groundwater at the SPS:

- Cobalt was not detected above reporting limits in surface water and groundwater samples collected down gradient of the FAP's monitoring well system (Table 4).
- Boron concentrations in surface water and groundwater at all sampled locations are below USEPA Regional Screening Levels (4,000 ug/L). The absence of boron concentrations above USEPA Screening Levels indicates plume migration is limited.
- Boron concentrations in water from MW-1R, MW-7, and MW-9 show concentrations above MDNR Screening Levels (2,000 micrograms per liter [µg/L]), but generally below USEPA Screening Levels (4,000 ug/L).
- Molybdenum is reported in shallow groundwater at down gradient monitoring well locations MW-1R, MW-7, and MW-9 at concentrations greater than the GWPS of 100 ug/L. However, molybdenum concentrations reported in surface water samples and in all other shallow groundwater monitoring locations are considerably (4x) lower than the GWPS, indicating contaminant migration is limited.
- Molybdenum is reported in two of the three deeper groundwater samples collected from Well "B" at concentrations above the GWPS. However, vertical aquifer profiling of the screened interval of Well "B" indicates that only the upper half of the screened interval (133 to 150 feet below ground) exceeded the GWPS standard. Molybdenum concentrations were less than the GWPS in the deeper sample collected at a depth of 167 feet below ground in this well.
- Sampling results for groundwater collected from temporary piezometers (DP-1, and DP-2) down gradient of Well "B" do not indicate molybdenum concentrations above GWPS limits.
- Groundwater samples collected at DP-3 from depths of 74 feet and 144 feet below ground do not contain concentrations of molybdenum above the GWPS. This indicates limited vertical (downward) migration of molybdenum from the area adjacent to the FAP. These observations support the conclusion that elevated molybdenum concentrations in deeper samples at Well "B" are the result of drawdown and comingling of shallower groundwater due to the effects of historical long-term pumping in this high-capacity well.
- Arsenic is either below detection limits or only present at low concentrations in surface water (2.4 µg/L or less) and shallow groundwater (2.2 µg/L or less) at the FAP. Generally, arsenic at deeper depths also remains below GWPS limits except for samples collected in Well "B". These results suggest the source of arsenic is naturally occurring and unrelated to a release from the FAP.

3.0 RISK ASSESSMENT AND EXPOSURE EVALUATION

SBMU has conducted detailed environmental evaluations of the SPS and its surroundings. These evaluations are detailed in the Human Health and Ecological Risk Evaluation for the FAP (Appendix B). The purpose of the risk evaluation is to identify whether current groundwater conditions pose a risk to human health or the environment and, if so, whether the corrective measures identified in this report mitigate such risk.

This Human Health and Ecological Risk Evaluation (Appendix B) describes and explains the CSM, constituents of concern, potential exposure pathways, and a summary of findings. As explained in the report, the COC (cobalt, molybdenum, and possibly boron) concentrations from the SPS are not associated with a potential for adverse impact to human health or ecological receptors (plants and animals) in nature.

3.1 Alluvial Aquifer – Irrigation and Drinking Water

Groundwater sampling results from the CCR FAP monitoring wells shown on Figure 1 are summarized in Table 4. These data demonstrate that only the down gradient wells adjacent to the FAP exceed the GWPS for cobalt and/or molybdenum in the shallow groundwater.

Sample results for NE-3, MW-4, MW-5, MW-8 and MW-10 were used to evaluate irrigation exposure scenarios. None of these sample results exceeded their respective and appropriate criteria for Irrigation and Livestock Watering, and Wildlife Protection (10 CSR 20-7) for boron, cobalt, molybdenum, or any of the other CCR groundwater monitoring constituents.

Sample results for Well “A” (150 feet), Well “B” (167 feet), Well “D” (130 feet), DP-1-150, and DP-2-150 were used to evaluate potable use exposure scenarios. None of these data exceeded their respective criteria for potable use provided by USEPA Regional Screening Levels for Tap Water for boron, cobalt, molybdenum, or any of the other CCR groundwater monitoring constituents.

3.2 Surface Water – Aquatic Ecology

RDD#4 sampling results (Table 4) do not indicate impact of CCR Rule Appendix III and IV constituents. Sample results for NE-1, NE-2, NE-3, MW-4, MW-5, and MW-8 were used to evaluate aquatic ecological receptor exposure scenarios. None of these data exceeded the Chronic Freshwater Screening Values provided by USEPA for boron, cobalt, molybdenum, or any of the other CCR groundwater monitoring constituents.

3.3 Risk Assessment Results

In summary, there are no adverse impacts on human health or the environment from either surface water or groundwater uses resulting from coal ash management practices at the FAP. There are no users of groundwater near the FAP. While the purpose of this report is to evaluate remedies to address the SSLs of cobalt and molybdenum detected near the FAP boundary, the current conditions at the FAP, even prior to closure, do not pose an unacceptable risk to human health or the environment. This risk-based evaluation provides additional support for the selection of a corrective measure for this site.

3.4 Trace COCs in Coal Ash

Coal ash is comprised of inorganic minerals and elements that are naturally present in the environment. Cobalt and molybdenum are trace elements, because they are present in soils, rocks, coal, and coal ash at very low concentrations (measured in milligrams per kilogram, or parts per million). Cobalt, molybdenum, and other trace elements collectively make up less than one percent of the earth's soils and rocks.

Every monitored constituent in coal ash occurs naturally in our environment. United States Geological Survey National Geochemical Survey (2023) data demonstrate the prevalence of these constituents across our country. Because these natural elements are in the soils in our yards, and communities, they are also present in our food. Some are recommended for daily consumption as vitamins and minerals. Cobalt is needed to make vitamin B12 and aids carbohydrate metabolism in our bodies. Molybdenum is an essential trace mineral in foods and supplements and is a component of four different enzymes that the body uses to break down proteins, alcohol, and toxins. Fact sheets for cobalt and molybdenum have been prepared and are provided in Appendices D and E.

4.0 CORRECTIVE MEASURE ALTERNATIVES

The CCR Rule has a set of criteria that must be followed for all corrective measures considered. Each set of these criteria has a minimum standard, with respect to evaluation of the remedy and ranking. A summation of the potential remedies, their ranking, and the factors considered as listed in 40 CFR 257.97(d) can be found in Section 5.0.

4.1 Objectives

The overarching objectives of this assessment of corrective measures are:

- Identify and evaluate the suitability of potential corrective measures intended to prevent release of Appendix IV constituents above their GWPS.
- Remediate releases of Appendix IV constituents exceeding their GWPS, and
- Restore groundwater in the affected area to conditions that do not exceed GWPS for those constituents.

The following subsections discuss the corrective measures evaluations and provide analysis of the effectiveness/suitability/appropriateness of four potential corrective measures for the FAP. The requirements and objectives of remedies described in 40 CFR 257.97 provide the basis for the evaluations. Additionally, this assessment will also evaluate the following Evaluation Criteria Categories as required in 40 CFR 257.96(c):

- The performance, reliability, ease of implementation, and potential impacts of appropriate potential remedies, including safety impacts, cross-media impacts, and control of exposure to any residual contamination;
- The time required to begin and complete the remedy; and
- The institutional requirements, such as state or local permit requirements or other environmental or public health requirements, that may substantially affect implementation of the remedy(ies).

These Evaluation Criteria Categories are included as part of 40 CFR 257 and described in Section 1.4 of this report.

4.2 Groundwater Flow and Geochemical Modeling

Numerical groundwater flow and transport models are tools utilized to estimate flow and transport of COCs in groundwater at the FAP. Groundwater flow and geochemical modeling utilizing MODFLOW 2000 and MT3DMS was performed to evaluate groundwater flow and geochemical transport at the FAP. MT3DMS is the numerical chemical transport software used to predict solute movement conservatively assuming that hydrodynamic dispersion is the only process that attenuates the chemicals modeled, meaning that no retardation or chemical reactions are assumed to slow migration or remove dissolved mass.

4.3 Groundwater Treatment Evaluation

Dissolved metals concentrations in groundwater can be reduced through stabilization of the metals through precipitation of a metal compound, co-precipitation of the target metal within the surface structure of another compound and/or sorption of the target metal on to other compounds in the subsurface. This may be accomplished with amendments to groundwater in the aquifer to expedite chemical reaction that attenuates metals through precipitation or sorption.

Chemical precipitation is a treatment technology that is known, available, has been demonstrated to be effective, and is recognized by USEPA and in use to remediate releases from ash ponds elsewhere in Missouri. Localized groundwater geochemistry can have profound impact on metals mobility, in that some metal compounds may be more soluble under highly oxidative conditions while others are more soluble in reducing conditions. Metals solubilities are also highly pH dependent.

Loureiro Engineering Associates, Inc. (Loureiro) was retained to conduct research and development of appropriate corrective measures for COCs. Based on site-specific data and bench-scale effectiveness assessments, two treatment options (corrective measures) are presented as Alternatives #2 and #3. Loureiro has conducted similar evaluations at other power plants in Missouri with similar (alluvial) aquifers and has demonstrated effectiveness at reducing COC concentrations under specific pH conditions.

4.4 Evaluated Corrective Measures

Corrective measures are the actions that may be taken to address the objectives introduced in Section 4.1 and ultimately to correct groundwater impacted as a result of a release (seepage) from the FAP. This ACM evaluates four corrective measures. The corrective measures will conclude when groundwater impacted by the FAP no longer has Appendix IV constituent concentrations exceeding the respective GWPS for three consecutive years of groundwater monitoring. In accordance with 40 CFR 257.97, the groundwater corrective measures must meet the following base requirements to be considered for this evaluation:

- Be protective of human health and the environment;
- Attain the GWPS as specified pursuant to 40 CFR 257.95(h);
- Control the source(s) of releases so as to reduce or eliminate, to the maximum extent feasible, further releases of constituents listed in Appendix IV into the environment;
- Remove from the environment as much of the contaminated material that was released from the CCR unit as is feasible, taking into account factors such as avoiding inappropriate disturbance of sensitive ecosystems; and
- Comply with standards for management of wastes as specified in 40 CFR 257.98(d) (comply with all applicable Resource Conservation and Recovery Act (RCRA) requirements).

The corrective measures presented explore three options for Closure In-Place (CIP) and Closure By Relocation of CCR (CBR). Both CIP and CBR are permissible under 40 CFR 257 (the CCR Rule). The four alternatives are listed below:

- **Alternative #1**: CIP with Monitored Natural Attenuation (MNA)
- **Alternative #2**: CIP with Use of Existing SPS Cooling Tower Process Well Pumping (CTP) and MNA.
- **Alternative #3**: CIP with Groundwater Interception, Treatment, Reinjection (GITR), and MNA
- **Alternative #4**: CBR and MNA.

4.4.1 Alternative #1 - CIP with MNA

Alternative 1 proposes leaving some or all of the ash in the FAP, installation of an engineered, low-permeability cap that substantially reduces precipitation infiltration and resulting seepage from the FAP, followed by MNA of COCs down gradient of the FAP. It is noted that partial CBR options are being considered to address drainage, dewatering, and stability concerns of the FAP following closure. The reduction or elimination of infiltration into the FAP with an engineered cap has the result of isolating the source (CCR) material. A geomembrane and soil capping system has a specified maximum permeability of 1 x 10^{-7} centimeters per second (cm/s), which exceeds the minimum CCR Rule permeability standards (1 x 10^{-5} cm/s) by a factor of 100 for capping systems. Artificial turf capping systems can have even lower permeability values.

The cap system results in significantly less infiltration into the FAP (based on the results of Hydraulic Evaluation of Landfill Performance (HELP) modeling), decreased head on the bottom liner of the FAP, and as a result, seepage from the FAP to groundwater significantly decreases and COC concentrations in groundwater rapidly attenuate down gradient of the FAP as a result of hydraulically isolating the source. Infiltration (HELP) modeling results indicate that post-closure seepage from the FAP is reduced by over 99% for both cap options, and because of the vertical separation between the FAP and the uppermost aquifer, upgradient groundwater will not flow through and be impacted by the ash. Upon completion of the dewatering process and cap placement, any potential for precipitation water contact of ash is practically eliminated.

Based on predictive numerical modeling results, COC concentrations in the uppermost aquifer attenuate to below GWPS before reaching the SPS property line. Predicted COC concentrations above the GWPS in shallow groundwater model layers dissipate within six years of completing any CIP alternative. COC concentrations in deeper groundwater are predicted to attenuate below the GWPS within 10 years of completing this alternative. The modeled, predictive results are based on conservative assumptions of continued SPS operation (and associated deep groundwater pumping for power production) with continued operation of Well “C” at 700 GPM and precipitation rates to those observed during 2023, which were reported by SPS and the National Centers for Environmental Information (an agency within the National Oceanic and Atmospheric Administration (NOAA)), respectively, to be generally similar to the pumping and precipitation rates since groundwater monitoring was initiated at the Site in 2016. Based on the 40+ year operating record, SPS wells pumped approximately 1,250 GPM (collectively) and annual precipitation has averaged about 49 inches per year. Predictive simulations were run with assumptions of typical pumping rates (based on historical records, assumptions of (only) Well “C” operating at 700 GPM to conservatively assess COC control in the future, and with the assumption that the SPS wells would cease pumping entirely.

CIP is safe to complete, complies with applicable federal and state rules and regulations, and is protective of public health and the environment. Temporary construction dewatering, site preparation, construction and installation of the cap system are anticipated to require less than 12 months to complete.

MNA is a state and federally recognized viable remedial technology for removal of inorganic compounds in groundwater. MNA is a passive remedial approach whereby naturally occurring subsurface processes, such as advection, dispersion, sorption, and degradation (biological and abiotic), are assessed via an environmental monitoring program to ensure that these processes:

- Allow for sufficient reductions in COC concentrations so that corrective measure goals will be attained;

- Minimize further down gradient COC migration at the plume boundaries (i.e., plume is stable); and
- Restore the dissolved-phase plume to levels appropriate for current and future beneficial uses to the extent practicable (USEPA, 1998).

The naturally occurring subsurface processes include a multitude of physical, chemical, or biological processes that, under favorable conditions, act without intervention to reduce, mass, mobility, volume, concentration, and/or toxicity of contaminants. When paired with a low-permeability CIP system to isolate the source of COCs and substantially reduce seepage from the FAP, MNA will reduce concentrations of COCs in groundwater at the FAP boundary (MW-1R, MW-7, and MW-9) in four years or less based on groundwater modeling discussed in Section 4.2.

Following installation of the engineered cap system, SBMU would implement post-closure care activities. These include routine cap system maintenance and long-term groundwater monitoring until groundwater conditions become consistent with regulatory requirements. Future development of the capped surface could be used for solar photovoltaic arrays or other site staging/ancillary operational needs. Once implemented, the concentrations of COCs in groundwater are expected to attenuate. The timeline for Alternative #1 is expected to be within 10 years for COC concentrations in groundwater to attenuate to levels less than the GWPS across the site. Groundwater monitoring will continue (at minimum) until COC concentrations in groundwater remain in compliance with the GWPS for a period of three consecutive years.

4.4.2 Alternative #2 - CIP with CTP and MNA

Alternative 2 is like Alternative 1 in that it also proposes leaving some or all of the ash in the FAP, installation of the same engineered, low-permeability cap, followed by MNA of COCs down gradient of the FAP. However, it also includes CTP to provide additional migration control of COCs. As with Alternative 1, the permeability of the proposed cap exceeds the minimum CCR Rule permeability standards by a factor of 100 or more. Since the high-water table at the FAP is below the level of the deposited ash residuals, the cap will serve to isolate the source materials from both infiltrating precipitation and underlying groundwater flow. Over a relatively short period of time, COCs in the underlying groundwater will be flushed from under the FAP and the concentration of COCs in down gradient groundwater will attenuate. With a maintained cap and no groundwater contact with the stored ash, future COCs impact to groundwater associated with the FAP is unlikely. Groundwater modeling, discussed in Section 4.2, projects that the shallow groundwater underlying the FAP will be flushed of COCs (i.e. COC concentrations will be lower than GWPS) within three years post-cap completion or less based on groundwater modeling.

At any given time, SPS power generation uses up to five high-capacity wells located on the Site to provide cooling water for system operations. The pumps, located in Wells “C”, “E”, “F”, “G” and “H”, are operated in various pumping schemes to produce a sufficient volume of water for the cooling process. Particle tracking models performed for the site evaluation, as presented in Section 4.2, demonstrate that operation of the high-capacity wells not only captures groundwater underlying the footprint of the FAP but also captures groundwater across the entire SPS property when Well “C” is included in these multiple well operation scenarios. This capture includes the identified area of groundwater above GWPS throughout the Site. The discharged water from the cooling towers is directed to an on-site settling pond and a process waste pond (Figure 1). The main sources of water to these ponds are from the high-capacity wells or from precipitation events. These ponds have the capacity to maintain several days of retention prior to discharge to NPDES Outfall #003. The discharge from NPDES Outfall #003 runs directly westward to RDD#4 (Figure 1). Multiple samples collected from NPDES Outfall #003 over the period from April 2020 to present demonstrate that the COCs measured are below the required GWPS criteria.

The varied operational scenarios of the high-capacity wells can both shift COC-impacted groundwater flow direction and contain the COC impacts to within the property boundaries. Blending of the extracted well waters using defined operation scenarios prior to use for the SPS cooling towers is sufficient to reduce COCs in groundwater to below the GWPS criteria. The use of groundwater as a water source for SPS operations pre-dates the existence of releases from the FAP. While the well operations serve as a primary cause of COC migration on-site, these operations also serve as the primary method of COC migration control. As the SPS operations managers select which wells to use at any given time to supply the cooling waters for the SPS, it will be necessary to perform additional modeling using the site-specific calibrated groundwater flow model to develop a recommended high-capacity well operating plan for the SPS to maintain control of the on-site COC-impacted groundwaters. This plan will describe operation scenarios to maintain control of flow direction and groundwater capture. It will identify specific wells to operate in conjunction with each other to obtain sufficient water volume for cooling purposes while controlling groundwater flow direction and COC migration.

Post-installation of the low-permeability cap and ensuring compliance with the proposed high-capacity well operating plan, post-closure care activities would be implemented. These activities would include recording the well operations, long-term groundwater sampling to monitor system performance, and cap cover system maintenance. The required short-term periods of specific well downtime, for maintenance requirements, will not affect long-term control of the COC-impacted groundwater as the projected radius of influence of any specific well will capture the COC-impacted groundwater shortly after well pumping is resumed. Periodic review and optimization of the operating plan will be required.

Future development of the capped surface could be used for solar photovoltaic arrays or other site staging/ancillary operational needs. Once implemented, the concentrations of COCs in groundwater are expected to attenuate and any required well pumping operations under the operating plan could be eliminated at that time. The timeline for Alternative #2 is expected to be within 10 years of alternative completion for COC concentrations in groundwater to attenuate to levels less than the GWPS across the site.

It is noted that this is about the same duration (10 years) as predicted for Alternative 1. The similarity of the durations for different alternatives is coincidental. COCs are predicted to be flushed at different rates in some areas of the model domain based on the aquifer stresses associated with each alternative (such as operation of SPS's high-capacity wells). While some areas may achieve compliance earlier, both Alternatives 1 and 2 require about 10 years for COC concentrations in groundwater to attenuate to levels less than the GWPS across the site, and control would then continue (at minimum) until COCs concentrations in groundwater remain in compliance with the GWPS for a period of three consecutive years.

4.4.3 Alternative #3 - CIP with GITR and MNA

The FAP would be closed in place with Alternative 3 leaving some or all of the ash in the FAP, the installation of the same engineered, low-permeability cap outlined in Alternatives 1 and 2, with groundwater intercepted at the FAP edge, treated, and reinjected to reduce COC migration. As with Alternatives 1 and 2, the permeability of the proposed cap exceeds the minimum CCR Rule permeability standards by a factor of 100 or more, and since the high-water table at the FAP is below the level of the deposited ash residuals, the source materials will be isolated from both infiltrating precipitation and underlying groundwater flow. Over a relatively short period of time, COCs in the underlying groundwater will be flushed from under the FAP and the concentration of COCs in down gradient groundwater will attenuate. With a maintained cap and no groundwater contact with the stored ash, future COCs impact to groundwater, associated with the FAP, is unlikely. Groundwater modeling, discussed in Section 4.2 of this ACM, projects that the shallow groundwater underlying the FAP will be flushed of COCs within three years post cap completion.

Control of COC migration (prevent impacted groundwater migration to compliance wells) would be maintained with groundwater pumping from a series of extraction wells located along the western boundary of the FAP (Figure 6). The extracted groundwater will be treated via an ex-situ treatment train of technologies using pH adjustments to cause COC precipitation, filtration to remove precipitants, followed by adsorption of non-precipitated COCs using ion-specific resin. The treated groundwater will then be injected into a series of new wells, down gradient of the extraction wells and upgradient of the compliance wells. Figure 6 presents the approximate locations for the extraction, injection, and system compliance wells. The process would be designed via groundwater modeling to have a net-zero impact on the natural groundwater flow through the Site while maintaining hydraulic control and treatment of groundwater migrating from under the pond. A site-specific laboratory treatability study will be conducted to refine the treatment train specific parameters and demonstrate the effectiveness of the treatment system for the Site. To confirm that the laboratory study results can be adequately replicated at full-scale, a pilot-scale system would typically be operated at the Site prior to finalization of the full-scale system design. Given the project timeframe to flush the impacted groundwater from under the pond, the cost and time to implement a pilot study to refine a full-scale system would be an inefficient use of resources.

As stated above, a site-specific calibrated groundwater flow model will be used to refine the design of the required extraction and injection well locations and screened intervals. Based on modeling results, extraction wells and injection wells will be installed to control the groundwater flow from under the FAP and the treated groundwater will be injected upgradient from compliance points determined under the CCR Rule. Extracted groundwater is pumped to a process area where the COCs are removed, and the treated water is then returned to the aquifer via the injection wells. Natural groundwater flow is then re-established for a net zero removal or change in flow direction or rate outside of the hydraulic control zone developed from the extraction and injection well systems. Approval and permitting would be required for the injection of the treated groundwater back into the aquifer. This approval requirement typically requires seven to twelve months to complete.

A typical schematic for a potential treatment system design is provided on Figure 7. As a result of this example treatment process the potential for sludges from settling tanks and wastes from backwash waters for filters and resin are projected. Accordingly, wastes will be generated for offsite disposal. Precipitant sludges containing the COCs will be removed, as necessary, in secondary containers and processed onsite for transport and disposal offsite. Backwash fluids generated from the filters will be redirected to the initial settling tank for additional processing and settlement. Regeneration waste from the resin filtration system will be neutralized as part of the regeneration process and contained in secondary containers for offsite disposal. All generated waste will be handled, transported and disposed of in accordance with all applicable state and federal regulations.

Following the installation of the low-permeability cap and groundwater interception and treatment system, post-closure care activities would be implemented that includes operation and maintenance of the treatment system, long-term groundwater sampling to monitor system performance, and cover system maintenance. Future development of the capped surface could be used for solar photovoltaic arrays or other site staging/ancillary operational needs. Once implemented, the concentrations of COCs are expected to attenuate to meet the GWPS and the groundwater control and treatment system would cease over time. The timeline for Alternative #3 is expected to be within 10 years of alternative completion for COC concentrations in groundwater to attenuate to levels less than the GWPS across the site.

It is noted that this is about the same duration (10 years) as predicted for Alternatives 1 and 2. The similarity of the durations for different alternatives is coincidental. COCs are predicted to be flushed at different rates in some areas of the model domain based on the aquifer stresses associated with each alternative (such as operation of SPS's high-capacity wells). While some areas may achieve compliance earlier, Alternatives 1, 2, and 3 require about 10 years for COC concentrations in groundwater to attenuate to levels less than the GWPS across the site, and control would then continue (at minimum) until COCs concentrations in groundwater remain in compliance with the GWPS for a period of three consecutive years.

4.4.4 Alternative #4 CBR and MNA

This corrective measure alternative consists of removal of FAP contents and relocation to one of the following types of receiving facilities:

- A permitted Subtitle D solid waste facility (landfill); or
- A cement producer that accepts fly ash at no cost for reuse of fly ash as an alternative raw material in cement production; or
- A cement producer pays for the raw material value for beneficial reuse.

CBR is followed by ash pond decontamination, and eventually MNA of COCs in down gradient groundwater. This alternative is the only corrective measure that removes the source. However, there are substantial limitations, including costs (financially and environmentally), timeline, and logistical concerns associated with this remedial alternative.

A CBR study completed by ANE Engineering (ANE) (Appendix C) states that exhuming the FAP can theoretically be completed in five years based on reduction of moisture content and maximization of driver and truck usage, but the actual project duration may exceed 18 years depending on acceptance rate (daily volume) and criteria the receiving facility can accommodate. However, it is noted that the landfill or cement producing facility may reduce the CCR acceptance rate to accommodate other waste or raw material streams provided by other clients or for other operational reasons that could result in protracting CBR to 30 years or more.

Like the other corrective measures assessed (Alternatives 1, 2, and 3), concentrations of COCs in down gradient groundwater will eventually decrease via natural attenuation. However, COC attenuation would not be observable down gradient until exhumation and decontamination of the ash pond is completed, which may exceed 18 years to accomplish. Regardless of which receiving facility is utilized, the FAP and its contents would remain exposed to the elements and would be subjected to precipitation/inflow/run-on, and seepage through the base of the pond for the duration of the removal and decontamination process. In other words, the groundwater impact down gradient of the FAP will likely worsen during the excavation and removal process. It will only begin to improve once the CBR process is completed. In contrast, the other corrective measures considered in this assessment include installation of a low permeability cap, which is effective at reducing pond seepage immediately upon completion. CBR requires a significant amount of time to exhume ash and decontaminate the pond prior to any expectation of attenuation of COC concentrations in down gradient groundwater.

5.0 COMPARISON OF CORRECTIVE MEASURES ALTERNATIVES

This section presents evaluation, comparison, and rank of each of the four corrective measures using the evaluation criteria provided in 40 CFR 257.97 and summarized in this section.

As summarized in Section 1.4, the CCR Rule is prescriptive in regard to the process for assessing corrective measures. As discussed, the rule provides minimum requirements (listed in 40 CFR 257.97(b)) that any corrective measure must meet in order to be considered. Following that, each corrective measure is then compared to one another utilizing criteria listed in 40 CFR 257.97(C) and in the following sections. Each of the first three Evaluation Criteria Categories has several sub-criteria to consider while ranking suitability of each corrective measure proposed. A summation of the ranking is then used to select the most suitable corrective measure based on these collective criteria.

5.1 Evaluation Criteria

The CCR Rule provides guidance for evaluating corrective measures that meet the criteria provided in 40 CFR 257.97. Following the establishment that the minimum criteria have been met, the CCR Rule provides evaluation criteria. The first three Evaluation Criteria Categories are addressed in this report, while the final evaluation criteria pertain to Sikeston’s community concerns:

- **Evaluation Criteria Category #1:** The long- and short-term effectiveness and protectiveness of the potential remedy(ies), along with the degree of certainty that the remedy will prove successful
    - **Sub-Criterion #1:** Magnitude of reduction of existing risks
    - **Sub-Criterion #2:** Magnitude of residual risks in terms of likelihood of further releases due to CCR remaining following implementation of a remedy
    - **Sub-Criterion #3:** The type and degree of long-term management required, including monitoring, operation, and maintenance
    - **Sub-Criterion #4:** Short-term risks that might be posed to the community or the environment during implementation of such a remedy, including potential threats to human health and the environment associated with excavation, transportation, and re-disposal of contaminant
    - **Sub-Criterion #5:** Time until full protection is achieved
    - **Sub-Criterion #6:** Potential for exposure of humans and environmental receptors to remaining wastes, considering the potential threat to human health and the environment associated with excavation, transportation, re-disposal, or containment
    - **Sub-Criterion #7:** Long-term reliability of the engineering and institutional controls
    - **Sub-Criterion #8:** Potential need for replacement of the remedy

- **Evaluation Criteria Category #2:** The effectiveness of the remedy in controlling the source to reduce further releases based on consideration of the following factors
    - **Sub-Criterion #1:** The extent to which containment practices will reduce further releases
    - **Sub-Criterion #2:** The extent to which treatment technologies may be used

- **Evaluation Criteria Category #3:** The ease or difficulty of implementing a potential remedy(ies) based on consideration of the following types of factors
    - **Sub-Criterion #1:** Degree of difficulty associated with constructing the technology
    - **Sub-Criterion #2:** Expected operational reliability of the technologies

- **Sub-Criterion #3:** Need to coordinate with and obtain necessary approvals and permits from other agencies
- **Sub-Criterion** #4: Availability of necessary equipment and specialists
- **Sub-Criterion #5:** Available capacity and location of needed treatment, storage, and disposal services

- **Evaluation Criteria Category #4:** The degree to which community concerns are addressed by a potential remedy(ies)

In accordance with the CCR Rule, each remedial alternative must satisfy the five minimum requirements listed in in 40 CFR 257.97 and summarized in Section 4.4. Each of the four remedial alternatives are then compared to the first three Evaluation Criteria Categories with associated sub-criteria summarized below to allow comparative analysis for each corrective measure.

Following the comparison of each corrective measure based on Evaluation Criteria Categories 1 through 3 with associated sub-criteria, the final evaluation criteria will be assessed at a public meeting held for the purpose of understanding public concerns and evaluating the degree to which community concerns are addressed by a potential remedy(ies). A schedule for implementing and completing the selected corrective measure will be completed taking into consideration the factors listed in 40 CFR 257.97(d).

5.2 Comparison of Alternatives

Below is a list of the first three Evaluation Criteria Categories with sub-criteria on which each corrective measure will be ranked. Table 5 is provided to visually summarize the favorability of each corrective measure based on each sub-criteria listed below. A ranking of 1 indicates favorable, a rank of 0 indicates less favorable, and a ranking of -1 indicates unfavorable.

5.2.1 Evaluation Criteria Category #1 (Performance)

These criteria are intended to gauge the long-term and short-term effectiveness of the corrective measures being compared.

5.2.1.1 Category #1 (Performance) Sub-Criterion #1

This sub-criterion addresses the comparison for the magnitude of reduction of existing risks. As concluded by the Human Health and Ecological Risk Evaluation conducted for this site (Appendix B), the FAP COCs are not associated with a potential for adverse impact to human health or ecological receptors (plants and animals in nature). In this regard, none of the remedial alternatives are necessary to reduce risk posed by COCs from the FAP in groundwater, because adverse risk is not present. Regardless, each remedial alternative offers its own challenges, impacts, and concerns that are discussed.

The remedial alternatives associated with the least amount of external risk, and external impact are Alternatives 1 (CIP and MNA) and 2 (CIP with CTP and MNA), because they are conducted in place and most components of these systems (except the cap construction) already exist and therefore involve the least amount of construction. Alternative 3 (CIP with GITR and MNA) is associated with a slightly higher level of risk resulting from construction of arrays of extraction and injection wells. Alternative 4 (CBR with MNA) is ranked as least favorable because of the highest potential for impact due to years of construction and truck traffic. While in transit, accidents and spills can occur, which are risks not associated with the other alternatives. Additionally, the FAP would remain open to the environment for a prolonged period of time as the ash is removed, and the public and environment will be exposed to the ash longer than the relatively short time required to install a cap.

5.2.1.2 Category #1 (Performance) Sub-Criterion #2

This sub-criterion addresses the comparison for the magnitude of residual risks in terms of likelihood of further releases due to CCR remaining following implementation of a remedy. Removal of the CCR (Alternative 4) has the lowest very-long reduction of risk in that the source material is removed, but doing so will require almost twenty years to complete. During this source material removal time period, the ash will be exposed to precipitation and is open to the environment. The remaining alternatives (1, 2, & 3) require closing in place by installing a low permeability cap (less than 1×10^{-7} cm/s) that essentially isolates the CCR by essentially eliminating precipitation from percolating through the ash and into the underlying groundwater aquifer. Moreover, capping can be completed in a timeframe measured in months rather than years.

Alternatives 1 and 4 rely on MNA to address the COCs dissolved in groundwater, while Alternatives 2 and 3 provide additional measures to ensure treatment and/or control of the impacted groundwater. The lowest residual risk is associated with Alternative 2 (CIP with CTP and MNA) and with Alternative 3 (CIP with GITR and MNA).

5.2.1.3 Category #1 (Performance) Sub-Criterion #3

This sub-criterion addresses the type and degree of long-term management required, including monitoring, operation, and maintenance. Alternative 1 (CIP with MNA) is most favorable for this sub-criterion because it requires the least amount of long-term maintenance and does not involve mechanical systems requiring operational management. By contrast, Alternative 4 (CBR with MNA) is least favorable because tracking of the CCR during removal and transport over a 20-year, or more time-period will require significant management efforts, as will coordination efforts with the receiving facilities that dictate acceptance rates. Therefore, the duration of the risk is outside the control of SPS. Development of a utility waste landfill on the site is not practical because the complexity of design, permitting, and construction would delay the project five years or longer. Alternatives 2 and 3 both require pumping and treatment, which requires a level of sampling, management, and maintenance that is greater than Alternative 1, but less than Alternative 4.

5.2.1.4 Category #1 (Performance) Sub-Criterion #4

This sub-criterion addresses the short-term risks that might be posed to the community or the environment during implementation of such a remedy, including potential threats to human health and the environment associated with excavation, transportation, and re-disposal of contaminant. The highest short-term risk is associated with Alternative 4 (CBR and MNA), as a result of the length of time the ash remains open to the environment (during dewatering and excavation), the duration of construction hazards, the increased truck traffic, fugitive dust emissions, noise, and other risks associated with a multi-year (possibly multi-decade) construction project of this type. The remaining alternatives involve minimal short-term risk to the community or environment during implementation because they can be completed relatively quickly and without increased short-term risk.

5.2.1.5 Category #1 (Performance) Sub-Criterion #5

This sub-criterion addresses the time until full protection is achieved. There currently is not a potential for adverse impact to human health or ecological receptors (plants and animals in nature) associated with the groundwater at the FAP (Appendix B). However, based on predictive modeling, Alternatives 1, 2, and 3 all result in attenuation of COCs in groundwater to concentrations below GWPS within 10 years.

By contrast, Alternative 4 (CBR and MNA) is estimated to require more than five years to exhume the ash, and depending on the receiving facility's acceptance rate it will require closer to 20 years. Meanwhile, the FAP will remain open to the environment and allow for aquifer recharge by COC-impacted water for several decades while CBR is implemented. Following removal of the ash, groundwater monitoring will continue to verify natural attenuation. Similar monitoring will be required for Alternatives 1, 2 and 3, but it is expected that the sampling will begin following capping, which is expected to require less than 6 months to complete. Alternative 3 requires extensive analysis to design and construct arrays for extraction points and re-injection points of treated groundwater.

5.2.1.6 Category #1 (Performance) Sub-Criterion #6

This sub-criterion addresses the potential for exposure of humans and environmental receptors to remaining wastes, considering the potential threat to human health and the environment associated with excavation, transportation, re-disposal, or containment. Alternatives 1 (CIP with MNA) and 2 (CIP with CTP and MNA) are similar in that they both have minimal potential for exposure of humans and environmental receptors to remaining wastes during construction of the cap, monitoring well installation, and any additional high-capacity well construction. Alternative 1 is most favorable in this category due to the lack of additional construction necessary to complete relative to the other alternatives. Similarly, Alternative 2 is not expected to add potential for exposure of humans and environmental receptors to remaining wastes. However, Alternative 3 (CIP with GITR and MNA) will involve installation of extraction wells at the waste boundary or potentially under the waste, which would involve drilling through the ash and potentially exposing workers. Alternative 4 (CBR with MNA) is least favorable in that it involves the most extensive exposure and longest duration of construction to complete.

5.2.1.7 Category #1 (Performance) Sub-Criterion #7

This sub-criterion addresses the long-term reliability of engineering and institutional controls. Alternatives 1 (CIP with MNA), 2 (CIP with CTP and MNA), and 4 (CBR with MNA) are expected to have high long-term reliability in that capping and long-term monitoring are familiar methods for long-term waste management. Alternative 3 (CIP with GITR and MNA) is also a reliable, familiar, and proven technology, but requires considerable testing and scaling of treatment from lab to environment with confirmation of treatment, and therefore it is the least favorable alternative. Alternative 1 is most favorable because changes to operation and maintenance are not required (groundwater sampling, analysis, and reporting is already being conducted). Alternative 2 is almost as favorable but requires coordination of production wells used for plant operations. Alternative 4 is similarly favorable after the construction is completed but has a significant timeline difference.

5.2.1.8 Category #1 (Performance) Sub-Criterion #8

This sub-criterion addresses the potential need for replacement of the remedy. Alternative 4 (CBR with

MNA) is considered permanent and can be effective in the right situation. In this regard the need to replace the remedy, source removal, is permanent but takes the longest time to complete. The remaining alternatives are expected to result in permanent closure with capping in place. If monitoring suggests that the alternative in use is not effective at reducing the COC concentrations over time, alternate and/or additional remedial alternatives may be considered and implemented in the future.

5.2.1.9 Summary of Category #1 (Performance)

Table 5 summarizes the favorability of each corrective measure based on each sub-criterion. In consideration of the sub-criteria, the long- and short-term effectiveness and protectiveness of the potential remedy, and the degree of certainty that the remedy will prove successful, Alternatives 1 (CIP with MNA) and 2 (CIP with CTP and MNA) are the most favorable. Modeling suggests that Alternatives 1, 2, and 3 will achieve COC concentrations below GWPS within 10 years of completion of construction. Alternative 1 requires the least amount of time to implement, because there is the least amount of construction associated with this alternative. Alternative 2 requires a limited amount of engineering and planning to develop a successful pumping plan for SPS water production that also maintains control. Alternative 3 requires more time and engineering design to construct and tune the extraction and injection system and treatment train. Alternative 4 is least favorable in that it requires the most time to complete and will involve the greatest amount of exposure of humans and the environment to COCs.

5.2.2 Evaluation Criteria Category #2 (Constructability)

These criteria consider the ability of the corrective measures being compared to control a release and the extent to which the associated technologies may be used.

5.2.2.1 Category #2 (Constructability) Sub-Criterion #1

This sub-criterion addresses the extent to which containment practices will reduce further releases. Alternatives 1 (CIP with MNA), 2 (CIP with CTP and MNA), and 3 (CIP with GITR and MNA) all incorporate a low-permeability cap to reduce or eliminate precipitation from entering and percolating through the ash and seeping into groundwater. Alternatives 2 and 3 offer additional favorability because they incorporate active control technologies and treatment of groundwater to inhibit down gradient migration of COCs. Alternative 4 (CBR with MNA) offers the least risk of future release, but only after a lengthy excavation, hauling, and relocation project has been completed. Similarly, Alternative 1 lacks active control technology and therefore is ranked slightly lower than Alternatives 2 and 3.

5.2.2.2 Category #2 (Constructability) Sub-Criterion #2

This sub-criterion addresses the extent to which treatment technologies may be used. Alternatives 1 (CIP with MNA) and 4 (CBR with MNA) do not utilize treatment technologies, meaning that there would be no additional operation and maintenance considerations. The required coordination and scale of construction of Alternative 4 renders Alternative 1 as the more attractive alternative of these two options. Alternative 3 (CIP with GITR and MNA) utilizes additional technologies to treat extracted water prior to reinjection that could result in spent treatment agents or concentrated water that could not be reinjected but would instead require offsite disposal. Because Alternative 2 (CIP with CTP and MNA) incorporates a low permeability cap and down gradient groundwater control and COC capture via pumping, it is the most favorable of the four corrective measures being considered (even though Alternatives 1, 2, and 4 all scored favorably). The low permeability cap and pumping of existing SPS high-capacity wells (as they have been operating on-site for over a decade) were modeled to confirm that Alternative 2 will control and capture COCs from the FAP.

5.2.2.3 Summary of Category #2 (Constructability)

Table 5 summarizes the favorability of each corrective measure based on the two sub-criteria. In consideration of these two sub-criteria regarding the effectiveness of the remedy in controlling the source to reduce further releases, Alternative 2 (CIP with CTP and MNA) is the most favorable. Modeling suggests that the low permeability cap utilized in Alternatives 1, 2, and 3 is effective in isolating the source material from groundwater by preventing infiltration into the pond. Because Alternative 2 uses the low permeability cap and a system of high-capacity pumping wells (which already exist and are required to be operated for production needs) and has been demonstrated with modeling to capture COC impacted water associated with the FAP, it is the most attractive alternative for controlling the source to reduce further releases. Alternative 4, while possible, requires a duration of time to complete removal of the source before reduction of COC concentrations in groundwater can begin. The probable duration of time associated with removal of CCR is longer than the duration of time required to fully implement and achieve groundwater compliance for Alternatives 1, 2, and 3.

Alternative 1 requires the least amount of time to implement, because there is the least amount of construction associated with this alternative. Alternative 2 requires a limited amount of engineering and planning to develop a successful pumping plan for SPS water production that also maintains control. Alternative 3 requires more time and engineering to design, construct and tune the extraction and injection system and treatment train. Alternative 4 is least favorable because it requires the most time to complete and will involve the greatest amount of exposure of humans and the environment to COCs for the duration of the CBR process.

5.2.3 Evaluation Criteria Category #3 (Implementation Concerns)

These criteria consider the ability of each corrective measure being compared to control a release and the extent to which the associated technologies may be used.

This criterion considers the following five sub-criteria that are intended to gauge the ease of implementation of the corrective measures being compared. They are used for considering technical and logistical challenges necessary to complete the measure. Equipment availability and available capacity at receiving facilities are also considered.

5.2.3.1 Category #3 (Implementation Concerns) Sub-Criteria #1

This sub-criterion addresses the degree of difficulty associated with constructing the technology. Alternative 1 (CIP with MNA) is relatively un-complicated and can be implemented with standard construction techniques. Alternative 2 (CIP with CTP and MNA) is essentially the same degree of difficulty as Alternative 1 in that the SPS is already operating the pumping system that effectively treats the groundwater as a byproduct of plant operations. Alternative 3 (CIP with GITR and MNA) adds a layer of difficulty in that the extraction/injection system will require tuning, and pilot studies may be necessary to optimize the treatment system. Therefore, Alternative 3 is less favorable than Alternatives 1 and 2.

Alternative 4 (CBR with MNA) is the most difficult alternative to implement due to technical and logistical challenges. This option requires transportation of a very large volume of material to a receiving facility (or facilities) over public roadways near residential areas. Receiving facilities may have special requirements and limits that will require additional levels of coordination, adding to the difficulty and rendering Alternative 4 the least favorable option.

5.2.3.2 Category #3 (Implementation Concerns) Sub-Criteria #2

This sub-criterion addresses the expected operational reliability of the technologies. Alternative 1 (CIP with MNA) is highly favorable from an operational standpoint because it is a proven technology. Alternative 2 (CIP with CTP and MNA) is essentially the same but adds reliability via control with existing infrastructure and operations. Similarly, Alternative 4 (CBR with MNA) is considered very reliable in that the source will be removed; however, the time required to achieve reliability should be considered. Alternative 3 (CIP with GITR and MNA) is considered reliable but because it involves ex-situ treatment technologies, reliability may change over time and require tuning or adjustments. For these reasons, Alternatives 1, 2, and 4 are considered the most reliable.

5.2.3.3 Category #3 (Implementation Concerns) Sub-Criteria #3

This sub-criterion addresses the need to coordinate with and obtain necessary approvals and permits from other agencies. Alternatives 1 (CIP with MNA) and 2 (CIP with CTP and MNA) are the most favorable in this sub-criterion because they will require the least amount of outside permitting but will involve internal policy (for high-capacity well water production). Alternative 3 (CIP with GITR and MNA) is relatively straightforward in terms of permitting and approvals. Alternative 4 (CBR with MNA) will require extensive permitting for such a large-scale construction effort. Alternative 4 will require the greatest need for coordination, permitting, and approval from receiving facility(ies) rendering it the least favorable in this sub-criterion.

5.2.3.4 Category #3 (Implementation Concerns) Sub-Criteria #4

This sub-criterion addresses the availability of necessary equipment and specialists. Alternative 1 (CIP with MNA) is highly favorable because the treatment requires no special equipment or specialists to implement. Similarly, Alternatives 2 (CIP with CTP and MNA) and 3 (CIP with GITR and MNA) are favorable because specialists for these alternatives are available. By contrast Alternative 4 (CBR with MNA) is least favorable in that this alternative requires specialty contractors to implement successfully, and transportation of material to receiving facilities will require a large amount of coordination, equipment, and qualified drivers.

5.2.3.5 Category #3 (Implementation Concerns) Sub-Criteria #5

This sub-criterion addresses the available capacity and location of needed treatment, storage, and disposal services. Alternatives 1 (CIP with MNA), 2 (CIP with CTP and MNA), and 3 (CIP with GITR and MNA) all involve closure in place and therefore none of these alternatives will require storage and/or acceptance and/or disposal of CCR. However, Alternative 3 involves ex-situ treatment, which may generate a concentrated waste stream requiring on-site treatment or off-site transportation and disposal (or treatment) that the other alternatives do not require. Alternative 4 (CBR with MNA) was studied (Appendix C) in depth and evalu3.ation for beneficial reuse as raw material, and/or disposal in landfills in reasonable proximity to SPS. For these reasons Alternatives 1 and 2 are favorable due to their lack of dependance on capacity for treatment, storage, and/or disposal services, and Alternatives 3 and 4 are less favorable because of their dependance on off-site treatment, storage, and/or disposal services.

5.2.3.6 Summary of Category #3 (Implementation Concerns)

Table 5 summarizes the favorability of each corrective measure based on each sub-criterion. In consideration of the five implementation concern sub-criteria, Alternatives 1 (CIP with MNA) and 2 (CIP with CTP and MNA) are the most favorable because both are relatively un-complicated, proven technologies that can be implemented with common construction techniques. Alternatives 1 and 2 will require the least amount of outside permitting compared to other alternatives. No specialists or special equipment is required to implement these options, and neither option requires storage and/or acceptance and/or disposal of CCR by facilities outside of the SPS.

By comparison, Alternative 3 (CIP with GITR and MNA) offers the same favorability as Alternatives 1 and 2 regarding availability of equipment and specialists necessary to implement but is less favorable in every other sub-criterion in this (ease of implementation) category. Alternative 4 (CBR with MNA) is the least favorable alternative in this category largely due to the duration of time, difficulty of implementation, permitting complexities, and the number of specialists and specialized equipment necessary to complete this alternative.

5.2.4 Evaluation Criteria Category #4 (Community Concerns)

These criteria consider the public feedback for each corrective measure being compared. It is noted that public input and feedback will be considered during this process.

6.0 SUMMARY

This document evaluated the following corrective measures to address the COCs in groundwater resulting from the FAP at the SPS:

- Alternative #1- CIP with MNA
- Alternative #2 - CIP with CTP and MNA
- Alternative #3 - CIP with GITR and MNA
- Alternative #4 - CBR with MNA

As a condition of CCR Rule 40 CFR 257.97, all of the measures listed above fulfil the following requirements:

- Be protective of human health and the environment;
- Attain the GWPS as specified pursuant to 40 CFR 257.95(h);
- Control the source(s) of releases so as to reduce or eliminate, to the maximum extent feasible, further releases of constituents in appendix IV to 40 CFR 257 into the environment;
- Remove from the environment as much of the contaminated material that was released from the CCR unit as is feasible, taking into account factors such as avoiding inappropriate disturbance of sensitive ecosystems; and
- Comply with standards for management of wastes as specified in 40 CFR 257.98(d) (comply with all applicable RCRA requirements).

Each of these corrective measures have been evaluated in accordance with and using the criteria provided in CCR Rule 40 CFR 257.96:

- Evaluation Criteria Category #1: The long- and short-term effectiveness and protectiveness of the potential remedy(ies), along with the degree of certainty that the remedy will prove successful
    - Sub-Criterion #1: Magnitude of reduction of existing risks
    - Sub-Criterion #2: Magnitude of residual risks in terms of likelihood of further releases due to CCR remaining following implementation of a remedy
    - Sub-Criterion #3: The type and degree of long-term management required, including monitoring, operation, and maintenance
    - Sub-Criterion #4: Short-term risks that might be posed to the community or the environment during implementation of such a remedy, including potential threats to human health and the environment associated with excavation, transportation, and re-disposal of contaminant
    - Sub-Criterion #5: Time until full protection is achieved
    - Sub-Criterion #6: Potential for exposure of humans and environmental receptors to remaining wastes, considering the potential threat to human health and the environment associated with excavation, transportation, re-disposal, or containment
    - Sub-Criterion #7: Long-term reliability of the engineering and institutional controls
    - Sub-Criterion #8: Potential need for replacement of the remedy
- Evaluation Criteria Category #2: The effectiveness of the remedy in controlling the source to reduce further releases based on consideration of the following factors
    - Sub-Criterion #1: The extent to which containment practices will reduce further releases

  - Sub-Criterion #2: The extent to which treatment technologies may be used

- Evaluation Criteria Category #3: The ease or difficulty of implementing a potential remedy(ies) based on consideration of the following types of factors
  - Sub-Criterion #1: Degree of difficulty associated with constructing the technology
  - Sub-Criterion #2: Expected operational reliability of the technologies
  - Sub-Criterion #3: Need to coordinate with and obtain necessary approvals and permits from other agencies
  - Sub-Criterion #4: Availability of necessary equipment and specialists
  - Sub-Criterion #5: Available capacity and location of needed treatment, storage, and disposal services

The information presented in this document and community input provided during the public comment period, will be utilized to select the corrective measure to be implemented at the SPS.

7.0 REFERENCES

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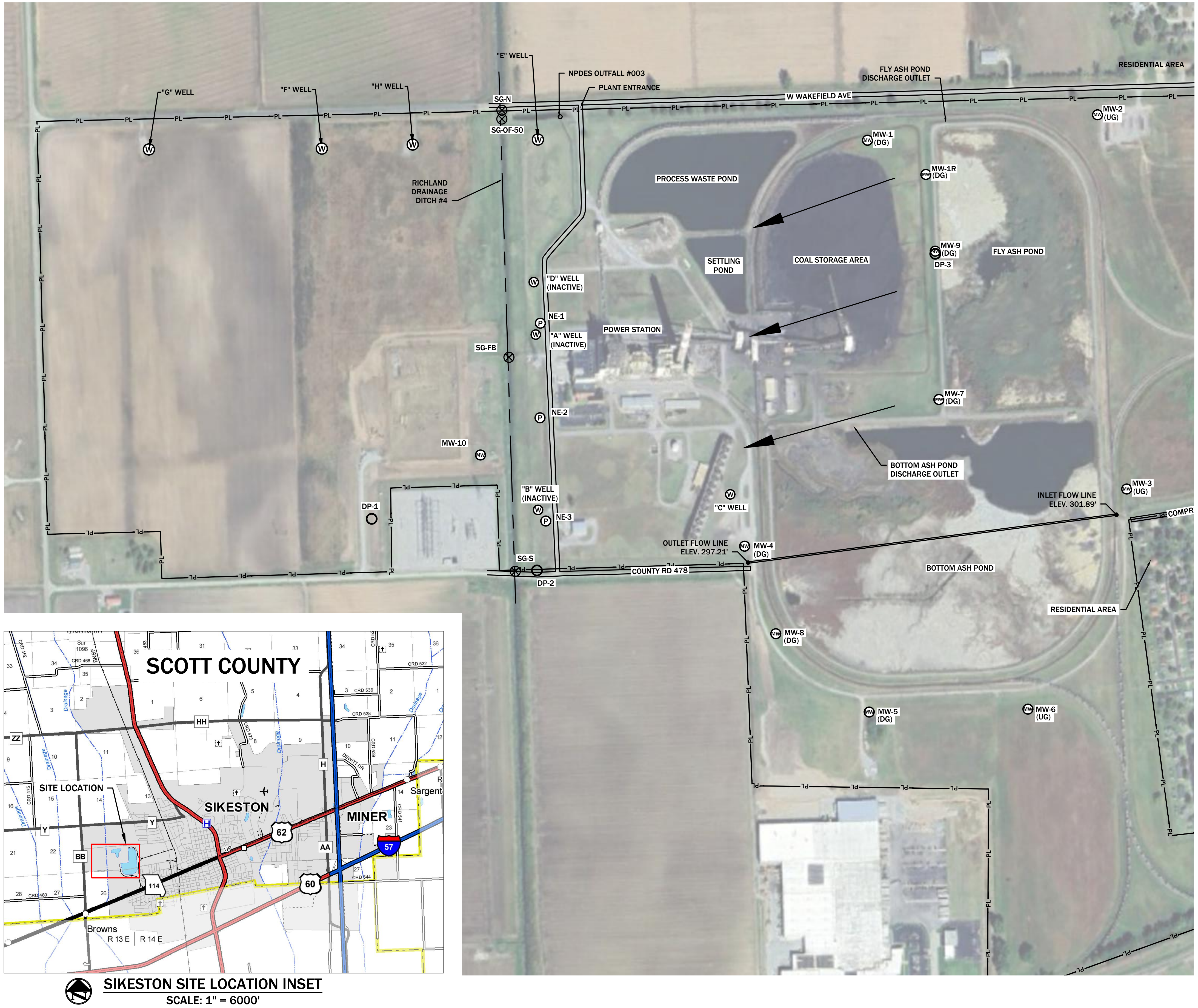
Figures



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SCALE: 1" = 600'

0 300 600

LEGEND

PROPERTY LINE (APPROX.)	—PL—	
MONITORING WELL	MW	MW-10
TEMPORARY PEIZOMETER	P	NE-3
RICHLAND DRAINAGE DITCH #4 WATER ELEVATION GAUGE AND/OR SAMPLE LOCATION	⊗	SG-S
HIGH-CAPACITY WELL	W	"D"
DIRECT PUSH GROUNDWATER SAMPLE LOCATION	○	DP-3
UP GRADIENT MONITORING LOCATION	UG	
DOWN GRADIENT MONITORING LOCATION	DG	
GROUNDWATER FLOW	←	

NOTES:

1. IMAGE PROVIDED BY BING MAPS.
2. MONITORING WELL LOCATIONS, CASING ELEVATIONS & UNDERGROUND CULVERT ELEVATIONS SURVEYED BY BOWEN ENGINEERING & SURVEYING.
3. LOCATIONS DP-1, DP-2, AND DP-3 ARE APPROXIMATE.
4. MW-10, NE-1, NE-2, NE-3, SG-N, SG-FB, SG-S, AND SG-OF-50 INSTALLED DURING FIRST PHASE OF NATURE AND EXTENT CHARACTERIZATION.
5. DP-1, DP-2, AND DP-3 DRILLED AND SAMPLED DURING SECOND PHASE OF NATURE AND EXTENT CHARACTERIZATION.
6. HIGH-CAPACITY WELLS "A", "B", AND "D" ARE INACTIVE (PUMPS HAVE BEEN REMOVED).
7. HIGH-CAPACITY WELLS "C", "E", "F", "G", AND "H" ARE CURRENTLY ACTIVE AND SHOWN FOR LOCATION PURPOSES ONLY.
8. COORDINATE SYSTEM FOR ALL POINTS IS STATE PLANE NAD 83, EAST ZONE

MONITORING WELL ID	CASING ELEVATION (FEET)	NORTHING	EASTING
MW-1	312.77	383,119.51	1,078,467.90
MW-1R	314.34	382,926.45	1,078,801.61
MW-2	308.01	383,207.42	1,079,751.30
MW-3	308.55	381,130.00	1,079,946.62
MW-4	305.61	380,804.62	1,077,766.95
MW-5	305.91	379,858.94	1,078,477.85
MW-6	307.72	379,874.77	1,079,384.36
MW-7	315.03	381,584.50	1,078,847.00
MW-8	304.77	380,311.20	1,077,940.08
MW-9	314.68	382,429.94	1,078,825.60
MW-10	304.28	381,324.39	1,076,261.22
NE-1	308.53	382,075.47	1,076,602.42
NE-2	306.30	381,536.65	1,076,600.17
NE-3	303.40	380,948.04	1,076,633.18
SG-N	305.42	383,289.97	1,076,382.88
SG-FB	306.00	381,881.66	1,076,423.14
SG-S	304.80	380,661.54	1,076,458.95
"A"	311.75	382,010.47	1,076,576.72
"B"	309.84	381,011.18	1,076,589.61
"C"	312.92	381,110.52	1,077,715.49
"D"	312.22	382,309.74	1,076,564.50
DP-1	N/A (TEMPORARY)	380,960*	1,075,639*
DP-2	N/A (TEMPORARY)	380,666*	1,076,582*
DP-3	N/A (TEMPORARY)	382,471*	1,078,818*

*LOCATION APPROXIMATE

FIGURE 1
SITE LOCATION MAP

SIKESTON POWER STATION
ASSESSMENT OF
CORRECTIVE MEASURES

SURVEYED	DESIGNED	DRAWN	CHECKED	APPROVED	DATE	SCALE	PROJECT NAME	FILE NAME	SHEET #
N/A	KE	CM	KE	MCC	02/25	1" = 600'	SIKESTON ACM	Base-Site-01	1 OF 1

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FILE PATH: O:\CADDFiles\SIKESTON\AOCM\DRAWINGS\Base-Site-01.dwg

ORIGINAL SHEET SIZE: 8.5" X 11"

PRINTED ON: 3/19/25 BY: cm

FILE PATH AND FILENAME: O:\CADDFiles\SIKESTON\AOCM\DRAWINGS\Base-Site-03.dwg

SOURCE: U.S. GEOLOGICAL SURVEY (MILLER, 1993)

FIGURE 2 PHYSIOGRAPHIC PROVINCES OF MISSOURI

SIKESTON POWER STATION ASSESSMENT OF CORRECTIVE MEASURES

GREDELL
ENGINEERING RESOURCES
CIVIL • GEOTECHNICAL • ENVIRONMENTAL • GEOLOGY • EARTH SCIENCES
1505 East High Street
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MO CORP. ENGINEERING LICENSE NO. E-2001001669-D

DATE	SCALE	PROJECT NAME	REVISION
02/25	AS NOTED	SIKESTON ACM	NA
DRAWN	APPROVED	FILE NAME	SHEET #
BM	MCC	BASE-SITE-03	1 OF 1

ORIGINAL SHEET SIZE: 8.5" X 11"

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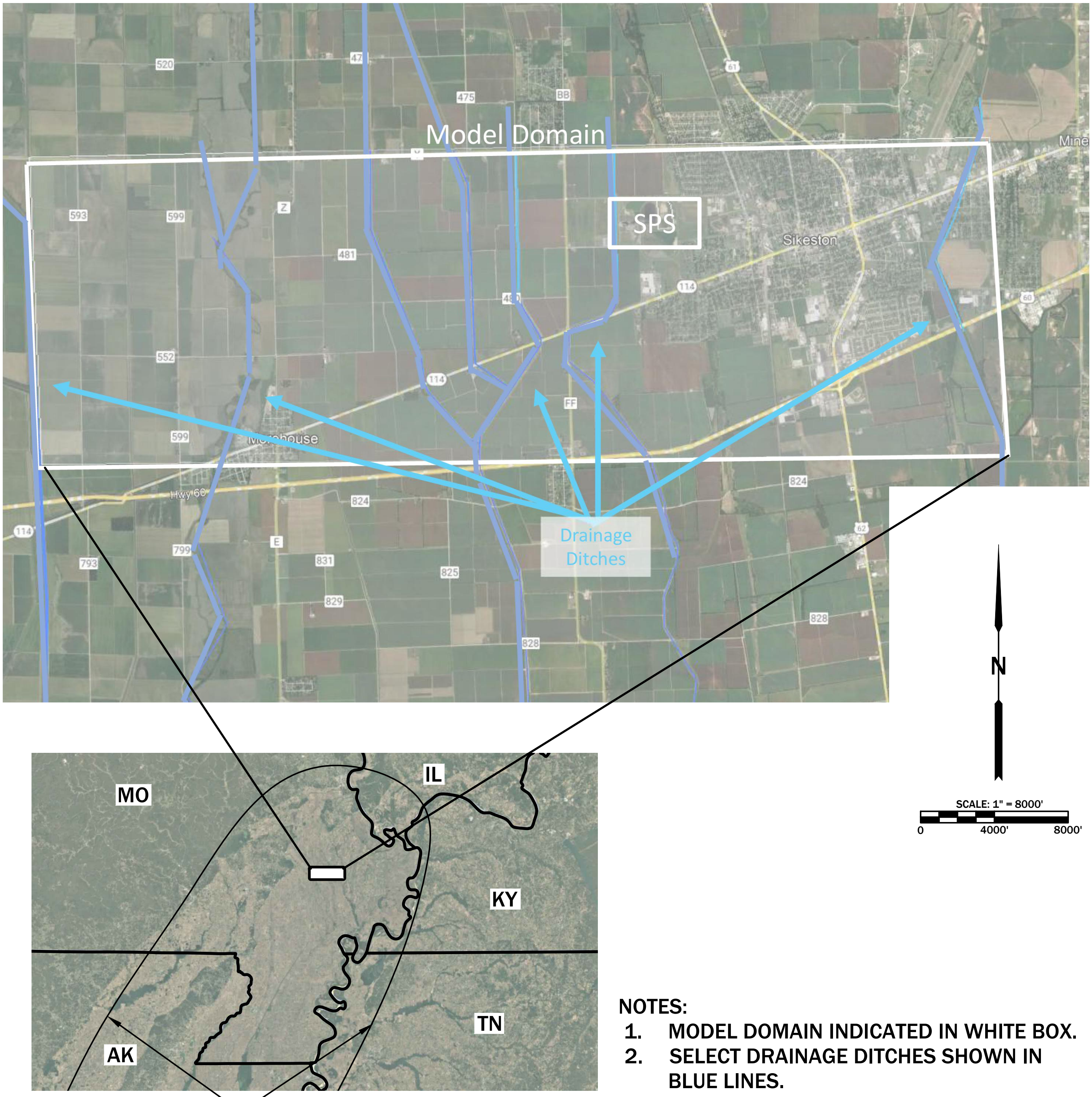
FILE PATH AND FILENAME: O:\CADDFiles\SIKESTON\AOCM\DRAWINGS\Base-Site-04.dwg



APPROXIMATE EXTENT OF SURFICIAL ALLUVIUM (SOUTHEASTERN LOWLAND PHYSIOGRAPHIC PROVINCE)

NOTES:

1. MODEL DOMAIN INDICATED IN WHITE BOX.
2. SELECT DRAINAGE DITCHES SHOWN IN BLUE LINES.

FIGURE 3 REGIONAL SITE LOCATION MAP AND MODEL DOMAIN

SIKESTON POWER STATION ASSESSMENT OF CORRECTIVE MEASURES

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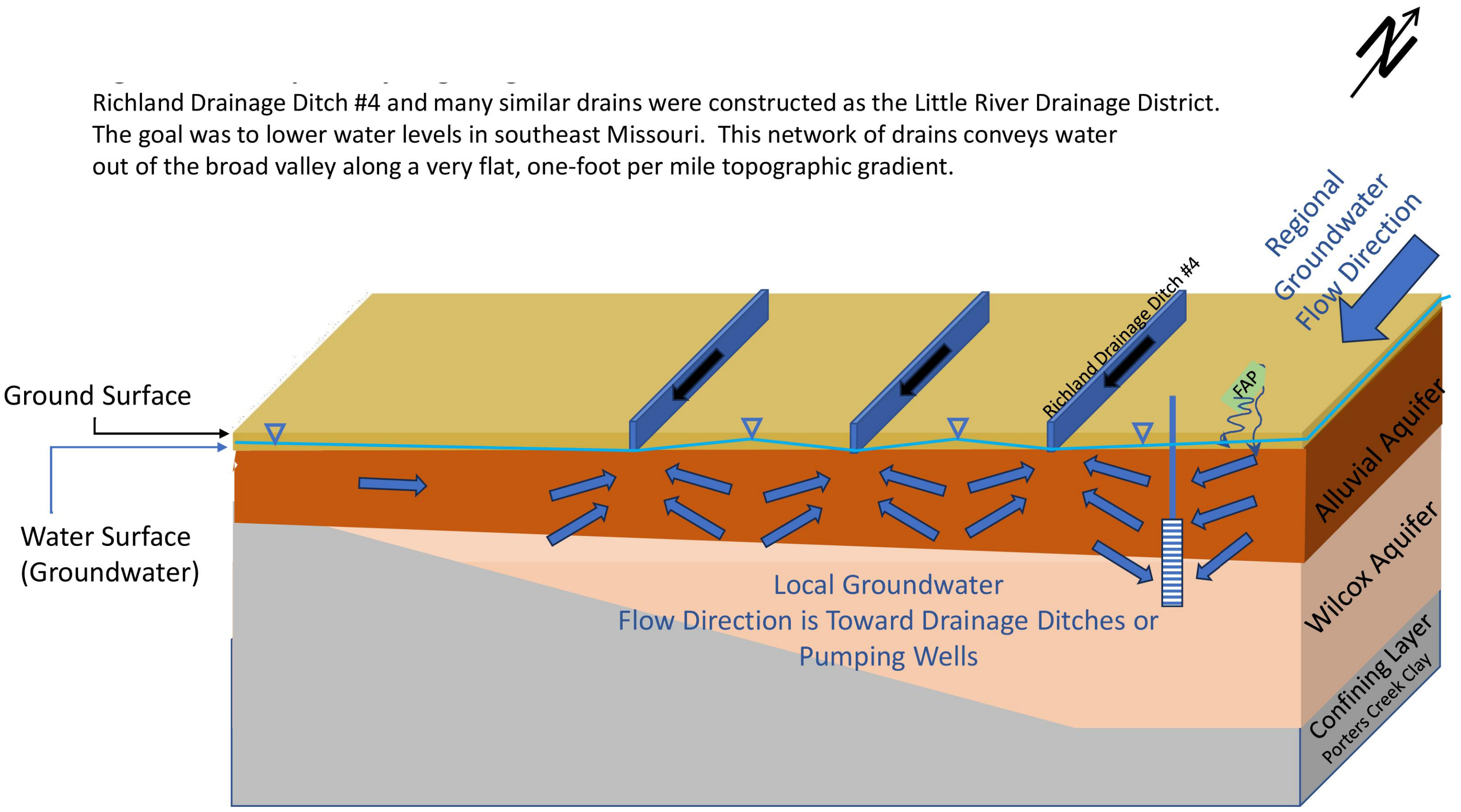
02/25	AS NOTED	SIKESTON ACM	N/A
DRAWN	APPROVED	FILE NAME	SHEET #
BM	MCC	BASE-SITE-04	1 OF 1



Richland Drainage Ditch #4 and many similar drains were constructed as the Little River Drainage District. The goal was to lower water levels in southeast Missouri. This network of drains conveys water out of the broad valley along a very flat, one-foot per mile topographic gradient.

Local Groundwater
Flow Direction is Toward Drainage Ditches or
Pumping Wells

CONCEPTUAL DRAWING:
NOT TO SCALE HORIZONTALLY OR VERTICALLY

FIGURE 4A CONCEPTUAL HYDROGEOLOGIC MODEL - POST DRAIN CONSTRUCTION

SIKESTON POWER STATION ASSESSMENT OF CORRECTIVE MEASURES

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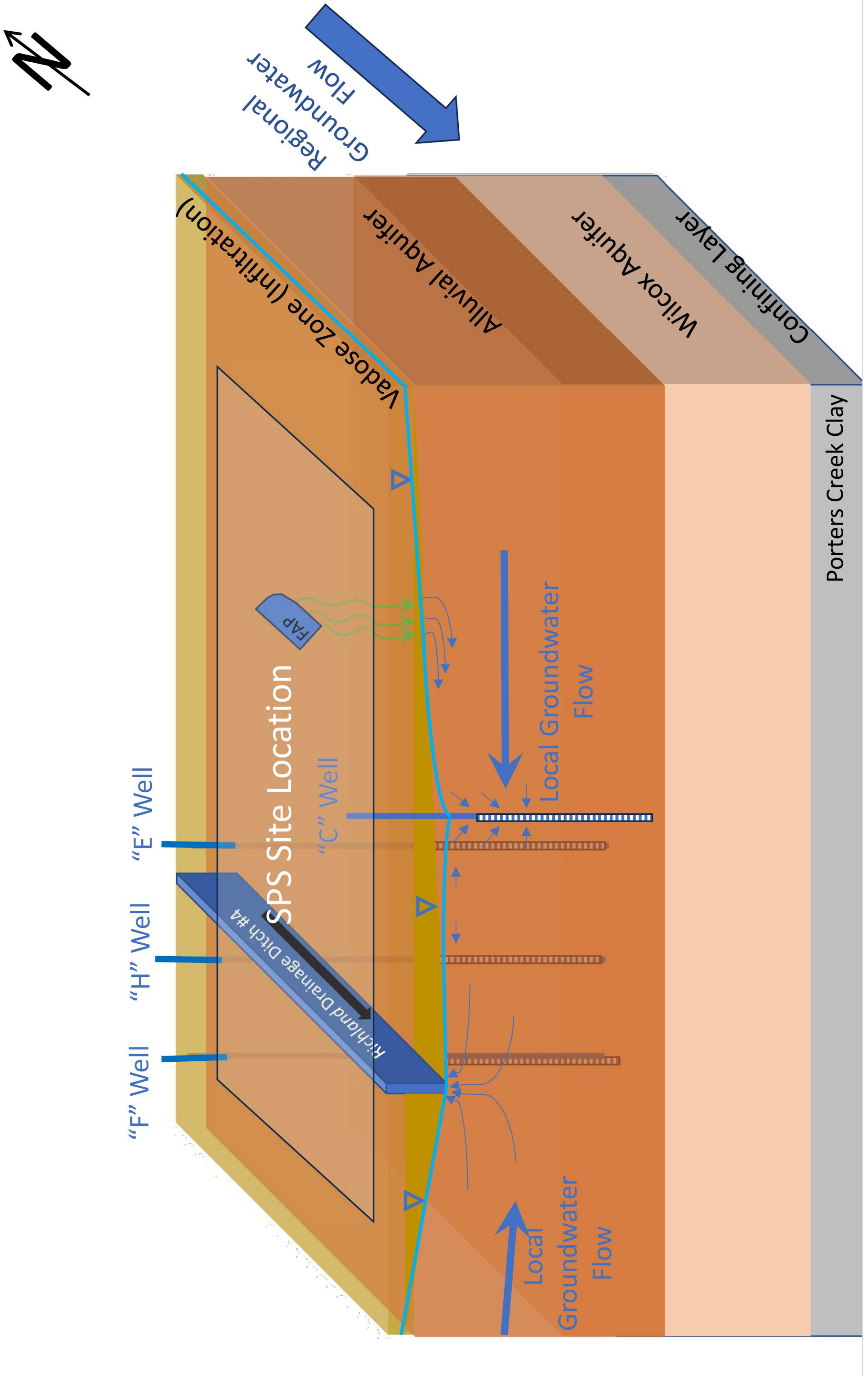
DATE	SCALE	PROJECT NAME	REVISION
02/25	N.T.S.	SIKESTON ACM	N/A
DRAWN	APPROVED	FILE NAME	SHEET #
BM	MCC	BASE-SITE-04	1 OF 1

ORIGINAL SHEET SIZE: 8.5" X 11"



CONCEPTUAL DRAWING:
NOT TO SCALE HORIZONTALLY OR VERTICALLY

FIGURE 4B CONCEPTUAL HYDROGEOLOGIC SITE MODEL - POST DRAIN CONSTRUCTION - SITE SCALE

SIKESTON POWER STATION
ASSESSMENT OF CORRECTIVE MEASURES

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DATE	SCALE	PROJECT NAME	REVISION
02/25	N.T.S.	SIKESTON ACM	N/A
DRAWN	APPROVED	FILE NAME	SHEET #
BM	MCC	BASE-SITE-04	1 OF 1

PRINTED ON: 3/19/25 BY: cm

FILE PATH AND FILENAME: O:\CADDFiles\SIKESTON\AOCM\DRAWINGS\Base-Site-04.dwg

ORIGINAL SHEET SIZE: 8.5" X 11"

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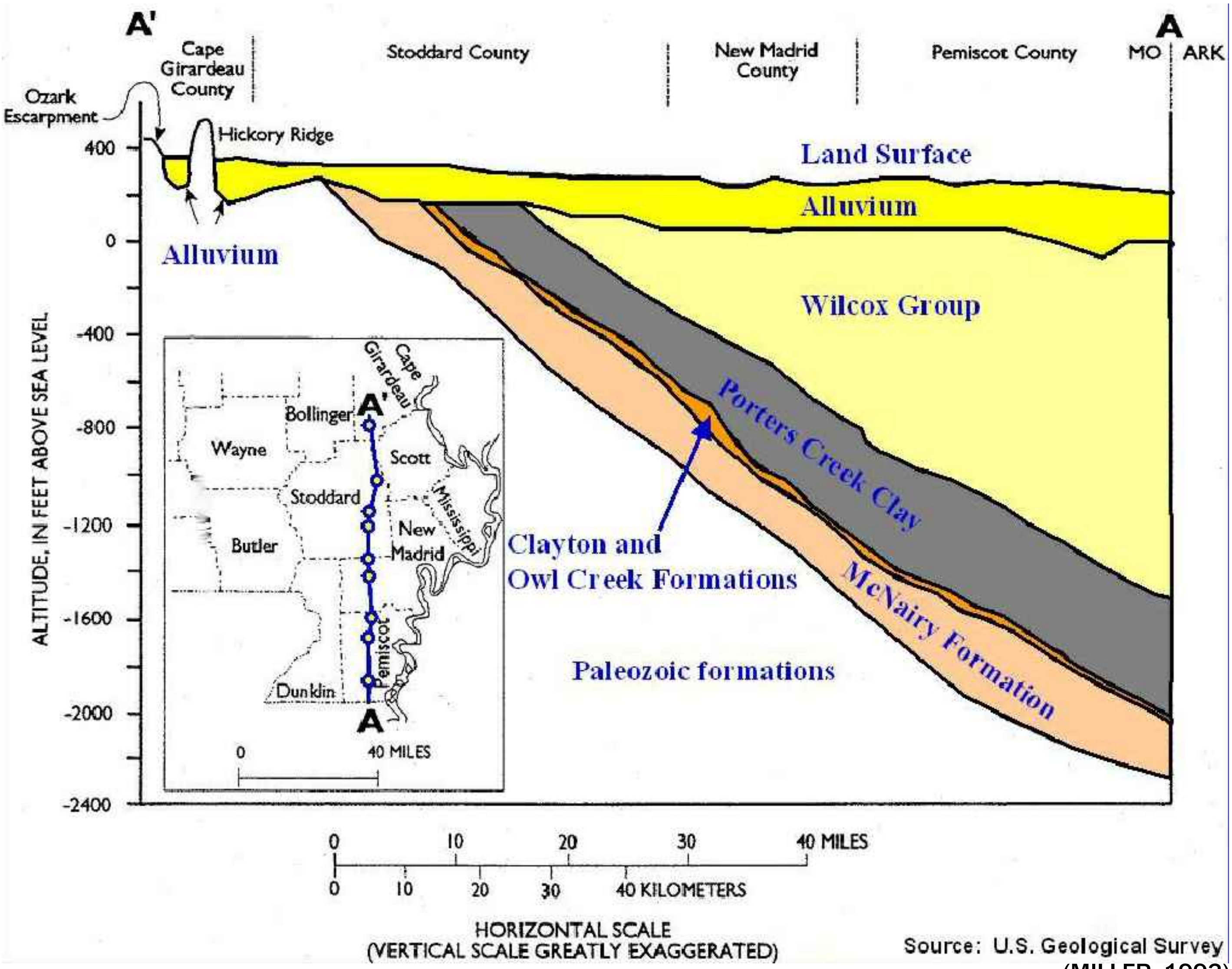
FILE PATH AND FILENAME: O:\CADDFiles\SIKESTON\AOCM\DRAWINGS\Base-Site-04.dwg



Source: U.S. Geological Survey
(MILLER, 1993)

FIGURE 5 GENERALIZED GEOLOGIC SECTION THROUGH SOUTHEAST MISSOURI

SIKESTON POWER STATION
ASSESSMENT OF CORRECTIVE MEASURES

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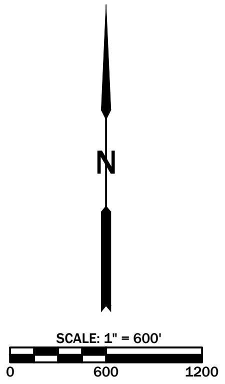
DATE	SCALE	PROJECT NAME	REVISION
02/25	AS NOTED	SIKESTON ACM	N/A
DRAWN	APPROVED	FILE NAME	SHEET #
BM	MCC	BASE-SITE-04	1 OF 1



LEGEND

PROPERTY LINE (APPROX.)	—PL—
MONITORING WELL	MW MW-10
SAMPLE LOCATION	
UP GRADIENT MONITORING LOCATION	UG
DOWN GRADIENT MONITORING LOCATION	DG
GROUNDWATER FLOW	←

NOTES:

1. IMAGE PROVIDED BY BING MAPS.
2. MONITORING WELL LOCATIONS, CASING ELEVATIONS & UNDERGROUND CULVERT ELEVATIONS SURVEYED BY BOWEN ENGINEERING & SURVEYING.

FIGURE 6
CONCEPTUAL LOCATIONS FOR CM#3 EXTRACTION AND INJECTION SYSTEM WELLS

SIKESTON POWER STATION
ASSESSMENT OF
CORRECTIVE MEASURES

SHEET #	1 OF 1
FILE NAME	Base-Site-02
PROJECT NAME	SIKESTON ACM
SCALE	N.T.S.
DATE	02/25
APPROVED	MCC
CHECKED	KE
DRAWN	CM
DESIGNED	KE
SURVEYED	N/A

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FILE PATH: O:\CADDFiles\SIKESTON\AOCM\DRAWINGS\Base-Site-02.dwg

ORIGINAL SHEET SIZE: 8.5" X 11"

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FILE PATH AND FILENAME: O:\CADDFiles\SIKESTON\AOCM\DRAWINGS\Base-Site-04.dwg

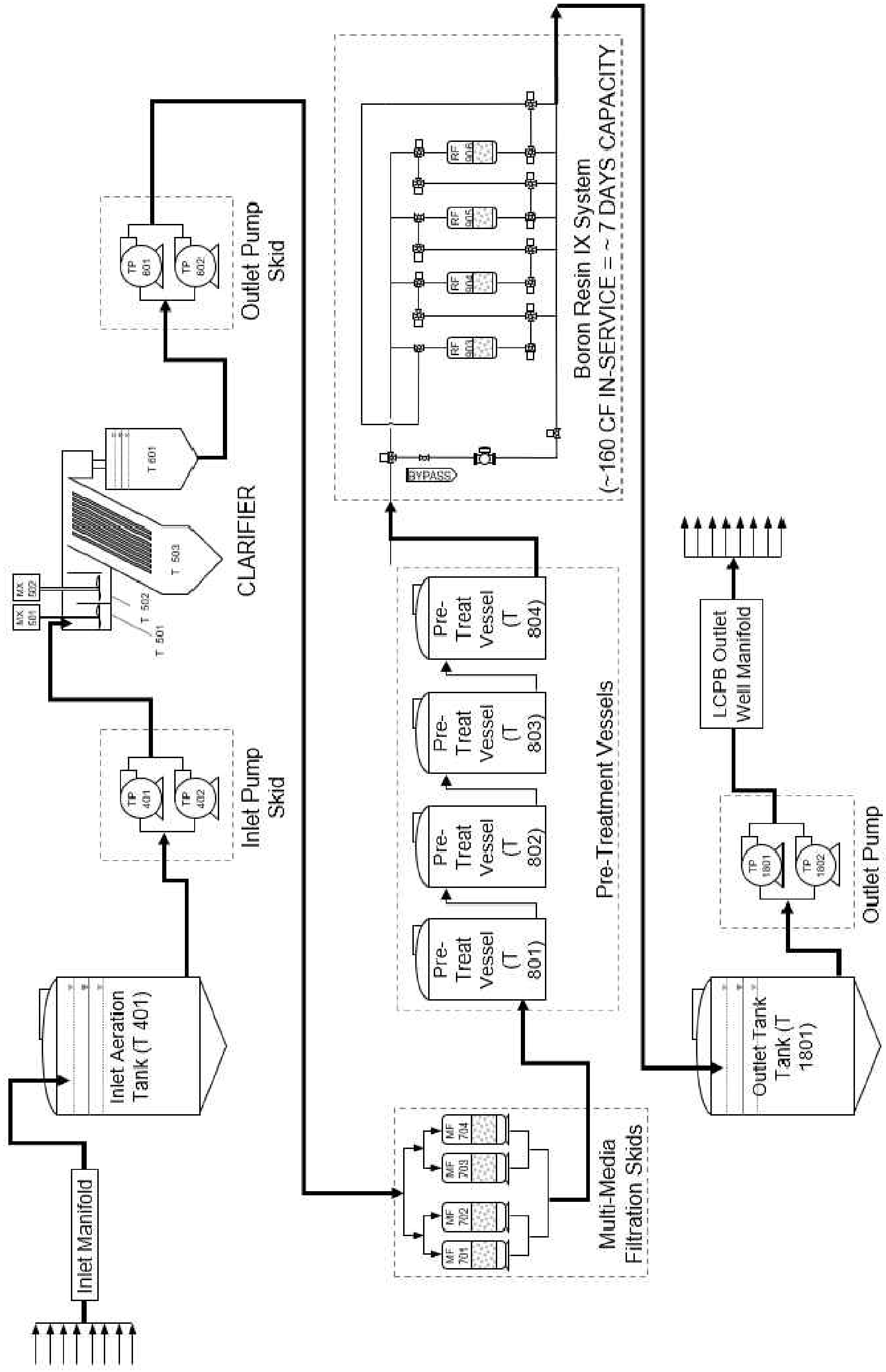

FIGURE 7 TYPICAL CCR GROUNDWATER TREATMENT SYSTEM

SIKESTON POWER STATION ASSESSMENT OF CORRECTIVE MEASURES

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DATE	SCALE	PROJECT NAME	REVISION
02/25	N.T.S.	SIKESTON ACM	N/A
DRAWN	APPROVED	FILE NAME	SHEET #
BM	MCC	BASE-SITE-04	1 OF 1

Tables

Assessment of Corrective Measures Report for Fly Ash Pond
SBMU - Sikeston Power Station
Scott County, Missouri

Table 1
Groundwater and Surface Water Sampling Location Summary

Well ID[1,2]	Previous ID (if any)	CCR Compliance Monitoring System	NPDES Groundwater Monitoring System	Northing Location[3,4]	Easting Location[3,4]	Ground Surface Elevation[3,4] (feet)	Top of Riser Elevation[3,4] (feet)	Well Depth[5] (feet)	Base of Well Elevation[6] (feet)	Screen Length[7] (feet)	Top of Screen Elevation (feet)
MW-1*	TPZ-1	none	Yes	383119.51	1078467.90	310.41	312.77	37.84	274.93	10	285.1
MW-1R	none	FAP	No	382926.45	1078801.61	311.41	314.34	38.16	276.10	10	286.4
MW-2	TPZ-2	FAP	Yes	383207.42	1079751.30	305.53	308.01	37.42	270.59	10	280.8
MW-3	TPZ-3	FAP & BAP	Yes	381130.00	1079946.62	306.11	308.55	37.21	271.34	10	281.5
MW-4	TPZ-4	BAP	Yes	380804.62	1077766.95	303.26	305.61	37.55	268.06	10	278.3
MW-5	TPZ-5	BAP	Yes	379858.94	1078477.85	303.57	305.91	37.17	268.74	10	278.9
MW-6	TPZ-6	BAP	Yes	379874.77	1079384.36	305.37	307.72	38.03	269.69	10	279.9
MW-7	none	FAP	Yes	381584.50	1078847.00	312.70	315.03	37.37	277.66	10	287.9
MW-8	none	BAP	Yes	380311.20	1077940.08	302.37	304.77	37.41	267.36	10	277.6
MW-9	none	FAP	Yes	382429.94	1078825.60	311.85	314.68	37.28	277.40	10	287.6
MW-10	none	FAP	No	381324.39	1076261.22	300.70	304.28	32.9	271.38	10	281.4
NE-1	none (Nature and Extent Characterization Piezometers)	none (Nature and Extent Characterization Piezometers)	No	382075.47	1076602.42	306.0	308.53	32.5	276.0	10	286.2
NE-2			No	381536.65	1076600.17	303.3	306.30	33.0	273.3	10	283.5
NE-3			No	380948.04	1076633.18	300.1	303.40	32.3	271.1	10	281.3
"A" Well	none (Inactive High-Capacity Well)	none (Inactive High-Capacity Well)	No	382010.47	1076576.72	312	311.75	175	140	43	183
"B" Well			No	381011.18	1076589.61	310	309.84	179	136	43	179
"C" Well	none (High-Capacity Well)	none (High-Capacity Well)	No	381110.52	1077715.49	313	312.92	181	135	47	182
"D" Well	none (Inactive High-Capacity Well)	none (Inactive High-Capacity Well)	No	382309.74	1076564.50	312	312.22	166	151	40	191
DP-1-150 [9]	none (Nature and Extent Characterization Temporary Piezometers)	none (Nature and Extent Characterization Temporary Piezometers)	No	380960	1075640	300	none (temporary)	151	156.0	2	157
DP-2-150 [9]			No	380667	1076583	303	none (temporary)	154	159.0	2	158
DP-3-75 [9]			No	382472	1078818	312	none (temporary)	79	238.00	2	237
DP-3-150 [9]			No	382471	1078855	312	none (temporary)	144	168.00	2	167

NOTES:

1. Refer to Figure 1 for monitoring well locations.
2. Refer to Sikeston Power Station On-Site Operating Record for well construction diagrams.
3. Monitoring well survey data provided by Bowen Engineering & Surveying, Inc.
4. Horizontal Datum: Missouri State Plane Coordinates - NAD 83 (Feet), Vertical Datum: NAVD 88 (Feet).
5. Depth measurements relative to surveyed point on top of well casing.
6. Sump installed at base of screen (0.2 feet length).
7. Actual screen length (9.7 feet) is the machine-slotted section of the 10-foot length of Schedule 40 PVC pipe.
8. * = MW-1 removed from Fly Ash Pond Monitoring System following installation and completion of background sampling of MW-1R on March 2, 2022.
9. Temporary Piezometers installed with Direct Push Drilling. Locations approximated with GPS.

Prepared by: KAE
Checked by: MCC
Approved by: TRG

Prepared by: GREDELL Engineering Resources, Inc.

Assessment of Corrective Measures Report for Fly Ash Pond
SBMU - Sikeston Power Station
Scott County, Missouri

Table 2
Historical Groundwater Level Summary

Well ID	MW-1*	MW-2	MW-3	MW-7	MW-9	MW-1R
Date	Groundwater Elevation (feet MSL)					
05/12/16	297.50	298.66	298.13	NM	NM	NM
06/28/16	296.60	298.01	297.58	NM	NM	NM
07/15/16	296.57	297.86	297.37	NM	NM	NM
08/08/16	295.62	297.06	297.05	NM	NM	NM
09/08/16	296.06	297.27	296.76	NM	NM	NM
10/05/16	295.86	296.96	296.40	NM	NM	NM
11/01/16	295.47	296.66	296.10	NM	NM	NM
11/30/16	295.45	296.60	296.03	NM	NM	NM
01/24/17	NM	NM	296.35	NM	NM	NM
01/26/17	295.77	296.76	296.35	NM	NM	NM
02/22/17	NM	NM	296.00	NM	NM	NM
02/24/17	295.47	296.40	296.00	NM	NM	NM
03/20/17	296.11	296.96	296.45	NM	NM	NM
04/19/17	296.04	296.86	296.35	NM	NM	NM
04/27/17	NM	NM	296.72	NM	NM	NM
05/17/17	NM	NM	297.81	NM	NM	NM
06/08/17	NM	NM	297.81	NM	NM	NM
07/13/17	NM	NM	296.98	NM	NM	NM
10/31/17	NM	NM	295.22	NM	NM	NM
03/21/18	295.92	296.96	296.65	295.83	296.13	NM
04/15/18	297.07	297.86	297.60	296.95	297.18	NM
05/23/18	296.78	298.01	297.62	296.66	296.98	NM
06/13/18	NM	NM	297.33	NM	NM	NM
06/27/18	296.37	297.61	297.21	296.26	296.56	NM
08/01/18	295.22	296.60	296.15	295.08	295.48	NM
09/05/18	294.79	296.11	295.68	294.71	295.01	NM
11/06/18	295.01	296.21	295.74	294.85	295.17	NM
11/26/18	NM	NM	295.63	NM	NM	NM
12/12/18	295.12	296.21	295.79	295.06	295.36	NM
01/08/19	295.66	296.72	296.38	295.53	295.80	NM
02/05/19	NM	NM	296.73	NM	NM	NM
02/22/19	297.70	298.67	298.35	297.59	297.84	NM
03/27/19	297.69	298.93	298.51	297.58	297.93	NM
04/16/19	298.15	299.29	298.93	298.01	298.38	NM
05/14/19	298.27	299.66	299.25	298.15	298.52	NM
05/28/19	NM	NM	298.95	NM	NM	NM
06/12/19	297.82	299.24	298.82	297.76	298.10	NM
07/17/19	297.32	298.77	298.38	297.25	297.55	NM
07/24/19	297.40	298.80	298.41	297.33	297.65	NM
08/14/19	296.61	298.15	297.80	296.65	296.96	NM
08/28/19	NM	NM	297.55	NM	NM	NM
09/16/19	296.24	297.70	297.22	296.14	296.50	NM
09/24/19	296.09	297.53	297.05	295.98	296.33	NM
10/10/19	295.92	297.29	296.84	295.80	296.13	NM
10/22/19	295.92	297.24	296.80	295.74	296.12	NM
11/04/19	NM	NM	297.34	NM	NM	NM
01/28/20	297.61	298.73	298.34	297.42	297.80	NM
02/18/20	NM	NM	299.00	NM	NM	NM
03/30/20	NM	NM	300.09	NM	NM	NM
04/06/20	299.16	300.40	300.00	298.99	299.41	NM
05/21/20	298.50	300.02	299.55	NM	298.71	NM
09/22/20	296.53	297.97	297.47	296.33	296.78	NM
12/08/20	296.63	298.00	NM	NM	NM	NM
01/26/21	NM	NM	NM	296.51	296.82	NM
04/17/21	297.32	298.49	298.05	297.08	297.48	NM
10/20/21	295.36	296.55	296.04	295.08	295.53	295.69
04/09/22	NM	298.06	297.60	296.78	297.18	297.29
08/02/22	NM	297.01	296.55	295.38	295.85	296.04
11/02/22	NM	295.79	295.24	294.33	294.78	294.96
03/12/23	NM	297.21	296.75	295.80	296.27	296.45
12/11/23	NM	296.31	295.81	294.86	295.28	295.44
04/23/24	NM	296.71	296.20	295.38	295.83	296.30

NOTES:

1. Refer to Figure 1 for monitoring well locations.
2. Refer to Sikeston Power Station On-Site Operating Record for well construction diagrams.
3. NM - Not Measured.
4. Maximum and minimum groundwater elevations are shaded.
5. * = MW-1 removed from Fly Ash Pond Monitoring System following installation and completion of background sampling of MW-1R on March 2, 2022.

Prepared by: KAE
Checked by: MCC
Approved by: TRG

Assessment of Corrective Measures Report for Fly Ash Pond
SBMU - Sikeston Power Station
Scott County, Missouri

Table 3
Groundwater Protection Standards for Assessment Monitoring Constituents

Constituent	Units	MCL or Health-Based Groundwater Protection Standards
Antimony	ug/L	6
Arsenic	ug/L	10
Barium	ug/L	2000
Beryllium	ug/L	4
Cadmium	ug/L	5
Chromium	ug/L	100
Cobalt	ug/L	6
Fluoride	mg/L	4
Lead	ug/L	15
Lithium	ug/L	40
Mercury	ug/L	2
Molybdenum	ug/L	100
Selenium	ug/L	50
Thallium	ug/L	2
Radium 226/228 (Combined)	pCi/L	5

NOTES:

1. ug/L - micrograms per liter.
2. mg/L - milligrams per liter.
3. pCi/L - picocuries per liter.
4. MCL - Maximum Contaminant Level per CFR 40 Subchapter D Part 141 subpart G Section 141.62 & 141.66, or Part 257 subpart D Section 257.95(h)(2).

Prepared by: KAE
Checked by: MCC
Approved by: TRG

Assessment of Corrective Measures Report for Fly Ash Pond
SBMU - Sikeston Power Station
Scott County, Missouri

Table 4
Groundwater and Surface Water Quality Data Summary

			Appendix III Monitoring Constituents (Detection)							Appendix IV Monitoring Constituents (Assessment)													
Well	Approx. Sample Elevation	Date Sampled	pH	Chloride	Fluoride	Sulfate	TDS	Boron	Calcium	Antimony	Arsenic	Barium	Beryllium	Cadmium	Chromium	Cobalt	Lead	Lithium	Mercury	Molybdenum	Selenium	Thallium	Radium 226/228 (Combined)
ID	ft		S.U.	mg/L	mg/L	mg/L	mg/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	pCi/L
Site Specific Groundwater Protection Standard[3]										6	10	2000	4	5	100	6	15	40	2	100	50	2	5
NE-1	276.0	2/15/2023	6.78	**9.9**	<0.250	**86**	**360**	**580**	**90**	<3.0	<1.0	**190**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**9.8**	<1.0	<1.0	< 0.741
NE-2	273.3	2/15/2023	7.04	**18**	**0.256**	**42**	**300**	**120**	**72**	<3.0	**1.0**	**470**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**2.6**	<1.0	<1.0	< 0.985
NE-3	271.1	2/15/2023	7.14	**1.5**	<0.250	**33**	**300**	**77**	**82**	<3.0	**1.5**	**300**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**2.2**	**1.3**	<1.0	< 0.000
MW-1	280.4	2/22/2023	7.21	**5.4**	<0.250	**15**	**170**	**300**	**35**	<3.0	**1.1**	**180**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	<1.0	<1.0	<1.0	< 0.260
MW-1R	282.4	3/12/2023	6.60	**10**	<0.250	**140**	**300**	**3,000**	**70**	(NA)	(NA)	**52**	(NA)	(NA)	(NA)	**7.9**	(NA)	<20	(NA)	**180**	<1.0	(NA)	< 1.03
MW-2	276.5	3/12/2023	6.51	**1.3**	<0.250	**8.7**	700 H	**29**	**12**	(NA)	(NA)	**100**	(NA)	(NA)	(NA)	<2.0	(NA)	<20	(NA)	<1.0	<1.0	(NA)	< 0.630
MW-3	277.1	3/12/2023	6.51	<1.0	<0.250	**13**	**93 H**	**31**	**14**	(NA)	(NA)	**110**	(NA)	(NA)	(NA)	<2.0	(NA)	<20	(NA)	<1.0	<1.0	(NA)	< 0.779
MW-4	274.3	10/20/2022	7.4	**17**	<0.250	**96**	**330**	**1000**	**80**	<3.0	<1.0	**82**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**5.7**	<1.0	<1.0	< 0.375
MW-5	274.6	10/20/2022	6.9	**15**	<0.250	**220**	**590**	**360**	**120**	<3.0	<1.0	**80**	<1.0	<1.0	<4.0	**3.1**	<1.0	<20	<0.20	<1.0	<1.0	<1.0	< 0.610
MW-6	276.4	10/20/2022	7.0	**2.4**	<0.250	**24**	**250**	**47**	**49**	<3.0	**3.4**	**210**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	<1.0	<1.0	<1.0	< 1.579
MW-7	282.7	3/12/2023	7.40	**3.7**	**0.635**	**190**	**520**	**2,600**	**140**	(NA)	(NA)	**77**	(NA)	(NA)	(NA)	**4.1**	(NA)	**27**	(NA)	**120**	**4.1**	(NA)	< 0.976
MW-8	272.4	10/20/2022	7.2	**56**	<0.250	**130**	**460**	**510**	**110**	<3.0	<1.0	**77**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	<1.0	<1.0	<1.0	< 1.384
MW-9	281.9	3/12/2023	7.43	**11**	**1.02**	**160**	**480**	**3,600**	**95**	(NA)	(NA)	**85**	(NA)	(NA)	(NA)	<2.0	(NA)	<20	(NA)	**160**	<1.0	(NA)	< 1.50
MW-10	270.7	2/15/2023	7.02	**14**	<0.250	**120**	**360**	**340**	**78**	<3.0	**6.7**	**140**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**23**	<1.0	<1.0	< 0.773
MW-10 (dup)	270.7	2/15/2023	7.02	**13**	<0.250	**120**	**340**	**340**	**81**	<3.0	**6.9**	**150**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**25**	<1.0	<1.0	< 0.681
SG-N	~293 [9]	2/15/2023	7.99	**8.8**	<0.250	**33**	**190**	**18**	**47**	<3.0	**1.6**	**310**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	<1.0	<1.0	<1.0	< 0.549
SG-OF-50	~293 [9]	2/15/2023	8.04	**9.3**	<0.250	**47**	**180**	**36**	**50**	<3.0	**1.8**	**300**	<1.0	**2.2**	<4.0	<2.0	<1.0	<20	<0.20	**1.5**	<1.0	<1.0	< 1.32
SG-S	~293 [9]	2/15/2023	7.86	**9.7**	<0.250	**70**	**210**	**81**	**62**	<3.0	**2.4**	**320**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**3.9**	<1.0	<1.0	< 0.287
"A" Well (150')	162	2/15/2023	7.32	**14**	<0.250	**83**	**320**	**1,100**	**77**	<3.0	**6.4**	**150**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**58**	<1.0	<1.0	< 0.436
"B" Well (133')	177	3/22/2023	7.44	NT	NT	NT	NT	NT	NT	NT	**10.0**	NT	NT	NT	NT	NT	NT	NT	NT	**110**	NT	NT	NT
"B" Well (133') (dup)	177	3/22/2023	7.44	NT	NT	NT	NT	NT	NT	NT	**15.0**	NT	NT	NT	NT	NT	NT	NT	NT	**165**	NT	NT	NT
"B" Well (150')	160	2/15/2023	7.43	**27**	<0.250	**180**	**470**	**980**	**87**	<3.0	**14.0**	**350**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**150**	<1.0	<1.0	< 0.258
"B" Well (150')	160	3/22/2023	7.28	NT	NT	NT	NT	NT	NT	NT	**27.0**	NT	NT	NT	NT	NT	NT	NT	NT	**170**	NT	NT	NT
"B" Well (150') (dup)	160	3/22/2023	7.28	NT	NT	NT	NT	NT	NT	NT	**17.5**	NT	NT	NT	NT	NT	NT	NT	NT	**114**	NT	NT	NT
"B" Well (167')	143	3/22/2023	7.41	NT	NT	NT	NT	NT	NT	NT	**8.9**	NT	NT	NT	NT	NT	NT	NT	NT	**56**	NT	NT	NT
"B" Well (167') (dup)	143	3/22/2023	7.41	NT	NT	NT	NT	NT	NT	NT	**10.2**	NT	NT	NT	NT	NT	NT	NT	NT	**52**	NT	NT	NT
"C" Well	182 - 135 [10]	2/15/2023	7.34	**12**	<0.250	**71**	**180**	**360**	**78**	<3.0	**9.9**	**130**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**52**	<1.0	<1.0	< 0.851
"D" Well (130')	182	2/15/2023	7.25	**24**	<0.250	**25**	**140**	**290**	**50**	<3.0	**7.7**	**190**	<1.0	<1.0	<4.0	<2.0	<1.0	<20	<0.20	**14**	<1.0	<1.0	< 0.608
DP-1-150	156 [11]	8/2/2023	7.42	NT	NT	NT	NT	NT	NT	NT	**8.7**	NT	NT	NT	NT	NT	NT	NT	NT	**80.5**	NT	NT	NT
DP-2-150	159 [11]	8/3/2023	7.36	NT	NT	NT	NT	NT	NT	NT	**2.2**	NT	NT	NT	NT	NT	NT	NT	NT	**28.5**	NT	NT	NT
DP-3-75	238 [11]	8/1/2023	7.34	NT	NT	NT	NT	NT	NT	NT	0.4 "J"	NT	NT	NT	NT	NT	NT	NT	NT	**54.5**	NT	NT	NT
DP-3-150	168 [11]	8/4/2023	7.44	NT	NT	NT	NT	NT	NT	NT	**7.6**	NT	NT	NT	NT	NT	NT	NT	NT	**26.5**	NT	NT	NT

NOTES:

1. All data transcribed from analytical lab data sheets or field notes.
2. Barium, Chromium, Cobalt, Lithium, Molybdenum, Selenium, and Radium 226/228 shaded to indicate these constituents were detected during Noveber 2022 Fly Ash Pond assessment groundwater monitoring.
3. Site Specific Groundwater Protection Standard developed for SBMU-SPS FAP per 40 CFR 257.95(h).
4. Less than (<) symbol denotes concentration not detected above reportable limits. Bold values indicate analyte detected at or above reporting limit.
5. NT denotes that analysis was not conducted.
6. Radium 226 and 228 (Combined) concentration not detected above minimum detectable concentration for samples presented above.
7. (NA) denotes that constituent was not analyzed as a result of not being detected during November 2022 sampling event per 40 CFR 257.95(d).
8. Radium 226/228 (Combined) assumes a concentration of 0 for negative values reported.
9. Surface water sample of Richland Drainage Ditch #4.
10. Sample taken with sample port of pumping well. Screen interval shown for sample collection depth.
11. Temporary Piezometers installed with Direct Push Drilling, Locations Approximated with GPS.

Prepared by: KAE
Checked by: MCC
Approved by: TRG

Assessment of Corrective Measures Report for Fly Ash Pond
SBMU - Sikeston Power Station
Scott County, Missouri

Table 5
Corrective Measure Alternative Comparison - Fly Ash Pond

Evaluation Criteria Category # 1 (Performance) Long and Short Term Effectiveness, Protectiveness, and Certainty of Success		Alternative 1 CIP & MNA	Alternative 2 CIP, CTP & MNA	Alternative 3 CIP, GITR & MNA	Alternative 4 CBR & MNA
Sub-Criteria	Sub-Criterion #1 Magnitude of reduction of risks	1	1	0	-1
	Sub-Criterion #2 Magnitude of residual risk in terms of likelihood of further release	0	1	1	-1
	Sub-Criterion #3 Type and degree of long-term management required	1	0	0	-1
	Sub-Criterion #4 Short term risk to community or environment during implementation	1	1	1	-1
	Sub-Criterion #5 Time until full protection is achieved	1	1	0	-1
	Sub-Criterion #6 Potential for exposure of humans and environmental receptors to remaining wastes	1	1	0	-1
	Sub-Criterion #7 Long-term reliability of engineering and institutional controls	1	1	0	1
	Sub-Criterion #8 Potential need for replacement of the remedy	0	0	0	1
Evaluation Criteria Category #1 (Performance) - SUMMARY		**(6) Favorable**	**(6) Favorable**	**(2) Less Favorable**	**(Less than Zero) Unfavorable**

Evaluation Criteria Category #2 (Constructability) Effectiveness in controlling the source to reduce further releases		Alternative 1 CIP & MNA	Alternative 2 CIP, CTP & MNA	Alternative 3 CIP, GITR & MNA	Alternative 4 CBR & MNA
Sub-Criteria	Sub-Criterion #1 Extent to which containment practices will reduce further releases	0	1	1	0
	Sub-Criterion #2 Extent to which treatment technologies may be used	1	1	0	1
Evaluation Criteria Category # 2 (Constructability) - SUMMARY		**(1) Less Favorable**	**(2) Favorable**	**(1) Less Favorable**	**(1) Less Favorable**

NOTES:

1. Alternatives are ranked relative to one another considering the criteria provided in 40 CFR 257.97 (and listed above) with the following quantitative rating sysytem:
   Alternatives that are the most favorable considering criteria above are ranked as 1 and colored green.
   Alternatives that are favorable, but less favorable than some of all other alternatives considered are ranked 0 (no points) and colored orange.
   Alternatives that are not favorable in consideration of the criterion are ranked -1 (subtract a point) and colored red.
2. Rank for each alternative is summed for Evaluation Criteria #1, #2, and #3 with totals provided in parenthesis and ranked qualitatively as less favorable, favorable, or unfavorable.

Prepared by: KAE
Checked by: MCC
Approved by: TRG

Assessment of Corrective Measures Report for Fly Ash Pond
SBMU - Sikeston Power Station
Scott County, Missouri

Table 5
Corrective Measure Alternative Comparison - Fly Ash Pond

Evaluation Criteria Category #3 (Implementation Concerns) **Ease of implementation**		**Alternative 1** CIP & MNA	**Alternative 2** CIP, CTP & MNA	**Alternative 3** CIP, GITR & MNA	**Alternative 4** CBR & MNA
Sub-Criteria	Sub-Criterion #1 Degree of difficulty associated with constructing the technology	1	1	0	-1
	Sub-Criterion #2 Expected operational reliability of the technologies	1	1	0	1
	Sub-Criterion #3 Need to coordinate with and obtain necessary approvals and permits from other agencies	1	1	0	-1
	Sub-Criterion #4 Availability of necessary equipment and specialists	1	1	1	-1
	Sub-Criterion (v) Available capacity and location of needed treatment, storage, and disposal services	1	1	0	0
Evaluation Criteria Category #3 (Implementation Concerns) - SUMMARY		**(5) Favorable**	**(5) Favorable**	**(1) Less Favorable**	**(Less than Zero) Unfavorable**

Evaluation Criterion #4 (Community Concerns) **The degree to which community concerns are addressed by a potential remedy(s)**	**Alternative 1** CIP & MNA	**Alternative 2** CIP, CTP & MNA	**Alternative 3** CIP, GITR & MNA	**Alternative 4** CBR & MNA

NOTES:

1. Alternatives are ranked relative to one another considering the criteria provided in 40 CFR 257.97 (and listed above) with the following quantitative rating sysytem:
   Alternatives that are the most favorable considering criteria above are ranked as 1 and colored green.
   Alternatives that are favorable, but less favorable than some of all other alternatives considered are ranked 0 (no points) and colored orange.
   Alternatives that are not favorable in consideration of the criterion are ranked -1 (subtract a point) and colored red.
2. Rank for each alternative is summed for Evaluation Criteria #1, #2, and #3 with totals provided in parenthesis and ranked qualitatively as less favorable, favorable, or unfavorable.

Appendices

Appendix A

Analytical Data Summaries for FAP Groundwater Sampling for the CCR Rule

Sikeston Board of Municipal Utilities - Sikeston Power Station
Fly Ash Pond Baseline Groundwater Statistical Evaluation
Scott County, Missouri

Appendix A - Analytical Data Summaries for FAP Groundwater Sampling for the CCR Rule

			Field Parameters						**Appendix III Monitoring Constituents (Detection)**						**Appendix IV Monitoring Constituents (Assessment)**																
Well	Date	Monitoring Purpose	Spec. Cond.	Temp.	ORP	D.O.	Turbidity	pH	Chloride	Fluoride	Sulfate	TDS	Boron	Calcium	Antimony	Arsenic	Barium	Beryllium	Cadmium	Chromium	Cobalt	Fluoride	Lead	Lithium	Mercury	Molybdenum	Selenium	Thallium	Radium 226	Radium 228	Radium 226/228 (Combined)
ID			μmhos/cm	°C	mV	mg/L	NTU	S.U.	mg/L	mg/L	mg/L	mg/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	pCi/L	pCi/L	pCi/L
Federal MCL									None	4.0	None	None	None	None	6	10	2000	4	5	100	6	4	15	40	2	100	50	2			5
MW-1R (DG) Baseline	10/20/2021	Background	511.3	15.25	32.2	6.41	4.62	6.55	**11**	<0.250	**130**	**330**	**2200**	**64**	<3.0	**1.3**	**40**	<1.0	<1.0	<4.0	**6.3**	<0.250	<1.0	**10**	<0.20	**160**	<1.0	<1.0	0.184	(0.0411)	0.184 (ND)
	11/1/2021	Background	532.4	12.98	16.9	0.60	5.38	6.55	**12**	**0.286**	**110**	**330**	**2100**	**58**	<3.0	**1.5**	**38**	<1.0	<1.0	<4.0	**5.4**	**0.286**	<1.0	<10	<0.20	**160**	<1.0	<1.0	0.0676	0.516	0.600(ND)
	11/16/2021	Background	540.4	11.47	41.9	0.94	1.27	6.54	**15**	**0.366**	**150**	**360**	**2800**	**73**	<3.0	<1.0	**49**	<1.0	<1.0	<4.0	**8.5**	**0.366**	<1.0	**10**	<0.20	**170**	<1.0	<1.0	0.513	0.552	1.065(ND)
	12/7/2021	Background	576.3	9.14	11.2	0.98	0.91	6.58	**13**	<0.250	**140**	**400**	**2300**	**61**	<3.0	<1.0	**37**	<1.0	<1.0	<4.0	**7.1**	<0.250	<1.0	**11**	<0.20	**190**	<1.0	<1.0	(0.298)	0.530	0.53(ND)
	12/27/2021	Background	757.3	8.40	21.7	1.28	1.32	6.48	**17**	<0.250	**210**	**390**	**3100**	**97**	<3.0	<1.0	**52**	<1.0	<1.0	<4.0	**9.6**	<0.250	<1.0	**19**	<0.20	**200**	<1.0	<1.0	(0.286)	0.430	0.430(ND)
	1/17/2022	Background	707.3	4.56	-0.3	1.02	1.46	6.56	**17**	<0.250	**190**	**440**	**2800**	**89**	<3.0	<1.0	**44**	<1.0	<1.0	<4.0	**7.9**	<0.250	<1.0	**17**	<0.20	**200**	<1.0	<1.0	(0.406)	0.556	0.556(ND)
	2/7/2022	Background	794.4	3.14	21.9	0.84	1.04	6.55	**19**	<0.250	**200**	**450**	**3500**	**90**	<3.0	<1.0	**51**	<1.0	<1.0	<4.0	**13.0**	<0.250	<1.0	**11**	<0.20	**210**	<1.0	<1.0	0.364	(0.007)	0.364(ND)
	3/2/2022	Background	515.0	2.07	36.1	0.91	4.31	6.57	**12**	<0.250	**130**	**290**	**2800**	**78**	<3.0	<1.0	**41**	<1.0	<1.0	<4.0	**8.6**	<0.250	<1.0	<10	<0.20	**190**	<1.0	<1.0	0.393	0.907	1.300
MW-1R (DG) Compliance	4/9/2022	Detection 7	671.2	-1.69	52.4	1.04	1.59	6.66	**12**	<0.250	**150**	**300**	**3,100**	**73**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	<0.250	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	8/2/2022		687.8	18.18	60.3	0.56	4.87	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	11/2/2022	Det 8/ Ass 1	609.3	17.48	7.6	0.51	2.79	6.55	**14**	<0.250	**170**	**440**	**2,400**	**72**	<3.0	<1.0	**30**	<1.0	<1.0	<4.0	**8.5**	<0.250	<1.0	<10	<0.20	**150**	<1.0	<1.0	0.0595	0.775	**0.853**
	3/12/2023	Det 9/ Ass 2	577.8	14.68	31.0	0.38	1.06	6.60	**10**	<0.250	**140**	**300**	**3,000**	**70**	(NA)	(NA)	**52**	(NA)	(NA)	(NA)	**7.9**	<0.250	(NA)	<20	<0.20	**180**	<1.0	(NA)	(0.0842)	1.030	1.03(ND)
	12/11/2023	Det 10/ Ass 3	489.0	16.07	791.4	0.54	1.35	6.55	**9**	<0.25	**118**	**310**	**1,980**	**58.6**	<3.0	**2.2**	**45.5**	<1.0	<1.0	<4.0	**5.8**	<0.25	<1.0	**16.1**	<0.20	**204**	<1.0	<1.0	0.17	0.38	<2.0
	4/23/2024	Det 11/ Ass 4	584.0	16.74	1161.3	0.61	1.56	6.47	**14**	<0.25	**188**	**424**	**3,770**	**95.9**	(NA)	<1.0	**55.5**	(NA)	(NA)	(NA)	**10.4**	<0.25	(NA)	**10.2**	(NA)	**199**	<1.0	(NA)	(NA)	(NA)	(NA)

Notes:

1. All data and Qualifiers transcribed from analytical lab data sheets or field notes.
2. Less than (<) symbol denotes concentration not detected at or above reporting limits. Bold values indicate analyte detected above reporting limit.
3. (ND) denotes Radium 226 and 228 (combined) concentration not detected above minimum detectable activity.
4. (NA) denotes analysis not conducted, not available at time of report, or not confirmed/replaced by resampling.
5. Baseline monitoring per USEPA 40 CFR 257.93.
6. Detection monitoring per USEPA 40 CFR 257.94. Detection Monitoring database comprised of analytical results for pH, Chloride, Fluoride, Sulfate, TDS, Boron, and Calcium.
7. Assessment monitoring per USEPA 40 CFR 257.95. Note Fluoride included in both Assesment and Detecion Monitoring Constituents, but data screening may be conducted over a different range.
8. Shaded cells indicate resampling occurred. Data that were not confirmed or were replaced by resample data is indicated with (NA) in shaded cell.
9. Red text with black border represent outlier values identified by Sanitas.
10. Blue shaded cells with black border indicate data removed for correction of a trend identified by Sanitas (Sen's Slope / Mann-Kendall).
11. Analytical Data Qualifiers provided by Laboratory:
    a. "J" - Analyte detected below quantitation limits
    b. "S" - Spike Recovery outside recovery limits

7/3/2024
Prepared by: JTF
Checked by: KAE
Approved by: MCC

Sikeston Board of Municipal Utilities - Sikeston Power Station
Fly Ash Pond Baseline Groundwater Statistical Evaluation
Scott County, Missouri

Appendix A - Analytical Data Summaries for FAP Groundwater Sampling for the CCR Rule

Well	Date	Monitoring Purpose	Spec. Cond.	Temp.	ORP	D.O.	Turbidity	pH	Chloride	Fluoride	Sulfate	TDS	Boron	Calcium	Antimony	Arsenic	Barium	Beryllium	Cadmium	Chromium	Cobalt	Fluoride	Lead	Lithium	Mercury	Molybdenum	Selenium	Thallium	Radium 226	Radium 228	Radium 226/228 (Combined)
ID			µmhos/cm	°C	mV	mg/L	NTU	S.U.	mg/L	mg/L	mg/L	mg/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	pCi/L	pCi/L	pCi/L
Federal MCL									None	4.0	None	None	None	None	6	10	2000	4	5	100	6	4	15	40	2	100	50	2			5
MW-2 (UG) Baseline	3/21/2018	Background	157.8	15.86	65.3	2.72	3.41	6.35	**3.4**	<0.250	**16**	**110**	**28**	**16**	<3.0	<1.0	**130**	<1.0	<1.0	<4.0	<2.0	<0.250	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.514	0.382	0.896 (ND)
	4/15/2018	Background	159.8	14.04	64.7	0.87	4.05	6.36	**2.3**	**0.335**	**18**	**63**	**23**	**14**	<3.0	<1.0	**120**	<1.0	<1.0	<4.0	<2.0	**0.335**	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.381	0.102	0.483 (ND)
	5/23/2018	Background	175.3	17.40	121.7	0.58	1.72	6.18	**4.2**	<0.250	**20**	**100**	**36**	**18**	<3.0	<1.0	**170**	<1.0	<1.0	<4.0	<2.0	<0.250	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.119	1.080	1.199 (ND)
	6/27/2018	Background	172.1	18.38	243.8	0.27	5.30	6.16	**4.7**	<0.250	**18**	**87**	**42**	**19**	<3.0	<1.0	**180**	<1.0	<1.0	<4.0	<2.0	<0.250	<1.0	<10	<0.20	<1.0	**1.4**	<1.0	0.488	0.518	1.006 (ND)
	8/1/2018	Background	184.2	18.48	80.7	0.75	2.61	6.11	**5.9**	<0.250	**19**	**140**	**43**	**20**	<3.0	<1.0	**200**	<1.0	<1.0	<4.0	<2.0	<0.250	<1.0	<10	<0.20	<1.0	**2.0**	<1.0	0.308	0.443	0.751(ND)
	9/5/2018	Background	187.9	19.26	83.8	0.68	2.58	6.09	**6.8**	<0.250	**18**	**110**	**46**	**22**	<3.0	<1.0	**220**	<1.0	<1.0	<4.0	<2.0	<0.250	<1.0	<10	<0.20	<1.0	**2.2**	<1.0	0.801	0.933	**1.734**
	11/6/2018	Background	174.3	17.77	79.7	0.60	1.19	6.19	**4.2**	**0.272**	**19**	**100**	**43**	**20**	<3.0	<1.0	**170**	<1.0	<1.0	<4.0	<2.0	**0.272**	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.353	1.230	**1.583**
	12/12/2018	Background	186.3	16.78	82.3	0.67	5.78	6.13	**5.5**	**0.254**	**21**	**140**	**48**	**21**	<3.0	<1.0	**210**	<1.0	<1.0	<4.0	**2.0**	**0.254**	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.624	0.556	1.180 (ND)
	3/27/2019	Detection 1	165.9	15.87	70.4	0.72	2.60	6.25	**3.3**	<0.250	**20**	**130**	**31**	**17**	NA	NA	NA	NA	NA	NA	NA	<0.250	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9/24/2019	Detection 2	189.4	18.75	71.3	0.61	1.16	6.1	**6.6**	<0.250	**17**	**130**	**58**	**22**	NA	NA	NA	NA	NA	NA	NA	<0.250	NA	NA	NA	NA	NA	NA	NA	NA	NA
	4/6/2020	Detection 3	148.7	16.04	58.2	1.36	4.70	6.3	**2.1**	**0.336**	**16**	**140**	NA	**15**	NA	NA	NA	NA	NA	NA	NA	**0.336**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	5/21/2020		168.1	16.47	-0.8	6.90	2.76	NA	NA	NA	NA	NA	**36**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9/22/2020	Detection 4	189.8	18.34	-9.6	6.52	0.62	6.2	**4.8**	<0.250	**17**	**150**	NA	**21**	NA	NA	NA	NA	NA	NA	NA	<0.250	NA	NA	NA	NA	NA	NA	NA	NA	NA
	12/8/2020		186.5	16.90	223.4	5.56	0.79	NA	NA	NA	NA	NA	**49**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	4/17/2021	Detection 5	178.9	14.70	21.7	12.02	1.68	6.3	**3.8**	<0.250	**17**	NA	**41**	**19**	NA	NA	NA	NA	NA	NA	NA	<0.250	NA	NA	NA	NA	NA	NA	NA	NA	NA
	6/15/2021		165.4	17.03	55.1	18.10	1.55	NA	NA	NA	NA	**350**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
MW-2 (UG) Compliance	10/20/2021	Detection 6	188.0	14.85	19.6	5.97	1.36	6.25	**4.2**	<0.250	**15**	**140**	(NA)	**19**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	<0.250	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	12/27/2021		161.0	8.90	17.7	0.88	1.53	6.31	(NA)	(NA)	(NA)	(NA)	**43**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	4/9/2022	Detection 7	156.4	-1.47	71.9	1.20	3.31	(NA)	**2.9**	<0.250	**15**	**150**	(NA)	16	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	<0.250	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	8/2/2022		185.6	18.26	83.4	0.28	2.95	6.21	(NA)	(NA)	(NA)	(NA)	**53**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	11/2/2022	Det 8/ Ass 1	218.4	17.64	101.7	0.74	6.51	6.23	**7.4**	<0.250	**15**	180	**81**	**24**	<3.0	<1.0	**220**	<1.0	<1.0	<4.0	**2.4**	<0.250	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.403	1.51	**1.913**
	3/12/2023	Det 9/ Ass 2	120.5	15.40	54.5	0.61	3.33	6.51	**1.3**	<0.250	**8.7**	700 H	**29**	**12**	(NA)	(NA)	**100**	(NA)	(NA)	(NA)	<2.0	<0.250	(NA)	<20	(NA)	<1.0	<1.0	(NA)	(0.150)	0.630	0.630(ND)
	12/11/2023	Det 10/ Ass 3	197.2	17.35	733.0	0.59	0.79	6.21	**4**	<0.25	**15**	**108**	**47.8**	**18.6**	<3.0	<1.0	**193**	<1.0	<1.0	<4.0	<2.0	<0.25	<1.0	<10.0	<0.20	**1.4**	<1.0	<1.0	0.19	1.2	<2.0
	4/23/2024	Det 11/ Ass 4	176.8	17.55	518.1	0.67	1.02	6.23	**4**	<0.25	**15**	**104**	**42.9**	**20.4**	(NA)	<1.0	**192**	(NA)	(NA)	(NA)	<2.0	<0.25	(NA)	<10.0	(NA)	<1.0	<1.0	(NA)	(NA)	(NA)	(NA)

Notes:

1. All data and Qualifiers transcribed from analytical lab data sheets or field notes.
2. Less than (<) symbol denotes concentration not detected at or above reporting limits. Bold values indicate analyte detected above reporting limit.
3. (ND) denotes Radium 226 and 228 (combined) concentration not detected above minimum detectable activity.
4. (NA) denotes analysis not conducted, not available at time of report, or not confirmed/replaced by resampling.
5. Baseline monitoring per USEPA 40 CFR 257.93.
6. Detection monitoring per USEPA 40 CFR 257.94. Detection Monitoring database comprised of analytical results for pH, Chloride, Fluoride, Sulfate, TDS, Boron, and Calcium.
7. Assessment monitoring per USEPA 40 CFR 257.95. Note Fluoride included in both Assesment and Detecion Monitoring Constituents, but data screening may be conducted over a different range.
8. Shaded cells indicate resampling occurred. Data that were not confirmed or were replaced by resample data is indicated with (NA) in shaded cell.
9. Red text with black border represent outlier values identified by Sanitas.
10. Blue shaded cells with black border indicate data removed for correction of a trend identified by Sanitas (Sen's Slope / Mann-Kendall).
11. Analytical Data Qualifiers provided by Laboratory:
    - a. "J" - Analyte detected below quantitation limits
    - b. "S" - Spike Recovery outside recovery limits

7/3/2024
Prepared by: JTF
Checked by: KAE
Approved by: MCC

Sikeston Board of Municipal Utilities - Sikeston Power Station
Fly Ash Pond Baseline Groundwater Statistical Evaluation
Scott County, Missouri

Appendix A - Analytical Data Summaries for FAP Groundwater Sampling for the CCR Rule

Well ID	Date	Monitoring Purpose	Spec. Cond.	Temp.	ORP	D.O.	Turbidity	pH	Chloride	Fluoride	Sulfate	TDS	Boron	Calcium	Antimony	Arsenic	Barium	Beryllium	Cadmium	Chromium	Cobalt	Fluoride	Lead	Lithium	Mercury	Molybdenum	Selenium	Thallium	Radium 226	Radium 228	Radium 226/228 (Combined)
			µmhos/cm	°C	mV	mg/L	NTU	S.U.	mg/L	mg/L	mg/L	mg/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	pCi/L	pCi/L	pCi/L
Federal MCL									None	4.0	None	None	None	None	6	10	2000	4	5	100	6	4	15	40	2	100	50	2			5
MW-3 (UG) Baseline	3/21/2018	Background	220.7	15.22	40.7	0.38	14.88	6.57	**1.4**	**0.274**	**18**	**120**	**17**	**19**	<3.0	<1.0	**96**	<1.0	<1.0	<4.0	<2.0	**0.274**	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.836	0.404	1.240 (ND)
	4/15/2018	Background	224.7	14.05	39.2	0.45	10.81	6.48	**1.5**	**0.386**	**20**	**120**	**25**	**18**	<3.0	<1.0	**100**	<1.0	<1.0	<4.0	<2.0	**0.386**	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.556	0.919	1.475 (ND)
	5/23/2018	Background	221.3	17.77	43.2	0.39	13.39	6.49	**1.4**	<0.250	**20**	**100**	**20**	**18**	<3.0	<1.0	**100**	<1.0	<1.0	<4.0	<2.0	<0.250	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.526	0.468	0.994 (ND)
	6/27/2018	Background	198.7	17.81	123.8	0.45	17.03	6.45	**1.2**	<0.250	**17**	**110**	**27**	**18**	<3.0	<1.0	**100**	<1.0	<1.0	<4.0	<2.0	<0.250	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.214	(0.187)	0.214 (ND)
	8/1/2018	Background	209.2	16.74	41.4	0.43	10.96	6.55	**1.3**	<0.250	**17**	**150**	**21**	**18**	<3.0	<1.0	**91**	<1.0	<1.0	<4.0	<2.0	<0.250	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.315	(0.0763)	0.315(ND)
	9/5/2018	Background	196.8	17.62	56.8	0.46	6.21	6.51	**1.2**	**0.308**	**15**	**100**	**22**	**17**	<3.0	<1.0	**98**	<1.0	<1.0	<4.0	<2.0	**0.308**	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.344	0.516	0.860(ND)
	11/6/2018	Background	206.7	16.84	63.3	0.49	2.37	6.49	**1.3**	**0.313**	**16**	**130**	**26**	**17**	<3.0	<1.0	**100**	<1.0	<1.0	<4.0	<2.0	**0.313**	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.547	0.792	**1.339**
	12/12/2018	Background	195.6	15.39	48.7	0.40	3.10	6.50	**1.4**	**0.334**	**18**	**160**	**28**	**17**	<3.0	<1.0	**99**	<1.0	<1.0	<4.0	<2.0	**0.334**	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.414	0.386	0.800 (ND)
	3/27/2019	Detection 1	196.0	15.07	52.2	0.84	12.50	6.36	**1.5**	<0.250	**19**	**140**	**22**	**16**	NA	NA	NA	NA	NA	NA	NA	<0.250	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9/24/2019	Detection 2	191.4	17.07	58.1	0.53	2.28	6.5	**1.2**	**0.332**	**16**	**130**	**26**	**17**	NA	NA	NA	NA	NA	NA	NA	**0.332**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	4/6/2020	Detection 3	198.4	14.94	61.3	1.17	7.37	6.4	NA	**0.371**	**20**	NA	**29**	**16**	NA	NA	NA	NA	NA	NA	NA	**0.371**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	5/21/2020		205.5	15.25	14.9	13.48	7.29	NA	**1.5**	NA	NA	**130**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9/22/2020	Detection 4	194.1	16.65	36.7	8.29	2.13	6.5	**1.1**	<0.250	**17**	**120**	**31**	**17**	NA	NA	NA	NA	NA	NA	NA	<0.250	NA	NA	NA	NA	NA	NA	NA	NA	NA
	4/17/2021	Detection 5	196.8	14.04	34.3	12.04	3.47	6.6	<1.0	<0.250	**15**	**150**	**16**	**17**	NA	NA	NA	NA	NA	NA	NA	<0.250	NA	NA	NA	NA	NA	NA	NA	NA	NA
MW-3 (UG) Compliance	10/20/2021	Detection 6	189.0	12.85	33.6	10.32	1.35	6.52	<1.0	<0.250	**13**	**130**	**30**	**14**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	<0.250	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	4/9/2022	Detection 7	197.6	-2.74	66.7	2.86	2.58	6.67	<1.0	<0.250	**13**	**130**	(NA)	**15**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	<0.250	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	8/2/2022		163.7	16.97	52.6	0.47	4.88	(NA)	(NA)	(NA)	(NA)	(NA)	**21**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	11/2/2022	Det 8/ Ass 1	161.8	16.28	9.1	0.36	9.56	6.93	<1.0	<0.250	**10**	**160**	**29**	**17**	<3.0	<1.0	**73**	<1.0	<1.0	<4.0	<2.0	<0.250	<1.0	<10	<0.20	<1.0	<1.0	<1.0	0.0589	1.16	**1.16**
	3/12/2023	Det 9/ Ass 2	177.2	14.09	73.2	1.35	3.90	6.51	<1.0	<0.250	**13**	**93 H**	**31**	**14**	(NA)	(NA)	**110**	(NA)	(NA)	(NA)	<2.0	<0.250	(NA)	<20	(NA)	<1.0	<1.0	(NA)	0.221	0.558	0.779(ND)
	12/11/2023	Det 10/ Ass 3	178.5	16.25	720.9	0.90	1.11	6.62	<4	<0.25	**10**	**102**	**17.4**	**13.7**	<3.0	<1.0	**71.0**	<1.0	<1.0	<4.0	<2.0	<0.25	<1.0	<10.0	<0.20	<1.0	<1.0	<1.0	(0.03)	0.72	<2.0
	4/23/2024	Det 11/ Ass 4	178.6	15.40	495.9	1.45	1.06	**6.65**	**1 "J"**	<0.25	**10**	**94**	**13.0**	**15.0**	(NA)	<1.0	**85.1**	(NA)	(NA)	(NA)	<2.0	<0.25	(NA)	<10.0	(NA)	<1.0	<1.0	(NA)	(NA)	(NA)	(NA)

Notes:

1. All data and Qualifiers transcribed from analytical lab data sheets or field notes.
2. Less than (<) symbol denotes concentration not detected at or above reporting limits. Bold values indicate analyte detected above reporting limit.
3. (ND) denotes Radium 226 and 228 (combined) concentration not detected above minimum detectable activity.
4. (NA) denotes analysis not conducted, not available at time of report, or not confirmed/replaced by resampling.
5. Baseline monitoring per USEPA 40 CFR 257.93.
6. Detection monitoring per USEPA 40 CFR 257.94. Detection Monitoring database comprised of analytical results for pH, Chloride, Fluoride, Sulfate, TDS, Boron, and Calcium.
7. Assessment monitoring per USEPA 40 CFR 257.95. Note Fluoride included in both Assesment and Detecion Monitoring Constituents, but data screening may be conducted over a different range.
8. Shaded cells indicate resampling occurred. Data that were not confirmed or were replaced by resample data is indicated with (NA) in shaded cell.
9. Red text with black border represent outlier values identified by Sanitas.
10. Blue shaded cells with black border indicate data removed for correction of a trend identified by Sanitas (Sen's Slope / Mann-Kendall).
11. Analytical Data Qualifiers provided by Laboratory:
    a. "J" - Analyte detected below quantitation limits
    b. "S" - Spike Recovery outside recovery limits

Sikeston Board of Municipal Utilities - Sikeston Power Station
Fly Ash Pond Baseline Groundwater Statistical Evaluation
Scott County, Missouri

Appendix A - Analytical Data Summaries for FAP Groundwater Sampling for the CCR Rule

Well	Date	Monitoring Purpose	Spec. Cond.	Temp.	ORP	D.O.	Turbidity	pH	Chloride	Fluoride	Sulfate	TDS	Boron	Calcium	Antimony	Arsenic	Barium	Beryllium	Cadmium	Chromium	Cobalt	Fluoride	Lead	Lithium	Mercury	Molybdenum	Selenium	Thallium	Radium 226	Radium 228	Radium 226/228 (Combined)
ID			μmhos/cm	°C	mV	mg/L	NTU	S.U.	mg/L	mg/L	mg/L	mg/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	pCi/L	pCi/L	pCi/L
Federal MCL									None	4.0	None	None	None	None	6	10	2000	4	5	100	6	4	15	40	2	100	50	2			5
MW-7 (DG) Baseline	3/21/2018	Background	901.8	14.85	41.8	0.58	1.61	7.30	**12**	**0.752**	**190**	**440**	**1900**	**110**	<3.0	<1.0	**41**	<1.0	<1.0	<4.0	<2.0	**0.752**	<1.0	**25**	<0.20	**160**	**5.4**	<1.0	0.457	0.426	0.883 (ND)
	4/15/2018	Background	936.4	14.04	40.0	0.51	0.96	7.24	**12**	**0.794**	**210**	**420**	**1900**	**110**	<3.0	<1.0	**43**	<1.0	<1.0	<4.0	**2.0**	**0.794**	<1.0	**19**	<0.20	**170**	**2.3**	<1.0	0.062	(0.036)	0.062 (ND)
	5/23/2018	Background	899.1	18.05	46.5	0.38	0.25	7.25	**11**	**0.650**	**220**	**480**	**1800**	**120**	<3.0	<1.0	**44**	<1.0	<1.0	<4.0	<2.0	**0.650**	<1.0	**22**	<0.20	**170**	**28**	<1.0	0.517	0.379	0.896 (ND)
	6/27/2018	Background	891.4	17.91	66.4	0.22	5.84	7.22	**11**	**0.592**	**220**	**500**	**2000**	**140**	<3.0	<1.0	**48**	<1.0	<1.0	<4.0	**2.1**	**0.592**	<1.0	**26**	<0.20	**160**	**53**	<1.0	0.335	0.818	1.153 (ND)
	8/1/2018	Background	958.3	18.03	53.0	0.28	1.77	7.22	**9.1**	**0.608**	**230**	**590**	**2300**	**140**	<3.0	<1.0	**47**	<1.0	<1.0	<4.0	**2.2**	**0.608**	<1.0	**30**	<0.20	**160**	**54**	<1.0	0.473	0.411	0.884(ND)
	9/5/2018	Background	873.3	19.46	69.3	0.28	2.29	7.29	**10**	**0.700**	**220**	**520**	**2100**	**130**	<3.0	<1.0	**47**	<1.0	<1.0	<4.0	**2.0**	**0.700**	<1.0	**27**	<0.20	**150**	**42**	<1.0	0.474	0.178	0.652(ND)
	11/6/2018	Background	787.9	18.12	344.4	0.44	0.44	7.35	**6.3**	**0.693**	**170**	**450**	**2000**	**120**	<3.0	<1.0	**43**	<1.0	<1.0	<4.0	**2.0**	**0.693**	<1.0	**26**	<0.20	**150**	**15**	<1.0	1.090	0.388	1.487(ND)
	12/12/2018	Background	784.8	17.26	51.6	1.05	0.41	7.27	**6.8**	**0.746**	**180**	**440**	**1800**	**120**	<3.0	<1.0	**44**	<1.0	<1.0	<4.0	**2.1**	**0.746**	<1.0	**26**	<0.20	**150**	**11**	<1.0	0.355	0.620	0.975 (ND)
	3/27/2019	Detection 1	797.4	16.39	52.6	0.32	2.37	7.25	**6.6**	**0.670**	**170**	**480**	**1800**	**110**	NA	NA	NA	NA	NA	NA	NA	**0.670**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9/24/2019	Detection 2	751.7	18.88	119.0	0.31	0.59	7.3	**3.9**	**0.684**	**150**	**470**	**1900**	**120**	NA	NA	NA	NA	NA	NA	NA	**0.684**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	4/6/2020	Detection 3	865.6	16.34	68.3	0.24	1.62	7.2	**4.0**	**0.737**	**200**	**540**	**2200**	**120**	NA	NA	NA	NA	NA	NA	NA	**0.737**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9/22/2020	Detection 4	720.5	17.40	-80.8	3.63	0.50	NA	**3.1**	**0.628**	**110**	**460**	**1700**	**100**	NA	NA	NA	NA	NA	NA	NA	**0.628**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	1/26/2021		823.6	16.40	-49.2	0.27	0.41	7.4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
MW-7 (DG) Compliance	4/17/2021	Detection 5	870.0	15.17	-19.6	3.40	0.85	7.4	**1.8**	**0.522**	**160**	**520**	**2200**	**120**	NA	NA	NA	NA	NA	NA	NA	**0.522**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	10/20/2021	Detection 6	855.3	14.58	-44.0	3.75	0.75	7.35	**3.7**	**0.375**	**160**	**520**	**1,900**	**120**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	**0.375**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	4/9/2022	Detection 7	958.3	-1.31	17.1	0.67	0.60	(NA)	**4.1**	**0.488**	**240**	**510**	**3,200**	**130**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	**0.488**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	8/2/2022		835.0	17.59	64.1	0.23	1.77	7.31	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	11/2/2022	Det 8/ Ass 1	874.2	18.26	56.8	0.44	2.60	7.36	**3.1**	**0.476**	**130**	**500**	**2,300**	**120**	<3.0	<1.0	**62**	<1.0	<1.0	<4.0	**3.5**	**0.476**	<1.0	**33**	<0.20	**100**	**4.7**	<1.0	-0.0488	2.31	**2.310**
	3/12/2023	Det 9/ Ass 2	880.0	15.09	35.7	0.49	0.54	7.40	**3.7**	**0.635**	**190**	**520**	**2,600**	**140**	(NA)	(NA)	**77**	(NA)	(NA)	(NA)	**4.1**	**0.635**	(NA)	**27**	(NA)	**120**	**4.1**	(NA)	0.0773	0.899	0.976(ND)
	12/11/2023	Det 10/ Ass 3	840.1	16.69	172.5	0.48	0.91	7.28	**3 "J"**	**0.57**	**141**	**460**	**2,270**	**105**	<3.0	<1.0	**66.7**	<1.0	<1.0	<4.0	**2.7**	**0.57**	<1.0	**49.2**	<0.20	**127**	**3.0**	<1.0	0.16	1.29	<2.0
	4/23/2024	Det 11/ Ass 4	723.4	16.59	761.7	0.38	0.93	7.29	**3 "J"**	**0.53**	**93**	**390**	**2,260**	**111 "S"**	(NA)	<1.0	**65.2**	(NA)	(NA)	(NA)	<2.0	**0.53**	(NA)	**30.6**	(NA)	**122**	**2.8**	(NA)	(NA)	(NA)	(NA)

Notes:

1. All data and Qualifiers transcribed from analytical lab data sheets or field notes.
2. Less than (<) symbol denotes concentration not detected at or above reporting limits. Bold values indicate analyte detected above reporting limit.
3. (ND) denotes Radium 226 and 228 (combined) concentration not detected above minimum detectable activity.
4. (NA) denotes analysis not conducted, not available at time of report, or not confirmed/replaced by resampling.
5. Baseline monitoring per USEPA 40 CFR 257.93.
6. Detection monitoring per USEPA 40 CFR 257.94. Detection Monitoring database comprised of analytical results for pH, Chloride, Fluoride, Sulfate, TDS, Boron, and Calcium.
7. Assessment monitoring per USEPA 40 CFR 257.95. Note Fluoride included in both Assesment and Detecion Monitoring Constituents, but data screening may be conducted over a different range.
8. Shaded cells indicate resampling occurred. Data that were not confirmed or were replaced by resample data is indicated with (NA) in shaded cell.
9. Red text with black border represent outlier values identified by Sanitas.
10. Blue shaded cells with black border indicate data removed for correction of a trend identified by Sanitas (Sen's Slope / Mann-Kendall).
11. Analytical Data Qualifiers provided by Laboratory:
    - a. "J" - Analyte detected below quantitation limits
    - b. "S" - Spike Recovery outside recovery limits

Sikeston Board of Municipal Utilities - Sikeston Power Station
Fly Ash Pond Baseline Groundwater Statistical Evaluation
Scott County, Missouri

Appendix A - Analytical Data Summaries for FAP Groundwater Sampling for the CCR Rule

Well ID	Date	Monitoring Purpose	Spec. Cond. µmhos/cm	Temp. °C	ORP mV	D.O. mg/L	Turbidity NTU	pH S.U.	Chloride mg/L	Fluoride mg/L	Sulfate mg/L	TDS mg/L	Boron ug/L	Calcium mg/L	Antimony ug/L	Arsenic ug/L	Barium ug/L	Beryllium ug/L	Cadmium ug/L	Chromium ug/L	Cobalt ug/L	Fluoride mg/L	Lead ug/L	Lithium ug/L	Mercury ug/L	Molybdenum ug/L	Selenium ug/L	Thallium ug/L	Radium 226 pCi/L	Radium 228 pCi/L	Radium 226/228 (Combined) pCi/L
Federal MCL									None	4.0	None	None	None	None	6	10	2000	4	5	100	6	4	15	40	2	100	50	2			5
MW-9 (DG) Baseline	3/21/2018	Background	979.8	14.98	25.1	0.52	1.60	7.35	**17**	**0.929**	**230**	**480**	**4700**	**65**	<3.0	<1.0	**49**	<1.0	<1.0	<4.0	<2.0	**0.929**	<1.0	**19**	<0.20	**630**	<1.0	<1.0	0.0898	0.401	0.491 (ND)
	4/15/2018	Background	972.7	14.63	24.9	1.73	2.32	7.37	**21**	**1.09**	**240**	**460**	**5100**	**57**	<3.0	**1.2**	**49**	<1.0	<1.0	<4.0	<2.0	**1.09**	<1.0	**11**	<0.20	**680**	<1.0	<1.0	(0.132)	0.982	0.982 (ND)
	5/23/2018	Background	1020.5	18.70	25.9	0.48	0.64	7.34	**17**	**1.05**	**240**	**520**	**5800**	**55**	<3.0	<1.0	**45**	<1.0	<1.0	**8.1**	<2.0	**1.05**	<1.0	**15**	<0.20	**840**	<1.0	<1.0	0.260	0.0989	0.359 (ND)
	6/27/2018	Background	902.9	19.33	25.2	0.42	4.97	7.32	**15**	**0.910**	**220**	**520**	**4600**	**73**	<3.0	<1.0	**47**	<1.0	<1.0	<4.0	<2.0	**0.910**	<1.0	**15**	<0.20	**560**	<1.0	<1.0	0.000	0.327	0.327 (ND)
	8/1/2018	Background	942.6	19.10	20.7	0.47	2.03	7.28	**16**	**0.916**	**220**	**560**	**4500**	**76**	<3.0	<1.0	**47**	<1.0	<1.0	<4.0	<2.0	**0.916**	<1.0	**18**	<0.20	**500**	<1.0	<1.0	0.248	0.1700	0.418(ND)
	9/5/2018	Background	829.2	19.85	20.9	0.45	2.68	7.31	**16**	**0.957**	**180**	**420**	**4400**	**80**	<3.0	<1.0	**48**	<1.0	<1.0	<4.0	<2.0	**0.957**	<1.0	**17**	<0.20	**460**	<1.0	<1.0	(0.076)	0.707	0.707(ND)
	11/6/2018	Background	732.8	18.19	428.8	0.60	0.45	7.34	**11**	**0.885**	**130**	**410**	**3800**	**79**	<3.0	<1.0	**47**	<1.0	<1.0	<4.0	<2.0	**0.885**	<1.0	**13**	<0.20	**420**	<1.0	<1.0	0.570	0.903	1.473(ND)
	12/12/2018	Background	742.9	16.95	36.5	0.48	0.63	7.33	**12**	**0.972**	**170**	**360**	**3700**	**78**	<3.0	<1.0	**53**	<1.0	<1.0	<4.0	<2.0	**0.972**	<1.0	**17**	<0.20	**420**	<1.0	<1.0	0.452	0.780	1.232 (ND)
	3/27/2019	Detection 1	673.2	16.74	22.1	0.51	0.96	7.40	**11**	**0.827**	**120**	**440**	**3100**	**70**	NA	NA	NA	NA	NA	NA	NA	**0.827**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9/24/2019	Detection 2	891.5	19.25	38.3	0.41	0.62	7.4	**16**	**0.847**	**220**	**540**	**5000**	**87**	NA	NA	NA	NA	NA	NA	NA	**0.847**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	4/6/2020	Detection 3	967.5	17.60	61.6	0.34	0.92	7.3	**18**	**0.816**	**250**	NA	**4900**	**92**	NA	NA	NA	NA	NA	NA	NA	**0.816**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	5/21/2020		1024.4	17.09	-51.1	4.95	0.59	NA	NA	NA	NA	**560**	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9/22/2020	Detection 4	891.9	17.59	-70.4	4.18	0.64	7.5	**15**	**0.832**	**210**	**550**	**5000**	**80**	NA	NA	NA	NA	NA	NA	NA	**0.832**	NA	NA	NA	NA	NA	NA	NA	NA	NA
	1/26/2021		971.7	16.07	-69.1	0.34	0.47	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	4/17/2021	Detection 5	1098.1	15.16	-19.7	7.52	0.91	7.4	**21**	**0.775**	**250**	**630**	**6200**	**57**	NA	NA	NA	NA	NA	NA	NA	**0.775**	NA	NA	NA	NA	NA	NA	NA	NA	NA
MW-9 (DG) Compliance	10/20/2021	Detection 6	1020.5	15.70	13.1	6.16	0.87	7.52	**18**	**1.33**	**240**	(NA)	**5,500**	**5**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	**1.330**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	12/27/2021		886.0	8.57	-21.5	0.70	0.87	(NA)	(NA)	(NA)	(NA)	**520**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	4/9/2022	Detection 7	894.7	-0.98	1.9	0.86	0.70	(NA)	11	(NA)	160	**330**	**3,800**	**64**	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	8/2/2022		681.8	18.12	27.6	0.30	2.29	7.39	(NA)	0.860	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	0.860	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)	(NA)
	11/2/2022	Det 8/ Ass 1	785.3	19.11	6.4	0.44	2.67	7.39	**12**	**1.03**	**160**	**540**	**3,000**	**97**	<3.0	<1.0	**78**	<1.0	<1.0	<4.0	<2.0	**1.03**	<1.0	**21**	<0.20	**210**	<1.0	<1.0	0.164	0.648	0.812 (ND)
	3/12/2023	Det 9/ Ass 2	764.4	16.07	26.7	0.42	0.34	7.43	**11**	**1.02**	**160**	**480**	**3,600**	**95**	(NA)	(NA)	**85**	(NA)	(NA)	(NA)	<2.0	**1.02**	(NA)	<20	(NA)	**160**	<1.0	(NA)	0.451	1.05	1.50(ND)
	12/11/2023	Det 10/ Ass 3	804.1	16.27	782.2	0.52	1.13	7.15	**13**	**0.70**	**171**	**466**	**2,750**	**101**	<3.0	<1.0	**84.1**	<1.0	<1.0	<4.0	<2.0	**0.70**	<1.0	**34.9**	<0.20	**102**	<1.0	<1.0	0.16	1.14	<2.0
	4/23/2024	Det 11/ Ass 4	801.5	17.45	1035.7	0.44	1.06	7.05	**14**	**0.58**	**203**	**512**	**3,700**	**103**	(NA)	<1.0	**102**	(NA)	(NA)	(NA)	<2.0	**0.58**	(NA)	**23.0**	(NA)	**89.8**	<1.0	(NA)	(NA)	(NA)	(NA)

Notes:

1. All data and Qualifiers transcribed from analytical lab data sheets or field notes.
2. Less than (<) symbol denotes concentration not detected at or above reporting limits. Bold values indicate analyte detected above reporting limit.
3. (ND) denotes Radium 226 and 228 (combined) concentration not detected above minimum detectable activity.
4. (NA) denotes analysis not conducted, not available at time of report, or not confirmed/replaced by resampling.
5. Baseline monitoring per USEPA 40 CFR 257.93.
6. Detection monitoring per USEPA 40 CFR 257.94. Detection Monitoring database comprised of analytical results for pH, Chloride, Fluoride, Sulfate, TDS, Boron, and Calcium.
7. Assessment monitoring per USEPA 40 CFR 257.95. Note Fluoride included in both Assesment and Detecion Monitoring Constituents, but data screening may be conducted over a different range.
8. Shaded cells indicate resampling occurred. Data that were not confirmed or were replaced by resample data is indicated with (NA) in shaded cell.
9. Red text with black border represent outlier values identified by Sanitas.
10. Blue shaded cells with black border indicate data removed for correction of a trend identified by Sanitas (Sen's Slope / Mann-Kendall).
11. Analytical Data Qualifiers provided by Laboratory:
    - a. "J" - Analyte detected below quantitation limits
    - b. "S" - Spike Recovery outside recovery limits

Sikeston Board of Municipal Utilities - Sikeston Power Station
Fly Ash Pond Baseline Groundwater Statistical Evaluation
Scott County, Missouri

Appendix A - Analytical Data Summaries for FAP Groundwater Sampling for the CCR Rule

Well	Date	Monitoring Purpose	Spec. Cond.	Temp.	ORP	D.O.	Turbidity	pH	Chloride	Fluoride	Sulfate	TDS	Boron	Calcium	Antimony	Arsenic	Barium	Beryllium	Cadmium	Chromium	Cobalt	Fluoride	Lead	Lithium	Mercury	Molybdenum	Selenium	Thallium	Radium 226	Radium 228	Radium 226/228 (Combined)
ID			µmhos/cm	°C	mV	mg/L	NTU	S.U.	mg/L	mg/L	mg/L	mg/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	pCi/L	pCi/L	pCi/L
Federal MCL									None	4.0	None	None	None	None	6	10	2000	4	5	100	6	4	15	40	2	100	50	2			5
MW-10 (DG) Baseline	2/15/2023	Background	599.92	18.30	-64.8	0.14	8.51	7.02	**14**	<0.250	**120**	**360**	**340**	**81**	<3.0	**6.9**	**150**	<1.0	<1.0	<4.0	<2.0	<0.250	<1.0	<20	<0.20	**25**	<1.0	<1.0			<0.773
	8/21/2023	Background	677.61	20.31	-29.0	0.34	5.79	6.91	**17**	**0.31**	**141**	**465**	**233**	**90.1**	<3.0	**5.7**	**139**	<1.0	<1.0	<4.0	<2.0	**0.31**	<1.0	**31.0**	<0.20	**15.4**	<1.0	<1.0	0.19	0.86	<2.00
	9/5/2023	Background	695.13	20.58	-36.5	0.28	1.86	6.85	**18**	**0.30**	**168**	**490**	**240**	**83.5**	<3.0	**7.4**	**134**	<1.0	<1.0	<4.0	<2.0	**0.30**	<1.0	**34.7**	<0.20	**24.8**	<1.0	<1.0	0.18	0.85	<2.00
	9/20/2023	Background	693.51	19.95	-82.5	0.33	0.40	6.79	**21**	**0.28**	**182**	**450**	**249**	**86.4**	<3.0	**5.6**	**141**	<1.0	<1.0	<4.0	<2.0	**0.28**	<1.0	**32.2**	<0.20	**21.7**	<1.0	<1.0	-0.02	0.05	<2.00
	10/2/2023	Background	720.70	20.81	-44.2	0.26	2.62	6.98	**19**	**0.29**	**171**	**440**	**265**	**87.6**	<3.0	**5.5**	**157**	<1.0	<1.0	<4.0	<2.0	**0.29**	<1.0	**36.2**	<0.20	**20.7**	<1.0	<1.0	0.17	0.59	<2.00
	10/17/2023	Background	726.4	19.44	-101.1	0.33	0.72	7.05	**20**	**0.42**	**164**	**412**	**284**	**86.5**	<3.0	**6.1**	**146**	<1.0	<1.0	<4.0	<2.0	**0.42**	<1.0	**40**	<0.20	**24.2**	<1.0	<1.0	0.19	0.58	<2.00
	11/2/2023	Background	722.98	19.46	198.7	0.42	0.53	6.84	**20**	**0.30**	**161**	**394**	**282**	**86.3**	<3.0	**8.7**	**141**	<1.0	<1.0	<4.0	<2.0	**0.30**	<1.0	**40.6**	<0.20	**18.0**	<1.0	<1.0	0.35	1.29	<2.0
	11/15/2023	Background	181.18	19.51	383.6	0.30	0.74	6.87	**21**	**0.30**	**187**	**400**	**342**	**91.7**	<3.0	**6.3**	**151**	<1.0	<1.0	<4.0	<1.0	**0.30**	<1.0	**13.4**	<0.20	**24.0**	<1.0	<1.0	0.24	1.11	<2.0
MW-10 (DG) Compliance	12/11/2023	Det 10/ Ass 3	720.43	18.48	98.6	0.35	0.60	7.06	**19**	**0.29**	**166**	**455**	**378**	**88.8**	<3.0	**5.9**	**142**	<1.0	<1.0	<4.0	<2.0	**0.29**	<1.0	**11.4**	<0.20	**25.2**	<1.0	<1.0	0.12	1.38	<2.0
	4/23/2024	Det 11/ Ass 4	680.1	18.28	432.0	0.31	9.96	6.93	**8**	<0.25	**140**	**420**	**241**	**90.4**	(NA)	**6.6**	**138**	(NA)	(NA)	(NA)	<2.0	<0.25	(NA)	**<10.0**	(NA)	**19.3**	<1.0	(NA)	(NA)	(NA)	(NA)

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3. (ND) denotes Radium 226 and 228 (combined) concentration not detected above minimum detectable activity.
4. (NA) denotes analysis not conducted, not available at time of report, or not confirmed/replaced by resampling.
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8. Shaded cells indicate resampling occurred. Data that were not confirmed or were replaced by resample data is indicated with (NA) in shaded cell.
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11. Analytical Data Qualifiers provided by Laboratory:
    a. "J" - Analyte detected below quantitation limits
    b. "S" - Spike Recovery outside recovery limits

Appendix B

Human Health and Ecological Risk Evaluation – Fly Ash Pond Sikeston Power Station (Loureiro, 2024)

HUMAN HEALTH AND ECOLOGICAL RISK EVALUATION

Fly Ash Pond
Sikeston Power Station
Scott County, Missouri

March 2025

Prepared for

GREDELL Engineering Resources

1505 East High Street

Jefferson City, Missouri

Engineering • Construction • EH&S • Energy
Waste • Facility Services • Laboratory

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An Employee-Owned Company

Comm. No. 035GE4.01

HUMAN HEALTH AND ECOLOGICAL RISK EVALUATION

Fly Ash Pond, Sikeston Power Station
Scott County, Missouri

March 2025

Prepared for

GREDELL Engineering Resources

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Table 1 Exposure Points and Monitoring Results

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1. INTRODUCTION

This risk evaluation has been performed to assess the potential for unacceptable levels of risk to human and ecological receptors associated with the constituents of concern present in groundwater associated with the Sikeston Power Station (SPS) facility (hereinafter the "Site"). As presented in the November 2023 *Nature and Extent Characterization*, *Summary of Findings for Fly Ash Pond for Sikeston Power Station* report prepared by GREDELL Engineering Resources, Inc. for Sikeston Board of Municipal Utilities (hereinafter "*NEC*"), cobalt and molybdenum have been identified as the constituents of concern (COCs) associated with the groundwater monitoring system for the Fly Ash Pond (FAP), as these two constituents have been reported in representative monitoring wells at Statistically Significant Levels (SSLs) greater than their respective Groundwater Protection Standards (GWPS) established in accordance with §257.95(h). In addition, as discussed within the NEC, boron was identified in groundwater and surface water at the SPS. Although a GWPS has not been established for boron, it has been included as a constituent of concern within this risk assessment as evidence suggests that the detections of boron are likely attributable to the FAP. As additionally discussed in the NEC, although arsenic has also been detected above the GWPS in wells downgradient from the FAP, its presence is attributed to an alternate, naturally occurring source and is not believed to be associated with a release from the FAP. Therefore, arsenic has not been included as a constituent of concern within this risk assessment.

The following sections present the approaches used in the completion of this risk evaluation, as well as the conclusions of the risk evaluation.

2. RISK EVALUATION

The overall purpose of the risk evaluation is to identify whether current concentrations of constituents of concern associated with the FAP pose unacceptable levels of risk to human health and the environment, and to guide decisions regarding potential corrective measures to mitigate those risks.

2.1 **Approach**

There are four main components to the evaluation of risk: 1) Hazard Identification, 2) Toxicity Assessment, 3) Exposure Assessment, and 4) Risk Characterization.

Potential hazards associated with the Site were identified using groundwater and surface water data collected in 2023 as part of the FAP Nature and Extent Evaluation, summarized within the

NEC. The collection methods and results are described in detail within the *NEC*. As discussed in Section 1.0, the COCs associated with the FAP, which warrant further evaluation as part of this risk assessment under 40 Code of Federal Regulations (CFR) 257.95, were identified by comparing concentrations against risk-based Site Specific Groundwater Protection Standards within 40 CFR 257.95(h), which consider the toxicities of individual compounds.

Using physical setting information and data regarding groundwater flow directions and lithology, a conceptual site model (CSM) was developed as part of this risk evaluation to identify human and ecological receptors that may be exposed to the groundwater and receiving surface water at or emanating from the FAP. Using this conceptual site model and understanding of potential human and ecological receptors, certain groundwater and surface water sampling locations were selected to represent exposure points for human and ecological receptors.

The COCs associated with the FAP in groundwater and surface water at these locations were then evaluated using risk-based screening levels promulgated by the United States Environmental Protection Agency and the State of Missouri to evaluate human health and ecological risk. For each exposure scenario, it can be concluded that exposure of a receptor to a COC at concentrations below appropriate risk-based screening levels is not expected to result in a condition of unacceptable risk. Conversely, exposure of a receptor a COC at concentrations above appropriate screening levels indicates that further evaluation is warranted, which may result in implementation of risk mitigation measures.

2.2 Conceptual Site Model

A CSM was developed for the groundwater associated with the FAP in order to evaluate the potential for human and/or ecological exposure to COCs associated with the FAP. The CSM identifies the FAP as the source of the COCs. As presented in greater detail in prior investigation reports prepared for SPS, the finished subgrade elevation of the FAP base is 300 feet, and a two-foot clay liner was constructed on the floor and interior slopes. During normal operations, the only source of surface water entering the FAP is from direct precipitation. The uppermost continuous aquifer under the ash ponds is approximately 90 feet thick, representing the saturated thickness of the sand above the documented clay layer. The uppermost continuous aquifer was determined to be uniform in terms of permeability of the granular materials; therefore there is likely a lack of preferential flow pathways beneath the site. Precipitation is a recharge source for the uppermost continuous aquifer but the relationship between precipitation and groundwater elevation was noted to be highly variable. Hydraulic conductivity values calculated are consistent with values for the upper range of silty sands or mid-range clean sands (Freeze and Cherry, 1979), and consistent with the aquifer matrix composition. Groundwater velocity values in the area of the FAP were previously calculated to be 0.1 to 2 feet per day.

Drainage ditches were constructed beginning in the early 1900s, which run north to south toward the Mississippi River to convey shallow groundwater out of region. As a result, the current water table is approximately ten to twenty feet below ground near the Site, and groundwater flow at the Site is generally to the west-southwest toward Richland Drainage Ditch #4. However, high-capacity industrial wells influence flow direction during their operation by SPS. Regionally, groundwater movement is along a shallow hydraulic gradient estimated at approximately one foot per mile (Miller and Vandike, 1997), consistent with the topography of the region.

Given the Site setting and hydrogeologic conditions, the CSM used to evaluate potential human and ecological exposure to COCs associated with the FAP consists of dissolution of constituents present in ash within the FAP into infiltrating water and interacting with shallow groundwater as it moves beneath the coal ash impoundments. Constituents then move with groundwater as it flows to the west-southwest toward the Richland Drainage Ditch #4 and the high-capacity pumping wells operated by SPS.

2.3 **Constituents of Concern**

Cobalt and molybdenum have been identified as the constituents of concern associated with the Fly Ash Pond (FAP) groundwater monitoring system, as these two constituents have been reported in representative monitoring wells at SSLs greater than their respective GWPS established in accordance with 40 CFR 257.95(h). In addition, as discussed within the *NEC*, boron was identified in groundwater and surface water at the SPS. Although a GWPS has not been established for boron it has been included as a constituent of concern within this risk assessment as evidence suggests that the detections of boron are likely attributable to the FAP.

As additionally discussed in the *NEC*, although arsenic has also been detected above the GWPS in wells downgradient from the FAP, its presence is attributed to an alternate, naturally occurring source and is not believed to be associated with a release from the FAP. Therefore, arsenic has not been included as a constituent of concern within this risk assessment.

2.4 **Exposure Pathways**

The SPS facility is located within the western city limits of Sikeston. The topography is relatively flat, and the SPS is bounded to the north, west, and south by land primarily used for agricultural (row-crop) production. A residential development is located to the east; the closest residence is approximately 400 feet east of the ash pond area. There are no users of shallow groundwater present between the FAP and the Richland Drainage Ditch #4. According to the Well Information Management System (WIMS) database maintained by the Missouri Department of Natural Resources (MDNR) there are 2 domestic wells and 2 public wells recorded within a one-mile radius of the facility. Both of the domestic wells are located upgradient of the SPS. The domestic well nearest to the SPS is approximately 1,300 feet north of the northern property boundary. This well (reference number 00178292) is associated with the SPS and is constructed with a bottom depth of 139 feet below grade.

One of the public wells is located upgradient and to the east of the SPS (reference number 00361493). The public well that is located downgradient from the SPS is approximately 3,000 feet southwest of the southwest property boundary. This well (reference number 00560854) is steel cased to 219 feet below grade. The nearest high-yield well, which is used for irrigation purposes, is located downgradient from the SPS, approximately 1,825 feet southwest from the southwest property boundary. This well (reference number 00360541) is plastic cased to 60 feet below grade, with the pump set at 60 feet below grade, and pumps 3,000 gallons per minute.

To supplement the review of the WIMS database, a 2017 Environmental Database Resource (EDR) with GeoCheck® report prepared for the Site was evaluated for the presence of any additional wells. No additional potable wells were identified in the EDR report. Should any unrecorded potable wells exist within the area surrounding the Site, they would likely be screened within the deep aquifer (assuming at least 140 feet below grade if consistent with the domestic well with reference number 00178292).

Groundwater flow at the Site is generally to the west-southwest toward Richland Drainage Ditch #4. Richland Drainage Ditch #4 is the nearest surface water body that may receive groundwater emanating from the SPS, and for the purposes of this risk assessment is considered an exposure point for aquatic ecological receptors.

Therefore, the environmental media, their respective exposure pathways, and the representative exposure points included in this risk evaluation are as follows:

- **Human Exposures: Use of groundwater for potable purposes (domestic and public):**
  - Exposure media: Groundwater from the deeper aquifer, downgradient from the SPS.
  - Representative exposure points: Wells/Piezometers DP-1, DP-2, B Well (167’), A, and D. Approximate sample elevations range from 143 feet (B Well (167’)) to 182 feet (D well).

- **Human Exposures: Use of groundwater for irrigation purposes:**
    - Exposure media: Groundwater within the shallow aquifer, downgradient from the SPS.
    - Representative exposure points: Wells/Pieozmeters MW-10, NE-3, MW-4, MW-8, MW-5. Approximate sample elevations range from 270.7 feet (MW-10) to 274.6 feet (MW-5).

- **Ecological Exposures: Exposure of aquatic ecological receptors**
    - Exposure media: Surface water in Richland Drainage Ditch #4.
    - Representative exposure points: Surface water within Richland Drainage Ditch #4: Surface water sample location SG-S; Shallow groundwater that may interact with surface water within Richland Drainage Ditch #4: Wells/Piezometers NE-3, NE-2, NE-1, MW-4, MW-8, MW-5. Approximate sample elevations range from 271.1 (NE-3) to 276 (NE-1).

A summary of the groundwater monitoring results for the site-specific COCs evaluated in this risk assessment, is presented by exposure scenario in **Table 1**.

2.5 Risk Evaluation Methods

The evaluation of risk associated with the two potential human health exposure scenarios and one potential ecological exposure scenario was performed via comparison of exposure point concentrations to risk-based screening levels promulgated by Federal and State sources. These screening levels are designed to provide a conservative evaluation of the potential for adverse human or ecological health effects.

2.5.1 Derivation of Exposure Point Concentrations

Exposure point concentrations for each representative exposure point for a given exposure scenario were derived by using the maximum concentration of a site-specific COC within the representative exposure points. As a note, total concentrations of molybdenum, rather than the dissolved fraction, were used to generate exposure point concentrations. The use of the maximum concentration of each site-specific COC is in line with the guidance in Table 1 of Missouri Title 10 CSR 25-18a and is a conservative approach.

Exposure point concentrations for exposure of aquatic ecological receptors were derived from concentrations in surface water in Richland Drainage Ditch #4 as well as in shallow groundwater proximate to Richland Drainage Ditch #4 that may intercept this receiving surface water body.

Higher concentrations of the site-specific COCs were observed in the shallow groundwater than in the surface water sample itself. The practice of evaluating a surface water screening value against a groundwater sample is conservative as it does not account for dilution and attenuation in the aquifer prior to interaction with the receiving surface water body.

The exposure point concentrations utilized for each exposure scenario are presented on **Table 2**, along with the human health or ecological screening value appropriate for the exposure scenario.

2.5.2 Risk-Based Screening Levels

Exposure point concentrations for each of the selected potential exposure scenarios were compared to risk-based screening levels promulgated by Federal and State sources, as described below.

Human Exposures: Use of groundwater for potable purposes (domestic and public)

Typically, Maximum Contaminant Levels (MCLs) promulgated under the National Primary Drinking Water Regulations are used as risk-based screening levels for evaluating the potable water exposure pathway. However, no MCLs or State of Missouri Drinking Water Supply criteria (which are found in Missouri Code of State Regulations (CSR) – Title 10 CSR 20-7) are available for the site-specific COCs. Therefore, the United States Environmental Protection Agency (EPA) risk-based regional screening levels (RSLs) for tapwater were used to evaluate potential risk to human health via use of groundwater for potable purposes. Per the risk evaluation guidance found in Table 1 of Missouri Title 10 CSR 25-18, a hazard quotient of 1 and an individual compound excess lifetime cancer risk (ELCR) of 1×10^{-5} were used as the risk thresholds in generating the RSLs.

Human Exposures: Use of groundwater for irrigation purposes

Potential risk to human health and livestock via use of shallow groundwater for irrigation and livestock watering and feeding purposes was evaluated by comparing exposure point concentrations to irrigation supply standards (found in Missouri Title 10 CSR 20-7 Table A1). In the absence of such a standard for molybdenum, the RSL for tapwater for molybdenum was used, which is a conservative approach.

Ecological Exposures: Exposure of aquatic ecological receptors

Criteria were not available in Missouri Title 10 CSR 20-7 Table A1 for aquatic life protection for the site-specific COCs. Therefore, the freshwater screening values (chronic) found in Table 1a, Surface Water Screening Values for Hazardous Waste Sites of EPA's *Region 4 Ecological Risk*

Assessment Supplemental Guidance (March 2018) were used to evaluate risk to ecological aquatic receptors.

2.6 **Risk Evaluation Results**

As presented on Table 2, all exposure point concentrations for each of the identified exposure scenarios (use of groundwater for potable use, use of groundwater for irrigation, or exposure of aquatic ecological receptors) are below their respective screening values. Therefore, groundwater emanating from the SPS is not associated with the potential for adverse impacts on human health or ecological receptors.

3. CONCLUSIONS

An evaluation of potential human and ecological risk posed by the constituents of concern present in groundwater associated with the Fly Ash Pond at the Sikeston Power Station facility was performed. The evaluation focused on site-specific COCs, cobalt and molybdenum, which have been reported in representative monitoring wells at SSLs greater than GWPS established in accordance with 40 CFR 257.95(h), as well as boron, as evidence suggests that the detections of Boron are likely attributable to the Fly Ash Pond. Given the site setting and conceptual site model, exposure scenarios evaluated included use of groundwater for potable use, use of groundwater for irrigation, and exposure of aquatic ecological receptors. None of the exposure point concentrations exceeded their respective risk-based screening value for the chosen exposure scenario. Therefore, this risk evaluation indicates that groundwater emanating from the Site is not associated with a potential for adverse impacts to human health or ecological receptors.

TABLES

Table 1 - Exposure Points and Monitoring Results

Fly Ash Pond
Sikeston Power Station
Scott County, Missouri

	Exposure Points Used to Evaluate Irrigation Exposure Scenario					
Well ID	**NE-3**	**MW-4**	**MW-5**	**MW-8**	**MW-10**	**MW-10 (dup)**
Elevation (ft)	271.1	274.3	274.6	272.4	270.7	270.7
Sample Date	2/15/2023	10/20/2022	10/20/2022	10/20/2022	2/15/2023	2/15/2023
Boron (ug/L)	77	1000	360	510	340	340
Cobalt (ug/L)	<2.0	<2.0	3.1	<2.0	<2.0	<2.0
Molybdenum (ug/L)	2.2	5.7	<1.0	<1.0	23	25

	Exposure Points Used to Evaluate Potable Use Exposure Scenario					
Well ID	**"A" Well (150')**	**B Well (167')**	**B Well (167') (dup)**	**"D" Well (130')**	**DP-1-150**	**DP-2-150**
Elevation (ft)	162	143	143	182	156	159
Sample Date	2/15/2023	3/22/2023	3/22/2023	2/15/2023	8/2/2023	8/3/2023
Boron (ug/L)	1100	NT	NT	290	NT	NT
Cobalt (ug/L)	<2.0	NT	NT	<2.0	NT	NT
Molybdenum (ug/L)	58	56	52	14	80.5	28.5

	Exposure Points Used to Evaluate Aquatic Ecological Receptor Exposure Scenario						
Well ID	**NE-1**	**NE-2**	**NE-3**	**MW-4**	**MW-5**	**MW-8**	**SG-S**
Elevation (ft)	276.0	273.3	271.1	274.3	274.6	272.4	293
Sample Date	2/15/2023	2/15/2023	2/15/2023	10/20/2022	10/20/2022	10/20/2022	2/15/2023
Boron (ug/L)	580	120	77	1000	360	510	81
Cobalt (ug/L)	<2.0	<2.0	<2.0	<2.0	3.1	<2.0	<2.0
Molybdenum (ug/L)	9.8	2.6	2.2	5.7	<1.0	<1.0	3.9

Notes:
< = Not detected less than reporting limit indicated
NT = Not tested
ug/L = micrograms per liter
SG-S = Surface water sample

Table 2 - Exposure Point Concentrations and Screening Results

Fly Ash Pond

Sikeston Power Station

Scott County, Missouri

	Irrigation - Risk Assessment		*Potable Use - Risk Assessment*		*Aquatic Ecological Receptor - Risk Assessment*	
	Exposure Point Concentration	**IRR/LWP**	**Exposure Point Concentration**	**RSL**	**Exposure Point Concentration**	**FSV**
Boron (ug/L)	1,000	2,000	1,100	3,990	1,000	7,200
Cobalt (ug/L)	3	1,000	0	6	3	19
Molybdenum (ug/L)	25	99.8*	81	100	10	800

Notes:

IRR/LWP = Criteria for Irrigation and Lifestock and Wildlife Protection (10 CSR 20-7 Table A1)

*EPA Regional Screening Level for Tap Water used

RSL = EPA Regional Screening Level (Tap Water) - using HI 1 and ELCR 1E-05

FSV (Chronic) = Freshwater Screening Value (Chronic) (Region 4 Ecological Risk Assessment Supplemental Guidance (2018), Table 1a)

Exposure Point Concentration = Maximum concentration from exposure points used to evaluate a given exposure scenario

Appendix C

Fly Ash Pond Study of Closure by Extraction and Relocation Options (ANE, 2024)

Closure by CCR Removal (CBR) from the Fly Ash Pond (FAP) at Sikeston Power Station

Removal of the CCR and decontamination of the FAP CCR unit

In accordance with 40 CFR 257.102 (b) conducting closure of the FAP will require a written closure plan that covers the following key provisions:

- A narrative description of how the FAP will be closed
- Procedures to remove the CCR
- Procedures to decontaminate the FAP after removal of ash
- An estimate of the maximum inventory of CCR in the pond
- A schedule for completing all activities
- Discussion of necessary permits by other agencies

The Initial Closure Plan was completed April 17, 2018 and will be updated to cover these provisions.

The Sikeston Power Station has requested the evaluation of several options for closure by CCR removal. For each of these options a budgetary cost estimate has been developed. Also, a brief discussion of the impacts on the environment and future liability for the Sikeston Power Station is provided. The closure by removal options evaluated include:

Option 1: Landfilling the CCR in an approved Subtitle D landfill
Option 2 : Beneficially reusing the CCR as an alternate raw material in cement production ($0 raw material value)
Option 3 : Beneficially reusing the CCR as an alternate raw material in cement production (with cement plant paying for raw material value)

Closure by Removal Benefits and Liabilities

There are potential long-term obligations and environmental liabilities if the FAP is closed in place. Will environmental regulations change? Will environmentally sensitive areas emerge under future regulations, and/or will groundwater regulations become more stringent causing undue economic hardship for future compliance during post-closure? Are there future land use benefits to closing by removal of the CCR from the 30-acre site? Are there current environmental benefits from closure by removal of the CCR? Closure by removal could address some or all of the items referenced above.

Environmental regulations are significantly different today than they were when the Power Station was constructed and placed into service. The regulatory standards for groundwater impacts have changed, becoming more stringent and the possibility for future, more stringent contamination limits exist.

Environmental liability can be reduced or eliminated by removing the CCR. By removing all CCR and decontaminating the pond, the future threat of added impacts to groundwater contamination are eliminated as the regulated ash is no longer onsite. Even removing a portion of the CCR will reduce liability from potential future regulatory changes. Any future changes to regulations for management of closed-in-place FAP will also be eliminated. Closure by removal of the entire 30-acre site would allow for higher value future land use when the power plant is decommissioned.

Beneficially reusing the CCR as an alternate raw material at a cement production plant will provide environmental benefits by reducing total carbon emissions from the cement plant's air emissions via the stack. Since the CCR is a result of the prior combustion of coal, the use of CCR as an alternate raw material to replace the normal silica-based material at the cement plant will create insignificant CO_2 emissions. Not only will the use of CCR benefit the environment surrounding the power plant, but it will also benefit the cement plant in meeting its net zero carbon emission goals. There may be a future economic value, as a carbon credit, associated with eliminating carbon emissions in the cement production process.

Background information on the FAP

The FAP occupies approximately 30 acres with a maximum berm elevation of approximately 322 feet. The pond depth is approximately 20' with an estimated total volume of ash ranging from 810,00 CY to 860,000 CY of material. The FAP was used for the disposal of CCR from the initiation of plant operations in 1981 to August 31, 2020.

FAP CONSTRUCTION: The construction of the FAP was conducted between 1978 and 1979. The original ground surface was stripped of topsoil, clay, and vegetation to a minimum depth of six inches. The surface was then excavated or backfilled to the desired subgrade elevation. The finished design subgrade elevation of the FAP was 300 feet. The FAP was lined with an approximate two-foot-thick compacted clay liner (CCL) on the bottom and interior slopes.

In more recent years, Disposal operations were conducted by transporting the CCR by truck, in a dry state, from the power station to the FAP. CCR was disposed of in the FAP by pumping existing stormwater from within the FAP, mixing the stormwater with the dry CCR, and sluicing the slurry into the FAP. No new process water from the power station was being added to the FAP by disposal operations.

Closure by Removal Plan Provisions

Excavation and hauling CCR offsite must be completed in order to close the pond by removal. Sending the CCR to either a landfill or beneficially reusing the CCR as an alternate raw material for cement production are potential end destinations for the CCR. Following is a description of the excavation/removal process.

A narrative description of how the FAP will be closed

This plan provides for either a complete removal and closure of the entire FAP or a partial removal of CCR in a smaller portion of the pond followed by capping the remainder of the pond area. Leaving CCR in place and capping is described in more detail in other sections of this report.

The FAP area to be closed by removal will require the following activities:

- Dewater existing surface ponded water
- Dewater pore water from the FAP to the optimal moisture level for shipment
- Commence excavation from the south end of the FAP
- Prepare a loadout pad onsite in an approved area accessible to dump trailers

- Haul removed CCR, using mining type haul trucks, to the loadout pad
- Load and haul CCR on 40 CY dump trailers offsite to either the landfill or cement plant
- Following excavation of the CCR, decontaminate the bottom and berms of the pond via over excavation of the soil base.
- Ship decontamination materials to the landfill, cement plant or use these materials as an initial cover material in low areas for any portion of the FAP closed by capping.
- If only a portion of the CCR is removed, complete the capping of the FAP
- Conduct final grading, seeding and mulching of the site

Procedures to remove the CCR

1. **Dewater existing surface ponded water**
   Water ponded on the FAP will be removed either passively (by gravity drainage) or actively (by pumps or trenches). To dewater portions of the surface impoundment, the CCR material may be moved and stockpiled within the footprint of the impoundment to allow surface water to drain from the surface of the ponded ash. Surface water removed will be conveyed directly to the Process Pond and discharged in accordance with the existing NPDES permit.

2. **Dewater the FAP**
   Dewatering free liquids within the FAP is needed prior to excavating CCR. Free liquids will be removed to control, minimize, or eliminate, to the maximum extent feasible, releases of leachate or CCR contaminated run-off to the ground, surface water, or groundwater. Free liquids within the CCR will be removed utilizing one or more of the following methods:
   - Excavation of trenches to facilitate draining of free liquids.
   - Excavation of one or more sumps within the CCR material to collect free liquids.
   - Excavation of the south end of the FAP material to facilitate drainage and drainage of liquids.

   Accumulated free liquids would be pumped directly to the Process Pond and eventually discharged through the existing NPDES permit outfall.

3. **Commence excavation from the south end of the FAP**
   A tracked excavator will be utilized to remove the CCR from the pond. The excavator will have the capability to excavate the 20' depth of the CCR. The CCR and any original soil placed on the liner will be excavated down to the original clay liner bottom of the pond. The 2' clay liner will not be disturbed during this initial excavation. Decontamination of the interface layer between the CCR and clay liner is addressed below.

   The density of the CCR material is expected to be greater at the south end since CCR was sluiced into the pond from that end. The larger CCR particles remained near the inlet with the finer CCR particles moving away from the inlet. Moisture content is also expected to be lower in the free draining of larger CCR particles. This was confirmed by digging test pits in the south and north ends of the FAP on January 5, 2024. A picture of each test pit follows.

Test Pit South

Test Pit North

By starting excavation on the south end of the pond where the larger CCR particles are present, working conditions will be better than in the north side of the FAP where the finer particle CCR solids have migrated away from the pond inlet location. Smaller particle sized CCR was observed in the test pit at the north end of the FAP.
A ten-foot-wide trench, with 2:1 side slope, will be excavated from the south end of the FAP to the north end. Approximately 48,000 CY of ash will be excavated and placed in the FAP on each side of the initial trench for air drying. By allowing two to three months (or more) of air drying, lower moisture, higher quality CCR can then be shipped. The target moisture level for the CCR would be 15% with a maximum of 20% moisture. By excavating the trench from the south end through the middle of the pond to the north end, dewatering of the CCR can be accomplished more easily in the south end due to the larger particle materials. After CCR has been removed from the south end, the more difficult to dewater CCR in the north end of the pond can then drain to south end. Pumping of free liquids from the FAP can then be performed to increase the recovery of usable CCR .

If the final decision is to close only a portion of the FAP by removal, the same trench technique will be utilized but the trench will have a much shorter length. Removing a portion of the CCR so that the final size of the closed pond is as small as practicable (in acres) will reduce long-term liability. The pond area where the partial removal is performed can be utilized for liquid removal of the remainder of the pond and incorporated into the closure design for capping the FAP.

4. **Haul excavated CCR, using mining type haul trucks, to a loadout pad onsite**
   The excavator removing the CCR will place the CCR material directly onto haul trucks. The haul road may need to be evaluated and possibly improved to handle the extra weight and volume of haul trucks. When full, the truck will haul the CCR to the designated loadout pad onsite where it will be dumped on the pad. Hauling and dumping CCR on a separate loadout pad, with appropriate containment and stormwater control, will be performed to efficiently remove CCR from the pond and then load the CCR on dump trailers to the maximum hauling capacity of the truck for offsite shipment. A small stockpile of CCR (less than 12,000 CY or tons) will be placed on the loadout pad area that will allow for some additional drying of remaining CCR liquids. The loadout pad will be placed in an accessible loading area for outbound trucks hauling CCR material.

5. **Load and haul CCR on dump trailers offsite to either the landfill or cement plant**
   The cost of transporting CCR offsite will be significant. By having a small stockpile of CCR and loader available at the loadout pad location, dump trailers permitted for highway usage, can be loaded for outbound shipment with the maximum allowable weight. The weighing device on the loader will be utilized to maximize the weight on each load. To optimize both driver and truck usage on a daily basis, efficient loading and unloading will allow for four roundtrips per truck to be performed. The nearest landfill and the nearest cement plant are located approximately 30 miles from the site. The landfill and cement plant both have weigh scales for inbound trucks where the final weight of the CCR in each truck will be determined and recorded.

6. **Following excavation, decontaminate the bottom of the pond**
   Once all CCR materials have been removed from the pond, final decontamination of the pond will be performed. An additional 6” of material at the interface of the CCR and the clay bottom liner will be removed. This same procedure will be conducted on the berms of the FAP. For the 30-acre FAP, approximately 25,000 CY of this interface material will be removed.

   Following removal, the FAP bottom will be divided into a grid of six equal areas. In conformance with composite sampling under ASTM D6061-15, six grab samples, from 0” to 6” deep, will be composited from each grid and tested. Testing will consist of a total metals analysis for the constituents as listed in 40 CFR 257.90(e) Table 2 Appendix IV. A background soil sample will also be taken near the plant entrance in an undisturbed area. For the background sample, three grab samples will be taken at 6”, 12” and 18” depth and then composited. This composite background sample will be tested for the same Appendix IV constituents. Each of the six composite samples from the FAP will be compared to the background sample contaminants. To be considered decontaminated, a sample must have contaminants that are equal to or lower than background soil levels or less than Statistically Significant Levels as compared to the background sample. Further soil removal will be required for those grids with higher than background contaminant levels present. Following additional soil removal from the CCR pond, further sampling and soil retesting will be performed to document that decontamination has been performed.

The decontaminated material removed can be hauled to the landfill or to the cement plant for beneficial reuse to replace the cement plant's normal clay based raw material. If the final decision is made to only close a portion of the FAP by removal, some of the decontaminated interface material can be used to improve the necessary elevations needed before the final cap can be placed.

7. **Ship decontamination materials to the landfill, cement plant or use these materials as a filler material in low areas for any portion of the pond where CCR has not been removed.** CCR hauled for closure by removal is an acceptable material for landfilling. Only the Lemons Landfill (Republic Services) located in Dexter, MO less than 30 miles from the FAP is a reasonable distance from the Sikeston Power Station.

   CCR hauled for closure by removal can also be an acceptable material for use as an alternate raw material for the cement production process. CCR has a high silica content and also contains iron, alumina and calcium. All of these constituents are needed as raw material ingredients for producing cement clinker. Composite samples were obtained from test pits in the FAP showing that 88% of the CCR is composed of the four needed ingredients. The results of the testing show that the CCR is an acceptable raw material substitute at the Buzzi Unicem, Cape Girardeau, MO cement plant. The decontamination material, including portions of the clay liner material, are also an acceptable alternate raw material for the cement production process.

8. **Conduct final grading, seeding and mulching of the site**
   A final grading plan will be designed as part of the closure by removal plan for the FAP. The grading plan will identify areas where stormwater will be directed in accordance with NPDES requirements for long-term management. Once final grading is completed the entire disturbed area will be seeded and mulched. The type of seed and volume of mulch will be specified in the final design plan for closure by removal.

An estimate of the maximum inventory of CCR in the pond

The 30-acre pond has a depth of 20'. Based upon the design dimensions and interior slopes of the Fly Ash Pond, an estimated total ash volume ranges from 810,000 CY to 860,000 CY of material. The density of the material will vary with depth and moisture content. Given an average CCR density of 75 lbs./CF, from 820,000 tons to 870,000 tons of ash is estimated in the pond. One cubic yard of CCR following dewatering and some air drying is expected to weigh 2000 lbs. For cost estimating purposes, it was assumed that one cubic yard of ash will weigh one ton.

A schedule for completing all activities

The plan for removal of the ash will be dependent upon if the entire pond is to be closed by removal or only a portion. For CCR materials to be hauled offsite, a schedule will be based upon the acceptable inbound rate for either the landfill or the cement plant.

If all CCR must be removed from the pond within a 5-year period, the following average rate per day of 700 CY (or 700 tons/day) must be hauled. Assuming a total of 850,000 CY of ash will be removed, approximately 1200 days of excavation and hauling will be required. This will require 48 weeks/year of ash removal over the 5-year period. Final decontamination will be accomplished within 6-months of removal of the final CCR. If CCR is to be hauled offsite at a rate of 200 tons/day or 1000 tons per week (48,000 tons/year), which would be the rate expected for beneficially reusing the CCR as an alternate raw material, then nearly 18 years would be required for complete removal of the CCR.

Discussion of necessary permits by other agencies

Closure by removal of CCR from the pond will comply with the closure requirements of 40 CFR 257. The following agency permitting requirements were reviewed:

Sikeston Power Station: Requirements include obtaining approval from Missouri One Call before excavation may commence. Missouri One Call obtains clearance from the Sikeston Street Dept, Sikeston Municipal Utilities and ATT. In addition, the Sikeston Power Station also has an approval/sign off procedure by the appropriate staff before excavation work can commence.

MDNR Air Program: Since the CCR will require dewatering, particulate emissions (PM_{10}) will be de minimis during the excavation activities. Given that approximately 170,000 tons per year of CCR material will be hauled from the site over a 5-year period, a final evaluation will be required to determine if fugitive PM_{10} emissions from haul roads will require an air construction permit. From initial calculations, it is expected that PM_{10} will be below the 15-ton/year threshold where a construction air permit would be required.

MDNR Solid Waste: No solid waste permit will be required for excavating and hauling the CCR offsite.

MDNR Water Protection: The existing FAP stormwater discharge is currently under the NPDES permit for the site. No additional stormwater permitting is required. Since all CCR excavation will occur inside the bermed FAP, a land disturbance permit should not be required. Groundwater monitoring and management activities are covered as part of the closure program and are described in other sections of this document. Stormwater discharge from the loadout pad will have to be incorporated in the existing NPDES permit and preparation of the pad may require a Land Disturbance Permit.

Option 1: Landfilling the CCR in an approved Subtitle D landfill

Disposal of excavated CCR from the FAP can be shipped via forty cubic yard dump trailers and deposited in a sanitary landfill. The nearest landfill to the Sikeston Power Station is the Lemons Landfill located in Dexter, MO. The distance to the landfill is 21 miles. The Lemons Landfill is now owned by Republic Services. A call was placed to Lemons Landfill requesting approval and a tipping fee price for disposing CCR. The standard disposal rate was quoted. Additional discussion is needed with Republic Services on the disposal rate that would be applied to the CCR based upon the daily volume of CCR that could be delivered. A significant volume of available airspace in the landfill would be consumed by the +/- 850,000 cubic yards of CCR. If hauled over a 5-year period, approximately 700 cubic yards of CCR per day would need to be excavated and hauled. This daily volume may be difficult for the landfill to manage.

In the initial disposal fee discussion, the Republic Services representative proposed a tipping fee of $125 per ton. The tipping fee is higher than observed at many other Missouri landfills where more landfill competition exists. The next nearest landfill, in Missouri, to the Sikeston Power Station is the Timber Ridge Landfill located in Richwoods Missouri (southwest of St. Louis), 148 miles away. The high transportation fee hauling from Sikeston to Richwoods, in addition to the Timber Ridge tipping fee, would result in a similar (or higher) landfilling cost as compared to Republic's Lemons Landfill. The economics for landfilling the CCR is the highest cost option as shown in the economic analysis below.

Option 2 : Beneficially reusing the CCR as an alternate raw material in cement production

Buzzi Unicem USA owns and operates a cement production plant on the south side of Cape Girardeau, MO. The plant is located 35 miles from the Sikeston Power Station. The cement plant produces approximately 950,000 tons per year of cement clinker. The raw material mineral needs for the cement plant include calcium, silica, alumina and iron. Limestone provides approximately 80% of the volume for its calcium content. Clay, Tripoli and bauxite are several sources of silica and alumina. From 14% to 17% of the volume for silica and alumina content is provided by these natural raw materials. The clay and Tripoli are the portion of the raw materials that can be replaced by the CCR as an alternate raw material. Since the cement constituent chemistry will not be the same for CCR as compared to clay or Tripoli, approximately 50,000 tons per year is expected as the maximum amount of CCR that could be reused at the Buzzi plant.

Discussions were held with the quality control manager at Buzzi. A representative composite sample of the CCR was requested. On January 5, 2024, Dumey Contracting excavated a test pit from the surface down to near the clay liner in the CCR pond. Since the proposed excavation would involve digging from the top to the bottom of the pond, a composite sample from the test would be representative of future excavated CCR. Grab samples were taken from each bucket as the CCR was excavated. These samples were composited into one representative sample of the CCR and provided to Buzzi for evaluating the cement chemistry.

The results of the testing confirm that there are differences in chemistry between the current natural raw materials and the CCR. The silica, alumina, calcium, and iron content are all good. The two items of concern in the CCR are the moisture content at 48% and the potassium content at 2.44%. Air drying of the CCR before shipment would be required. A copy of the test results is provided in Appendix 2.

The test results show that the Sikeston CCR is a suitable alternate raw material. Given the differences in chemical makeup, particularly the potassium, the quantity that can be utilized to replace current raw materials must be tested at scale and carefully controlled. Buzzi would like to start with a pilot test of 1000 tons of CCR. This volume will be ramped up to a feed rate of 500 tons per week. Impacts to the process and the cement clinker will be evaluated daily for the ASTM quality parameters.

From the pilot testing, Buzzi will be able to determine the volume of CCR that can be utilized on a weekly basis. Buzzi will also be able to observe the handling characteristics of the high moisture CCR as an alternate raw material. From this pilot test run, Buzzi will also be able to evaluate if the CCR has value and whether to just accept the CCR at no charge or pay a fee for the CCR.

Assuming at a minimum, 500 tons week of CCR can be utilized, approximately 23,000 tons per year of the CCR could be incorporated into the raw mix for cement production. It is likely that the weekly volume would double after utilizing this CCR for a period of time when the overall raw mix chemistry is maximized for CCR usage. The maximum volume of CCR estimated to be used as an alternate raw material is 48,000 tons/year. Buzzi would want to sign a long-term contract to insure a continuous supply of the CCR.

As previously stated, the economics involved with beneficially reusing the CCR will be dependent upon the 1000-ton pilot test. Not only will the cement chemistry of the CCR be important, but also the moisture content and handling characteristics of the CCR will be observed at full scale. If the CCR can be managed similarly to the current raw materials and the chemistry proves compliant with ASTM standards, then the CCR will have value for Buzzi. For Option 2, a worst-case situation was assumed where Buzzi would recognize a lower CCR raw material value and not pay Sikeston a tipping fee for the CCR. If the CCR chemistry allows replacement of higher volumes of natural raw materials and the CCR handles well, Buzzi would then see a value for the CCR and would pay a fee for delivered CCR. Option 3 has been prepared assuming that Buzzi would pay $20/ton for the CCR. The fee will need to be negotiated with Buzzi following the pilot test. There is a cost to Sikeston for the pilot test estimated from $25,000 to $35,000. There is a risk that the future value of the ash could be less than $20 per ton. A more detailed economic evaluation follows showing the impacts of the value of the ash.

Economic Analysis

Closure by removal of all ash from an ash pond followed by decontamination of the pond is typically more expensive than leaving the ash in place and capping the site. Closure by removal does provide a significant reduction in long-term liabilities as compared to a capped CCR pond. An economic summary of the options evaluated for closure by removal are provided below. The excavation costs are the same for each option, but the landfill disposal cost and cement reuse options are quite different. Until the pilot test is completed a range of fees as shown in Option 2 and Option 3 has been estimated from past experience with usage of alternate raw materials and discussions with Buzzi.

The cost estimates are based upon budgetary costs as provided by the following entities:

- Excavation: Dumey Contracting, Benton, MO
- Trucking: Buchheit Logistics, Scott City, MO
- Landfill: Republic Services, Lemons Landfill, Dexter, MO
- Cement plant reuse: Buzzi Unicem USA cement plant, Cape Girardeau, MO

The budgetary values utilized in the preliminary cost estimates include:

- 850,000 CY of ash @ 74 lbs./CF = 850,000 tons total
- Fee for excavation, stockpiling, air drying = $1.25/CY
- Fee to load and haul ash from the pond to the loadout pad = $5.00/CY
- Daily loadout rate to cement plant = 200 tons per day, 5-days/week

- Dump trailers can make four round trips per day
- Loading and hauling cost = $20.00/CY

Cost Summary for 850,000 CY of CCR

Excavation, stockpiling and air drying = $1,062,500

Load/haul CCR from pond to loadout pad = $4,250,000

Loading & Hauling CCR Cost = $17,000,000

Disposal/Reuse

- Option 1: Disposal cost at Lemons Landfill = $106,250,000
- Option 2: Reuse at Buzzi Unicem = $0.00 assuming no CCR value
- Option 3: Reuse at Buzzi Unicem = $17,000,000 income assuming CCR value at $20/ton

Option 1 Total Cost = $128,562,500 landfilling

Option 2 Total Cost = $22, 312, 500 ($0 fee at Buzzi) alternate raw material for cement

Option 3 Total Cost = $5,312,500 (Buzzi pays $20/ton for the CCR**) alternate raw material for cement**

A more detailed breakdown of the costs for each option is provided in Appendix 1.

Other Costs and Impacts from Closure by Removal of the CCR

The following summary of information is based upon 200 tons/day or a 1000 tons/week of ash removal. Due to cement plant annual outages, CCR would only be hauled for 48 weeks per year. This volume will provide a comparative analysis of the impacts of ash removal.

- **Emissions**
    - Operating equipment at the site: Heavy construction equipment is regulated under 40 CFR 1039 for emissions. Since 2011, emissions from this equipment, including total hydrocarbon, carbon monoxide, particulate, and organic material hydrocarbon equivalent has been regulated. A specific emission standard for CO2 was not promulgated under the 1039 regulation. Currently, the cement plant is obtaining a clay-based material that must be mined using heavy construction equipment. The same type of excavators currently mining clay will be used for removal of CCR. Therefore, the emissions released from this heavy equipment will be similar since the volumes will also be similar. No new emissions will be produced but the location of the emissions will change.
    - Hauling emissions: Using EPA emission factors for CO2 released from heavy truck hauling, the data shows that 189 metric tons per year of CO2 will be released to the atmosphere from hauling an estimated 48,000 tons/year ash to the cement plant. There are other emissions including total hydrocarbon, carbon monoxide, particulate, and organic material hydrocarbon equivalent. These same emissions would be occurring from the natural clay based raw materials as this clay is being hauled from Southern IL to

    the cement plant. Therefore, both the CO2 emissions and other emissions will be a net zero change due to hauling of either type of silica based raw material.
  - Stack emissions at the cement plant: There will be a positive impact to CO2 emissions at the cement plant from the use of the CCR. CCR is considered a decarbonized material that will replace a clay-based material. Using loss on ignition test data as an indicator of the carbon content, typical clay raw material has from 6% to 10% carbon content. The CCR will be less than 1% carbon. Therefore, the reduction in CO2 emissions resulting from replacement of clay with the decarbonized CCR produces savings of approximately 3000 metric tons per year of CO2 emissions.

- **<u>Hauling impacts on Highways</u>**
  - Impact to roadway maintenance: Hauling an assumed volume of 48,000 tons per year of CCR will have an impact on the highways. The current clay-based materials are being hauled out of southern Illinois on two lane highways. The majority of the haul from Sikeston to Cape Girardeau will be on Interstate 55. Both types of roadways are designed for 80,000 lb. maximum loads but the interstate is designed for a higher volume of heavy trucks. MO DOT shows that the damage impact from a semi-truck as compared to a sedan vehicle calculates to more than 2500 times higher damage.   Given that the interstate is designed for higher volumes of heavier trucks than the two-lane highway, a slightly less amount of damage to the highways could result from hauling the same volume of silica materials. The location of the damage will change.
  - Increases in traffic: Based upon the MO DOT traffic volume map, 12059 total vehicles traveling in one direction utilize Interstate 55 near Cape Girardeau. Of this total 2335 (19%) are semi-trailers. The daily volume of trucks hauling CCR would average eight trucks. This represents a 0.3% increase in semi-trailers and 0.07% in overall traffic.
  - Safety to the public in over-the-road hauling: MO DOT is extremely focused on highway safety particularly on highway deaths. In Cape Girardeau and Scott counties, over a 5-year period, thirteen deaths involved commercial vehicles which represents 15% of the total deaths (89) over this same period. Six of these deaths did occur on Interstate 55. Accidents are a safety concern for all materials being hauled to the cement plant whether it be the current natural clay-based materials or CCR.

<u>Schedule of Activities for Closure by Removal of the CCR</u>

- Coordinate Excavation Permits for Pilot Test = 2 weeks
- Conduct Pilot Testing of 1000 tons of CCR = 8 weeks (includes drying time)
- Determine if Reuse is an option and negotiate the value of the CCR = 4 weeks
- Coordinate Permits or Approvals for closure by removal = 2 months
- Dewater CCR FAP = 6 months
- Complete Closure by Removal Design = 4 months
- Select Closure Contractor = 2 months
- IMPLEMENT CLOSURE PER 257.102
- SPS Place Notice of Intent to Close in Operating Record = 1 day
- Complete CCR Removal within 18 Years of Initiation (requires extension of the 5-year limit)

- Decontaminate FAP within 6-months
- ALL REMOVAL COMPLETED WITHIN 18-YEARS
- Final revisions to Stormwater Management = 1 month
- Seed, Fertilize and Mulch = 4 weeks
- Estimated Final Project Completion Date : 2043
- NOTIFICATIONS REQUIRED BY 257.102
- Certificate Closure by Removal and Decontamination Complete per 257.102
- Place Notice of Closure in Operating Record 1 day

Summary of Closure by Removal

There are significant liability reduction benefits to the Sikeston Power Station if closure by removal of the CCR in the pond can be accomplished. Beneficial reuse of the CCR as a valuable alternate raw material, where Buzzi pays a $20/ton fee for the CCR, upon delivery at the cement plant can be economically competitive with capping the site. Buzzi would like to conduct the 1000-ton pilot test to determine the actual impacts to handling of the higher moisture CCR as well evaluating the impacts to clinker quality before negotiating a fee for beneficially reusing the CCR.

Therefore, expenses will have to be expended to determine how much CCR could be used at the cement plant as well as the value of the CCR. The projected cost for a 1000-ton pilot test ranges from $25,000 to $35,000.

If the pilot test does not prove that the CCR has value and Buzzi only offers to take the CCR at no fee, the economics are not attractive as compared to capping the site. By removing 1000 tons of CCR from the pond, benefits could still be realized if capping the site will be required. Some excavation will be required to dewater the pond prior to commencing the capping project.

If the Sikeston Power Station wants to determine if beneficial reuse and closure by removal is economically feasible, the pilot test will be required.

Appendix 1

Cost Estimate Details

Appendix 1 - Sikeston Flyash Ponds - Cost Estimates

Fly ash pond	30	acres		*(assumes 20% air drying)*	
	1306800	SF		**ash density**	lbs/CF
	1800	ft length		sample 1 FA	79
	726	width		sample 2 FA	69
	20	ft depth		**Avg =**	**74**
volume based upon modeling		850,000	CY		
		849,981	tons	*@74 PCF*	
		(1 CY ash = 1 ton)			
Excavating and Loading ash					
excavate, stockpile, air dry flyash/yr	48000	CY/year	$ 1.25	*per CY*	$ 60,000.00
load/haul: ash pond to loadout pad	48000	CY/year	$ 5.00	*per CY*	$ 240,000
loadout and haul to Buzzi/yr	48000	CY/year	$ 20.00	*per CY*	$ 960,000
				yearly total =	**$ 1,260,000**
years for complete removal	**17.7**	years	**$ 26.25**	***per CY or ton***	**$ 22,312,500**
Option 1 = Landfill (assumes hauling over 5-years)			**170000**	**tons/year**	
excavate, stockpile, air dry flyash	850,000	CY	$ 1.25	*per CY*	$ 1,062,500
load/haul: ash pond to loadout pad	850,000	CY	$ 5.00	*per CY*	$ 4,250,000
loadout and haul to lndfill	850,000	CY	$ 20.00	*per CY*	$ 17,000,000
Disposal at Lemmons		$ 125.00	*per CY*		$ 106,250,000
				Total	$ 128,562,500
Option 2 = Cement Kiln raw material (assumes ongoing volume at 48,000 tons/yr)					
excavate, stockpile, air dry flyash				Total =	$ 1,062,500
load/haul: ash pond to loadout pad					$ 4,250,000
loadout and haul to Buzzi					$ 17,000,000
		per ton fee at Buzzi			
Reuse at Buzzi Cement		$ 0.00			$ -
				Total	$ 22,312,500
Option 3 = Cement Kiln raw material with value (assumes ongoing volume at 48,000 tons/yr)					
excavate, stockpile, air dry flyash				Total =	$ 1,062,500
load/haul: ash pond to loadout pad					$ 4,250,000
loadout and haul to Buzzi					$ 17,000,000
		per ton fee paid by Buzzi			
Reuse at Buzzi Cement		$ (20.00)	*$ (960,000.00)*	*rev/yr*	$ (17,000,000)
				Total	$ 5,312,500
Project Total: Excavation, Hauling and End Use or Disposal					
Option 1 - Landfill					**$ 128,562,500**
Option 2 - reuse as raw material at cement plant ($0/ton)					**$ 22,312,500**
Option 3 - reuse as raw material at cement plant with value ($20)/ton)					**$ 5,312,500**

Appendix 2

CCR Mineral Constituents

```
                                                                      2024-01-10
                                 BUZZI UNICEM USA
                                CAPE GIRARDEAU, MO
-----------------------------------------------------------------RMX XRF PW2400
\UQ4\JOB\JOB.135    2024-01-10
Sample ident  =  SIKESTON POWER STATION FLY ASH
Remark        =  LOSS=2.82  MOISTURE=47.95
2400 Rh 60kV LiF220 Ge111 TlAP
\UQ4\ASC\Kdata.asc 2015-02-06  ..\ChData.asc 2015-02-03
Calculated as :  Oxides        Matrix (Shape & ImpFc):  1 Teflon
X-ray path    =  Vacuum        Film type = No supporting film
Case number   =  0  Known Mass, Area, Rest, Dilution
Eff.Diam.     = 25.0 mm        Eff.Area  = 490.6 mm2
KnownConc     =  0    %
Rest          =  0    %                     Viewed Mass    = 2080.078 mg
Dil/Sample    =  0.065  Cellulose           Sample Height = 2.00 mm
          <    means that the concentration is <  20 mg/kg
          <2e  means wt% < 2 StdErr. A + or & means: Part of 100% sum
 Z        wt%     StdErr   Z          wt%     StdErr   Z          wt%     StdErr
========================= ========================= =========================
SumBe..F   0.078   0.027   29+CuO     0.0110  0.0011  52 TeO2    <
11+Na2O    0.528   0.045   30+ZnO     0.0533  0.0015  53 I       <
12+MgO     1.23    0.02    31+Ga2O3   0.0037  0.0008  55 Cs2O    <
13+Al2O3  19.50    0.20    32+GeO2    0.0024  0.0009  56+BaO     0.0390   0.0080
14+SiO2   47.14    0.27    33+As2O3   0.0097  0.0030  SumLa..Lu  0.099    0.044
15 P                       34+SeO2    <               72 HfO2    <
15+P2O5    0.115   0.003   35 Br      <               73 Ta2O5   <
16+SO3     6.12    0.12    37+Rb2O    0.0145  0.0010  74+WO3     0.0103   0.0020
16 S                       38+SrO     0.0252  0.0016  75 Re2O7   <
17+Cl      0.0211  0.0015  39+Y2O3    0.0054  0.0008  76 OsO4    <
18 Ar      <               40+ZrO2    0.0215  0.0011  77 IrO2    <
19+K2O     2.44    0.17    41 Nb2O5   <               78 PtO     <
20+CaO     9.39    0.16    42 MoO3    <               79 Au      <
21+Sc2O3   0.0032  0.0011  44 RuO4    <               80 HgO     <
22+TiO2    0.819   0.056   45 Rh2O3   <               81 Tl2O3   <
23+V2O5    0.0480  0.0028  46 PdO     <               82+PbO     0.0128   0.0013
24+Cr2O3   0.0970  0.0025  47 Ag2O    <               83 Bi2O3   <
25+MnO     0.0604  0.0030  48 CdO     <               90 ThO2    <
26+Fe2O3  12.10    0.08    49 In2O3   <               92 U3O8    <
27+Co3O4   0.0119  0.0014  50 SnO2    <               94 PuO2    <
28+NiO     0.0155  0.0014  51 Sb2O3   <               95 Am2O3   <
==== Light Elements ====== ==== Noble Elements ===== ====== Lanthanides ======
SumBe..F   0.078   0.027   44 RuO4    <               57+La2O3   0.0109   0.0018
 4 BeO                     45 Rh2O3   <               58 CeO2    <
 5 B2O3                    46 PdO     <               59 Pr6O11  <
 6 CO2                     47 Ag2O    <               60 Nd2O3   <
 7 N                       75 Re2O7   <               62+Sm2O3   0.0211   0.0060
 8 O                       76 OsO4    <               63 Eu2O3   <
 9 F       0.078   0.027   77 IrO2    <               64 Gd2O3   0.0071   0.0025
                           78 PtO     <               65 Tb4O7   <2e      0.0055
                           79 Au      <               66 Dy2O3   0.0074   0.0032
                                                      67 Ho2O3   <
                                                      68+Er2O3   0.0363   0.0032
                                                      69 Tm2O3   <
                                                      70 Yb2O3   <2e      0.0020
                                                      71 Lu2O3   <2e      0.0019
KnownConc= 0                    REST= 0                 D/S= 0.065Cellulose
Sum Conc's before normalisation to 100% :   105.5 %
```

Appendix D

Chemical Constituents in Coal Combustion Products: Cobalt, (EPRI, 2019)

ELECTRIC POWER
RESEARCH INSTITUTE

Chemical Constituents in Coal Combustion Products: Cobalt

2019 TECHNICAL REPORT

Chemical Constituents in Coal Combustion Products: Cobalt

3002016497

Final Report, June 2019

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ABSTRACT

Cobalt is a constituent that can be present in coal and coal combustion products (CCPs) and can be found in CCP leachate. This chemical profile assembles and summarizes existing information on cobalt's environmental characteristics, with a focus on conditions associated with CCP management. Extensive references provide a means for obtaining more detailed information on specific subject areas. The following topics are covered: 1) occurrence and sources of cobalt; 2) geochemistry fate and transport in groundwater; 3) cobalt leaching from CCPs; 4) human health and ecological toxicology, including health and risk benchmarks; 5) environmental sampling and analysis, and 6) groundwater remediation and treatment technologies. Chemical profiles have been completed for arsenic, beryllium, boron, cobalt, chromium, lithium, molybdenum, radium, selenium, and thallium.

Keywords
Coal combustion products
Cobalt
Remediation
Leachate
Toxicology

EXECUTIVE SUMMARY

Deliverable Number: 3002016497

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PRIMARY AUDIENCE: Environmental managers responsible for groundwater monitoring programs

SECONDARY AUDIENCE: Risk managers

KEY RESEARCH QUESTION

Cobalt is a metal that naturally occurs in soil, water, and coal. Cobalt generally has low solubility and relatively low leachability from coal combustion products (CCPs). However, cobalt has low (typically <1 µg/L) concentration in background groundwater, and it can leach from CCPs at concentrations higher than the United States Environmental Protection Agency (USEPA) regional screening level (RSL) of 6 µg/L, and therefore can be a constituent of interest (COI) in groundwater.

The objective of this research was to assemble and synthesize information on cobalt regarding its environmental occurrence, environmental behavior, human and ecological toxicology, sampling and analysis, and treatment and remediation, with specific emphasis on the implications for CCP management.

RESEARCH OVERVIEW

The project team performed a literature search using several databases to compile relevant information on cobalt. Key secondary sources and relevant EPRI reports and data were also reviewed. Cobalt concentrations in CCP leachates were obtained from EPRI's CPInfo database. Information from these sources was summarized so that key data and references could be contained and accessed easily in one report.

KEY FINDINGS

- Cobalt compounds vary greatly in solubility, but in the environment, cobalt is found mainly in the solid phase.
- Naturally occurring cobalt concentrations in groundwaters are typically lower than 1 µg/L.
- Cobalt's solubility is sensitive to redox chemistry, with the oxidized form (Co^{3+}) being less soluble than the reduced form (Co^{2+})
- Adsorption of cobalt in soils and sediments primarily occurs on iron and manganese (oxy)hydroxides and clay minerals. The process is pH dependent, with very little sorption occurring at pH less than 4 SU.
- Mean distribution coefficients (K_d) reported for cobalt were 60 L/kg in sandy soil and higher in other soil types, except for in low-pH environments, where a mean K_d of 12 L/kg was reported for radiocobalt. These values are indicative of an element with moderate to low mobility in groundwater.
- Median concentrations for cobalt in porewater from different types of CCPs were typically less than 4 µg/L, although higher concentrations were noted at some sites.
- Human exposure to cobalt occurs primarily through dietary sources, including ingestion of the essential cobalt-containing vitamin cobalamin (vitamin B_{12}). The diet is the primary source of cobalt exposure in the general population. Most dietary cobalt is in inorganic forms, with a small percentage as vitamin B_{12}. Cobalt is essential only as a component of vitamin B_{12}, which is not produced in the human body and is required to maintain proper health.

- There are no studies available on humans or laboratory animals that adequately address carcinogenic risks from oral exposure to cobalt. Nevertheless, the National Toxicology Program concluded that metallic cobalt and cobalt compounds that release metal ions are reasonably anticipated to be human carcinogens, based on inhalation studies in rodents combined with mechanistic data indicating that that in vivo exposure to cobalt ions is a key event for cobalt-induced carcinogenicity.
- USEPA derived a tap water RSL for cobalt of 6 µg/L that is protective of residential water consumption.
- The form of cobalt present in the environment may affect its bioavailability to organisms and thus its ecological effects. Typically, cobalt found in soil is not readily bioavailable to organisms because cobalt readily complexes with organic matter and precipitates as carbonate and hydroxides.
- When cobalt is a COI at a CCP site, there are a variety of remediation alternatives that can be effective, including monitored natural attenuation, groundwater pump and treat, in situ immobilization, containment using barrier walls, in situ solidification/stabilization, or other isolation methods (capping, excavation and disposal, and liner retrofitting).

WHY THIS MATTERS

Because CCPs disposed of in landfills and surface impoundments have the potential to impact the environment, particularly groundwater, it is important to have a complete understanding of the key constituents in CCPs. In particular, it is important to understand the leaching behavior of these constituents under different environmental conditions, the environmental levels of these constituents that may lead to potential exposures and adverse human health and ecological effects, and the remediation technologies that may be effective if such environmental concentrations occur.

HOW TO APPLY RESULTS

Results of this research provide background on cobalt occurrence and concentrations in nature, as well as in CCP leachate. Results can be used to evaluate appropriate human and ecological risk-based criteria, laboratory analytical issues, and prospective remediation technologies for lithium.

LEARNING AND ENGAGEMENT OPPORTUNITIES

- EPRI has previously published chemical profiles, and technical briefs summarizing and updating profiles, for arsenic (full profile: 1015550, tech brief: 1021212), beryllium (full profile: 1012583), boron (full profile: 1005258, tech brief: 1023737), chromium (tech brief: 1022143), lithium (full profile: 3002012311), molybdenum (full profile: 1021815), radium (full profile: 3002016496), selenium (full profile: 3002001237, tech brief: 3002003761), and thallium (full profile: 1016801, tech brief: 3002001155).
- This research may be of interest to other industries where cobalt is monitored in groundwater, in particular the solid waste management industry and the mining industry.

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PROGRAM: Coal Combustion Products – Environmental Issues, P49

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1

INTRODUCTION

Coal combustion products (CCPs), produced when coal is burned to generate electricity, contain a variety of trace elements. Characterizing the potential human health, ecological, and environmental risks that can result from the management of CCPs has been an important research topic for the Electric Power Research Institute (EPRI) and federal regulatory agencies, such as the U.S. Environmental Protection Agency (USEPA), for several decades. These issues gained heightened attention in recent years, and in 2015, USEPA issued the Coal Combustion Residuals (CCR) Rule (40 CFR Part 257 and 261), modifying the regulation of CCP disposal practices.[1]

Because CCPs disposed of in landfills and surface impoundments have the potential to impact the environment, particularly groundwater, it is important to have a complete understanding of the key constituents in CCPs. In particular, it is important to understand the leaching behavior of these constituents under different environmental conditions and the environmental levels of these constituents that may lead to potential exposures and adverse human health and ecological effects.

Cobalt (Co) is a trace element often present in CCPs and in CCP leachate. In the USEPA human health and ecological risk assessment of CCPs, USEPA indicates that cobalt was in a second category of constituents "for which the risk assessment and the damage cases did not agree" where risk modeling showed "risk at the 90th percentile but no damage cases had been proven as of 2007" (USEPA, 2010). Although cobalt does not have a maximum contaminant level (MCL), USEPA included cobalt in the CCR Rule Appendix IV list of constituents for assessment monitoring "because cobalt was found to be a risk driver in the 2014 risk assessment, based on certain waste management disposal practices that lead to highly acidic wastes conditions" (40 CFR Part 257 and 261). Specifically, USEPA stated that certain constituents including cobalt "presented higher risks when considered in waste management units that co-dispose both ash and coal refuse at more acidic pHs or [flue gas desulfurization] FGD wastes at more basic pHs" (40 CFR Part 257 and 261). USEPA further stated in the original CCR Rule that "if a constituent has no MCL (i.e., cobalt, lead, lithium and molybdenum), their groundwater protection standards will be their background levels" (40 CFR Part 257 and 261). USEPA subsequently revised the CCR Rule (USEPA 2018a), specifying a Groundwater Protection Standard (GWPS) of 6 µg /L, or background if higher, for cobalt. This GWPS was based on the Regional Screening Level (RSL).[2] Furthermore, USEPA left open the possibility that further changes to the CCR Rule could be considered that may enable the use of risk-based alternative standards for constituents without MCLs (USEPA 2018a).

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[1] Coal combustion residuals (CCR) is a term used by USEPA for the same materials referred to as CCPs in this document.

[2] RSLs are subject to periodic revision.

The inclusion of cobalt in the Appendix IV list of constituents underscores the importance of understanding its potential to leach from waste management units and whether those releases can occur at levels that may exceed background concentrations and/or impact human and ecological receptors. In addition, in the absence of a fully peer-reviewed reference dose (RfD) and an established drinking water standard for cobalt, compiling the available toxicological information is necessary to evaluate risk-based alternative standards and site-specific risk management programs before closure of CCP facilities.

This report describes the current understanding of cobalt occurrence and behavior in the environment as well as in CCPs and CCP-related waste streams. Section 2 summarizes occurrences, uses, and sources of cobalt. Section 3 covers the geochemistry and fate and transport of cobalt, and Section 4 addresses leaching of cobalt from CCPs. Sections 5 and 6 discuss potential health and ecological impacts. Section 7 discusses sampling and analysis methods, and Section 8 discusses treatment and remediation options. Section 9 summarizes key points from the preceding sections.

Numerous online search engines (e.g., ProQuest, PubMed, Google Search, and Google Scholar) were used to identify relevant research articles, reports, and reviews. Information and data presented here are comprehensive, though not exhaustive.

2

OCCURRENCES, USES, AND SOURCES

2.1 Occurrence and Forms

Cobalt is an element that occurs naturally in water, rocks, and soil, and in small amounts in animals and plants. In the environment, cobalt is associated with iron and manganese and is often found with nickel. Cobalt is the 33rd most abundant element in the Earth's crust (Young 1956). Typical environmental media concentrations are provided in Table 2-1.

2.1.1 Rock and Soil

In the Earth's crust, cobalt is found at a concentration of approximately 25 mg/kg (Taylor 1964 cited in Hamilton 1994), which varies with mineral type. Basic and ultrabasic rocks have a low silica content and contain approximately 100 mg/kg cobalt, basalts contain 40 to 50 mg/kg cobalt, and granites contain 1 to 10 mg/kg cobalt (Hamilton 1994). Chief ores of cobalt are cobaltite (CoAsS) and skutterudite ($CoAs_3$; also known as smaltite). Other cobalt-containing minerals include linnaeite (Co_3S_4), erythrite ($Co_3[AsO_4]_2 \cdot 8H_20$), and glaucodot ([Co, Fe]AsS) (Emsley 1998).

In surface soils (1,311 samples from across the United States), cobalt concentrations were reported to range from <0.1 to 216 mg/kg, with a median of 7.7 mg/kg (Smith et al. 2014). An earlier study by Shacklette and Boerngen (1984) found cobalt to have an overall geometric mean of 6.7 mg/kg with concentrations varying between the eastern and western United States (geometric mean of 5.9 mg/kg in eastern soils versus 7.1 mg/kg in western soils). Smith et al. (2014) found the highest cobalt concentrations in soil to be in the northwestern continental United States as well as in the general area of the Appalachian basin. USEPA's Ecological Soil Screening Level document (USEPA 2005) reports cobalt concentrations to range between 1 and 15 mg/kg dry weight (dw) in soil from the eastern United States and between 7 and 20 mg/kg dw in soil from the western United States. Wetland soils, dark brown clay soils, and limestone soils have higher than average cobalt concentrations, with values reported at 10 to 12 mg/kg (Baralkiewicz 1999).

In soils near industrial facilities (e.g., smelters) or other anthropogenic sources, cobalt concentrations can be up to 800 mg/kg (Kloke et al. 1984; Smith and Carson 1981 as cited in ATSDR 2004a). Elevated soil or sediment levels of cobalt can result from anthropogenic activities such as application of sludge or phosphate fertilizers to soil, mining and mineral processing, power generation by electric utilities, disposal of industrial waste, and atmospheric deposition from smelting, refining, and fossil fuel combustion (ATSDR 2004a).

Sediment cobalt concentrations are similar to those in soils. More than 74,000 stream sediments collected from throughout the United States as part of the National Geochemical Survey had a median value of 9 mg/kg and ranged from not-detected (ND) to 695 mg/kg, with a mean of 10.9 mg/kg (USGS 2004).

Table 2-1
Cobalt concentration ranges reported for environmental media

Medium (Location)	Cobalt Concentration Mean (Min–Max)	Reference
Air		
Ambient levels–remote global	0.0005–0.9 ng/m^3 [a]	ATSDR (2004b)
Open ocean atmosphere	0.0004–0.08 ng/m^3 [a]	Chester et al. (1991) as cited in ATSDR (2004b)
Ambient levels–urban U.S.	0.2–83 ng/m^3 [a]	ATSDR (2004b)
Atmosphere near a U.S. smelter	(maximum: 610 ng/m^3)	ATSDR (2004b)
Water		
Groundwater (U.S.)	8.1×10^{-4} mg/L (ND–0.095 mg/L)	Groschen et al. (2009)
Ocean water (Atlantic)	(2×10^{-7}–5×10^{-6} mg/L)	Saito and Moffett (2002)
Ocean water (Pacific)	(4×10^{-7}–3×10^{-6} mg/L)	Martin and Gordon (1988); Martin et al. (1989); Sunda and Huntsman (1995); all as cited in Saito and Moffett (2002)
Land		
Earth's crust (worldwide)	20 mg/kg	Emsley (1998)
	25 mg/kg	Taylor and Mclennan (1985) as cited in Hamilton (1994)
Upper continental crust (worldwide)	10–18 mg/kg	EarthRef (2018)
Soil (worldwide)	1.6–21.5 mg/kg[a]	McBride (1994)
Soil (U.S.)	7 mg/kg (1–40 mg/kg) 6.7 mg/kg (<0.3–>70 mg/kg) 1–17 mg/kg[a]	Smith and Carson (1981) as cited in ATSDR (2004b) Shacklette and Boerngen (1984) McBride (1994)
Soil (eastern U.S.)	(1–15 mg/kg)	USEPA (2005)
Soil (western U.S.)	(7–20 mg/kg)	USEPA (2005)
River sediments (U.S.)	10.9 mg/kg (ND–695 mg/kg)	USGS (2004)

Note: ND – not detected.
[a] Range of means.
[b] In areas without cobalt minerals.

2.1.2 Coal

Coal can include many trace elements incorporated during formation or during subsequent alteration. Cobalt is found in trace quantities in coal, varying widely among geographical regions and deposits. The highest levels of cobalt in coal are associated with coal containing marine black shales (Merian et al. 1985 as cited in Hamilton 1994).

There are 7,529 measurements of cobalt in coal reported in the U.S. Geological Survey (USGS) Coal Quality Database (Palmer et al. 2015). The concentration of cobalt in these coal samples ranges from ND to 322 mg/kg, with a median value of 4.8 mg/kg and a mean of 6.3 mg/kg (Figure 2-1). The concentration of cobalt varies with coal types. Median values range from 1.6 mg/kg for lignite to 6.5 mg/kg for anthracite (Figure 2-2). There is also variability between coal regions, with coal from the Pacific Coast having the highest median cobalt value (9.2 mg/kg) and coal from the Great Northern Plains having the lowest (1.4 mg/kg; Figure 2-3).

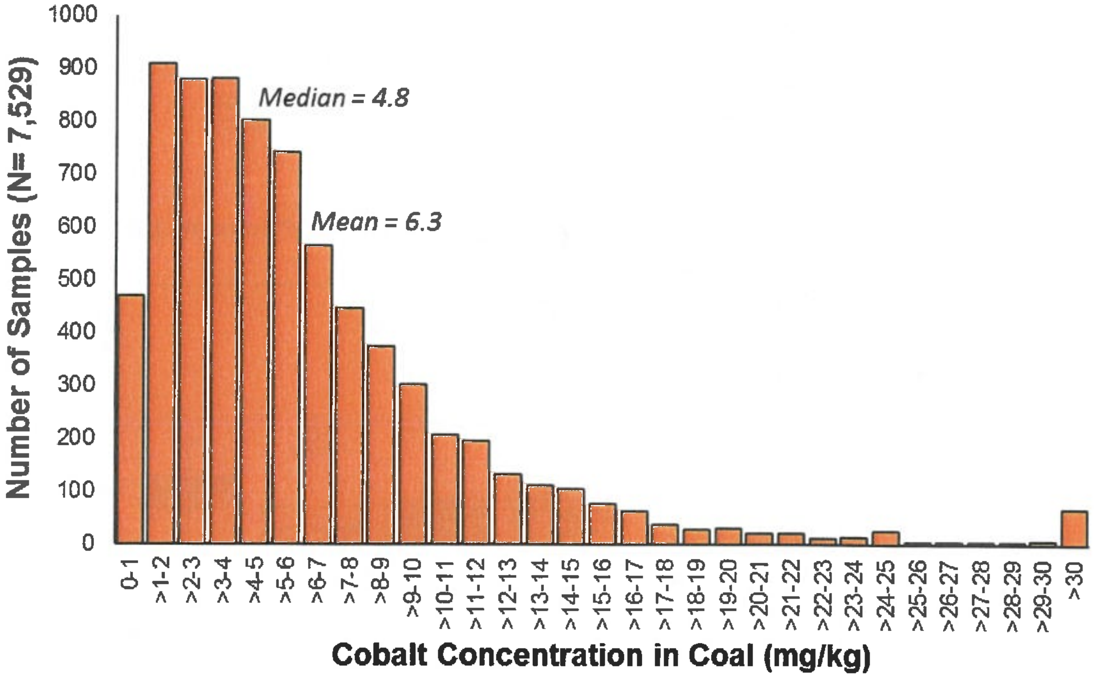
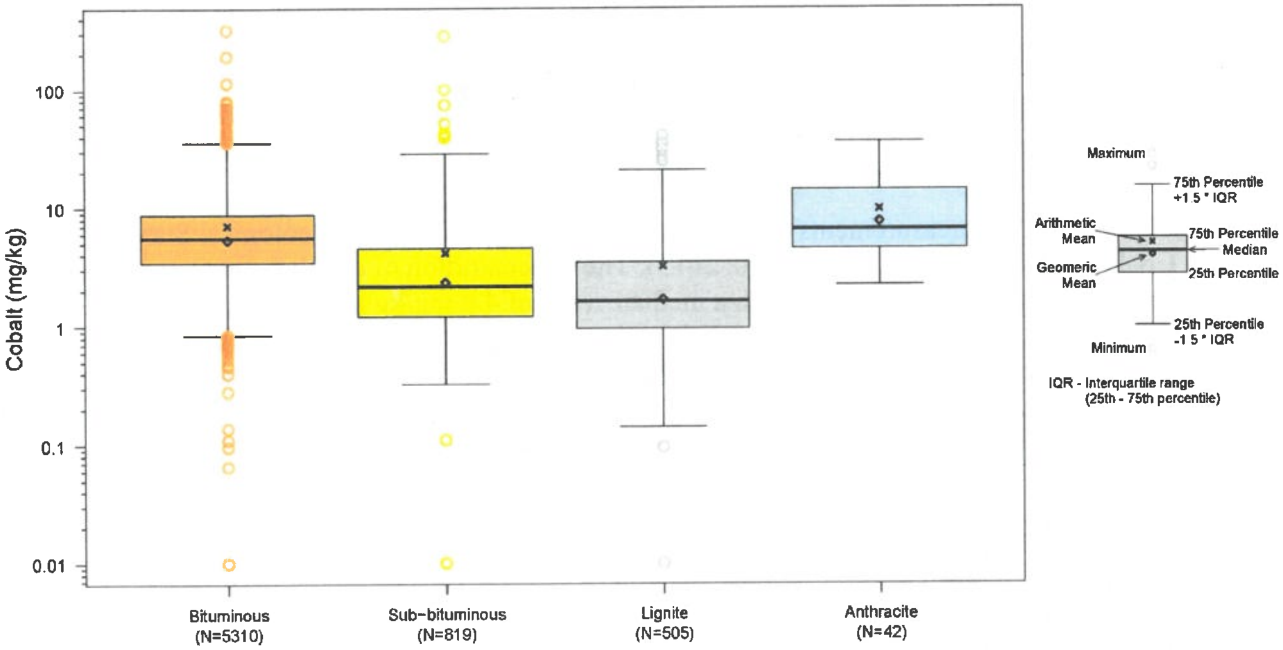


Figure 2-1
Cobalt concentration distribution in domestic coal (histogram) (Palmer et al. 2015)

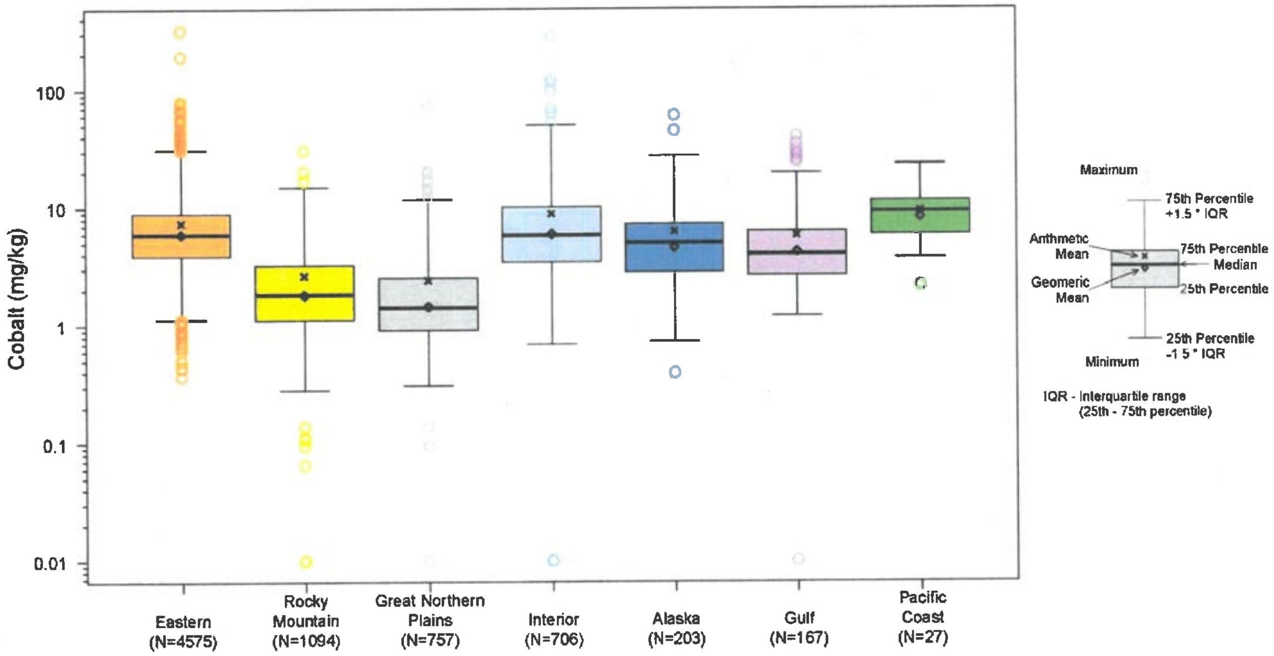
A review of experimental and observational studies of coal found that the mode of cobalt occurrence varied between coals and/or experimental systems. Cobalt was associated with pyrite and other sulfide minerals in some studies but not others, and the authors hypothesized that some fraction of the measured cobalt was present associated with organic material (Finkelman 1994).

Cobalt has been measured in fly ash (mean: 25 mg/kg) and flue gas (100–700 mg/m^3) from coal-burning power plants (ATSDR 2004b).



Not-detected (ND) results shown at 0.01 mg/kg

Figure 2-2
Comparison of cobalt concentrations in coal by type (data from Palmer et al. 2015)



Not-detected (ND) results shown at 0.01 mg/kg

Figure 2-3
Comparison of cobalt concentrations by coal province (data from Palmer et al. 2015)

2.1.3 Water

In a study of groundwater collected from 847 groundwater wells drilled into the glacial aquifer system, which provides nearly 50% of the drinking water to the United States, cobalt was detected in approximately half (451) of the samples with a median value of 0.21 µg/L and an average value of 0.81 µg/L (range: ND to 95 µg/L) (Groschen et al. 2009). Concentrations of cobalt in groundwater were generally higher in the central United States than in coastal areas, and monitoring wells installed as part of the USGS National Water-Quality Assessment Program were found to have a higher concentration than drinking water wells (Groschen et al. 2009). A more extensive survey of 3,026 samples from multiple aquifer systems did not find cobalt above detection limits (typically DL was 1 µg/L) in 72% of the samples but found higher maximum values (range: ND to 680 µg/L; USGS 2011). Even though the range reported by USGS (2011) was higher, the calculated median of 0.17 µg/L was similar to the median reported by Groschen et al. (2009). USGS (2011) found that more than 75% of the groundwater samples analyzed had cobalt concentration lower than 1 µg/L (Table 2-2). Higher cobalt (along with iron, manganese, lead, and aluminum) concentrations were found in humid regions compared with dry regions. Within the dry regions, higher cobalt was found in wells in urban areas compared to agricultural areas, but no association between cobalt concentrations and land use was found in humid regions. Concentrations of cobalt were higher in mixed or anoxic aquifers compared to aquifers with oxygen present, which is consistent with mobilization of cobalt from iron and manganese minerals under reducing conditions (Section 3.3.2; USGS 2011).

Table 2-2
Cobalt concentrations in principal aquifers of the United States

Aquifer Type	Percent Detected	Median[a] (µg/L)	75th Percentile[a] (µg/L)	90th Percentile (µg/L)
All	27.7%	0.17	0.48	1.1
Sand & Gravel	28.9%	0.14	0.33	0.77
Glacial Sand & Gravel	35.3%	0.20	0.58	1.8
Semiconsolidated Sand	51.9%	0.28	1.1	4.1
Sandstone	21.5%	<1	<1	4
Sandstone & Carbonate	3.2%	<1	<1	<1
Carbonate	11.6%	<1	<1	<1
Basaltic/Volcanic	0%	<1	<1	<1
Crystalline	9.8%	<1	<1	<1

Source: USGS 2011.

[a] Median and 75th Percentile values were calculated at values lower than the reporting level when sufficient data and a sufficient number of values higher than the MDL were available.

In surface water, cobalt was ND in 67% of stream and lake samples in a 1970 study that collected samples from surface waters in the 50 states and Puerto Rico, but for samples where cobalt was detected, concentrations were typically in the range of 1 to 5 µg/L (Durum et al. 1970). These samples were collected from public water supply sources as well as locations downstream of urban or industrial sites.

Ocean concentrations of cobalt tend to be lower than freshwater, e.g., ranging from 0.0001 to 0.004 µg/L in the Atlantic, a range that was reported to be consistent with values previously reported for the Pacific. In the oceans, cobalt exhibits behavior similar to both scavenged and nutrient-type elements,[3] consistent with the behavior of iron (Saito and Moffett 2002).

2.1.4 Air

Cobalt is nonvolatile but present in the atmosphere in association with airborne particulates. Typical atmospheric concentrations of cobalt are 0.4 to 2.0 ng/m^3 (ATSDR 2004b). Concentrations greater than 10 ng/m^3 have been measured in source areas, such as at a nickel refinery (Smith and Carson 1981, cited in ATSDR 2004b).

2.2 Uses

Historically, the characteristic blue color of cobalt made it useful as a pigment in paints and glasses (Young 1956). Today, cobalt's physical and chemical properties make it useful in a wide variety of industries, including aerospace, industrial equipment, and healthcare. In particular, cobalt's strength at high temperatures and resistance to wear result in its use in "superalloys" specifically designed for use at higher temperatures. These alloys are found in jet engines, power plants, and other locations where strength at higher temperatures is required and are currently the largest use of cobalt by industry in the United States (USGS 2018; Figure 2-4). Cobalt is increasingly being used in the rechargeable battery industry, leading to an increase in demand (USGS 2015, 2018; Figure 2-5). Worldwide, batteries make up 30% of cobalt use, as of 2011 (Slack et al. 2017).

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[3] Elements exhibiting nutrient-like profiles show a decrease in concentration with depth because of uptake by organisms in surface waters. Scavenged elements generally decrease with depth because of their association with particulate matter that is most prevalent in surface waters.

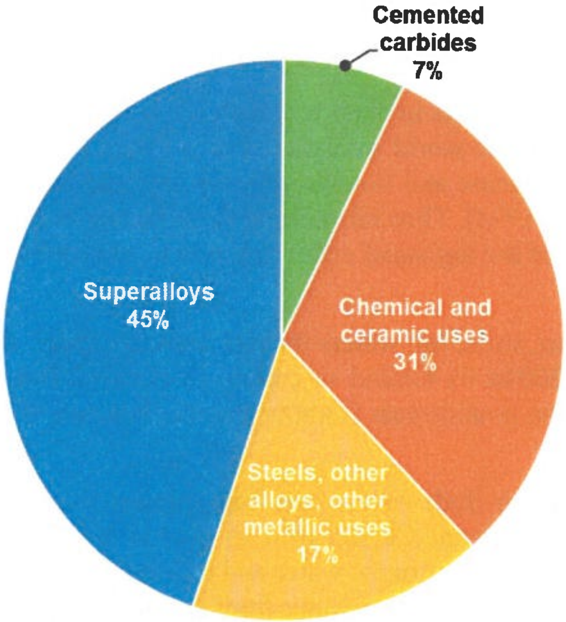

Figure 2-4
Uses of cobalt in the United States in 2017 (data from USGS 2018)

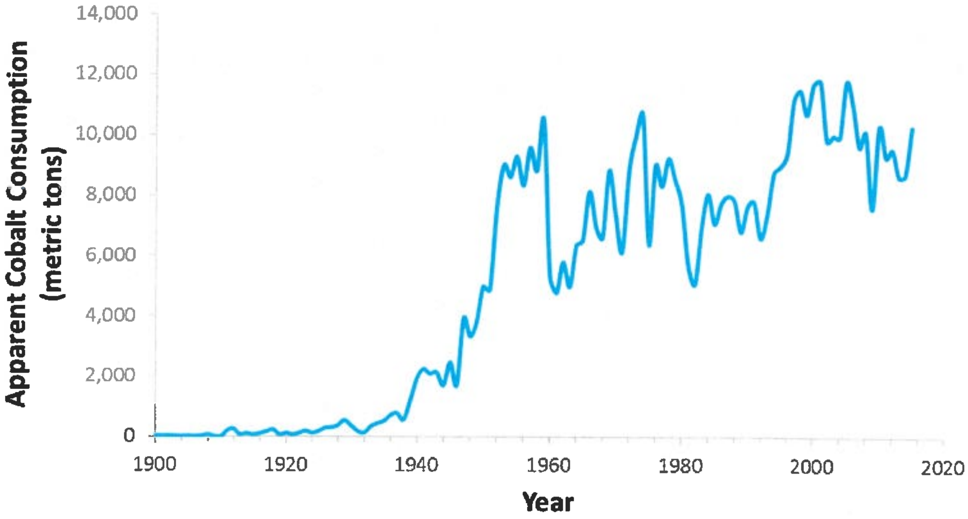

Figure 2-5
Historical cobalt consumption in the United States, metric tons (modified from USGS 2015)

2.3 Sources

Cobalt has been mined commercially since 1905 and has been recovered from the processing of copper ores since 1926 (Hamilton 1994). As of 2017, more than half the world's mined cobalt came from the Congo (Kinshasa) where it was extracted from copper-containing deposits (USGS 2018). In the United States, cobalt has historically been produced as a byproduct of mining for other metals (ATSDR 2004b). In 2017, a small amount of cobalt was obtained from a cobalt-bearing nickel concentrate mined in Michigan, but most of the cobalt used by the United States was imported or from recycled sources (Slack et al. 2017).

An additional reservoir of cobalt occurs in deep-sea manganese nodules and other deposits, which contain more than 80% of the world's cobalt deposits (Slack et al. 2017). These structures are formed of precipitated manganese and iron (oxy)hydroxides and have been found to contain 0.56 to 1.5% cobalt (Hamilton 1994). Thus far, mining these resources has not been commercially viable because of the logistical effort required to obtain them, but work is ongoing (Park and Yang 2009).

Natural sources of cobalt to air, soils, and waters include seawater spray, dust, forest fires, and volcanic eruptions (ATSDR 2004a, b). Global air emissions of cobalt from natural sources are estimated to be 13 to 15 million pounds/year (Lantzy and Mackenzie 1979; Nriagu 1989 as cited in ATSDR 2004b).

Sources of anthropogenic cobalt include wastewater from mining operations, refinery processes, and chemical manufacturing (Smith and Carson 1981 as cited in ATSDR 2004b). Additional sources include municipal discharges, process water and effluent from coal residue and gasification processes, and discharge of wastewater from pigment manufacturing. Runoff and leaching of cobalt from soil into water bodies also occurs from both anthropogenic and natural sources (ATSDR 2004b). Radioisotopes of cobalt, while not naturally occurring, may be present in effluent from nuclear reactors and may be detected in water and sediments downstream of release points.

Anthropogenic sources are estimated to contribute 9.7 million pounds/year to atmospheric emissions (ATSDR 2004b). The Toxic Chemical Release Inventory (TRI) reported the release of cobalt and cobalt compounds into water, soil, and air from U.S. facilities in 2016 as 2,467,182 pounds (USEPA 2018d).

3

GEOCHEMISTRY AND FATE AND TRANSPORT

This section provides a review of the geochemistry and fate and transport of cobalt in the environment. Section 3.1 presents the basic chemical and physical properties of cobalt; Section 3.2 discusses the chemistry of cobalt in solids including minerals, soil, sediment, and coal; Section 3.3 focuses on the aqueous geochemistry of cobalt; and Section 3.4 discusses fate and transport of cobalt in the environment.

Cobalt is found in many different minerals, often associated with arsenic, iron, manganese, nickel, or copper. Chemically, cobalt behaves similarly to other divalent metal cations. In water, soils, and sediments, cobalt cycles together with manganese and iron because of similar chemical properties.

3.1 Basic Chemical and Physical Properties

Cobalt is a transition metal with an atomic number of 27 and an average atomic mass of 58.933195. Additional properties of cobalt are summarized in Table 3-1. There is only one naturally occurring isotope of cobalt, ^{59}Co (100%), but multiple synthetic radioisotopes have been generated. Of the radioisotopes, ^{60}Co is the most important. It is formed through the neutron activation of ^{59}Co and has a half-life of approximately 5.3 years. The gamma rays produced by ^{60}Co are used in a variety of industrial applications (Emsley 1998).

Table 3-1
Properties of cobalt

Property	Value
Symbol	Co
Atomic Number	27
Atomic Mass	58.9
Chemical Series	Group 9, Transition metals
Valence States	Common: +2, +3 Less common: -1, 0, +1, +4, +5
Room Temperature Phase	Solid
Solid Density (293 K)	8,900 kg/m^3
Liquid Density (melting point)	7,670 kg/m^3
Melting Point	1,768 K
Boiling Point	3,143 K
Heat of Fusion (melting point)	15.2 kJ/mol
Heat of Vaporization	382.4 kJ/mol

Source: Emsley (1998).
Note: K – Kelvin.

3.2 Solid-Phase Geochemistry

3.2.1 Geochemistry in Mineral Forms

Cobalt is a structural component of more than 70 mineral species, but there are no discrete cobalt minerals found in surface sediments and soils (Ames and Rai 1978). Instead, cobalt occurs in solution with other elements of similar charge and size, such as iron, manganese, copper, and nickel (Hamilton 1994). Cobalt is found most frequently associated with sulfides, oxides, and arsenic-containing compounds (Hamilton 1994). Major minerals include cobaltite, erythrite, and skutterudite (Emsley 1998). Additionally, cobalt can be incorporated into sulfide minerals such as pyrite. Weathering leaches some cobalt from these minerals, which is mobilized as Co^{2+} and either enters surface or groundwater or is incorporated into new mineral forms.

3.2.2 Geochemistry in Soil and Sediment

The behavior of cobalt in soils and sediments is primarily controlled by the cycling of iron and manganese, where solid oxides form under aerobic conditions and dissolve under reducing conditions. In addition to manganese and iron (oxy)hydroxides, cobalt can be associated with aluminosilicates (ATSDR 2004b). Cobalt also binds to organic matter in soils, such as humic substances. If soil conditions become more reducing, cobalt may become more mobile as iron and manganese oxides dissolve.

3.3 Aqueous Geochemistry

3.3.1 Speciation

In natural waters, cobalt primarily exists in the +2 and +3 oxidation states, with Co^{2+} being the most common form. Cobalt forms complexes with hydroxide, fluoride, sulfate, phosphate, chloride, and organic ligands. In the dissolved form, cobalt commonly occurs as $CoCO_3$ or Co^{2+} in freshwater (Groschen et al. 2009). Cobalt's solubility is sensitive to redox chemistry, with the oxidized form (Co^{3+}) being less soluble. Oxidation of cobalt from the +2 to +3 oxidation state is mediated by manganese oxidation. Co^{3+} is a strong oxidant and is unstable under the Eh-pH conditions typically found in natural waters. However, Co^{3+} may be present in oxide phases and dissolved Co^{3+} may exist in complexes with organic ligands.

3.3.2 Solid-Liquid Partitioning

Cobalt compounds vary greatly in solubility, but in the environment cobalt is found mainly in the solid phase. Solubility information for selected cobalt compounds is presented in Table 3-2.

Table 3-2
Selected cobalt compound solubility

Compound	Formula	Solubility in Water
Cobalt	Co	Insoluble
Cobalt(II) chloride	$CoCl_2$	450 g/L (7°C)
Cobalt(II) hydroxide	$Co(OH)_2$	0.0032 g/L
Cobalt(II) carbonate	$CoCO_3$	1.8 g/L at 15°C
Cobalt(III) oxide	Co_2O_3	Insoluble

Source: ATSDR 2004b.

In rivers, Albrecht (2003) found that greater than 90% of the cobalt was associated with the suspended particulate fraction. A study of lakes using a cobalt radiotracer showed that cobalt was associated with inorganic particulate matter, and the presence of dissolved organic matter increased the amount of cobalt that remained in solution, likely because of complexation (Parker and Hasler 1969).

In the aqueous environment, cobalt partitioning is controlled by the interaction with solid phases, particularly manganese and iron (oxy)hydroxides. These processes may involve precipitation-dissolution and/or adsorption-desorption reactions. Studies have shown that, because of the structure of the manganese (oxy)hydroxides, more cobalt tends to be associated with these structures than with iron (oxy)hydroxides (Stockdale et al. 2010). Cobalt can adsorb to the surface of manganese (oxy)hydroxides, but may also be oxidized to Co^{3+} and incorporated directly into the oxide structure (Tebo et al. 2004). The adsorption is controlled by many geochemical and physical parameters, such as pH, Eh, organic ligand concentrations, temperature, biological activity, and flow conditions (Tebo et al. 2004). For example, Brooks (1995) showed that cobalt sorption to sand and iron- and manganese-oxide-coated sand decreased at lower temperatures and in the presence of citrate, which was available to form soluble complexes.

3.3.2.1 Adsorption/Desorption

Adsorption of cobalt in soils and sediments primarily occurs on iron and manganese (oxy)hydroxides and clay minerals. The process is pH dependent, with very little sorption occurring at pH less than 4 (Krupka and Serne 2002). Experiments comparing sorption to two iron minerals and two manganese minerals showed that more cobalt was adsorbed to manganese minerals relative to iron minerals and that desorption was slower than adsorption. Adsorbed cobalt species become more resistant to desorption over time. When cobalt was allowed to adsorb for longer periods of time, desorption became even slower, especially for iron oxyhydroxide (goethite), suggesting the transfer over time of bound cobalt to sites with slower desorption kinetics (Backes et al. 1995). Wendling et al. (2009) also found increased retention over time and attributed this to oxidation and precipitation of the adsorbed cobalt.

The presence of soluble organic ligands can decrease adsorption of cobalt onto soils and sediments through the formation of soluble complexes that increase the mobility of cobalt. However, the presence of humic substances bound to surfaces can increase adsorption, especially at slightly acidic pH (Masset et al. 2000; Zachara et al. 1994 as cited in Krupka and Serne 2002). Additionally, some inorganic ligands, such as cyanide and nitrite, can also decrease adsorption through the formation of soluble complexes (Krupka and Serne 2002).

In the environment, radioactive cobalt is expected to react like stable cobalt; however, ^{60}Co that enters the environment through effluent from nuclear reactors and associated wastes may co-occur with the synthetic ligand EDTA, resulting in increased mobility compared to stable cobalt because of the relatively stable ^{60}Co-EDTA complexes formed (Krupka and Serne 2002).

3.3.2.2 Precipitation-Dissolution

Manganese oxides have been shown to oxidize cobalt, which is then incorporated into their structure. The initial oxide produced by bacterially mediated manganese oxidation has been shown to oxidize and immobilize cobalt at faster rates than more crystalline manganese oxide minerals (Murray et al. 2007), so cobalt immobilization through oxidation and coprecipitation with manganese oxides is expected to be most rapid at redox boundaries4 where active biological manganese oxidation is occurring. Under anaerobic conditions, such as those found in some sediments, cobalt may also precipitate as sulfide minerals.

Bacterial reduction of iron oxides results in the release of incorporated cobalt. The fate of the released cobalt is dependent on environmental conditions. It may move into solution, sorb to different mineral surfaces, or be precipitated into additional minerals (Zachara et al. 2001).

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[4] The term *redox boundaries* refers to the transition between aerobic (oxygen-containing) and anaerobic (sulfide-containing) sediments. Bacterial manganese oxidation occurs in these zones, which can contain both oxygen and a source of dissolved manganese.

Stockdale et al. (2010) examined the mobilization of cobalt, iron, and manganese in fresh and aged sediment experiments using diffusive gradient thin film samplers. In fresh sediments, cobalt correlated with iron ($r^2 = 0.76$) and not manganese ($r^2 = 0.28$), while the opposite was found in aged sediments (r^2 of 0.03 for iron, r^2 of 0.85 for manganese). The authors interpreted these differences as the result of the lack of mobilized manganese in the fresh sediments and the formation of sulfides in the aged systems, as manganese sulfides are much less soluble.

3.4 Environmental Fate and Transport

The majority of cobalt that enters the environment through surface water ultimately becomes associated with particles and ends up in sediments. Once in soil or sediment, cobalt can be remobilized through desorption or reduction of the associated solid phases such as the iron and manganese minerals discussed above. The (re)mobilization of cobalt may be enhanced by lower pH, reducing Eh conditions, or increased dissolved organic matter. For example, a study of the application of organic wastes applied to soil columns exposed to cobalt at the column surface showed that the organic matter increased the mobility of cobalt through the columns compared to the untreated control (Al-Wabel 2011).

3.4.1 Distribution Coefficients

The mobility of cobalt in groundwater can be described by the bulk soil-water distribution coefficient (K_d). This value represents the ratio of the mass of cobalt adsorbed to the solids over the mass in the aqueous phase, reported in units of L/kg or m^3/kg. A K_d of zero indicates a conservative element—that is, the element remains in solution and moves at the same speed as the groundwater. Overall, cobalt is highly associated with the particulate phase, in the absence of organic ligands. Krupka and Serne (2002) reported typical values of K_d for soil that range from 10^3 to 10^5 L/kg, and ATSDR (2004b) reported values from 0.2 to 3,800 L/kg. Thibault et al. 1990 compiled K_d values for different soil types and found that cobalt was expected to be most mobile in sandy soils (see Table 3-3 below).

Table 3-3
K_d values (L/kg) for cobalt in a variety of soil types

Group	N	Geometric Mean	Min	Max
Silty soil	23	1,300	100	9,700
Clayey soil	15	550	20	14,000
Organic-rich soil	6	1,000	120	4,500
Sandy soil	33	60	0.07	9,000

Source: Thibault et al. 1990.

Gil-Garcia et al. (2009) compiled published K_d values for radiocobalt in a variety of soils with varying chemical conditions (see Table 3-4 below). Results showed that cobalt was most strongly associated with clayey soils and least strongly associated with organic rich soils. Cobalt was more mobile at pH lower than 5, consistent with the dissolution of manganese and iron oxide phases at these pHs.

Table 3-4
K_d values (L/kg) for radiocobalt in a variety of soil types

Group	N	Geometric Mean (GSD)	Min	Max
All soils	*118*	*480 (16)*	*2*	*103,595*
Soil Type				
Sandy	18	260 (18)	5	36,756
Loamy	71	810 (15)	2	103,595
Clayey	10	3,800 (6)	540	99,411
Organic rich	17	87 (9)	4	5,800
pH group (mineral soils only)				
pH <5	21	12 (5)	2	153
5≤ pH <6.5	50	1,100 (5)	29	99,411
pH ≥6.5	26	4,600 (4)	547	103,595

Source: Gil-Garcia et al. 2009.
Note: GSD – geometric standard deviation.

Overall, the movement of cobalt in the various soil types tested in the studies summarized above was likely controlled by competing factors described in the sections above. These include the presence of solid-phase iron and manganese oxides, which can bind (and therefore slow the movement of) cobalt, and the presence of organic ligands, which can bind cobalt to keep it in solution. Soil type alone is not likely predictive of the mobility of cobalt at a specific site, and other geochemical conditions, particularly manganese chemistry, should be considered (Tebo et al. 2004).

4

COBALT LEACHING FROM COAL COMBUSTION PRODUCTS

4.1 Data Source

This section reviews the concentration of cobalt in three types of CCP leachate:

- *Porewater samples collected at CCP management facilities.* Porewater samples were collected from monitoring wells or drive-points screened in CCP, from lysimeters placed within or immediately beneath CCP, and from leachate collection systems. Porewater samples with cobalt results were available for 46 landfills and 13 impoundments, as well as 3 additional facilities. Most porewater samples were from the landfill facilities (394 of 449 total samples).
- *Contact water samples collected at CCP management facilities.* Contact water samples were taken from sluice lines, from water in CCP impoundments, and from impoundment outfalls. Runoff water is also categorized as contact water in the database, although there are few runoff samples. The contact water samples largely represent cobalt concentrations from impoundments (44 of 47 samples), plus three landfill samples. Contact water represents leaching at a higher water-to-solids ratio than porewater, and the chemistry of contact water may reflect influences other than CCP leaching, for example the major ion chemistry of the raw water used for sluicing. However, the high water-to-solids ratio does not necessarily indicate that the contact water samples are more dilute than porewater. For example, the CCP samples with the highest total dissolved solids (TDS) concentrations are contact water samples taken from impoundments where sluice water is recirculated.
- *Laboratory leachate samples generated from solid CCP samples.* A variety of leaching methods have been used in these tests. The methods have not always been indicated in detail, with most results classified as "Other Batch." Specified batch methods include Synthetic Precipitation Leaching Procedure (SPLP) SW-846 Method 1312 and Toxicity Characteristic Leaching Procedure (TCLP) SW-846 Method 1311, where a specified volume of solid is placed in a container with a leaching solution that may consist of water or a weak acid for a test-specific period. In addition, there are samples analyzed using ASTM D3987-85 Shake Extraction of Solid Waste with Water, which specifies shaking the solid sample with a neutral reagent water (e.g., deionized water) to extract leachate. Other methods include displacement and extraction. Extraction methods extract tightly held porewater from a solid sample by vacuum, whereas displacement extracts porewater with a gas or centrifuge. Laboratory leachate samples are useful for comparing relative concentrations between materials; however, they are less useful for estimating field leachate concentrations because the liquid-to-solid ratio, pH, and redox in the laboratory test may not match field conditions. Laboratory leach test results are shown in Figure 4-1 but are not used elsewhere in this data review.

Leachate data were obtained from EPRI's CPInfo database, which contains analytical results for field-collected leachate samples, laboratory-derived leachate samples, and solid samples for coal ash, FGD products, and miscellaneous power plant (e.g., low-volume) wastes from studies performed by EPRI over the past 25 years. The CPInfo database also contains data collected by individual power companies, and from the Effluent Limitation Guidelines data published by USEPA. The database provides a large volume of high-quality analytical data that can be used to broadly evaluate CCP characteristics. Leachate data are represented in this section using box and whisker plots (Figure 4-1).

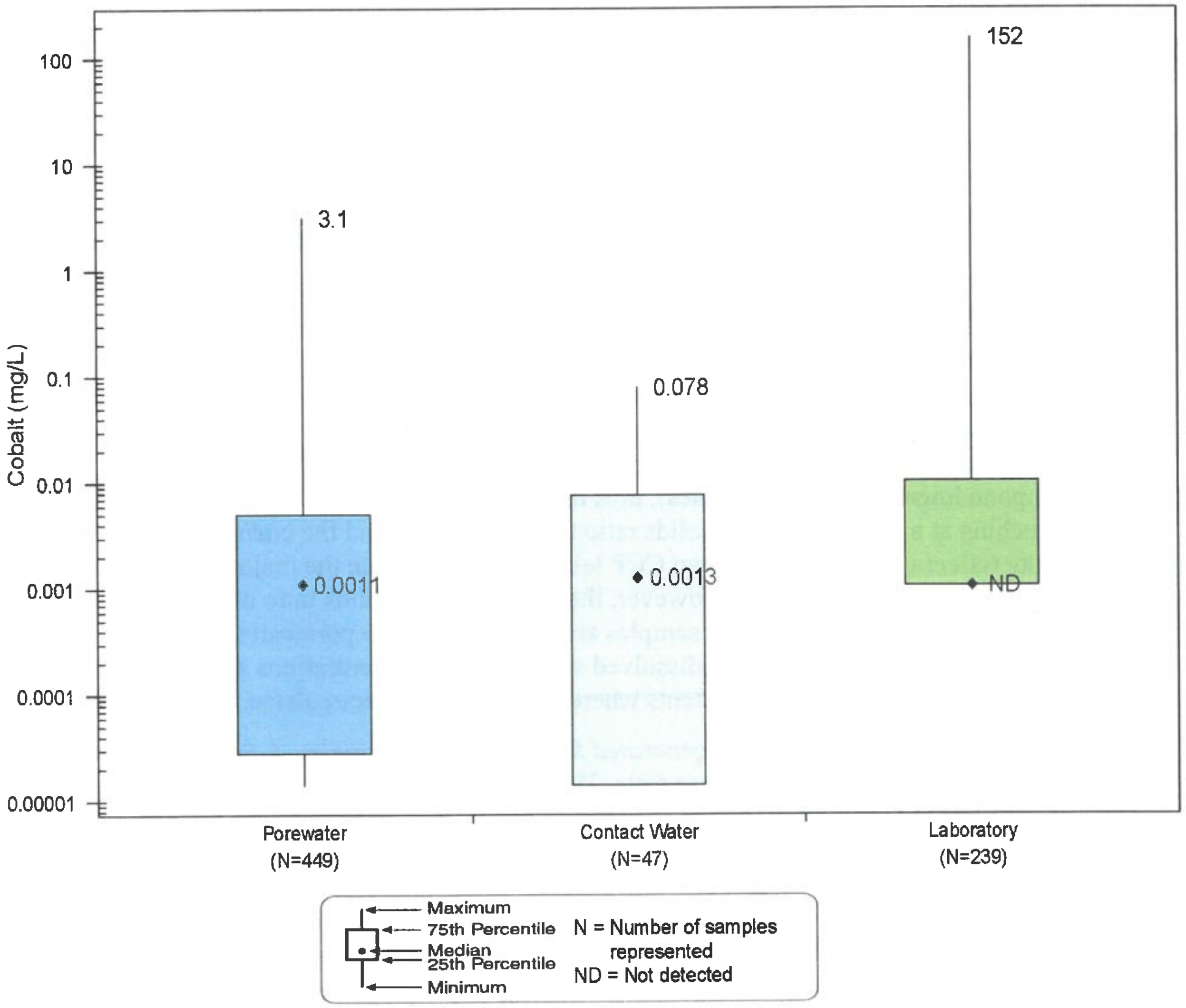

Figure 4-1
Box and whisker plot showing range of cobalt concentrations in the CPInfo database

4.2 Cobalt Concentrations in CCP Leachate

4.2.1 Data Preparation

The CPInfo database contains cobalt analytical results from 496 field-collected samples, consisting of porewater and contact water, and 239 laboratory leachate extracts (Table 4-1). Some sites had more than 30 cobalt results, while many others had fewer than 5 results. When summarizing and evaluating the data, to avoid potential bias based on those sites with many samples, site averages were calculated. Field leachate site averages were calculated for each management facility at a power plant. Laboratory leachate site averages were calculated based on the sample collection point (for example, a hopper or a CCP management facility). Table 4-2 lists the number of cobalt site averages in CPInfo.

The distributions of site averages were slightly higher compared with individual sample results for porewater, contact water, and laboratory leachate. Although the difference is small, it indicates that sites with many cobalt results have lower cobalt concentrations, which biases the average of individual results low.[5] The highest site averages are similar to the range of individual results for all three sample types, i.e., porewater, contact water, and laboratory leachate (Figure 4-2).

In this report, individual results were used to determine the total range of cobalt concentrations in CCP leachate and to evaluate inter-sample relationships—for example, the relationship of cobalt concentration to pH—while site averages were used to compare the range of concentrations in different types of CCP leachate.

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[5] Note that the tendency for sites with many cobalt results to have lower cobalt concentrations relative to sites with few results is not a cause-and-effect relationship.

Table 4-1
Number of available individual cobalt results by sample source and CCP type

Sample Source	Mixed Coal Ash	Fly Ash	Fixated FGD	CCP Mixture[a]	FGD Solids[b]	FGD Gypsum[c]	SDAM[d]	Bottom Ash	FBC Ash
Laboratory extract	85	44	4	0	9	23 / 9	8	44	13
Field leachate – porewater	243	22	66	84	4	16	14	0	0
Field leachate – contact water	28	10	2	0	7	0	0	0	0
Total	356	76	72	84	20	48	22	44	13

Note: CCP - coal combustion product
FBC - fluidized bed combustion ash
FGD - flue gas desulfurization
SDAM - spray dryer absorber material

[a] CCP mixture consists of leachate from units where coal ash was managed with either FGD solids or FGD gypsum.

[b] FGD solids consist of $CaSO_3$ produced by a natural- or inhibited-oxidation flue gas desulfurization system.

[c] FGD gypsum laboratory extract includes 23 results for washed and 9 results for unwashed FGD gypsum.

[d] SDAM: Spray dryer absorber material refers to reaction products, unspent sorbent, and fly ash collected from the bag house at power generation units equipped with spray dryer FGD systems.

Table 4-2
Number of available site-average cobalt results by sample source and CCP type

Sample Source	Mixed Coal Ash	Fly Ash	Fixated FGD	CCP Mixture[a]	FGD Solids[b]	FGD Gypsum[c]	SDAM[d]	Bottom Ash	FBC Ash
Laboratory extract	23	42	2	0	9	22 / 9	4	44	10
Field leachate – porewater	31	10	7	7	2	4	3	0	0
Field leachate – contact water	11	6	1	0	4	0	0	0	0
Total	65	58	10	7	15	35	7	44	10

Note: CCP - coal combustion product
FBC - fluidized bed combustion ash
FGD - flue gas desulfurization
SDAM - spray dryer absorber material

[a] CCP mixture consists of leachate from units where coal ash was managed with either FGD solids or FGD gypsum.

[b] FGD solids consist of $CaSO_3$ produced by a natural- or inhibited-oxidation flue gas desulfurization system. CPInfo does not contain any field results for FGD gypsum.

[c] FGD gypsum laboratory extract includes 22 results for washed and 9 results for unwashed FGD gypsum.

[d] SDAM: Spray dryer absorber material refers to reaction products, unspent sorbent, and fly ash collected from the bag house at power generation units equipped with spray dryer FGD systems.

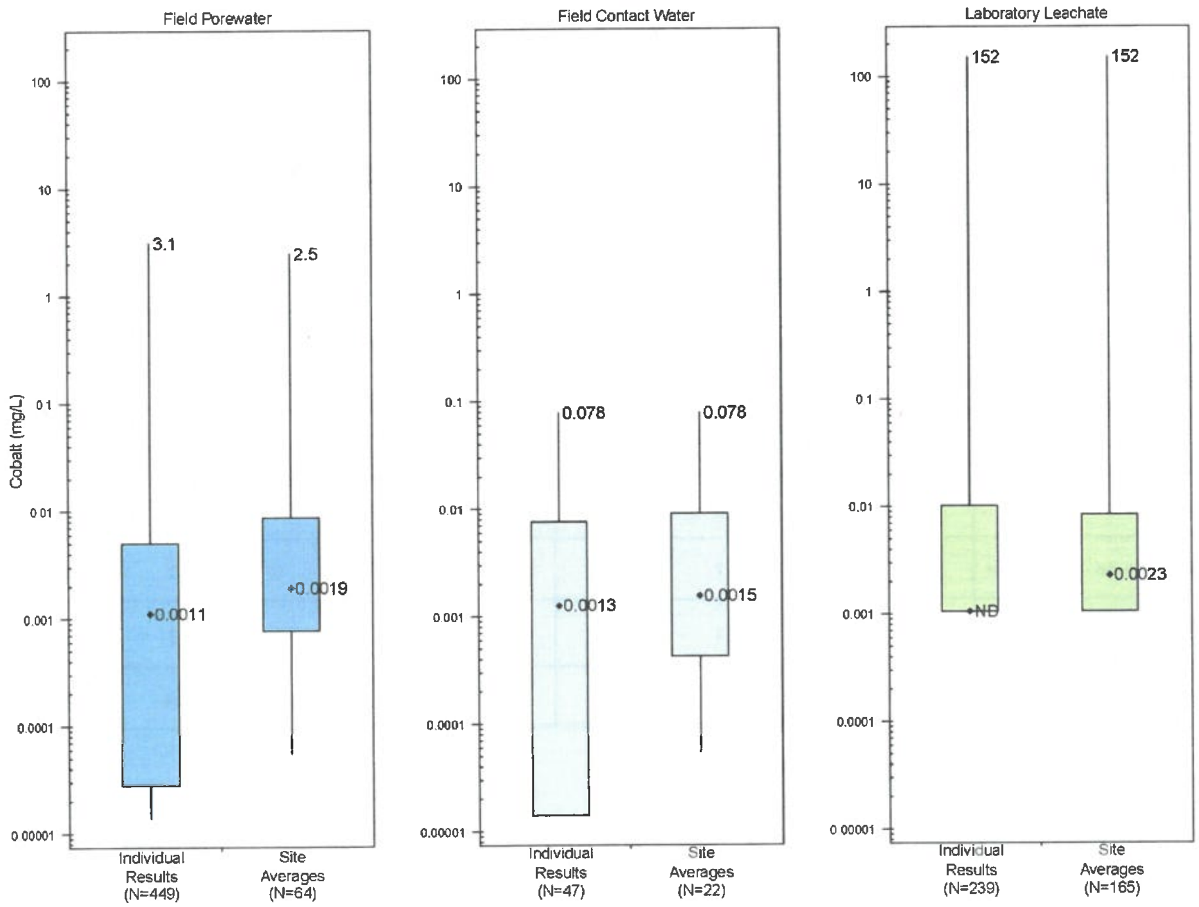

Figure 4-2
Comparison of cobalt site averages to individual sample results

4.2.2 Evaluation of Field Leachate Data

Cobalt concentrations in individual CCP porewater and contact water samples ranged from less than analytical detection limits[6] to 3.1 mg/L (Table 4-3 and Table 4-4, respectively). Cobalt was typically detected in field leachate from all CCP types sampled. Median values were lower than 0.0040 mg/L in all materials except fly ash and fixated FGD contact water. Graphical comparison of the distribution of concentrations indicates that relative cobalt concentrations for CCP porewater are ordered as follows: CCP mixture > FGD gypsum > fly ash > mixed coal ash (Figure 4-3), though there is overlap in the range of concentrations for all types. For contact water, cobalt concentrations were ordered as follows: FGD solids > fly ash > mixed coal ash, though there were only four sites with cobalt results for FGD solids. Mixed coal ash was measured at the most sites (n=11) and had the lowest concentrations (Figure 4-3).

The distributions (Figure 4-3) for porewater from FGD solids, FGD gypsum, and spray dryer absorber material (Table 4-3) and field contact water from fixated FGD and FGD solids (Table 4-4) are based on too few sites (<5) to provide a reliable comparison.

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[6] Detection limits were variable depending on data source and were equal to or less than 0.02 mg/L.

Table 4-3
Summary of cobalt concentrations in field porewater samples by CCP type

CCP Type	Count[a]	Min[b] (mg/L)	Median[a] (mg/L)	Max[b] (mg/L)	% Detected[b]
All	*449 / 64*	*BDL*	*0.0011 / 0.0019*	*3.1*	*75%*
Mixed Coal Ash[c]	243 / 31	BDL	0.00029 / 0.0015	0.11	64%
Fly Ash	22 / 10	BDL	0.00080 / 0.0017	0.13	68%
Fixated FGD	66 / 7	BDL	0.0016 / 0.0020	0.031	95%
CCP Mixture	84 / 7	BDL	0.0039 / 0.033	3.1	92%
FGD Solids	4 / 2	BDL	0.0028 / 0.0030	0.0061	75%
FGD Gypsum	16 / 4	0.00071	0.0012 / 0.0013	0.32	100%
SDAM	14 / 3	BDL	0.00061 / 0.00085	0.0097	57%

Note: BDL - below detection limit
CCP - coal combustion product
FGD - flue gas desulfurization
SDAM - spray dryer absorber material

[a] Individual results / site averages.
[b] Based on individual results.
[c] Includes facilities where fly ash and bottom ash were both managed.

Table 4-4
Summary of cobalt concentrations in field contact water samples by CCP type

CCP Type	Count[a]	Min[b] (mg/L)	Median[a] (mg/L)	Max[b] (mg/L)	% Detected[b]
All	*47 / 22*	*BDL*	*0.0013 / 0.0015*	*0.078*	*66%*
Mixed Coal Ash[c]	28 / 11	BDL	0.00010 / 0.00053	0.022	50%
Fly Ash	10 / 6	BDL	0.0071 / 0.0044	0.019	90%
Fixated FGD	2 / 1	0.0080	0.0090 / 0.0090	0.010	100%
FGD Solids	7 / 4	BDL	0.0020 / 0.017	0.078	86%

Note: BDL - below detection limit
CCP - coal combustion product
FGD - flue gas desulfurization

[a] Individual results / site averages.
[b] Based on individual results.
[c] Includes facilities where fly ash and bottom ash were both managed.

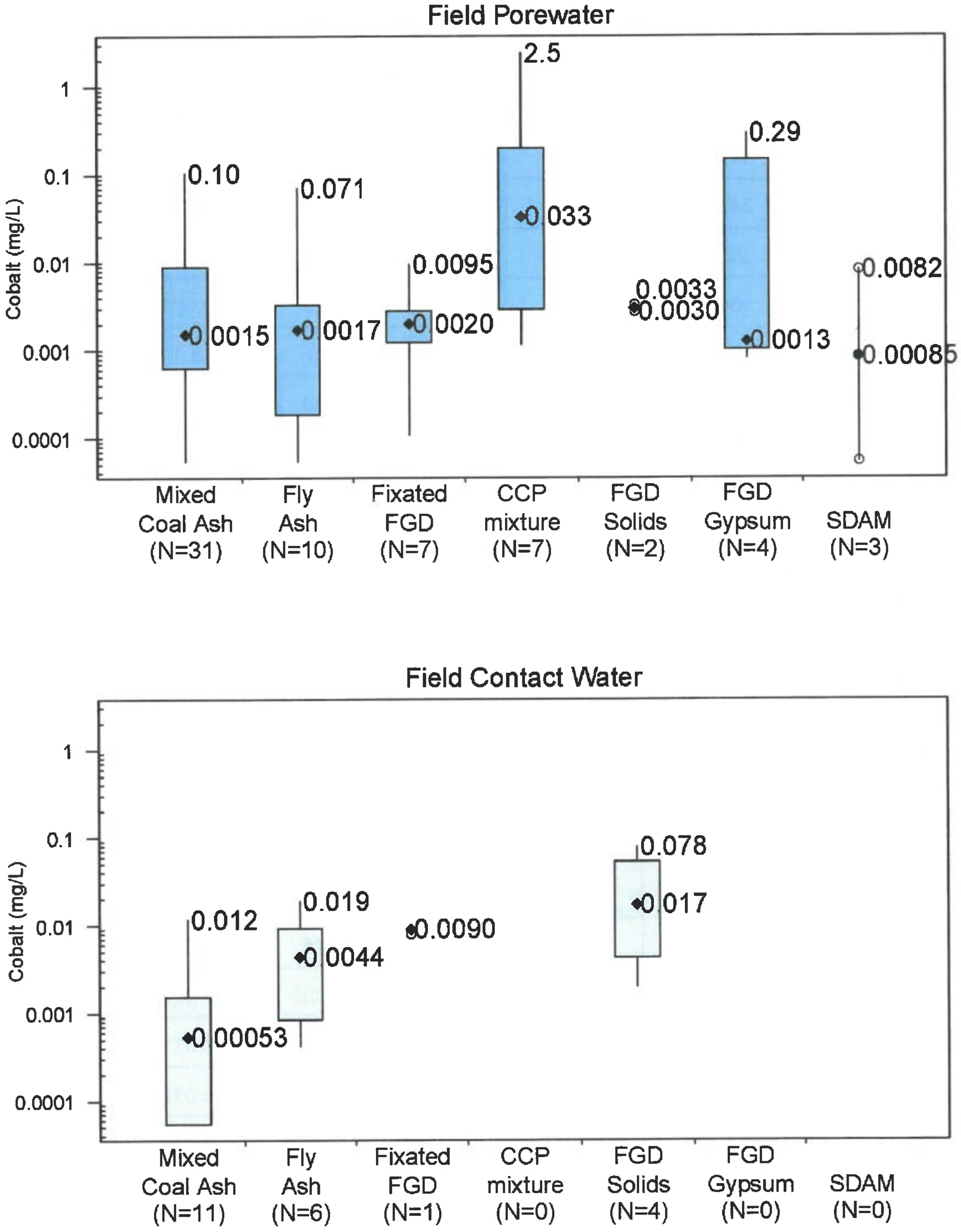

Figure 4-3
Comparison of cobalt site average concentration ranges by CCP type for porewater and contact water

Cobalt site average concentrations were further reviewed to evaluate differences based on source coal and whether the CCP was managed dry in landfills or sluiced to impoundments. The following comparisons focus on fly ash, because it is the most robust dataset in CPInfo. In addition, fly ash and mixed coal ash results were combined for this evaluation because the leachate chemistry for the mixed coal ash is dominated by the fly ash. Fly ash contact water was only sluiced (not dry managed) and summarized to provide comparisons with sluiced porewater.

Figure 4-4 provides comparison of site average cobalt concentrations based on management approach, i.e., dry-managed in landfills or sluiced to impoundments. Additionally, the same sample concentrations are depicted by coal type to allow direct comparisons of samples from the same coal type that were managed differently. There were insufficient lignite data for meaningful comparison.

The highest cobalt concentrations generally come from dry-managed ash in landfills. Ash sluiced to impoundments has lower cobalt concentrations, with porewater samples lower than contact water (Figure 4-4). Coal blend cobalt concentrations are inconsistent relative to bituminous or sub-bituminous, not showing a consistent pattern by management or sample type, although site average counts are small for this category

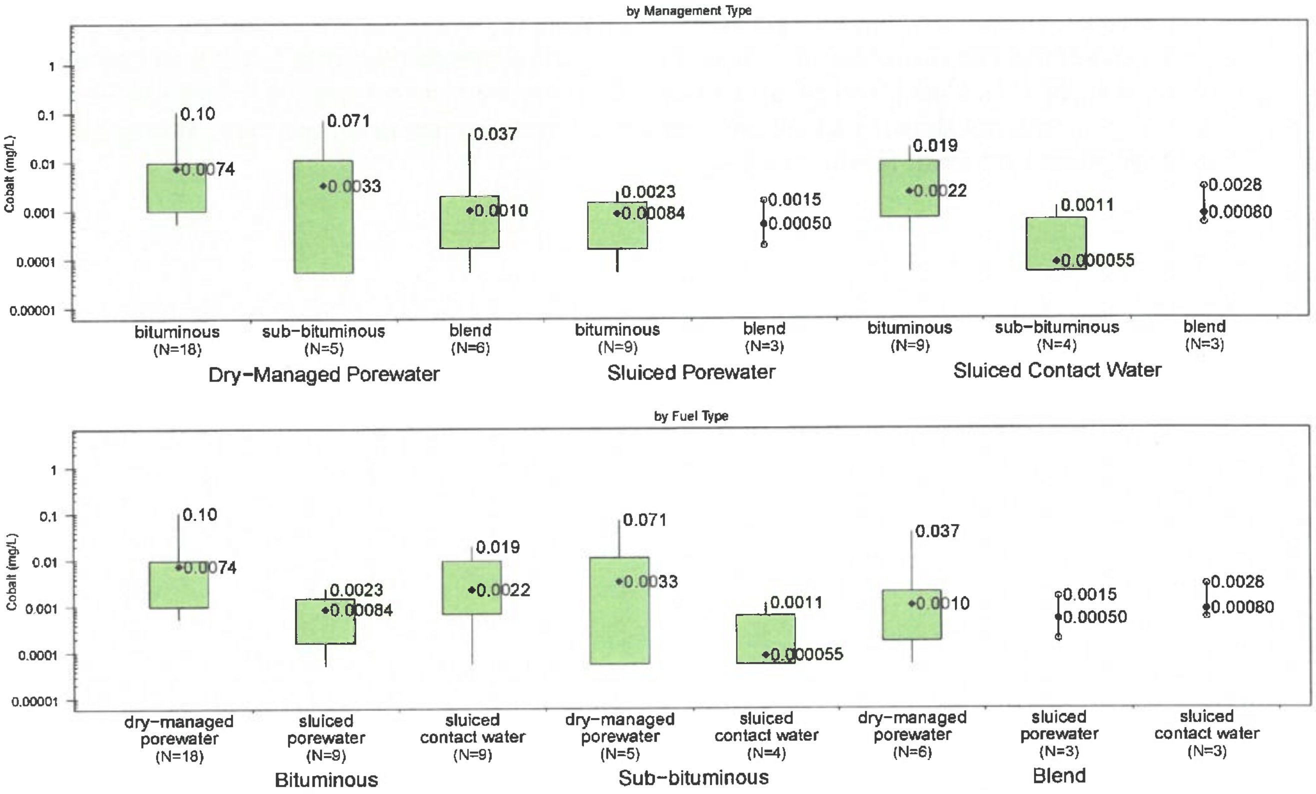

Figure 4-4
Comparison of cobalt site average concentration ranges by management type and fuel type

4.3 Empirical Cobalt Relationships in Field Leachate Samples

Cobalt concentrations were plotted against other constituents analyzed in the same sample to evaluate the presence of any empirical relationships between constituents. To reduce variability, this evaluation was limited to mixed coal ash from bituminous and sub-bituminous sources and coal or other blends, and did not include other CCPs. Correlations evaluated porewater and contact water separately by coal type. Cobalt concentrations were compared against other constituents with sufficient detected results for meaningful analysis:[7] alkalinity, bicarbonate, inorganic and organic carbon, chemical oxygen demand (COD), dissolved oxygen, electrical conductivity (EC), hardness, pH, redox potential, TDS, temperature, total suspended solids (TSS), boron, iron, lead, lithium, and manganese.

Correlation analyses were used to identify the strength of relationships between cobalt and other constituents, including standard Pearson correlations and non-parametric Spearman correlations. Log-transformations were used for all constituents except pH and TDS. The results did not identify consistent relationships between cobalt concentrations and the other parameters for different coal types. Lead, lithium, and alkalinity showed the strongest relationships with porewater cobalt concentrations, yet there were inconsistencies between fuel types. Lead was positively correlated with cobalt for sub-bituminous and blends but inversely correlated for bituminous (Figure 4-5). There were many samples with high concentrations of cobalt and lithium that increased the correlation value, despite the variability at lower concentrations (Figure 4-6). Samples of bituminous porewater with results for alkalinity and cobalt were divided into two clusters (alkalinity around 100 and 400, respectively), which inflated the correlation value (Figure 4-7).

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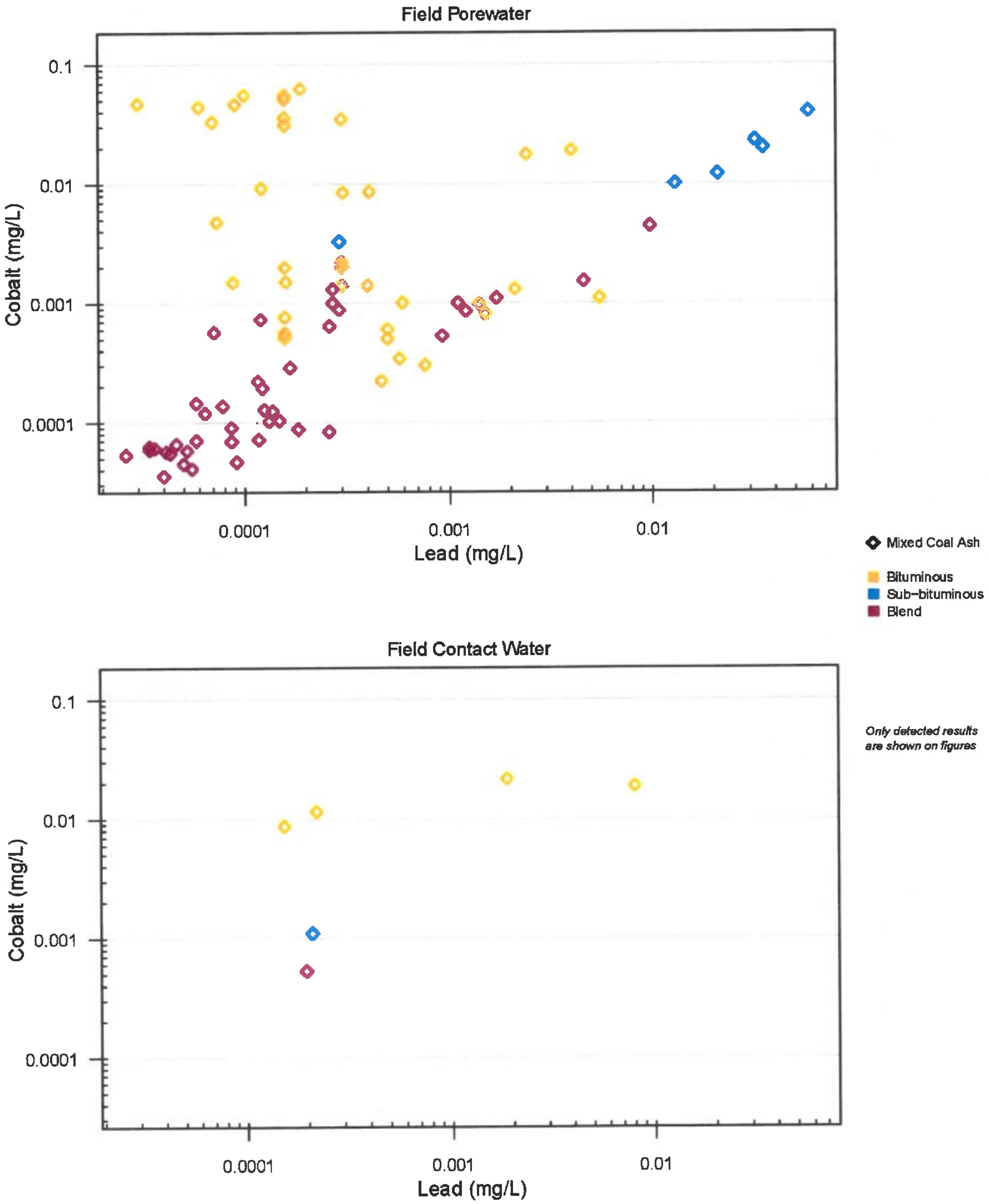
[7] Constituents with more than five results and more than 50% detected results.


Field Porewater

Field Contact Water

Only detected results are shown on figures

Figure 4-5
Relationship between lead and cobalt concentrations in mixed coal ash

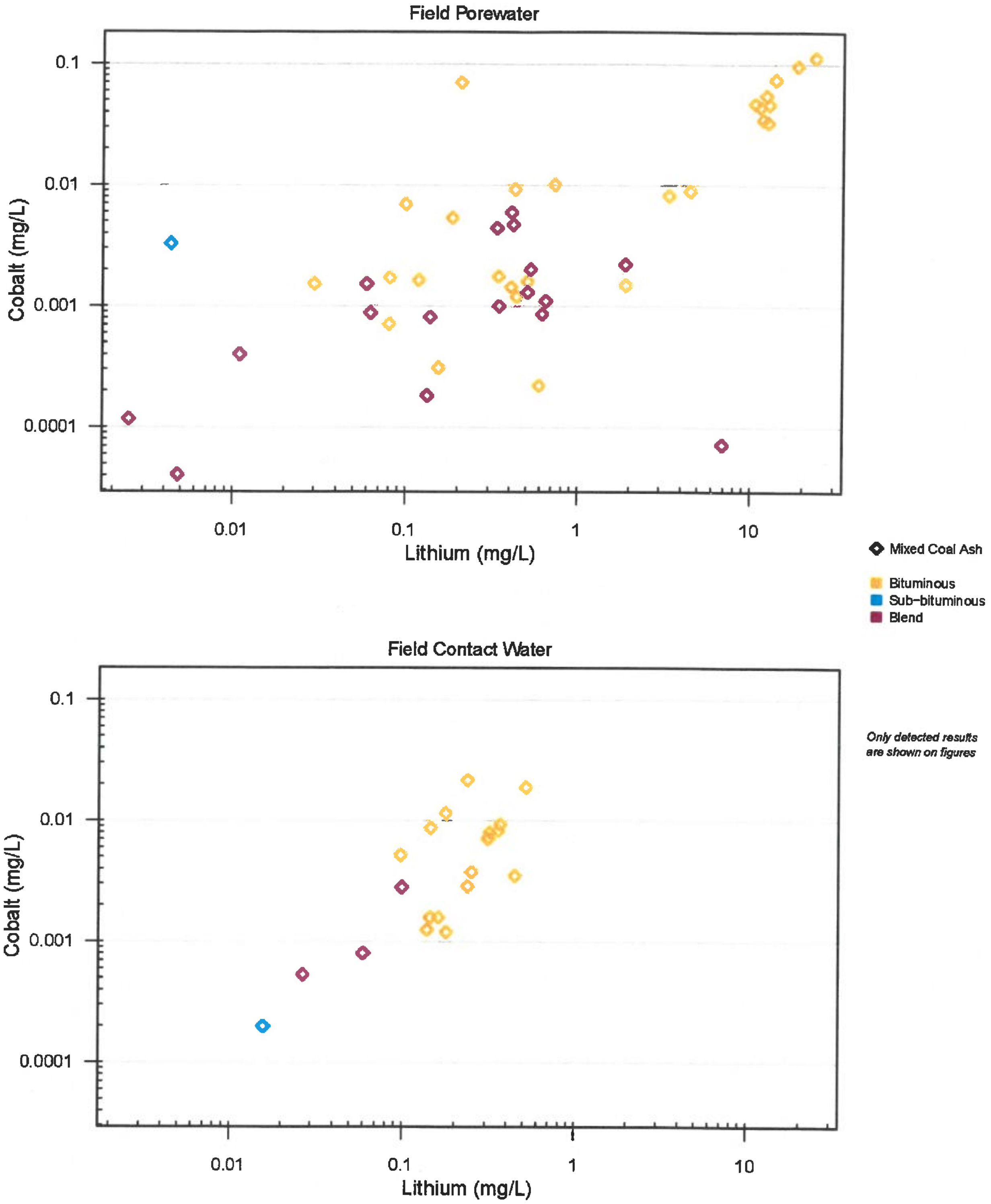


Figure 4-6
Relationship between lithium and cobalt concentrations in mixed coal ash

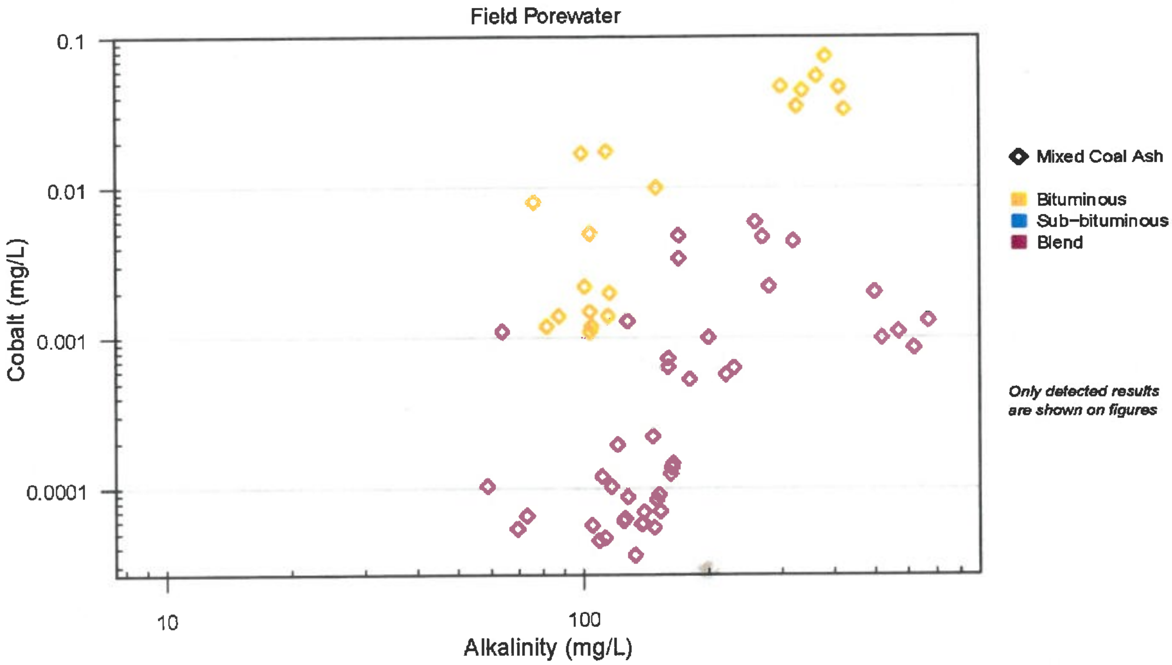


Figure 4-7
Relationship between alkalinity and cobalt concentrations in mixed coal ash

5

HUMAN HEALTH TOXICOLOGY

Human exposure to cobalt occurs primarily through dietary sources, including ingestion of inorganic cobalt supplements and the essential cobalt-containing vitamin cobalamin (Vitamin B_{12}). This section summarizes cobalt's pharmacokinetics, levels found in the body with and without therapeutic use, cancer and non-cancer health effects, toxicity factors used in risk assessment, and health-based regulatory benchmarks.

5.1 Absorption, Metabolism, Distribution, and Excretion

Absorption of cobalt depends on the chemical form; soluble forms are more readily absorbed through the gastrointestinal tract (ATSDR 2004b, Paustenbach et al. 2013, NTP 2016a, b). Gastrointestinal absorption has been reported to be 20–45% for water soluble forms of inorganic cobalt (e.g., cobalt chloride) and 10–25% for more insoluble forms (e.g., cobalt oxide) (Unice et al. 2014). Cobalt absorption appears to be higher in women than men (NTP 2016a). This could be related to anemia and iron status because cobalt absorption is increased in people with iron deficiency, which is more common in women. Cobalt and iron may share a common uptake mechanism in the gastrointestinal tract that is regulated by iron status (Paustenbach et al. 2013).

Inorganic cobalt is primarily distributed to the liver, as well as the kidney, heart, and spleen (ATSDR 2004b, NTP 2016a). Smaller amounts are found in bone, lymph, brain, and pancreas. Cobalt can transfer to human milk and across the placenta (NTP 2016a). Excretion of the majority of absorbed cobalt occurs rapidly in urine, with a small proportion distributed throughout the body and excreted over weeks to months. A smaller proportion of about 10% is retained in tissues for longer, with a half-life of 2 to 15 years (Iarc 2006, NTP 2016a). Orally administered cobalt that is not absorbed is excreted in the feces. Although most absorbed cobalt is excreted in the urine, as noted above, a smaller fraction of absorbed cobalt is secreted back to the GI tract and also excreted in feces (NTP 2016a). Smith et al. (1972) administered cobalt chloride by intravenous infusion to human volunteers and followed cobalt distribution by whole-body radioisotope scans for up to 1,000 days. Plasma levels decreased rapidly, as the cobalt dose was distributed throughout the body. Approximately 20% of the administered dose was initially distributed to the liver. Excretion through the kidney occurred relatively rapidly, but 9 to 16% of the initial dose was retained, with a half-life of approximately 800 days.

5.2 Measurement in Human Biological Media

Cobalt is included among chemicals measured in biomonitoring in the United States as part of the National Health and Nutrition Examination Survey (NHANES). The most recent data available for urinary and blood samples from 2009 and 2010 are summarized below.

Urinary cobalt levels in the general population had geometric mean and 95th percentile values of 0.369 and 1.40 µg/L, respectively (CDC 2015). Geometric mean and 95th percentile values were generally higher in females (0.403 and 1.68 µg/L) than males (0.336 and 0.96 µg/L).

Blood cobalt levels have been measured in non-occupationally exposed people in the range of 0.1 to 0.5 µg/L (Paustenbach et al. 2013, NTP 2016a). Approximately 90 to 95% of blood cobalt in humans is bound to leukocytes or plasma proteins, predominantly albumin, with only a small percentage present as the more cytotoxic, free form, cobalt ions (Paustenbach et al. 2013, Tvermoes et al. 2015, NTP 2016a). Free cobalt is taken up into red blood cells via a membrane calcium ion pump, where it then binds to hemoglobin (NTP 2016a). Four volunteers who received oral cobalt supplementation of 0.4 mg/day for two weeks had a mean blood cobalt level of 3.6 µg/L (range, 1.8 to 5.1 µg/L) (Tvermoes et al. 2013). Five male and five female volunteers administered 1,000 µg/day oral cobalt supplementation for 89 days had mean blood cobalt levels of 20 µg/L (range, 12 to 33 µg/L) and 53 µg/L (range, 6 to 117 µg/L), respectively (Finley et al. 2013). Unice et al. (2014) used a pharmacokinetic model to predict blood cobalt levels for various intake rates. The modeling indicated that daily supplementation marketed in the United States with doses of 0.2, 0.4, and 1 mg/day would result in blood cobalt levels of 5.7 µg/L (range, 2.7 to 9.8 µg/L), 11 µg/L (5 to 19 µg/L), and 26 µg/L (11 to 46 µg/L), respectively. Blood cobalt levels of 1,300 µg/L (510 to 2,300 µg/L) were estimated to be associated with a cobalt dose of 68 mg/day for 30 days, which has been used therapeutically to treat anemia in the past (Unice et al. 2014).

5.3 Cobalt in the Diet

The diet is the primary source of cobalt exposure in the general population (NTP 2016a). The 1984 U.S. Food and Drug Administration (FDA) Total Diet Study reported a mean cobalt intake from food for the U.S. general population of 0.0034 to 0.0116 mg/day, depending on age and sex (NTP 2016b). ATSDR (2004b) reported mean cobalt intake from food in the United States in the range of 0.005 to 0.04 mg/day. Mean cobalt intake rates from diet in Canada ranged from 0.004 to 0.015 mg/day, depending on age and sex (ATSDR 2004b). Most dietary cobalt is in inorganic forms, with a small percentage as Vitamin B_{12}. Cobalt is essential for humans only as a component of vitamin B_{12}, which is not produced in the human body and is required to maintain proper health (ATSDR 2004b).

5.4 Health Effects

The focus of this health effects review is on oral exposure to cobalt. Some discussion of effects associated with inhalation exposure to cobalt is included to provide context and to support hazard assessment where oral exposure data are lacking.

For non-cancer effects, the primary organ systems affected by oral exposure to cobalt include the blood, thyroid, heart, and secondarily the liver (ATSDR 2004b). Adverse effects on the developing fetus have also been observed, but inconsistently and typically at dose levels higher than those associated with maternal toxicity. These types of effects are discussed in more detail in the following sections. Two studies in patients with renal disease treated with oral cobalt supplements (25 to 50 mg/day) to address hemodialysis-associated anemia identified hearing loss as a side effect in a total of 4 out of 26 patients (Duckham and Lee 1976, Bowie and Hurley 1975). However, these patients all had serum cobalt levels around 500 µg/L and above (>2,000 µg/L in one patient), far higher than would occur with environmental exposures.

Although there are inadequate studies to address the potential for carcinogenic effects from oral exposure to cobalt in humans, the National Toxicology Program (NTP) concluded that metallic cobalt and cobalt compounds that release metal ions are "reasonably anticipated to be human carcinogens" based on inhalation and injection studies in rodents combined with supporting mechanistic data (NTP 2016a, b).

5.4.1 Non-Cancer Health Effects

5.4.1.1 Blood

Cobalt causes polycythemia (elevated hematocrit, or the percentage of red blood cells in blood) and thus has been administered to treat anemia, sometimes with iron, including in pregnant women and children with sickle cell anemia (ATSDR 2004b). Based on previous reports that cobalt induces polycythemia, Duckham and Lee (1976) treated 12 anephric hemodialysis patients with 25 to 50 mg/day cobalt chloride for up to 32 weeks for the purpose of therapeutically increasing hemoglobin levels. Eight patients completed the trial; one patient died, two became ill for reasons unrelated to cobalt exposure, and one discontinued the study because of presumed cobalt-related nausea and constipation. Six of eight patients receiving 50 mg/day showed significantly increased hemoglobin levels. Hemoglobin levels returned to pretrial levels after cessation of treatment. Four patients entered a second trial with the same cobalt chloride dose (25 to 50 mg/day). All four patients again had increased hemoglobin levels, demonstrating the reproducibility of the effect.

Cobalt chloride administered as a 2% solution in water or milk for up to 22 days induced transitory polycythemia (increased red blood cell count) in six healthy men (20 to 47 years old) (Davis and Fields 1958). Five of the six received 150 mg/day cobalt for the entire exposure period, and the sixth received 120 to 150 mg/day. Cobalt treatment induced an approximately 16–20% increase in red blood cell count that returned to normal within 15 days after cessation of treatment. Cobalt treatment also increased hemoglobin levels but less so than the red blood cell count. In five of the six subjects, reticulocyte (immature red blood cells) levels were elevated, reaching at least twice the pre-experiment values. Thrombocyte and total leukocyte counts were not affected.

Unlike the earlier studies evaluating high dose cobalt exposure, recent controlled human dosing studies reported no clinically significant effects on the blood system (Finley et al. 2013, Tvermoes et al. 2014). Ten volunteers (5 male/5 female) ingested a daily liquid cobalt chloride supplement (approximately 1,000 µg/day; 10-19 µg cobalt per day) for 31 days without clinically significant adverse effects on red blood cell count, hemoglobin, or hematocrit (Finley et al. 2013). Similarly, Tvermoes et al. (2014) reported no polycythemia or other effects in a study of 10 volunteers (5 men and 5 women) taking over-the-counter cobalt supplements at the recommended dose of 1,000 µg cobalt per day (as $CoCl_2$) for up to 90 days.

Studies of occupationally exposed cohorts have shown either decreases in hemoglobin and red blood cell counts or no effect at all. (Swennen et al. 1993) reported slightly but statistically significantly lower hemoglobin and red blood cell count in cobalt refinery workers exposed to mean cobalt air concentrations of 125 µg/m^3 (range, 1 to 7,772 µg/m^3) for an average of 8 years (range, 4 months to 39 years) compared to an age and sex matched control group. A later study of workers from the same refinery showed no differences in hemoglobin or red blood cell count in exposed workers compared to controls (Lantin et al. 2011).

Polycythemia and other effects on blood parameters have been reported in rats and mice (ATSDR 2004b, Finley et al. 2012a). In an 8-week exposure study, Stanley et al. (1947) reported a no-observed-adverse-effect level (NOAEL) of 0.6 mg/kg-day and a lowest-observed-adverse-effect level (LOAEL) of 2.5 mg/kg-day for increased red blood cell count in rats administered cobalt chloride (ATSDR 2004b). Shrivastava et al. (1996) reported elevated hemoglobin, hematocrit, and red blood cell count in rats administered 12.5 mg/kg-day cobalt chloride for 7 days compared to controls administered distilled water. In an unpublished, GLP-compliant study following OECD guidelines, CD rats (10/sex/group) were administered 0, 3, 10, or 30 mg/kg-day cobalt chloride by oral gavage for 90 days (ECHA 2019). Although there were no effects at the lowest dose level, there were statistically significant increases in red blood cell count, hemoglobin, and hematocrit at both 10 (males only) and 30 mg/kg-day (males and females). The NOAEL for this study was identified as 3 mg/kg-day cobalt chloride based on the hematological effects.

5.4.1.2 Thyroid

Thyroid dysfunction was identified as the critical effect of oral cobalt chloride exposure by USEPA (2008) based primarily on two studies conducted in the mid-1950s: a case series of five severely ill children with sickle cell anemia (Kriss et al. 1955) and a study of 12 adults reported in a letter to the editor (Roche and Layrisse 1956). The five sickle cell cases described by Kriss et al. (1955) were severely ill and it is unclear what role their compromised health status may have played. In a study of patients receiving cobalt orally as a therapeutic treatment for two weeks, Roche and Layrisse (1956) reported reduced iodine uptake into the thyroid. Interpretation of this study is limited for several reasons. First, although the health status of the patients included in the study was not detailed, they were all "hospitalized for varying reasons." Second, this study included only a single, extremely high-dose group with a limited number of participants (n=12) and no control group for comparison. Homeostatic controls exerted by the body could result in a threshold for effects. However, the study design did not allow for determination of a NOAEL. Third, this study was published as a letter to the editor, with limited supporting information on methods and results.

In contrast, three studies published during the same time frame of the mid-1950s do not support the conclusion that thyroid dysfunction is the most sensitive effect for cobalt. Jaimet and Thode (1955) reported no significant change in thyroid function of 17 children who received 1, 2, 4, or 6 mg/kg-day cobalt chloride for 10 weeks. The patients exhibited no signs of either goiter or hypothyroidism. Similarly, no thyroid effects were reported in 78 pregnant women who received 60 to 100 mg/day cobalt chloride for 3 to 6 months (Holly 1955). Thyroid enlargement did not occur in any of the women or any of the children born to these women. Wolf and Levy (1954) treated four adult sickle-cell patients and seven other patients without sickle cell (but with non-specified diseases) with oral doses of 300 mg/day cobalt chloride, divided into three daily doses in orange juice, for six weeks. Although several effects were identified (skin rashes, GI effects, anorexia, and in one case, reversible deafness), no thyroid effects were reported.

Two more recent studies evaluated inhalation exposures in people occupationally exposed to cobalt. Although the exposure route differs, these studies provide additional information on the potential for thyroid dysfunction as a result of cobalt exposure. Swennen et al. (1993) conducted a cross-sectional study of workers exposed to metallic and inorganic cobalt compounds at a plant producing these materials from cobalt metal cathodes and scrap metal. The mean cobalt exposure concentration was 125 μg/m^3 (range, 1 to 7,772 μg/m^3). Exposure durations ranged from less than 1 year to 39 years, with an average exposure of 8 years. Despite a 10- to 14-fold difference in urinary cobalt compared to the control group, measures of thyroid function were not consistently affected. Although 3',5,3-triiodothyronine (T3) levels were slightly but significantly decreased, there was no significant difference in T3 uptake, or serum levels of thyroxine (T4) or thyroid stimulating hormone (TSH), nor were there any clinical changes in thyroid volume. The post-work shift geometric mean blood cobalt level for these workers was 11 and 12.7 μg/L on Monday and Friday, respectively. For context, these cobalt blood levels are similar to the blood cobalt level predicted by the refined pharmacokinetic model of Unice et al. (2014) for a daily oral intake of 400 mg/day from dietary supplements (Unice et al. 2014). Prescott et al. (1992) conducted a cross-sectional study on the effects of cobalt exposure on thyroid function and volume in 61 female plate painters. The plate painters in this study had 10-fold higher urinary cobalt levels than the control group. Unlike Swennen et al. (1993), T3 levels were not significantly different than the control group. However, serum and free T4 were slightly but significantly increased. TSH and thyroid volume were not significantly different. Taken together, these two studies suggest only minimal and inconsistent effects on thyroid function despite significant long-term occupational exposures (10 or more times greater than background). Furthermore, thyroid volume was not significantly affected in either study.

Two recent dietary supplementation studies reported no effect of cobalt supplements on thyroid biochemical parameters. Tvermoes et al. (2014) administered 1 mg/day cobalt chloride supplements to 10 healthy adult volunteers (5 male/5 female) for 90 days and measured various blood biochemical thyroid function parameters. There were no treatment-related effects on either TSH or T4 levels in either males or females during the treatment period. T4 was slightly increased in females at 1 week post-dosing but returned to normal at 2 weeks post-dosing. Similarly, Finley et al. (2013) reported that 1 mg/day cobalt chloride supplementation for 30 days did not significantly affect thyroid function indicators.

Evidence for thyroid effects from laboratory animals is inconsistent. Shrivastava et al. (1996) reported histopathological changes in the thyroids of mice exposed to 400 ppm cobalt chloride in drinking water for 15, 30, and 45 days. However, Holly (1955) reported no effects on thyroid function, size, or histopathology in mice injected intraperitoneally with 10 mg/kg-day cobalt chloride for 10 days or in rats either injected intraperitoneally with 10 mg/kg-day cobalt chloride for 5½ months or orally dosed with 40 mg/kg-day cobalt chloride for 4 months. There were no significant effects on iodine metabolism, thyroid function, thyroid weight, or body weight gain in rats administered 60 mg/kg-day cobalt chloride in drinking water for 44 days, although polycythemia did occur (Scott and Reilly 1955).

In 13-week inhalation studies of cobalt chloride in F344/N rats and B6C3F$_1$ mice, NTP (1998) reported only minimal effects on thyroid function parameters. The results clearly indicated that thyroid dysfunction was not the critical effect in rodents exposed to cobalt concentrations up to 30 mg/m^3. The authors concluded, "thyroid function as indicated by serum triiodothyronine (T3), thyroxin (T4), and thyrotropin (TSH) concentrations did not appear to be consistently affected in rats in the current studies. These results support the conclusion of Sederholm et al. (1968) that effects of cobalt on the thyroid gland have not been clearly demonstrated in studies with rats, mice, or rabbits." A chronic, 2-year inhalation study in mice did report increased levels of follicular cell hyperplasia in the thyroid in all dose groups (0.3, 1.0, and 3.0 mg/m^3) for males, but the severity was mild and not dose dependent (NTP 1998). This effect did not occur in females. There was not an increased incidence of thyroid tumors.

5.4.1.3 Cardiovascular

Cardiomyopathy (diseases of the heart muscle) leading to death in many cases occurred in the 1960s in Canada and the United States in a small fraction of people who drank large quantities of beer (8–30 pints per day over a period of years) that contained cobalt sulfate as a foam stabilizer (ATSDR 2004b). Approximately 18% of patients died within several days of hospital admission and over 40% died within several years of initial admittance. Respiratory effects (pulmonary edema and rales) were also reported in this population and attributed to the cardiomyopathy. The estimated cobalt dose from the beer was 0.04–0.14 mg/kg-day (ATSDR 2004b); however, it should be noted that the symptoms appeared to be similar to alcoholic cardiomyopathy. Furthermore, therapeutic treatment of anemic patients with much higher cobalt doses (0.6 to 1 mg/kg-day) did not result in mortality, nor were cardiac or respiratory effects reported (Holly 1955, Davis and Fields 1958), except in very rare cases involving higher doses in vulnerable patients (anemic 6-month old infant weighing 10.5 lbs, Little and Sunico 1958; anephritic 17-year on dialysis with severe chronic anemia, Manifold et al. 1978). In the former case, despite having a large goiter and serious cardiomyopathy, the infant made a full recovery once cobalt therapy was stopped. The cardiomyopathy and mortality reported in the beer drinker cohort was likewise associated with a number of risk factors unrelated to cobalt or that could increase susceptibility to cobalt, including chronic alcohol abuse, ischemically-modified blood proteins, and deficiencies in protein and nutrients such as vitamins and other minerals from malnutrition. In particular, protein deficiency and ischemic modification of serum proteins reduces protein binding of cobalt, resulting in higher circulating levels of free cobalt, the cytotoxic form (Catalani et al. 2011, Tvermoes et al. 2015). The occurrence of cardiomyopathy in malnourished alcoholics, though not those with sufficient nutrition but similarly high consumption of beer with cobalt, is consistent with the protective effect of protein binding of cobalt (Kesteloot et al. 1968, Tvermoes et al. 2015). Cardiomyopathy was observed in guinea pigs administered cobalt sulfate daily by oral gavage, but at a dose (20 mg/kg-day) that was lethal for 20–25% of the animals (Mohiuddin et al. 1970). Co-administration of ethanol did not modify the effect. Cardiac effects (e.g., increased heart weight, histopathological effects, ventricular hypertrophy, and enzyme level changes) have also been produced in rats administered cobalt doses ranging from 8.4 to 30.2 mg/kg-day for multiple weeks and in rats administered a single oral dose of cobalt of either 176.6 mg/kg or 795 mg/kg (ATSDR 2004b).

5.4.1.4 Liver

Liver injury (central hepatic necrosis) with increased serum bilirubin and serum enzymes was reported in the cardiomyopathy patients exposed to high levels of cobalt sulfate in beer (ATSDR 2004b). The liver injury may have been secondary to ischemic injury associated with the cardiomyopathy or, more likely, a result of alcohol abuse in these patients. Liver function tests were not affected in pregnant women administered up to 0.6 mg/kg-day cobalt chloride for 90 days (Holly 1955). A single dose of 68.2 mg/kg cobalt fluoride or 157.3 mg/kg cobalt oxide resulted in liver toxicity in rats (ATSDR 2004b). In contrast, 2.5 to 30.2 mg/kg-day cobalt chloride administered to rats by gavage or in the drinking water for 3 to 7 months did not affect liver weight, morphology, or function (ATSDR 2004b).

5.4.1.5 Reproductive and Developmental

An unpublished, OECD guideline compliant, repeat-dose toxicity study with a one-generation reproductive and an added developmental toxicity screening component evaluated the effects of 0, 30, 100, 300, or 1000 mg/kg-day cobalt powder administered to Sprague Dawley rats (10/sex/group) by oral gavage beginning 2 weeks prior to mating through 3 days postpartum (for females; 2 weeks prior to mating through mating for males) (ECHA 2019). The dams in all but the lowest dose group had reduced food consumption, piloerection, lethargy, and soft feces. Dose-dependent decreases in body weight and increases in mortality also occurred beginning in the 100 mg/kg-day dose group, with all 10 females and 9 of 10 males in the high dose group dying prematurely. The study also reported increased mortality among offspring and reduced viability index in all but the lowest dose group. A significant decrease in live births, reduced litter weight, and increased post-implantation loss occurred in the 300 mg/kg-day dose group (no data for the 1000 mg/kg-day group because of 100% maternal mortality). The NOAEL for both maternal and reproductive effects was 30 mg/kg-day.

No birth defects were identified in the infants of women therapeutically administered up to 0.6 mg/kg-day cobalt chloride for 3–6 months during pregnancy (Holly 1955). No other studies in humans are available evaluating developmental effects and oral cobalt exposure.

Animal studies provide mixed results. In an unpublished, OECD guideline compliant developmental toxicity study, pregnant CD rats (25/group) were administered 0, 25, 50, or 100 mg/kg-day cobalt dichloride hexahydrate by oral gavage from gestational days 6 through 19 (ECHA 2019). A NOAEL of 25 mg/kg-day was identified for maternal toxicity based on reduced body weight and food consumption, increased incidence of clinical observations (e.g., behavior, lethargy) and hematological effects (increased hematocrit, hemoglobin, and red blood cell count) beginning at 50 mg/kg-day. No treatment-related effects were observed in offspring at any dose level. Thus, the developmental NOAEL was 100 mg/kg-day for cobalt dichloride hexahydrate. Oral administration of cobalt chloride to pregnant rats from gestational day 14 to postnatal day 21 resulted in a decreased growth rate at 5.4 mg/kg-day and reduced survival at 21.8 mg/kg-day (Domingo et al. 1985, ATSDR 2004b). However, these dose levels were also associated with reduced food consumption and maternal toxicity, including decreased body weight and effects on blood parameters. Szakmary et al. (2001) reported effects on reduced growth, delayed skeletal development, and urogenital malformations in pups of Sprague-Dawley rats orally administered cobalt sulfate during gestation. The effects occurred at all dose levels, with a LOAEL of 5.2 mg/kg-day. Maternal toxicity only occurred at the highest dose level (21 mg/kg-day). In the same study, developmental effects (delayed skeletal development, and eye, kidney and skeletal malformations) were also reported in C57BI mice in the absence of maternal toxicity at 10.5 mg/kg-day. Rabbits were more sensitive to cobalt sulfate in this study, with high maternal mortality and fetal resorptions in all dose groups (20, 100, and 200 mg/kg-day on gestational days 6 to 20).

5.4.2 Cancer Health Effects

There are no studies available in humans or laboratory animals that adequately address carcinogenic risks from oral exposure to cobalt. Nevertheless, NTP classified metallic cobalt and cobalt compounds that release metal ions as "reasonably anticipated to be human carcinogens" based on inhalation and injection studies in rodents combined with mechanistic data indicating that *in vivo* exposure to cobalt ions is a key event for cobalt-induced carcinogenicity (NTP 2016a, b). NTP's designation includes all forms of both water soluble and poorly soluble cobalt, with the exception of vitamin B_{12}, which is stable in the body and excreted without releasing cobalt ions. The mechanism of action for carcinogenicity for cobalt ions is not fully understood but, as summarized by NTP, involves inhibition of DNA repair, genotoxicity, generation of reactive oxygen species (ROS) resulting in oxidative damage, and stabilization of hypoxia-inducible factor 1α (HIF-1α) (NTP 2016a, b). HIF-1α increases expression of cell survival genes under low oxygen conditions. These events lead to oxidative damage to macromolecules, including to DNA, genomic instability, resistance to apoptosis (programmed cell death), and, ultimately, unchecked cell growth and proliferation.

NTP (2016a, 2016b) concluded that the cancer studies in humans, including by inhalation exposures, are inadequate to evaluate the relationship between cobalt and cancer. Most studies are limited by co-exposure to other known or suspected carcinogens (tungsten and carbon for hard metal workers), particularly lung carcinogens, low numbers of cases, and poor exposure assessment. NTP considered studies of metal-on-metal (MoM) hip implant patients uninformative for their analysis because of inadequate exposure assessment and co-exposure to other metals (NTP 2016a, b). The weight of evidence from available epidemiological studies does not indicate a pattern of increased risk of cancer associated with MoM implants (Smith et al. 2012, Lalmohamed et al. 2013, Christian et al. 2014, Makela et al. 2014, Hunt et al. 2018, Ekman et al. 2018). When small increases in some cancers have been reported, they have generally been attributed to confounding factors, bias, and issues related to multiple comparisons (Signorello et al. 2001).

In animal studies, tumors have been produced in rats and mice exposed to metallic cobalt or water-soluble cobalt compounds (cobalt sulfate and cobalt chloride) by inhalation, and to a poorly water-soluble cobalt compound (cobalt oxide) by intratracheal instillation (NTP 2016a, b). In particular, cobalt compounds have been shown to induce lung cancer after lifetime inhalation exposures as low as 1.25 mg/m^3: both metallic cobalt and cobalt sulfate produce alveolar/bronchiolar adenoma and carcinoma in rats and mice, and cobalt metal inhalation is associated with squamous cell lung tumors in female rats (NTP 1998, 2013). NTP (2013) also reported tumors in rats at sites other than the portal of entry (lungs), including the pancreas (males), blood system (mononuclear cell leukemia; females), and adrenal gland. In addition to the lung tumors, NTP (1998) reported an increased incidence of adrenal tumors (pheochromocytomas) in female rats and blood vessel tumors (hemangiosarcomas) in male mice associated with cobalt sulfate inhalation exposure. Injection of primarily cobalt powders and pellets in rats resulted in sarcomas at the injection/implantation site (IARC 1999, NTP 2016a). Cobalt concentrations experienced by tissue in contact with these solid materials would be much higher than systemic levels that might result from oral exposure.

5.5 Human Health Risk Assessment

USEPA's Office of Superfund Remediation and Technology Innovation provides a hierarchy of human health toxicity values for use in Superfund risk assessments. Most state agencies rely on USEPA's or a similar hierarchy:

1. USEPA Integrated Risk Information System (IRIS)
2. USEPA Provisional Peer-Reviewed Toxicity Values (PPRTVs)

3. Other peer-reviewed values, including:
    a. Agency for Toxic Substance and Disease Registry's (ATSDR) Minimal Risk Levels (MRLs)
    b. California Environmental Protection Agency (CalEPA) values
    c. USEPA's Health Effects Assessment Summary Tables (HEAST)

USEPA derives toxicity criteria under the IRIS program, including RfDs to evaluate non-cancer effects and cancer slope factors (CSFs) to evaluate cancer risks after oral exposure to chemicals. IRIS values have undergone multi-level internal and external peer review. For some chemicals that have not been reviewed under the IRIS program, USEPA develops toxicity values under the PPRTV program specifically for the Superfund program. PPRTV values have undergone internal peer review but not the full external peer-review process necessary to be placed in IRIS.

USEPA develops RfDs to evaluate noncarcinogenic risks from chemical exposures via the oral route. An RfD is an estimate of the level of daily oral exposure that is likely to be without appreciable risk of adverse health effects over a lifetime, even in sensitive populations. In human health risk assessment, exposure estimates are compared to RfDs to predict whether exposure might exceed a threshold for noncarcinogenic health effects. The following sections discuss derivation of an oral RfD, other potentially relevant safe intake values, and regulations and screening criteria.

5.5.1 Derivation of the USEPA Oral Reference Dose

USEPA has not derived an RfD for cobalt under the IRIS program (USEPA 2018b). However, USEPA developed PPRTV RfDs (p-RfDs) for both subchronic (<9 years) and chronic (>9 years) exposures based on thyroid effects (USEPA 2008).

The subchronic p-RfD value of 0.003 mg/kg-day for cobalt was based on reduced thyroid uptake of iodine at the LOAEL for cobalt of 1 mg/kg-day (Roche and Layrisse 1956). A composite uncertainty factor of 300 was applied to the LOAEL to arrive at the subchronic p-RfD (10 for extrapolation from a LOAEL to a NOAEL; 10 to address the potential for sensitive populations; 3 for deficiencies in the toxicological database, including lack of reproductive toxicity data). The chronic p-RfD value of 0.0003 mg/kg-day included an additional uncertainty factor of 10 to extrapolate from subchronic to chronic exposure. This is based on data from Kriss et al. (1955) suggesting the potential for more severe thyroid effects with longer exposures (although at higher doses of 2 to 4 mg/kg-day of cobalt chloride). USEPA reported low-to-medium confidence in the study on which the p-RfDs are based. Additionally, as noted above, three studies released around the same time did not detect thyroid dysfunction in relation to therapeutic oral administration of cobalt chloride (Wolf and Levy 1954, Holly 1955, Jaimet and Thode 1955).

An earlier version of the PPRTV support documentation based a subchronic p-RfD on increased hemoglobin in anemic patients after treatment with cobalt (Davis and Fields 1958, Duckham and Lee 1976). Although increased hemoglobin and red blood cell count (polycythemia) would be beneficial for someone with anemia, USEPA considered polycythemia to be potentially harmful for people with normal or already elevated levels. Davis and Fields (1958) identified a LOAEL for this study of 0.18 mg/kg-day (lower than the LOAEL for thyroid effects reported by Roche and Layrisse (1956)) and applied an uncertainty factor of 10 (3 to extrapolate from a minimal effect LOAEL to a NOAEL; 3 for deficiencies in the toxicological database). The resulting subchronic p-RfD was 0.02 mg/kg-day. Support for this endpoint includes the larger database for defining a point of departure dose and the lack of support for thyroid effects at doses below those used in the treatment of anemia.

5.5.2 Other Potentially Relevant Safe Intake Values

Finley et al. (2012b) derived an oral RfD for cobalt based on the study by Jaimet and Thode (1955) that evaluated thyroid function in children who received 1, 2, 4, or 6 mg/kg-day cobalt chloride (0.45, 0.90, 1.8, or 2.7 mg cobalt/kg-day, as calculated by Finley et al.) for 10 weeks. The dose levels were selected because they were representative of doses that would be expected from a commercially available cobalt-iron medication for thyroid hyperplasia. In addition, the high dose had previously been indicated as safe for children. Although the original publication did not include a statistical analysis of the data, Finley et al. (2012b) conducted repeated ANOVA tests on the raw data presented by Jaimet and Thode (1955) and concluded there were no statistically significant effects on hematological or thyroid function measurements at any dose level (Finley et al excluded the highest dose group of 2.7 mg/kg-day from their analysis because the dosing regime was interrupted in this group in the original study). Finley et al. selected the 0.9 mg/kg-day dose as the "point of departure" for deriving an RfD because the next highest dose of 1.8 mg/kg-day was higher than LOAELs reported in other studies. They applied an uncertainty factor of 30 (10 for inter-individual variability; 3 in consideration of deficiencies in the toxicological database) to derive an RfD of 0.03 mg/kg-day. Finley et al. considered this RfD applicable to chronic exposures because if the precursor event (i.e., inhibition of iodide uptake) does not occur, then the functional effect of thyroid dysfunction will not occur, nor would a longer duration of exposure at a no effect dose result in thyroid dysfunction. The authors provide the analogy of USEPA's conclusion regarding perchlorate RfD (also based on thyroid iodide uptake), for which an uncertainty factor for a study duration of less than chronic exposure was not included by USEPA for the same reason.

The ATSDR derived an intermediate duration MRL for oral exposures to cobalt of less than 1 year (ATSDR 2004b). The MRL is based on polycythemia reported in six male patients administered 120 to 150 mg/day cobalt chloride for up to 22 days (Davis and Fields 1958). Red blood cell count and hemoglobin levels increased in all 6 patients. ATSDR estimated a LOAEL of 1 mg/kg-day and applied an uncertainty factor of 100 (10 to extrapolate from a LOAEL to a NOAEL; 10 to account for inter-individual variability in response) to arrive at the intermediate-duration MRL of 0.01 mg/kg-day. ATSDR did not derive a chronic duration MRL because of a lack of adequate data for effects associated with chronic exposures. Application of an uncertainty factor of 10 to extrapolate from the intermediate duration MRL to a chronic exposure would result in a chronic duration value of 0.001 mg/kg-day.

FDA derived a permissible daily exposure level (PDE) for cobalt present as an impurity in orally administered drug products based on studies in humans (FDA 2015). In one study, cobalt chloride administered as a 2% solution in water or milk for up to 22 days induced polycythemia (increases red blood cell count) in six healthy men (20 to 47 years old) (Davis and Fields 1958). In another study, no treatment-related effects (including polycythemia and on thyroid biochemical function parameters) were reported in healthy human volunteers administered 1 mg/day cobalt chloride supplements for 90 days (Tvermoes et al. 2014). FDA considered the NOAEL for oral cobalt ingestion to be 1 mg/day and applied an uncertainty factor of 20 (10 for potential individual sensitivity; 2 to extrapolate from subchronic to chronic exposure) to derive an oral PDE of 0.05 mg/day. For comparison to the USEPA p-RfD of 0.0003 mg/kg-day, conversion of the PDE to a dose for a 70-kg adult would be 0.0007 mg/kg-day.

Cobalt is a structural component of the required dietary vitamin B_{12}, the lack of which can result in pernicious anemia. Because of this dietary requirement, cobalt/B_{12} is included in many multi-vitamin and mineral supplements. Accordingly, international and national health agencies have provided guidance on allowable intake levels for B_{12} and/or cobalt. In 2010, the Institute of Medicine of the National Academies released updated values for dietary reference intakes (DRIs). DRIs establish both adequate and upper level intake thresholds for dietary intake of vitamins and minerals (Nasem 2016). There are no DRI values for cobalt, but the DRI recommended dietary allowance (RDA) or adequate intake (AI) for the cobalt-containing vitamin B_{12} ranges from 0.4 µg/day (AI; infants 0 to 6 months of age) to 2.8 µg/day (RDA; lactating mothers of any age) (Nasem 2010). No DRI tolerable upper intake level (UL) has been recommended for vitamin B_{12} because of a lack of suitable data.

A joint committee of the United Nations Food and Agricultural Organization and the World Health Organization (FAO/WHO) recommended an upper limit for vitamin B_{12} intake of 1 mg/day, which corresponds to a cobalt intake of 0.044 mg/day (based on the relative molecular weights of cobalt/B_{12} of 59/1,355) and notes that this level of intake "has never been reported to have any side effects" (FAO and WHO 2001). Thus, the FAO/WHO upper limit is based on a lack of effects at the highest doses for which there is information rather than any report of effects. Similarly, Health Canada provides guidance on the amount of vitamins and minerals allowed in supplements (Health Canada 2007). Health Canada provided RDAs for cobalt ranging from 0.00004 mg/day (children 1 to 3 years of age) to 0.00012 mg/day (breastfeeding mothers of any age) based on the Institute of Medicine RDA for vitamin B_{12} and the molar contribution of cobalt to the molecule. Health Canada also provided an acceptable dose range for cobalt in supplements of 0.000004 to 0.044 mg/day.

The Danish Ministry of Family and Consumer Affairs compiled intake values for vitamins and minerals in 2006 (DVFA 2006). The compilation relied on data from expert panels to report intake limits. Based on information from the United Kingdom Expert Group on Vitamins and Minerals, vitamin B_{12} and cobalt have guidance levels of 2 and 0.0014 mg/day respectively. It is important to note that these guidance levels are based on limited data.

In their most recent toxicological assessment of cobalt, USEPA stated, "[s]tudies for evaluation of the oral carcinogenic potential for cobalt were not located" (USEPA 2008) Accordingly, USEPA did not derive an oral CSF for cobalt in USEPA's IRIS (USEPA 2018b).

5.5.3 Regulations and Screening Criteria

USEPA has not promulgated an MCL for cobalt in drinking water, nor are there any other enforceable regulatory criteria for oral exposure to cobalt. USEPA derives RSLs for evaluating chemical concentrations in the environment, screening hazardous waste sites to identify chemicals of potential concern for future evaluation, and to provide initial screening levels (USEPA 2018b). RSLs are risk-based concentrations derived using standard risk equations and exposure assumptions combined with toxicity data for individual chemicals. Based on the p-RfD, USEPA derived a tap water RSL for cobalt of 6 µg/L protective of residential water consumption. USEPA also derived soil RSLs for cobalt protective of residential (23 mg/kg) and industrial (350 mg/kg) exposure to soil and for leaching of cobalt from soil to groundwater and use of that water as residential drinking water (0.27 mg/kg). The WHO has not developed a guideline value for cobalt in drinking water. **Error! Reference source not found.**Table 5-1 summarizes available guidance levels, toxicity factors, and dietary recommendations for oral exposure to cobalt.

Table 5-1
Guideline values for cobalt

Type	Value	Units	Reference
CCR Rule Groundwater Protection Standard (GWPS)			
GWPS[a]	6	μg/L	USEPA (2018a)
Toxicity			
USEPA PPRTV Reference dose	0.0003	mg/kg-day	USEPA (2008)
ATSDR Intermediate minimal risk level[b]	0.01	mg/kg-day	ATSDR (2004b)
FDA Permissible daily exposure level[c]	0.05	mg/day	FDA (2015)
Regional Screening Levels[d]			
Tap water	6	μg/L	USEPA (2018c)
Residential soil	23	mg/kg	USEPA (2018c)
Industrial soil	350	mg/kg	USEPA (2018c)
Soil screening level for protection of groundwater	0.27	mg/kg	USEPA (2018c)
Recommended Dietary Allowance			
IOM (B_{12})[e]	0.0004 to 0.0028	mg/day	NASEM (2010)
Health Canada (cobalt / B_{12})[f]			
1–3 years old	0.00004 / 0.0009	mg/day	Health Canada (2007)
4–8 years old	0.00005 / 0.0012	mg/day	Health Canada (2007)
9–13 years old	0.00008 / 0.0018	mg/day	Health Canada (2007)
>13 years old	0.0001 / 0.0024	mg/day	Health Canada (2007)
Pregnancy	0.00011 / 0.0026	mg/day	Health Canada (2007)
Breastfeeding	0.00012 / 0.0028	mg/day	Health Canada (2007)

Note:
ATSDR - Agency for Toxic Substances and Disease Registry
FDA - U.S. Food and Drug Administration
ICH - International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use
IOM - Institute of Medicine
PPRTV - provisional peer reviewed toxicity value
RDA - recommended dietary allowance
THQ - target hazard quotient

[a] Background may be used as the GWPS if higher than 6 µg/L.

[b] ATSDR intermediate duration minimal risk level. ATSDR did not derive a chronic minimal risk level.

[c] FDA and ICH recommendation for permissible daily exposure to cobalt as an impurity in an orally. administered drug product. For comparison to USEPA and ATSDR toxicity values, the FDA value would be 0.007 mg/kg-day, assuming 70 kg body weight.

[d] USEPA regional screening levels based on a THQ of 1.

[e] The range of values is summarized in the table entry values for Health Canada, although Health Canada did not adopt the IOM value of 0.0004 mg/day for infants.

[f] Health Canada RDAs for cobalt are based on Institute of Medicine RDAs for vitamin B_{12} and the molar contribution of cobalt to vitamin B_{12}.

6

ECOLOGICAL TOXICOLOGY

This section reviews the potential for ecological effects from cobalt exposure, particularly through soil and water exposure pathways, and includes discussion of bioaccumulation, bioavailability, factors influencing uptake, toxicity, and ecological regulatory criteria and screening levels.

Extensive reviews have previously been developed for cobalt, including ATSDR's 2004 cobalt profile (ATSDR 2004b), reviews on the effects of cobalt on plants (Palit et al. 1994, Nagajyoti et al. 2010), and documents developed by USEPA (Baldessarini and Tarazi 2001, USEPA 2005). These reviews and numerous additional relevant publications were identified in literature searches and evaluated. Information and data presented here are comprehensive, though not exhaustive.

6.1 Factors Affecting Cobalt Bioavailability and Toxicity in Ecological Receptors

The form of cobalt present in the environment (see Sections 2 and 3) may affect its bioavailability to organisms and thus its ecological effects. Typically, the bulk of cobalt found in aerobic soil is not readily bioavailable to organisms because cobalt tends to exist in the solid phase, either complexed with organic matter or precipitated as a carbonate or hydroxide mineral (Perez-Espinosa et al. 2005). Cobalt adsorption within soil is relatively fast, occurring within 1 to 2 hours (Kim et al. 2006), but cobalt adsorbed to mineral phases in the soil will exist in equilibrium with the soil porewater and may be available for uptake by biota. However, as adsorbed cobalt ages, it can be immobilized and made unavailable through incorporation into mineral phases (Wendling et al. 2009). Cobalt mobility and bioavailability can also be altered via environmental changes such as changes in available adsorption sites, pH, and redox conditions (Kim et al. 2006). Higher pH in soil increases cobalt adsorption to minerals, and a lower pH increases cobalt mobility. Soils with high cation exchange capacity, exchangeable calcium, and high water content have increased adsorption (Kim et al. 2006). For plants, uptake of cobalt and other heavy metals is influenced by soil conditions: pH, soil aeration, temperature, available chelating and complexing agents, redox conditions, plant competition, form of metal (speciation), presence of fertilizers, organic matter content, plant size and root structure, soil moisture, water content, mineral content, and clay content (Kim et al. 2006, Gal et al. 2008, Wendling et al. 2009 as cited in Nagajyoti et al. 2010). All of these factors affect the potential for plant toxicity. Soil concentrations at which toxicity is reported for plants exposed to cobalt can vary by up to two orders of magnitude, as a function of many factors including species, endpoint measured, and differences in soil conditions such as pH, cation exchange capacity, and exchangeable soil calcium (Li et al. 2009).

In aquatic systems, the availability of cobalt is similarly limited by precipitation and adsorption. The proportions of dissolved and particle-associated cobalt in freshwater are highly variable

(Nagpal 2004), and the cobalt distribution coefficient in water is influenced by redox conditions, pH, ionic strength, and dissolved organic matter (Mahara and Kudo 1981 as cited in Kim et al. 2006). In any given body of water, cobalt is found in the following forms: dissolved, adsorbed, precipitated, within inorganic solids, in oxide coatings, complexed with organics, and in crystalline sediments (Smith and Carson 1981 as cited in Nagpal 2004). In waters with high concentrations of organic matter, the majority of the cobalt may exist as soluble organic matter-bound cobalt complexes (Smith and Carson 1981 as cited in Kim et al. 2006).

Cobalt toxicity to aquatic species is also affected by the chemical properties of the water. For example, toxicity in *Daphnia magna* and *Ceriodaphnia dubia* is influenced by water hardness; increasing hardness decreases cobalt toxicity. The LC_{50} (the lethal concentration at which 50% of test organisms died) values for *D. magna* were 1.1 mg/L Co in soft water (45.3 mg/L hardness as $CaCO_3$), 3.4 mg/L Co in hard water (124–128 mg/L hardness as $CaCO_3$), and 5.2 mg/L Co in very hard water (220 mg/L hardness as $CaCO_3$) (Diamond et al. 1992). At a very high water hardness level (800 mg/L hardness as $CaCO_3$), the 48-hour LC_{50} for *Ceriodaphnia dubia* was greater than 5.3 mg/L Co. This is a factor of 60 times greater than the LC_{50} value at 48 hours for 50 mg/L hardness (as $CaCO_3$) for the same organism (Diamond et al. 1992). No-observable-effect concentrations (NOECs) increased by an order of magnitude, 0.05 to 0.6 mg/L, from 400 to 800 mg $CaCO_3$/L (Diamond et al. 1992). A 24-hour LC_{50} also doubled from 2.4 to 5.3 mg/L from 50 to 800 mg $CaCO_3$/L (Diamond et al. 1992).

Information regarding bioavailability of forms of cobalt other than cobalamin (vitamin B_{12}) in mammals or birds was not widely found in the literature. One example found related to bioavailability was in ruminants, in which cobalt bioavailability depends on the form of cobalt; carbonates were found to be more available than oxides in ruminants (Kawashima et al. 1997, EFSA 2012).

The following sections provide more detailed information on cobalt bioaccumulation and toxicity, typically related to common bioavailable forms in the environment or used in toxicity testing such as ionic, chloride, nitrate, or sulfate, discussed by types of organisms.

6.2 Bioaccumulation in Aquatic and Terrestrial Organisms

Cobalt has been found to bioaccumulate in aquatic organisms (Subrahmanyam 1990) but not to biomagnify (ATSDR 2004b). For terrestrial organisms that consume plants, cobalt also does not biomagnify (Smith and Carson 1981, Evans et al. 1988, Freitas et al. 1988, Barceloux and Barceloux 1999 all as cited in ATSDR 2004b).

Bioconcentration factors (BCFs, the tissue concentration on a dry weight basis divided by the water and food concentrations) for freshwater molluscs ranged from approximately 1 to 300 in soft tissues and ranged from approximately 6 to 84 in whole bodies of marine molluscs (ATSDR 2004b). BCFs ranged from less than 10 to 1,000 for freshwater fish and from approximately 100 to 4,000 for marine fish (Smith and Carson 1981 as cited in ATSDR 2004b). BCFs for radioactive cobalt in the freshwater alga, *Selenastrum capricornutum*, ranged from 2,300 to 18,000 (Corisco and Carreiro 1999).

Food sources, such as plants, can provide the cobalt essential to humans and animals (ATSDR 2004b). Cobalt distribution in plants varies widely and depends on the species. Cobalt largely accumulated in plant roots (Gal et al. 2008), but was also found in the edible parts of plants (seeds, grain, and fruit). Concentrations were highest in roots, followed in decreasing order by leaves, seeds, and stems (Palit et al. 1994). In general, cobalt in most plant tissues was typically 1 mg/kg, with plant shoot concentrations at 2 mg/kg (Perez-Espinosa et al. 2005). Though plants can uptake cobalt from the soil, the transfer coefficient of cobalt from roots to shoots, defined as the ratio of plant concentration to soil concentration, was low (0.01 to 0.3), and low quantities of cobalt were found in plant tissue (Smith and Carson 1981, Mascanzoni 1989 both as cited in Kim et al. 2006). Exceptions occur where plants that grow in the presence of sewage sludge or serpentine soils had higher concentrations in leaves and stems (Perez-Espinosa et al. 2005). Some plants also absorb cobalt through active transport (Palit et al. 1994).

Bioaccumulation has also been observed in microorganisms: *Euglena viridis* concentrated up to 0.007 mg Co/mg cell dry weight when in Bold's basal media containing 3 mg/L of cobalt (Coleman et al. 1971).

6.3 Essentiality and Health Benefits in Aquatic and Terrestrial Organisms

A chemical profile on cobalt published by WHO (WHO 2006) cites a number of studies indicating that cobalt is essential for growth of bacteria, algae, and plants and is a component of vitamin B_{12}, an essential nutrient for ruminants, horses, and other mammals (WHO 2006). A publication by the National Research Council (NRC) on the mineral tolerance of animals indicates that cobalt is required at 0.10 to 0.15 mg Co/kg in the diet of ruminants in order for ruminal bacteria to synthesize necessary amounts of vitamin B_{12} (NRC 2005). Cobalt had a positive effect on algae and microorganisms at low doses resulting in growth (Diamond et al. 1992, WHO 2006) but the absence of cobalt resulted in growth inhibition and the inability to fix nitrogen in some species (WHO 2006). Low cobalt concentrations generally found in the range of 0.1 to 0.5 mg/L are required by numerous algae, yeast, and bacteria (Holm-Hansen et al. 1954, Sawada et al. 1955, Enari 1958, Patterson 1960 all as cited in Diamond et al. 1992). However, some studies indicated that cobalt concentrations ranging from 0.4 to 0.5 mg/L inhibited the growth of freshwater algae (Diamond et al. 1992).

6.4 Aquatic Toxicity

6.4.1 Toxicity to Algae and Microorganisms

A number of studies are available on the effects of cobalt to freshwater algae and aquatic microorganisms and are summarized in Table 6-1. While low concentrations of cobalt generally improve growth rates of simple algae to complex plants, higher concentrations are often toxic. Though cobalt can affect various organisms, overall, cobalt toxicity is typically limited in aquatic environments because cobalt complexes with humic acids (Ennis and Brogan 1961 as cited in Gadd and Griffiths 1978, Watanabe et al. 2017).

Cobalt was found to have beneficial effects at low concentrations in green alga, *Chlamydomonas reinhardtii* (Lavoie et al. 2012), such as mitigating toxicity effects from other metals. When increasing environmentally relevant Co^{2+} concentrations from 6×10^{-7} mg/L Co^{2+} to 6×10^{-5} mg/L Co^{2+}, a decrease in cadmium uptake and a decrease in toxicity occurred (Lavoie et al. 2012). Microbial processes supplemented with trace amounts of metals often show improved performance, whereas a higher dose with the same metal resulted in toxicity (Paulo et al. 2017). In a methanogenic culture, 0.618 mg/L of cobalt increased methane production by approximately

10% when compared to the control, but 1,800 mg/L of cobalt caused a reduction in methane production by 53% when compared to the control (Paulo et al. 2017). Adding sulfide led to metal precipitation, which reduced toxicity, and also reduced methane production by favoring sulfate-reducing bacteria within the microbial community (Paulo et al. 2017).

In freshwater microorganisms, cobalt toxicity effects have been observed over a concentration range of 0.6 mg/L for a 12-day lowest-observed-effect-concentration (LOEC) test to 66.2 mg/L for 24-hour LC_{50} (effective concentration that impacts 50% of organisms tested) test (Table 6-1). In general, cobalt exposures may have the following effects on various algal and plant species: decrease in growth, lowering of cellular weight, and inhibition of sporulation (Palit et al. 1994). Relatively high cobalt concentrations (0.6–50 mg/L) compared to background environmental levels (groundwater average of 0.0008 mg/L, Table 2-1) caused toxicity and decreased growth in microorganisms found in natural waters. For example, growth of algal species, *Pediastrum tetras*, *Euglena viridis*, and *Chlorella vulgaris* decreased when exposed to cobalt nitrate at 0.6 mg/L (Coleman et al. 1971). In bacteria commonly found in wastewater treatment plants, *Zoogloea ramigera*, a pronounced lag phase and decreased growth rate were observed when exposed to 1 mg/L, 5 mg/L, and 10 mg/L Co^{2+} (Norberg and Molin 1983). At 10 mg/L, no growth was noted for *Z. ramigera* (Norberg and Molin 1983). Cobalt toxicity in cyanobacteria (formally bluegreen algae, now *Anabaena variabilis*) was observed at 50 mg Co/L and for the marine diatom *Witzschia closterium* at 10.2 mg Co/L (Ahluwalia and Manjit 1988 as cited in Palit et al. 1994).

Little has been reported on cobalt toxicity to marine microorganisms. The marine diatom *Witzschia closterium* is the only marine microorganism with cobalt toxicity data readily available. Measurable cobalt toxicity was noted for *Witzschia closterium* at 10.2 mg/L (Rosko and Rachlin 1975 as cited in Palit et al. 1994).

Cobalt can also disrupt metabolic processes within microorganisms. In cyanobacteria, cobalt chloride inhibited many cellular activities including ammonia uptake and enzyme activity of nitrate reductase (Palit et al. 1994). Toxic concentrations within algae inhibited active ion transport (Palit et al. 1994). In yeast, cobalt impacted mitochondrial respiration and oxidative phosphorylation; both are important pathways for providing energy to the cell (Tuppy and Sieghart 1973 as cited in Palit et al. 1994). In general, elevated concentrations of cobalt disrupted iron metabolism in organisms, which is vital for growth (Stewart 1963 as cited in Coleman et al. 1971).

A number of factors control the degree of toxicity observed in microorganisms. Examples include tolerance of the organism and environmental conditions that negate cobalt toxicity, such as oxygen content, pH, or the presence of humic acids. Multiple species of fungus exhibited resistance to elevated cobalt concentrations; mechanisms of resistance include intracellular detoxification, mutations, transport, or alternative forms of metabolism (Palit et al. 1994). Numerous bacterial and algal species have shown tolerance or resistance to cobalt (Manning and Cooke 1972 as cited in Gadd and Griffiths 1978, Strauss 1986 as cited in Palit et al. 1994, Wu et al. 1994). Such studies and others (Hashem and Bahkali 1994, Kumar et al. 2016) support the potential use of microorganisms in bioremediation of cobalt-impacted environments. One of the factors influencing the degree of toxicity of cobalt is pH. In the green alga *Scenedesmus bijuga*, increasing pH led to decreasing cobalt uptake, and increasing cobalt concentrations led to decreases in growth (Fathi and Al-Omar 2006). For example, during a 0.0001 to 0.1 mg/L cobalt chloride exposure, *S. bijuga* had similar total cell counts compared to the control, whereas 13 to 130 mg/L cobalt chloride resulted in mortality (Fathi and Al-Omar 2006). A lower pH range from 4 to 6 SU resulted in cell death compared to the control, whereas a higher pH range from 8 to 10 SU showed a decrease in toxicity compared with the control (Fathi and Al-Omar 2006). Cobalt accumulation was higher at pH ranging from 4 to 8 SU, which may have led to the increase in toxicity (Fathi and Al-Omar 2006).

The median cobalt groundwater concentration in the United States is 0.0008 mg/L (Table 2-1). In comparison, the toxicity studies discussed above used cobalt exposure concentrations approximately 3 to 5 orders of magnitude higher than what is typically found in groundwater, indicative of the degree of contamination needed to cause ecological effects.

6.4.2 Toxicity to Aquatic Invertebrates

Invertebrates are common model organisms used to assess metal toxicity because of their sensitivity and prevalence in all freshwater bodies. Common endpoints included mortality, growth, behavior, and reproduction. The available studies reported a number of toxicity effects over a range of 0.0095 to 239 mg Co/L for freshwater invertebrates, depending on the species, life stage, endpoint, and exposure duration. Typically, acute toxicity endpoints are expressed as lethality (LC_{50}) or effect concentrations (EC_{50}). Chronic toxicity tests last longer in duration and typically have endpoints including survival, growth, and/or reproduction. Commonly used model invertebrates, *Daphnia magna* (water flea) and *Lumbriculus variegatus* (*worm*), had a 96-hour LC_{50} (concentration causing 50% lethality) of 3.2 and >100 mg/L, respectively (Table 6-1). Additionally, the data for over 20 freshwater invertebrates provided in Table 6-1 indicate varying levels of sensitivity within species (larva vs. adult) and sensitivity among species.

Cobalt toxicity to freshwater invertebrates were reported over a range between 3.2 (*D. magna*; Ewell et al. 1986) and 239 mg/L (*Tubifex tubifex*; Rathore and Khangarot 2002 as cited in Kim et al. 2006) based on 96-hour LC_{50} tests (Table 6-1). *D. magna* appears to be the most sensitive freshwater invertebrate based on the 96-hour LC_{50}, whereas *Hyalella azteca* (amphipod) is the most sensitive based on a 4-week LC_{50} (Table 6-1), with larger freshwater species such as snails, worms, and crayfish showing less sensitivity (WHO 2006; Table 6-1). Limited studies on cobalt and marine invertebrates have been conducted; these studies are listed in Table 6-2.

Acute toxicity tests with aquatic invertebrates in the laboratory can be useful for evaluating whether concentrations of cobalt in natural waters pose a potential risk. For the amphipod *Hyalella azteca*, a common laboratory test species, chronic toxicity was reported as 0.0095 mg/L after a four-week exposure (Norwood et al. 2007). Based on 96-hr TL_m (medium tolerance limit at 96 hours), cobalt caused mortality to *Ephemerella subvaria* at 16 mg/L and to *Hydropsyche betteni* at 64 mg/L (Warnick and Bell 1969). Additional studies evaluated seven juvenile forms of aquatic invertebrate species representing five phyla with a cobalt chloride concentration up to 100 mg/L (Ewell et al. 1986). Survival and behavior were monitored daily (Ewell et al. 1986). In the tests, water fleas were overall more sensitive to cobalt chloride than the other species tested (water flea, flatworm, shrimp, snail, segmented worm, and fish). Similar results were reported by Kimball (1978) with toxicity effects in *Daphnia magna* (water flea) at 6 mg/L 48-hour LC_{50}. Other LC_{50} results are provided in Table 6-1, with several species showing acute toxicity at cobalt concentrations as low as a 3.2 mg/L 96-hour LC_{50} (*D. magna*). However, most LC_{50} values were in the parts per million range. Another study exposed six freshwater mussel species to cobalt chloride in soft water (42 mg/L $CaCO_3$) for 24 to 72 hours (Markich 2017). All mussel species had an increased sensitivity of 2.5-fold to cobalt chloride from 24 to 72 hours (Markich 2017). The endpoint tested was sensitivity, i.e., valve closure of the larvae, which is not a typical toxicity endpoint for LC_{50} data, and thus was not tabulated in Table 6-1. Of the six species, *Alathyria profuga* and *Velesumio ambigus* were the two most sensitive species to cobalt chloride (Markich 2017).

Limited data are available for marine invertebrates; however, available studies have reported adverse effects to marine invertebrates at concentrations that ranged from 1.7 to 454 mg Co/L (Table 6-2).

In general, invertebrate toxicity studies showed a range of effects from reproduction to mortality. The above toxicity studies and those found in Table 6-1 used exposure cobalt concentrations up to approximately 1 to 5 orders of magnitude higher than what is typically found in the environment (ATSDR 2004b, Groschen et al. 2009).

Another consideration when comparing laboratory studies to field conditions is that organisms are rarely exposed to a single contaminant. For example, CCR contains many elements, and therefore interactions among metals may reduce or increase the toxicological effects of cobalt. The following studies assessed toxicity observed when exposing organisms to multiple contaminants. A study using the model organism *Enchytraeus crypticus*, an annelid worm, observed the effects of cobalt and nickel, both individually and as co-contaminants (He et al. 2015). Concentrations tested for each metal ranged from 0.2 to 13 mg/L for nickel and 3 to 96 mg/L for cobalt. The LC_{50} for the cobalt ion when tested alone was 30.1 mg/L at 4 days, 24 mg/L at 10 days, and 23 mg/L at 14 days. During a mixed cobalt and nickel exposure, cobalt decreased the uptake of nickel by 20 to 70%, while nickel did not have an effect on the uptake of cobalt (He et al. 2015). This study indicated that cobalt can act as an antagonist, modifying the uptake and bioaccumulation of nickel. For *H. azteca*, mortality increased with an increasing bioaccumulation of cobalt and resulted in growth reduction (Norwood et al. 2007). Bozich et al. (2017) conducted a study simulating exposure to battery components using lithium nickel manganese cobalt oxide and lithium cobalt oxide (Bozich et al. 2017). Chronic studies up to 21 days showed that lithium nickel manganese cobalt oxide and lithium cobalt oxide exposures were associated with a decrease in reproduction and survival at 0.3 and 1.0 mg/L for the two compounds (Bozich et al. 2017). The study represents potential realistic environmental exposures that would consist of multiple compounds (Bozich et al. 2017). The freshwater bivalve mollusc, *Andonta cygnea*, was used to study the effects of a cobalt-containing nanoscale-polymeric complex and free Co^{2+} (Falfushynska et al. 2012). A 14-day exposure using 0.05 mg/L of the cobalt nanoscale material or the free Co^{2+} showed that the cobalt-containing nanoscale-polymeric substance caused cobalt accumulation, increased metallothionein production, and decreased oxyradical production whereas the free Co^{2+}, caused cytotoxicity and increased oxyradical production (Falfushynska et al. 2012).

Table 6-1
Acute and chronic toxicity values for cobalt to freshwater aquatic organisms

Organism	Cobalt (mg/L)	Cobalt Form[a]	Endpoint	Reference
Algae, Protozoa, Cnidarian				
Chlorella vulgaris (alga)	2	Nitrate	21-day LOEC (growth)	Coleman et al. (1971) as cited in Who (2006)
Euglena viridis (single-cell flagellate)	0.6	Nitrate	21-day LOEC (growth)	Coleman et al. (1971) as cited in Who (2006)
Hydra magnipapillata (polyp)	66.2	Chloride	24-hour LC_{50}	Zeeshan et al. (2017)
	21.2	Chloride	48-hour LC_{50}	Zeeshan et al. (2017)
	16	Chloride	72-hour LC_{50}	Zeeshan et al. (2017)
	14	Chloride	96-hour LC_{50}	Zeeshan et al. (2017)
Pediastrum tetras (alga)	0.6	Nitrate	21-day LOEC (growth)	Coleman et al. (1971) as cited in Who 2006
Spirostomum ambiguum (protozoa)	12	Nitrate	24-hour LC_{50}	Nalecz-Jawecki and Sawicki (1998) as cited in Kim et al. (2006)
Spirulina platensis (cyanobacteria)	11	Chloride	96-hour EC_{50}	Sharma et al. (1987) as cited in Kim et al. (2006)
Tetrahymena pyriformis (ciliate)	56	Chloride	9-hour IC_{50} (growth)	Sauvant et al. (1995) as cited in Kim et al. (2006)
	24	Chloride	36-hour IC_{50} (growth)	Sauvant et al. (1995) as cited in Kim et al. (2006)
Invertebrates				
Austropotamobius pallipes (crayfish)	9	Chloride	96-hour LC_{50}	Boutet and Chaisemartin (1973) as cited in Kim et al. (2006)
Asellus intermedius (isopod crustacean)	>100	Chloride	96-hour LC_{50}	Ewell et al. (1986)
Branchiura sowerbyi (worm)	132.62	Chloride	96-hour LC_{50}	Das and Kaviraj (1994)

Table 6-1 (continued)
Acute and chronic toxicity values for cobalt to freshwater aquatic organisms

Organism	Cobalt (mg/L)	Cobalt Form[a]	Endpoint	Reference
Invertebrates (continued)				
Cyclops abyssorum (plankton)	16	Chloride	48-hour LC_{50}	Baudouin and Scoppa (1974) as cited in Kim et al. (2006)
Crangonyx pseudogracilis (amphipod)	39.2	Chloride	96-hour LC_{50}	Martin and Holdich (1986) as cited in Kim et al. (2006)
Chironomus tentans (midge)	57	Chloride	48-hour LC_{50}	Khangarot and Ray (1989) as cited in Kim et al. (2006)
Ceriodaphnia dubia (water flea)	>5.3	Chloride	48-hour LC_{50}	Diamond et al. (1992)
Diaptomus forbesi (copepod)	3.4	Chloride	96-hour LC_{50}	Das and Kaviraj (1994)
Daphnia magna (water flea)	2	Chloride	48-hour LC_{50}	Khangarot and Ray (1989) as cited in Kim et al. (2006)
	1.1	Chloride	48-hour LC_{50}	Biesinger and Christensen (1972) as cited in Kim et al. (2006)
	6	Sulfate	48-hour LC_{50}	Kimball (1978) as cited in Sample et al. (1997)
	3.2	Chloride	96-hour LC_{50}	Ewell et al. (1986)
	0.02	Chloride	21-day LC_{50}	Biesinger and Christensen (1972) as cited in Kim et al. (2006)
	0.01	Chloride	21-day EC_{50} (reproduction)	Biesinger and Christensen (1972) as cited in Kim et al. (2006)
	0.03 to–0.05	N/A	21-day NOEC (reproduction and survival)	Nagpal (2004) as cited in Kim et al. (2006)
	0.03	Sulfate	28-day LC_{50}	Kimball (1978) as cited in WHO (2006)
	0.003	Sulfate	28-day NOEC (reproduction)	Kimball (1978) as cited in WHO (2006)

Table 6-1 (continued)
Acute and chronic toxicity values for cobalt to freshwater aquatic organisms

Organism	Cobalt (mg/L)	Cobalt Form[a]	Endpoint	Reference
Invertebrates (continued)				
Daphnia hyalina (water flea)	1.3	Chloride	48-hour LC_{50}	Baudouin and Scoppa (1974) as cited in Kim et al. (2006)
Dugesia tigrina (flatworm)	25	Chloride	96-hour LC_{50}	Ewell et al. (1986)
Ephemerella subvaria (mayfly)	16	Sulfate	96-hour LC_{50}	Warnick and Bell 1969
Eudiaptomus padanus (copepod)	4	Chloride	48-hour LC_{50}	Baudouin and Scoppa (1974) as cited in Kim et al. (2006)
Gammarus fasciatus (freshwater shrimp)	>100	Chloride	96-hour LC_{50}	Ewell et al. (1986)
Hyalella azteca (amphipod)	0.0095	Chloride	4-week LC_{50}	Norwood et al. (2007)
Helisoma trivolvis (snail)	>100	Chloride	96-hour LC_{50}	Ewell et al. (1986)
Lumbriculus variegatus (worm)	>100	Chloride	96-hour LC_{50}	Ewell et al. (1986)
Orconectes limosus (crayfish)	10.2	Chloride	96-hour LC_{50}	Boutet and Chaisemartin (1973) as cited in Kim et al. (2006)
Philodina acuticornis (rotifer)	28	Chloride	24-hour LC_{50}	Buikema et al. (1984) as cited in Kim et al. (2006)
Tubifex tubifex (worm)	95.4 to 239	Chloride	96-hour LC_{50}	Rathore and Khangarot (2002) as cited in Kim et al. (2006)
Fish				
Carassius auratus (goldfish)	67	Cobalt(II)	96-hour LC_{50}	AQUIRE database accessed 1996 by Sample et al. (1997)
	333	Chloride	96-hour LC_{50}	Das and Kaviraj (1994) as cited in Kim et al. (2006)
	0.8	Nitrate	7-day LC_{50}	Birge et al. 1979 as cited in Kim et al. (2006)
Catla catla, (carp, 60 day old)	113 to 132	Chloride	96-hour LC_{50}	Yaqub and Javed (2012)

Table 6-1 (continued)
Acute and chronic toxicity values for cobalt to freshwater aquatic organisms

Organism	Cobalt (mg/L)	Cobalt Form[a]	Endpoint	Reference
Fish (continued)				
Cirrhin mrigala, (carp, 90 day old)	153 to 155	Chloride	96-hour LC_{50}	Yaqub and Javed (2012)
Colisa fasciatus (gourami)	102	Chloride	96-hour LC_{50}	Srivastava and Agrawal (1979) as cited in Kim et al. (2006)
Cyprinus carpio (carp)	83	Cobalt(II)	96-hour LC_{50}	AQUIRE database accessed 1996 by Sample et al. (1997)
Danio rerio (zebrafish)	4	Chloride	16-day NOEC (hatching rate)	Dave and Xiu (1991)as cited in Who (2006)
	0.06	Chloride	16-day NOEC (survival)	Dave and Xiu (1991) as cited in Who (2006)
Labeo rohita, (carp, 60 day old)	113 to 132	Chloride	96-hour LC_{50}	Yaqub and Javed (2012)
Lepidocephalichthyes guntea (loach)	500	Chloride	24-hour LC_{50}	Shivaraj and Patil (1985)
	400	Chloride	48-hour LC_{50}	Shivaraj and Patil (1985)
	378	Chloride	72-hour LC_{50}	Shivaraj and Patil (1985)
	344.4	Chloride	96-hour LC_{50}	Shivaraj and Patil (1985)
Pimephales promelas (Fathead minnow)	4	Sulfate	96-hour LC_{50}	Kimball (1978) as cited in WHO (2006)
	13	Formate	96-hour LC_{50}	Curtis and Ward (1981) as cited in Kim et al. (2006)
	48	Chloride	96-hour LC_{50}	Ewell et al. (1986)
	1.2 to 3.8	Chloride	7-day NOEC (survival)	Diamond et al. (1992) as cited in Who (2006)
	24.8	Bromide	96-hour LC_{50}	Curtis and Ward (1981) as cited in Kim et al. (2006)

Table 6-1 (continued)
Acute and chronic toxicity values for cobalt to freshwater aquatic organisms

Organism	Cobalt (mg/L)	Cobalt Form[a]	Endpoint	Reference
Fish (continued)				
Oncorhynchus mykiss (Rainbow trout)	0.1	N/A	96-hour LC_{50}	Birge et al. (1979) as cited in Diamond et al. (1992)
	1.4	Chloride	96-hour LC_{50}	Marr et al. (1998)
	112.9 without UV light	Potassium hexacyanocobaltate	96-hour LC_{50}	Little et al. (2007)
	0.38 with UV light (cobalt cyanide)	Potassium hexacyanocobaltate	96-hour LC_{50}	Little et al. (2007)
	0.49	N/A	28-day Chronic LC_{10}	Birge et al. (1980) as cited in Marr et al. (1998)
Amphibian				
Rana hexadactyla (frog)	18	Cobalt(II)	96-hour LC_{50}	AQUIRE database accessed 1996 by Sample et al. (1997)
Gastrophryne carolinensis (toad)	0.05	Nitrate	7-day LC_{50}	Birge et al. (1979) as cited in Kim et al. (2006)

Note:

LC_{50}	-	lethal concentration at which 50% of the test organisms were impacted.
EC_{50}	-	effective concentration that impacts 50% of organisms tested.
IC50	-	half maximal inhibitory concentration; measure of substance potency in inhibiting biological function.
NOEC	-	no-observed-effects concentration.
LOEC	-	lowest-observed-effects concentration.
UV	-	ultraviolet.

[a] Various forms of cobalt were tested, including Co^{2+}, cobalt nitrate, cobalt sulfate, cobalt chloride, cobalt formate, and cobalt bromide. Cobalt form was listed where information was available; N/A indicates that the cobalt form was unclear or unstated.

Table 6-2
LC_{50} and EC_{50} values for cobalt to marine aquatic organisms

Organism	Cobalt (mg/L)	Cobalt Form[a]	Endpoint	Reference
Diatom				
Ditylum brightwellii diatom)	0.3	Chloride	5-day EC_{50} (growth)	Canterford and Canterford (1980) as cited in Kim et al. (2006)
Nitzschia closterium (diatom)	10.2	N/A	96-hour EC_{50}	Rosko and Rachlin (1975) as cited in Kim et al. (2006)
Invertebrates				
Artemia salina (brine shrimp)	172	Nitrate	48-hour LC_{50}	Watling and Watling (1982) as cited in Kim et al. (2006)
Carcinus maenus (crab, adult)	227 to 454	Chloride	96-hour LC_{50}	Amiard (1976) as cited in Kim et al. (2006)
C. maenus (crab, larva)	23	Chloride	96-hour LC_{50}	Amiard (1976) as cited in Kim et al. (2006)
Homarus vulgaris (lobster, larva)	5–23	Chloride	96-hour LC_{50}	Amiard (1976) as cited in Kim et al. (2006)
Idotea baltica (isopod)	10	Chloride	52-day LC_{50}	El-Nady and Atta (1996) as cited in Kim et al. (2006)
Monhystera disjuncta (nematode)	94	N/A	96-hour LC_{50}	Vranken et al. (1991) as cited in Kim et al. (2006)
Palaemon serratus (prawn, adult)	227 to 454	Chloride	96-hour LC_{50}	Amiard (1976) as cited in Kim et al. (2006)
P. serratus (prawn, larva)	22.7 to 45.4	Chloride	96-hour LC_{50}	Amiard (1976) as cited in Kim et al. (2006)
Perna perna (mussel)	1.7	Chloride	1-hour EC_{50}	Watling and Watling (1982) as cited in Kim et al. (2006)
Fish				
Blennius pholis (Shanny)	454 to 681	Chloride	96-hour LC_{50}	Amiard (1976) as cited in Kim et al. (2006)
Fundulus heteroclitus (mummichog)	275	Chloride	96-hour LC_{50}	Dorfman (1977) as cited in Kim et al. (2006)

Table 6-2 (continued)
LC_{50} and EC_{50} values for cobalt to marine aquatic organisms

Organism	Cobalt (mg/L)	Cobalt Form[a]	Endpoint	Reference
Fish (continued)				
F. heteroclitus (mummichog)	>1,000	Carbonic acid with cobalt	96-hour LC_{50}	Dorfman (1977) as cited in Kim et al. (2006)
Terapon jarbua (Crescent bass)	52.5	Sulfate	96-hour LC_{50}	Krishnakumari et al. (1983) as cited in Kim et al. (2006)

Note:

LC_{50} - lethal concentration at which 50% of the test organisms were impacted.
EC_{50} - effective concentration that impacts 50% of organisms tested.

[a] Various forms of cobalt were tested, including Co^{2+}, cobalt nitrate, cobalt sulfate, cobalt chloride, cobalt formate, and cobalt bromide. Cobalt form was listed where information was available; N/A indicates that the cobalt form was unclear or unstated.

6.4.3 Toxicity to Fish

Numerous freshwater fish studies on cobalt toxicity have been conducted, as summarized in Table 6-1. Acute toxicity tests are short-term exposures and typically are defined as an exposure duration of <96 hours. Chronic toxicity tests last longer in duration and typically have endpoints including survival, growth, and/or reproduction.

Cobalt toxicity tests have primarily focused on three model organisms, *Pimephales promelas* (fathead minnow), *Oncorhynchus mykiss* (rainbow trout), and *Danio rerio* (zebrafish). One study described the acute and chronic toxicity of cobalt to *P. promelas* as a function of water hardness (Diamond et al. 1992). In a range of 50 to 200 mg/L hardness, the study found that cobalt acute toxicity was inversely correlated with water hardness, and based on the findings, proposed a tentative cobalt acute criteria of 0.29 mg/L and 0.87 mg/L cobalt in soft and hard water, respectively. Other work with *P. promelas* measured a 96-hour LC_{50} of 4 mg/L (Kimball 1978), which is approximately four to five orders of magnitude greater than the amount of cobalt found in natural surface waters. Chronic toxicity tests with *P. promelas* showed that the NOEC (no observable effect concentration) increased with increasing water hardness: 1.2 mg/L (50 mg/L hardness as $CaCO_3$) to 4 mg/L (800 mg/L as $CaCO_3$) (Diamond et al. 1992). Although the water hardness was not reported, low chronic toxicity (LC_{10}) was reported in rainbow trout at approximately 0.1 mg/L (Birge et al. 1979 as cited in Diamond et al. 1992).

Gills are a primary target of metal toxicity in fish (Lock et al. 2006). Ions such as H^+, Na^+, and Ca^{2+} inhibited short-term cobalt accumulation in the gills of rainbow trout (Richards and Playle 1998 as cited in Lock et al. 2006). Marr et al. (1998) showed in rainbow trout (*Oncorhynchus mykiss*) that lethality was observed between 72 to 192 hours, which demonstrates that a 96-hour toxicity test may not be optimal for understanding cobalt toxicity in this species, since toxicity was observed at up to 8 days (Marr et al. 1998, WHO 2006).

In zebrafish (*D. rerio*), abnormal development included changes in morphology, such as white pigmentation, behavioral changes, delayed hatching, retarded growth, and bradycardia (Cai et al. 2012). The effects of cobalt on hatching and survival of zebrafish embryos were monitored for 16 days following exposure to cobalt in the blastula stage (2 to 4 hour after fertilization). Overall, effects on survival were not observed until day 9, when concentrations ranging from 0.6 to 15.4 mg Co/L inhibited hatching (Dave and Xiu 1991). In another study with zebrafish, embryos were exposed to 0 to 100 mg Co/L between 1 and 144 hours post fertilization (Cai et al. 2012). Survival and development were not impacted when Co <100 mg/L (Cai et al. 2012). However, exposures that were >100 mg Co/L showed reduced survival and abnormal development (Cai et al. 2012). The study also indicated that oxidative stress in zebrafish embryos occurred at 0.1 and 0.5 mg Co/L and apoptosis occurred at 0.5 mg Co/L (Cai et al. 2012). A study focusing on cobalt-induced genotoxicity from environmental exposures in male zebrafish found that chronic exposure caused DNA damage in sperm, reduced reproductive success, and induction of DNA repair genes in the testes (Reinardy et al. 2013). Specifically, the LC_{50} for larval zebrafish was determined at 35.3 mg Co/L during a 96-hour exposure to 0 to 50 mg Co/L (Reinardy et al. 2013). During a 12-day sub-lethal exposure to 0 to 25 mg Co/L, adult zebrafish had reduced reproduction and decreased hatchling survival at 25 mg Co/L (Reinardy et al. 2013). It should be noted that DNA damage in sperm returned to control levels after adult males were transferred to clean water for six days (Reinardy et al. 2013). The work suggests that chronic exposure to cobalt can result in DNA damage in sperm, induction of repair genes within testes DNA, and reduced reproductive success.

Toxicity testing with various freshwater fish species have shown that acute toxicity ranges over two orders of magnitude in cobalt concentrations (Table 6-1). In a study with seven aquatic species, the fathead minnow (*P. promelas*) had a 96-hour LC_{50} of 48 mg/L (Ewell et al. 1986). However, another study reported a 96-hour LC_{50} for the fathead minnow (Kimball 1978 as cited in WHO 2006). Carp (*Cyprinus carpio*) had a 96-hour LC_{50} of 83 mg/L, and goldfish (*Carassius auratus*) had a 96-hour LC_{50} of 67 mg/L (AQUIRE database accessed in 1996 by Sample et al. [1997]). At a cobalt concentration of 233 mg/L for up to 96 hours, *Colisa fasciatus*, a freshwater fish species, displayed erratic movements, restlessness (more movement to surface), and increased mucus production (Nath and Nishith 1988). Carbohydrate metabolism also decreased for all time intervals measured between 3 and 96 hours, with a maximum decrease in metabolism of 26% at 96 hours (Nath and Nishith 1988). Lactic acid level in blood increased (hyperlacticemia), with a 78% increase at 96 hours. In three carp species (*Catla catla, Labeo rohita, Cirrhina mrigala*), juveniles were exposed to sub-lethal concentrations in water and food (Javed 2013). Waterborne exposure concentrations ranged from 30 to 40 mg Co/L, or approximately one-third of the LC_{50}, and dietary exposure concentrations ranged from approximately 68 to 81 mg Co/kg, or approximately one-third of the dietary LD_{50} (amount of substance causing 50% lethality; Javed 2013). Details were not provided on the LC_{50} and LD_{50} selected for the study (Javed 2013). In carp treated with cobalt, a reduction in body tissue protein was also observed at 5 mg Co/L over the course of a week (Singh et al. 2016). During a 40-day exposure with the same species at 5 mg Co/L, a reduction in liver protein content was observed (Singh and Kumar 2013). Behavioral changes, such as aversion and reduced exploratory behaviors, were more pronounced in the waterborne exposure than dietary exposure; organisms in the waterborne exposure also showed a greater loss in appetite and a reduction in growth and weight (Javed 2013). The study indicated increased sensitivity between the three species, but also showed that the waterborne exposure pathway played an important role in increasing sub-lethal effects compared to the dietary exposure pathway (Javed 2013).

For marine fish species, there are limited toxicity data; however, available studies have reported adverse effects to marine fish at concentrations that ranged from 52.5 to >1,000 mg Co/L (Table 6-2).

In summary, fish species show a wide range of toxicity to cobalt. *O. mykiss* may be the most sensitive species studied to date, with a 96-hour LC_{50} of 0.1 to 1.4 mg/L (Birge et al. 1979 as cited in Diamond et al. 1992, Marr et al. 1998). In other studies, a range of adverse effects were noted such as abnormal development, including changes in morphology, such as white pigmentation, behavioral changes, delayed hatching, retarded growth, and bradycardia, with some effects occurring as low as 0.6 mg Co/L (Cai et al. 2012). Adverse effects occurred one to five orders of magnitude above levels of cobalt found in natural surface water and groundwater (ATSDR 2004b, Groschen et al. 2009).

6.4.4 Toxicity to Amphibians

Limited information is available for other aquatic vertebrates. The frog, *Rana hexadactyla,* has been studied for cobalt toxicity, and the 96-hour LC_{50} was 18 mg/L (AQUIRE database accessed 1996 by Sample et al. 1997; Table 6-1).

6.4.5 Toxicity to Aquatic Plants

Only two published articles on toxicity to aquatic plant species were identified. At concentrations of 1–10 ppm cobalt chloride, the sex ratio of the algae duckweed *Lemna acquinoclatis* was altered, with more male flowers prevalent (Wang et al. 1990 as cited in Palit et al. 1994). It should be noted that cobalt effects on the sex ratio of plants may be similar to changes in sex ratio caused by salinity-induced water stress (Freeman et al. 1980). The WHO summarized additional plant toxicity work: a 96-hour EC_{50} was observed for two aquatic plants, *Azolla pinnata* and *Spirodela polyrhiza*, at 0.1 to 0.2 mg/L (WHO 2006; Table 6-3).

6.4.6 Species Sensitivity Distribution for Aquatic Species

Figure 6-1 provides a species sensitivity distribution (SSD) for freshwater and marine aquatic species (invertebrates, fish, and amphibians) that was constructed with acute toxicity data (24-, 48-, or 96-hour LC_{50} and EC_{50} values) from Tables 6-1 and 6-2 using USEPA's SSD generator (USEPA 2016). Consistent with derivation of aquatic life water quality criteria (Stephen et al. 1985), geometric means were taken for each species where more than one acute toxicity value was available.

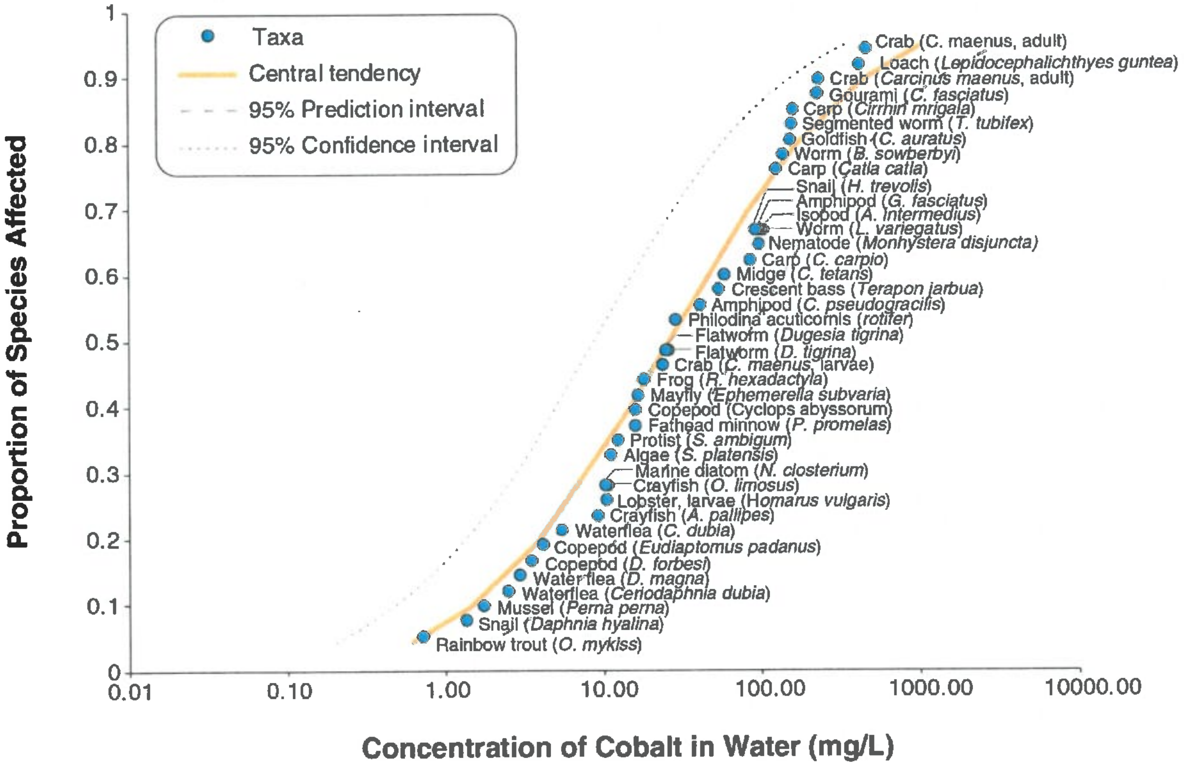


Figure 6-1
Species sensitivity distribution of acute toxicity of cobalt to aquatic organisms

As shown in Figure 6-1, acute toxicity of cobalt to aquatic species span over approximately three orders of magnitude, with aquatic invertebrate species being the most sensitive compared to fish and algae species. Cobalt forms were not taken into account for the SSD curve; however, the majority of exposures documented in Figure 6-1 and also listed in Tables 6-1 and 6-2 are for cobalt chloride.

Insufficient data were available to construct a chronic aquatic toxicity species sensitivity distribution curve that would represent a suitable comparison among numerous species.

6.5 Terrestrial Toxicity

The majority of cobalt toxicity research in terrestrial organisms has been conducted in plants. Limited research exists on the effects to soil dwelling organisms such as microorganisms and invertebrates. Summaries of plant and terrestrial invertebrate studies are provided in Table 6-3; mammalian toxicity studies are summarized in Table 6-4, and bird toxicity studies are summarized in Table 6-5.[8] For terrestrial species, standard endpoints such as growth, survival and reproduction were reviewed, and some genotoxicity studies were also reviewed.

6.5.1 Effects on Soil Microorganisms and Processes

Little information is available for cobalt effects to terrestrial microorganisms, as compared to aquatic microorganisms. A soil microbial community showed a 23% reduction in respiration when exposed to 1,362 mg Co/kg soil (Lighhart et al. 1977 as cited in Sample et al. 1997). Lichens, an organism formed by a relationship between algae and cyanobacteria, grow in areas of high cobalt concentrations such as smelters. Lichens were found to tolerate high concentrations of anthropogenic cobalt sources because of their ability to accumulate metals. Absence of lichens from industrial areas if an indicator that heavy metals have affected the photosynthesis process and decreased cellular potassium levels, altering membrane permeability (Nash 1975, Puckett 1976 both as cited in Palit et al. 1994).

Cobalt toxicity in yeast, *Saccharomyces cerevisiae*, was impacted by histidine levels (Pearce and Sherman 1999). Intracellular histidine was suggested to diminish pH-related toxicity, with cellular growth occurring between pH 5 to 6.5 in the presence of histidine, and no growth occurring in the absence of histidine (Pearce and Sherman 1999).

Another study supplemented soils with varying cobalt chloride levels (0 to 800 mg $CoCl_2$/kg soil dry matter (Zaborowska et al. 2016) and examined the biological activity, specifically microbial enzymatic activity, within the soil. Cobalt reduced, on average, enzyme activity by 25% across all cobalt concentrations, and was shown to be the strongest inhibitor of enzymatic activity when compared to tin and molybdenum at the same concentrations (Zaborowska et al. 2016). As little as 25 mg Co^{2+}/kg soil dry matter caused enzymatic inhibition by 9 to 25% (Zaborowska et al. 2016). Dehydrogenase and urease were the most sensitive to cobalt (Zaborowska et al. 2016). Research has shown that soil enzymatic activity is a good indicator for abiotic stress from accumulated heavy metals (Zaborowska et al. 2016). In particular, dehydrogenase was regarded as the most sensitive factor used to evaluate contamination effects on soil (Zaborowska et al. 2016).

In *Streptomyces fradiae* SCG-5, cobalt chloride at 50 mg/L stimulated enzymatic activity, though growth inhibition was observed at higher concentrations (>130 mg/L) (Kowser and Joseph 1979). However, the addition of magnesium, iron, zinc, or copper salts during exposure to higher

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[8] Tables 6-3, 6-4, and 6-5 are presented at the end of Section 6.5.

concentrations reversed the growth inhibition caused by cobalt chloride (Kowser and Joseph 1979).

The average concentration of cobalt in U.S. soil is 7 mg/kg, with a range between 1 and 40 mg/kg (Smith and Carson 1981 as cited in ATSDR 2004b). Adverse effects seen in soil and terrestrial microorganisms in the literature were typically observed at cobalt concentrations one to two orders of magnitude higher than concentrations found in soil.

6.5.2 Effects on Terrestrial Plants

A large quantity of information is available for cobalt toxicity to plants. Cobalt affects plants by inhibiting overall growth, and root growth, and by causing cytological, physiological, and morphological changes. These changes occurred in protein levels, catalase activity, chlorophyll content, iron content in leaves, respiration, translocation of essential elements from roots to shoots, water potential, and transpiration (Chatterjee and Chatterjee 2000, Kukier et al. 2004, Bakkaus et al. 2005, Li et al. 2009, Ali et al. 2014 all as cited in Nagajyoti et al. 2010, Satsukyevich and Lyshyevich 1975 as cited in Palit et al. 1994). The function of the chloroplast, a cellular component necessary for transferring sunlight into energy, was destroyed by cobalt through altering the membrane integrity and structure (Tripathy and Mohanty 1981 as cited in Palit et al. 1994). The changes to plants caused by cobalt ultimately affected the overall growth and viability of the plant. Plant toxicity effects are listed in Table 6-3, with examples of visual toxicity symptoms discussed in more detail below. However, it should be noted that cobalt toxicity has historically not had practical importance because soils containing cobalt contamination have also often contained high levels of nickel. Nickel phytotoxicity is dominant over any effects caused by cobalt (Pinkerton et al. 1981, Chaney 1983, Robinson et al. 1999a, Robinson et al. 1999b all as cited in Gal et al. 2008).

Cobalt has many visual toxicity effects: discolored veins, premature leaf closure, leaf fall, and reduced shoot height (Palit et al. 1994). In oats, toxicity symptoms in plants included interveinal chlorosis and discolored banding (Anderson et al. 1973). Chlorosis is the loss of color caused by a depletion in chlorophyll. Mild toxicity in oats has been observed at a soil concentration of 2 mg/kg (Anderson et al. 1973). Visual cobalt toxicity symptoms were similar to those caused by nickel—including chlorotic banding and "longitudinally striped colorless (necrotic) areas which replaced a slight mottling at the tips of the first leaves"—and occurred at a range of 75 to 225 mg/L (Anderson et al. 1973). These symptoms extended along the plant tissue so that the middle and upper parts of leaves were covered (Hewitt and Jones 1949 as cited in Anderson et al. 1973). In the white bean (*Phaseolus vulgaris* L. var. Kentwood), four day exposures to 2.3, 8, 16, 31, and 62 mg/L of cobalt sulfate in a hydroponic system showed significant reduction in root dry matter at 62 mg/L of cobalt sulfate (Rauser 1978). Leaf discoloration in the white bean was observed at three days in veins and at four days in stems at 62 mg/L of cobalt sulfate, with starch accumulation occurring after two days (Rauser 1978).

In the white bean plant (*Phaseolus vulgaris* L. var. Kentwood), a range of cobalt concentrations were tested, from 1 to 24 mg/L in a hydroponic system (Rauser 1978). Cobalt reduced root dry weight mass at concentrations over 12 mg/L, but shoot biomass was unaffected at the same concentrations (Rauser 1978). White bean leaves presented additional physiological changes (orientation/position) after two days at ~3 mg/L; leaf damage served as an early sign of metal toxicity and may be caused by a disruption in leaf water potential (Rauser 1978). Cobalt also caused a rise in starch concentration within leaves at 24 mg/L; this result suggested that cobalt interfered in carbohydrate metabolism or that cobalt altered starch translocation from leaves to other plant tissue (Rauser 1978).

Cobalt can also have positive effects on plant species. For example, cobalt reduced leaf senescence and increased drought resistance (Tarabrin and Teteneva 1979, Tosh et al. 1979 both as cited in Palit et al. 1994). Cobalt has also been shown to regulate potentially toxic compounds within plant tissue (Palit et al. 1994). Other metals may influence the effects of cobalt in plants. For example, zinc and cobalt have a competitive absorption and a mutual transport activation in wheat seedlings and pea plants (Chaudhry and Loneragan 1972, Babalakova et al. 1986 both as cited in Palit et al. 1994). As a benefit for plants but a detriment for fungus, cobalt has an antifungal property (Parashar et al. 1987 as cited in Palit et al. 1994). Cobalt is also an essential element for plants and has a role in vitamin B_{12} formation and fixation of nitrogen in *Alnus glutinosa* root nodules in leguminous plants at low concentrations (Bond and Hewitt 1962 as cited in Palit et al. 1994).

Some plant families exhibit tolerance to cobalt. Serpentine-rich soil, common in certain areas of the western United States and often high in cobalt, is an environment in which native plants may have developed cobalt tolerance (Palit et al. 1994). Tolerance mechanisms include the ability to inhibit uptake or accumulation of cobalt, an exclusion mechanism (Morrison et al. 1979 as cited in Palit et al. 1994), or a compensation mechanism by taking up increased amounts of calcium to mitigate cobalt effects (Palit et al. 1994). In barley, calcium reduced cobalt toxicity at 6 mg Co/L (Lwalaba et al. 2017). Another tolerance mechanism may be that calcium reduces cobalt exposure via competition for root binding sites for uptake (Li et al. 2009). *Agrostis gigantea*, a perennial grass, showed a wide variety of metal tolerance depending upon the clone tested, with one clone showing tolerance to copper, cobalt, and nickel, likely because of exposure to copper and nickel in its native environment (Hogan and Rauser 1979). Other clones tested had either tolerance to nickel only, or no tolerance to any of the three metals tested (Hogan and Rauser 1979).

In industrial areas, cobalt concentrations were found to range between 10.2 and 13 mg/kg dry matter in shoots of four species (Hoodaji et al. 2009). Here, the research indicated that atmospheric pollution may be a source of cobalt found in soil and plants near industrial areas (Hoodaji et al. 2009). As stated above, the average concentration of cobalt in U.S. soil is 7 mg/kg, with a range between 1 and 40 mg/kg (Smith and Carson 1981 as cited in ATSDR 2004b). Adverse effects reported for plants occur at cobalt concentrations one to two orders of magnitude lower and up to two orders of magnitude higher, compared to background cobalt concentrations found in soil. Therefore, depending on background levels and the sensitivity of specific plant species, some background levels of cobalt found in soil could cause toxicity. However, a number of bioavailability factors may inhibit the uptake of cobalt by plants. For example, humic acid concentrations of 5% in soils have been observed to decrease cobalt content in plant tissues by 2 to 3 times (Freiberg 1970 as cited in Palit et al. 1994). Therefore, the overall cobalt concentration in soil may not be predictive of the plant uptake or toxicity without measuring factors that affect the bioavailability of cobalt.

6.5.2.1 Beneficial Uses of Plants for Cobalt-Based Environmental Remediation

More information can be found in Section 8 on bioremediation and phytoremediation of cobalt. *Spirulina platensis* and *Ficus carica* show promise as bioremediators (Murali et al. 2014, Dabbagh et al. 2015). Sunflower roots are also promising for cobalt phytoremediation (Lotfy and Mostafa 2014).

6.5.3 Effects on Terrestrial Invertebrates

Terrestrial invertebrates' sensitivities to cobalt are species dependent. Reported adverse effects include changes in lifespan, development, behavior, and reproduction. For the springtail, *Folsomia candida*, the EC_{50} was 490 mg/kg soil but may be as high as 1,480 mg/kg depending on soil characteristics and cobalt availability (Lock et al. 2004 as cited in Gal et al. 2008). The potworm, *Enchytraeus albidus*, had an LC_{50} range of 0.2 to 12.4 mg/L Co^{2+} (Lock et al. 2006, Gal et al. 2008), with Ca^{2+}, Mg^{2+}, and H^+ ions effectively reducing toxicity effects.

In a multi-generational chronic toxicity test conducted using the nematode *Caenorhabditis elegans*, cobalt caused multiple biological effects and altered the lifespan, development, behavior (locomotion), reproduction, and behavioral plasticity (chemotaxis) (Wang et al. 2007), with many effects being transferred to offspring from the parental generation. Specifically, when exposed to nominal concentrations of 4.4 and 12 mg/L, the *C. elegans* lifespan was reduced by 6 to 8 days compared to the control (23-day lifespan); similar decreases in lifespan were seen in the progeny (Wang et al. 2007). Body size (mm) significantly decreased in all tested cobalt concentrations (0.2, 4.4, and 12 mg/L, nominal concentrations), with the first-generation offspring showing the same effect (Wang et al. 2007). Low reproductive speed, measured by a longer generation time, was noted for the parental generation and the first progeny generation at reduced rates of 13 to 55% and 7 to 25%, respectively, when exposed to all tested concentrations (Wang et al. 2007). Brood size produced by the parental generation was also reduced by 61% (0.2 mg/L), 68% (4.4 mg/L), and 75% (12 mg/L) (Wang et al. 2007). Furthermore, it was found that cobalt caused a transferrable stress response from parents to offspring (Wang et al. 2007).

In the earthworm *Lumbricus rubellus*, 0.03 mg Co/g soil was added as cobalt nanoparticles or cobalt ions to food (horse manure) once a week for five weeks to investigate earthworm health and cobalt impacts to the microbial communities within the soil and earthworm feces (Antisari et al. 2016). Two to three times more cobalt accumulated in earthworm tissues than in the control, and histological observations showed toxicosis also occurred (Antisari et al. 2016). In earthworms exposed to either form of cobalt, the fecal microbial community structure shifted to a higher amount of gram-negative bacteria (Antisari et al. 2016). In the soil microbial community exposed to either form of cobalt, data suggested the soil community showed stress under exposure conditions (Antisari et al. 2016).

6.5.4 Effects on Terrestrial Vertebrates

Cobalt toxicity to mammals and predatory birds occurs through ingestion of a food source that has accumulated cobalt concentrations (Gal et al. 2008). In general, cobalt toxicosis is considered rare in vertebrates and suspected cases of toxicosis are due to excessive cobalt in water, feed, or in pastures (NRC 2005). Cobalt toxicity effects span a range of symptoms in mammals: cytotoxicity, genotoxicity, oxidative DNA damage, and cellular apoptosis and necrosis with inflammation at even higher concentrations (Simonsen et al. 2012). Cobalt accumulation occurred in mammals in bone and multiple organs such as the heart, liver, pancreas, and kidney, and the skeleton (Simonsen et al. 2012). Cobalt caused myocytolysis in the myocardium in animal studies and decreased fertility and sperm production in rodent studies during cobalt exposure (FSA 2003 as cited in Gal et al. 2008).

For wildlife, a source of cobalt exposure can also come from ingestion of cobalt-contaminated water (Nagpal 2004). While vertebrates do consume plants that may contain cobalt, further biomagnification of cobalt up the food chain is not known to occur (Baudin et al. 1990, Lux et al. 1995, ATSDR 2004b both as cited in Gal et al. 2008). Predators of small mammals are typically excluded in cobalt toxicity studies; little information currently exists for these organisms (Gal et al. 2008). Rather, bird feathers, feces, and eggs have been used as biomonitoring tools to assess animal exposure in contaminated environments (Gal et al. 2008). Currently, laboratory mammals and livestock exposure studies are used in ecological risk assessments to assess cobalt toxicity to wildlife. The limited field studies and wildlife data that are available are not described here, to avoid reporting on co-occurring contaminants and toxicity effects not solely linked to cobalt. Table 6-4 and Table 6-5 present available information for terrestrial mammal and avian cobalt toxicity developed and published by USEPA in 2005 (USEPA 2005). This toxicity information was used to develop Ecological Soil Screening Levels (Eco-SSLs) for exposure to cobalt found in soil. Toxicity reference values (TRVs) for avian (7.6 mg Co/kg body weight/day) and mammalian (7.3 mg Co/kg body weight/day) organisms were developed following a comprehensive review and selection process (USEPA 2005 as cited in Gal et al. 2008).

Research using rodent models represents a large portion of toxicity studies with mammals. Oral LD_{50} values of 1,700 mg cobalt oxide/L and 180 mg cobalt chloride/L were reported for the rat (Christensen and Luginbyh 1974 as cited in Sample et al. 1997). At doses of approximately 3 to 40 mg/kg body weight, body weight and thymus size were reduced, and production of hematocrit, agglutinins, plaque forming cells, and hemoglobin were reduced (Chetty et al. 1979). Adult rats displayed testicular atrophy and cobalt accumulation in bone, blood, hair, brain, kidney, small intestine, testes, and liver (Nation et al. 1983). Work with pregnant rats during days 6 to 15 of gestation showed a decrease in maternal growth and food consumption and fetuses had stunted growth (Paternain et al. 1988). In a 98-day study, rats showed degenerative and necrotic lesions in the seminiferous tubes, polycythemia (increase blood hemoglobin concentration), cyanosis (discoloration of skin from inadequate oxygenation) and engorgement of testicular vasculature (Corrier et al. 1985). Damaged testicular tubules contained degenerated spermatocytes, calcified necrotic debris, and sloughed cells (Corrier et al. 1985). Reproductive effects were reported in mice, such as decreased sperm concentration, fertility, and testicular weight at an ingested dose of 72 mg/kg/day during a 13-day exposure (Pedigo et al. 1988 as cited in Sample et al. 1997).

In livestock, ruminant toxicity occurred at 10 mg/kg when cobalt was added to the diet (NRC 1980, Chaney 1983 both as cited in Gal et al. 2008). A beneficial effect of cobalt was shown in sheep, which had a delayed onset of ryegrass toxicity after exposure to 4 or 16 mg Co/day (Davies et al. 1995). A similar study showed a protective effect of cobalt to the liver when exposed to toxin-containing ryegrass (Davies et al. 1993).

As with mammals, reduced body weight was observed in birds exposed to cobalt (Diaz et al. 1994). Table 6-5 discusses toxicity to birds. Birds displayed effects not observed in mammals when exposed to 250–500 mg/kg in the diet (Diaz et al. 1994). Lesions occurred in smooth and skeletal muscle in ducklings (Van Vleet et al. 1981 as cited in Sample et al. 1997). Similar work showed lesions in the gizzard, pancreas, duodenum, heart, liver, and skeletal muscle following exposure to 200 or 500 mg/kg cobalt chloride in the diet (Van Vleet et al. 1981 as cited in Diaz et al. 1994). Chicks gained only 24.4 and 80% of body weight measured in the control group when exposed to 250 mg/kg and 500 mg/kg of cobalt, respectively (Diaz et al. 1994). However, negative effects such as weight loss and a decreased capacity in feeding in birds was improved by adding cysteine or methionine to the diet. At the 250 mg/kg dose, cysteine eliminated weight loss when added as 1–18% of the diet (Paulov 1971 as cited in Sample et al. 1997). In meat-type chickens, cobalt caused an increased risk of right ventricular hypertrophy (thickening of ventricle wall) in the heart and ventricle failure, and 18.3% of exposed chickens developed ascites (abdominal swelling) (Diaz et al. 1994). In another study, 2-day old Peking ducklings fed cobalt chloride had reduced growth, increased in β-globulin production, and decreased albumin production (Paulov 1971). In chicks, excess dietary iron (1,000 mg/L) reduced cobalt toxicity (Blalock and Hill 1983). Chicks exposed to 0 to 400 mg/L cobalt with the addition of iron showed no reduction in growth when compared to cobalt exposure with an iron deficient diet (10 mg/L iron). Cobalt concentrations were also reduced in chick kidneys in the iron excess diet (Blalock and Hill 1983). In general, a high iron:cobalt ratio, regardless of the cobalt concentration, caused a decrease in cobalt toxicity (Blalock and Hill 1983).

The European Food Safety Authority published a scientific opinion on the safety and efficacy of cobalt compounds used as feed additives for animal species (EFSA 2012). The use of supplemental cobalt is considered safe for animal species at 2 mg Co/kg feed, though it has been recommended to lower the feed supplement for animals to 1 mg Co/kg feed (EFSA 2012). Cobalt is considered an essential element for mammals, specifically ruminants, able to synthesize vitamin B_{12} from cobalt using their gastrointestinal microbial community (EFSA 2012). The dietary requirement for ruminants and horses for cobalt intended for vitamin B_{12} conversion is 0.1 to 0.3 mg Co/kg feed (EFSA 2012). The U.S. National Research Council set 25 mg Co/kg feed as the maximum tolerable level of cobalt for chicks, rats, cattle, and sheep and 100 mg Co/kg feed as the maximum tolerable level for swine (NRC 2005).

Given that the maximum tolerable level for agricultural animals is 12 to 50 times greater than cobalt supplemental levels found in feed (2 mg Co/kg feed), cobalt toxicity is not considered a problem for agricultural animals (EFSA 2012). However, field cases of cobalt toxicosis in calves were previously reported, likely because of their reduced rumen function (EFSA 2012). Cobalt toxicity has similar symptoms as cobalt deficiency; therefore, confirming cobalt deficiency before adding food supplementation is recommended to avoid chronic toxicity in agricultural animals (EFSA 2012). Another study administered cobalt chloride hexahydrate at 0 to 180 mg/kg feed from days 1 to 70, followed by 0 to 600 mg/kg as supplemental cobalt from days 71 to 108. Weight loss was observed at all doses; however, no additional effects such as lesions, anemia, anorexia, or toxicosis were observed (EFSA 2012), indicating that supplemental levels of cobalt in feed may have a limited role in toxicosis in agricultural animals.

In summary, cobalt has a range of effects in terrestrial organisms. In microorganisms, enzymatic activity was adversely affected at 25 mg Co^{2+}/kg soil dry matter (Zaborowska et al. 2016). Adverse effects in plants include the following: inhibition of overall growth, root growth, and cytological, physiological, and morphological changes. These changes occurred in protein expression, catalase activity, chlorophyll content, iron content in leaves, respiration, translocation of essential elements from roots to shoots, and water potential and transpiration.

Effects in plants were seen across four orders of magnitude of cobalt concentrations, from 0.2 to 225 mg/L. A similar concentration range was also responsible for adverse effects in terrestrial invertebrates. In terrestrial vertebrates, LOAELs ranged between 0.9 and 81 mg/kg/day. However, as mentioned previously, cobalt found in soil is not readily bioavailable to organisms because cobalt readily complexes with organic matter and precipitates as carbonate and hydroxides (Perez-Espinosa et al. 2005), therefore reducing the potential for toxicity. Additionally, cobalt toxicity in terrestrial environments, and therefore uptake in terrestrial species, was found to be limited by numerous soil conditions such as pH, soil aeration, temperature, organic matter content, soil moisture, water content, mineral content, and clay content (Kim et al. 2006, Gal et al. 2008, Wendling et al. 2009 as cited in Nagajyoti et al. 2010).

Table 6-3
Toxicity of cobalt to terrestrial plants and invertebrates

Organism	Cobalt[a]	Cobalt Form	Effect or Endpoint[b]	Reference
Plants				
Agrostis gigantea (bentgrass)	85 to 170 mmol/m^3	Sulfate	50% reduction in root growth	Hogan and Rauser (1979)
Azolla pinnata (fern)	0.2 mg/L	Chloride	96-hour EC_{50}	Gaur et al. (1994) as cited in Kim et al. (2006)
Helianthus annus (sunflower)	2,360 to 5,890 mg/L	Co^{2+} ion	Inhibition of lipase and peroxidase activity	Arora et al. (1987) as cited in Palit et al. (1994)
Hordeum vulgare (barley)	29.8 and 36.4 mg/kg dw	N/A	EC_{20}	TN & Associates (2000) as cited in USEPA (2005)
Lycopersicon esculentum cv. *Pusa ruby* (tomato)	29.5 mg/L	Sulfate	Visible symptoms such as chlorosis and necrosis	Gopal et al. (2003)
Medicago sativa (alfalfa)	0.60 and 13.4 mg/kg dw	N/A	EC_{20}	TN & Associates (2000) as cited in USEPA (2005)
Nicotiana tabacum (tobacco)	0.03, 0.1, and 0.5 % cobalt sulfate	Sulfate	Germination decreases	Siegel (1977) as cited in Palit et al. (1994)
Nigella damascene annual)	2,360 to 5,890 mg/L	N/A	Inhibition of lipase and peroxidase activity	Rudyk and Korchagina (1977) as cited in Palit et al. (1994)

Table 6-3 (continued)
Toxicity of cobalt to terrestrial plants and invertebrates

Organism	Cobalt[a]	Cobalt Form	Effect or Endpoint[b]	Reference
Plants (continued)				
Phaseolus vulgaris L. var. Kentwood (white bean plant)	23.6 mg/L	Sulfate	Roots brown and stunted; root biomass reduced by 66%	Rauser (1978)
	After three days at 23.6 mg/L	Sulfate	Tissue discoloration, deep red-brown color in veins	Rauser (1978)
	Two days at 3 mg/L or after 4 days at 1 mg/L	Sulfate	Chlorosis	Rauser (1978)
	24 mg/L	Sulfate	1.5x increase in starch concentration within leaves	Rauser (1978)
Pinus sylvestris (Scots pine)	0.03, 0.1, and 0.5 % cobalt sulfate	Sulfate	Germination decreases	Volkorezov (1968) as cited in Palit et al. (1994)
Raphanus sativus (radish)	15 and 45.2 mg/kg dw	N/A	EC_{20}	TN & Associates (2000) as cited in USEPA (2005)
Spirodela polyrhiza (duckweed)	0.1 mg/L	Chloride	96-hour EC_{50}	Gaur et al. (1994)
Vigna radiate (mung bean)	0.3 mg/L	N/A	Inhibition seedling growth	Liu et al. (2000)
Multiple species	31 mg/kg	Chloride	Growth, survival; EC_{20} soil screening value	Kapustka et al. (2006)
Invertebrates				
Enchytraeus albidus (annelid worm)	0.2 to 12.4 mg/L	Chloride, expressed as Co^{2+} activity	14-day LC_{50}	Lock et al. (2006)
Folsomia candida (springtail)	490 mg/kg–1,480 mg/kg soil	N/A	EC_{50}	Lock et al. (2004) as cited in Gal et al. (2008)

Note: dw - dry weight
EC_{20} - effective concentration that impacts 20% of organisms tested
EC_{50} - effective concentration that impacts 50% of organisms tested

[a] Various forms of cobalt were tested, including Co^{2+}, cobalt nitrate, cobalt sulfate, and cobalt chloride. Cobalt form was listed when information was available; N/A indicates that the cobalt form was unclear or was unstated.

[b] Reported, if available.

Table 6-4
Cobalt dose adverse effect levels for mammals

Measurement and Organism	NOAEL (mg/kg-day)	LOAEL (mg/kg-day)	Reference
Biochemical			
Cow	0.3	None	Maro et al. (1980)
Rat	19.3	28.9	Chetty et al. (1979)
	None	20.0	Kadiiska et al. (1985)
	None	118	Derr et al. (1970)
Behavioral			
Rat	1.5	None	Gershbein et al. (1983)
	None	20.0	Bourg et al. (1985)
Pig	None	7.1	Huck and Clawson (1976)
Physiological			
Rat	None	9	Haga et al. (1996)
Pathology			
Rat	2	None	Gershbein et al. (1983)
	5	10	Chetty et al. (1979)
	None	9	Haga et al. (1996)
	None	118	Derr et al. (1970)
Pig	None	19.3	Van Vleet et al. (1981)
Mouse	None	82	Seidenberg et al. (1986)
Reproductive			
Rat	5.0	20.0	Nation et al. (1983)
	6	11	Domingo et al. (1985)
	30	None	Paternain et al. (1988)
	None	20.0	Corrier et al. (1985)
	None	24.2	Mollenhauer et al. (1985)
Mouse	82	None	Seidenberg et al. (1986)
	None	10.0	Pedigo et al. (1988)
	None	14	Anderson et al. (1993)
	None	43.4	Anderson et al. (1993)
	None	56	Pedigo et al. (1988)

Table 6-4 (continued)
Cobalt dose adverse effect levels for mammals

Measurement and Organism	NOAEL (mg/kg-day)	LOAEL (mg/kg-day)	Reference
Growth			
Cow	0.30	None	Maro et al. (1980)
Rat	2	None	Gershbein et al. (1983)
	20.0	None	Bourg et al. (1985)
	None	0.9	Chetty et al. (1979)
	None	6.2	Paternain et al. (1988)
	None	122	Derr et al. (1970)
Pig	2.4	None	Huck and Clawson (1976)
	None	20.2	Van Vleet et al. (1981)
Mouse	19.0	33.0	Pedigo et al. (1988)
	None	43.4	Anderson et al. (1993)
Guinea pig	20.0	None	Mohiuddin et al. (1970)
Survival			
Pig	19.3	None	Van Vleet et al. (1981)
Mouse	82	None	Van Vleet et al. (1981), Seidenberg et al. (1986)
Guinea pig	None	20.0	Mohiuddin et al. (1970)

Source: All references, except Nation et al. (1983) and Corrier et al. (1985), are as cited in USEPA (2005).

Note: LOAEL - lowest-observed-adverse-effects level
NOAEL - no-observed-adverse-effects level

Table 6-5
Cobalt dose adverse effect levels for birds

Measurement Type and Organism	NOAEL (mg/kg-day)	LOAEL (mg/kg-day)	Reference
Biochemical			
Chicken	0.9	5	Diaz et al. (1994)
	9.3	19	Ling and Leach (1979)
Behavioral			
Chicken	13.0	29.0	Diaz et al. (1994)
	None	5	Diaz et al. (1994)
Pathology			
Chicken	13.0	29.0	Diaz et al. (1994)
	None	5	Diaz et al. (1994)
Duck	None	15.3	Van Vleet et al. (1981)
Growth			
Chicken	4	8	Hill (1979)
	4.1	8.2	Ling and Leach (1979)
	4.3	9	Hill (1974)
	25.2	None	Berg and Martinson (1972)
	None	17.0	Hill (1979)
	None	12.0	Diaz et al. (1994)
	None	22	Brown and Southern (1985)
	None	22.3	Southern and Baker (1981)
	None	30	Diaz et al. (1994)
Duck	15	148	Paulov (1971)
Survival			
Chicken	5	None	Diaz et al. (1994)
	6	12	Hill (1979)
	12.3	27	Diaz et al. (1994)
	17.0	None	Hill (1979)
	22.0	None	Ling and Leach (1979)
Duck	15.0	None	Van Vleet et al. (1981)
	None	38.0	Van Vleet et al. (1981)

Source: All references are as cited in USEPA (2005).
Note: LOAEL - lowest-observed-adverse-effects level
NOAEL - no-observed-adverse-effects level

6.6 Ecological Regulatory Criteria and Screening Guidelines

To date, USEPA has not established ecologically based regulatory standards, such as aquatic life criteria values, for cobalt. In addition, very few screening levels exist for cobalt; those available are summarized in Table 6-6. Such screening levels are derived from studies in which adverse effects (e.g., mortality, reduced growth, and reduced reproduction) were observed following exposure to a given chemical. More details regarding these guidelines are discussed below. It should be noted that screening levels and guidelines are often produced using conservative assumptions about exposure and toxicity. Therefore, exceedance of these values does not necessarily indicate environmental harm would occur but rather that additional evaluation may be warranted.

The USEPA Region III Biological Technical Advisory Group (BTAG) freshwater screening benchmark for cobalt is 0.023 mg/L (USEPA 2006), which is based on the Tier II value (Suter and Tsao 1996). The USEPA Region III BTAG Freshwater Sediment Screening Benchmark for cobalt is 50 mg/kg (USEPA 2006). The National Oceanic and Atmospheric Administration (NOAA) also provides a comprehensive document for soil screening benchmarks in various soil and water sources (Buchman 2008). When available, NOAA lists the USEPA Eco-SSLs for cobalt.

USEPA develops Eco-SSLs for a contaminant to provide adequate protection to three groups: 1) plants, 2) birds and mammals, and 3) soil invertebrates that contact soil or ingest biota living in the soil. An Eco-SSL is a concentration of the contaminant and is used in a screening step to identify contaminants of potential concern at a site (USEPA 2005). For cobalt, the Eco-SSL are 13 mg/kg for plants, 120 mg/kg for birds, and 230 mg/kg for mammals (USEPA 2005). A cobalt Eco-SSL was not developed for soil invertebrates given that insufficient information was available.

The Canadian Water Quality Guidelines (CWQG) allow for 0.05 mg/L of cobalt in irrigation waters with continuous use on soils and for livestock watering at 1 mg/L (CCREM 1987 as cited in Nagpal 2004). As of 2004, the British Columbia Ministry of Water, Land, and Air Protection (BC MWLAP) has issued 0.11 mg/L for acute and 0.004 mg/L for chronic guidelines to protect freshwater aquatic life (CCREM 1987 as cited in Nagpal 2004).

The USEPA Region III Biological Technical Advisory Group (BTAG) freshwater screening benchmark for cobalt is 0.23 mg/L (USEPA 2006), which is based on the Tier II value (Suter and Tsao 1996). A Tier II value is used to establish aquatic benchmarks when fewer data are available when compared to benchmarks set using the National Ambient Water Quality Criteria. The Toxicological Benchmarks for Screening Potential Contaminants of Concern for Aquatic Biota Report developed a Tier II secondary acute value of 1.5 mg/L and a secondary chronic value of 0.023 mg/L for cobalt (Suter and Tsao 1996). The USEPA Environmental Restoration Division (ERD) aquatic TRV for cobalt is also 0.023 mg/L in surface water (SRS 1999). NOAA (Buchman 2008) presented acute and chronic freshwater screening levels for cobalt as 1.5 and 0.003 mg/L based on the Tier II values (Suter and Tsao 1996) and EcoUpdate.[9] Additional Tier

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[9] https://www.epa.gov/risk/eco-update-bulletin-series; accessed May 30, 2018.

II benchmarks were mined from the Great Lakes Initiative database[10]; values published after 2000 were added to Table 6-6. Additional screening levels for sediments or soils are also presented in Table 6-6.

Table 6-6
Ecological screening values for cobalt

Media, Entity, and Screening Type	Cobalt Concentration	Reference
Surface Water—Freshwater		
USEPA		
Tier II chronic value	0.023 mg/L	Suter and Tsao (1996)
Tier II acute value	1.5 mg/L	Suter and Tsao (1996)
USEPA		
Region III BTAG freshwater screening benchmark	0.023 mg/L	USEPA (2006)
ERD aquatic TRV	0.023 mg/L	SRS (1999)
US Department of Energy		
Preliminary Remediation Goals	0.023 mg/L	Efroymson et al. (1997)
Michigan DEQ		
Aquatic maximum value	0.74 mg/L	MDEQ (2015)
Ohio EPA		
Tier II Acute Aquatic Value	0.22 mg/L	Ohio EPA (2006)
Chronic Aquatic Value	0.024 mg/L	Ohio EPA (2006)
British Columbia Ministry of Water, Land, and Air Protection		
Acute guidelines to protect freshwater aquatic life	0.11 mg/L	CCREM (1987) as cited in Nagpal (2004)
Chronic guidelines to protect freshwater aquatic life	0.004 mg/L	CCREM (1987) as cited in Nagpal (2004)
Netherlands National Institute of Public Health and Environmental Protection		
Maximum permissible concentration for freshwater organisms	0.003 mg/L	Van De Plassche et al. (1992)
Canadian Water Quality Guidelines (CWQG)		
Irrigation waters	0.05 mg/L	CCREM (1987) as cited in Nagpal (2004)
Livestock waters	1 mg/L	CCREM (1987) as cited in Nagpal (2004)

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[10] https://www.epa.gov/gliclearinghouse/about-great-lakes-initiative; accessed May 22, 2019.

Table 6-6 (continued)
Ecological screening values for cobalt

Media, Entity, and Screening Type	Cobalt Concentration	Reference
Surface Water—Marine		
Netherlands National Institute of Public Health and Environmental Protection		
Maximum permissible concentration for saltwater organisms	0.003 mg/L	Van De Plassche et al. (1992)
Sediment—Freshwater		
USEPA		
Region III BTAG freshwater sediment screening benchmark	50 mg/kg	USEPA (2006)
Sediment—Marine		
NOAA		
Adverse effect threshold	10 mg/kg	SQuiRT (Buchman 2008)
Soil		
USEPA		
Eco-SSL for plants	13 mg/kg	USEPA (2005)
Eco-SSL for birds	120 mg/kg	USEPA (2005)
Eco-SSL for mammals	230 mg/kg	USEPA (2005)
ASTM E1963-98 derived SSL[11]		
Eco-SSL for plants	30.6 mg/kg	Kapustka et al. (2006)
US Department of Energy		
Preliminary remediation goals for soils	20 mg/kg	Efroymson et al. (1997)
Los Alamos National Laboratory		

Note: BTAG - Biological Technical Assistance Group
CCREM - Canadian Council of Resource and Environment Ministers
CWQG - Canadian Water Quality Guidelines
ERD - Environmental Restoration Division
ESL - ecological screening level
SSL - soil screening level
Eco-SSL- ecological soil screening level
TRV - toxicity reference value

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[11] Publication describing an ecological soil screening level derived from testing funded by USEPA using methods based on ASTM E1963-98 Standard Guide for Conducting Terrestrial Plant Toxicity Tests (Kapustka et al. 2006).

7
ANALYTICAL METHODS AND INTERFERENCES

This section presents sample preparation methods (digestion) and analytical methods for cobalt in CCP-impacted matrices including aqueous matrices, such as CCP leachates and water, and solid or bulk CCP matrices, and discusses potential analytical interferences.

7.1 Laboratory Methods for Analyzing Cobalt

There are many digestion and analytical methods available for analyzing cobalt in aqueous and solid matrices. The majority of the methods involve inductively coupled plasma (ICP) analyses (i.e., ICP-atomic emission spectrometry [ICP-AES], ICP-optical emission spectrometry [ICP-OES], or ICP-mass spectrometry [ICP-MS]) and are multi-elemental, allowing for quantitation of multiple metals simultaneously. In contrast, the flame atomic absorption (FLAA) and graphite furnace atomic absorption (GFAA) methods are specific to only cobalt. In general, the ICP-MS and atomic absorption (AA) methods offer lower detection limits than the ICP-AES methods. Digestion and analytical methods appropriate for cobalt are listed in Table 7-1.

Table 7-1
Methods for laboratory analysis of cobalt

Source	Method Number	Method Name	Approximate Detection Level
Aqueous Matrices (Water and Leachates)			**µg/L**
USEPA Drinking Water Methods	200.2	Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements (sample preparation method)	NA
	200.7	Determination of Metals and Trace Elements in Water and Wastes by ICP-AES	2[a]
	200.8	Determination of Trace Elements in Water and Wastes by ICP-MS	0.09 and 0.004[a,b]
Standard Methods for the Examination of Water and Wastewater	3111B	Metals by FLAA Spectrometry	30
	3113B	Metals by Electrothermal AA Spectrometry	1
	3120B	Metals by Plasma Emission Spectroscopy	7
	3125B	Metals by ICP-MS	0.002

Table 7-1 (continued)
Methods for laboratory analysis of cobalt

Source	Method Number	Method Name	Approximate Detection Level
Aqueous Matrices (Water and Leachates) (continued)			**µg/L**
USEPA SW-846	3005A	Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy (sample preparation method)	NA
	3010A	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy (sample preparation method)	NA
	6010C	ICP-AES	4.7
	6020	ICP-MS	0.006 to 0.2
	7010	GFAA Spectrophotometry	1
ASTM	D1976-12	Standard Test Method for Elements in Water by ICP-AES	7
	D5673-96	Standard Test Method for Elements in Water by ICP-MS	0.03
USGS-NWQL	I-1241-85	Cobalt, GFAA Spectrometric (dissolved)	0.5
	I-1239-85/I-3239-85	Cobalt, FLAA Spectrometric (dissolved and total recoverable)	50
	I-4471-97	Metals in Water by ICP-OES, Whole-Water Recoverable	7
	I-4472-97	Metals in Water by ICP-MS, Whole-Water Recoverable	0.04
Solid/Bulk CCP Matrices			**mg/kg**
USEPA Drinking Water Methods	200.2	Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements (sample preparation method)	NA
	200.7	Determination of Metals and Trace Elements in Water and Wastes by ICP-AES	0.4[a]
	200.8	Determination of Trace Elements in Water and Wastes by ICP-MS	0.04[a]

Table 7-1 (continued)
Methods for laboratory analysis of cobalt

Source	Method Number	Method Name	Approximate Detection Level
Solid/Bulk CCP Matrices (continued)			**mg/kg**
USEPA SW-846	3050B	Acid Digestion of Sediments, Sludges, and Soils (sample preparation method; environmentally available digestion)	NA
	3051A	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils (microwave-assisted acid alternative to methods 200.2 and 3050B)	NA
	3052	Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices (sample preparation method; total digestion)	NA
	6010C	ICP-AES (performed on 3050B, 3051A, or 3052 digestate)	Not listed
	6020B	ICP-MS (performed on 3050B, 3051A, or 3052 digestate)	Not listed
	6200	Field Portable X-ray Fluorescence (XRF) Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment	60

Note: NA - not applicable.
USGS-NWQL - U.S. Geological Survey, National Water Quality Laboratory.

[a] Concentration is based on original matrix with allowance for sample pre-concentration during digestion.
[b] Scanning mode and selection ion monitoring mode, respectively.

7.2 Analytical Interferences

Cobalt is susceptible to matrix interferences caused by high levels of various other metals. ICP-AES analysis is susceptible to spectral, physical, chemical, and memory interferences (USEPA 1994a, 2000). Spectral interferences are probably the most common ICP-AES interferences, and are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra (USEPA 2000). Spectral interferences need to be evaluated on each individual instrument since they are dependent on instrument-specific optical resolution and operating conditions (USEPA 1994a, 2000). For example, high concentrations of metals such as barium, cadmium, chromium, iron, molybdenum, nickel, and titanium may cause spectral interferences when their wavelengths overlap with cobalt at wavelength 228.616, resulting in false positives (USEPA 1994a, 2000). High concentrations of interfering metals can also suppress the signals of other metals, causing false negatives as a result of baseline shifts (USEPA 1994a, 2000). Physical interferences also may occur when analyzing samples with high dissolved solids or acid content because of increasing sample viscosity, which affects absorption, nebulization (conversion of the liquid into an aerosol that can be transported), and sample transport (Boss and Fredeen 1997). The high dissolved solids can also cause salt to build up on the nebulizer tip, which affects how the sample is introduced into the instrument, resulting in instrument drift or instability (Gaines 2005).

ICP-MS analysis is susceptible to interferences such as isobaric elemental, isobaric molecular/doubly-charged ion, physical, and memory interferences (USEPA 1994b, 1998). For example, isobaric elemental interferences may occur because of isotopes of different elements that have similar nominal mass-to-charge ratios as the isotope of interest. Many of the isobaric interferences have been identified in the literature and can be corrected based on natural isotope abundances (USEPA 1998). Physical interferences (high solids, high viscosity) may hinder transport of the sample into the plasma by mechanisms similar to that described above for ICP-AES analysis (Gaines 2005).

Analytical method documents (ICP-AES, ICP-MS, AA, and FLAA) provide a wealth of information and guidance regarding interferences and how to detect and correct for them during sample analysis. Background correction techniques, such as inter-element corrections for spectral interferences in ICP-AES and background correction (e.g., Zeeman or Smith Hieftje corrections) in GFAA, can be used to correct and minimize interferences (USEPA 1994a, APHA 1999, USEPA 2000, Gaines 2016). Many of the ICP-MS polyatomic isobaric interferences can be eliminated by use of collision/reaction cells (CRCs). The CRC allows for more selective choice of ions by minimizing the polyatomic isobaric interferences (Agilent 2010, 2015, Gaines 2016, Prus and Zhdanyuk 2016). Internal standards can also help detect and monitor interferences encountered during ICP-MS (USEPA 1998). Physical and memory interferences may be eliminated by diluting the sample or may require longer rinse periods between samples (USEPA 1998, 2000). The specific analytical methods can be referenced for additional information regarding interferences.

8
TREATMENT AND REMEDIATION

When cobalt is a constituent of interest (COI) at a CCP site, there are a variety of remediation alternatives that can be effective. EPRI (2018b) discusses implementation and relative costs for widely used site remediation technologies, briefly discussed below in Section 8.1 in the context of cobalt treatment. Specific technologies for treating cobalt in solution are described in Section 8.2, and emerging technologies for removal of cobalt from wastewater, soil, and groundwater are reviewed in Section 8.3.

Other constituents may also be considered when choosing appropriate removal technologies for cobalt. Chemically, cobalt behaves similarly to other divalent metal cations, and treatments targeting metals such as copper and zinc can be appropriate for cobalt removal. In fact, cobalt has been used as a proxy for the group of divalent heavy metals in experimental work related to bioremediation (Krumholz et al. 2003).

8.1 Overview of Site Remediation Approaches

Standard approaches to site remediation that can be effective for the immobilization or removal of cobalt include:

- *Monitored natural attenuation (MNA):* Because the solubility and mobility of cobalt (and many other inorganics typical in coal ash leachate) are controlled by pH and the presence of manganese and iron oxide minerals (Section 3), the principal MNA mechanism for cobalt is sorption to the solid phase under chemical conditions favorable to iron and manganese oxidation (Brady et al. 2003). However, in the presence of adequate ligands, cobalt may remain mobile even under conditions favorable to sorption. Under strongly reducing conditions, cobalt can also precipitate as a metal sulfide (Krumholz et al. 2003). As with all metals undergoing redox-based immobilization, if conditions change, there is the potential for remobilization of the contaminant. An MNA protocol for CCP sites is described in EPRI (2018a).
- *Groundwater extraction (Pump and Treat):* Cobalt-affected groundwater can be collected via wells, drains, or other groundwater capture systems, followed by removal by ex situ treatment methods that employ filtration to remove cobalt associated with particulate matter, and ion exchange resins or other methods to remove dissolved cobalt (these treatment methods are discussed in the following sections). Whether or not cobalt treatment will be included in system design will be dependent on the concentration of cobalt in the extracted water and requirements of the receiving water body (e.g., NPDES discharge point, plant treatment system, public sewage treatment system). Specific removal technologies, including several experimental approaches, are discussed in Section 8.2.
- *In situ immobilization, e.g., via injections or permeable reactive barriers (PRBs):* Reagents and media for treatment of cobalt do not appear to have been applied in CCP settings; however, they have been evaluated in other applications such as for treatment of acid-mine

drainage and chemical spills. Cobalt has been shown to be removed from groundwater via multiple types of PRBs, including lime drains and compost-based sulfate-reducing barriers (Cravotta and Trahan 1999, Ludwig et al. 2005). However, field measurements in one study showed an increase in dissolved cobalt downstream of the PRB, which was interpreted to be caused by the presence of reducing conditions downgradient of the PRB having mobilized sorbed cobalt from soils (Savoie et al. 2004). Zeolites such as clinoptilolite and clays such as bentonite have been shown to exhibit cobalt-sorbing characteristics in a laboratory setting, making them candidates for future in situ injection and PRB application studies. Section 8.2.7.1 reviews these mineral sorbents, as well as other experimental sorbents including biopolymers and engineered materials.

- *Barrier walls:* Cobalt can be physically contained by barrier walls similarly to other potential constituents derived from CCPs. When gradient control pumping is included in the barrier wall design, the need to treat for cobalt will be dependent on the concentration of cobalt in the extracted water and requirements of the receiving water body (e.g., NPDES discharge point, plant treatment system, public sewage treatment system).
- *In-situ stabilization/solidification (ISS):* Leaching of cobalt and other elements can be significantly reduced by the solidification component of this technology. There is currently no information on chemical stabilization of cobalt in CCPs; however, cobalt has low solubility at high pH, which suggests that in situ chemical stabilization—which typically occurs at high pH—may be effective. EPRI's ISS technology profile indicated that chemical binding of elements such as cobalt, for which there is little laboratory and field data, could be a topic of future research (EPRI 2016).
- *Capping, excavation and removal, and liner retrofitting:* Cobalt poses no special challenges to these technologies and will be contained as effectively as other potential constituents in CCPs.

Each of these remediation technologies has been reported to be applicable to radioactive cobalt at CERCLA sites by the USEPA (USEPA 2007), and should be applicable to stable cobalt, which has similar characteristics. Additional treatment technologies and specific remedial approaches that may also be applicable for cobalt are discussed in the following sections.

8.2 Treatment Technologies for Removal of Cobalt from Solutions

In aqueous solutions, dissolved cobalt is found as Co^{2+}, a positively charged divalent ion (i.e., a divalent cation). Divalent cations are amenable to treatment by several existing and experimental processes that take advantage of cobalt's ionic charge. Existing treatment processes include precipitation and co-precipitation, ion exchange, reverse osmosis (RO) and other membrane-driven processes, and adsorption. Experimental treatment processes currently in development include a variety of sorbents derived from natural sources, such as vegetative or mineral materials, and from synthesis and assembly of engineered materials, including nanomaterials, as described below.

8.2.1 Precipitation and Co-Precipitation

Precipitation and co-precipitation are often used to remove dissolved metals from solutions in a variety of applications, including environmental remediation, industrial waste treatment, and mining/resource recovery. "Precipitation" refers to normally insoluble compounds in a solution that may precipitate out of a solution depending on pH, temperature, and/or other physicochemical parameters. "Co-precipitation" refers to normally soluble compounds in a solution that may precipitate from a solution by being incorporated into precipitating solids of less-soluble species from the same solution. Precipitation and co-precipitation rely on pH adjustment of solution to an optimal pH range by addition of acids or bases, and, depending on the solution, addition of precipitating agents in the form of metal oxides and metal (oxy) hydroxides.

Precipitation can be utilized for removal of cobalt from aqueous solutions by increasing the pH of solution with sodium hydroxide above 8.2 (Huang et al. 2004, Yuzer et al. 2008). For example, a complex multimetallic aqueous mixture containing 1.3 mg/L of cobalt, 10,016 mg/L of zinc, 1,643 mg/L of iron, 238 mg/L of manganese, and trace amounts of other metals was precipitated with 5 M sodium hydroxide solution up to pH of 9.5, resulting in cobalt reduction to <0.025 mg/L, iron to 0.14 mg/L, and manganese to 3.12 mg/L (Vocciante et al. 2017). The cobalt hydroxide precipitate formed around pH of 8 is porous and gel-like and easier to filter out compared to dense amorphous aggregates formed at pH of 10 or above (Huang et al. 2004).

Cobalt can be co-precipitated with ferrites and can be removed from a liquid solution by magnetic filters that attract the ferrite-cobalt precipitates (Becker et al. 2012). Sodium hydroxide adjustments to pH 10.5 resulted in >99% incorporation of cobalt to ferrite (Becker et al. 2012).

8.2.2 Ion Exchange

Because of its ionic form in aqueous solutions, cobalt is amenable to ion exchange by strong acid cation resins. For aqueous solutions with relatively low dissolved solids, strong acid cation resins (e.g., Dowex™ G 26 H and Lewatit® MonoPlus SP 112) are typically employed, while chelating resins (e.g., Lewatit MonoPlus TP 220 and Dowex M4195) are employed in treating acidic wastewater (Grinstead 1984, Diniz et al. 2005, Kołodyńska et al. 2014). Weakly acidic cation exchange resins (e.g., DOWEX MAC 3) may be utilized when targeting preferential removal of multivalent ions, including cobalt.

A bench-scale evaluation specifically for cobalt removal from aqueous solution using Lewatit MonoPlus SP 112, a strong acid resin, determined the optimal operating pH range to be between 4 and 8 and the maximum adsorption capacity to be 22 mg Co/g resin. The optimal resin regeneration (100% desorption of cobalt) was achieved by using either a 2 M HCl or a 2 M H_2SO_4 solution (Aşçı and Kaya 2013).

8.2.3 Activated Carbon

Adsorption is an effective technique for cobalt removal from aqueous solutions. The performance of activated carbon is presented first because of its wide use in water treatment applications. Other less common and experimental adsorbents and their ability to remove cobalt are presented separately below.

A comprehensive study for removal of cobalt (and lead and copper) was performed in 1984 using 10 commercially available activated carbons (Netzer and Hughes 1984). Of all the evaluated activated carbons, the Barney Cheney NL 1266 (hereafter referred to as NL 1266) was found to adsorb the largest percentage of cobalt (as well as lead and copper). Note that the NL 1266 is no longer produced. NL 1266 was a hardwood-derived activated carbon, the only one of its kind among the 10 tested. Other activated carbons were derived from nut shells, coal, wood, and petroleum (Netzer and Hughes 1984).

Overall, the key parameters affecting the adsorption of cobalt to activated carbon are the pH of the solution, the concentration of cobalt in a monometallic solution, and the concentration of competing ions in multimetallic solutions. The onset of cobalt adsorption occurs at pH 3 (Baes Jr. and Mesmer 1976 as cited in Netzer and Hughes 1984). After 2-hour contact time, the NL 1266 removed 99% of cobalt (initial cobalt concentration was 10 mg/L) at pH 3, while the next three best activated carbons removed between 44 and 58% of cobalt (Netzer and Hughes 1984). The NL 1266 maintained >98% removal performance up to pH 8 using the initial 10 mg/L cobalt concentration and 2-hour contact time (Netzer and Hughes 1984).

Prabakaran and Arivoli (2013) demonstrated the concentration effect of cobalt on a wood-based activated carbon, i.e., lower removal performances with increased cobalt concentration: >95% removal for cobalt concentrations in a 5 mg/L range, 85 to 92% for 10 mg/L, 78 to 86% for 15 mg/L, and 43 to 52% for 25 mg/L (Prabakaran and Arivoli 2013). Also, the removal efficiency dropped off substantially in the 8–12 pH range (Prabakaran and Arivoli 2013).

The presence of the other metals (a multimetallic solution) has a pronounced effect on cobalt adsorption. Cobalt removal was substantially reduced when copper, or copper and lead, were in solution. For example, NL 1266, the best-performing carbon, only removed 15% of cobalt when lead and copper were present at 7.6 and 10.0 mg/L, respectively, and cobalt was initially dosed at 11.4 mg/L at pH 4 (Netzer and Hughes 1984).

Cobalt also requires substantially longer contact time with activated carbon to achieve the same removal as other metals. For example, under identical conditions, cobalt requires 2 hours to achieve the same removal that was achieved for lead and copper in 30 minutes (Netzer and Hughes 1984).

Because of a large number of variables in the adsorption of cobalt by activated carbon and the complexity of the carbon surface chemistry and water chemistry, no single carbon property appears to be dominant in determining the adsorptive characteristics from aqueous solutions. Therefore, bench-scale testing can be performed to identify activated carbon products with optimal cobalt removal characteristics for application-specific conditions.

8.2.4 Reverse Osmosis

Cobalt in the Co^{2+} ionic form is effectively removed by reverse osmosis (RO). In a bench-scale study of a simulated wastewater containing several monovalent (Na, K, etc.) and divalent (Ca, Mg) ions and surfactants, the RO membranes made from polyamide (Filmtech SW 20HR-2540) exhibited rejection rates of 99.9%, while RO membranes made from cellulose acetate (Osmone 192 SR CA) rejected up to 93% of influent cobalt (Park et al. 2001). Other RO performance tests show cobalt rejection rates reaching 90% (Kong and Tian 2012). Cobalt rejection increased with increasing pH, with optimal cobalt rejection at pH 9.

It should be noted that cobalt may be present as an impurity in some metabisulfite solutions commonly used to dechlorinate RO influent or store mothballed RO membranes. Metalbisulfite is used to protect the RO membranes from irreversible chlorine attack; however, any cobalt impurities in the metabisulfite solution reportedly may degrade RO membranes, particularly those made from polyamide (Kucera 2010). RO membrane manufacturers recommend using food-grade non-cobalt-activated metabisulfite. Therefore, RO membrane cobalt resistance is a consideration as a selection criterion, particularly for systems where cobalt is a primary constituent of interest.

RO often requires pre-treatment to remove particulates and dissolved species that may cause RO membrane scaling and fouling. Pre-treatment may involve the use of additional porous membranes, including nanofiltration (NF) and ultrafiltration (UF) systems. Based on removal studies described below for NF and UF, those treatment methods may be used individually or together with RO to achieve the required cobalt removal.

8.2.5 Nanofiltration

Depending on membrane selection, NF is effective for removing cobalt from both multimetallic and monometallic solutions. Some NF membranes (e.g., Nitto Denko NTR7410, NTR7250, and NTR729HF) are capable of >95% cobalt rejection at pH>7 from monometallic solutions (Choo et al. 2002), while others (e.g., PCI Membrane System's AFC 30) are not (Bouranene et al. 2008).

Testing of PCI Membrane System's AFC 30 NF membrane showed cobalt rejection in multimetallic solutions was >95% between pH 3 and 7 (Bouranene et al. 2008). Conversely, the rejection of cobalt in a monometallic solution was substantially lower for AFC 30, from >95% rejection at pH 3 to only 50% rejection at pH 7 (Bouranene et al. 2008). This behavior is opposite of that described for activated carbon, where other metals in a multimetallic solution preferentially competed with cobalt for adsorption sites. Given these factors, NF membranes are selected based on source water quality.

8.2.6 Ultrafiltration

UF aided by addition of water-soluble polymers is a viable membrane-based technology for removing heavy metals, including cobalt. Polyethyleneimine (PEI), a water soluble polymer with strong chelating properties, complexes the cobalt ions in solution, making the complex amenable to UF. Under experimental conditions, cobalt rejection of 96.7% was achieved (from initial cobalt concentration of 65 mg/L) using a 5-kilo Dalton regenerated cellulose UF membrane at pH 6.8 (Cojocaru et al. 2009a, Cojocaru et al. 2009b).

8.2.7 Adsorption

Experimental research is making substantial progress in several approaches for removing cobalt from aqueous solutions. Major research initiatives focus on low-cost adsorption media, including biopolymers and minerals, novel engineered adsorbents, and nanomaterials. As described below, coal fly ash also appears to be a viable adsorbent for cobalt. While still in the research phase, adsorption technologies appear to be effective alternatives to the more conventional water treatment processes described above.

8.2.7.1 Biopolymers

Chitosan (CTS) and Montmorillonite (MMT) Composite (CTS-MMT)—Chitosan is the second-most abundant natural biopolymer on earth after cellulose. It is made by treating the chitin shells of shrimp and other crustaceans with sodium hydroxide or other alkalis. Chitosan is a versatile natural adsorbent with multiple molecular functional groups with affinity for heavy metal ions, including cobalt. Montmorillonite is a clay mineral with a porous structure and high surface area. A composite of MMT and CTS was developed to evaluate the synergy of two natural adsorbents (Wang et al. 2014). The CTS-MMT achieved an adsorption capacity of 150 mg of Co/g CTS-MMT, substantially higher than other mineral adsorbents (clay, kaolinite, zeolites, silica gel, etc. [0.9–38.6 mg/g]) and vegetative adsorbents (green almond hulls, lemon peel, coir pith, etc. [12–22 mg/g]). The CTS-MMT adsorption capacity was equivalent to a sugarcane-derived activated carbon (154 mg/g) (Wang et al. 2014). Virgin, unmodified chitosan adsorbs 50% of Co^{2+} from a 250 mg/L solution at pH 7 and >99% at pH 9 (Negm et al. 2015).

Other Biopolymers—Depending on location and available materials, other locally sourced biopolymers may be considered for cobalt removal from aqueous solutions. Research is being performed on a variety of biopolymers including swine bone char (Pan et al. 2009) and hydroxyapatite (Handley-Sidhu et al. 2016), coconut shells (Maruthamuthu et al. 2015), pine sawdust (Musapatika et al. 2012), and hemp fibers (Tofan et al. 2013).

8.2.7.2 Minerals

Bentonite—Bentonite is an absorbent clay consisting primarily of montmorillonite. Bentonite exhibits substantial affinity to cobalt; however, results from several studies indicate that competing ions may be synergistic or antagonistic for cobalt removal, based on initial ion concentrations (Triantafyllou et al. 1999, Al-Shahrani 2014). At initial cobalt concentration of 5 mg/L, bentonite removal efficiency ranged between 50 and 80% for pH 3.5 to 5 (Triantafyllou et al. 1999). Bentonite removed 90% of cobalt from a 25 mg Co^{2+}/L solution but only 50% from a 120 mg Co^{2+}/L solution at pH 7 (Al-Shahrani 2014). Bentonite removal efficiency increased with rising pH, resulting in >99% cobalt removal for pH 8–10 (Al-Shahrani 2014). It should be noted that bentonite is naturally alkaline, with a 5% bentonite suspension having a pH of 10.5 (Triantafyllou et al. 1999). Hence, addition of bentonite can lead to cobalt co-precipitation.

Clinoptilolite—Clinoptilolite is a natural zeolite comprised of silica and alumina. Clinoptilolite was shown to remove 65% of Co^{2+} from a 120 mg Co/L solution after 1-hour contact time at pH 6.5 (Mamba et al. 2009).

8.2.7.3 Engineered Materials

A nano-conjugate adsorbent (NCA) with high Co^{2+} selectivity was developed by anchoring organic ligands on an inorganic substrate (Awual et al. 2015). Under optimal pH of 8, NCA adsorption is relatively rapid, with 92% of Co^{2+} adsorbed after 30 minutes contact time and 99% after 40 minutes from a starting concentration of 4 mg/L Co. The used cobalt-saturated NCA can be regenerated with hydrochloric acid and put back into operation. NCA is highly selective for cobalt, with over 98% selection efficiency, compared to approximately 2% selection for sodium, potassium, lithium, mercury, barium, calcium, zinc, magnesium, lead, cadmium, nickel, and strontium in a multimetallic solution test (Awual et al. 2015). The same research team also developed a dual conjugate adsorber (DCA) that is effective for removing Co^{2+} and Cu^{2+}. This DCA exhibited higher capacity for cobalt at 205 mg Co/gram of adsorber compared to NCA's capacity of 165 mg/L (Awual et al. 2014, Awual et al. 2015). Overall, there is substantial progress being made in the development of engineered adsorption materials for cobalt.

Nanoscale Zero-Valent Iron—Nanoscale zero-valent iron (NZVI) particles supported on natural montmorillonite substrate removed >95% of Co^{2+} from an initial solution containing 50 mg/L Co (Prus and Zhdanyuk 2016). The NZVI was effective over a pH range from 4 to 8.

Graphene Oxide—Graphene oxide (GO), a carbonaceous layered material produced by oxidation of graphite, adsorbs >95% of cobalt from a 1,000 mg Co/L solution when the solution pH is between 5 and 8. The research indicates that 1 g of GO is needed per liter of solution to achieve maximum Co^{2+} adsorption (Lingamdinne et al. 2016).

Carbon Nanotubes—Carbon nanotubes have been employed extensively as a new adsorbent for the removal of several heavy metals from water, including cobalt (Wang et al. 2011, Chen et al. 2012, Gupta and Diwan 2017).

Magnetic chitosan nanoparticles—Chitosan impregnated with magnetic nanoparticles achieved a maximum cobalt removal (27.5 mg/g) over a pH range from 3 to 7 with 1 minute contact time (Chang et al. 2006 as cited in Ali 2012).

8.2.7.4 Industrial Byproducts

Coal Fly Ash—South African coal fly ash was found to be effective for removing cobalt from a synthetic petrochemical wastewater containing cobalt (50 mg/L), other heavy metals (50 mg/L total of nickel, iron, and lead), and phenol (110 mg/L). The research indicated that 40 g of coal ash per liter of wastewater was required to achieve >99% cobalt removal (Musapatika et al. 2010). Also, the experiments showed that adsorption of cobalt increased with increasing pH and decreasing adsorbent dose. Coal fly ash also exhibited high adsorption capacity for cobalt (0.4 mg/g) compared to various mineral- and vegetation-derived materials (see Chitosan and Montmorillonite Composite (CTS-MMT) section, above) (Musapatika et al. 2010). It should be noted that while coal fly ash is effective for cobalt removal, any leaching from coal ash used in treatment may result in release of other inorganic constituents.

As described here and in the prior sections, several classes of adsorbents appear to have affinity to cobalt, and some appear to have unique selectivity for cobalt as well. While all of the above-described adsorbents are still in a research and development stage for water treatment applications, many of these adsorbents appear to be potential candidates for in situ cobalt remediation. At the time of preparation of this chemical profile, EPRI was testing blast oxygen furnace slag, electric arc furnace slag, and several proprietary media to determine potential use as in situ treatments of cobalt and other inorganic constituents in groundwater.

8.2.7.5 Microbial Biosorption

Currently, biosorption of cobalt remains in the research and development stage, but both natural and modified microorganisms exhibit potential for future field bioremediation applications. Biosorption is utilization of biomaterials, such as bacteria and algae, to absorb and concentrate environmental pollutants. Biosorption is generally regarded as a cost-effective biotechnological option for treatment of high-volume and low-concentration complex wastewaters containing heavy metal(s) in the range of 1–100 mg/L (Murali et al. 2014). Ongoing experimental research on several types of organisms is focused on identifying metal-tolerant species with high accumulation capacity (i.e., “hyperaccumulators”) for specific metals or groups of metals. Biosorption of some organisms is studied on “natural” unmodified organisms found in nature, while other organisms are bioengineered to increase their accumulation capacity, tolerance, or a range of other factors to make metal uptake more efficient.

For example, in an experimental study, *E. coli* was modified through genetic engineering to enhance cobalt uptake, with a goal of using the modified organisms as a biofilter (Duprey et al. 2014). The modified *E. coli* in a 3 mg/L Co solution has accumulated 6 mg Co/g dry weight of *E. coli* after only 10 minutes of contact time (Duprey et al. 2014).

Microbiological byproducts also show promise as biosorbents, although they vary in their ability to accumulate cobalt. Exopolysaccharide (EPS), a polymer released by bacteria to protect it against harsh pH and temperature conditions, exhibits anionic properties that make it effective for sequestration of positively charged heavy metal ions. EPS derived from *Chryseomonas luteola* immobilized in calcium alginate resulted in adsorption of 55.3 mg Co/g of EPS (Gupta and Diwan 2017). Other tested biosorbents either have no affinity for cobalt (such as various *Spirulina* species) or have relatively moderate affinity of 13–15 mg/g for *Spirogyra hyalina* and *Oscillatoria angustissima*, respectively (Suresh Kumar et al. 2015).

8.3 Remediation of Cobalt-Impacted Water and Soil

Most of the available scientific and professional literature involving remediation of cobalt is not specific to cobalt alone, but focuses on other divalent metals, including mercury, cadmium, lead, zinc, and nickel, or mixtures of contaminants. However, radioactive cobalt (^{60}Co) has been specifically studied due to its presence as a contaminant associated with nuclear activities, and the results from these studies should be applicable to stable cobalt at other sites (USEPA 2007).

Based on the general behavior of cobalt and its similarity to other well-studied metals, many different approaches to metal remediation in contaminated water and soil should be applicable to cobalt. An overview of studies for aquatic phytoremediation, soil flushing, bioremediation, and phytoremediation strategies specific to cobalt removal is presented below.

8.3.1 Water

Constructed Wetlands—Constructed wetlands take advantage of physical, chemical, and biological processes for immobilizing or degrading COIs that occur in naturally occurring wetlands, in a more controlled flow-through setting. These have been used extensively for treatment of effluent from coal mines and other industries, and were studied as an alternative to treat CCP leachate at a site in Pennsylvania (Ye et al. 2001). Results from the two-year study showed immobilization of iron and manganese (the target constituents) starting in the first year, and near-complete removal of up to 0.022 mg/L cobalt beginning in year two. The cobalt was immobilized within the sediment and associated with fallen litter.

Aquatic Phytoremediation—The aquatic macrophyte *Pistia stratiotes* (water lettuce) has been extensively used for phytoremediation of several heavy metals. It is a free-floating plant with only its root system completely submerged. In experimental setting, *Pistia stratiotes* was effective in removing 70% of cobalt from an initial 5 mg/L cobalt solution after 2 days and 86% of cobalt after 4 days (Prajapati et al. 2012).

Bioremediation—Several groups of naturally occurring microbes can facilitate the immobilization of cobalt through enzymatic redox processes. Under highly reducing conditions, cobalt may be precipitated as a metal-sulfide through the activities of sulfate-reducing bacteria, and experimental work using sediments and soil columns has suggested that this is a viable strategy for immobilizing cobalt in subsurface groundwater (Krumholz et al. 2003). The cobalt sulfide is insoluble and stable under reducing conditions. Conversely, conditions that promote the bacterial oxidation of manganese can indirectly promote the oxidation of cobalt from Co^{2+} to Co^{3+} and subsequent precipitation of oxidized cobalt associated with oxide minerals (Murray et al. 2007). These oxides can also adsorb cobalt from solution, further removing it from solution (Tebo et al. 2004). Manipulation of environmental conditions to facilitate specific microbial processes through the addition of nutrients or the control of oxygen availability can promote cobalt immobilization and prevent movement with groundwater, such that the cobalt will remain within the soil or sediment.

8.3.2 Soil

Since the mode of release from CCP landfills and impoundments is via leaching to groundwater, soil contamination is not relevant to most corrective actions at CCP sites. However, selected information on soil remediation is presented here for completeness.

Electrochemically Assisted Soil Flushing—ElectroKinetic Remediation Technology (EKRT) is a type of experimental electrochemically assisted soil flushing currently being implemented on a pilot scale (Vocciante et al. 2017). EKRT deployment consists of a grid array of electrode wells across an impacted site. Effective implementation of the EKRT approach consists of an initial saturation of soil with a suitable electrolyte solution, which facilitates the mobilization of target constituent(s) under the action of an electric field through complexation phenomena. The constituents are then removed from the soil together with the electrolytic solutions extracted at the electrode/dewatering wells or as a result of electrodeposition on electrodes. EKRT requires substantial capital costs consisting of electrode well deployment and electrolyte delivery equipment and operational costs consisting of electrical energy and water consumption. Researchers are still evaluating and optimizing strategies for treatment and management of the liquid waste, including precipitation, ion exchange, and different (non EKRT) electrochemical processes (Vocciante et al. 2017). In an experimental pilot run with a multimetallic soil contamination with initial cobalt concentration of 10 mg/kg, and an electrolytic solution of KI 0.02 M in 0.02 M HNO_3, the EKRT achieved a removal rate of 2 mg Co/day/m^3 at current density of 1.6 A/m^2 and 8 mg Co/day/m^3 at 16.6 A/m^2 (Vocciante et al. 2017). A pilot-scale electrokinetic system was developed at a site in South Korea contaminated with radioactive ^{60}Co and ^{137}Cs to test the removal of these metals from soils, in an experimental system. The removal efficiency of ^{60}Co and ^{137}Cs from artificially contaminated site soil was concentration dependent, but showed ^{60}Co removal of greater than 90% within a week from soils with 245 mg/kg cobalt (Kim et al. 2010).

Phytoremediation—Plants that hyperaccumulate, or concentrate at levels higher than normally seen, cobalt and other metals within their above-ground biomass have been studied as a minimally invasive approach to removing cobalt from contaminated soils. These plants are generally endemic to locations with high soil metal concentrations, and many taxa have been found that hyperaccumulate cobalt (Baker et al. 1994). Numerous factors have to be considered to achieve successful phytoremediation, including the plant's climate tolerance, water demand, and soil conditions, among others. Additionally, the resulting biomass with the accumulated cobalt requires removal and disposal.

The cobalt accumulator *Nyssa sylvatica* and the nickel hyperaccumulators *Alyssum murale* and *Alyssum corsicum* show promise for cleanup of cobalt from soil. A study of the three plants found that they all concentrate cobalt in their shoots to levels far exceeding those in soil (Malik et al. 2000). Further, *Berkheya coddii*, a South African hyperaccumulator, was measured to have a bioaccumulation coefficient of 50x (Keeling et al. 2003). Soil amendments to increase phytoaccumulation can be investigated thoroughly before application to specific plants. For example, addition of calcium and magnesium carbonates and chelating agents (NTA, DPTA, and EDTA) to *Berkheya coddii* caused substantial reductions in the plant's ability to absorb nickel, while not impacting cobalt absorption (Robinson et al. 1999a). Conversely, adding sulfur and acid mine tailings resulted in a significant increase in both cobalt and nickel uptakes (Robinson et al. 1999a).

9

SUMMARY

- Cobalt is a transition metal with an atomic number of 27 and an average atomic mass of 58.933. Cobalt is the 33rd most abundant element in the Earth's crust. Cobalt is found most frequently associated with sulfides, oxides, and arsenic-containing compounds. In the environment, cobalt is associated with iron and manganese and is often found with nickel.
- Cobalt compounds vary greatly in solubility, but in the environment cobalt is found mainly in the solid phase. Cobalt occurs naturally in water, rocks, soil, and in small amounts in animals and plants. Cobalt is also found in higher than average concentrations in wetland soils, dark brown clay soils, and limestone soils.
- Major uses of cobalt include batteries and applications in various industries, such as aerospace, industrial equipment, and healthcare. Cobalt alloys are found in jet engines, power plants, and other locations where strength at higher temperatures is required. Historically, the characteristic blue color of cobalt made it useful as a pigment in paints and glasses.
- Natural sources of cobalt to air, soils, and waters include seawater spray, dust, forest fires, and volcanic eruptions.
- Sources of anthropogenic cobalt include wastewater from mining operations, refinery processes, chemical manufacturing, municipal discharges, process water and effluent from coal combustion and gasification processes, and discharge of wastewater from pigment manufacturing. Runoff and leaching of cobalt from soil into water bodies also occurs from both anthropogenic and natural sources.
- Naturally occurring cobalt concentrations in groundwater are typically lower than 1 μg/L.
- There is only one naturally occurring isotope of cobalt, ^{59}Co; however, radioisotopes of cobalt are created in nuclear reactors.
- Cobalt's solubility is sensitive to redox chemistry, with the oxidized form (Co^{3+}) being less soluble than the reduced form (Co^{2+})
- Adsorption of cobalt in soils and sediments primarily occurs on iron and manganese (oxy)hydroxides and clay minerals. The process is pH dependent, with very little sorption occurring at pH less than 4 SU.
- The presence of soluble organic ligands can decrease adsorption of cobalt onto soils and sediments through the formation of soluble complexes that increase the mobility of cobalt. However, the presence of humic substances bound to surfaces can increase adsorption, especially at slightly acidic pH.
- Distribution coefficients reported for cobalt vary over a wide range; mean values were 60 L/kg in sandy soil and higher in other soil types, except for in low pH environments, where a mean K_d of 12 L/kg was reported for radiocobalt. These values are indicative of an element with moderate to low mobility in groundwater.

- Cobalt occurs in leachates from coal combustion products, with concentrations in field leachates (CCP porewater and contact water) ranging from less than the analytical detection limit[12] to 3.1 mg/L. Median concentrations for porewater from different types of CCPs were typically less than 0.004 mg/L (4 µg/L).
- Human exposure to cobalt occurs primarily through dietary sources, including ingestion of the essential cobalt-containing vitamin cobalamin (vitamin B_{12}). The diet is the primary source of cobalt exposure in the general population. Most dietary cobalt is in inorganic forms, with a small percentage as vitamin B_{12}. Cobalt is essential only as a component of vitamin B_{12}, which is not produced in the human body and is required to maintain proper health.
- For non-cancer effects, the primary organ systems affected by oral exposure to cobalt include the heart, thyroid, blood, and liver, and possibly the developing fetus. These effects have been observed only with high-dose exposures.
- There are no studies available in humans or laboratory animals that adequately address carcinogenic risks from oral exposure to cobalt. Nevertheless, the NTP concluded that metallic cobalt and cobalt compounds that release metal ions are reasonably anticipated to be human carcinogens, based on inhalation studies in rodents combined with mechanistic data indicating that that in vivo exposure to cobalt ions is a key event for cobalt-induced carcinogenicity.
- USEPA has not derived an RfD for cobalt under the IRIS program. However, USEPA developed p-RfDs for both subchronic (<9 years) and chronic (>9 years) exposures based on thyroid effects.
- The ATSDR derived an intermediate-duration MRL for oral exposures to cobalt of less than 1 year at the intermediate-duration MRL of 0.01 mg/kg-day.
- FDA derived an oral PDE of 0.05 mg/day for cobalt present as an impurity in orally administered drug products, based on studies in humans.
- In 2010, the Institute of Medicine of the National Academies released updated values for DRIs. DRIs establish both adequate and upper-level intake thresholds for dietary intake of vitamins and minerals. There are no DRI values for cobalt, but the DRI RDA or AI for the cobalt-containing vitamin B_{12} ranges from 0.4 µg/day (AI; infants 0–6 months of age) to 2.8 µg/day (RDA; lactating mothers of any age).
- Based on the p-RfD, USEPA derived a tap water RSL for cobalt of 6 µg/L that is protective of residential water consumption. USEPA also derived soil RSLs for cobalt protective of residential (23 mg/kg) and industrial (350 mg/kg) exposure to soil and for leaching of cobalt from soil to groundwater and use of that water as residential drinking water (0.27 mg/kg).
- The form of cobalt present in the environment may affect its bioavailability to organisms and thus its ecological effects. Typically, cobalt found in soil is not readily bioavailable to organisms because cobalt readily complexes with organic matter and precipitates as carbonate and hydroxides.
- Cobalt has been found to bioaccumulate in aquatic organisms, but not to biomagnify.

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[12] Detection limits were variable depending on data source and were equal to or less than 0.5 mg/L.

- When cobalt is a COI at a CCP site, there are a variety of remediation alternatives that can be effective, including monitored natural attenuation, groundwater pump and treat, in situ immobilization, containment using barrier walls, in situ solidification/stabilization, or other isolation methods (capping, excavation and disposal, and liner retrofitting).
- In aqueous solutions, cobalt is found as Co^{2+}, a positively charged divalent ion (i.e., a divalent cation). Divalent cations are amenable to several existing and experimental treatment processes that take advantage of cobalt's ionic charge. For example, cobalt is effectively removed by RO, precipitation, ion exchange, adsorption, UF, and NF.
- Biologically mediated remediation of cobalt is also an option and includes bioremediation (e.g., via precipitation as a metal-sulfide through the activities of sulfate-reducing bacteria), and phytoremediation strategies (e.g., using hyperaccumulators, or constructed wetlands that combine physical, chemical, and biological removal processes).

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Appendix E

Chemical Constituents in Coal Combustion Products: Molybdenum, (EPRI, 2011)

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REPORT SUMMARY

This report provides comprehensive information on the environmental occurrence and behavior of molybdenum (Mo), with specific emphasis on Mo derived from coal combustion products (CCPs). Included are discussions of Mo's occurrence in water and soil, potential human health and ecological effects, geochemistry, occurrence in CCPs, leaching characteristics from CCPs, measurement techniques, and treatment/remediation options.

Background

Mo is a metal that naturally occurs in air, water, soil, and coal. Due to its presence in coal, coal-fired power plants produce CCPs containing Mo as a byproduct of electricity generation. Mo has the capacity to leach from coal ash when stored, and it has relatively high mobility in groundwater. Although the United States Environmental Protection Agency (US EPA) has not established a maximum contaminant level for Mo in water, nonenforceable standards have been developed for water and soil. To manage CCP sites effectively, it is important to understand available information regarding Mo's leaching potential, environmental behavior, and concentrations in various media, as well as the exposure levels associated with adverse human and ecological effects.

Objective

- To assemble and synthesize information on molybdenum with respect to the environmental occurrence, environmental behavior, and potential human health effects, with specific emphasis on the implications for CCP management

Approach

The project team performed a literature search using several databases, focusing on environmental data and human health information, in order to compile relevant information on Mo. Key secondary research sources and relevant EPRI reports and data were also collected and reviewed. Information from these sources was summarized so that key data and references could be contained and accessed easily in one report.

Results

Mo occurs at relatively low levels in soil and water. Worldwide concentrations of Mo in soils vary from about 0.1 to 10 mg/kg, with an average concentration of approximately 1–2 mg/kg. Mo concentrations are typically around 1 µg/L in fresh surface water and up to 10 µg/L in groundwater. Mo concentrations in coal are similar to concentrations in soil; Mo is enriched in CCPs, with mean concentrations around 10–20 mg/kg.

Mo is an essential element that is necessary for optimal health. Because of this, the Institute of Medicine (IOM) of the National Academy of Sciences (NAS) has established a recommended dietary allowance (RDA) for Mo of 34–45 µg/day for nonpregnant adults. Although Mo at low levels is necessary for optimal health, Mo can also be associated with adverse effects via oral exposure at higher concentrations. The most common and sensitive health effects observed are increased uric acid production and gout. Based on these endpoints and a margin of safety, the EPA has established a reference dose for Mo of 0.005 mg/kg-day. This is lower than the tolerable upper intake level developed by IOM of 0.03 mg/kg-day. The EPA also determined that the information available to evaluate Mo's carcinogenic potential in humans or animals is inadequate.

Molybdate is the principal form of Mo that is encountered in oxic waters. Molybdate has relatively high mobility in groundwater, with distribution coefficient values ranging from 0.6 to 501 L/kg. Mo adsorption on both minerals and organic matter is highly pH dependent, with peak adsorption at pH < 5 and limited adsorption above a pH of 8.

Mo is typically present in CCP leachate at concentrations from about 0.25 up to a few mg/L. The highest Mo concentrations at CCP disposal sites are associated with fly ash in landfills; the lowest are associated with flue gas desulphurization gypsum. The leaching behavior of Mo from CCPs depends on several factors, including pH, CCP composition, and the CCP weathering state.

The most viable remediation technologies for the treatment of aqueous Mo are adsorption and chemical precipitation, although biological treatment and membrane filtration are promising—but not yet proven—remediation techniques. Both *ex situ* (using conventional "pump-and-treat") and *in situ* (using permeable reactive barriers and subsurface injection) methods can be used to remediate Mo. As with most metals, pH control is an important consideration for Mo remediation.

Keywords

Coal combustion products
Ecological effects
Geochemistry
Human health
Leachate
Molybdenum

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1

INTRODUCTION

Coal combustion products (CCPs), which are produced when coal is burned to generate electricity, contain a variety of trace metals. Characterizing the potential human health, ecological, and environmental risks that can result from the management of CCPs has been an important research topic for the Electric Power Research Institute (EPRI) and federal regulatory agencies, such as the United States Environmental Protection Agency (US EPA), for several decades. These issues have gained heightened attention in recent years, and US EPA is currently proposing changes to the regulation of CCP disposal practices.

Because CCPs disposed of in landfills and surface impoundments have the potential to impact surface water, groundwater, soil, and sediment, it is important to have a complete understanding of the key constituents in CCPs. In particular, it is important to understand the leaching behavior of these constituents under different environmental conditions and the environmental levels of these constituents that may lead to potential exposures and adverse human health and ecological effects.

Molybdenum (Mo) is one of the trace elements present in CCPs. While less studied than some other trace elements in CCPs (*e.g.*, arsenic, selenium, mercury), Mo can pose an environmental concern if CCPs are managed improperly. In fact, the recent US EPA human health and ecological risk assessment of CCPs determined that Mo could pose a potential human health risk (US EPA, 2010a). While US EPA's analysis was hypothetical and relied on a considerable number of conservative assumptions and simplifications (particularly with regard to metal fate and transport), the risk assessment findings underscore the importance of understanding the potential for Mo to leach from waste management units, and whether those releases are at levels that can impact human and ecological receptors, under more realistic, real-world conditions.

This report describes the current understanding of Mo occurrence and behavior in the environment as well as in CCPs and CCP-related waste streams. Mo concentrations in various media, as well as in CCPs, are summarized in Chapter 2. In Chapters 3 and 4, the potential health and ecological impacts are discussed. Chapter 5 covers the fate and transport of Mo, and Chapter 6 addresses CCP leaching behavior specifically. Sampling and analyses related to Mo are discussed in Chapter 7. Lastly, Chapter 8 discusses treatment and remediation options.

2
OCCURRENCE, USES, AND SOURCES

2.1 Occurrence and Forms

Molybdenum (Mo) is a naturally occurring transition metal that can be found in the environment in several different valence states; the most common valence states for naturally occurring Mo are Mo (+4) and Mo (+6). In the Mo (+4) valence state, Mo is usually complexed with sulfur to form the compound molybdenite (MoS_2). Not only is molybdenite the most abundant form of Mo in ores, but it is also the most commercially valuable form. Other common Mo minerals include a lead complex called wulfenite ($PbMoO_4$) and a calcium complex called powellite ($CaMoO_4$). In soil, Mo is generally found adsorbed to iron or aluminum oxides, clay, and/or organic matter. In water, the Mo (+6) valence (molybdate ion, MoO_4^{2-}) dominates Mo aqueous speciation except under low pH (< 4) and anoxic conditions. In Chapter 5, Mo chemical and physical properties are described in more detail.

Table 2-1
Typical Molybdenum Concentrations in Environmental Media

Environmental Media		Concentration Mean/*Median*[1] (Min-Max)	Reference
US soil (mg/kg)		1.0 / *0.77* (0.08-21)	EPRI, 2010
Rocks and minerals (mg/kg)		*1.6* (< 0.05-640)	EPRI, 2010
Water (µg/L)	Surface freshwater	68[2] (4-1100)	Hem, 1985
	Groundwater	20 / *9* (4-5292)	USGS, 2011
	Drinking water supplies	*1.4* (ND[3]-68 µg/L)	WHO, 2003
Atmosphere (µg/m^3)	Rural areas	(0.0001-0.003)	Eisler, 1989
	Urban areas	(0.01-0.03)	Eisler, 1989
US coal (mg/kg)		*1.7* (0.03-280)	USGS, 1998a
CCPs (mg/kg)		19.2 / *11.2* (0.04-236)	EPRI, 2011a
CCP leachate (mg/L)		1.1 / *0.25* (< 0.1-60.8)	EPRI, 2011a

Notes: *[1] The central tendency estimate was reported as a mean or median (in italics), depending on the reference source.*

[2] Based on one-third of the data which was above the detection level (thus, this reported mean is skewed high).

[3] ND = not detected.

2.1.1 Soil

Mo is the least abundant of the biologically essential trace elements in soil. The mean concentration of Mo in the upper continental crust, from which soil is formed, is 1.4 mg/kg (Wedepohl, 1995). Typical concentrations in soil, rocks, and minerals are listed in Table 2-1 and shown in Figure 2-1. Worldwide concentrations of Mo in soils vary from about 0.1-10 mg/kg, with an average concentration of about 1-2 mg/kg (Eisler, 1989, p. 8; US EPA, 1979, p. 31). Recent surveys in the US have reported average concentrations of about 1 mg/kg and median levels of 0.77 mg/kg, with a range of 0.08-21 mg/kg (EPRI, 2010, Table 4-1). Soils in highly mineralized areas have reported Mo concentrations ranging from 27-190 ppm (US EPA, 1979, p. 32). In addition, soil irrigated with effluent from a uranium mill in Colorado was found to contain as much as 72 mg/kg Mo (Eisler, 1989).

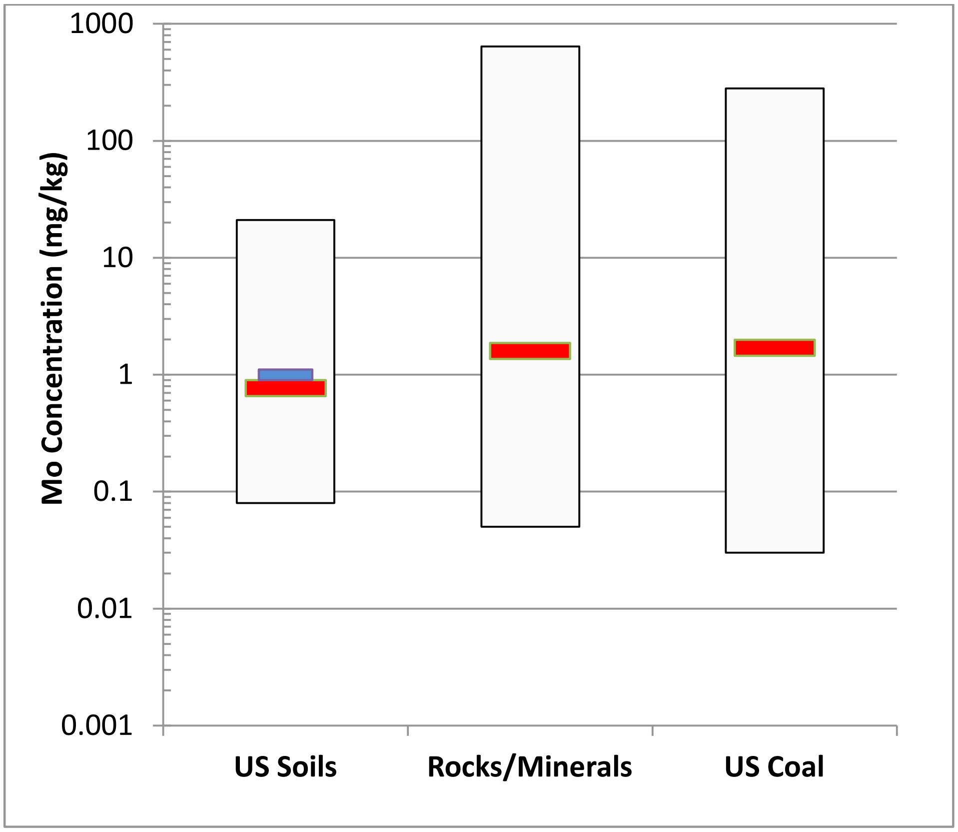

Figure 2-1
Comparison of Molybdenum Concentration in US Soils, Rocks and Minerals, and US Coal

Notes: Red lines indicate median concentration, blue lines indicate mean concentration.

Source: US Soils, Rocks and Minerals: EPRI, 2010; US Coal: USGS, 1998a.

2.1.2 Water

There is a wide range of concentrations of naturally occurring Mo in water. Typical Mo concentrations in water are listed in Table 2-1 and shown in Figure 2-2. Fresh surface waters are reported to typically contain approximately 1 µg/L Mo, while the Mo concentration in oxic seawater is reported to be approximately 10 µg/L (Ryzhenko, 2010; Bertine and Turekian, 1973).

Background concentrations of Mo in groundwater are on the order of 1-10 µg/L, but increase with alkalinity, reaching up to hundreds of µg/L (Ryzhenko, 2010).

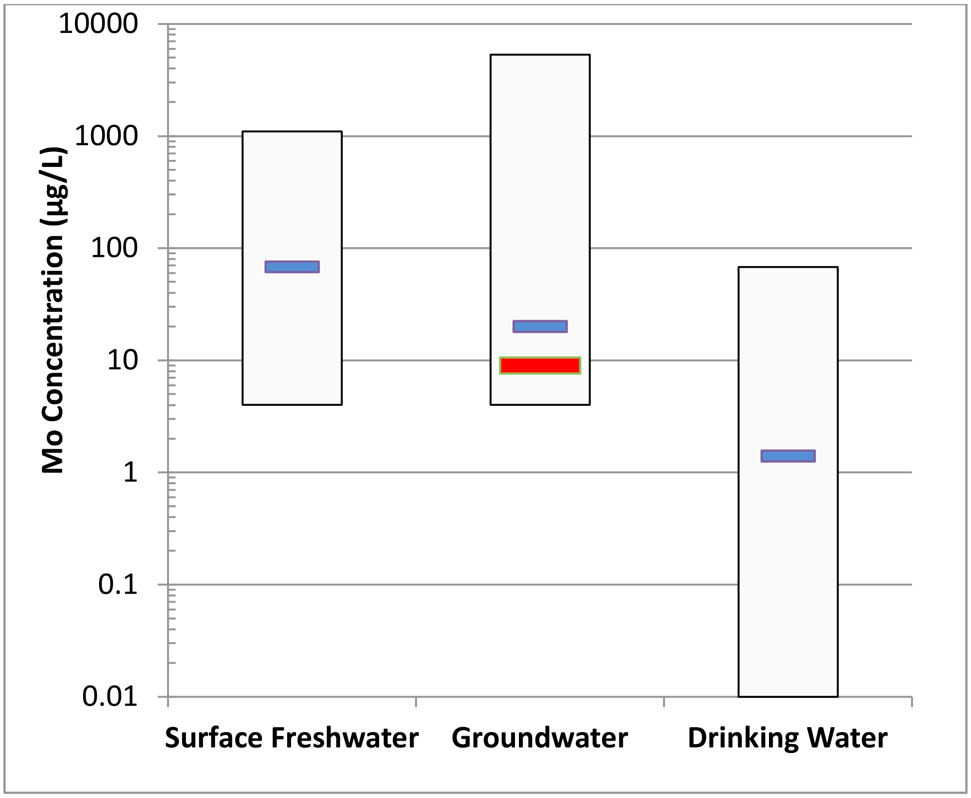

Figure 2-2
Range of Molybdenum Concentrations

Notes: *Red lines indicate median concentration, blue lines indicate mean concentration.*

Mean surface freshwater concentrations are skewed high, as they represent only the one-third of samples that were above detectable levels.

Sources: Surface freshwater: Hem, 1985; groundwater: USGS, 2011; drinking water: WHO, 2003.

As reviewed in the World Health Organization's (WHO's) background document for development of its drinking-water quality guidelines, surveys of Mo in water supplies were conducted in the US, although these data are quite dated (WHO, 2003). For example, in a 1967 survey, 32.7% of surface water samples from 15 major river basins had detectable levels of Mo, with concentrations ranging from 2-1500 µg/L and a mean for detected samples of 60 µg/L. Similarly, Koop and Kroner (1968, as cited in Hem, 1985) reported Mo concentrations for 1,500 stream water samples from 130 locations that were detectable in only one-third of the samples (detection levels ranged from 3-5 µg/L). The mean of the detectable samples was 68 µg/L (Koop and Kroner, 1968, cited in Hem, 1985).

In a survey of groundwater conducted in 1944, Mo levels ranged from non-detectable to 270 µg/L, with no mean/median reported (WHO, 2003). Treated water supplies were reported in a 1964 survey to have lower Mo concentrations, ranging from non-detectable to 68 µg/L, with a median of 1.4 µg/L (WHO, 2003). More recently, data available from the state of Minnesota reported a median concentration of Mo in groundwater monitoring wells of < 4.2 µg/L (MPCA, 1999). Data from Wisconsin showed that only 20% of the 2,700 water supply wells tested had detectable levels of Mo. The median of the detected concentrations was 4 µg/L, with 95% of wells containing < 11 µg/L. The highest level measured was 3,499 µg/L, but there was no information on whether this maximum concentration was due to a specific source of contamination (WDHSD, 2010). In North American rivers and lakes, Mo concentrations generally range from 0.4-4.1 µg/L, with > 100-10,000 µg/L in surface water associated with mining activities (Eisler, 1989).

2.1.3 Air

Environmental concentrations of Mo in air are generally low and constitute a minor pathway of exposure for the general population. Overall, surveys show that Mo concentrations in air range from 0.0001-0.003 $\mu g/m^3$ in rural environments and 0.01-0.03 $\mu g/m^3$ in urban environments in the US (Friberg *et al.*, 1975, and Friberg and Lener, 1986, as cited in Eisler, 1989). In 1961, reported atmospheric concentrations of Mo in the United Kingdom (UK) in rural areas ranged from 0.00029-0.00129 $\mu g/m^3$ and from 0.00057-0.00700 $\mu g/m^3$ in a steelworks area (as cited in Chappell and Peterson, 1977, p. 362). Air concentrations of Mo in the vicinity of Mo-related industrial activities (*i.e.*, areas of active mining) and in occupational settings (*e.g.*, smelters) can be much higher. In a 1975 study of respirable Mo in dust, concentrations as high as 6 mg/m^3 were measured during ore crushing operations. Smelting operations can also result in similarly elevated occupational exposures to Mo via air (Chappell and Peterson, 1977).

2.1.4 Diet

Mo is an essential nutrient for humans; the recommended daily intake is 45 µg/day for adult men and women (IOM, 2001). Mo is readily taken up by a variety of plants and, as a result, plants are the major source of Mo in the human diet. In particular, legumes, grain products, and nuts are rich sources of Mo in the human diet (Pennington and Jones, 1987, Tsongas *et al.*, 1980, as cited in IOM, 2001). A limited amount of information is available on typical Mo intake in the human diet. In a 1980 US study, Mo concentrations were reported to range from 120-240 µg/day, with an average intake of 180 µg/day (Tsongas *et al.*, 1980, as cited in IOM, 2001). In 1987, the US Food and Drug Administration (US FDA) reported an average Mo intake of 76 µg/day for women and 109 µg/day for men (Pennington and Jones, 1987, as cited in IOM, 2001). These intakes are well above the recommended daily intake of 45 µg/day.

2.2 Uses

The chemical properties of Mo, namely its high melting temperature (*i.e.*, it has the sixth-highest melting temperature of all elements) and high thermal and electrical conductivity in the absence of thermal expansion, make it a commonly used material in manufacturing. US mines produced 56,000 tons of Mo in 2010; this is approximately one-quarter of 2010 total world production (USGS, 2011). About 75% of mined Mo is used as a component in stainless steel, other steel products, and cast iron. Mo is also used in superalloys, electronics, spark plugs, X-ray tubes, filaments, screens, and grids for radio valves, and in the production of tungsten, glass-to-metal seals, nonferrous alloys, and pigments. Mo disulfide is also widely used as a lubricant additive for machines and engines (IMOA, 2010a; WHO, 2003).

Mo is an essential nutrient for both plants and animals and, thus, it is added to some fertilizers and even sold as a dietary supplement. As a dietary supplement, Mo is usually in the form of sodium molybdenate or ammonium molybdenate and is a common ingredient in over-the-counter multivitamins (Hendler and Rorvik, 2008). Although Mo is added to a number of supplements, Mo nutritional requirements are met in a typical US diet.

2.3 Sources

Contributions to Mo soil concentrations can result from natural weathering processes and are dependent on the types of rock in the area; black shale and phosphorite have the highest concentrations of Mo on average and are associated with soil rich in Mo (US EPA, 1979, p. 31). Anthropogenic sources of Mo in soils include several industrial sources such as mining, milling, and smelting, as well as soils amended with fly ash, liquid sludge, or other Mo-enriched media for agricultural purposes (Eisler, 1989, p. 10).

Industries also contribute to elevated Mo in surface water bodies, streams, and groundwater. In particular, the mining, milling, and smelting of Mo can contaminate nearby water bodies. Other industries that may release excess amounts of Mo into the environment (and particularly water) include uranium and copper mining and milling, shale oil production, and coal-fired power generation (US EPA, 1979). Of these other sources, in particular, uranium extraction from ore is associated with Mo contamination. This is because these two compounds are often co-located (US EPA, 1979).

Lastly, additional sources contributing to elevated Mo concentrations include industrial uses in alloys, flame retardants, catalysts, lubricants, and corrosion inhibitors (Barceloux, 1999; Buekers *et al*., 2010). Also, biosolid application as fertilizer may increase Mo soil concentrations (O'Connor *et al*., 2001).

3

HUMAN HEALTH EFFECTS

This chapter focuses on the human health effects of Mo, including its essential and beneficial properties at lower doses and the adverse effects that can occur at higher exposures, beginning with a brief discussion of the human metabolism of Mo. This discussion includes information garnered from primary and secondary literature, and it is comprehensive with respect to human studies via oral exposure. Overall, human studies involving oral exposure are limited. Thus, to provide more insight into potential Mo toxicity, supplementary information on inhalation exposure and data from animal studies are also briefly reviewed. Additionally, this chapter describes how health-based information on Mo was used to develop toxicity criteria, cancer classifications, and other regulatory limits.

3.1 Uptake, Bioavailability Metabolism, and Excretion in the Human Body

When ingested, water-soluble forms of Mo are readily absorbed by the gastrointestinal tract, while poorly soluble compounds (*e.g.*, Mo disulfide) are minimally absorbed (Barceloux, 1999; Vyskocil and Viau, 1999). Overall, several key studies conducted in humans indicate that Mo absorption ranges from 28-95% following oral intake (Alexander *et al*., 1974; Robinson *et al*., 1973; Turnlund *et al*., 1995). In these studies, however, the chemical form of ingested Mo was not described, and therefore the solubility and bioavailability of Mo in these tests cannot be ascertained; this may account for the wide range of absorptions measured. Animal studies provide information on the forms of Mo that undergo the most significant absorption. Vyskocil and Viau (1999) report that absorption of various forms of Mo (from highest to lowest) is: $MoO_4^{2-} > MoO_3 > (NH_4)_2MoO_4 > MoS_2$ (V). Recent evidence suggests that food-bound Mo has lower bioavailability than purified Mo (Novotny and Turnlund, 2006).

Once absorbed, Mo distributes rapidly to the blood and most organs (Barceloux, 1999; Vyskocil and Viau, 1999). Blood Mo concentrations have been reported to be 5 µg/L on average, but levels as high as 400 µg/L have been measured after elevated exposures (Allaway *et al*., 1968). Upon exposure, the highest concentrations of Mo have been found in the kidney and liver, with lower levels in the adrenal glands and long bones (Barceloux, 1999; Vyskocil and Viau, 1999). Mo does not bioaccumulate in tissues and, after exposure cessation, tissue concentrations decrease to steady-state levels in a relatively short timeframe in most organs (Schroeder *et al*., 1970; Barceloux, 1999; Vyskocil and Viau, 1999). The biological half-time for Mo in humans has not been studied extensively. Limited studies suggest that half-times in animals vary from a few hours to several days (Vyskocil and Viau, 1999).

Mo is excreted primarily via the urine or feces (Barceloux, 1999; Vyskocil and Viau, 1999; Turnlund *et al*., 1995). Animal and human studies show similar excretion profiles and indicate that very little Mo is excreted via the bile (Vyskocil and Viau, 1999). In addition, Mo compounds have been found to readily cross the placental barrier (Bougle *et al*., 1989; Barceloux, 1999).

3.2 Measurement in Human Biological Media

The analysis of Mo concentrations in biological media is difficult because of background contamination issues (Barceloux, 1999). Urinary concentrations are the preferred measure of exposure because this is the primary excretion route of Mo, and urinary concentrations have been found to be highly correlated with dietary intake (IOM, 2001). The National Health and Nutrition Examination Survey (NHANES III) of US residents reported a 95th percentile concentration of 168 mg Mo/L in urine (Paschal *et al*., 1998; Barceloux, 1999). Although urinary measurements may be more reliable, a recent study has demonstrated that plasma Mo can reflect differential dietary intakes of Mo and may be a useful indicator of Mo exposure under certain conditions (Turnlund and Keyes, 2004).

3.3 Health Effects

Very little information exists on the health effects of Mo in humans, both beneficial and adverse (Barceloux, 1999). As described in more detail in the following sections, some of the more informative studies on potential adverse health effects come from studies in populations living in areas rich in Mo. Occupational studies also provide some information on health impacts from inhalation exposure. Much of the toxicology information available, however, is from animal studies.

3.3.1 Essentiality and Health Benefits

Mo is essential to normal biological function. Mo serves as a co-factor for several enzymes in humans and animals that are important for metabolism of sulfur amino acid and heterocyclic compounds (IOM, 2001). For example, Mo is a co-factor for sulfite oxidase, an enzyme that catalyzes the oxidation of sulfite to sulfate and is necessary for metabolism of sulfur amino acids (IOM, 2001; Turnlund *et al*., 1995). Sulfite oxidase deficiency or absence leads to neurological symptoms and early death (IOM, 2001; Turnlund *et al*., 1995). Also, Mo is necessary for xanthine oxidase activity, which is involved in xanthine metabolism and the normal production of uric acid (IOM, 2001; Turnlund *et al*., 1995). Low dietary Mo leads to low urinary and serum uric acid concentrations and excessive xanthine excretion (IOM, 2001; Turnlund *et al*., 1995). While these biochemical changes have not been reported to be associated with clinical signs of Mo deficiency in adults, metabolic defects of molybdoenzymes in infants have been reported to result in mortality or severe neurological abnormalities (IOM, 2001). Based on potential health concerns associated with Mo deficiency, the Institute of Medicine (IOM) of the National Academy of Sciences (NAS) has developed recommended dietary allowances (RDAs). These RDAs are presented in Table 3-1. Consistent with these RDAs, recent studies of Mo metabolism have demonstrated that an intake of 43 μg/day would be sufficient to maintain plasma Mo levels at the necessary steady state in healthy adults (Novotny and Turnlund, 2006; 2007).

Table 3-1
Recommended Dietary Allowances for Molybdenum

Life Stage Group	RDA (µg/day)[1]
Infants	
0-6 mo	2 (adequate intake)
7-12 mo	3 (adequate intake)
Children	
1-3 y	17
4-8 y	22
Males/Females	
9-13 y	34
14-18 y	43
19 to > 70 y	45
Pregnancy/Lactation	
≤18 y	50
19-30 y	50
31-50 y	50

Notes: [1] RDA = Recommended Dietary Allowance; the average daily dietary nutrient intake level sufficient to meet the nutrient requirement of nearly all healthy individuals in a particular life stage and gender group.

Source: IOM (2001).

3.3.2 Antagonistic Effects

Mo metabolism is affected by the presence of copper, sulfate, and tungsten (NTP, 1997). Mo salts can alter copper absorption by forming copper molybdate or thiomolybdate compounds, two compounds that are poorly absorbed (Vyskocil and Viau, 1999; NTP, 1997). Sulfate can alleviate Mo toxicity by reducing gastrointestinal absorption; however, in copper deficient states, sulfate can aggravate symptoms in mammals (Vyskocil and Viau, 1999; NTP, 1997). Copper, sulfate, and copper-sulfate have been used to treat health effects associated with excessive Mo intake (NTP, 1997). Conversely, ammonium tetrathiomolybdate has been used to alleviate chronic copper poisoning in ruminants, and it has been suggested as a possible treatment for Wilson's disease (Haywood *et al*., 1998; Brewer, 2003). Similarly, because copper has been suggested to play a role in Alzheimer's disease, animal studies have demonstrated that treatment with tetrathiomlybdate can reduce beta amyloid levels (a hallmark of Alzheimer's disease) and memory impairment (Quinn *et al*., 2010). Tungsten and Mo also act antagonistically and, as a result, tungsten can alter both the absorption and function of Mo (De Renzo, 1962; Cohen *et al*., 1973; NTP, 1997).

3.3.3 Acute Health Effects

Available information on the acute effects following high Mo exposures, particularly in humans, is limited. Momcilovic (1999) reported an incident of Mo poisoning from a nutritional supplement. A cumulative dose of 13.5 mg Mo (300-800 µg Mo/day[1]) was consumed over 18 days and resulted in a number of neurological effects that were persistent a year after exposure (Momcilovic, 1999). No information on lethal doses in humans is available. Lethal doses for animals range from 3-333 mg/kg-day, depending on the exposure period and animal species (Vyskocil and Viau, 1999).

3.3.4 Chronic Non-Cancer Health Effects

3.3.4.1 Oral Exposures

Four studies have evaluated the potential health effects from chronic Mo exposure in humans (Koval'skiy *et al*., 1961; Deosthale and Gopalan, 1974; US EPA, 1979; Meeker *et al*, 2010). In a cross-sectional epidemiology study in Armenia, Koval'skiy *et al*. (1961) correlated the dietary intake of Mo with serum uric acid levels and several other biochemical endpoints with a gout-like sickness affecting the adult population in two settlements. This region had a naturally high Mo content in the soil and plants (38 and 190 times that of the control area) and a low content of copper. Dietary Mo intake was estimated at doses of 0.14-0.21 mg/kg-day for a 70-kg adult. Medical exams performed in highly exposed areas indicated that 57 adults (31% of the adult population) from one settlement and 14 adults (17.9% of the adult population) from the other had gout-like symptoms, compared with 1-4% on average for the area. This condition was characterized by pain, swelling, inflammation and deformities of the joints, and, in all cases, an increase in the uric acid content of the blood (Koval'skiy *et al*., 1961). In a number of cases (exact number not reported), this condition was accompanied by illnesses of the gastrointestinal tract, liver, and kidneys (US EPA, 2003). Both serum Mo and serum xanthine oxidase activity were positively correlated with serum uric acid levels. Increasing urinary excretion of copper was inversely correlated to increasing serum levels of Mo.

Ingestion of Mo in drinking water was investigated in two Colorado cities over a two-year period (US EPA, 1979). Urinary levels of Mo and copper and serum levels of ceruloplasmin (the major copper-carrying protein in the blood) and uric acid were examined. The Mo intake was ≥ 7 µg/kg-day (≥ 0.0001 mg/kg-day) in the exposed group. Higher daily urinary Mo was associated with higher Mo intake; however, no adverse biochemical or systemic effects were noted (US EPA, 1979).

A recent cross-sectional epidemiology study explored the associations between exposure to metals and testosterone levels in 219 men recruited from infertility clinics (Meeker *et al*., 2008, 2010). The authors reported a significant association ($p = 0.001$) between reduced testosterone levels and increased blood Mo levels (70th and 85th percentile blood Mo concentrations were 1.0 and 1.5 µg/L, respectively). The authors and reviewers of the study, however, noted several study limitations (*e.g.*, small sample size, uncertain blood Mo detection limits). Thus, further research is needed to confirm this association and its clinical relevance (Meeker *et al*., 2008, 2010; Sorahan and Sullivan, 2009).

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[1] For a 70-kg adult, this translates to a dose of 0.004-0.01 mg/kg-day.

Lastly, in a controlled experiment, Deosthale and Gopalan (1974) examined the effects of dietary Mo exposure on uric acid and copper excretion in four adult men given diets based on sorghum varieties differing widely in Mo content for 10 days. The urinary excretion of uric acid was unaltered at Mo intake levels up to 1,540 µg/day (approximately 0.022 mg/kg-day), but copper excretion increased with increasing Mo dose (Deosthale and Gopalan, 1974; Vyskocil and Viau, 1999).

3.3.4.2 Inhalation Studies

In occupational settings, there have been reports that inhalation of Mo (*i.e.*, metallic Mo dusts or Mo-trioxide, MoO_3) may adversely affect health. Pneumoconiosis (restrictive lung disease) has been reported following inhalation exposure (Vyskocil and Viau, 1999). For example, in a study of 19 molybdenum wire workers exposed for four to five years to Mo in dust at concentrations ranging from 1-19 mg Mo/m^3, three workers showed signs of pneumoconiosis (Mogilevskaya, 1967; Vyskocil and Viau, 1999). In a plant producing Mo-trioxide, an eight-hour exposure to Mo-trioxide dusts was measured at 9.47 mg/m^3 (Walravens *et al*., 1979). Mean serum uric acid levels of 25 male workers were significantly (1.18-fold) higher, and mean serum ceruloplasmin (copper transport protein) levels were also significantly (1.65-fold) higher than those of unexposed workers (Walravens *et al.*, 1979; NTP, 1997). In this study, the authors reported no evidence of a gout-like syndrome (Walravens *et al.*, 1979; NTP, 1997). Gout and multiple sclerosis, however, have been reported in several case studies of humans exposed to high Mo concentrations in air (Pitt, 1976; Walravens *et al.*, 1979; US EPA, 1975; Selden *et al*., 2005). For example, complaints of pain in joints (arthralgia) were reported in 37 copper-molybdenum plant workers with elevated serum uric acid levels (US EPA, 1975; NTP, 1997). Detailed methods and results are not available for these studies; thus, evaluating the validity of results is not possible (US EPA, 1975).

3.3.4.3 Animal Studies

Overviews of animal toxicity studies of Mo via oral exposure are available from several different sources (NTP, 1997; Vyskocil and Viau, 1999). Based on these publications, the health effects and associated levels of exposure are summarized in Table 3-2. Briefly, acute symptoms of Mo toxicity include diarrhea, coma, and death from cardiac failure (NTP, 1997). Sub-chronic or chronic exposures mainly lead to growth retardation, anemia, diarrhea, and changes to the thyroid, kidney, and liver (NTP, 1997; Vyskocil and Viau, 1999). Mo also was found to disturb bone metabolism, giving rise to lameness, bone joint abnormalities, osteoporosis, and high serum phosphatase levels (NTP, 1997; Vyskocil and Viau, 1999). Elevated Mo exposure also was found to adversely affect reproduction (*e.g.*, decreased gestation weight and offspring survival) (Vyskocil and Viau, 1999). The lowest observed adverse effect level (LOAEL) of Mo for the chronic symptoms described above range from 1.5-80 mg/kg-day and varied by animal species (Table 3-2).

Table 3-2
Lowest and No Observed Effect Concentrations from Animal Studies

Species	Effect	Exposure Duration (Form of Mo)	LOAEL (mg/kg-day)[1]	NOAEL (mg/kg-day)[1]	Source
Rat	Prolonged estrus cycle, decreased gestation weight, effect on embryogenesis	9 weeks (Na_2MoO_4)	16	0.9	Fungwe *et al*., 1990
Rat	Growth depression	13 weeks ($NaMoO_4$)	2	-	Jeter and Davis, 1954
Rat	Bone deformities	6 weeks (Na_2MoO_4)	7.5	-	Miller *et al*. 1956
Rat	Growth depression	13 weeks ($NaMoO_4$)	8	2	Jeter and Davis, 1954
Rat	Infertility	13 weeks ($NaMoO_4$)	8	2	Jeter and Davis, 1954
Rat	Anemia	5 weeks (Na_2MoO_4)	50	-	Ostrom *et al*., 1961
Rat	Diarrhea	5-8 weeks (Na_2MoO_4)	50	-	Cox *et al*., 1960
Rat	Renal failure	8 weeks ($[NH_4]_6\ Mo_70_{24}$)	80	40	Bompart *et al*., 1990
Rat	Male reproductive toxicity	2 months (tetrathiomolybdate-TTM)	12 (TTM) 4.4 (Mo)	4 (TTM) 1.5 (Mo)	Lyubimov *et al*., 2004
Rabbit	Reduced growth and histological changes in kidney and liver	6 months (MoO_2SO_4)	5	0.5	Asmanagulyan, 1965
Rabbit	Reduced growth, skeletal abnormalities, anemia	4 months (Na_2MoO_4)	23	46	Arrington and Davis, 1953
Rabbit	Skeletal abnormalities, anemia	5 weeks (Na_2MoO_4)	25	-	McCarter *et al*., 1962
Rabbit	Thyroidal injury	1 month (Na_2MoO_4)	66	-	Widjajakusuma *et al*., 1973
Rabbit	Testes histology and clinical chemistry	14 days ($[NH_4]_6\ Mo_70_{24}$)	1.2	-	Bersenyi *et al*., 2008
Guinea pig	Reduced growth	8 weeks (Na_2MoO_4)	75	-	Arthur, 1965
Mouse	Failure to breed, deaths of offspring and litters	3 generations (Molybdate salt)	1.5	-	Schroeder and Mitchener, 1971

Notes: *[1] NOAEL and LOAEL doses are based on molybdenum ion.*
LOAEL = lowest observed adverse effect level; NOAEL = no observed adverse effect level.
Adapted from Vyskocil and Viau (1999).

3.3.5 Cancer Health Effects

Information available to assess the carcinogenicity of Mo compounds is inconclusive (US EPA, 2003). Only a few human and animal studies have evaluated an association between Mo exposure and cancer incidence, and those have reported mixed results. Furthermore, data suggest that Mo deficiency may be associated with an increase in cancer incidence. A summary of cancer studies is provided below.

3.3.5.1 Human Studies

Studies regarding the carcinogenicity of Mo compounds in humans are limited, and these studies suffer from poor experimental designs and conflicting results (NTP, 1997). Robinson and Clifford (1968) found no correlation between an above-normal incidence of nasopharyngeal carcinoma and the concentrations of Mo in food crops and soil in the high-altitude areas of Kenya. In a case-control study, the relationship between lung cancer and Mo occupational exposure was investigated by questionnaires administered to male lung cancer patients (Droste *et al.*, 1999). The authors reported an association between occupational exposure (primarily inhalation) to Mo and lung cancer (Droste *et al.*, 1999). The authors commented that their study was the first to report a significant association, but they also noted methodological problems (*e.g.*, measures of exposure, job descriptions, and self assessments) that limited the reliability of the results. In contrast, low intake (deficiency) of Mo has been attributed to high incidences of esophageal cancer in South Africa among the Bantu of Transkei (Burrell *et al.*, 1966) and in China (Luo *et al.*, 1983) and Russia (Nemenko *et al.*, 1976, as cited in NTP, 1997).

3.3.5.2 Animal Studies

Carcinogenicity studies in animals are also limited. No long-term bioassays to test Mo carcinogenicity via the oral route were identified. Two-year inhalation studies (6 hours/day, 5 days/week, 105 weeks) were conducted with rats and mice exposed to 0, 10, 30, or 100 mg/m^3 Mo-trioxide (NTP, 1997). Based on these studies, the National Toxicology Program (NTP) concluded that the evidence in rats was equivocal or negative, while in mice there was “some evidence of carcinogenicity…based on increased incidences of alveolar/bronchiolar adenoma and adenoma or carcinoma” (NTP, 1997).

Mo (III) trioxide was also found to be weakly carcinogenic in a short-term lung adenoma assay with mice (Stoner *et al.*, 1976). In this study, three groups of 20 mice were intraperitoneally injected with 50, 144, or 250 mg Mo (III) trioxide per kg body weight in normal saline three times per week for a total of 19 injections. The total doses received by each group were 950, 2,735, and 4,750 mg/kg. After 30 weeks, the frequency of lung tumors in the 4,750 mg/kg group was significantly higher than that in the controls, while tumor incidences in the two lower dose groups were similar to the controls (Stoner *et al.*, 1976).

Conversely, sodium molybdate was reported to reduce the incidence of tumors in rodents induced by nitroso compounds (NTP, 1997). Genotoxicity assays with bacterial strains and chromosomal aberration studies with Chinese hamster ovary cells generally have been negative for Mo compounds (NTP, 1997).

Overall, there is no evidence that Mo is carcinogenic via the oral route of exposure and, while there is some evidence of carcinogenicity in animals via inhalation, the human evidence is weak.

US EPA has concluded that the carcinogenicity of Mo has not been evaluated adequately in humans or animals (US EPA, 2003) and, therefore, it has not made a determination as to the carcinogenic potential of Mo.

3.4 Human Health Risk Assessment

Non-cancer and cancer toxicity information is used to develop chemical-specific toxicity factors that are used to quantitatively evaluate human health risks. Reference doses (RfDs) are used to assess non-cancer risks, and cancer slope factors (CSFs) are generally used to evaluate cancer risks. All US EPA-derived toxicity factors are published on the Integrated Risk Information System (IRIS). The IRIS database serves as an important resource because it allows scientists to standardize the risk assessment process by using a common set of toxicity criteria.

3.4.1 Evaluation of Non-Cancer Risks

As defined by US EPA, an RfD is intended to represent a level of daily human exposure, experienced over the course of a lifetime, that is likely to be without an appreciable risk of deleterious effects, even for susceptible members of the population (US EPA, 1993). For non-cancer risks, a threshold for chemical toxicity is typically assumed (*i.e.*, there is a dose below which adverse health effects are not observed). To derive an RfD, the chemical-specific threshold dose must be defined. This is accomplished by identification of a LOAEL and/or a no observed adverse effect level (NOAEL), from either human epidemiology or laboratory animal toxicology studies. After determining the NOAEL or LOAEL, this dose is divided by uncertainty factors (UFs) to account for potential uncertainties (including inter- and intra-species differences in sensitivity, insufficient study durations, use of a LOAEL instead of a NOAEL, and data deficiencies) to arrive at a final RfD. The application of UFs in the derivation of the RfD helps ensure that the RfD is health-protective. It should be noted that, according to US EPA, “it should not be categorically concluded that all doses below the RfD are ‘acceptable’ (or will be risk-free) and that all doses in excess of the RfD are ‘unacceptable’ (or will result in adverse effects)” (US EPA, 1993).

3.4.2 Derivation of the US EPA Oral Reference Dose

US EPA (2003) derived an oral RfD for Mo in 1993 based on the results of a six-year to lifetime dietary exposure study (Koval’skiy *et al*., 1961). This study, which was described in more detail in Section 3.3.4.1, demonstrated that dietary intake of Mo was correlated with serum uric acid levels, several biochemical endpoints, and a gout-like sickness in an adult population in two Armenian settlements. Estimates of daily intake in the Mo-rich area for an average adult were 10-15 mg, corresponding to doses of 0.14-0.21 mg/kg-day for a 70-kg adult. In comparison, the control-area adults ingested 1-2 mg of Mo daily (0.014-0.029 mg/kg-day). Further analysis was conducted to correlate uric acid levels to Mo intake. It was estimated that a Mo intake of 0.14 mg/kg-day may result in serum uric acid levels above the range typically measured in adult populations (US EPA, 2003).

The Mo intake of 0.14 mg/kg-day was selected by US EPA (2003) as the critical value (*i.e.*, LOAEL) for use in developing an RfD. A final RfD of 0.005 mg/kg-day was derived by applying

UFs to the LOAEL. A UF of 3 was applied to protect sensitive human populations,[2] and a factor of 10 was applied for the use of a LOAEL, rather than a NOAEL, from a long-term study in a human population. US EPA (2003) indicated that the level of confidence in the oral RfD for Mo is "medium." According to IRIS, this confidence rating was based on the use of a study from a relatively large population and the fact that the proposed RfD satisfies Mo nutrient requirements for all healthy members of the population (US EPA, 2003).

3.4.3 Derivation of the Tolerable Upper Intake Levels

Although not used as commonly in risk assessment, IOM (2001) has recently developed a Tolerable Upper Intake Level (TUL) for Mo (Table 3-3). Under the IOM definition, the TUL is the highest level of a daily nutrient intake that is likely to pose no risk of adverse health effects for almost all individuals. IOM (2001) examined the available data and identified a NOAEL of 0.9 mg/kg-day[3] for Mo based on reproductive effects identified in rats and mice reported by Fungwe *et al*. (1990). This value was divided by a UF of 30 to obtain a safe dose level of 0.03 mg/kg-day for humans. Lastly, TULs were estimated for the various age groups by multiplying the safe dose of 0.03 mg/kg-day by average body weights, as shown in Table 3-3 (IOM, 2001). For example, 0.03 mg/kg-day multiplied by 68.5 kg (average adult male body weight) resulted in a TUL of 2,000 μg/day (rounded).

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[2] US EPA determined a full UF of 10 was not necessary for the protection of sensitive human populations because the study was conducted in a relatively large human population (US EPA, 2003).

[3] The US EPA RfD and IOM TUL are different due to the selection of different critical studies for developing the threshold level. The US EPA RfD is based on a study in humans, while the IUM TUL is based on an animal study. In addition, the RfD and TUL values were developed using differing UFs and assumptions.

Table 3-3
Tolerable Upper Intake Levels Established by the IOM

Life Stage Group	TUL (µg/day)
Infants 0-6 mo 7-12 mo	not established
Children	
1-3 y	300
4-8 y	600
Males/Females	
9-13 y	1,100
14-18 y	1,700
19 to > 70 y	2,000
Pregnancy/Lactation	
≤18 y	1,700
19-30 y	2,000
31-50 y	2,000

3.4.4 Evaluation of Cancer Risks

As discussed above, studies on the cancer effects associated with Mo exposure are limited and US EPA has concluded that this information is not adequate to evaluate Mo's carcinogenic potential in humans or animals (US EPA, 2003). Therefore, US EPA (2003) has not derived a CSF for Mo. In addition, Mo has not been evaluated formally by the International Agency for Research on Cancer (IARC) for its carcinogenic potential.

3.4.5 Regulations and Screening Criteria in Tap Water and Soils

Regulatory standards and criteria for environmental media are derived using toxicity criteria (RfDs and CSFs), human exposure assumptions, and other information. For drinking water, US EPA establishes Maximum Contaminant Level Goals (MCLGs) and Maximum Contaminant Levels (MCLs). An MCLG is a non-enforceable regulatory standard that, according to US EPA, reflects "the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety" (US EPA, 2009b). An MCL is set as close to the MCLG as possible while considering factors such as feasibility and cost benefit. US EPA has not established an MCLG or MCL for Mo; however, a health advisory and drinking water equivalent level (DWEL) has been published by US EPA (2009b) (See Table 3-4). A health advisory is an "estimate of acceptable drinking water levels for a chemical substance based on health effects information" and "is not a legally enforceable Federal standard, but serves as technical guidance to assist Federal, State, and local officials." A DWEL is "lifetime exposure concentration protective of adverse, non-cancer health effects, which assumes that all of the exposure to a contaminant is from drinking water" and is not an enforceable standard (US EPA, 2009b).

US EPA Regions III, VI, and IX have harmonized risk-based screening levels for use at Superfund Sites (US EPA, 2010b). These screening criteria are called regional screening levels (RSLs). RSLs are risk-based concentrations derived from standardized equations combining exposure information assumptions with US EPA toxicity data. RSLs are considered by US EPA to be protective for humans (including sensitive groups) over a lifetime. The RSLs are used for site "screening" and as initial cleanup goals, if applicable (US EPA, 2010b). RSLs are not *de facto* cleanup standards and should not be applied as such (US EPA, 2010b). The role of the RSL in site "screening" is to help identify areas, contaminants, and conditions that require further federal attention at a particular site. Chemical concentrations above the RSL would not automatically designate a site as "dirty" or trigger a response action; however, exceeding an RSL suggests that further evaluation of the potential risks by site contaminants is appropriate (US EPA, 2010b). RSLs for Mo in tap water and soils are presented in Table 3-4.

In addition to US EPA assessments, WHO has established a guideline for Mo in drinking water. As shown in Table 3-4, the WHO guideline is 0.07 mg/L. This value was derived based on epidemiological studies conducted in Colorado (see Section 3.3.4.1) (WHO, 2003).

Table 3-4
Regulatory Screening Criteria for Molybdenum in Soil, Water, and Air

Source	Media	Criteria Concentration
US EPA Health Advisory[1]	Drinking Water	0.08 mg/L
US EPA DWEL[2]	Drinking Water	0.2 mg/L
WHO Drinking Water Guideline	Drinking Water	0.07 mg/L
US EPA RSL[3]	Tap Water	0.18 mg/L
	Residential Soil	390 mg/kg
	Industrial Soil	5,100 mg/kg
	Soil Screening Value Protective of Groundwater	3.7 mg/kg

Notes: *[1] Health advisory for 1- or 10-day exposure for a 10-kg child.*

[2] DWEL = drinking water equivalent level; DWEL is estimated using the RfD (0.005 mg/kg-day) and assumes a 2 Liter/day drinking water intake and a 70 kg body weight.

[3] RSL = regional screening level.

3.5 Risk Assessment of Molybdenum in Coal Combustion Products

A recent draft US EPA risk assessment found that CCPs stored in unlined landfills pose a potential Mo health risk (US EPA, 2010a). US EPA estimated that Mo leaching of coal combustion waste (CCW) from unlined waste management units to groundwater could reach levels that, if consumed by humans, would exceed the RfD by 8-fold (US EPA, 2010a). This exceedance was for a maximally exposed individual (90th percentile) only; the RfD was not exceeded for an individual when modeling a more typical exposure scenario. It should be noted that the calculated risk exceedance reflects several health protective assumptions with regard to the leaching model, exposure assumptions, and toxicity criteria. The fate and transport of Mo and leaching behavior are discussed in more detail in Chapters 5 and 6.

An earlier risk assessment conducted by US EPA on the storage of CCPs focusing on non-groundwater pathways (*i.e.*, residential exposures from soil ingestion, inhalation, gardening, beef and dairy consumption, and erosion and overland transport) did not identify an Mo-related risks (US EPA, 1998).

3.6 Human Health Risk Assessment Toolbox

Government websites and reports provide useful information on risk assessment. The list below presents some of the key human health risk assessment resources. Some resources are specific to Mo, while others present information on a wider range of environmental contaminants.

3.6.1 Molybdenum-Specific Resources

- US EPA's IRIS file for Mo (CASRN 7439-98-7) (US EPA, 2003) Website: http://www.epa.gov/iris/subst/0425.htm
- International Molybdenum Association's (IMOA) Database of Molybdenum in Human Health and the Environment Website: http://www.imoa.info/HSE/environmental_data/database.html
- Molybdenum in Drinking-water: Background Document for Development of WHO Guidelines for Drinking-water Quality http://www.who.int/water_sanitation_health/dwq/chemicals/molybdenum.pdf

3.6.2 General Resources

- US EPA's RSL Summary Table: http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/Generic_Tables/pdf/master_sl_table_run_MAY2010.pdf

4
ECOLOGICAL EFFECTS

As discussed in Chapter 3, Mo is an essential nutrient for microorganisms, plants, and animals, but adverse effects can result from exposures in excess of nutritional requirements. Both natural and anthropogenic sources can result in elevated levels of Mo in soil and water, two of the critical exposure routes for ecological receptors (*e.g.*, plants and animals). In this chapter, Mo bioavailability, uptake, bioaccumulation, and toxicity in aquatic and terrestrial organisms are summarized. In addition, available ecological screening benchmarks (*i.e.*, threshold concentrations above which adverse ecological effects might occur) and regulatory guidelines for protection of ecological receptors are presented.

Extensive reviews of Mo ecotoxicity were performed by the US Fish and Wildlife Service (US FWS) in 1989, US Department of the Interior (US DOI) in 1998, and the Dutch National Institute for Public Health and the Environment (RIVM) in 1992 and 2005 (Eisler, 1989; US DOI, 1998; van de Plassche *et al*., 1992; RIVM, 2005). These Mo ecotoxicity data compilations and reviews are the primary sources of data reviewed here. US EPA's Ecotoxicological (ECOTOX) Database was also queried (November 2010) and all data not overlapping in Eisler (1989), US DOI (1998), and/or RIVM documents (van de Plassche *et al*., 1992; RIVM, 2005) were also evaluated. In addition, recent publications on Mo ecotoxicity were searched on several sources (*e.g.*, PubMed, WorldCat, Scopus, and Google). All relevant publications were identified and included for review. Data presented here should be considered comprehensive but not exhaustive.

4.1 Bioavailability, Uptake, and Bioaccumulation in Ecological Receptors

4.1.1 Factors Affecting Molybdenum Bioavailability in Ecological Receptors

Molybdate is the predominant water-soluble Mo species under environmental conditions. Molybdate is also the Mo species that plants and animals take up most readily from soil and water. Several different environmental factors influence the extent of Mo uptake, bioaccumulation, and toxicity. For example, differences in soil pH, soil organic carbon (OC), aluminum and iron oxide, and soil sulfate (SO_4^{2-}) were examined across 10 soils (van Gestel *et al*., 2010). These factors influenced Mo toxicity in soil invertebrates (*e.g.*, earthworms, collembola, and enchytraeids), with toxicity varying between 18- to > 47-fold across the 10 soils (van Gestel *et al*., 2010). Similarly, Mo toxicity in higher plants (*e.g.*, oilseed rape, red clover, ryegrass, and tomato) varied between 66- to 609-fold across the 10 different soils (McGrath *et al*., 2010a,b).

By sequestering Mo, soil iron and aluminum oxides reduce the molybdate concentration in soil pore water, especially in acidic soils, thus limiting Mo uptake in plants and other soil organisms (Bibak and Borggaard, 1994; US EPA, 1998, Appendix I; McGrath *et al*., 2010b; van Gestel *et al*., 2010). Similarly, increased soil OC decreases Mo toxicity. Mo sequestration by iron oxides bound to soil OC and/or direct Mo sequestration by soil OC are believed to reduce the amount of Mo available for uptake (McGrath *et al*., 2010b). Direct Mo adsorption to soil humic acid (a major fraction of soil OC) also has been demonstrated to reduce uptake and, ultimately, toxicity (Bibak and Borggaard, 1994).

Molybdate and sulfate have similar structures and environmental behavior (Zimmer and Mendel, 1999; McGrath *et al*., 2010b; van Gestel *et al*., 2010). This explains why sulfate in soil competes with Mo uptake by some plants and can modulate Mo toxicity. In Mo-deprived soils, specific Mo transporters maintain essential Mo status in plants, but in Mo-rich soils much of the Mo is taken up via the sulfate transporters (McGrath *et al*., 2010b).

The presence of other metals (*e.g*., copper) and anions (*e.g*., phosphate) also can affect Mo bioavailability and toxicity in the environment. Interactions between copper, Mo, and sulfur are known to alter Mo effects in ruminants (*e.g*., livestock) (Suttle, 1991; O'Connor *et al*., 2001; Helz and Erickson, 2011). For example, studies indicate ruminants feeding on diets low in Mo and sulfur and moderate in copper content can succumb to copper toxicity; conversely, diets high in Mo and sulfur and moderate in copper content can result in copper deficiency (Suttle, 1991; O'Connor *et al*., 2001). Phosphate also competes with molybdate to bind to aluminum oxide (Goldberg, 2010); therefore, its presence in environmental media may increase Mo bioavailability.

Studies on the environmental factors affecting Mo interactions are focused largely on soils. The environmental factors that affect Mo uptake and/or toxicity, however, are likely to be operational in other environmental media (*e.g*., in water and sediment) because similar interactions among the substrates can also take place in these media.

4.1.2 Bioaccumulation in Ecological Receptors

Mo uptake by various forage plants (including grains and cereals) has been reviewed by O'Connor *et al*. (2001) in the context of assessing risks toward mammals grazing on pasture receiving biosolids. In this review, O'Connor *et al*. (2001) reported plant uptake factors ranging from < 0.1 (in non-legume forage) to 4.3 (in legumes in alkaline soils). Unlike plants, wildlife species do not appear to accumulate high levels of Mo. Mo levels were low (0.1-4.0 mg/kg dry wt) in livers and kidneys of nine wildlife species – including deer, squirrel, chipmunk, badger, beaver, marmot, and pika – collected from areas of high environmental Mo, with no evidence of adverse effects (Kienholz, 1977, as cited in Eisler, 1989).

Available bioconcentration data for aquatic species indicate that bioconcentration factors (BCFs) for algae and plants are generally higher than those for invertebrates and fish (Table 4-1). Mo bioconcentration by freshwater algae can result in residues up to 20 mg/kg without apparent damage (Sagaguchi *et al*., 1981, as cited in Eisler, 1989). BCFs of up to 25 have been reported for marine plankton (Goyer, 1986, as cited in Eisler, 1989), with much higher BCFs (up to 3,570) reported for periphyton[4] (Table 4-1).

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[4] Periphyton is a complex matrix of algae and heterotrophic microbes attached to submerged substrata in almost all aquatic ecosystems (http://www.epa.gov/bioiweb1/html/periphyton.html).

Table 4-1
Molybdenum Bioconcentration in Aquatic Organisms

Species	Test Concentration (µg/L)	Exposure Duration	BCF[1]	Reference
Aquatic Plants				
Blue-green alga (*Anabaena oscillaroides*)	0.005	1h	3,300	Ter Steeg *et al*. (1986) as cited in Eisler (1989)
	0.073	1h	550	
	25	1h	7-24	
Green alga (*Chlorella vulgaris*)	10,000	1h	490	Sakaguchi *et al*. (1981) as cited in Eisler (1989)
		20h	2,000	
Freshwater alga (*Nitella flexilis*)	0.014	25d	628	Short *et al*. (1971) as cited in Eisler (1989)
	3,300	24d	39	
Bryophyte (*Hygrohypnum ochraceum*)	30.3	10d	370	Carter and Porter (1997) from US EPA, 2007
Lake periphyton	0.014	24d	3,570	Short *et al*. (1971) as cited in Eisler (1989)
Aquatic Invertebrates				
Amphipod (*Gammarus sp.*)	3,300	24d	4.8	Short *et al*. (1971) as cited in Eisler (1989)
Clam (*Margaretifera margaretifera*)		15-24d	0.3-1.8[2]	
Crayfish (*Pacifiastacus leniusculus*)		24d	5.7-9.8[3]	
Fish				
Steelhead trout (*Oncorhynchus mykiss*)	0.014	Chronic	1,143[4]	Short *et al*. (1971) as cited in Eisler (1989)
	3,300	24d	0.6-5.4[5]	

Notes: *[1] Unless noted otherwise, the BCF values are based on whole body tissue residue.*
[2] Muscle/soft parts/shell.
[3] Muscle/carapace.
[4] Liver.
[5] Gastrointestinal-tract/gill/muscle/liver/spleen.

Aquatic animals showed large interspecies differences in their ability to accumulate Mo. Marine bivalve mollusks generally demonstrated 30-90 times (and up to 1,300 times) more Mo in their body than the ambient seawater (Eisler, 1981, as cited in Eisler, 1989). In contrast, other aquatic invertebrates shown in Table 4-1 have BCFs < 10. In fish collected from surface water (rainbow trout, *Oncorhynchus mykiss*), Mo concentrations in water only slightly affected tissue Mo accumulation; tissue residues ranged from 5-118 µg/kg wet wt in water with trace (< 6 µg/L) Mo concentrations, 10-146 µg/kg in water with low (6 µg/L) Mo concentrations, and 13-322 µg/kg in water with high (300 µg/L) Mo concentrations (Ward, 1973, cited in Eisler, 1989). A similar pattern was observed for kokanee salmon (*Oncorhynchus nerka*) collected from the same surface waters (Ward, 1973, cited in Eisler, 1989). Short *et al*. (1971, cited in Eisler, 1989; Table 4-1) have reported a BCF of 1,143 in the liver of steelhead trout chronically exposed to 0.014 µg/L Mo, but this observation appears to be atypical.

4.2 Essentiality and Health Benefits in Aquatic and Terrestrial Organisms

Mo is present in enzymes with essential biological functions involved in the biochemical cycle of nitrogen, sulfur, and phosphorus, including nitrate reduction, nitrogen fixation, and oxidase reactions (van Gestel *et al*., 2010). In plants, Mo's essential biochemical role in growth via its involvement in nitrogen fixation and nitrate reduction is well recognized (Schroeder *et al*., 1970, as cited in Eisler, 1989). For example, insufficient Mo retards nodulation and limits nitrogen fixation in legumes (IMOA, 2010b). Mo also is essential for growth in animals, as it influences purine oxidation, protein synthesis, phosphate ester hydrolysis, sulfide oxidation and sulfur metabolism, and iron transport and utilization (IMOA, 2010c). Additionally, metabolic relationships between Mo and other trace elements also may have beneficial effects. For example, in mammals, Mo can protect against poisoning by copper, mercury, chromium, and likely other trace elements (Eisler, 1989).

4.3 Aquatic Toxicity

The available data on the toxicity of Mo in aquatic organisms are presented in Tables 4-2, 4-3, and 4-4. Acute toxicity data were available for both freshwater and marine organisms; chronic toxicity data were available only for freshwater organisms.

As noted earlier, because of its environmental relevance, molybdate [either as sodium molybdate (Na-molybdate, Na_2MoO_4) or ammonium molybdate (NH_4-molybdate, $(NH_4)_6(Mo_7O_2)_4$) is the most commonly used form of Mo in ecotoxicity studies. Occasional studies have used Mo-trioxide, but, under environmentally relevant conditions, Mo-trioxide readily transforms into molybdate, causing slight acidification (*i.e.*, pH lowering) in the process. Consequently, the apparent differences in molybdate versus Mo-trioxide ecotoxicity are due not to the Mo valence state but rather to the pH effects (De Schamphelaere *et al*., 2010). Therefore, as a matter of simplification, the studies below describe Mo toxicity in general, with the assumption that observed toxicity occurred from the molybdate ion.

4.3.1 Acute Toxicity

Acute toxicity tests are conducted for short durations (compared to the test species' entire life span), and the toxicological endpoints are generally based on observed gross effects, such as mortality or immobilization. Table 4-2 presents acute toxicity information on Mo for several species of freshwater invertebrates (annelids, crustaceans, and insects) and fish species. The studies have been conducted at environmental pH of 6.7-8.5 and over a wide range of temperatures and water hardness levels. Reported endpoints are the 50% lethal concentration (LC50) and/or 50% effect concentration (EC50). Based on the reported endpoint values, acute toxicity of Mo to aquatic organisms varies by several orders of magnitude depending on organism species and environmental conditions. The LC50 values vary about 10-fold within fish species; as a group, however, they appear to be more tolerant to Mo toxicity than invertebrates. Upon further investigation, the remarkably low LC50 values (0.36-4.6 mg/L) for a midge

(*Chironomus plumsus*) and an annelid (*Tubifex tubifex*) reported by Fargasova (1997, 1998, and 1999, cited in RIVM, 2005) were determined to be unreliable in a regulatory evaluation by RIVM (2005). Based on the rest of the data in Table 4-2, the lethality of Mo ranges from 211 mg/L (*N. botia* 96h LC50) to > 2,000 mg/L (*O. nerka* 96h LC50); a single sub-lethal effect concentration of 29 mg/L (*T. tubifex* 96h EC50) also was reported.

Table 4-3 presents available data on acute toxicity of Mo for marine organisms. Several species of mollusks, crustaceans, and fish have been tested at various pH, salinity, and temperature conditions. Lethality to these marine species ranges from > 79.8 mg/L (*M. saxatilis* 96h LC50) to 2,600 mg/L (*C. variagtus* 96h LC50); sub-lethal effect concentrations range from 150 mg/L (*M. edulis* 96h EC50) to 1,900 mg/L (*C. virginica* 96h EC50). These acute toxicity values generally indicate that marine species are more tolerant to Mo exposures than freshwater species.

4.3.2 Chronic Toxicity

Chronic tests encompass a significant fraction of the test species' life span. The chronic endpoints are generally based on sub-lethal effects such as growth and reproduction. De Schamphelaere *et al*. (2010) compiled and critically reviewed the quality of available Mo chronic toxicity data on aquatic species and found that available data were inadequate to derive a no observed effect concentration (NOEC) for aquatic organisms in surface waters. Consequently, De Schamphelaere *et al*. (2010) conducted several supplementary chronic toxicity studies that provided more relevant data on chronic toxicity of Mo in fresh water organisms, including algae, higher plants, and amphibians. All available data on the chronic toxicity of Mo in freshwater organisms (sub-lethal effects only), regardless of their quality, are presented in Table 4-4. Generally, the reported endpoints are either NOECs or the 10% effects concentrations (EC10) for growth or reproduction. No chronic toxicity data for marine species were found.

A species sensitivity distribution based on EC10 values (Table 4-4) is depicted in Figure 4-1. Based on the EC10 values for Mo, species sensitivity are as follows: fish (*O. mykiss*, 36.9 mg/L) > water flea (*D. magna*, 62.8 mg/L) > algae (*P. subcapitata*, 74.3 mg/L) > frog (*X. laevis*, 115.9 mg/L) > midge (*C. riparius*, 121.4 mg/L) > rotifer (*B. calciflorus*, 193.6 mg/L) > snail (*L. stagnalis*, 211.3 mg/L) > duckweed (*L. minor*, 241.5 mg/L). The EC10 values vary among species by roughly 6-fold and vary within species by < 2-fold (*e.g.*, fish EC10 ranges from 36.9-90.9 mg/L; water flea EC10 ranges from 62.8-105.6 mg/L). While NOEC data are also available, an analysis comparing NOECs to establish sensitivity among species would be unreliable. This is because the NOECs may be driven largely by the test concentrations and, thus, may not give a completely accurate depiction of a "true" NOEC for a particular species.

Two studies using Mo-trioxide report NOEC/EC10 values that are generally lower than those using molybdate for the same species (HRC, 1996, and Kimball, 1978, cited in De Schamphelaere *et al*., 2010). As discussed previously, the apparently higher toxicity of Mo-trioxide compared to molybdate is likely due to pH effects. De Schamphelaere *et al*. (2010), however, deemed both of these studies to be unreliable.

Table 4-2
Acute Toxicity of Molybdenum to Freshwater Organisms

Species	Test Compound[1]	Test Conditions			Exposure Duration	Endpoint[2]	Value (mg/L)	Reference[3]
		pH	Temp (ºC)	Hardness (mg $CaCO_3$/L)				
Invertebrates								
Annelids								
Tubificid worm (*Tubifex tubifex*)	Na-molybdate	7.6	24.5	ND	96h	EC50	29	Khangarot (1991)
	NH_4-molybdate	7.8	20	311	96h	LC50	4.6[4]	Fargašová (1999)
Crustaceans								
Amphipod (*Crangonyx pseudogracilis*)	Na-molybdate	6.7-6.8	45-55	ND	96h	LC50	2,700	Martin and Holdich (1986)
Insects								
Midge (*Chironomus plumosus*)	NH_4-molybdate	7.7	20	ND	96h	LC50	0.36[4]	Fargašová (1997)
	NH_4-molybdate	7.8	20	80	96h	LC50	0.46[4]	Fargašová (1998)
Fish								
Sucker (*Catostomus latipinnis*)	Na-molybdate	7.9	25	144	96h	LC50	1940	Hamilton and Buhl (1997)
Mummichog (*Fundulus heteroclitus*)	Mo-trioxide	ND	20	7.9, 18.8	96h	LC50	230, 315[5]	Dorfman (1977)

Table 4-2
Acute Toxicity of Molybdenum to Freshwater Organisms (continued)

Species	Test Compound[1]	Test Conditions	Exposure Duration	Endpoint[2]	Value (mg/L)	Reference[3]	211	Pundir (1989)
Fish								
Rainbow trout (*Oncorhynchus mykiss*)	Na-molybdate	6.9-7.2	8, 12	14-32	96h	LC50	800, 1,320	McConnell (1977)
Sockeye salmon (*Oncorhynchus nerka*)	Na-molybdate	7.4-7.6	15-18	107	96h	LC50	> 2,000	Reid (2002)
Ticto barb (*Puntius ticto*)	NH_4-molybdate	8	16	53	96h	LC50	550	Pundir and Saxena (1990)

Notes: *ND = no data*

[1] Na-molybdate is sodium molybdate (Na_2MoO_4); NH_4-molybdate is ammonium molybdate [$(NH_4)_6(Mo_7O_2)_4$]; Mo-trioxide is molybdenum trioxide (MoO_3).

[2] EC50 = 50% effect concentration (effect was immobility); LC50 = 50% lethal concentration.

[3] All references were cited in RIVM (2005).

[4] Rejected for use in derivation of environmental risk limits (ERLs) by RIVM (2005).

[5] Author reports that pH (which was < 4 at test completion) was probable cause of mortality.

Table 4-3
Acute Toxicity of Molybdenum to Marine Organisms

Species	Test Compound[1]	Test Conditions				Endpoint[2]	Value (mg/L)	Reference[3]
		pH	Temp (ºC)	Salinity (‰)	Exposure Duration			
Mollusks								
Blue mussel (*Mytilus edulis*)	NH_4-molybdate	8.4	26	ND	48h	EC50[4]	150	Morgan *et al*. (1986)
Eastern oyster (*Crassostrea virginica*)	Na-molybdate	ND	20	ND	96h	EC50[5]	1,900	Knothe *et al*. (1988)
Crustaceans								
Green crab (*Carcinus maenas*)	Na-molybdate	5	12-14	33.2	48h	LC50	1,018[6]	Abbott (1977)
Pink shrimp (*Penaeus duorarum*)	Na-molybdate	ND	25	ND	96h	LC50	1,900	Knothe *et al*. (1988)
Mysid shrimp (*Mysidopsis bahia*)	Na-molybdate	ND	27	ND	96h	LC50	1,100	Knothe *et al*. (1988)
Amphipod (*Allorchestes compressa*)	NH_4-molybdate	5.0-5.4	16	34.8	96h	LC50	247	Ahsannulah *et al*. (1982)
Fish								
Sheepshead minnow (*Cyprinodon variegatus*)	Na-molybdate	ND	ND	25	96h	LC50	2,600	Knothe *et al*. (1988)
Striped bass (*Morone saxatilis*)	Na-molybdate	8.27	20	21	96h	LC50	> 79.8[7]	Dwyer *et al*. (1992)

Notes: ND = no data

[1] Na-molybdate is sodium molybdate (Na_2MoO_4); NH_4-molybdate is ammonium molybdate [$(NH_4)_6(Mo_7O_2)_4$].

[2] EC50 = 50% effect concentration; LC50 = 50% lethal concentration.

[3] All references were cited in RIVM (2005).

[4] Reproduction effects.

[5] Growth effects.

[6] Test described very poorly; endpoint is reported as TLM (median tolerance limit).

[7] Exposure concentration = 80% of nominal concentration.

Table 4-4
Chronic Toxicity of Molybdenum to Freshwater Organisms

Species	Test Compound[1]	pH	Exposure Duration	Endpoint[2]	Effect	Value (mg/L)	Reference
Green Algae							
Scenedesmus sp.	NH_4-molybdate	ND	96h	NOEC	Growth	54	Bringmann and Kuhn (1959) as cited in RIVM (2005)
Scenedesmus subspicatus	NH_4-molybdate	ND	72h	NOEC	ND	25	HRC (1994a) as cited in De Schamphelaere *et al.* (2010)
	Na-molybdate	ND	72h	NOEC	ND	12.5	HRC (1994b) as cited in De Schamphelaere *et al.* (2010)
	Mo-trioxide	ND	72h	NOEC	ND	≥100	HRC (1994c,d) as cited in De Schamphelaere *et al.* (2010)
Pseudokirchneriella subcapitata	Na-molybdate	ND	72h	NOEC	ND	4.6	HRC (1996) as cited in De Schamphelaere *et al.* (2010)
	Na-molybdate	8.0-8.1	72h	EC10	Growth rate	74.3-164[3]	De Schamphelaere *et al.* (2010)
Plant							
Duckweed (*Lemna minor*)	Na-molybdate	ND	7d	NOEC EC10	Growth rate	24.7 241.5	De Schamphelaere *et al.* (2010)
Invertebrates							
Rotifer (*Brachionus calyciflorus*)	Na-molybdate	7.5	48h	NOEC EC10	Population growth rate	244 193.6	De Schamphelaere *et al.* (2010)
Water flea (*Daphnia magna*)	Na-molybdate	ND	21d	NOEC	Reproduction	136[4]	GEI (2009) as cited in De Schamphelaere *et al.* (2010)
	Na-molybdate	ND	21d	NOEC	ND	50	Diamantino *et al.* (2000) as cited in De Schamphelaere *et al.* (2010)
	Mo-trioxide	ND	21d	NOEC EC10	ND	4.41 6.98	Kimball (1978) as cited in De Schamphelaere *et al.* (2010)
	Na-molybdate	7.4-8.2	21d	NOEC EC10	Reproduction	49.9-112 62.8-105.6	De Schamphelaere *et al.* (2010)

Table 4-4
Chronic Toxicity of Molybdenum to Freshwater Organisms (continued)

Species	Test Compound[1]	pH	Exposure Duration	Endpoint[2]	Effect	Value (mg/L)	Reference
Invertebrates							
Water flea (*Ceriodaphnia dubia*)	Na-molybdate	ND	7d	EC20	Reproduction	77[4]	GEI (2009) as cited in De Schamphelaere *et al*. (2010)
	Na-molybdate	ND	8d	IC12.5	Reproduction	34	Naddy *et al*. (1995)
		7.6-7.9	7d	NOEC EC10	Reproduction	97.3 78.2	De Schamphelaere *et al*. (2010)
Midge (*Chironomus riparius*)	Na-molybdate	6.9-7.1	14d	NOEC EC10	Growth	393 121.4	De Schamphelaere *et al*. (2010)
Pond snail (*Lymnaea stagnalis*)	Na-molybdate	7.8-8.2	28d	NOEC EC10	Growth rate	200 211.3	De Schamphelaere *et al*. (2010)
Fish							
Rainbow trout (*Oncorhynchus mykiss*)	Na-molybdate	ND	32d 18mo	NOEC	ND	200-750 > 18.5	Davies *et al*. (2005) as cited in De Schamphelaere *et al*. (2010)
	Na-molybdate	7.4±0.1	78/84d	NOEC EC10	Biomass	48.9-<121.0 36.9-43.2	De Schamphelaere *et al*. (2010)
Fathead minnow (*Pimephales promelas*)	Na-molybdate	ND	28d	EC10	Growth	90.9[4]	GEI (2009) as cited in De Schamphelaere *et al*. (2010)
	Na-molybdate	7.5±0.05	34d	NOEC EC10	Biomass	27.7 39.3	De Schamphelaere *et al*. (2010)
Cutthroat trout (*Oncorhynchus clarki*)	Na-molybdate	ND	30d	NOEC	ND	> 87.8	Pickard *et al*. (1999) as cited in De Schamphelaere *et al*. (2010)
Coho salmon (*Oncorhynchus kisutch*)	Na-molybdate	ND	20wk	NOEC	ND	> 19.5	Ennevor (1993) as cited in De Schamphelaere *et al*. (2010)

Table 4-4
Chronic Toxicity of Molybdenum to Freshwater Organisms (continued)

Species	Test Compound[1]	pH	Exposure Duration	Endpoint[2]	Effect	Value (mg/L)	Reference
Amphibian							
African clawed frog (*Xenopus laevis*)	Na-molybdate	7.8	4d	NOEC EC10	Malformation	22.4 115.9	De Schamphelaere *et al*. (2010)

Notes: *ND = no data*

[1] Na-molybdate is sodium molybdate (Na_2MoO_4); NH_4-molybdate is ammonium molybdate [$(NH_4)_6(Mo_7O_2)_4$]; Mo-trioxide is molybdenum trioxide (MoO_3).

[2] NOEC = no observed (adverse) effect concentration; EC10 = 10% effect concentration.

[3] Geometric mean of four values.

[4] Geometric mean of two values.

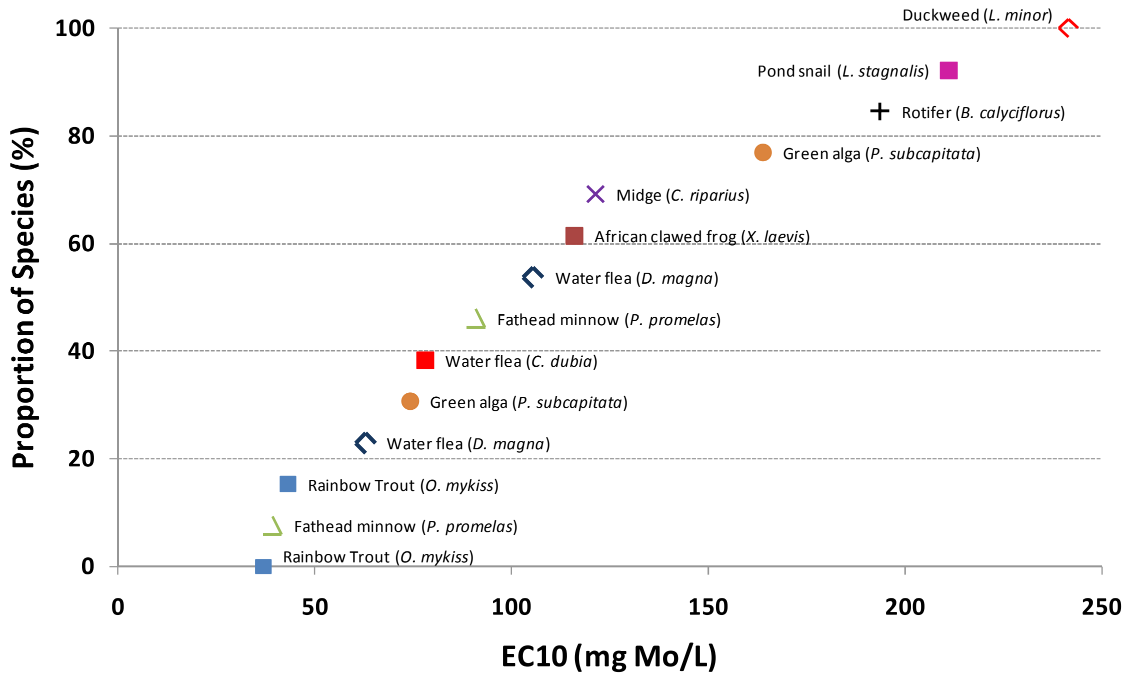


Figure 4-1
Species Sensitivity Distribution of Chronic Molybdenum Toxicity to Aquatic Organisms

Note: Only EC10 values for molybdate from Table 4-4 are included; when a range of values was available, both the minimum and the maximum values are included.

4.4 Terrestrial Toxicity

Most risk assessments for terrestrial organisms have focused on the likelihood of molybdenosis (a Mo-induced copper deficiency in ruminants) in cattle grazing on Mo-contaminated land (O'Connor *et al*., 2001). Effects on soil-dwelling organisms are relatively unexplored, and the limited data for microbial processes indicate that effects occur at high soil concentrations (> 480 mg/kg) that are not environmentally relevant (Buekers *et al*., 2010). Recently, Mo toxicity to invertebrates and plants has been investigated to support various regulatory risk assessments. A summary of these studies is presented in Table 4-5.

4.4.1 Effects on Soil Microbial Processes

Effects of Mo on several microbial processes and enzymatic activities have been tested in soils with wide-ranging properties [pH, soil organic matter (SOM), and clay contents]. The NOEC and EC10 values show a wide range (24-1,552 mg/kg dry wt soil) but generally exceed 120 mg/kg dry wt soil, indicating that soil microbes are generally tolerant of Mo exposure. However, it should be noted that, unlike aqueous solutions where experimental conditions can be controlled, transformation of test Mo compounds (Mo-trioxide, Na-,NH_4-,H_2-moblydate) in soils alters soil pH and salinity and, consequently, confounds effects attributable directly to Mo (Buekers *et al*., 2010). For example, as noted previously, the apparent effect of Mo-trioxide on highly pH-dependent nitrification (EC10 = 188 mg/kg in Table 4-5) was due entirely to changes in pH and salinity as Mo dose increased (Buekers *et al*., 2010). Therefore, after consideration of the confounding effects, Mo is expected to have relatively high toxicity thresholds for microorganisms.

4.4.2 Effects on Terrestrial Plants

As an essential trace element for the growth of all terrestrial plants, the presence of Mo in plants is not unexpected. In fact, all plants contain some Mo. The highest levels (> 20 mg/kg) are documented frequently in plants from contaminated areas. However, plants are generally tolerant of Mo and, in general, Mo accumulation in plants presents a greater concern to higher mammals exposed via their diet (such as mammals grazing on Mo-laden plants).

Buekers *et al*. (2010) studied the effects of Mo-trioxide and Na-molybdate on growth of wheat seedlings (*Triticum aestivum* L) in soil and determined EC10 values of 5 and 15 mg/kg, respectively (Table 4-5). However, after accounting for the confounding effects of pH and salinity, a lowest-effect concentration for Mo of 38 mg/kg was established for plants in soil. Based on these results, Buekers *et al*. (2010) recommended using Na-molybdate, with salinity controls, in soil toxicity studies. In another recent study, McGrath *et al*. (2010a) conducted plant growth studies using Na-molybdate in 10 soils with wide-ranging properties (Table 4-5). The EC50 values (not shown in Table 4-5) for a particular species varied by 66- to 609-fold across soils, whereas EC50s for a particular soil varied only 2- to 38-fold across the four species. The variability of toxicity thresholds across soils for a single species illustrates the importance of soil properties and their effects on Mo bioavailability (and ultimately toxicity). The toxicity threshold variability was less across different soils when they were based on soil solution Mo concentrations, highlighting that Mo bioavailability in soil depends on solubility. However, while using plant tissue as the metric produced a smaller range of EC50 values (compared to EC50 values derived using soil or soil solution concentrations), variability in Mo toxicity across soil types still persisted—indicating that Mo bioavailability is not explained by solubility alone. Effect concentration values quantified for Mo in plant shoots reflect a tolerance of plants to Mo uptake and accumulation. These studies showed that upwards of 200 mg Mo/kg plant tissue can accumulate without any adverse effects. Based on EC10 values, ryegrass was the most tolerant species.

Table 4-5
Molybdenum Toxicity to Soil Microbial Processes, Plants, and Invertebrates

Terrestrial Receptors	Soil Type/ Count	Test Compound [1]	Soil Properties			Test Conditions		Endpoint [3]	Effect	Value[4] (mg/kg dry wt)	Reference
			pH	SOM[2] (%)	Clay (%)	Temp (ºC)	Duration				
Microbial processes											
Nitrogen-mineralization	loam	H-molybdate	5.8	4.4	23	30	20d	EC10	Inhibition	480	Liang and Tabatabai (1977) as cited in RIVM (2005)
Nitrification	haplic luvisol	Mo-trioxide	5.0-6.4	ND	ND	ND	4d	EC10	Inhibition	188[5]	Buekers *et al.* (2010)
	haplic luvisol	Na-molybdate	6.2-6.6	ND	ND	ND	4d	EC10	Inhibition	1,552	
Alkaline phosphatase	silty clay loam	H-molybdate	7.4	9.3	34	37	0.5h	NOEC	Inhibition	120	Juma and Tabatabai (1977) as cited in RIVM (2005)
Arylsulfatase		H-molybdate	7	9	34	37	1h	NOEC	Inhibition	1,199	Al-Khafaji and Tabatabai (1979) as cited in RIVM (2005)
Urease	six soils	H-molybdate	5.1-7.8	2.6-9.3	17-42	37	0.5h	EC10	Inhibition	24-480	Tabatabai (1977) as cited in RIVM (2005)

Table 4-5
Molybdenum Toxicity to Soil Microbial Processes, Plants, and Invertebrates (continued)

Terrestrial Receptors	Soil Type/ Count	Test Compound [1]	Soil Properties				Test Conditions		Endpoint [3]	Effect	Value[4] (mg/kg dry wt)	Reference
Plants												
Wheat (*Triticum aestivum* L.)	haplic luvisol	Mo-trioxide/Na-molybdate	5.0-6.6	ND	ND	ND	21d		EC10	Growth (yield)	5-15[8]	Buekers *et al.* (2010)
Oilseed rape (*Brassica napus* L.)	10 field soils from Europe	Na-molybdate	4.4-7.8	0.6-30.7[9]	2-33	16-20	21d		ED10	Growth (shoot yield)	4-2,844	McGrath *et al.* (2010a)
Red clover (*Trifolium pratense* L.)											0.4-1,502	
Ryegrass (*Lolium perenne* L.)											14-3,476	
Tomato (*Lycopersicon esculentum* L.)											3-1,575	
Oilseed rape (*Brassica napus* L.)									EC10		2-140[6]	
Red clover (*Trifolium pratense* L.)											0.04-30[6]	
Ryegrass (*Lolium perenne* L.)											2-241[6]	
Tomato (*Lycopersicon esculentum* L.)											1.3-31[6]	
Oilseed rape (*Brassica napus* L.)									EC10		703 (185-1,220)[7]	
Red clover (*Trifolium pratense* L.)											225 (89-362)[7]	
Ryegrass (*Lolium perenne* L.)											228 (44-413)[7]	

Table 4-5
Molybdenum Toxicity to Soil Microbial Processes, Plants, and Invertebrates (continued)

Terrestrial Receptors	Soil Type/ Count	Test Compound [1]	Soil Properties			Test Conditions		Endpoint [3]	Effect	Value[4] (mg/kg dry wt)	Reference
Plants											
Tomato (*Lycopersicon esculentum* L.)										232 (63-402)[7]	
Invertebrates											
Earthworm (*Esenia andrei*)	10 field soils from Europe	Na-molybdate	4.4-7.8	0.6-30.7[9]	2-33	ND	4wk	NOEC	Repro-duction	8.88-≥2,744	van Gestel *et al.* (2010)
Enchytraeids (*Enchytraeus crypticus*)										78.1-≥2,820	
Collembola (*Folsomia candida*)										25.8-≥3,396	
Earthworm (*Esenia andrei*)								EC10		0.78-917	
Enchytraeids (*Enchytraeus crypticus*)										67.2-> 2,817	
Collembola (*Folsomia candida*)										38.9-> 3,396	

Notes: *ND = no data*

[1] Na-molybdate is sodium molybdate (Na_2MoO_4); H-molybdate is hydrogen molybdate (H_2MoO_4); Mo-trioxide is molybdenum trioxide (MoO_3).

[2] SOM = soil organic matter content.

[3] NOEC = no observed (adverse) effect concentration; EC10 = 10% effect concentration; ED10 = 10% effect dose.

[4] Unless noted otherwise, values are in terms of soil concentrations (in mg Mo/kg dry wt soil).

[5] Effects entirely due to changes in soil pH and not due to Mo.

[6] Values in terms of soil solution concentrations (in mg Mo/L soil solution).

[7] Values in terms of plant residue (in mg Mo/kg dry wt plant shoot), mean and range (all 10 soils).

[8] After correcting for the confounding effects, the EC10 is estimated to be 32 mg/kg.

[9] Organic carbon.

4.4.3 Effects on Terrestrial Invertebrates

Using the same 10 soils as the McGrath *et al*. (2010a) study, van Gestel *et al*. (2010) conducted studies of Mo toxicity on three species of soil invertebrates (earthworms, collembola, and enchytraeids). A summary of reported NOEC and EC10 values is shown in Table 4-5. Unlike for plants, toxicity thresholds varied more widely across species than across soil types, although Mo toxicity is dependent on both factors. The EC10 values for reproduction ranged from 0.78-917 mg/kg, 67.2 to > 2817 mg/kg, and 38.9 to > 3396 mg/kg for *E. andrei*, *E. crypticus*, and *F. candida*, respectively, indicating that *F. candida* was the most tolerant species, followed by *E. cryptis*; *E. andrei* was the most sensitive.

4.4.4 Effects on Terrestrial Vertebrates

We did not locate any studies on toxicity to birds in the environment. However, studies on domestic poultry exposed experimentally to a Mo-enriched diet were available. Based on these studies, birds appear to be tolerant to Mo. Adverse effects on growth were reported at dietary concentrations of 200-300 mg/kg, on reproduction at 500 mg/kg, and on survival at 6,000 mg/kg (Underwood, 1971, and Friberg *et al*., 1975, both as cited in Eisler, 1989). A few studies are available on the effects of Mo-related mining waste on animals (Kienholz, 1977, and King *et al*., 1984, both as cited in Eisler, 1989). Day-old chicks fed for 23 days with a diet containing 20% Mo mine tailings were unaffected; at 40% Mo mine tailings in diet, the chicks showed only a slight reduction in body weight (Kienholz, 1977, as cited in Eisler, 1989).

Studies on Mo ecotoxicity to mammalian wildlife are limited. Available studies focus mostly on domestic animals, such as livestock (cattle and sheep). Although direct effects of Mo on animal reproduction has been demonstrated (Phillippo *et al*., 1987, as cited in O'Connor *et al*., 2001), studies on livestock are almost always related to molybdenosis. Molybdenosis is characterized by Mo-induced copper deficiency (hypocuprosis) in ruminant animals, and was first identified in 1938 as the cause of severe diarrhea and emaciation in cattle grazing in areas called *teart* pastures (*e.g.*, pasture with alkaline pH and elevated Mo concentrations) in England (O'Connor *et al*., 2001). Ruminants are particularly sensitive to Mo, with adverse effects occurring at 2-20 mg/kg Mo in diet (when fed low copper diets) or when total daily Mo intake approaches 141 mg. The lethal dose to cattle is roughly 10 mg/kg body weight. Other mammals, including horses, pigs, rodents, and wildlife, are more tolerant to Mo. Mule deer (*Odocoileus hemionus*), for example, are at least 10 times more resistant than domestic ruminants; they can tolerate up to 1000 mg/kg, about the same as rabbits and rats (Ward and Naggy, 1977, and Anke *et al*., 1985, both as cited in O'Connor *et al*., 2001).

It is noteworthy that in the presence of excess sulfate, Mo may cause molybdenosis via copper-molybdenum-sulfate interactions, including formation of insoluble copper-molybdenum-sulfur complexes (*e.g.*, thiomolybdates). However, besides molybdenosis, there may be other causes of hypocuprosis. For example, as discussed in O'Connor *et al*. (2001), excess iron or sulfate may also exert an independent effect on copper availability, leading to hypocuprosis. Therefore, molybdenosis versus other causes of hypocuprosis needs to be evaluated carefully.

Overall, based on available data, birds (both wild and domestic) and mammalian wildlife are generally tolerant of elevated Mo exposures. Domestic mammals (cattle and sheep) appear to be the most sensitive. In 1980, the expert committee report of the NAS (the National Research

Council, or NRC) evaluated low-level, chronic Mo toxicity, and identified 5-10 mg/kg in soil as the critical level. This level is weakly associated with impaired bone development in young horses and cattle (NRC, 1980, as cited in O'Connor *et al*., 2001) and has been used in risk assessments of wild populations (O'Connor *et al*., 2001).

4.5 Ecological Risk Assessments

As noted in Chapter 2, mining activities, disposal of coal combustion residues (CCPs), and biosolids application constitute important anthropogenic sources of Mo in the environment. Although CCPs may be an anthropogenic source of Mo, recent US EPA risk assessments of CCPs have determined that Mo does not pose an ecological risk (US EPA, 1998, 2002, 2010a).

4.6 Ecological Regulatory Criteria and Screening Guidelines

Generally, the absence of regulatory criteria or guideline values for a substance may mean either that the substance is not a priority substance (*i.e.*, there is no potential environmental risk) or that there is a critical lack of data. For Mo, data on effects on mammalian species (domestic species) appear to be robust for deriving standards for protection from exposure via grazing (O'Connor *et al*., 2001), but data gaps have been identified for aquatic and other terrestrial species. Although some benchmarks based on the limited data do exist, new data using standard tests are being generated to support various risk assessments and the development of revised toxicity criteria for these ecological endpoints (De Schamphelaere *et al*., 2010; McGrath *et al*., 2010a; van Gestel *et al*., 2010). Available screening guideline values proposed for Mo by regulatory agencies and the scientific community are shown in Table 4-6 and discussed below.

Several surface water screening values for Mo are available from the National Oceanic and Atmospheric Administration's (NOAA's) Screening Quick Reference Tables (SQuiRTs) (Buchman, 2008) and RIVM (2005). The SQuiRTs were developed for screening purposes only and are very conservative (*i.e.*, over-protective). Environmental risk limits (ERLs) derived by RIVM serve as advisory values to set environmental quality standards (EQS) by the Dutch Ministry of Housing, Spatial Planning, and the Environment (VROM). The RIVM Maximum Permissible Concentration (MPC) is the concentration of a substance in a medium that should protect all species in ecosystems from adverse effects. The RIVM Ecological Serious Risk Concentration (SRC_{ECO}) is the concentration of a substance in a medium (soil, water, sediment, or air) at which an ecosystem's overall health will be seriously affected or is threatened. This is assumed when 50% of the species and/or 50% of the microbial and enzymatic processes could be affected. The Dutch Mo MPC of 30 µg/L for freshwater (Table 4-6) is very conservative, because it is based on a 100% protection (*i.e.*, no effects at all) whereas a protection for 95% of the species is typically considered in regulatory ecological risk assessments (ECB, 2003). To derive the Dutch freshwater MPC, a safety factor of 1,000 was applied to the EC50 (29 mg/L) for the annelid *T. tubifex* and added to the 90th percentile background surface water concentration in the Netherlands (1.3 µg/L).

Table 4-6
Regulatory and Scientific Molybdenum Screening Values and Standards for the Protection of Wildlife

Benchmarks	Symbol	Value	Units	Reference
Surface Water				
Dutch Guidance[1]				
Maximum Permissible Concentration	MPC	30	ug/L	RIVM (2005)
Ecological Serious Risk Concentration	SRC_{ECO}	54,000	ug/L	RIVM (2005)
NOAA SQuiRTs[2]				
Acute[a]		16,000	ug/L	Buchman (2008)
Chronic[b]		34	ug/L	Buchman (2008)
REACH Guidance Based[3]				
Median Hazard Concentration Affecting 5% of Species	HC_5	38,200	ug/L	De Schamphelaere *et al*. (2010)
Marine Water				
NOAA SQuiRTs[2]				
Chronic[b]		23	ug/L	Buchman (2008)
Groundwater				
NOAA SQuiRTs[2]				
Secondary Standards[c]		70	ug/L	Buchman (2008)
Dutch Standard[1]				
Target Value	TV_{GW}	5	ug/L	VROM (2009)
Soil				
NOAA SQuiRTs[2]				
Plants[d]	$Eco\text{-}SSL_{PLANTS}$	2	mg/kg	Buchman (2008)
Microbes[e]	$Eco\text{-}SSL_{MICROBES}$	200	mg/kg	Buchman (2008)
Dutch Guidance and Standards[1]				
Maximum Permissible Concentration	MPC	1.3	mg/kg	RIVM (2005)
Ecological Serious Risk Concentration	SRC_{ECO}	270	mg/kg	RIVM (2005)
Dutch Target Value[4]	TV_{Soil}	3	mg/kg	Buchman (2008)
Dutch Intervention Value[4]	IV_{Soil}	190	mg/kg	VROM (2009)

Benchmarks	Symbol	Value	Units	Reference
Biosolids Guidance[5]				
Ceiling Concentrations		75	mg/kg	O'Connor *et al*. (2001)
Cumulative Application Limit	RPc	40	kg/ha	O'Connor *et al*. (2001)
Alternate Pollutant Limit	APL	40	mg/kg	O'Connor *et al*. (2001)

Notes: [1] Dutch Guidance and Standards:

Maximum Permissible Concentration—Guidance concentration protective of all species in ecosystems from adverse effects.

Ecological Serious Risk Concentration—Guidance concentration that will seriously affect or threaten ecosystems (i.e., 50% of the species and/or 50% of the microbial and enzymatic processes are possibly affected).

Target Value (Standard)—Baseline concentration value below which compounds and/or elements are known or assumed not to affect the natural properties of the soil.

Intervention Value (Standard)—Maximum tolerable concentration above which remediation is required. This occurs if one or more compounds in concentrations equal to or higher than the intervention value are found in more than 25 m^3 of soil or 1000 m^3 of groundwater.

[2] National Oceanic and Atmospheric Administration Screening Quick Reference Tables, which were developed for screening purposes only (Buchman, 2008).

[a] Based on Tier II Secondary Acute Value: http://www.esd.ornl.gov/programs/ecorisk/tools.html.

[b] Based on Australian and New Zealand ECLs and Trigger Values: ANZECC Oct 2000, Volume 1, The Guidelines: www.mfe.govt.nz/publications.

[c] Based on World Health Organization's (WHO's) drinking water guidelines: http://www.who.int/water_sanitation_health/dwq/en.

[d] Based on ORNL Screening Benchmarks (Efroymson et al., 1997a).

[e] Based on ORNL (Efroymson et al.,1997b).

[3] Predicted No Environmental Effect Concentration (PNEC) determined in accordance with the REACH Technical Guidance Document (ECB, 2003).

[4] Concentrations in soil are shown for standard soil (10% organic matter and 25% clay).

[5] Standards for land-application of biosolids (40 CFR Part 503):

Ceiling concentration—Maximum permissible concentration in bulk sewage sludge or sewage sludge sold or given away in a bag or other container to be applied to the land.

Cumulative Application Limit—Maximum permissible cumulative loading rate.

Alternate Pollutant Limit—Maximum permissible concentration in the sewage sludge; all alternate pollutant limits (for eight other pollutants) must be met simultaneously.

Recent effects studies on aquatic and terrestrial species (De Schamphelaere *et al*., 2010; McGrath *et al*., 2010a; van Gestel *et al*., 2010) fill some of the data gaps and indicate that these MPCs are overly conservative. For example, De Schamphelaere *et al*. (2010) evaluated existing aquatic data and generated new data to derive an aquatic Hazard Concentration (HC) that is protective of 95% of the aquatic species using accepted regulatory guidance, *i.e.*, the European Union's Technical Guidance Document on Risk Assessment (ECB, 2003). Based on a species sensitivity distribution of the NOECs and/or EC10s for the most sensitive aquatic species, an aquatic HC of 38.2 mg/L was derived, which is orders of magnitude greater than the Dutch MPC of 30 µg/L, but only slightly lower than the Dutch SRC_{ECO} of 54 mg/L.

Similar to surface water MPCs, a soil MPC of 1.3 mg Mo/kg for soil (Table 4-6) is conservative because it is based on 100% protection (*i.e.*, no effects at all). To derive the soil MPC, a safety factor of 100 was applied to the NOEC (76 mg/kg) for urease activity inhibition and added to the 90th percentile background soil concentration in the Netherlands (0.5 mg/kg). The results of the McGrath *et al*. (2010a) and van Gestel *et al*. (2010) studies indicate the conservative nature of the Dutch standards. In 10 soils with wide-ranging properties, the NOECs and/or EC10s for several species of terrestrial plants and invertebrates varied widely (McGrath *et al*., 2010a; van

Gestel *et al*., 2010) and, generally, were significantly greater than the Dutch screening criteria in several cases. Like the Dutch criteria, the NOAA SQuiRTs soil screening levels were developed using conservative assumptions and limited data. In effect, soil Mo concentrations below these values can be used to indicate an absence of any adverse effects, but soil concentrations above these values do not necessarily indicate the presence of an ecological problem.

In 1994, US EPA promulgated risk-based values for the permissible levels of Mo in biosolids of 75 mg/kg in sludge (US EPA, 2007). However, most Mo standards were withdrawn following a legal challenge for reassessment and have not been redeveloped (40 CFR Part 503) (US EPA, 2007). In 2001, O'Connor *et al*. (2001) proposed new standards for Mo in biosolids (Table 4-6). They relied on newer and more reliable data (on biosolids Mo concentrations, background soil concentrations, and forage uptake coefficients from field studies using biosolids) and improved the algorithm to account for diet contribution from biosolids-receiving pastures/land and Mo leaching from soil. The resulting cumulative biosolids Mo application limit (RPc) was 40 kg/hectare, and an alternate concentration of Mo in biosolids of 40 mg/kg was proposed.

4.7 Ecological Benchmark Toolbox

Government and private websites and reports provide useful information on Mo ecotoxicity and ecological risk assessment. The list below presents some key resources.

- Cleanup Levels for Hazardous Waste Sites (US EPA examples)
    - Website: http://www.epa.gov/superfund/health/conmedia/soil/index.htm; http://water.epa.gov/drink/contaminants/index.cfm
    - US EPA soil screening guidance documents and drinking water guidance documents.
- Ecological Benchmark Tool (University of Tennessee, 2007)
    - Website: http://rais.ornl.gov/tools/eco_search.php
    - This website provides a searchable database with a comprehensive set of ecotoxicological screening benchmarks for surface water, sediment, and surface soil applicable to a range of aquatic organisms, soil invertebrates, and terrestrial plants. Also provided are the links to supporting technical reports from which the benchmarks were obtained.
- Ecological Risk Analysis: Guidance, Tools, and Applications (ORNL, 2003)
    - Website: http://www.esd.ornl.gov/programs/ecorisk/contaminated_sites.html
    - This page contains information that can be used to conduct screening and baseline ecological risk assessments at hazardous waste sites.
- The Ecotoxicological (ECOTOX) Database (US EPA, 2007)
    - Website: http://cfpub.epa.gov/ecotox/quick_query.htm
    - This searchable database provides aquatic and terrestrial life toxicity data and the associated primary literature references, and can be searched by chemical name.
- IMOA Database of Molybdenum in Human Health and the Environment
    - Website: http://www.imoa.info/HSE/environmental_data/database.html

  - IMOA’s database provides excerpts, summaries, and data from studies and resources pertaining to environmental effects and exposures of Mo.
- Molybdenum Consortium (Formed for REACH Registration)
  - Website: http://www.molybdenumconsortium.org/
  - This is a membership-only website for parties involved in registration of Mo compounds under REACH.
- NOAA’s SQuiRTs (Buchman, 2008)
  - Website: http://response.restoration.noaa.gov/book_shelf/122_NEW-SQuiRTs.pdf
  - SQuiRTs provide ecological screening levels compiled from various sources for Mo in soil, surface water, and groundwater.

5

GEOCHEMISTRY AND FATE AND TRANSPORT

This chapter focuses on the geochemistry and fate and transport of Mo in the environment. The basic chemical and physical properties are presented in Section 5.1, followed in Section 5.2 by a discussion of solid-phase Mo in minerals, soil, sediment, and coal. Section 5.3 describes the aqueous geochemistry of Mo, including speciation, dissolution-precipitation, adsorption-desorption, and oxidation-reduction. Section 5.4 discusses Mo fate and transport, including modeling.

As described in greater detail within this chapter, the most common mineral forms of Mo are molybdenite and wulfenite. It is a chalcophile element and is often associated with sulfidic sedimentary environments. In coal and black shales, Mo is associated with both pyritic and organic fractions (Querol *et al*., 1996; Eskanazy, 2009; Wang *et al*., 2009). Mo is mobilized by oxygenic weathering of black shales.

In oxic waters, molybdate is the principal form of Mo (Ryzhenko, 2010). Similar to other oxyanions such as Cr (VI) and Se (VI), molybdate is relatively mobile in groundwater (Hem, 1985; US EPA, 2005). Mo adsorption on both minerals and organic matter is highly pH-dependent, with peak adsorption at $\text{pH} < 5$ and limited adsorption above a pH of 8 (Goldberg and Forster, 1998). Increases in soil water pH or dissolution of oxide phases can readily mobilize Mo. In alkaline conditions, Mo behaves conservatively (*i.e.*, is mobile), and its dissolved concentration may be controlled by precipitation reactions (Wang *et al*., 1994; Meima *et al*., 2002; Essington, 1992). The environmental chemistry of Mo has been well described in the literature, but there have been fewer attempts to model its environmental fate and transport.

5.1 Basic Chemical and Physical Properties

Mo is a transition metal located in group 6 of the periodic table along with chromium and tungsten. In its pure state, Mo occurs as a silvery white metal (Cotton and Wilkinson, 1988). There are seven naturally occurring isotopes of Mo: 92 (natural abundance 14.84%), 94 (9.25%), 95 (15.92%), 96 (16.68%), 97 (9.55%), 98 (24.13%), and 100 (9.63%). Mo in compounds exists primarily in +4 and +6 oxidation states, but it may also form compounds with -2, 0, +1, +2, +3, and +5 oxidation states (Cotton and Wilkinson, 1988). The most common dissolved form of Mo is the molybdate oxyanion (Ryzhenko, 2010). Table 5-1 provides several additional chemical and physical properties for Mo.

Table 5-1
Basic Chemical and Physical Properties of Molybdenum

Property	Value	Property	Value
Symbol	Mo	Liquid Density (melting point)	9.33 g/cm^3
Atomic Number	42	Melting Point	2896 K; 2623°C
Atomic Mass	95.94 g/mol	Boiling Point	4912 K; 4639°C
Chemical Series	Transition metal	Heat of Fusion	37.48 kJ/mol
Valence States	6, 5, 4, 3, 2, 1, 0, -1, -2	Heat of Vaporization	617 kJ/mol
Room Temperature Phase	Solid	Heat Capacity	24.06 J/mol K
Solid Density (25°C)	10.29 g/cm^3		

5.2 Solid-Phase Geochemistry

5.2.1 Molybdenum Minerals

Mo is the least abundant of the biologically essential trace elements in soil. The mean concentration of Mo in the upper continental crust, from which soil is formed, is 1.4 mg/kg (Wedepohl, 1995). EPRI (2010) reported a range of Mo concentrations in rocks and minerals from < 0.05-640 mg/kg, with a median value of 1.6 mg/kg. There are over 50 identified Mo-bearing minerals, but the most common Mo minerals and primary ore sources are molybdenite and wulfenite. Molybdenite forms from high-temperature hydrothermal fluids associated with porphyry deposits (Smith *et al*., 1997). Wulfenite is usually found in the oxidized zone of mineral deposits containing Mo and lead (Smith *et al*., 1997). Mo is also associated with uranium ore deposits (Dahlkamp, 2009). It can be found in both hydrothermal uranium deposits and sedimentary-hosted uranium deposits associated with changes in redox conditions (Dahlkamp, 2009).

5.2.2 Molybdenum in Soil and Sediment

Pure-phase Mo minerals are generally not found in oxic soil environments. Instead, solid-phase Mo is commonly found adsorbed to iron or aluminum oxides, clay minerals, and/or organic matter such as humics and tannins (Goldberg *et al*., 1996; Wichard *et al*., 2009). In oxic sediment, Mo is often associated with ferromanganese oxides (Bertine and Turekian, 1973; Emerson and Huested, 1991; Morford and Emerson, 1999). In anoxic sediments and shales, Mo is associated with the iron sulfide pyrite (Vorlicek *et al*., 2004), and Mo concentrations in anoxic sediments can be as high as 140 mg/kg (Zheng *et al*., 2000).

5.2.3 Molybdenum in Coal

Coal contains minor amounts of many trace elements that can be incorporated into the coal at the time of deposition or by post-depositional changes, including by mineralizing fluids (Finkelman, 1995). The concentrations of trace elements in coal can vary widely, even within the same coal bed, and may be associated with clay mineral, sulfate, organic, or pyritic fractions (Finkelman, 1995).

The United States Geological Survey (USGS) Coal Quality Database contains 7,430 analyses of Mo in domestic coal samples (USGS, 1998a). Mo concentrations in these samples range from 0.03-280 mg/kg, with a median concentration of 1.7 mg/kg (Figure 5-1). There is not a significant difference in the median concentrations of Mo by coal type, which range from 1.3-2.1 mg/kg (Figure 5-2). There is a slightly wider range in median values, from 1.1-3.0 mg/kg, when coals are categorized by US coal province of origin (Figure 5-3). The higher Mo in interior coals may be related to its generally higher sulfur content (see Figure 5-4 and Section 5.2.3.1).

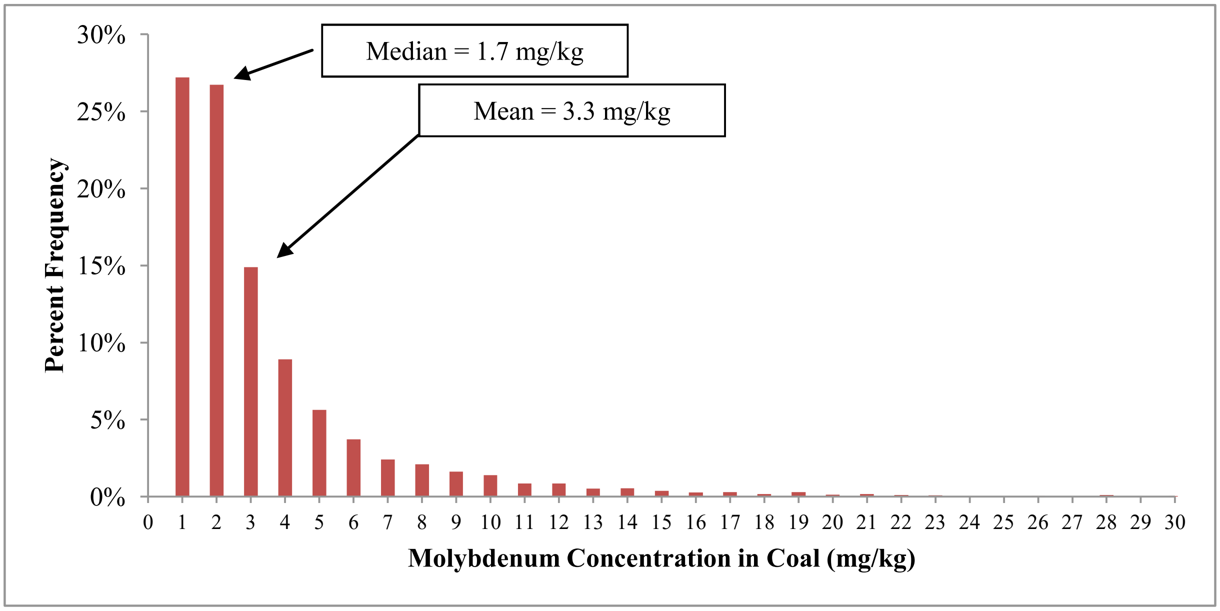


Figure 5-1
Molybdenum Concentration Distribution in Domestic Coal (Histogram)

Notes: Figure represents 99% of the analyses. The highest concentration samples were not plotted.
Data from USGS, 1998a.

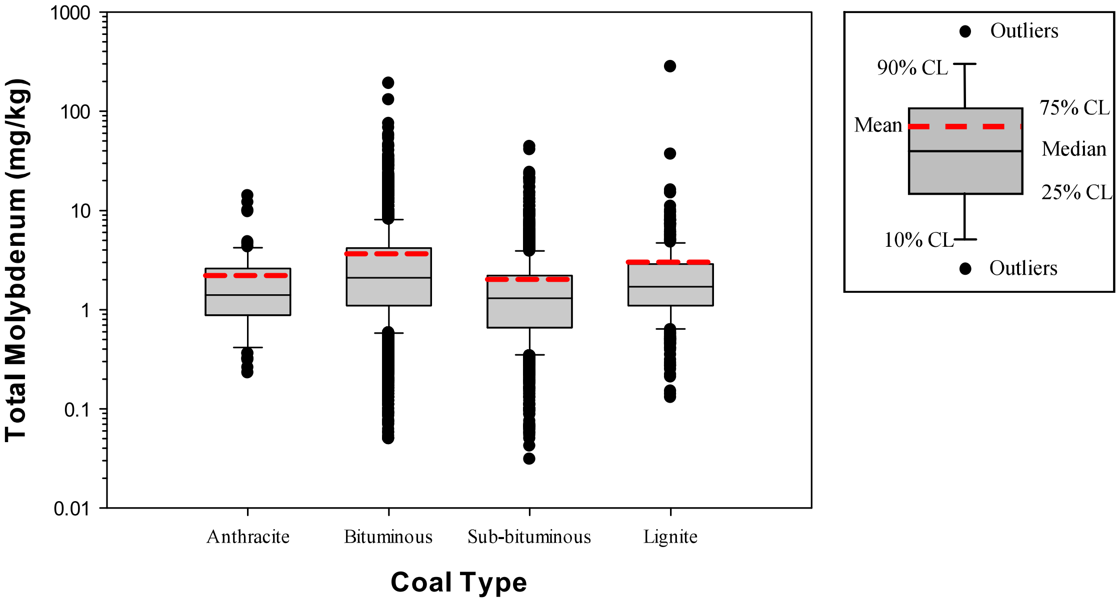


Figure 5-2
Comparison of Molybdenum Concentrations in Coal by Type

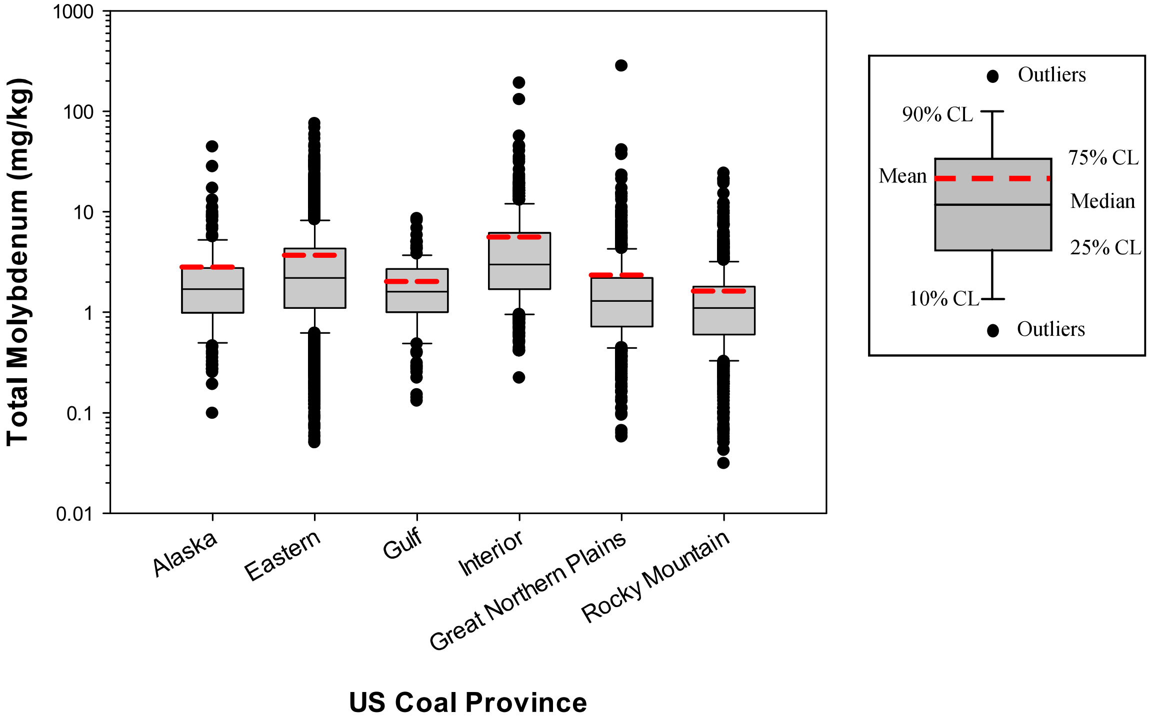


Figure 5-3
Comparison of Molybdenum Concentrations by US Coal Province

Note: Data for Figures 5-2 and 5-3 from USGS, 1998a.

5.2.3.1 Mode of Occurrence

While Mo appears to be associated with both organic and sulfide phases of coal based on leaching studies, x-ray and microprobe analysis have not been performed to confirm this, and there is currently no scientific consensus on this issue (Finkelman, 1995). Coal leaching studies (Querol *et al*., 1996; Eskanazy, 2009; Wang *et al*., 2009) show that Mo is optimally removed under pH conditions that target organic and sulfide-bound elements. Further, Mo's chalcophile tendencies lead to its association with pyrite (FeS_2). In the US, higher-sulfide coals from the Appalachian and Interior regions appear to have higher mean Mo concentrations than coals from other coal regions (Figure 5-4). Pyrites separated from eastern Canadian coal have concentrations of Mo ranging from 35-160 mg/kg (Zodrow and Goodarzi, 1993; Finkelman, 1995; Goodarzi, 2002).

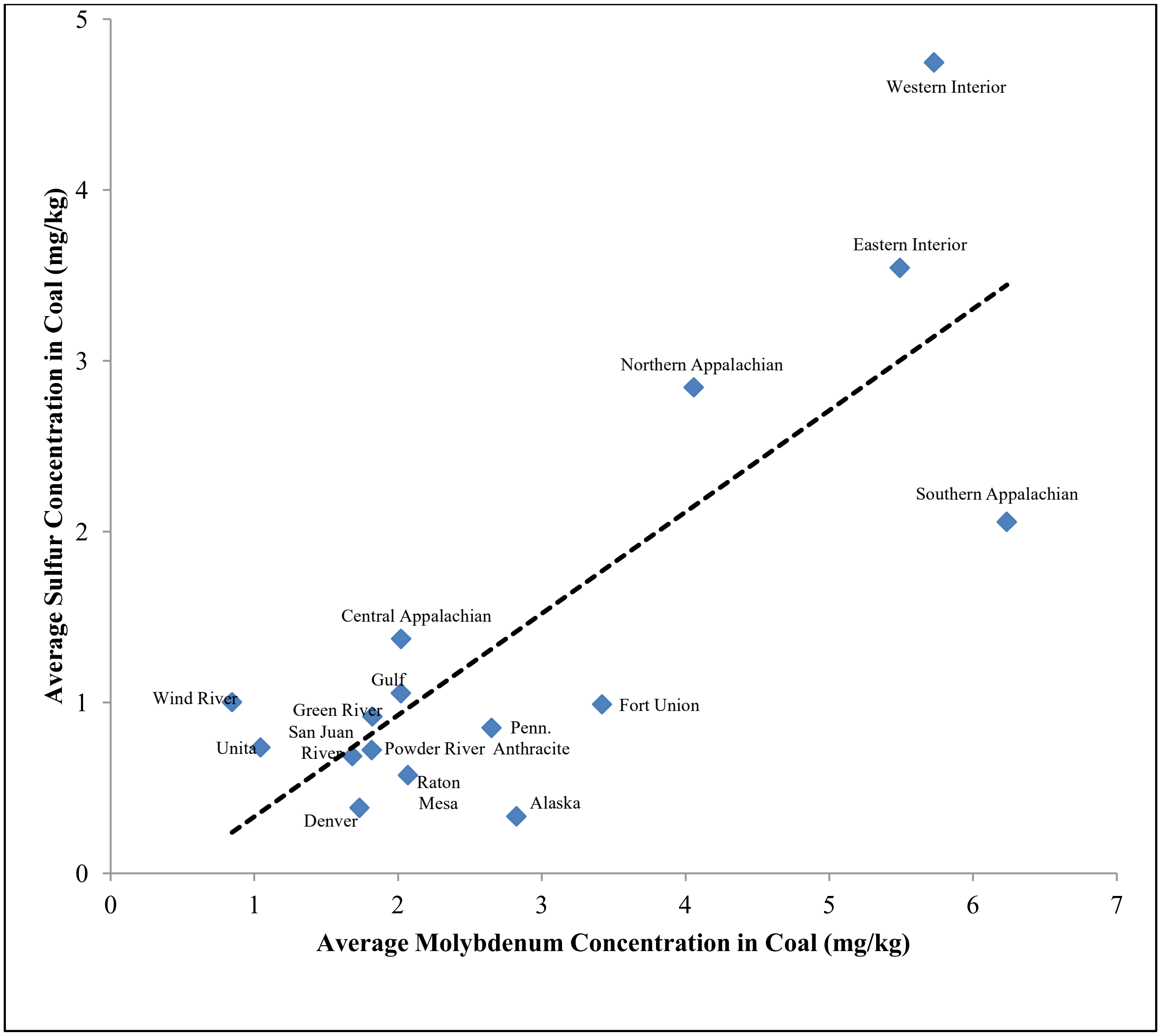


Figure 5-4
Molybdenum Versus Sulfur Concentrations in Coal by US Coal Regions

Note: Data from USGS, 1998a.

5.3 Aqueous Geochemistry

As discussed in Chapter 2, the concentration of Mo in water varies widely. Fresh surface waters and groundwater contain low levels of Mo that are typically below detection (approximately 5 µg/L Mo or less), but concentrations can increase with alkalinity up to hundreds of µg/L (Ryzhenko, 2010; Hem, 1985; WHO, 2003). Oxic seawater average Mo concentrations are higher, at about 10 µg/L (Hem, 1985; Manheim and Landergren, 1978; Ryzhenko, 2010; Bertine and Turekian, 1973). The factors controlling Mo aqueous geochemistry are discussed below.

5.3.1 Speciation

5.3.1.1 Redox State (Eh-pH Diagram)

Eh-pH diagrams represent the equilibrium speciation of a compound under a defined set of conditions (*i.e.*, "redox state"). As such, they are a useful theoretical tool for predicting speciation. It should be recognized, however, that most groundwater systems exist in a state of redox disequilibrium (Langmuir, 1997) due to kinetic or biologic control of reactions. Therefore, while thermodynamically favored, equilibrium may never be reached in some instances.

Ryzhenko (2010) calculated a recent Eh-pH diagram for the Mo-O-H-S system (Figure 5-5), which shows that the molybdate ion dominates Mo aqueous speciation except under low pH (< 4) and anoxic conditions. Molybdate is the most environmentally significant form of Mo (VI) in surface waters and soil solutions (De Schamphelaere *et al*., 2010). Hydrogenated molybdate species ($HMoO_4^-$ and H_2MoO_4) become important at lower pH, below their appropriate acid dissociation constants (pK_a). The acid dissociation constants of molybdate are in the range of pH 2-5, but there is no consensus in the literature (Table 5-2).

Under anoxic conditions, molybdenite is the thermodynamically favored species. The solubility of molybdenite is driven by the reaction:

$$MoS_2 + 12\ H_2O = MoO_4^{2-} + 2SO_4^{2-} + 24\ H^+ + 18e^-$$

Molybdenite dissolution is thought to be a source of Mo during weathering. However, although thermodynamically predicted, molybdenite precipitation rarely occurs under aqueous conditions below 300°C (Helz *et al*., 1996). Redox reactions are more likely than acid dissociation to be kinetically hindered. Molybdenite has not been identified in black shales or anoxic sediments (Vorlicek *et al*., 2004; Helz, *et al*., 1996).

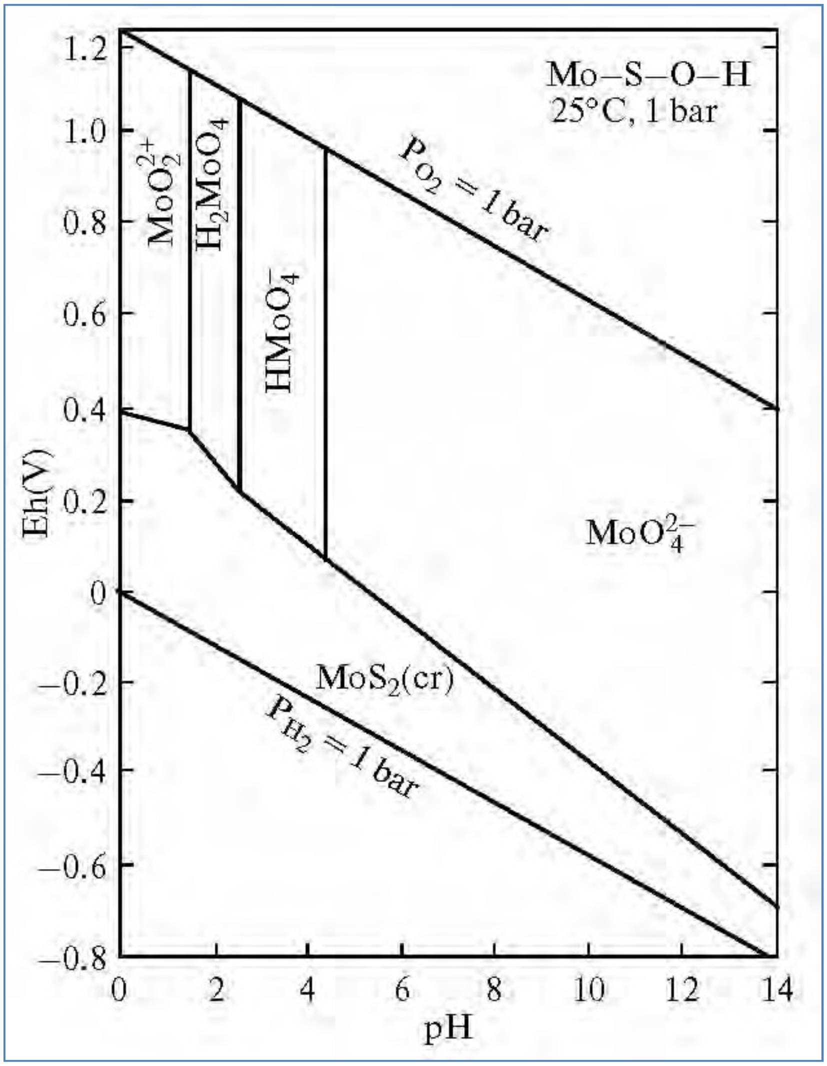


Figure 5-5
Eh-pH Diagram for the Mo-O-H-S System

Notes: *At 25 ° C, concentration of Mo is 10^{-8} M and S 10^{-3} M.*
From Ryzhenko, 2010.

Table 5-2
Molybdate Acid Dissociation Constants

Reaction	pK_a		
	Ryzhenko, 2010	Cruywagen, 1999	Lindsay, 1979
$H_2MoO_4 + 2H^+ = MoO_2^{2+} + 2H_2O$	1.40	N/A	N/A
$H_2MoO_4 = HMoO_4^- + H^+$	2.45	3.74	4.00
$HMoO_4^- = MoO_4^{2-} + H^+$	4.40	3.47	4.24

Note: N/A = not applicable.

5.3.1.2 Speciation with Hydrogen Sulfide

Another factor that influences Mo aqueous speciation is the aqueous concentration of hydrogen sulfide (H_2S). At H_2S concentrations > 10 mg/L, thiomolybdates have been shown to be stable in near-neutral to alkaline waters (Erickson and Helz, 2000). These species do not undergo a redox transition but are the result of replacement of the molybdate oxygen atoms with sulfide atoms, with tetrathiomolybdate as the end product: $MoO_4^{2-} \rightarrow MoO_3S^{2-} \rightarrow MoO_2S_2^{2-} \rightarrow MoOS_3^{2-} \rightarrow MoS_4^{2-}$ (Erickson and Helz, 2000; Ryzhenko, 2010). Tetrathiomolybdates are soft ligands and rapidly bind with other transition metals and particles. Tetrathiomolybdate has an extremely high affinity for copper, and it will also bind other trace elements (iron, zinc) to a lesser degree. Helz *et al*. (1996) have proposed the concept of a "sulfide switch" to describe this behavior, in which HS^- transforms the behavior of aqueous Mo from that of a conservative element to that of a particle reactive element. This mechanism removes the role of reduction in Mo scavenging in favor of forming Mo bonds with metals and organics via S bridges.

5.3.1.3 Speciation with Dissolved Organic Matter

Mo is not bound by most organic compounds, but there is some evidence that Mo may be associated with humic acids and tannins. Mo has the highest affinity for catechol groups such as those found in azotochelin, a compound produced by nitrogen-fixing soil bacteria that aids in the uptake of iron and Mo (the two metals required for nitrogen fixation). Tannins contain catechol groups that have been shown to bind Mo in leaf litter extract and also may bind Mo in the dissolved phase (Wichard *et al*., 2009). The interaction between Mo and organic matter is discussed further below.

5.3.2 Solid-Liquid Partitioning

As described previously, the aqueous concentration of Mo is affected by interaction with solid phases through the processes of precipitation-dissolution and adsorption-desorption. These processes are in turn influenced by dissolved phase speciation.

5.3.2.1 Precipitation-Dissolution

Many Mo minerals are highly soluble under neutral to basic conditions (see Table 5-3). For example, molybdenite is stable in acidic conditions but, under neutral or basic conditions, it is weathered and oxidized, mobilizing Mo as molybdate. As discussed above, molybdenite precipitation is kinetically hindered in most soil environments. While molybdate reduction and precipitation as molybdenite has long been thought to be the ultimate sink for Mo in anoxic sediments, empirical measurements have failed to identify molybdenite in anoxic sediments (Bostick *et al*., 2003; Helz *et al*., 1996). X-ray adsorption analyses of Mo-rich shales and sediments and in laboratory experiments with pyrite have found Mo absorbed to iron phases rather than precipitated as molybdenite (Helz *et al*., 1996; Bostick *et al*., 2003). These data suggest that adsorption of thiomolybdates, rather than direct precipitation as molybdenite, may be the mechanism for Mo removal in anoxic sediments. This has implications for the ease of remobilization of Mo in sediments. Adsorbed species are generally remobilized more easily than the less soluble molybdenite upon reoxygenation (Helz *et al*., 1996).

Table 5-3
Molybdenum Mineral Solubility

Mineral	Formula	Solubility (mg/L) 25°C pH 7.0	log Solubility Constant (K_{sp})
Ferrous Molybdate	$Fe(III)_3(MoO_4)_2$	20	NR
Ferrimolybdite	$Fe(II)MoO_4$	15	-7.76
Powellite	$CaMoO_4$	10	-7.02 to -8.51
Molybdite	MoO_3	2.6	-4.47
Molybdenite	MoS_2	0.2	NR
Wulfenite	$PbMoO_4$	Relatively Insoluble	-16

Notes: NR = not reported.

Source: Essington (1990); Wang et al. (1994).

Lindsay (1979) gave the following sequence for the solubility of Mo minerals in soils: $CuMoO_4 > ZnMoO_4 > MoO_3 > H_2MoO_4 > CaMoO_4 > PbMoO_4$. Wulfenite is an extremely stable Mo solid (log $K_{sp} = -16$). In environments where a source of lead is available, the formation of wulfenite may be a sink for Mo. Wang *et al*. (1994) investigated Mo solubility in soil from a surface coal mine, soil near a coal mine, and native soil in the Powder River Basin. These results suggested that, when corrected for the effect of fulvic acid complexation of lead, these soils were approaching saturations for wulfenite, implying that dissolved Mo concentrations in these soils may be controlled by wulfenite precipitation. In areas without a source of lead, powellite has been predicted to be the controlling phase for Mo in alkaline materials. Powellite is slightly soluble, with an estimated log K_{sp} ranging from -7.02 to -8.51 (Essington, 1990). Powellite has been suggested to be the controlling phase in alkaline municipal solid waste leachates (Meima *et al*., 2002). In natural waters with elevated Fe (II) concentrations, $Fe(II)MoO_4$ precipitation may occur; however, elevated Fe (II) is thermodynamically favored only at pH < 6 (Stumm and Morgan, 1981), a region where, as discussed below, significant Mo adsorption is expected.

5.3.2.2 Adsorption/Desorption

Mo adsorption is highly pH-dependent. Adsorption on all minerals investigated shows maximum Mo adsorption at $\mathrm{pH} < 5$ (Goldberg *et al*., 1996; Goldberg and Forster, 1998). Mo behaves conservatively in alkaline seawater (Emerson and Huested, 1991) and groundwater aquifers (Hodge *et al*., 1996). The pH effect on molybdate adsorption is likely related to the pH-dependent surface charges common in oxyhydroxides. Many oxyhydroxides have isoelectric points (IEPs, the pH at which oxide surface charge transitions from positive to negative) in the pH range of 4-8, where Mo adsorption drops off rapidly (Table 5-4). In addition, it is common for anions to exhibit peak adsorption that coincides with their $\mathrm{p}K_a$ values; for Mo, this occurs near pH 4 (Barrow, 1977, as cited in Chappell and Peterson, 1977).

Competing ions can limit Mo adsorption by soils and minerals. A variety of oxyanions (SO_4^{2-}, PO_4^{2-}, SeO_4^{2-}, WO_4^{2-}, SiO_4^{2-}, AsO_4^{2-}) have been investigated to determine their effect on Mo adsorption. Generally, oxyanions compete with each other for adsorption sites, and concentration ratios between oxyanions can play an important role in determining adsorption. The adsorption affinity for oxyanions on a volcanic soil was determined to be $PO_4^{2-} > SeO_3^{2-} > MoO_4^{2-} \geq AsO_4^{2-} > > SeO_4^{2} \geq CrO_4^{2-}$ (Saeki, 2008). Equimolar concentrations of phosphate, arsenate, selenate, or tungstate have been shown to depress Mo uptake on aluminum and iron oxides, but silicate had little effect (Xu *et al*., 2006; Goldberg, 2009). The presence of sulfate depresses Mo uptake on aluminum oxides (Goldberg, 2009) but not iron oxides (Xu *et al*., 2006), even at concentration ratios more reflective of natural systems (1:100). In soil, sulfate has been found to depress Mo adsorption occasionally, but not consistently (Goldberg *et al*., 1996). Phosphate decreased Mo adsorption in all soil tested (Goldberg *et al*., 1996; Goldberg and Forster, 1998).

The solid characteristics of the aborbent, including the surface area (S_A) and site density (N_S), describe the potential sorption capacity of the solid. These values set a limit on the total amount of Mo adsorption that can take place. Adsorption of trace elements can occur either by outer-sphere complexation, driven by electrostatic attraction between ions and the mineral surface, or inner-sphere complexation, which includes the formation of coordinate bonds between the ion and the mineral surface. Inner-sphere complexation tends to be stronger and less easily reversible than outer-sphere complexation. Table 5-4 describes properties of some Mo sorbents, which are discussed further below. Ferrihydrate shows the greatest number of potential sites for Mo adsorption on a per gram basis [adsorption sites available (sites/g) = N_S (sites/nm^2) x 10^{18} (nm^2/m^2) x S_A (m^2/g)], followed by fresh manganese oxides. These are also considered the two most important phases for Mo adsorption in nature (Goldberg *et al*., 1996). Appendix A provides more detail on specific Mo sorbents.

Table 5-4
Properties of Molybdenum Sorbents

Type	Solid	IEP (pH)	S_A (m^2/g)	N_S (sites/nm^2)
Fe/Mn Oxides and Oxyhydroxides	Fe_2O_3 (Hematite)	4.2-6.9	1.8	22-55
	$Fe(OH)_3$ (Ferrihydrate)	8.5-8.8	250-600	20
	FeOOH (Goethite)	5.9-6.7	45-169	2.6-16.8
	MnO_2 (Birnessite)	4.5	290 (fresh), 143 (weathered), 180 (natural)	18 (fresh), 2 (weathered)
Al Oxides and Clay Minerals	$Al(OH)_3$ (Gibbsite)	9.4	120	2-12
	$Al_2Si_2O_5(OH)_4$ (Kaolinite)	2.9	9.1-19.3	NR
Pyrite	FeS_2 (Pyrite)	7.6	NR	NR

Notes: S_A = surface area; N_S = number of adsorption sites; NR = not reported; IEP = isoelectric point.

Sources: Langmuir, 1997; EPRI, 2006a.

5.4 Environmental Fate and Transport in Groundwater

To summarize, Mo mobility in soils and groundwater is primarily controlled by adsorption-desorption and precipitation-dissolution reactions. The key factors controlling Mo mobility are groundwater pH, redox conditions, and the presence of competing oxyanions. Mo adsorption on both minerals and organic matter is highly pH-dependent, with peak adsorption at pH < 5 and limited adsorption above pH 8. Phosphate and several other oxyanions will depress Mo adsorption. Mo desorbs from most soils with a change in pH or competing ion concentrations (phosphate in particular). Permanent fixation of Mo requires anoxic conditions and pyrite. Thiomolybdates, formed by the replacement of the molybdate oxygen with sulfur when H_2S concentrations are elevated, appear to be irreversibly scavenged by pyrite. This mechanism has been proposed to sequester Mo in anoxic sediments. In neutral to alkaline conditions, Mo adsorption is minimal and Mo dissolved concentrations may be controlled by precipitation. In the presence of excess lead, precipitation of wulfenite has been shown to control dissolved Mo concentrations in soils near coal mines (Wang *et al.*, 1994). In the absence of elevated lead concentrations, Mo dissolved concentrations may be controlled by powellite precipitation, resulting in potential equilibrium Mo concentrations on the order of 10 mg/L (Meima *et al.*, 2002; Essington, 1992).

5.4.1 Distribution Coefficients

Soil-water bulk distribution coefficients (K_d) are used to estimate the mobility of an element in groundwater. The K_d is the ratio of the mass of a constituent adsorbed to the solids over the mass in solution, and it is generally reported as L/kg. When the K_d approaches zero, the constituent behaves conservatively and remains in the dissolved phase. It will travel at the same velocity as groundwater. When the K_d is above zero, the constituent reacts with the solid matrix and travels at a rate slower than the velocity of the groundwater. For example, a constituent with a K_d of approximately 2 L/kg will travel at approximately one-tenth the velocity of groundwater (EPRI, 2006a).

Relatively few experimental bulk distribution coefficients for Mo have been reported in the literature. After an extensive literature survey, US EPA (2005) found only eight reported values, with pH conditions ranging from 4-10. The median K_d was 12.6 L/kg, with a reported range of 0.6-501 L/kg. Mo distribution coefficients are similar to other oxyanions, all of which are highly mobile in groundwater under neutral to alkaline conditions (Table 5-5).

Table 5-5
Experimental Metal-Soil Water Distribution Coefficients

	Distribution Coefficient (K_d)				Median Retardation Factor	Median Velocity Relative to Groundwater[1]
Element	**Median (L/kg)**	**Minimum (L/kg)**	**Maximum (L/kg)**	**N**	**(R_d)**	**(V_c/V_{gw})**
As	2512	2.0	19900	22	15500	0.00006
Cr (III)	7940	10.0	50100	43	49000	0.00002
Cr (IV)	12.6	0.2	1990	24	79	0.013
Mo	12.6	0.6	501	8	79	0.013
Se	10.0	0.5	251	23	63	0.016
V	NA	12.6	501	2	NA	NA

Notes: *[1] $V_c/V_{gw} = 1/R_d = 1 + K_d$ * Bulk Density / Porosity; R_d = retardation coefficient; K_d = distribution coefficient. Assumes a bulk density of 1.85 kg/L and porosity of 0.3.*

Source: US EPA (2005).

K_d values can also be estimated for specific soil and groundwater conditions using aqueous speciation models. For the Human and Ecological Risk Assessment of Coal Combustion Wastes (US EPA, 2010a), US EPA used MINTEQA2 to model adsorption of groundwater constituents to soil for a range of conditions representing coal combustion leachate (US EPA, 2001). The resulting K_d values were all 2 L/kg or below (Table 5-6), suggesting that the US EPA model characterizes Mo as relatively mobile in groundwater at CCP sites.

Table 5-6
Distribution Coefficients Calculated for Coal Combustion Waste Leachate

Leachate Source	Land Fill/Surface Impoundment	Soil Zone	Distribution Coefficients (K_d) 10% CL (L/kg)	Mean (L/kg)	90% CL (L/kg)
Ash	LF	Saturated	< 0.0001	0.0018	0.37
	SI	Saturated	< 0.0001	0.0043	0.24
	LF	Unsaturated	0.023	0.34	2.0
	SI	Unsaturated	< 0.0001	0.16	1.3
Ash & Coal Refuse	LF	Saturated	< 0.0001	0.0025	0.27
	SI	Saturated	< 0.0001	0.011	0.31
	LF	Unsaturated	< 0.0001	0.21	2.0
Fluidized Bed Combustion	LF	Saturated	< 0.0001	0.0001	0.027
	LF	Unsaturated	< 0.0001	0.23	1.9

Notes: Source: US EPA, 2010a.
CL= Confidence Limit

5.4.2 Fate and Transport Models

Reactive transport models incorporate adsorption-desorption reactions via empirical relationships or surface complexation models (SCMs) that represent the adsorption process. Empirical models, which include a bulk K_d based on Langmuir and/or Freundlich isotherm equations, are more commonly incorporated into transport models, but they do not address the effects of variable chemical conditions like pH or other dissolved constituents. Most US EPA or USGS-supported transport codes use empirical relationships to describe adsorption (Goldberg *et al.*, 2007). SCMs describe adsorption as a process analogous to aqueous-phase reactions. Examples of SCMs applied to Mo adsorption, and references for further information on these models, include:

- Constant capacitance model (CCM): Goldberg *et al.*, 1996, 2002; Goldberg and Forster, 1998; Saripalli *et al.*, 2002
- Diffuse layer model (DLM): Dzombak and Morel, 1990; Stollenwerk, 1995; Gustafsson, 2003
- Triple layer model (TLM): Goldberg and Forster, 1998; Wu *et al.*, 2001
- CD-MUSIC model: Gustafsson, 2003; Xu *et al.*, 2006

SCM models may require a large number of variables to describe the adsorption process. These variables may not be known for a field site, which can make it difficult to incorporate SCMs into transport modeling. However, several researchers who have used SCMs to predict Mo adsorption on suites of soil samples have found that Mo adsorption can be described successfully using a relatively limited number of parameters:

- Goldberg *et al*. (2002) used the CCM to predict molybdate adsorption by soils. Mo adsorption was predicted successfully in 36 different soils by using four independently measured soil parameters: cation exchange capacity, OC content, inorganic carbon content, and iron oxide content.
- Dijkstra *et al*. (2009) used a multi-surface sorption model to predict trace metal leaching from a variety of industrial soils. This approach included aqueous speciation in combination with sorption to organic matter, iron/aluminum (hydr)oxides, and clay. The model relied on total available metal concentrations, concentrations of reactive surfaces (organic matter, iron/aluminum (hydr)oxides and clay), pH, and redox potential to estimate Mo leaching.
- Rodrigues *et al*. (2010) used a multiple regression analysis to compare trace metal concentrations measured in a suite of 136 Portuguese soils with those predicted using empirical Freundlich isotherms combined with a mechanistically based speciation model (ORCHESTRA with the NICA-Donnan model). They found that available Mo could be described successfully by total reactive metal content, pH, OC concentration, and clay concentration.

In one of the few successful applications of a field-scale SCM, Stollenwerk (1995) used a DLM calibrated to simulate molybdate transport in soil columns to predict Mo transport in a shallow sandy aquifer. This work was part of a large-scale natural gradient tracer test performed on Cape Cod, Massachusetts, where molybdate was used as a reactive tracer (in comparison to bromide, the non-reactive tracer). The Mo concentration distribution was asymmetric, with the maximum concentrations found at the leading edge with a long dilute tail. This is consistent with the understanding of molybdate rapid adsorption to soil, followed by a slow desorption. Stollenwerk (1995) identified pH, phosphate, and, to a lesser extent, sulfate concentrations as the primary factors affecting molybdate adsorption. Mo adsorption was the highest at the surface (which had low pH and phosphate and sulfate concentrations) and decreased at depth (which had higher pH and phosphate and sulfate concentrations). The DLM model was limited in its ability to simulate mass transfer, and the MINTEQ model used for chemical speciation was limited in its ability to account for reaction kinetics. The main results of these limitations appeared to be under-prediction of the amount of time it took for Mo to be removed from an aquifer.

More recently, Carroll *et al*. (2006) used the PHREEQC model to predict Mo transport in bio-solid amended, alkaline, agricultural soil. The K_d of Mo in the control and bio-solid amended soils was determined experimentally to be 0.29 L/kg and 1.24 L/kg, respectively. The adsorption of Mo was predicted using the DLM model, similar to Stollenwerk (1998). The Mo adsorption was higher in the amended soils and agreed with experimental results. Adsorption was rate-limited and reversible. The results showed that Mo was only temporarily adsorbed when applied to alkaline agricultural soils and was rapidly leached (Carroll *et al*., 2006).

6
COAL COMBUSTION PRODUCTS

This chapter discusses the occurrence of Mo in CCPs and leaching of Mo at CCP disposal sites.

6.1 Molybdenum Concentrations in Coal Combustion Products

Like coal, CCPs also contain minor amounts of trace elements, including Mo, the concentration of which varies depending on the CCP type. Mo volatilizes and is carried along with flue gas after coal is combusted (Vories and Throgmorton, 2002; Querol *et al*., 1995). Partial condensation in the particulate collection and FGD systems results in the capture and recovery of Mo in fly ash and FGD residuals (Querol *et al*., 1995).

6.1.1 Concentrations

This section describes the concentration of Mo in CCPs based on the EPRI (2011a) dataset. The EPRI dataset consists of 227 CCP samples collected from 76 power plants categorized into the following CCP types: fly ash, bottom ash, mixed coal ash (fly ash with bottom ash), FGD scrubber sludge (FGD SS) solids (calcium sulfite hemihydrate from wet scrubbers with inhibited or natural oxidation), and FGD gypsum (calcium sulfate dihydrate from wet scrubbers with forced oxidation). The concentration of Mo in these samples ranged from 0.04-236 mg/kg, with a mean of 19.2 mg/kg and a median of 11.2 mg/kg.

Table 6-1 presents summary statistics of Mo concentrations in the different CCP types. This table shows both discrete sampling results for each CCP type, as well as plant average data where all of the discrete samples collected from each plant for the stated CCP type have been averaged into a single value. Figure 6-1 depicts these plant-averaged concentrations by CCP type. As can be seen from Table 6-1 and Figure 6-1, the highest median and maximum concentrations of Mo are associated with fly ash and mixed coal ash, followed by bottom ash and FGD SS, then FGD gypsum. Figure 6-2 (a-e) displays further detail of the EPRI (2011a) dataset, showing the range in Mo concentration from discrete CCP samples collected at individual plants. Based on the EPRI (2011a) dataset, ash samples typically have concentrations of approximately 10-20 mg/kg Mo, but can range up to 100 mg/kg or more in some instances. The Mo concentration in FGD SS typically ranges from about 1 to10 mg/kg, and FGD gypsum samples typically have concentrations < 1 mg/kg Mo.

Table 6-1
Molybdenum Concentration in CCPs – Summary Statistics

CCP Type	# of Discrete Samples	# of Utility Plants	# of Non-Detects	Discrete Sample Data (mg/kg)[2]			Plant Average Data (mg/kg)[2]		
				Mean	Median	Range	Mean	Median	Range
Fly Ash	81	50	0	26.2	16.0	2.0-236.0	28.4	18.5	4.5-138.9
Bottom Ash	38	30	2	13.5	11.0	0.9-45.5	13.7	11.2	0.9-45.5
Mixed Coal Ash[1]	52	7	22	29.6	15.9	0.9-140	27.4	25.2	1.1-53.9
FGD SS[3]	22	10	9	7.1	5.6	0.6-52.6	10.2	7.4	0.8-52.6
FGD Gypsum	34	29	0	0.7	0.6	0.044-3.1	0.7	0.6	0.044-3.1

Notes: *[1] Mixed coal ash is a mixture of bottom ash and fly ash.*
[2] Non-detects included at one-half the reported detection limit.
[3] FGD scrubber sludge (calcium sulfite)

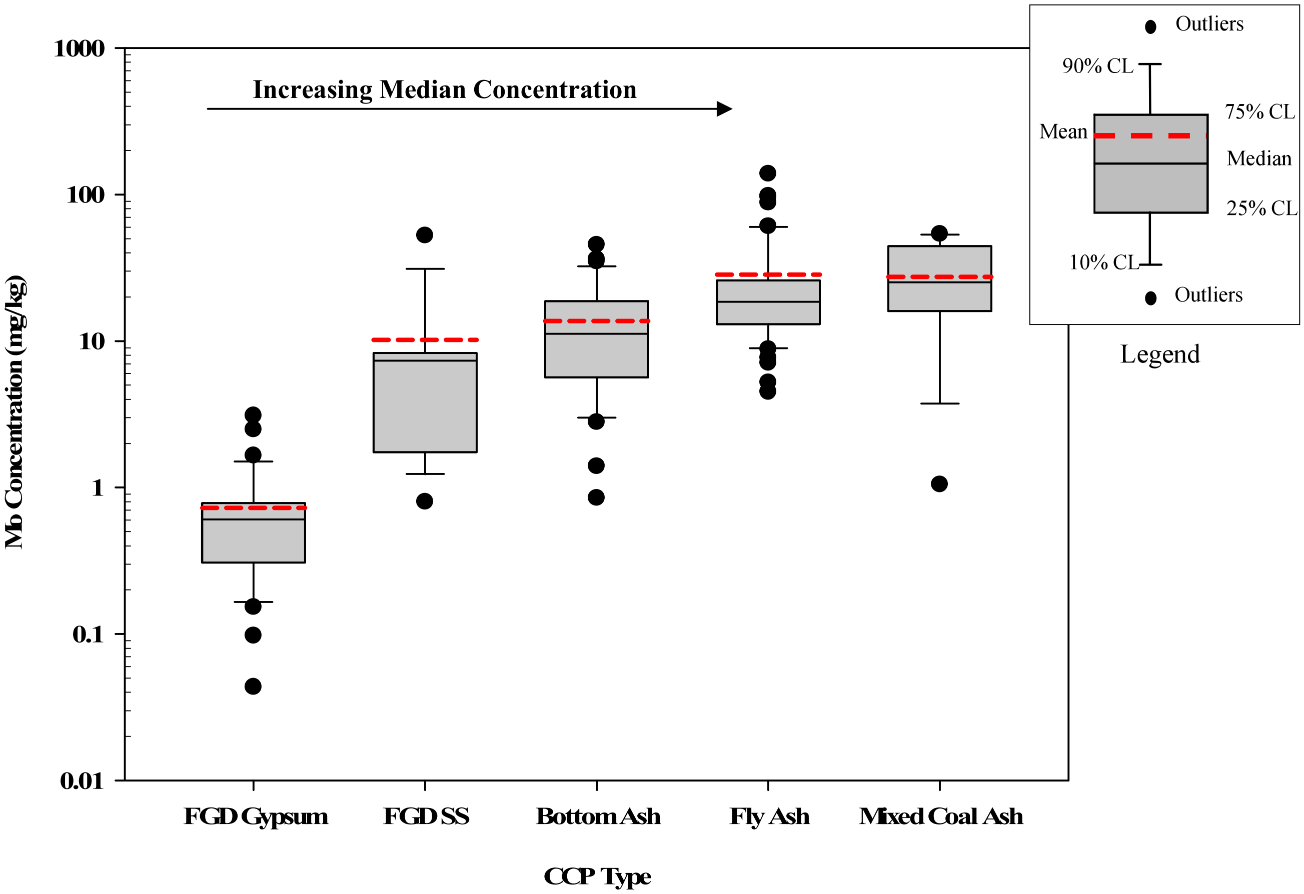
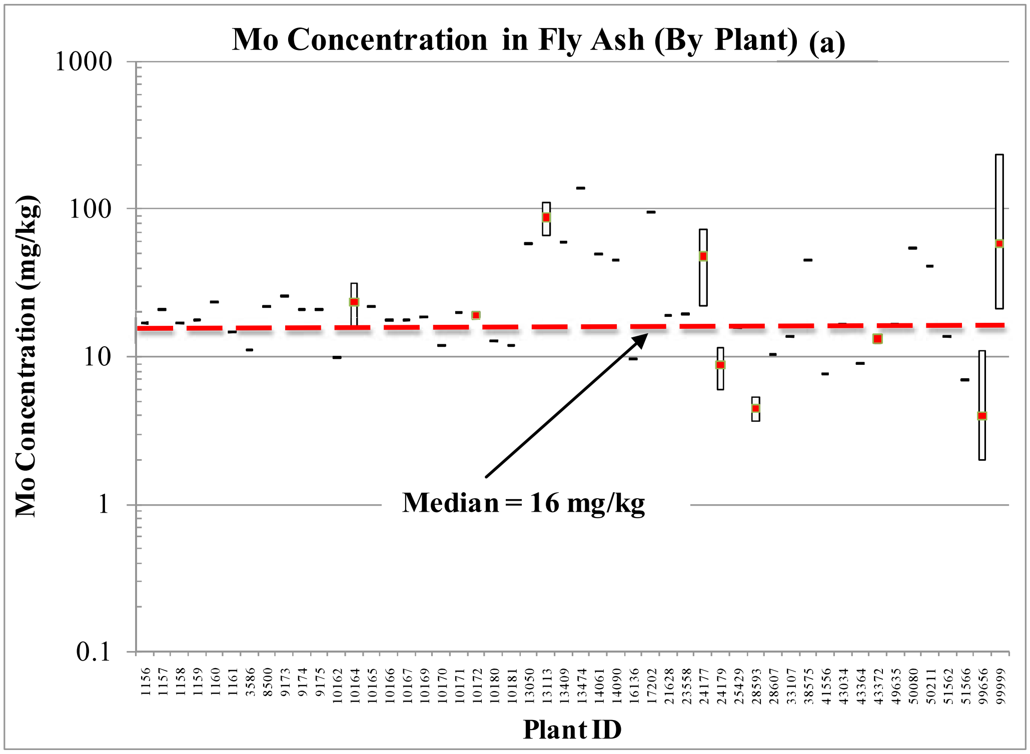
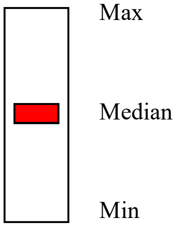
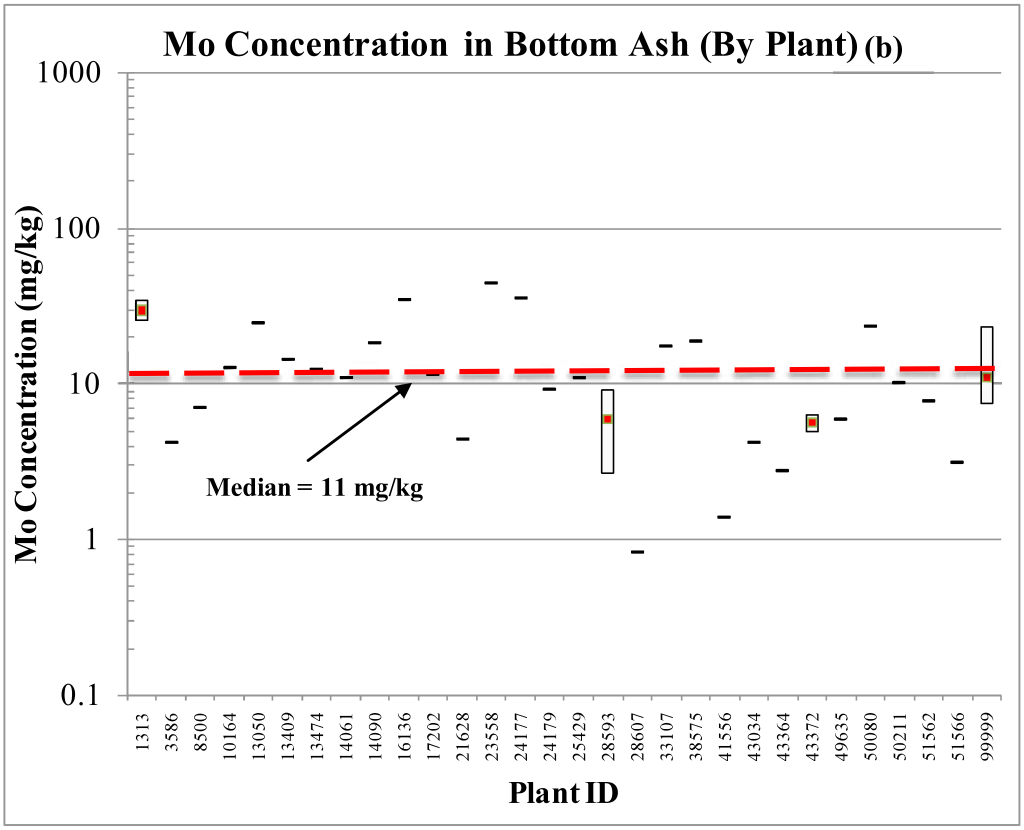


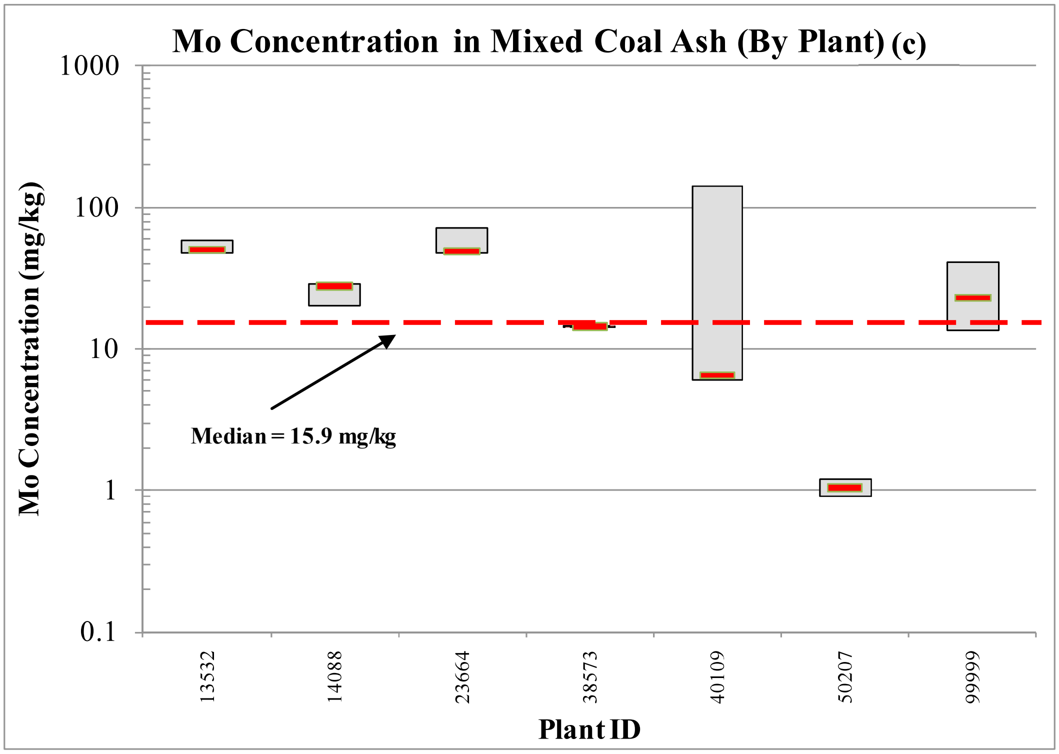
Figure 6-1
Molybdenum Concentrations in CCPs by CCP Type – Plant-Averaged Values

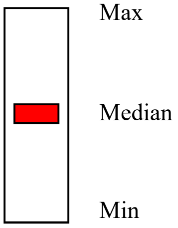
Notes: *See Table 6-1 for details.*
Data obtained from EPRI (2011a) dataset.

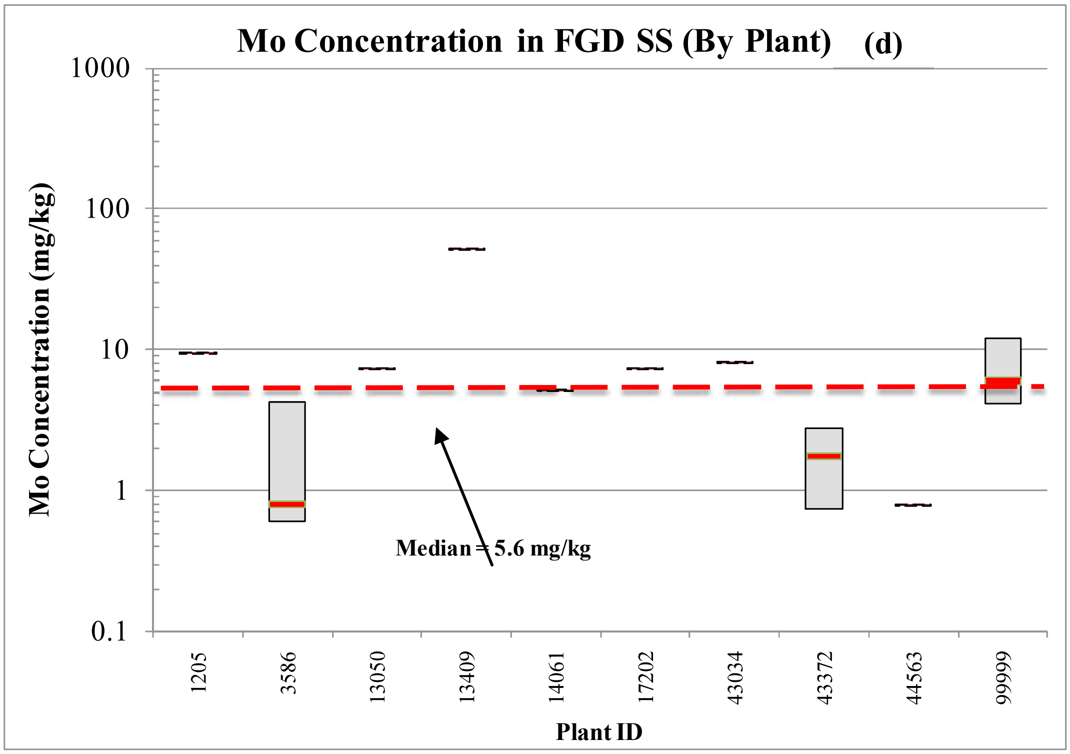

Mo Concentration in Fly Ash (By Plant) (a)
Mo Concentration (mg/kg)
1000
100
10
1
0.1
Median = 16 mg/kg
1156
1157
1158
1159
1160
1161
3586
8500
9173
9174
9175
10162
10164
10165
10166
10167
10169
10170
10171
10172
10180
10181
13050
1313
13409
13474
14061
14090
16136
17202
21628
23558
24177
24179
25429
28593
28607
33107
38575
41556
43034
43364
43372
49635
50080
50211
51562
51566
99656
99999
Plant ID


Max
Median
Min


Mo Concentration in Bottom Ash (By Plant) (b)
Mo Concentration (mg/kg)
1000
100
10
1
0.1
Median = 11 mg/kg
1313
3586
8500
10164
13050
13409
13474
14061
14090
16136
17202
21628
23558
24177
24179
25429
28593
28607
33107
38575
41556
43034
43364
43372
49635
50080
50211
51562
51566
99999
Plant ID


Mo Concentration in Mixed Coal Ash (By Plant) (c)
Mo Concentration (mg/kg)
1000
100
10
1
0.1
Median = 15.9 mg/kg
13532
14088
23664
38573
40109
50207
99999
Plant ID


Max
Median
Min


Mo Concentration in FGD SS (By Plant) (d)
Mo Concentration (mg/kg)
1000
100
10
1
0.1
Median = 5.6 mg/kg
1205
3586
13050
13409
14061
17202
43034
43372
44563
99999
Plant ID

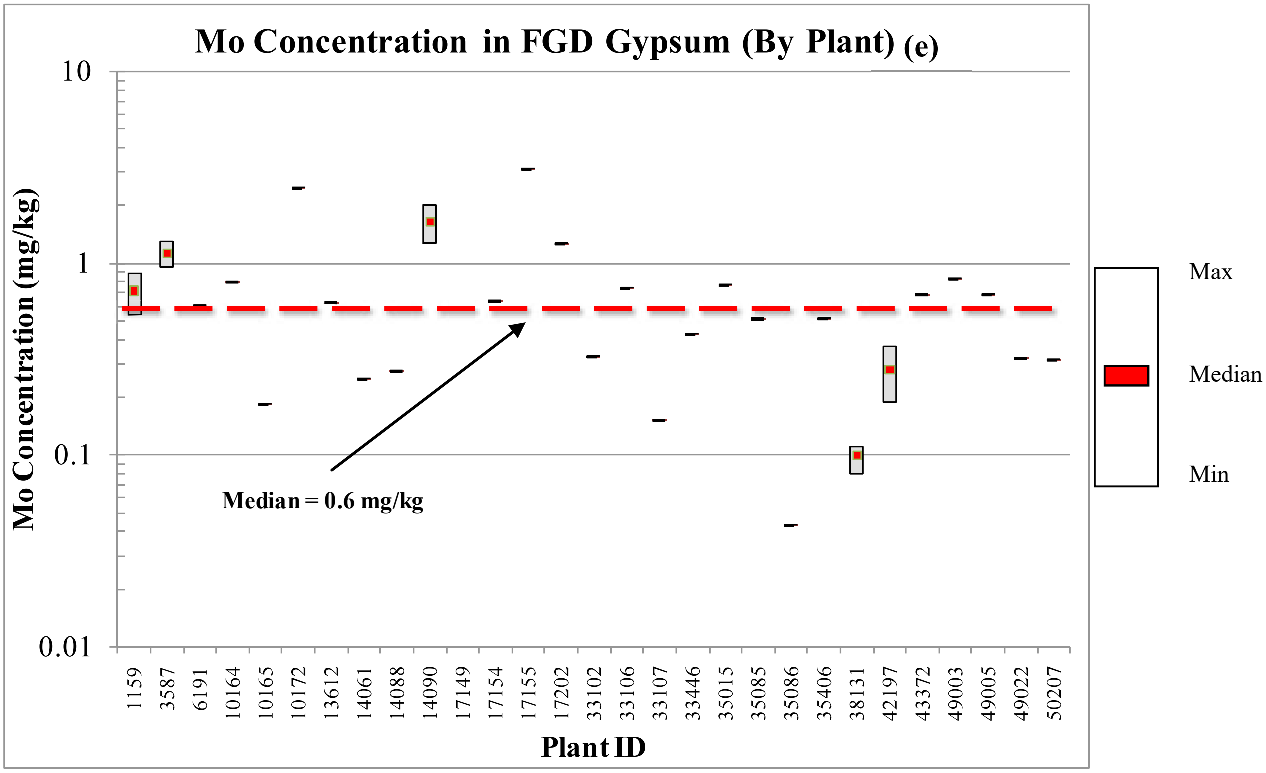


Figure 6-2 (a-e)
Molybdenum Concentrations in CCPs by Plant

The concentrations of Mo reported from the EPRI (2011a) dataset are generally consistent with other scientific literature. For example, Querol *et al*. (1995, 1996) determined the mean Mo concentrations in fly ash samples to be approximately 15 mg/kg. It was noted in the Querol *et al.* (1995, 1996) studies that Mo is more enriched in the smaller fly ash particles (< 2.5 µm) compared to larger size particles. In the Thorneloe *et al.* (2010) study, the range of Mo concentrations for 34 fly ash samples was 6.6-77 mg/kg, and the range of Mo concentrations in the FGD gypsum samples was 1.1-12 mg/kg. Querol *et al*. (1995) noted that Mo exhibited dual behavior during coal combustion: (1) volatilization during combustion; and (2) partial condensation of particles of high surface areas during flue gas and particulate removal (in the ESP and scrubbers), which would explain the observed Mo concentration in fly ash and FGD material. The variability within each CCP type can arise due to (1) variability in Mo concentration in the parent coal used; (2) variability due to differing combustion and emissions control technologies; and/or (3) the application of different analytical methods to measure Mo in CCPs. In addition, the waste management units typically accept CCPs generated from different coal types and separation technologies, potentially resulting in a concentration variance within an individual site.

6.1.2 Mode of Occurrence

Even though the characteristics and mineralogy of CCPs are well documented in literature, there is little information on the speciation and mode of occurrence of Mo in CCPs. The predominant mineral fractions in CCPs are oxides of aluminum (Al_2O_3), silicon (SiO_2), and iron (Fe_2O_3 or Fe_3O_4) (Hower *et al*., 2005). Other metal oxides, such as calcium and titanium oxide, also are present in coal ash and bottom ash in relatively minor quantities. Querol *et al*. (1996) noted that Mo has a greater affinity to iron oxides, calcium oxides, and calcium sulfate in CCPs. In their study, Querol *et al*. (1996) found that more than 40% of total Mo in fly ash was associated with readily leachable salts or oxides, such as metal sulfates and amorphous metal oxides. The remaining 60% of Mo was found to be associated with stable and/or recalcitrant minerals, such as crystalline iron oxides and alumino-silicate oxides. It was noted that, after combustion, Mo travels along with the flue gas and is captured with iron oxides, or it is sorbed onto calcium salts during the scrubbing process.

6.2 Molybdenum Concentrations in CCP Leachate

6.2.1 Factors that Affect Molybdenum Leaching Behavior in CCPs

6.2.1.1 pH

The pH of a CCP is determined primarily by the sulfur and calcium content of the parent coal and the type of coal combustion process that is used. The pH of CCPs affects the leachate pH, which in turn influences the mobility of metals, including Mo (Thorneloe *et al*., 2010; Carlson and Adriano, 1993; US EPA, 2009c). The effect of pH on the leaching behavior of Mo in CCPs is depicted in Figure 6-3, which is an illustrative leaching profile for fly ash at one plant as a function of pH (leaching profiles from other ashes included in US EPA, 2009c, show similar trends). This figure shows the general trend of higher Mo leaching in acidic and alkaline pH conditions and reduced leaching in the near neutral pH region. However, other factors besides pH (*e.g.*, total Mo concentration, the amount of calcium and sulfur present) influence both the shape of the leaching profile and the resulting leachate Mo concentrations.

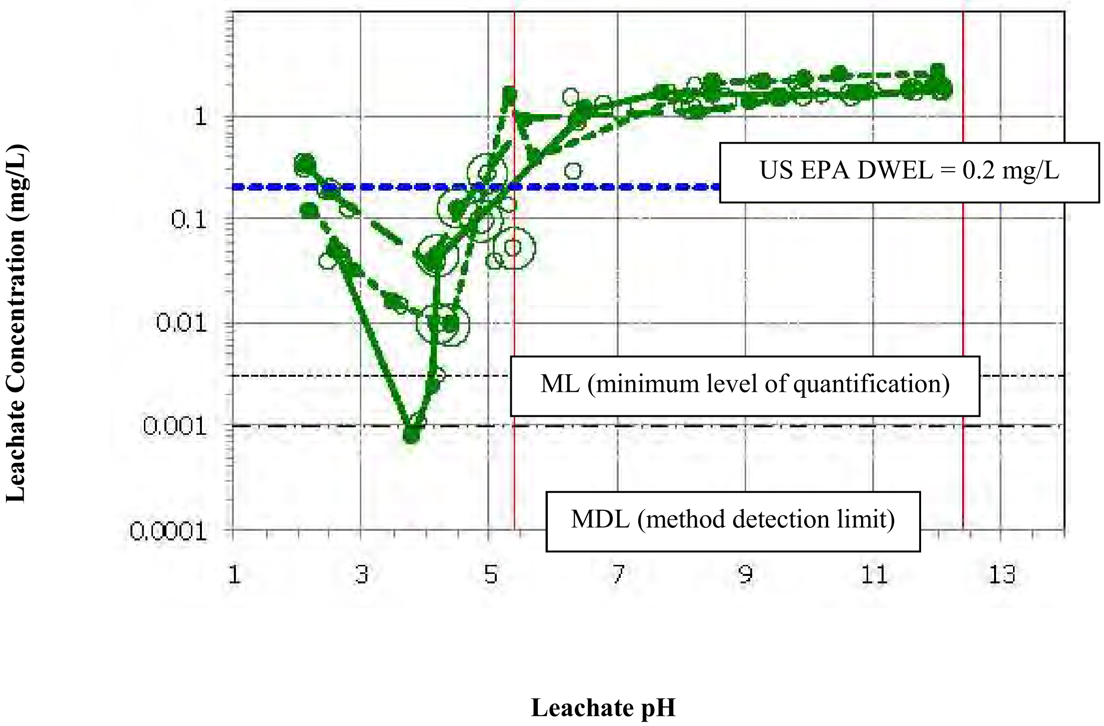


Figure 6-3
Illustrative Profile of Molybdenum Leaching from CCPs as a Function of pH

Note: Graph from US EPA, 2009c, "Facility E" leaching profile.

6.2.1.2 Mineralogical Composition

As stated previously, Mo has an affinity for iron oxides, calcium oxides, and calcium sulfate in CCPs (Querol *et al*., 1996). The relatively high leaching of Mo from coal fly ash, compared to other trace metals such as arsenic and selenium, in the Querol *et al*. (1996) study has been attributed to its association with soluble calcium salts.[5] Smichowski *et al*. (2008) noted that more than 40% of the total Mo in coal fly ash was associated with these soluble fractions. Tiruta-Barna *et al*. (2006) observed that Mo was associated predominantly with powellite, the dissolution of which controlled Mo leaching from coal ash.

6.2.1.3 CCP Weathering State

The weathering state of CCPs also influences Mo leaching. Dudas (1981) attributed higher Mo leaching from fresh, unweathered ash to its relatively higher fraction of soluble salts compared to weathered ash. With time, the amount of soluble salts decreases due to dissolution, resulting in decreased Mo leaching rates. EPRI (1987) and Al-Abed *et al*. (2008) reported similar findings on the effect of mineralogy on the leaching behavior of trace metals.

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[5] In general, calcium salts such as sulfates and carbonates in CCPs are readily soluble; leachable oxides such as amorphous iron oxides exhibit moderate solubility; and crystalline forms of iron, silicon, and aluminum oxides are less soluble (Querol *et al*., 1996).

6.2.2 Molybdenum Concentrations in CCP Leachate

This section presents data on Mo concentrations associated with CCP leachate. It is based on the EPRI (2011a) dataset, which includes Mo data from 306 field leachate samples collected from 34 plants, as well as 400 laboratory leachate samples from laboratory extraction tests performed on CCPs collected from 75 plants. Field samples were collected from surface impoundments and landfills from a variety of locations, including monitoring wells screened within the CCP zone, leachate collection systems, and surface impoundment outfalls from the various CCP disposal sites. Laboratory leachate samples were collected using different extraction methods to simulate variable leaching conditions. Data from scientific literature were used for comparison purposes.

Figure 6-4 shows the distribution of Mo concentrations in all samples from the EPRI (2011a) dataset, including all CCP types and all leachate types. The median concentration of Mo was 0.25 mg/L, while the mean value was approximately 1.1 mg/L.

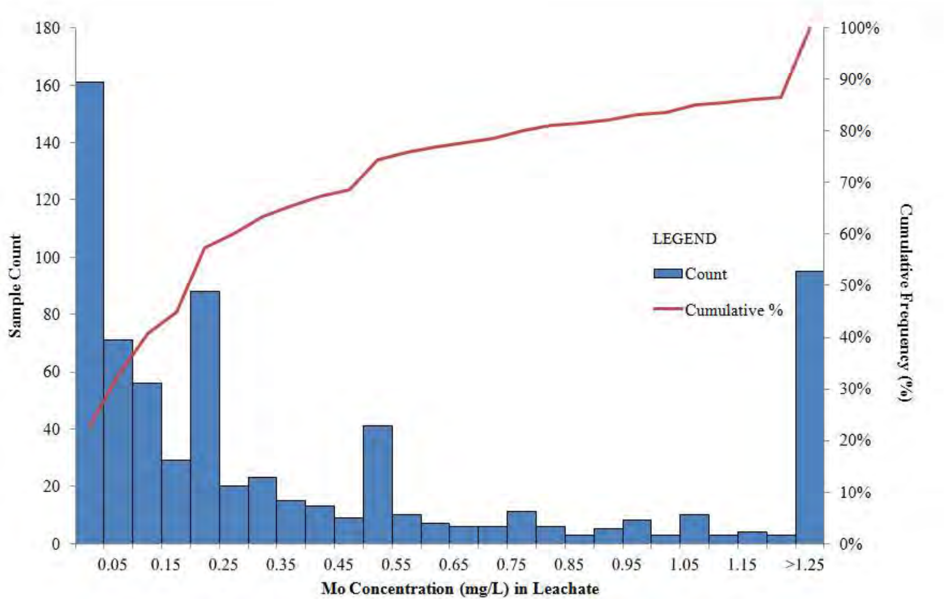

Figure 6-4
Molybdenum Concentration Distribution in Leachate – EPRI (2011a) Dataset

Notes: Includes all laboratory leachate and landfill and surface impoundment field leachate data from EPRI (2011a) dataset. The total number of discrete samples: n = 706 samples.

Non-detects were assumed to be half the detection limit.

Table 6-2 presents summary statistics of Mo leachate concentrations from the EPRI (2011a) dataset. These summary statistics are based on site-averaged data and classified by the CCP type reported in the dataset.[6] In general, the concentration of Mo in landfill field leachate samples was higher than in either laboratory leachate or surface impoundment field leachate samples. Among the different CCP types, the highest median and mean Mo concentrations were associated with leachate from fly ash and mixed coal ash (which is composed of fly ash with bottom ash) disposed of in landfills. FGD gypsum leachate had the lowest Mo concentrations.

Table 6-2
Molybdenum Concentration by CCP Type Site-Averaged Values[1]

CCP Type	Laboratory Leachate[2]					
	# of Plants	# of Sites	# of Discrete Samples	# of Non-Detects	Site-Averaged Data[3]	
					Mean (mg/L)	Median (mg/L)
Fly Ash	46	59	115	1	1.05	0.27
Bottom Ash	34	41	48	20	0.03	0.01
Mixed Coal Ash	13	19	160	71	0.42	0.28
FGD SS	10	13	27	14	0.52	0.11
FGD Gypsum	29	29	34	0	0.006	0.003
Fixated FGD	1	1	16	0	0.89	0.89
CCP Type	Field Leachate - Landfills[2]					
	# of Plants	# of Sites	# of Discrete Samples	# of Non-Detects	Site-Averaged Data[3]	
					Mean (mg/L)	Median (mg/L)
Fly Ash	8	9	32	0	6.85	4.48
Bottom Ash	-					
Mixed Coal Ash	5	8	47	6	2.11	1.03
FGD SS	-					
FGD Gypsum	-					
Fixated FGD	4	4	17	0	1.2	0.6

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[6] Most of the data within this chapter are described, evaluated, and presented on a “site-averaged basis.” Because the number of samples collected from each disposal site varies, as does the number of disposal sites at each plant, an initial step was performed on each dataset – the arithmetic mean (average) Mo concentration for each CCP type at each “site” was calculated – so that the results are not biased high or low because of the sampling frequency at individual sites. Thus, for example, a descriptive statistic such as the “median site-averaged Mo concentration” means that half the sites had average concentrations exceeding this value, half below. Non-detect values were assumed to be half the reported detection limit.

Table 6-2
Molybdenum Concentration by CCP Type Site-Averaged Values[1] (continued)

CCP Type	Field Leachate - Surface Impoundments[2]					
	# of Plants	# of Sites	# of Discrete Samples	# of Non-Detects	Site-Averaged Data[3]	
					Mean (mg/L)	Median (mg/L)
Fly Ash	12	13	78	10	0.36	0.25
Bottom Ash	9	9	28	22	0.26	0.25
Mixed Coal Ash	16	18	85	20	0.62	0.15
FGD SS	5	6	19	5	5.33	0.22
FGD Gypsum	-					
Fixated FGD	-					

Notes: *[1] Based on the EPRI (2011) dataset.*

[2] Laboratory leachate includes results from multiple extraction methods; landfill leachate includes results from all landfill field leachate sample types; surface impoundment water includes results from all surface impoundment sample types.

[3] Calculated using the mean for each plant "sub-site" as a discrete value

6.2.1 Molybdenum Concentration in Coal Combustion Products Determined in Laboratory Extraction Tests

The EPRI (2011a) dataset contains results from studies in which CCPs were subjected to different extraction tests, including the Synthetic Precipitation Leaching Procedure (SPLP), centrifuging, and hot-water/nitric acid extracts. Chapter 7 provides further details on these methods. The extracts from the different methods are referred to as “laboratory leachate.”

Figure 6-5 show the Mo concentration in laboratory leachate from different CCP types based on the EPRI (2011a) dataset. The median site-averaged Mo concentrations ranged from 0.003-0.28 mg/L as follows: FGD gypsum < bottom ash < FGD SS < fly ash < mixed coal ash (fly ash mixed with bottom ash).

Overall, the Mo concentration in laboratory leachate from the EPRI (2011a) dataset is comparable to values reported in the scientific literature. For example, Roy *et al*. (1984) reported Mo concentration in Illinois Basin coal fly ash leachate extracted using the EP TOX and water extraction tests to be from 0.02-14.5 mg/L. The range reported in Thorneloe *et al*. (2010) was 0.0005-130 mg/L[7] for coal fly ash leachate and 0.0003-1.9 mg/L for FGD gypsum leachate samples. Mo leachate concentration from bituminous fly ash subjected to TCLP and groundwater leaching tests ranged from 0.5-2.5 mg/L (Hassett *et al*., 2005).

Figure 6-6 displays the laboratory leachate sampling results for fly ash from the various laboratory batch leaching tests, as well as a limited number of centrifuge extraction test data (centrifuge extraction of porewater from field cores) based on the EPRI (2011a) dataset. The

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[7] Thorneloe *et al*. (2010) reported that the highest Mo concentration observed was in a leaching test conducted at a liquid-solid ratio of 1 using deionized water, compared to the liquid-solid ratio of 20 (as mandated in the TCLP or SPLP tests). Leachate concentrations generally decrease with increasing liquid-solid ratios (*i.e.*, the maximum concentration is observed at low liquid-solid ratios) (US EPA, 2009c).

means of the site-averaged Mo concentration ranged from 0.44-10.78 mg/L, depending on the type of extraction test, while the medians ranged from 0.19-9.43 mg/L. The mean and median leachate values were almost an order of magnitude higher in the centrifuge extractions of porewater, compared to the SPLP and "Other Batch" extraction techniques.

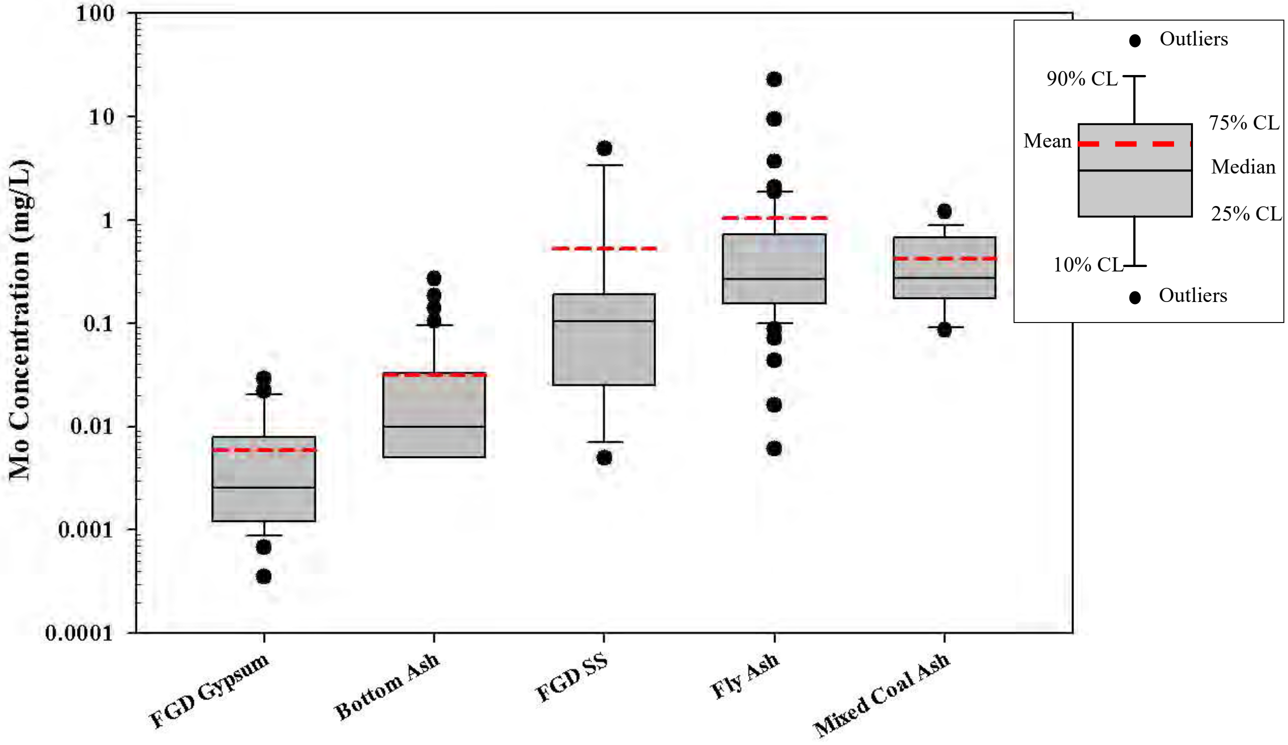

Figure 6-5
Molybdenum Concentrations in Laboratory Leachate

Notes: The total number of site-averaged values (n) are 1) Fly ash: n = 59; 2) bottom ash: n = 41; 3) FGD SS: n = 13; 4) Mixed coal ash: n = 19; and 5) FGD gypsum: n=29. Data from EPRI (2011a) dataset.

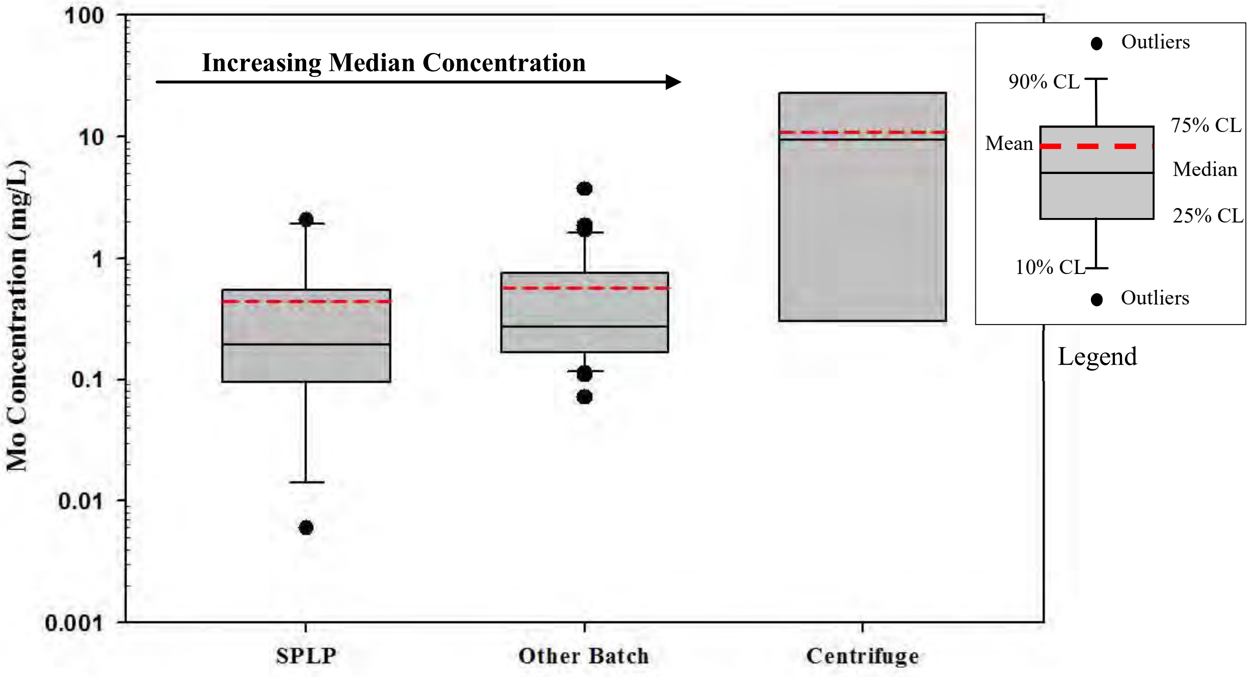

Figure 6-6
Molybdenum Concentrations in Fly Ash Leachate – Comparison of Laboratory Leachate Extraction Tests

Notes: The total number of site-averaged values (n) are 1) SPLP: n = 17; 2) Other Batch: n = 39; and 3) Centrifuge: n = 3. Data from EPRI (2011a) dataset.

6.2.2 Molybdenum Concentration in Landfill Leachate

Figure 6-7 presents the distribution of site-averaged Mo concentrations in landfill leachate from the EPRI (2011a) dataset. The site-averaged Mo concentration ranged from 0.1-25.4 mg/L for all CCP types. The mean and median of the site-averaged Mo concentration in the EPRI (2011a) dataset were highest in fly ash (6.85 and 4.48 mg/L, respectively; see Table 6-2). The highest site-averaged Mo concentration (25.4 mg/L) was observed for fly ash because of one sample that was almost 5-fold higher than the median value for fly ash. EPRI (2006a, p. 4-28) noted previously that leachate samples from this specific site had relatively high concentrations of elements (including Mo) because this power plant used a wider variety of fuel (*i.e.*, coal, petroleum coke, and tires) and high-temperature boilers.

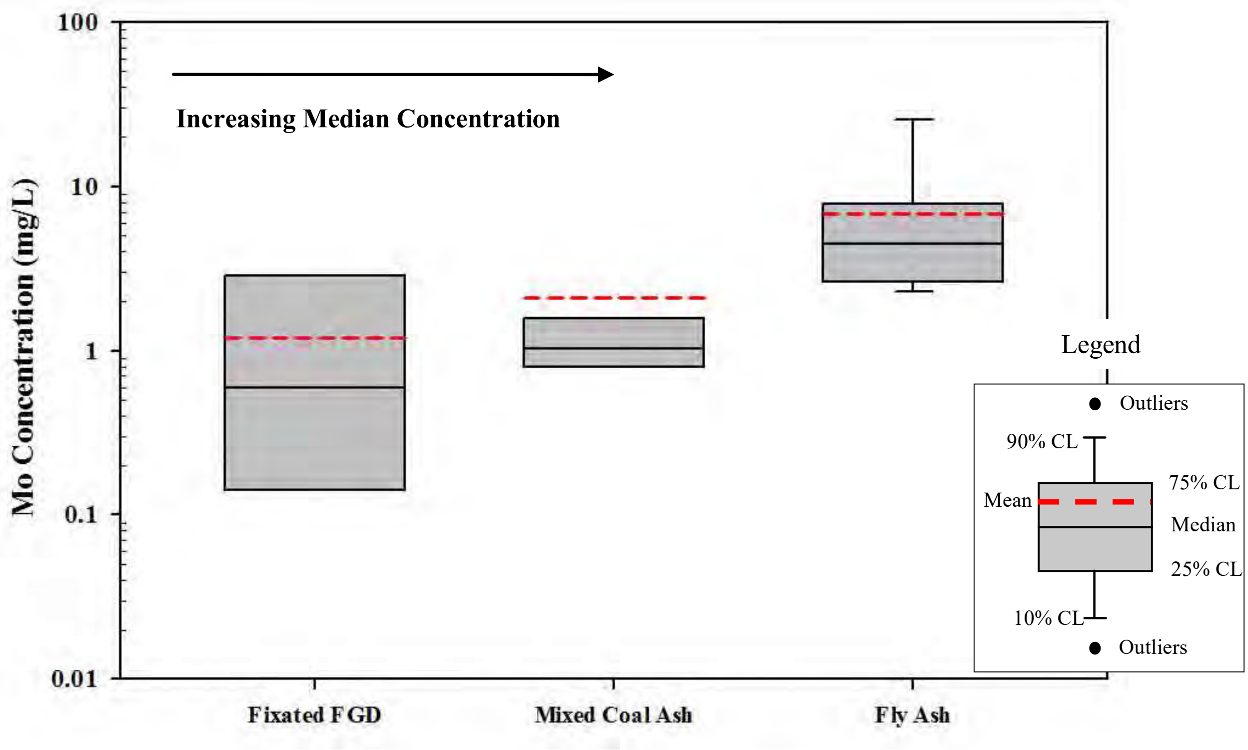

Figure 6-7
Molybdenum Concentrations in CCP Landfill Leachate

Notes: The total number of site-averaged values (n) are 1) fly ash: n = 9; 2) Mixed coal ash: n = 8; and 3) Fixated FGD: n = 4. Data from EPRI (2011a) dataset.

6.2.3 Molybdenum Concentration in Surface Impoundment Leachate

Figure 6-8 presents the distribution of site-averaged Mo concentrations in surface impoundment leachate from the EPRI (2011a) dataset. The mean and median concentrations were similar across all CCP types, except the mean FGD SS concentration, which appears to be skewed high because of one sample with a concentration of 60.8 mg/L (other samples collected from the same surface impoundment had much lower concentrations of Mo, < 1 mg/L). Overall, the Mo concentrations from surface impoundment samples were lower than from landfill leachate samples.

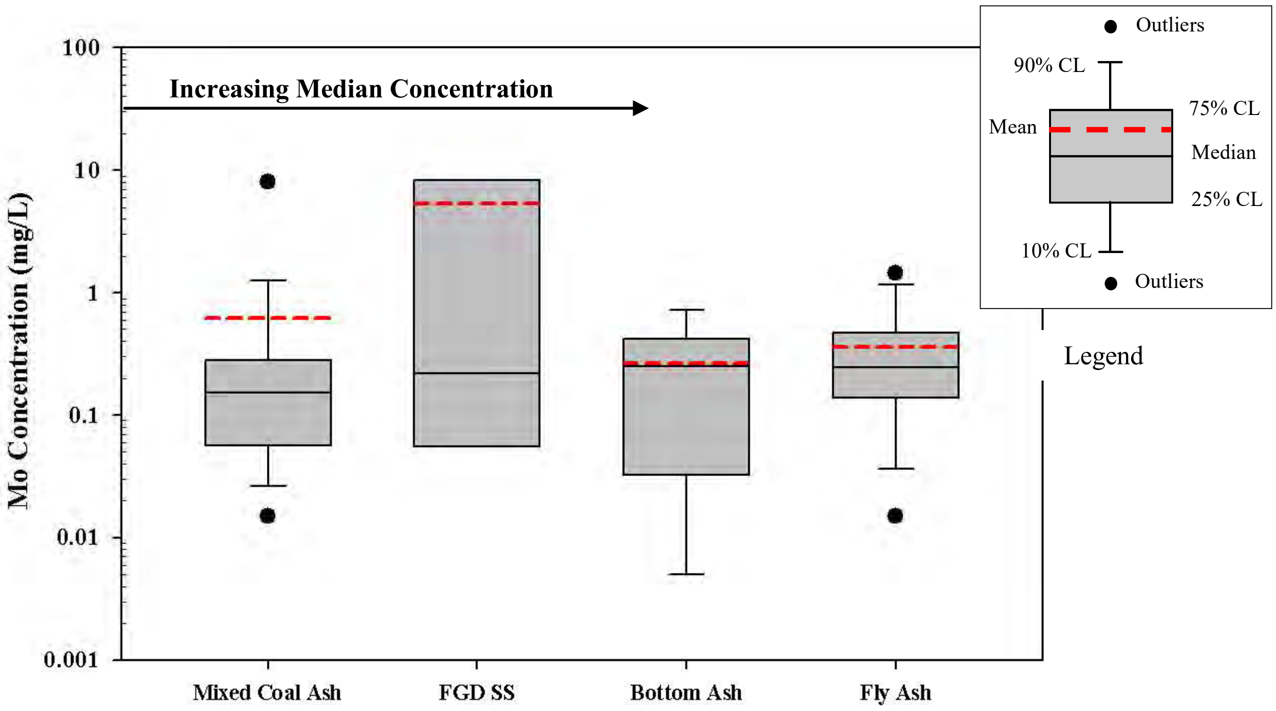

Figure 6-8
Molybdenum Concentrations in CCP Surface Impoundment Leachate

Notes: The total number of site-averaged values (n) are 1) fly ash: n = 13; 2) Bottom ash: n = 9; 3) Mixed coal ash: n = 18; and 4) FGD SS: n = 6. Data from EPRI (2011a) dataset.

6.3 Molybdenum Speciation in Coal Combustion Product Leachate

There is very little information on the speciation of Mo in CCP leachate. Mo is typically in the +6 oxidation state as an oxyanion (Morrison *et al*. 2006). At pH values > 5, Mo forms the water-soluble molybdate complex. Arai (2010) and LeGendre and Runnells (1975) noted that, under oxic environments and also high pH, Mo existed as molybdate oxyanions. Because CCP leachate in most landfills and surface impoundments has a pH > 5, it is more likely that the dominant form of Mo in leachate is molybdate.

7

ENVIRONMENTAL SAMPLING AND ANALYSIS

This chapter presents sample preparation and analysis methods for Mo in CCP-impacted matrices. Although the focus of this chapter is primarily aqueous matrices, such as CCP leachates and water, analysis methods for bulk CCP matrices are addressed briefly as well. Analyses of both solid and aqueous matrices are necessary to fully characterize potential exposure to Mo from environmental exposures.

7.1 Sample Preparation Methods for Coal Combustion Product Leachate

Laboratory leaching tests are widely used to determine the potential impact of metals and other constituents from CCPs on the environment (EPRI, 2005). Selection of an appropriate leaching method is highly dependent on overall data objectives, process/source of CCPs, intended management scenarios, and disposal conditions. Examples of leaching methods that have been investigated and implemented to characterize CCPs include those listed in Table 7-1.

Table 7-1
Examples of CCP Leaching Methods

Reference	Title	Comments
EPA SW846 Method 1311	Toxicity Characteristic Leaching Procedure (TCLP)	Simulates landfill disposal conditions.
EPA SW846 Method 1312	Synthetic Precipitation Leaching Procedure (SPLP)	Designed to evaluate the impact of contaminated soils on groundwater. Wastes can be sieved to < 2 mm to eliminate the particle size reduction step (see USGS, 2000).
ASTM D3987-85	Shake Extraction of Solid Waste with Water	Neutral extraction method.
18-hour leaching test	Modification of Shake Extraction of Solid Waste with Water	Extraction conditions are similar to ASTM D3987-85, but shaken for a duration of 18 hours.
30-day leaching test	Modification of Shake Extraction of Solid Waste with Water	Extraction conditions are similar to ASTM D3987-85, but shaken over 30 days.

Table 7-1
Examples of CCP Leaching Methods (continued)

Reference	Title	Comments
Ziemkiewicz, 2005; Ziemkiewicz and Knox, 2006	Mine Water Leaching Procedure (MWLP)	Evaluates behavior of ash in acidic conditions such as acid mine drainage. Involves a sequential extraction method that uses water from the intended application site. Accounts for chemical interactions between ions released from coal combustion by-products and those in the mine water. Continues leaching until all alkalinity is exhausted.
Hassett *et al*., 2005	Synthetic Groundwater Leaching Procedure (SGLP)	Simulates actual field conditions. Conditions similar to TCLP. Can incorporate Long Term Leaching (LTL) of 30- or 60-day equilibration times.
State of California, 2008	California Wet Extraction Test (WET)	Can be modified to use deionized water instead of citric acid (CWRCB, 2008).
ASTM D4874-95	Standard Test Method for Leaching Solid Material in a Column Apparatus	Flow-through column test involving aqueous leaching of a material in a dynamic partitioning manner.
ANSI/ANS-16.1-2003; R2008	Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure	Measures release from waste forms as a result of leaching in demineralized water for 5 days; similar methods have been used to evaluate leaching from CCPs reused to make cement (US EPA, 2008).
Leaching Environmental Assessment Framework (LEAF) (http://vanderbilt.edu/leaching/leaf/)	LEAF Method 1313 – pH Dependence	Evaluates chemical leaching as a function of pH.
	LEAF Method 1314 – Percolation Column	Assesses percolation through loosely packed material.
	LEAF Method 1315 – Mass Transfer Rates	Assesses the flux and cumulative chemical leaching as a function of leaching time.
	LEAF Method 1316 – Batch Liquid-Solid Partitioning	Evaluates leaching as a function of liquid-solid partitioning.

Some state agencies have expressed concern regarding the wide variety of leaching procedures available, the lack of correlation between these methods and/or bulk sample analyses, and the lack of data comparability (US EPA, 2009c). For example, it is possible that standard methods such as TCLP and SPLP will not be appropriate for determining leaching from CCPs *in situ* or under actual waste management conditions because these methods use standard leaching solutions and do not necessarily predict interactions between the solid waste and components of a specific mine water (Ziemkiewicz and Knox, 2006). A framework for more appropriate and reliable leaching methods (Leaching Environmental Assessment Framework, or LEAF) has been under examination by Vanderbilt University and US EPA so that CCP data comparability eventually may be improved; the methods evaluated by US EPA focus on leaching as a function of pH and liquid-to-solid (LS) ratio (US EPA, 2009c, 2010c). Additional testing methods following this framework (listed in Table 7-1) have been developed and currently are under review and validation for inclusion in US EPA's SW846 test method compendium.

7.2 Laboratory Methods for Analyzing Molybdenum

Numerous standard methods (Table 7-2) are available for analyzing Mo in leachates and CCP-impacted matrices. The majority of the methods involve inductively coupled plasma (ICP) analyses and are multi-element, allowing for characterization of multiple metals at once. In contrast, some of the flame and graphite furnace atomic absorption (AA) methods are specific to Mo. Detection limits range from 0.30-100 µg/L in aqueous matrices and 0.004-8 mg/kg in solid matrices. In general, the inductively coupled plasma/mass spectrometry (ICP-MS) and AA methods offer more sensitive detection limits than the ICP-atomic emission spectroscopy (ICP-AES) methods.

Table 7-2
Methods for Analysis of Molybdenum

Source	Method Number	Method Name	Approximate Detection Level
Aqueous Matrices (Water and Leachates)			**µg/L**
US EPA Drinking Water Methods	200.7	Metals in Water by ICP-AES	4
	200.8	Metals in Water by ICP-MS	0.3
	246.1	Molybdenum by Flame AA, Direct Aspiration	100
	246.2	Molybdenum by Graphite Furnace AA	1
Standard Methods for the Examination of Water and Wastewater	3113B	Metals in Water by GFAA	1
	3120B (total)	Metals (Total Recoverable) in Water by ICP	4
	3125	Metals in Water by ICP-MS	8
US EPA SW846	6010C	Trace Elements in Solution by ICP-AES	5.3
	6020A	ICP-MS	8
	6800	Elemental and Speciated Isotope Dilution Mass Spectroscopy	8
	7081	Graphite Furnace Atomic Absorption Spectrophotometry	1
AOAC International	990.08	Metals in Solid Wastes by ICP	8

Table 7-2
Methods for Analysis of Molybdenum (continued)

Source	Method Number	Method Name	Approximate Detection Level
Aqueous Matrices (Water and Leachates)			**µg/L**
ASTM	D1976	Elements in Water by ICP-AES	8
	D5673	Elements in Water by ICP-MS	2.8
USGS-NWQL	I-1472-87	Metals in Water by ICP	10
	I-1492-96	Molybdenum in Water by Graphite Furnace Atomic Absorption Spectrophotometry, Filtered	0.9
	I-3492-96	Molybdenum in Water by Graphite Furnace Atomic Absorption Spectrophotometry, Unfiltered	0.9
	I-4471-97	Metals in Water by Inductively Coupled Plasma/Optical Emission Spectrometry, Whole-Water Recoverable	34
	I-4472-97	Metals in Water by Inductively Coupled Plasma/Mass Spectrometer, Whole-Water Recoverable	0.4
Solid/Bulk CCP Matrices			**mg/kg**
US EPA Drinking Water Methods	200.2	Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements	Not applicable
US EPA SW846	3050B	Acid Digestion of Sediments, Sludges, and Soils (sample preparation method)	Not applicable
	3052	Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices	Not applicable
	6010C	Trace Elements in Solution by ICP-AES	5
	6020A	ICP-MS	0.004
	6200	Field Portable X-Ray Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment	20
	6800	Elemental and Speciated Isotope Dilution Mass Spectroscopy	8

Notes: *AA = Atomic Absorption Spectroscopy*
AOAC = Association of Official Agricultural Chemists
ASTM = American Society for Testing and Materials
GFAA = Graphite Furnace Atomic Absorption Spectroscopy
ICP = Inductively Coupled Plasma
ICP-AES = Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS = Inductively Coupled Plasma-Mass Spectrometry
USGS-NWQL = United States Geological Survey National Water Quality Laboratory

7.3 Analytical Interferences

It is possible that, due to high metal content, matrix interferences may occur, resulting in problems with the metal's quantitation and accuracy of results. For example, high concentrations of other metals (*e.g.*, aluminum and iron) may cause spectral interferences for Mo during ICP-AES analyses; these interferences occur when wavelengths from other analytes overlap with or are close to the wavelength of the analyte of interest, resulting in false positives. In other cases, concentrations of interfering analytes may be so high that they actually suppress analyte signals, causing false negatives. Physical interferences from high solids or acid content also may occur, increasing sample viscosity and affecting absorption, nebulization, and sample transport. Also, Mo can act as a spectral interferent for other analytes (*e.g.*, vanadium) in ICP-AES analyses.

There are several potential sources of interference during ICP-MS analyses. For example, isobaric elemental interferences may occur due to isotopes of different elements that form singly or doubly charged ions of the same nominal mass-to-charge ratio. Physical interferences (high solids, high viscosity) may hinder transport of the sample into the plasma. In addition, signals from relatively abundant isotopes can cause loss of resolution and poorer quantitation. Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom with the same nominal charge-to-mass ratio of the isotope of interest. Finally, memory interferences (carry-over) of isotopes can occur from previous sample runs. It should be noted that, at concentrations of 1 mg/L and above, Mo can cause molecular ion interferences and potential false positives for cadmium in ICP-MS analyses (USGS, 1998b). Also, Mo is used as a labeled standard in US EPA Method 6020A; this should be taken into consideration when designing any analysis program involving this method.

In general, the various published methods provide information and guidance regarding interferences and how to correct them during sample analysis. For example, background correction techniques (such as interelement corrections in ICP, Zeeman background correction in graphite furnace AA) can be implemented, while the use of internal standards generally alleviates interferences encountered during ICP-MS. Sulfate can interfere in the determination of Mo during graphite furnace AA analysis, but matrix modifiers such as magnesium nitrate and ammonium can minimize this interference. Mo also can form carbides, resulting in memory-effect (carry-over) interference; these can be eliminated by routine intermittent blank-sample analysis, a multistep high-temperature cleanout program, and the use of pyrolytically coated graphite tubes (USGS, 1997).

7.4 Molybdenum Speciation Analysis

At present, there appears to be little information available regarding Mo speciation in CCP matrices, and no standard methods were identified for Mo speciation analysis. This is most certainly an area requiring further research and development, specifically with regard to appropriate preservation methods, holding times, and factors affecting the stability of the species. The intended use and data objectives (*e.g.*, toxicity evaluations) of speciation data are critical to considering the need for speciation analysis or method development.

8

TREATMENT AND REMEDIATION

This chapter discusses remediation technologies for Mo at CCP disposal sites. The most viable remediation technologies for the treatment of aqueous Mo are adsorption and chemical precipitation, while biological treatment and membrane filtration are promising, but not yet proven, remediation techniques. Information sources used for this chapter include earlier EPRI reports on related topics (*e.g.*, EPRI (2006b)), scientific literature regarding metals remediation, and case studies for Mo-impacted sites. Mo is most often present as a co-contaminant of secondary concern at these sites (*i.e.*, it is not the primary remedy driver) and is often associated with other metals, including uranium.

At CCP disposal sites, impacted groundwater can be extracted and treated *ex situ* using conventional "pump-and-treat" (P&T) methods or *in situ* using permeable reactive barriers (PRBs) and subsurface injection. A PRB is used to hydraulically intercept and react with impacted groundwater that "passively" flows through some kind of reactive media using natural hydraulic gradients. As described in detail in EPRI (2006b), PRBs can be, and have been, used effectively to remediate metals such as Mo via precipitation and adsorption, often at lower estimated cost than P&T technology, although issues such as precipitate fouling could affect long-term performance. For example, Morrison *et al*. (2006) investigated the remediation of groundwater contaminated with uranium and Mo using a zerovalent iron PRB. Mo concentration in groundwater were reduced from 4.8 mg/L to < 0.1 mg/L over one year of operation, which was attributed to its precipitation or adsorption on iron oxides. McGregor *et al*. (2002) investigated the use of PRB to treat groundwater impacted by CCP leachate. It was noted in their study that PRB was successful in remediating Mo from groundwater, with removal efficiencies ranging from 80-99% (*i.e.*, Mo concentration reduced from almost 1 mg/L to < 0.07 mg/L). The data also indicated the removal of other trace elements, such as arsenic, selenium, and chromium, from groundwater.

Some of the key properties of Mo discussed in this report that are relevant to its treatment and remediation include:

- Mo has relatively low K_d values, ranging from 0.6-501 L/kg, which indicate that it has relatively high groundwater mobility. Other metals associated with CCP disposal sites that have similarly high mobility include boron, chromium, lithium, selenium, and strontium (EPRI, 2006b, Table 2-3).
- Mo typically exists as the negatively charged molybdate ion (MoO_4^{2-}) with pH-dependent behavior and sorption characteristics generally similar to those of other oxyanion-forming metals such as arsenic and selenium.
- Mo adsorption is highly pH-dependent. Peak adsorption for most sorbents (except maghemite nanoparticles) is at pH < 5 and limited adsorption occurs at pH > 8. In alkaline conditions, Mo behaves conservatively and its dissolved concentration is controlled by precipitation, not

adsorption, reactions. When present in sufficient concentrations, lead, then calcium, control Mo precipitation, forming wulfenite and powellite, respectively. For comparison, CCP leachates commonly have neutral to alkaline pH and are typically moderately to strongly oxidizing.

- Mo is typically present in CCP leachate at concentrations of about 0.25-1.1 mg/L, but concentrations can range up to 25 mg/L or more. US EPA has not established an MCL or MCLG for Mo, but the US EPA DWEL and tap water RSL of 0.2 mg/L and 0.18 mg/L, respectively, are non-enforceable federal regulatory screening criteria. Based on the EPRI (2011a) dataset, the site-average leachate Mo concentration exceeded 0.18 mg/L at about two-thirds of sites sampled.

The rest of this chapter provides an overview of individual remediation technologies for Mo.

8.1 Adsorption Techniques

Adsorption is a surface phenomenon by which constituents, such as dissolved Mo, become associated with solids. Adsorption can permanently or temporarily bind constituents and, as described in Chapter 5, can be quite geochemically complex. Adsorption techniques can be effective in treating Mo in water associated with CCPs, but most sorbents are not effective in alkaline conditions (except for maghemite nanoparticles, which studies indicate are effective even at high pH).

Adsorption techniques can be applied *ex situ* via groundwater extraction then treatment, or *in situ* via PRBs. Table 8-1 provides a summary of studies that have been performed on the use of sorbents, including iron and aluminum oxides, for Mo removal. The rest of this sub-section provides further details on these sorbents based on the studies referenced in Table 8-1.

Iron and Aluminum Oxides – As mentioned previously, studies of Mo sorption on iron and aluminum oxides and soil minerals have noted maximum Mo sorption (near complete removal) at the pH range 4-5. Mo sorption decreases with increasing pH > 5 (Goldberg *et al*., 2008; Arai, 2010).

The main mechanism of Mo sorption to oxides of iron and aluminum is through the formation of stable surface complexes (Goldberg *et al*., 2008). Xu *et al*. (2006) noted that the adsorption of Mo on the iron oxides pyrite and goethite is dependent on the Mo species present. Tetrathiomolybdate (MoS_4^{2-}) had greater sorption to goethite and pyrite than molybdate. Adsorption efficiency also was dependent on the presence and/or absence of competing ions, such as phosphate and sulfate. For example, the sorption of molybdate ions to goethite and pyrite decreased almost 30% in the presence of phosphate, while the sorption of tetrathiomolybdate decreased 15-20%. The presence of other competing ions, such as sulfate and silicate, did not have a significant effect on Mo sorption to goethite and pyrite.

Table 8-1
Summary of Sorbents for Molybdenum Remediation

Sorbent	Mo Removal	Factors Affecting Removal	Mechanism	Reference
Iron and aluminum oxides (*e.g.*, goethite, Al_2O_3, and pyrite, FeS_2)	Almost 100% removal observed at pH < 5	Presence of phosphate	Formation of surface complexes	Goldberg *et al*., 2008; Arai, 2010; Xu *et al*., 2006
Maghemite (Fe_2O_3) nanoparticles	Complete Mo removal across pH; fast sorption kinetics; sorption decreased with increasing pH	Slight decrease in Mo removal in the presence of sulfate ions	Surface complexation and electrostatic attraction	Afkhami and Norooz-Asl, 2009
Activated carbon	Maximum Mo sorption in acidic pH; significant decrease in removal with increasing pH	N/A	Electrostatic attraction	Afkhami and Conway, 2002
Hydrocalumite and ettringite	Strong Mo sorption at alkaline pH conditions; near complete removal	N/A	Ion substitution	Zhang and Reardon, 2003
Chitin	80-100% removal from mining effluent	Sorption decreases at alkaline pH	Electrostatic attraction	Moret and Rubio, 2003
Surface-modified zeolite	Only 30% Mo removal from 0.8-0.6 mg/L	N/A	N/A	Neupane and Donahoe, 2009

Note: N/A = not available.

Maghemite Nanoparticles – Maghemite nanoparticles have higher adsorption capacity due to their highly active surface sites and faster sorption kinetics than their macro-sized counterparts. They are also effective over a relatively wide pH range (2-10), unlike other Mo sorbents.

Afkhami and Norooz-Asl (2009) studied the removal of Mo using maghemite (γ-Fe_2O_3) nanoparticles. Mo removal was consistently high (> 75 %) over a wide pH range (2-10). The Mo concentration in the maghemite-treated water reduced from 100 mg/L to < 3 mg/L within a reaction time of 15 minutes. Unlike goethite and other iron oxides, maximum Mo sorption (*i.e.*, near complete removal) was observed at near neutral pH. A slight decrease in Mo sorption was observed at pH > 9. Afkhami and Norooz-Asl (2009) attributed this high Mo sorption to 1) electrostatic attraction of negatively charged molybdate ions to the positively charged maghemite surface at acidic pH; and 2) formation of iron-molybdate complexes at alkaline pH. Furthermore, it was observed in this study that the presence of common anions such as nitrate, chlorides, and sulfate had an insignificant effect on Mo adsorption.

Activated Carbon – Activated carbon has been used to remove Mo from aqueous solutions. Afkhami and Conway (2002) used a high surface area carbon cloth to remove molybdate from aqueous solutions. Similar to iron oxides, maximum Mo sorption was observed in acidic pH conditions, and the adsorption of Mo in near neutral pH was very low. Afkhami and Conway (2002) noted that, at extreme acidic conditions (pH 1.2), sorption of Mo decreased due to the formation of other condensed molybdates (*i.e.*, molybdates with octahedral structures).

Hydrocalumite and Ettringite **–** Zhang and Reardon (2003) studied the substitution of Mo on hydrocalumite and ettringite, as a mechanism of Mo removal. During the leaching of fly ash in alkaline environments, hydrocalumite (Ca2Al(OH)6.5Cl0.53(H2O)) and ettringite (Ca6Al2(SO4)3(OH)1226(H2O)) are formed as secondary precipitates, which can immobilize Mo via substitution/co-precipitation reactions. The authors observed that hydrocalumite and ettringite significantly removed dissolved Mo under alkaline pH conditions, and the mechanism involved was OH- and SO42- ion substitution. The Mo concentration was reduced to < 0.1 mg/L in treated water (from ~ 10 mg/L).

Chitin **–** Chitin is obtained from shells of crustaceans, such as shrimp and oysters. It can be described as cellulose with one hydroxyl group on each monomer substituted with an acetyl amine group, and it is rich in calcium carbonate and proteins. Chitin has been used successfully to treat Mo from aqueous solutions (Moret and Rubio, 2003). Moret and Rubio (2003) observed complete Mo removal from both mining effluents and synthetic aqueous solutions, attributing it to electrostatic attractions. Like other adsorbents, higher Mo sorption was observed in acidic pH. However, Mo desorption occurred at alkaline pH (pH 12), which would be useful in regenerating the adsorbent.

Zeolite **–** Mo also adsorbs to sorbents such as surface-modified zeolite (Neupane and Donahoe, 2009; EPRI, 2011b). Zhang and Reardon (2003) studied the adsorption of Mo from fly ash leachates and observed that up to 30% of Mo in the acidic and alkaline fly ash leachates was removed by zeolite treatment.

8.2 Chemical Precipitation

Chemical precipitation techniques, used widely to treat wastewater from coal-fired power plants, can be used to remediate Mo. In a chemical precipitation wastewater treatment system, chemicals are added to wastewater to alter the physical state of dissolved and suspended solids to facilitate settling and removal of the solids (US EPA, 2009a). Some of the common chemicals used as precipitating agents include lime (for hydroxide precipitation), ferrous or ferric chloride (iron co-precipitation), and sulfide salts (*e.g.*, sodium sulfide). Ferric chloride and a novel process of “electrocoagulation” have been used to chemically precipitate Mo from water, as described further below. Chemical precipitation is performed *ex situ* via groundwater extraction then treatment or *in situ* by injection of calcium polysulfide to precipitate soluble metals, for example.

LeGendre and Runnells (1975) observed a strong pH dependence on Mo removal using ferric chloride. Maximum Mo removal (almost 80%) was observed at acidic pH, and Mo removal decreased to 50-60% in the alkaline pH range. The ratio of Fe:Mo required for near-complete Mo removal (from an initial Mo concentration of 1.1-11.1 mg/L) was observed to be 10-100 (on a molar basis). US EPA data (2009c) obtained from four power plants that use chemical precipitation techniques for treating FGD wastewater showed a 50% decrease in Mo concentration with the use of lime and ferric chloride as precipitating agents.

Chellam and Clifford (2002) investigated the removal of Mo from leachate generated from the surface disposal of uranium mine tailings, using ferric chloride as a coagulant. Mo removal was greater at acidic pH (pH 4) than at alkaline pH. The increased Mo removal at acidic pH was attributed to the formation of inner-sphere complexes with iron, similar to those observed with goethite. Decreased removal at alkaline conditions was a result of electrostatic repulsion between the negatively charged Mo ions and negatively charged $Fe(OH)_4^-$ molecules (formed during the coagulation process). Also, increased removal efficiency by increasing iron concentration was noted.

Mills (2000) used a relatively new electrocoagulation process to remove Mo from leachate generated at mining sites. In this process, a series of electrolytic cells containing iron anodes and stainless steel cathodes were used. Application of direct current (DC) results in the generation of iron cations (*i.e.*, Fe^{3+}) at the anode and hydroxide ions (OH^-) at the cathode; the resulting iron hydroxide acts as a precipitating agent. The advantage of this process, as noted by Mills (2000), was the continuous generation of iron hydroxides. Almost 100% Mo removal, from 10 mg/L influent concentration to non-detect effluent concentration, was observed using this method. This technique also was effective in treating other trace elements such as arsenic and selenium. The presence of high concentrations of phosphate and sulfate had an insignificant effect on Mo removal efficiencies.

8.3 Biological Treatment

Bioremediation can be an effective technology for treating trace metals that are similar to Mo, such as arsenic and selenium. Microbial reduction of aqueous Mo could potentially immobilize Mo via the formation of insoluble Mo sulfides; however, very few studies have investigated this microbially mediated reduction, so the viability of this remediation technique at CCP disposal sites has not been demonstrated yet. These studies are described briefly below.

Kauffman *et al*. (1986) investigated the use of microbial treatment of uranium-impacted mine water that also contained Mo. Soils rich in sulfate-reducing bacteria were used in anaerobic reactors to treat uranium and Mo. The decrease in Mo concentration, from almost 1 mg/L to < 0.05 mg/L, was a result of the microbially mediated reduction of Mo to insoluble Mo sulfide (molybdenite).

In his review article, Lloyd (2003) noted that several sulfate-reducing bacteria (*e.g.*, *D. desulfuricans*, *T. ferrooxidans*) were able to immobilize Mo (VI) from solution at a very high efficiency.

Nelson *et al*. (2003) investigated the *in situ* anaerobic biological immobilization of Mo in groundwater using soil columns. The soils were rich in sulfate-reducing bacteria and the system was anoxic; *i.e.*, the redox potential was negative. The reduction of sulfate to sulfide, indicated by the generation of H_2S gas, resulted in reduction of Mo (VI) in the groundwater. The study observed complete Mo reduction (from an initial Mo concentration of up to 15 mg/L) over a 30-day period. Post-treatment flush tests to assess stability of the insoluble Mo sulfides showed minor remobilization of Mo.

Sivula *et al*. (2007) investigated the treatment of leachate generated from municipal solid waste incinerated (MSWI) bottom ash using anaerobic biological treatment. Leachates were treated in bioreactors containing digested sludge obtained from a municipal wastewater treatment plant

(WWTP). Sivula *et al*. (2007) noted almost 90% Mo reduction over a half-year period that was attributed to the formation of insoluble Mo sulfides and the complexation of Mo with organic matter. It was, however, observed that increasing the amount of organic matter increased formation of Mo-organic matter complexes. As a result, free Mo ions were not available for the microbial reduction process. The precipitation of calcium also inhibited the reduction process.

8.4 Membrane Filtration

Reverse osmosis (RO) is a physical separation process in which pretreated source water is delivered at moderate pressures against a semi-permeable membrane. The membrane rejects most solute ions and molecules while allowing water of very low mineral content to pass through. Nanofiltration is similar to RO in its mechanism, except that low pressures are applied. Chellam *et al*. (2002) found the efficacy of nanofiltration and RO techniques to achieve near complete removal of Mo, even from highly alkaline solutions (pH 10). Because anion repulsion is the predominant removal mechanism by the negatively charged membranes, greater ion rejection (or removal) was observed.

9
SUMMARY

- Mo is a naturally occurring transition metal that can be found in the environment in several different valence states; the most common valence state for naturally occurring Mo minerals is Mo (+4). In water, the Mo (+6) valence state (molybdate ion, MoO_4^{2-}) dominates Mo aqueous speciation except under low pH (< 4) and anoxic conditions.
- Mo is the least abundant of the biologically essential trace elements in soil. Worldwide concentrations of Mo in soils vary from about 0.1-10 mg/kg, with an average concentration of about 1-2 mg/kg. Overall, measured Mo concentrations in water appear to be highly variable, with a large percentage of surface and drinking water sources having levels below detection limits (about 5 µg/L or less). Averages for detectable levels of Mo in surface water have been reported to be below 100 µg/L.
- Mo is an essential nutrient that is necessary to normal biological function. The National Academy of Sciences has developed recommended dietary allowances for Mo ranging from 2-50 µg/day, depending on the age group.
- While Mo at low levels is necessary for optimal health, Mo at high levels can be associated with adverse effects via oral exposure. The most common health effects observed are increased uric acid production and gout. Based on these health endpoints and accounting for a margin of safety, US EPA has established an RfD for Mo of 0.005 mg/kg-day.
- According to US EPA, the information to evaluate the carcinogenic potential for Mo in humans or animals is inadequate. Also, Mo deficiency has been suggested to be associated with an increase in cancer incidence.
- Molybdate, which is an essential nutrient for microorganisms, plants, and animals, is the Mo species that plants and animals take up most readily from soil and water. Several different environmental factors (*e.g.*, pH, soil OC, aluminum and iron oxide, and soil sulfate) influence the extent of Mo uptake, bioaccumulation, and toxicity.
- Ruminants (*e.g.*, cows) are particularly sensitive to Mo toxicity and can develop a condition called molybdenosis, which is characterized by Mo-induced copper deficiency.
- Similar to other oxyanions such as Cr (VI) and Se (VI), molybdate is relatively mobile in groundwater. K_d values for molybdate range from 0.6-501 L/kg.
- Mo adsorption on both minerals and organic matter is highly pH-dependent, with peak adsorption at pH < 5 and limited adsorption above a pH of 8. Increases in soil water pH or dissolution of oxide phases can mobilize Mo.
- While the environmental chemistry of Mo has been well described in the literature, attempts to model its environmental fate and transport have been more limited. Surface complexation

models are promising and have been used to successfully model Mo adsorption using a relatively limited number of parameters.

- Overall, ash samples typically contain approximately 10-20 mg/kg Mo, but can have concentrations as high as 100 mg/kg or more. FGD SS typically contain 1-10 mg/kg Mo, and FGD gypsum samples typically contain < 1 mg/kg Mo. There is little information on the speciation of Mo in CCPs.
- Overall, Mo is typically present in CCP leachate of all types at concentrations of about 0.25 up to a few mg/L. These values exceed the US EPA's DWEL of 0.18 mg/L.
- The highest Mo leachate concentrations at CCP disposal sites are generally associated with fly ash disposed of in landfills (mean and median of 6.85 and 4.48 mg/L, respectively). The lowest leachate concentrations are associated with FGD gypsum (mean and median of 0.006 and 0.003 mg/L, respectively).
- The relatively high rate of leaching of Mo from fly ash, compared to the leaching rates of other trace metals such as arsenic and selenium, has been attributed to its association with soluble calcium salts. Over time, Mo leaching decreases as these salts become depleted from weathered CCPs.
- There is little information on the speciation of Mo in CCP leachate.

10

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A
SPECIFIC MOLYBDENUM SORBENTS

Iron/Manganese Oxides and Oxyhydroxides

Molybdate adsorption on iron oxides and oxyhydroxides (hematite, ferrihydrate, goethite, and amorphous iron oxides) has been shown to occur at a maximum at pH 4-5. Molybdate adsorption decreases rapidly above pH 5, with little to no molybdate adsorption occurring above pH 8 (Goldberg *et al*., 1996; Gustafsson, 2003). Molybdate adsorption by iron oxides has been modeled successfully using surface complexation models (SCMs) as inner-sphere complexation, forming strong coordinative bonds (Goldberg *et al*., 1996; Gustafsson, 2003; Xu *et al*., 2006). X-ray absorption spectroscopy (XAS) of Mo on goethite found that Mo surface complexation varies from tetrahedral to octahedral with decreasing pH, suggesting that Mo polymers may play an important role in the Mo adsorption mechanism at low pH (Arai, 2010). A Raman and Fourier transform infrared (FTIR) spectroscopic investigation of Mo on amorphous iron oxides found that Mo forms predominantly inner-sphere surface complexes at low pH and predominantly outer-sphere surface complexes at high pH (Goldberg *et al.*, 2008).

Mo is also adsorbed on manganese oxides. This relationship is especially apparent in marine systems where Mo is enriched in manganese oxide crusts, nodules, and sediments at a Mo:Mn molar ratio of 1.1×10^{-3} (Bertine and Turekian, 1973). The mechanism of Mo incorporation into manganese oxides is unknown.

Tetrathiomolybdate adsorption on goethite was investigated by Xu *et al*. (2006). Goethite showed a stronger affinity for tetrathiomolybdate than molybdate. At all pH levels, tetrathiomolybdate adsorption exceeded molybdate adsorption. Tetrathiomolybdate adsorption exhibited the same pH dependence seen for molybdate, with 100% adsorbed below pH 6 and a rapid decrease in adsorption until pH 8. Tetrathiomolybdate adsorption on goethite is more resistant to competition from phosphate (Xu *et al*., 2006). The resistance of goethite to tetrathiomolybdate desorption implies that tetrathiomolybdate may play an important role in the permanent fixation of Mo in soils and sediments.

Aluminum Oxides and Clay Minerals

Amorphous aluminum oxides, gibbsite, and aluminum-containing clay minerals have smaller adsorption capacity than iron and manganese oxides but can still represent a significant reservoir for Mo adsorption. Mo adsorption capacities in some soils have been shown to correlate with extractable aluminum (Barrow, 1977, as cited in Chappell and Peterson, 1977; Goldberg, 2010). These minerals adsorb molybdate very similarly to iron oxides, showing high adsorption at pH 4 followed by a rapid decrease in adsorption capacity (Goldberg *et al*., 1998). Molybdate adsorption on montmorillonite was best described using an outer-sphere, electrostatic attraction bond (Goldberg *et al*., 2008). Mo adsorption on aluminum oxides, kaolinite, and illite have all been best described as forming monodentate surface complexes with an inner-sphere adsorption mechanism (Goldberg *et al*., 2008). Again, complexation appears to be pH-dependent; the predominantly inner-sphere Mo-gibbsite surface complexes at low pH change to predominantly outer-sphere surface complexes at high pH. On gibbsite, this transition in complexation type occurs even more rapidly with increasing pH than on goethite, implying the Mo adsorbed onto aluminum oxides may be more easily desorbed than iron oxides (Goldberg *et al*., 2008).

Pyrite

Molybdate adsorption on pyrite has been investigated by Xu *et al*. (2006) and Bostick *et al*. (2003). Molybdate adsorbs strongly to pyrite under acidic pH, but it is readily desorbed with increased pH. X-ray absorption spectroscopy examination determined that molybdate forms bidentate, mononuclear complexes on FeS_2. Tetrathiomolybdate, on the other hand, appears to form highly stable Mo-Fe-S cubate-type clusters that resist desorption (Bostick *et al*., 2003). This supports the hypothesis that tetrathiomolybdate is the reactive Mo species in anoxic regions and ultimately may control Mo availability.

Organic Matter

Mo is not bound by most organic functional groups, but it is chelated by catechol groups (Wichard *et al*., 2009). Mo has been found to be bound and fixed by humic and fulvic acids (Smith *et al*., 1997). This adsorption appears to have an even greater pH dependence than iron oxides, with peak adsorption occurring at pH 3.5 on humic acid (Bibak and Borggard, 1994).

X-ray absorption spectra of Mo in black shales, anoxic sediments, and humic acid scavenging experiments have identified an organic form of Mo containing M-O double bonds and Mo-S-Fe bonds (Helz *et al*., 1996). Humic acid scavenging experiments (Helz *et al*., 1996) showed that, in oxic conditions, little Mo scavenging occurred above pH 5, but, in the presence of sulfide, humic acid was an effective scavenger at all pHs tested (5, 7, and 9). Helz *et al*. (1996) suggested that this was either the result of sulfidization of the humic acid or because the Mo-S-Fe bond is formed from humic bound iron. In oxic conditions, another X-ray absorption study (Wichard *et al*., 2009) found that Mo in the leaf litter of a temperate forest was bound by catechol-rich tannins; the authors found that molybdate will bind to leaf litter extract (LLE). This binding is pH-dependent, with the highest binding occurring at pH 6.1. It decreases slightly with decreased pH, but most Mo is still bound to the LLE at pH 4.7. At pH 9, only half the Mo is bound to the LLE. Binding to insoluble tannins may inhibit Mo leaching from surface soil and provide a source of bioaccessible Mo.

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