Leaching Environmental Assessment Framework (LEAF) How-To Guide

Understanding the LEAF Approach and How and When to Use It

SW-846 Update VII Revision 1 May 2019

NOTICE/DISCLAIMER

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Acronyms and Abbreviations

Acronym	Definition
ANC	acid neutralization capacity
CaFA	material specimen code for a coal combustion fly ash
CCR	coal combustion residue
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFS	material specimen code for a contaminated smelter site soil
COPC(s)	constituent(s) of potential concern
DAF(s)	dilution and attenuation factor(s)
DOC	dissolved organic carbon
EaFA	material specimen code for a coal combustion fly ash
EC	electrical conductivity [mV]
EDD	electronic data deliverable
EPACMTP	EPA Composite Model for Leachate Migration with Transformation Products
IWEM	Industrial Waste Management Evaluation Model
L/A	liquid-to-surface area ratio [mL/cm^3]
L/S	liquid-to-solid ratio [mL/g-dry]
LDR	Land Disposal Restrictions
LEAF	Leaching Environmental Assessment Framework
LLOQ	lower limit of quantification
LSP	liquid-solid partitioning
MCL	maximum contaminant level
MDL	method detection limit
MSWI	municipal solid waste incinerator
ORCHESTRA	Objects Representing Chemical Speciation and Transport
ORP	oxidation/reduction potential
QAPP	Quality Assurance Project Plan
QA/QC	quality assurance/quality control
POC	point of compliance
RCRA	Resource Conservation and Recovery Act
redox	reduction/oxidation
RSD_r	replicate standard deviation for repeatability
RSD_R	replicate standard deviation for reproducibility
RSL	Regional Screening Level
SAB	Science Advisory Board
SPLP	Synthetic Precipitation Leaching Procedure
SWA	material specimen code for a solidified waste form
TCLP	Toxicity Characteristic Leaching Procedure
U.S. EPA	United States Environmental Protection Agency

Abstract

This document provides guidance on the use and application of the Leaching Environmental Assessment Framework (LEAF) published by the United States Environmental Protection Agency (U.S. EPA or the Agency). The purpose of this guide is to provide an understanding of LEAF to facilitate its broader use in environmental assessment. LEAF is a leaching evaluation framework, which consists of four leaching tests (i.e., U.S. EPA Methods 1313, 1314, 1315 and 1316), data management tools, and approaches for estimating constituent release from solid materials. The LEAF tests consider the effect on leaching of key environmental conditions and waste properties known to significantly affect constituent release. This document provides background on the LEAF tests as well as information on how to perform the tests and how to understand the test results. This document also provides guidance on the application of LEAF to assess leaching potential of COPCs from solid waste matrices for beneficial use, disposal, treatment, and remediation applications. In addition, this document addresses frequently asked questions about the four LEAF test methods, data management and reporting using freely-available software, and potential applications of the LEAF approach.

The approach to testing and evaluation presented in this guide is progressive in that each of the different methods provide information on the effect of different environmental parameters on leaching. Therefore, investment in each increment of additional testing and evaluation may reward the user with increasingly refined estimates of leaching. Traditionally, the potential for environmental impact through leaching of COPCs from a solid material disposed or otherwise in contact with the land into ground water or surface water can be estimated using one or more single-point leaching tests that represent a specific scenario or set of environmental conditions. Alternatively, LEAF testing may provide more reliable release estimates by assessing the impact on leaching of environmental factors and waste properties that are known to significantly affect constituent leaching and which vary in the environment and across waste forms. By testing over a range of values for release-controlling factors, the LEAF approach allows for flexibility in that a single data set can be used to evaluate multiple potential management scenarios for a material (e.g., disposal or beneficial use) under varied or site-specific environmental conditions.

The four LEAF test methods presented in this document have undergone interlaboratory validation for use with inorganic constituents of potential concern (COPCs), such as metals and radionuclides, and have been incorporated into the U.S. EPA compendium of laboratory methods, SW-846 (see *https://www.epa.gov/hw-sw846/sw-846-compendium*). The Agency recognizes that the leaching of organic constituents will follow the same principles (i.e., that key environmental conditions or waste properties that significantly affect leaching can be identified) but may require different testing methods to address controlling properties. Therefore, the next steps for the Agency are to adapt these methods or develop new methods applicable to evaluating the potential release of organic COPCs from waste or other materials.

Key Definitions

Term	Definition
Assessment Ratio	The estimated maximum leaching concentration for a COPC divided by the threshold value for a scenario.
Available Content	The fraction of the total concentration of a constituent in the solid phase (mg/kg-dry) that potentially may leach over a reasonably near-term timeframe (e.g., 100 y).
Available Content-Limited Leaching	A liquid-solid partitioning endpoint at which the available content of a constituent in the solid phase limits the amount leached into aqueous phase (i.e., the aqueous phase is less than the saturation concentration and the solid phase is depleted of the constituent's available content).
Chemical Species	Particular forms of a chemical element or compound (e.g., ions, molecules, molecule fragments, etc.) that contribute to the measured concentration of a constituent in a given liquid or solid phase.
Constituent	A chemical element or species in the liquid or solid phase, typically chemically analyzed based on total content of chemical species or compound.
Constituent of Potential Concern (COPC)	A constituent that may be present at concentrations of regulatory, environmental, or human health significance due to their toxicity or other properties.
Eluant	The water or aqueous solution used to contact or extract constituents from a material during a laboratory test.
Eluate	The aqueous solution, analyzed as part of a laboratory test, which results from contact of an eluant with the tested material.
Equilibrium Limited Leaching	A liquid-solid partitioning endpoint at which the leaching of constituents is limited by the amount of material leached at equilibrium conditions (e.g., available content limited leaching, solubility-limited leaching.)
Flow-through	The water contact scenario when precipitation, infiltrating water, or groundwater flows around the external surface area of a low-permeability material (e.g., cement-treated wastes, compacted materials) and release occurs at the interface between the flowing water and the material.
Leachant	The water or aqueous solution contacting a material under field conditions (e.g., infiltrating water, groundwater).
Leachate	The aqueous solution resulting from leachant contact with a material under field conditions.
Mass Transport (diffusion) - Limited Leaching	The release from solid material when leaching potential is less than equilibrium liquid-solid partitioning, typically constrained by the rate of diffusion through the material being leached.
Percolation	The water contact scenario in which precipitation, infiltrating water, or groundwater, moves through the contiguous voids of a porous material and leaching occurs at the solid-liquid interface between the percolating fluid and the solid material.
Solubility-Limited Leaching	A liquid-solid partitioning endpoint at which the solubility of a constituent in the aqueous phase or eluant limits the leaching process (i.e., the aqueous phase concentration is at saturation yet available constituent remains in the solid phase).
Sorption-Controlled Leaching	A liquid-solid partitioning endpoint at which neither the solid nor the aqueous phase limits leaching, but sorption to mineral or organic matter

	surfaces controls the concentration measured in the aqueous phase or eluant.
Source Term	A numerical or model-based estimate of constituent release used to represent leaching from material in a field application and which may also be used for subsequent fate and transport modeling.
Total Content	The concentration of a constituent in the solid material (mg/kg-dry) accounting for all species.
Washout	A rapid release of constituents resulting from highly soluble species rapidly dissolving in water percolating through a material; usually indicated during Method 1314 by a decrease in leaching concentration of approximately one order of magnitude or more from L/S = 0.2 mL/g-dry to 2.0 mL/g-dry.

1. An Introduction to LEAF and this Guide

1.1 What is the Purpose of this Guide?

The purpose of this document is to provide information that improves understanding and supports application of the Leaching Environmental Assessment Framework (LEAF) published by the United States Environmental Protection Agency[1] (U.S. EPA, or the Agency) and, thereby, facilitate its broader use. LEAF is a leaching evaluation framework consisting of four leaching tests (i.e., U.S. EPA Methods 1313, 1314, 1315 and 1316; U.S. EPA, 2012f, 2013a, 2013b, 2013c) data management tools, and scenario assessment approaches that are designed to work together to provide an estimate of the release of constituents of potential concern (COPCs) from a wide range of solid materials. This document provides background and technical support for implementing LEAF to assess leaching potential of COPCs from solid waste matrices for beneficial use,[2] disposal, treatment and remediation applications. In addition, this document is designed to address frequently asked questions about the four EPA LEAF leaching test methods, data management and reporting using the freely available LeachXS™ Lite software,[3] and potential applications of the LEAF approach. For detailed information on EPA's SW-846 Methods, see *https://www.epa.gov/hw-sw846/sw-846-compendium*.

The LEAF test methods presented in this document have been validated for inorganic COPCs (U.S. EPA, 2012c, 2012d). The Agency believes the methodology in this guide is applicable to the leaching of heavy metals, and by extension, inorganic radionuclides.[4] Next steps for the Agency are to adapt these methods or develop new tests for estimating the leaching of organic COPCs. Although these leaching tests for organic COPCs will be based on the LEAF principles (i.e., testing protocols addressing identified environmental parameters having the greatest effect on COPC release), the specifics of organic COPC leaching may require development of different testing methods (i.e., different environmental factors may determine leaching behavior of organic COPC than for inorganic COPC). Every effort will be made to ensure the organic COPC test methods are compatible with the methods for inorganic COPC leaching, with the overall goal of creating an integrated set of tests that can be reliably used to evaluate the leaching potential of a broad range of wastes containing inorganic and/or organic COPCs.

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[1] EPA worked collaboratively with parallel efforts in the European Union to develop and harmonize test methods to support data comparisons. (Appendix A of this document identifies analogous leaching tests)

[2] EPA's *Methodology for Evaluating Beneficial Uses of Industrial Non-Hazardous Secondary Materials* presents a voluntary approach for evaluating the potential adverse impacts to humans and the environment from a wide range of industrial non-hazardous secondary materials and their associated beneficial uses. Prior to beneficially using secondary materials in any projects, interested individuals or organizations should consult with the relevant state and federal environmental agencies to ensure proposed uses are consistent with state and federal requirements.

[3] LeachXS™ Lite is a free, limited capability version of the LeachXS™ decision support software. As a data management tool for use with LEAF data, LeachXS™ Lite is available for licensing at no cost at www.vanderbilt.edu/leaching.

[4] Chemically, inorganic radionuclides behave similarly to inorganic species that are not radionuclides. Therefore, the LEAF leaching test methods may be applicable to estimating radionuclide leaching release provided appropriate modifications are taken to ensure adequate worker protection and materials management and disposal during and after testing. LEAF can be applied to radionuclides for the purposes of evaluating leaching potential; however, LEAF does not address radiological risks associated with radionuclides.

1.2 Who Can Benefit from this Guide?

The intended audience for this guide includes waste generators; decision-makers for waste management, such as beneficial use of non-hazardous industrial secondary materials, waste treatment effectiveness, and site remediation; risk assessors; technical consultants; state environmental agency officials; analytical laboratories; and other interested stakeholders to the degree that their use is consistent with existing federal and state regulations and policies.

1.3 What is LEAF?

Leaching of COPCs from solid materials to surrounding soils, groundwater, or surface water can occur in the environment whenever a material is placed on or in the ground. A leaching assessment provides an estimate of the extent and rate of COPC release to the environment through waterborne pathways. In addition, leaching assessments can provide insights into material durability under environmental conditions based on the dissolution and transport of the primary constituents that comprise the solid matrix. Laboratory leaching tests provide the basis for estimating which constituents will leach, the rate at which they will leach, and the factors that control leaching. In addition, the data obtained from leaching tests can be used to develop a quantitative description of the leaching behavior of a material, referred to as a leaching source term, representing the release of COPCs from a material under defined management scenario conditions.

Leaching Key Terms

Chemical Species—Particular forms of a chemical element or compound (e.g., ions, molecules, molecule fragments, etc.) that contribute to the measured concentration of a constituent in a given liquid or solid phase.

Constituent—A chemical element, species, or compound in the liquid or solid phase, typically chemically analyzed based on total content of chemical species or compound.

Constituents of Potential Concern (COPCs) — Constituents that may be present at concentrations of regulatory, environmental, or human health significance due to their toxicity or other properties.

Source Term— A numerical or model based estimate of constituent release used to represent leaching from material in a field application and which may also be used for subsequent fate and transport modeling.

LEAF is an integrated framework that includes four laboratory methods for characterizing the leaching behavior of solid materials under specified release conditions. It also provides data management tools for collecting leaching data, comparing leaching behavior between materials, reporting graphical and tabular results, and suggesting approaches for using leaching data to support leaching assessments. LEAF provides a consistent approach to estimate leaching of COPCs from a wide range of solid materials including as-generated wastes, treated wastes (e.g., solidified/stabilized soils and sediments), secondary materials (e.g., blast furnace slags), energy residuals (e.g., coal fly ash, air pollution control residues), industrial processing residuals (e.g., mining, and mineral processing wastes) and contaminated soil or sediments. The LEAF test methods consider the effect on leaching of important leaching factors, such as pH, liquid-to-solid ratio (L/S) and physical form of the material, that represent a range of plausible field conditions (U.S. EPA, 2010). Thus, a single set of leaching data can be used to evaluate multiple management options or scenarios.

The LEAF framework provides the flexibility to generate evaluations ranging from screening assessments to detailed source characterization for site-specific or national assessments. Generally, as used in this document, a screening level assessment means an evaluation based on the laboratory test results using the LEAF methods alone. A detailed source characterization uses the leach test results in a defined use scenario, including anticipated environmental conditions. Evaluating leach test results in the context of a particular scenario provides a more refined and detailed assessment of the likely impact of materials placement on land and COPC release under the conditions defined in the scenario. Therefore, testing can be tailored to address particular assessment objectives and the level of information needed to support decision-making. For some applications, leaching assessments using LEAF may be simple comparisons of leaching results to relevant benchmarks to evaluate performance of a material in a particular management scenario or identify COPCs with the potential for adverse impacts to the environment. In many cases, site-specific factors must be considered, and leaching test results may not directly reflect concentrations at the point of compliance. More complex assessments may require detailed characterization of leaching behavior sufficient to support groundwater (or surface runoff) fate and transport modeling between a source term and a point of compliance (POC), as determined by applicable state and federal regulations and policies. A number of models are available (U.S. EPA, 2015, 2017a) that can evaluate the fate and transport of COPCs in the environment using a source term derived from LEAF.

LEAF incorporates a consistent set of standardized testing methods and either generic or application-specific release models. Free publicly available data management and visualization software, LeachXS™ Lite including Microsoft Excel® templates, is provided to facilitate data management, evaluation, and reporting as part of LEAF assessments.

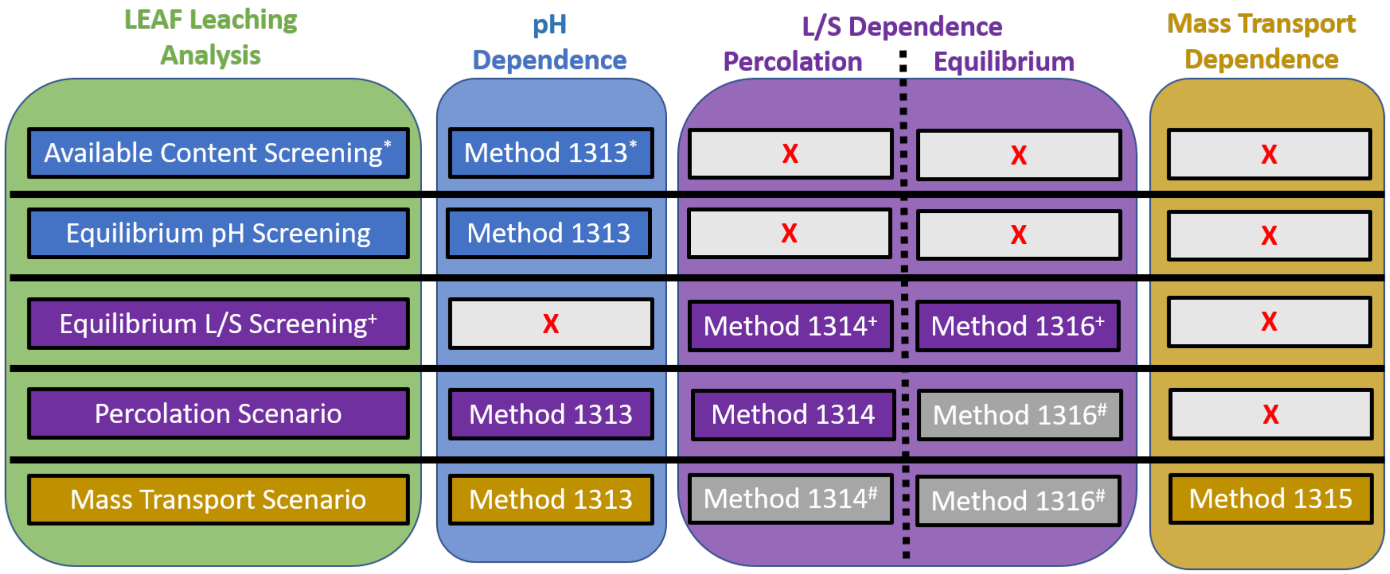
1.3.1 Why was LEAF Developed?

Traditionally, the potential for environmental impact through leaching of COPCs from a solid material disposed or otherwise in contact with the land into ground water or surface water has been estimated using one or more single-point leaching tests that represent a specific scenario or set of environmental conditions. For example, the Toxicity Characteristic Leaching Procedure, TCLP (U.S. EPA, 1992), simulates conditions that may be found within a municipal solid waste landfill while the Synthetic Precipitation Leaching Procedure, SPLP (U.S. EPA, 1994), mimics contact with a synthetic acidic infiltrate (U.S. EPA, 2010). Other single point test methods also simulate specific scenarios, e.g., ASTM D3987-12 (2012). Single-point test approaches can be appropriate for screening or classification purposes and TCLP remains required for specific regulatory applications such as hazardous waste classification under the toxicity characteristic regulation (40 CFR 261.24) and for many waste treatment regulatory standards. However, the U.S. EPA desired a flexible leaching characterization framework that can be tailored for use over a wide range of material types and release scenarios. Broad application of a uniform leaching characterization approach would enable comparison of leaching behavior between materials or between release scenarios.

Another approach that is sometimes used to assess constituent release in the environment involves defining liquid-solid partitioning as constants (K_d values) and modeling the movement of constituents through groundwater with constant partitioning values to soils and other media. This approach assumes that partitioning of COPCs from a solid material is proportional to the total COPC concentration (i.e., a linear partitioning relationship between the total content of the COPC in the material and contacting water). The K_d approach considers adsorption to mineral surfaces as a primary partitioning mechanism and may be a reasonable description for leaching or groundwater fate and transport of COPCs under dilute conditions. However, the partitioning of many constituents between a solid material and a contacting liquid is not linear over varying values of pH or L/S and, therefore, has many of the same drawbacks as single point leach tests. Similar to single point leach tests, a linear partitioning coefficient does not provide the mechanistic understanding nor represent the important processes and factors that control leaching (e.g., solubility constraints, available content, or the physical form of the material). Thus, the K_d approach would not be a reasonable description of leaching when COPC solubility limits leaching, when only a fraction of the COPC is leachable, or when the available content limits the observed solution concentration (Thorneloe, Kosson, Sanchez, Garrabrants, & Helms, 2010; U.S. EPA, 2014c).

In 1991 and 1999, the Science Advisory Board (SAB) of the U.S. EPA reviewed the Agency's leaching evaluation methodology (U.S. EPA, 1991, 1999) and recommended that EPA develop new, flexible evaluation approaches that consider how environmental parameters may affect the release of COPCs. The SAB also expressed concern about the over-broad use of the TCLP protocol to assess leaching for scenarios in which the test conditions were very different from the actual or plausible conditions or in cases where there was no regulatory requirement to use the test. In addition, the SAB also identified a number of technical concerns about the design and use of the TCLP (U.S. EPA, 1991).

While not answering all of these SAB concerns, LEAF was developed to provide an approach that addressed what EPA considered the most critical issues raised. Each method directly addresses one of three release-controlling factors for inorganic COPCs that may vary under plausible use or disposal conditions: pH, the L/S of the test material relative to the leaching environment, and whether leaching is controlled by chemical equilibrium or by mass transport rates (e.g., diffusion). By testing over a range of values for these release-controlling factors, the LEAF approach allows for flexibility in that a single data set can be used to evaluate multiple potential management scenarios for a material (e.g., disposal or beneficial use) under different environmental conditions. The LEAF leaching tests include batch equilibrium tests, percolation column tests and semi-dynamic leaching tests intended to characterize the leaching behavior of a solid material under equilibrium or dynamic conditions. The results from these tests may be interpreted individually or integrated to identify a solid material's characteristic leaching behavior. Figure 1-1 illustrates the chemical factors influencing leaching estimated by LEAF testing and the combination of tests utilized by the screening or scenario leaching assessments presented in this document.



LEAF Leaching Analysis	pH Dependence	L/S Dependence		Mass Transport Dependence
		Percolation	Equilibrium	
Available Content Screening*	Method 1313*	X	X	X
Equilibrium pH Screening	Method 1313	X	X	X
Equilibrium L/S Screening+	X	Method 1314+	Method 1316+	X
Percolation Scenario	Method 1313	Method 1314	Method 1316#	X
Mass Transport Scenario	Method 1313	Method 1314#	Method 1316#	Method 1315

* Method 1313 only requires pH endpoint 2, 9, and 13 for Available Content Screening
+ Equilibrium L/S Screening can use either Method 1314 or Method 1316
# Optional method for leaching analysis

Figure 1-1. LEAF test methods in leaching evaluations and the chemical factors influencing leaching estimated by each test method. Leaching analyses presented in this guide(left column) utilize the test methods in the boxes to the right of the analysis. Methods in grey are optional depending on the specifics of a scenario. A red X indicates the leaching analysis does not use test for the environmental parameter.

1.3.2 Why Perform Leaching Tests?

Leaching tests are used to measure the amount of constituent mass that is released from a solid material into a set volume of water under specified laboratory conditions. The data collected from leaching tests is not directly representative of field leachates but is used to estimate how a material will leach when managed in the field. Laboratory testing results can be combined with knowledge of how a material is managed (or potentially mismanaged) to develop a description of how the COPCs will leach from material in a defined scenario, often referred to as a source term. The source term can be used to evaluate the potential for adverse impacts from placement of the material into or onto the land and forms the basis for a determination of the appropriateness of the material in the proposed management scenario. Further, the movement of leached COPCs away from the leaching source may be simulated using source terms in conjunction within several available groundwater fate and transport models.

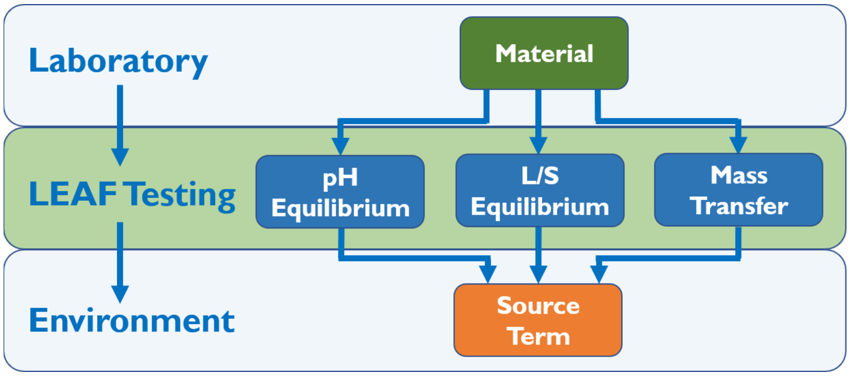


Figure 1-2. LEAF testing can estimate leaching from a material with varying environmental factors. A source term to represent leaching in the environment can be developed from LEAF testing.

1.3.3 When Can LEAF be Used?

The LEAF tests and approach is voluntary and not a requirement under the Resource Conservation and Recovery Act (RCRA). This guidance provides a general approach that needs to be tailoring to the specific application or regulation under which it is being used. For example, under RCRA, the TCLP test (EPA Method 1311) is used for classification of many wastes as hazardous (Subtitle C) or non-hazardous (Subtitle D) as part of the Toxicity Characteristic regulation (40 CFR 261.24). In addition, many RCRA land disposal restriction (LDR) treatment standards are based on the results from TCLP testing (40 CFR 268.40). LEAF is not a regulatory test but may be useful in support of evaluations not designed to meet requirements under the RCRA regulations. The use of LEAF on a site-specific basis needs to be tailored to the questions being asked. The usefulness of LEAF testing will depend on how well test results estimate environmental conditions for a specific application. Using data from ten case studies, comparisons have been made between LEAF testing and field leaching behavior over a range of materials and conditions (U.S. EPA, 2014c). Good agreement was found between field and laboratory results except for situations where redox or carbonation occurred. In these situations, geochemical speciation modeling was conducted in conjunction with the LEAF results, showing good agreement to what was found in field leaching behavior. (Garrabrants, Kirkland, Kosson, & van der Sloot, 2009; U.S. EPA, 2003, 2012b, 2014a, 2014b).

LEAF may also find application in support of cleanup decisions under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) that address specific contaminants on a site-specific basis. The performance values against which LEAF would be evaluated may differ depending on the specific regulatory program involved. For example, site-specific data is used to determine whether action is warranted at a site. Furthermore, under CERCLA as stated in the National Oil and Hazardous Substances Pollution Contingency Plan, “levels generally should be attained throughout the contaminated plume, or at and beyond the waste management area when waste is left in place” (55 FR 8753, March 8, 1990). Decision-makers should consult with the appropriate regulatory agency to ensure compliance when using LEAF testing in support of an evaluation.

Under CERCLA, cleanup decisions depend on site-specific factors. General guidance on use of LEAF data that would be applicable to all sites is impractical and beyond the scope of the How-to Guide. As such, EPA expects to provide additional guidance on the use of LEAF for CERCLA response actions as experience with LEAF evolves.

1.4 What Topics Are Covered in this Guide?

This document includes a range of topics, from background information on leaching to selecting a leaching test method and interpreting results. Some users of this guide may benefit from reading this material in a front to back manner while others may be better served by reviewing a selected section. The How-To Guide is modular in design but also builds upon previous sections. Specifically, the reader can learn about the following topics in each section.

Table 1-1. Overview of Topics in the How-To Guide

Section	Topics
Section 1: An Introduction to LEAF and this Guide	• The purpose of the How-To Guide • Who can benefit from the How-To Guide • Why LEAF was developed • The purpose of leaching tests
Section 2: Understanding the Leaching Process	• The definition of leaching • The definition of a source term • The definition of available content • An overview of fundamental leaching behavior including equilibrium control, mass transport control, and factors affecting leaching in the field
Section 3: An Overview of LEAF	• A description of analytical test methods and expected results for Methods 1313, 1314, 1315, and 1316 • The interlaboratory validation of LEAF methods • The field validation of LEAF methods • The suggested best practices for an analytical testing program • Best practices for quality assurance and quality control • Testing and analytical cost estimates for LEAF tests • Processing time estimates for LEAF tests

Table 1-1. Overview of Topics in the How-To Guide

Section	Topics
	• Laboratory data management discussion and tools
Section 4: Developing Leaching Evaluations using LEAF	• Some potential applications of LEAF • A general approach to developing an assessment framework • Assessment ratios and comparing test results to benchmark values • Developing a screening assessment • Developing a scenario assessment • Overview of environmental processes that can influence leaching • Determining available content • Interpolating data • Calculating water contact time • Identifying solubility and available content-limited leaching • Mass transport effects on leaching • Dilution and Attenuation in an Assessment Ratio • Using source terms from LEAF in environmental modeling
Section 5: Case Studies of Using LEAF for Assessments	• Screening Assessment Case Study: Evaluating Coal Combustion Fly Ash for Use as Structural Fill Material • Scenario Assessment Case Study: Evaluating Treatment Effectiveness of a Cement-Based Stabilization/Solidification (SS) Process
Section 6: Test Your Knowledge	• Exercises reviewing basic concepts using data from the screening assessment case study. • Calculating the available content of a material • Determining a plausible pH range for environmental conditions • Interpolating Method 1313 test results to environmental pH • Solubility versus available content limited leaching behavior
Section 7: Useful Resources	• A collection of related resources
Section 8: References	• References cited in this document

2. Understanding the Leaching Process

2.1 What is Leaching?

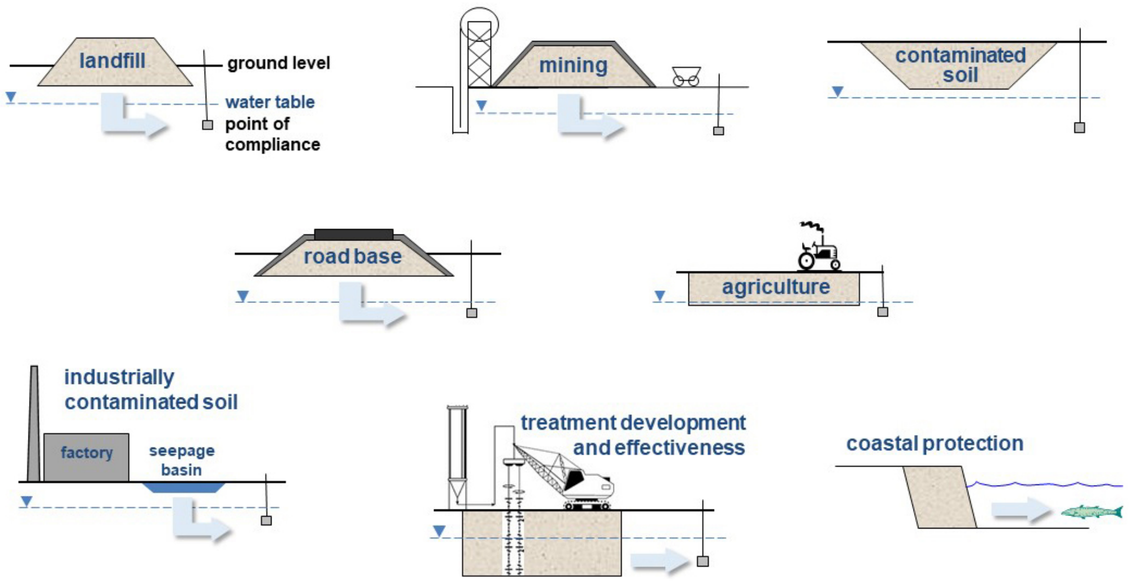
In an environmental context, leaching is the transfer of chemical species or compounds from a solid material into contacting water. In the environment, contacting water may result from infiltration of rainwater through overlying soils or through direct contact of the material with groundwater or surface water. Constituents that leach into the water have the potential to contaminate adjacent soils or disperse into groundwater or surface water bodies. The rate and extent of the release of inorganic constituents from a solid material are controlled by a combination of physical and chemical processes that depend on the properties of the solid material, the environmental exposure conditions or scenario, and the specific COPCs contained in the material.

2.2 What is a Source Term?

In leaching assessments, a leaching source term is a numerical description of constituent release from a material into contacting water under a defined set of environmental conditions. Figure 2-1 illustrates a variety of scenarios for which leaching from a solid material disposed or otherwise in contact with the land can be considered a primary source of environmental impact. In each of these scenarios, COPCs are released from material upon contact with water. This figure shows that these seemingly diverse applications often result in environmental release facilitated by water. For a chosen material, the leaching behavior at the source remains relatively constant based on environmental conditions in each of these scenarios, while the movement to groundwater or transport within groundwater can be significantly different between scenarios. For example, the POC may be considered at the boundary of the material or at some point down gradient of the source depending on applicable regulations.

The LEAF assessment approach provides a numerical estimate of COPC release (i.e., a source term) based on measured leaching data in the context of environmental conditions that a material might encounter in a chosen application. Leaching assessments typically include a description of the material in the field scenario, material geometry and placement relative to the groundwater, and ranges or changes to material properties or leaching conditions over time. While screening-level evaluation may utilize assumed or default values, detailed information will provide a more precise, and in some cases, more realistic estimate of release.

The selection of leaching test data to be used as a source term depends on the assessment objectives and the required level of detail, considering bounding cases and scenario uncertainties. Raw leaching test results may be used directly to formulate a generic source term that can be directly compared to relevant benchmarks or thresholds when the POC is at the material boundary. In some applications, LEAF test data may be compared between materials before and after treatment to evaluate the efficacy of treatment options (Kosson, van der Sloot, Sanchez, & Garrabrants, 2002). When detailed characterizations are required, the source term developed from LEAF may be used as an input to simple mass transport models, or with more-complex fate and transport models, to develop specific source terms for material- and site-specific applications. In addition, source terms may be developed considering variability as a basis for regional or national decisions (e.g., through Monte Carlo-based source terms used in fate and transport modeling for exposure assessment; U.S. EPA, 2014a, 2014b).



Adapted from van der Sloot, Kosson, and Hjelmar (2003).

Figure 2-1. Various environmental assessment scenarios showing a source term for leaching with transport to the water table and through the groundwater to a point of compliance. Note that the point of compliance may be at the unit boundary of the material for some applications.

2.3 What is the Available Content of a COPC?

All materials and wastes contain a number of chemical constituents, some of which may pose environmental hazards. The fraction of any COPC that is readily released into the environment is considered the "available content" for that COPC. The available content of a COPC is defined as the fraction of the total content that is not bound within decomposition-resistant (i.e., recalcitrant) phases, but that is "available" for release over the domain of leaching conditions. The sum of the recalcitrant and available fractions of a COPC is equal to the total content of the constituent in the material (U.S. EPA, 2014c). For inorganic constituents, available content is rarely the same as the total content because a fraction of the total mass may be tightly bound within the solid matrix and is not released under plausible field conditions. The available content can be determined from leaching tests as the mass release in milligram of constituent per kilogram of material calculated from the maximum leaching concentration tested at specific pH values (see Section 4.4.1). Determination of the available content provides a practical value of the potential release of constituents into the environment that may be used as a bounding estimate concentration for screening under assumed infinite source terms (see Section 4.2.4) or to place limits on the extent of leaching for finite source term approaches (see Section 4.2.5).

2.4 How Does Leaching Occur?

Leaching occurs when constituents within a material in the environment solubilize into contacting water. The leaching process is driven by the principles of mass transport, which defines the movement of constituents from a solid phase to contacting water to minimize gradients, or differences, in chemical activity within a phase or across the interface between phases (Bird, Stewart, & Lightfoot, 2001). In environmental conditions, which often have low ionic strength, gradients in chemical activities can often be estimated as concentration gradients. Thus, leaching may be considered the result of gradients in constituent concentrations between the pore solution of the solid and the contacting water. As leaching progresses and concentration gradients are minimized, mass transport slows, and the system approaches a state of chemical equilibrium (i.e., concentrations in the liquid phase are constant).

If the leaching process continues until concentration gradients are minimized and mass transport ceases, the scenario is considered to have reached chemical equilibrium. Due to slow dissolution of some minerals and other time-dependent processes, chemical equilibrium may be achieved for some constituents, but not for all constituents, within a defined duration (such as a short assessment interval or the duration of some laboratory tests). When chemical equilibrium is achieved, however, the leaching process can have one of several endpoints with respect to a constituent:

- Available Content Limit: The solid phase becomes depleted of leachable constituent such that the transfer from solid to liquid stops. When this endpoint occurs, the extent of leaching is considered available content-limited because the fraction of the total constituent content that is available for leaching has been released.
- Solubility Limit: The water phase becomes saturated with respect to the constituent and leaching stops although there remains a fraction of constituent in the solid available for leaching. For this case, the extent of leaching is considered solubility-limited because the chemical parameters of the liquid phase that define the solubility of a constituent constrain the amount that can be released[5].

The identification of leaching behavior as solubility-limited or available content-limited plays an important role in the estimation of COPC release for environmental purposes. Leaching behavior is interpreted through evaluation and comparison of equilibrium-based leaching tests results as described in Section 4.4.5. Discussion of relevant adsorption processes associated with sorption-controlled leaching is provided in Section 4.4.4.

In practical terms, the time that it takes a solid-liquid system to reach an equilibrium endpoint depends on (i) the geometric size of the material (i.e., particle size for granular materials or the dimension perpendicular to mass transport for monolithic materials and compacted granular fills), (ii) the L/S (i.e., the amount of liquid relative to the amount of solid), (iii) the chemical characteristics of the COPC, and (iv) the chemical composition of the liquid phase (i.e., pH, oxidation-reduction potential, ionic strength, composition). For example, when the material is granular (i.e., consists of many particles with relatively small dimension) and is contacted by a relatively small amount of water, the leaching process reaches an apparent endpoint within the practical time of bench-scale leaching tests. For these systems, the extent of leaching (i.e. the COPC mass released) is the practical measure of COPC release because the system is likely to achieve equilibrium quickly in the environment. The liquid-solid partitioning (LSP) of COPCs

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[5] While not constrained by the available content or aqueous solubility, a constituent may be distributed between the solid and water phase by adsorption to mineral or other phases under environmental conditions. Leaching at this endpoint is considered sorption-controlled because interfacial adsorption/desorption chemistry dictates the concentration of the constituent in the liquid phase. In basic leaching evaluations, sorption controlled processes are often not easily distinguishable from solubility-limited leaching and are thus treated similarly in this guide. LEAF data that indicate solubility-limited leaching, in fact, may reflect or consider the combined effect of solubility and adsorption as controlling processes. Depending on the surface charge of a granular material, adsorption can result in a constituent concentration in the leachate much lower than expected based on solubility alone. Chemical speciation modeling may be helpful in determining the chemical mechanisms that explain leaching concentrations when this level of information is needed.

between the contacting water and the solid material at equilibrium provides a measure of the extent of leaching with the available content representing the maximum extent of leaching. Conversely, larger particles, such as those within monoliths or compacted granular samples, require a longer time to reach an apparent endpoint to the leaching process. Thus, the rate of leaching becomes the dominant leaching characteristic that predicts the release of COPCs as measured by the rate of mass transport through the material to the interface between the material and the contacting water.

Therefore, over a wide range of environmental conditions, mass transport may be considered to control the rate of leaching while chemical equilibrium controls the extent of leaching. Ideally, comprehensive leaching assessment would address both the rate and the extent of constituent leaching as applicable based on the environmental conditions imposed by the combined influences of material and the management scenario.

2.4.1 The Extent of Leaching Through Liquid-Solid Partitioning (LSP)

LSP is the chemical equilibrium, or near-equilibrium, state that describes the distribution of a constituent between the solid phase and a contacting liquid. For many materials, LSP concentrations are the combined result of the available content, aqueous solubility of the various chemical species of the constituent, adsorption/desorption to (hydr)oxide surfaces and particulate carbon, and chemical reactions in the liquid phase. Thus, the LSP evaluated through leaching tests is intended to obtain one of the leaching process endpoints described above and to approximate chemical equilibrium between the aqueous and solid phases (U.S. EPA, 2010).

Important chemical factors influencing the measured constituent LSP include:

- **Eluant or leachate pH** that controls aqueous solubility of inorganic COPCs, dissolution of organic carbon, and sorption or desorption of COPCs to the surface of oxides, clays, minerals, and organic matter,[6]
- **Liquid-to-solid ratio (L/S)** defined as the volume of liquid in contact with a dry mass of solid,
- **Reduction/oxidation (redox) conditions** that may change the oxidation state of COPCs (e.g., Cr(III) to Cr(IV)) [7] and also the quantity of available surfaces for sorption; e.g. Fe(III) to Fe(II) results in a decrease in sorption to iron (hydr)oxide surfaces,
- **Dissolved organic matter** that can increase the measured concentration of COPCs through formation of soluble complexes with dissolved organic carbon (DOC),
- **Ionic strength and common ion effects** that suppress dissolution of some minerals, and
- **Biological activity** that result in pH changes or redox changes in the solid-liquid system.

Of these chemical factors, pH and L/S are the two parameters that are most important for the majority of inorganic constituents with regard to constituent leaching and are the two parameters that can be best controlled in the laboratory. Information about the other factors can be collected during testing and used to refine release estimates based on geochemical models when needed, as described in Section 4.4.8.

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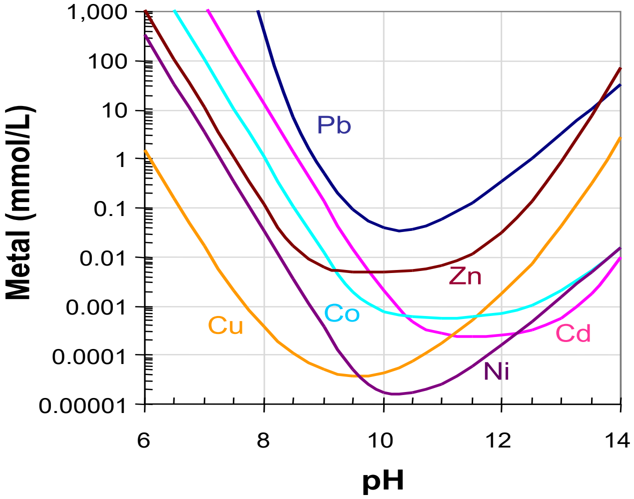
[6] The pH of the eluate or leachate is the combined effect of the acidity or alkalinity of the contacting solution and the buffering, or acid/base neutralization, capacity of the contacting material.

[7] Since a change in the oxidation state of an ion changes solid and aqueous species it can form, oxidation-reduction conditions also can have an impact on leaching in some cases.

2.4.1.1 pH-dependence

Typically, the aqueous solubility of many inorganic species, including many COPCs, is a strong function of solution pH. Figure 2-2 presents a graph of the solubility of metal hydroxides over the pH range from 6 to 14 which may be applicable for some environmental scenarios (e.g., used of solidification/stabilization with cement as a soil or waste treatment). The figure shows that the solubility of these metals reaches a minimum value at approximately pH 10 but can vary by several orders-of-magnitude with relatively small shifts in pH. The pH-dependent behaviors shown in this figure are for simple, single hydroxide minerals in solution. In comparison, the mineralogy of soil and waste systems is relatively complex with each COPC potentially present in several different mineral species, each with its own solubility behavior. In the field, a number of potential mineral species may affect the solubility. Regardless, this figure is helpful as an illustration of the significant influence that pH can have on the measured LSP of waste and soil systems.



Adapted from Stumm and Morgan (1996).

Figure 2-2. Solubility of metal hydr(oxides) in water as a function of pH.

2.4.1.2 L/S-dependence

The L/S dependence of a constituent allows for estimations of leaching behavior over a range of water contact rates. A constituent may initially leach as a highly soluble species. However, once a significant amount of water has contacted the solution and transported the constituent away, the depleted constituent concentration in the solid material limits further leaching. This transition would be seen in laboratory experiments at increasing L/S. Alternatively, leaching may be initially limited by the constituent solubility and a constituent may leach at a relatively constant rate over longer periods.

Figure 2-3 presents an illustration of how changes in L/S can influence the LSP leaching behavior. In this figure, the five light colored dots represent units of a COPC that are available to leach or have leached while the five dark colored dots represent units of a COPC that are present in recalcitrant minerals and are not available to leach. Therefore, the available content of this constituent is 50% of the total content (i.e., 5 units available out of 10 units). The panels on the left show that, at low L/S (e.g., the L/S associated with the porewater of a material), constituents in the liquid phase reach a saturation point of 0.1 unit/mL (i.e., 2 units leached into 20 mL of water) and the leaching behavior is considered solubility-limited. As the amount of water is doubled from 20 to 40 mL, additional constituent is leached such that the liquid concentration remains 0.1 unit/mL. Under solubility-limited release, the measured concentration for solubility-limited COPCs usually is a weak function of L/S as long as pH does not change significantly and complexing agents (e.g., DOC) are not present. As the volume of water increases to 60 mL, leaching continues and all of the available constituent mass is leached from the solid material; thus, the concentration in the liquid phase decreases to 0.08 unit/mL (5 units in 60 mL) and leaching has become limited by the available content. At this point, LSP becomes a strong function of L/S because the addition of water to 80 mL reduces the LSP concentration further to 0.06 units/mL because the same available mass of the constituent (5 units) is dissolved into a greater volume of water (80 mL).[8]

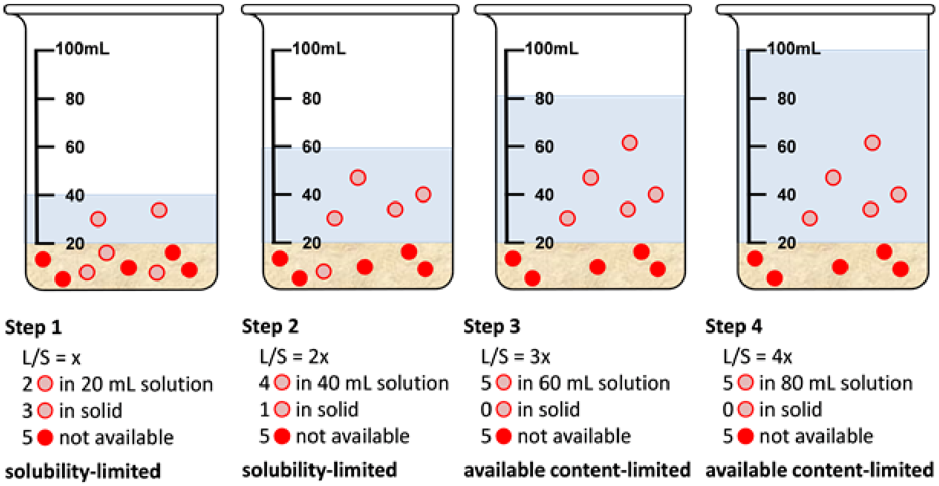


Figure 2-3. Illustration of the changes in LSP leaching behavior as the system L/S increases.

For many field scenarios, the L/S may be derived from the information on the rate of infiltration or groundwater contact and simple physical parameters of the material application. For example, the L/S of a landfill scenario can be determined by measuring the volume of leachate collected annually from the landfill and relative to the estimated volume of waste in the landfill or the landfill design capacity. When scenario-based information about the relative rate of water contact is known, laboratory data at varying L/S may be considered a surrogate for time that allows for the estimation of leaching as a function of time under field conditions or the prediction of the time required until constituents are depleted (see Section 4.4.3 for more on calculating L/S). The L/S may also be adjusted to account for the tendency of contacting water to preferentially flow on or around the material (See Section 4.4.4 for more on interpreting L/S from LEAF testing). In the laboratory, the L/S in a leaching test is varied by changing the relative proportions of test material and the leaching solution (i.e. leachant).

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[8] In addition to the effect on L/S illustrated above, concurrent changes in pH, ionic strength and the presence of other dissolved species that can also influence solubility. For example, according to the Davies Equation for calculation of activity coefficients (Stumm & Morgan, 1996) a 0.1 M solution of barium carbonate would result in an ionic strength of 0.4 M and activity coefficients of 0.292, resulting in solution activity substantially lower than measured solution concentration. An example of a common ion effect is the lower observed concentration of barium in field leachate compared to laboratory test results because of lower L/S and presence of higher sulfate concentrations from dissolved calcium sulfate that reduces the solubility of barium sulfate by Le Chatelier's principle (U.S. EPA, 2014c)

2.4.2 The Rate of Leaching (Mass Transport)

Mass transport describes a set of mechanisms (e.g., diffusion, dissolution, adsorption, or complexation) that collectively control the transfer of constituents from areas of higher concentration to areas of lower concentration over time. Within a solid material, constituents move via diffusion from areas of higher concentration to lower concentration and may interact with the minerals and other solid phases comprising the material through various chemical reactions (e.g., dissolution/precipitation, adsorption/desorption). The specific rate of diffusion, or the molecular diffusivity, is the speed at which a constituent travels unhindered by physical or chemical constraints through water, proportional to the magnitude of the concentration gradient (i.e., diffusion is faster when incremental difference in concentrations is greater). The observed rate of diffusion for a constituent moving through a porous material, however, is slowed by the distance that the constituent has to travel, the effective porosity of the material, the connectivity and tortuosity of the porous network, and chemical reactions that occur along the diffusion pathway. Often, local chemical equilibrium between the solid material and porewater is assumed during mass transport, such that all of the chemical parameters that influence LSP also effect the rate of mass transport.

2.4.3 Leachability of a Material in the Field

The rate and extent that constituents can leach from a material are determined by a number of chemical and physical factors that can vary between sites and are not likely to remain constant in the field because the environmental media, including local conditions and the solid materials, change over time. Slight changes in key factors can have substantial effects on the magnitude of releases by changing either the rate at which a constituent can be released or the equilibrium water concentration. Some examples of key factors include:

- Changes to the L/S from increased precipitation that results in a shift between solubility-limited and available content-limited leaching behavior;
- Changes to the pH that alter the solubility of a constituent in the water (e.g., from acid precipitation, uptake of atmospheric carbon dioxide, oxidation of reduced minerals or biological activity);
- Changes to the redox conditions (e.g., reduction from biological activity that alter the oxidation state of a constituent [e.g., Cr(III) to Cr(IV)] or oxidation through contact with air);
- Changes to the physical structure of the material (e.g., degradation from internal stress through freeze/thaw cycles or mechanical erosion that increase the ratio of surface area/volume);
- The tendency for contacting water to preferentially flow over or around material;
- Introduction of DOC from organic material decay; and,
- Changes to the chemical composition of the material (e.g., from co-disposal with other materials).
- Changes to a material from weathering or self-cementation.

3. An Overview of LEAF

LEAF is an integrated framework that uses the results from up to four different laboratory tests to characterize the leaching behavior of solid materials. Coordinated development of LEAF has occurred between research laboratories in the U.S. and the European Union to develop and harmonize test methods to support data comparisons. Test methods analogous to LEAF test methods are available in the EU with minor differences intended to address the different testing standards (e.g., quality control requirements, method description requirements, etc., See Appendix A). The four test methods, U.S. EPA Methods 1313, 1314, 1315 and 1316, are designed to account for the effects of major factors known to affect leaching behavior of inorganic constituents for most wastes and management scenarios (Kosson et al., 2002). Because the test methods take into consideration a range of material properties and potential environmental conditions, the resulting data can provide estimates of constituent leaching behavior that reflect plausible field conditions and considers the impact of a wide range of material management scenarios (U.S. EPA, 2014c). The overarching framework provides direction on how to interpret and apply the data collected based on the complexity and specificity of the evaluation, ranging from a simple and generalized screening analysis to a complex and site or scenario-specific probabilistic analysis. This section provides general descriptions of the components of LEAF.

3.1 Analytical Leach Test Methods

For characterization of inorganic constituents, LEAF includes four distinct leaching test methods. These test methods directly address one of three most important factors affecting leaching of inorganics: the final leachate pH, the amount of water in contact with the material, and the physical form (i.e., granular vs. monolithic) of the material (U.S. EPA, 2014c). The test methods also measure important parameters of the liquid such as pH, electrical conductivity (EC) and DOC under the final leaching conditions. Together, these methods provide information on the available content, peak leaching concentration, time-dependent release (Kosson et al., 2002; U.S. EPA, 2010). These methods can be applied individually or in combination, based on information needed to characterize the leaching behavior of the material of interest.

LEAF Leaching Tests

Method 1313: Liquid-Solid Partitioning as a Function of Extract pH using a Parallel Batch Extraction Procedure (U.S. EPA, 2012f)

Method 1314: Liquid-Solid Partitioning as a Function of Liquid-to-Solid Ratio for Constituents in Solid Materials using an Up-flow Percolation Column Procedure (U.S. EPA, 2013a)

Method 1315: Mass Transfer Rates of Constituents in Monolithic and Compacted Granular Materials using a Semi-Dynamic Tank Leaching Procedure (U.S. EPA, 2013b)

Method 1316: Liquid-Solid Partitioning as a Function of Liquid-to-Solid Ratio using a Parallel Batch Extraction Procedure (U.S. EPA, 2013c)

The LEAF tests are conducted under a specified set of conditions, which provides a standardized basis for comparison among different samples, materials, leaching tests, and management scenarios. The data can be used to evaluate a range of environmental conditions that a given material may be exposed to in the field (U.S. EPA, 2014c). Even when a particular value of interest has not been explicitly measured (e.g., leaching at a particular pH or L/S value), it is possible to interpolate between measured concentrations to more accurately reflect anticipated field conditions. Each of the four test methods have undergone interlaboratory and field validation for inorganic COPCs (U.S. EPA, 2012c, 2012d, 2014c). A summary of the parameters for each method is presented in Table 3-1 with a description in the following subsections.

A full detailed description of the validated methods can be found on the SW-846 website under validated methods (U.S. EPA, 2017b).

Table 3-1. Comparison of Test Parameters for LEAF Leaching Methods

Test Variable	Method 1313	Method 1314	Method 1315	Method 1316
Test Type	Equilibrium; pH-dependent	Equilibrium; percolation	Mass transfer	Equilibrium; L/S-dependent
Test Description	Parallel batch extractions	Column test in up-flow mode	Tank test with periodic eluant renewal	Parallel batch extractions
Sample Type and Dimension	Granular particle size of 85% by mass less than 0.3, 2.0 or 5.0 mm	Granular particle size of 85% by mass less than 2 mm with 100% less than 5 mm	*Monolith:* cylinder or cube; 40-mm minimum dimension *Compacted granular:* cylinder with 40 mm minimum height	Granular particle size of 85% by mass less than 0.3, 2.0 or 5.0 mm
Test, Extraction or Interval Duration	Extractions for 24, 48 or 72 hours based on maximum particle size	Continuous elution to L/S 10 mL/g-dry Estimated test time of 13 days based on constant flowrate of 0.75 L/S per day	Intervals of 2, 23, 23 hours, 5, 7, 14, 14, 7 and 14 days Cumulative leaching time of 63 days	Extractions for 24, 48 or 72 hours based on maximum particle size
Eluant Composition	Reagent water with additions of HNO_3 or NaOH	Reagent water or 1 mM $CaCl_2$	Reagent water	Reagent water
pH Range	2 to 13 at specified targets	As controlled by material being tested	As controlled by material being tested	As controlled by material being tested
Amount of Solid	Minimum 20 g-dry per extract; Approx. 400 g-dry each for pre-test and test replicate (collect 1 kg for first test; 500 g for each replicate)	Minimum 300 g; 600–700 g per column (collect 1 kg per test run)	*Monolith:* as specified *Compacted granular:* 500–750 g per test run + 5 pre-test samples (collect 4 kg for first test, 1 kg for each replicate)	Minimum 20 g-dry per extract; 20 to 400 g-dry each extract (collect 1 kg per test run)
Eluant Volume	L/S of 10 mL/g-dry	Eluates collected through cumulative L/S 10 mL/g-dry	Liquid-surface area ratio of 9 mL/cm^2	L/S of 10, 5.0, 2.0, 1.0, and 0.5 mL/g-dry
Number of Analytical Solutions per Test	9 extractions (10 if natural pH is outside target range)	9 eluate fractions	9 interval solutions	5 extractions

3.1.1 U.S. EPA Method 1313: pH-Dependent LSP

Method 1313 is designed to evaluate the partitioning of constituents between liquid and solid phases at near equilibrium conditions over a wide range of pH values. The method consists of 9 to 10 parallel batch extractions of a solid material (Figure 3-1) at various endpoint target pH values and at an L/S of 10 mL/g-dry. The pH of each extraction is controlled by additions of a known volume of dilute acid or base, derived from prior knowledge of the acid neutralization capacity (ANC) of the material or from determination of the ANC based on a pre-test titration step. Parallel extractions provide aqueous extracts at up to nine target pH values between pH 2 and 13, plus the natural pH of the material (i.e., when leached with DI water, and no acid or base is added). To achieve equilibrium conditions faster and reduce testing time, particle size reduction of the sample material may be required (U.S. EPA, 2010). The measured constituent concentrations and acid/base neutralization capacity can be plotted as a function of leachate pH. The measured values can be plotted and graphically compared to relevant benchmarks to facilitate the presentation and interpretation of the data. Given that leachate concentrations can vary by multiple orders of magnitude over the full pH range, it is recommended that the graph be log transformed for ease of presentation.

Total Content—The concentration [mg/kg-dry] of a constituent in the solid material on a total dry mass basis.

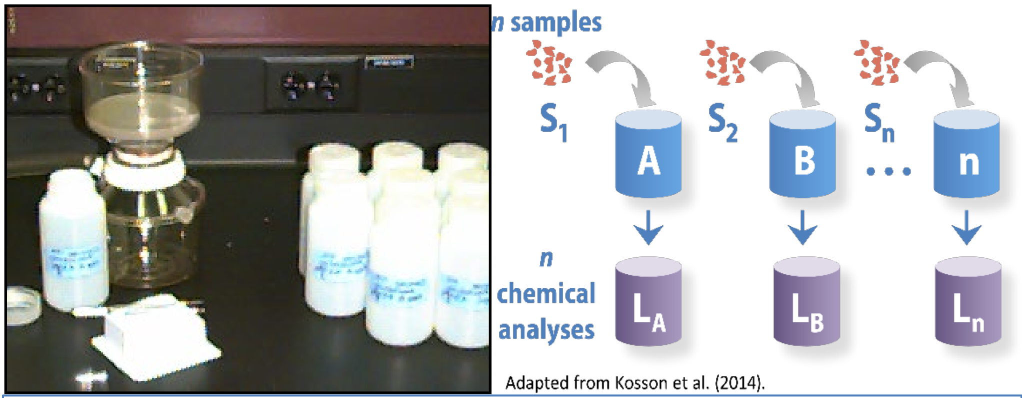
Available Content—The concentration [mg/kg-dry] of a constituent in a solid material on a total dry mass basis that potentially may leach over a reasonably near-term timeframe (e.g., 100 years). The available content is a fraction of the total content and, thus, less than or equal to the total content value.

Eluant—Water or aqueous solution used to contact or extract constituents from a material during a laboratory test.

Eluate—The aqueous solution, analyzed as part of a laboratory leaching test, that results from contact of an eluant with tested material.

Leachant—Water or aqueous solution contacting a material under field conditions (e.g., infiltrating water, groundwater).

Leachate—An aqueous solution resulting from leachant contact with a material under field conditions.



Adapted from Kosson et al. (2014).

Method 1313 consists of 9-10 parallel batch extractions (*A* through *n*) of subsamples of a particulate solid (*S*) in deionized water with various additions of acid or base intended to result in specified endpoint target pH values, approximating LSP as a function of pH.

Figure 3-1. Experimental scheme of U.S. EPA Method 1313 as a parallel batch extraction test.

Figure 3-2 presents an example of pH-dependent results from Method 1313 for the acid-base titration curve of a coal combustion fly ash (EaFA) and the LSP curve for chromium presented as eluate concentration and mass release (Kosson, Garrabrants, DeLapp, & van der Sloot, 2014). For batch extractions, mass release [mg/kg-dry] is calculated by multiplying eluate concentrations [mg/L] by the eluate-specific L/S [L/kg-dry]. Typically, eluate concentrations are plotted as a function of pH along with the method detection limit (MDL) and lower limit of quantitation (LLOQ). In Figure 3-2, the data corresponding to the natural pH extraction (i.e., the extraction where the material dictates the eluate pH) is indicated by a large circle about the data point.

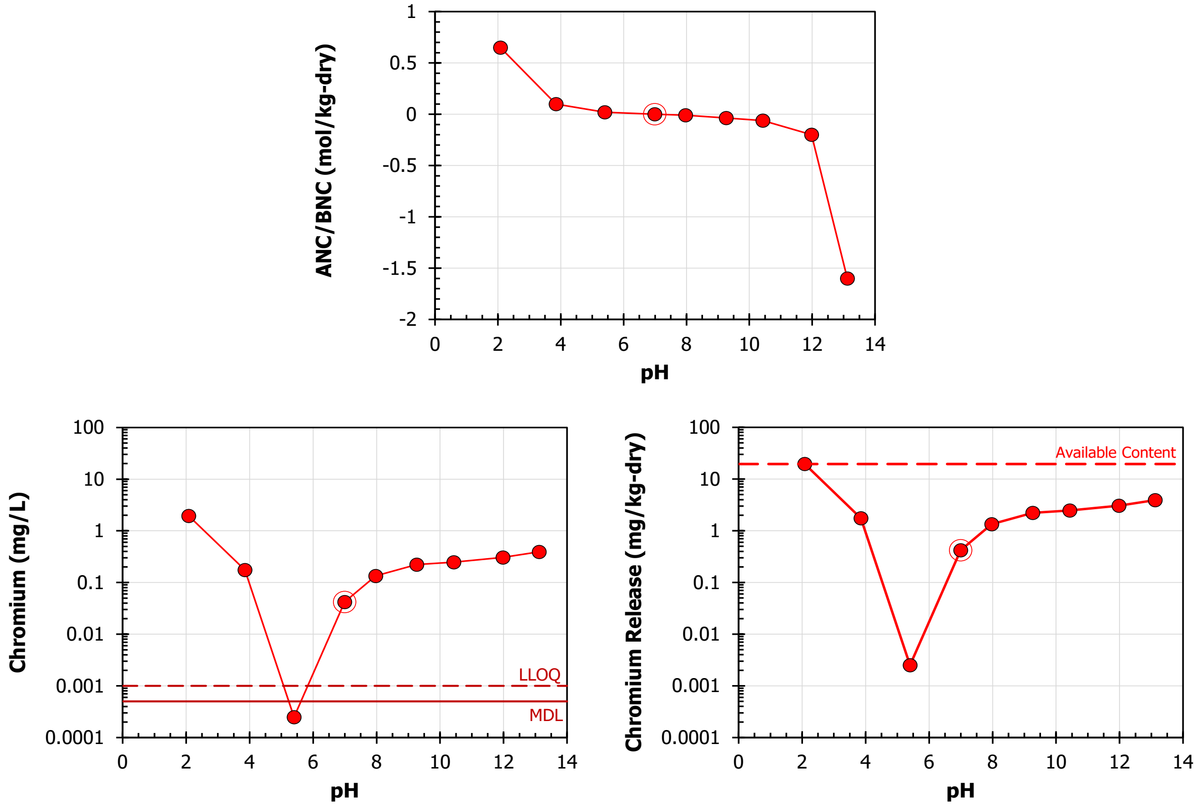


Figure 3-2. Example results from Method 1313 for leaching from a coal combustion fly ash (EaFA): Titration curve (top), chromium eluate concentration (lower, left) and chromium release with available content displayed (lower, right).

Many of the chemical processes that control liquid-solid partitioning are pH-dependent (e.g., solubility, mineral precipitation, adsorption reactions). Method 1313 provides an equilibrium partitioning curve as a function of pH that can be used to identify where leaching behavior is sensitive to changes in pH (i.e., where solubility may change significantly with a small change in pH). The method can also be used to estimate the leachable fraction, or available content, of constituents based on the maximum eluate concentration over the pH range (U.S. EPA, 2014c). LSP and available content information can be used as input into chemical speciation models to help understand the effects of physical and chemical factors that are difficult to control for in laboratory tests (e.g., material interactions, reducing conditions, reactions with atmospheric gases). Table 3-2 provides a summary of the potential applications of Method 1313 data.

Table 3-2. Potential Applications of Method 1313 Data

Data Collected	Potential Uses
Acid/base titration curve	• Impact on eluate pH from external sources of acidity or alkalinity (e.g., from mixing with other materials or from external sources such as acidic precipitation or ingress of carbon dioxide)
Equilibrium constituent concentrations at pH 2, 9, and 13	• Available content (i.e., the fraction of total content available for leaching based on maximum release at these 3 endpoint target pH values)
Equilibrium constituent concentrations at natural pH and at pH points within and bracketing scenario pH domain	• Determination of maximum potential leachate concentrations over scenario pH domain • Indication of solubility-limited or available content-limited leaching
Full suite of constituent concentrations for all test pH points	• Insights into chemistry controlling leaching • Comparison of characteristic constituent equilibrium partitioning as a function of pH between materials • Input for geochemical speciation modeling

3.1.2 U.S. EPA Method 1314: Percolation Column

Method 1314 is a percolation column test designed to evaluate constituent releases from solid materials as a function of cumulative L/S. The experimental scheme of Method 1314 is shown in Figure 3-3. The method consists of a column packed with granular material with moderate compaction to preserve the original porosity of the material. Particle size reduction of the sample material may be required to facilitate testing. Eluant is introduced through pumping of deionized water up through the column to minimize air entrainment and

Water Contact Key Terms

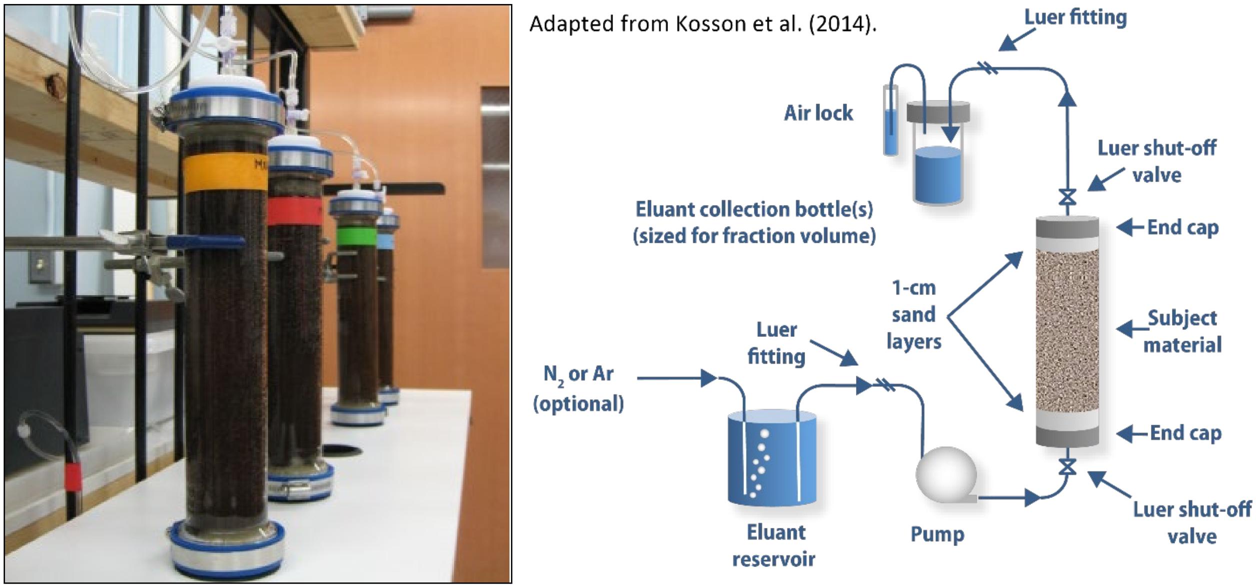
Percolation—The water contact scenario when precipitation, infiltrating water or groundwater, moves through the contiguous voids of a porous material and leaching occurs at the solid-liquid interface between the percolating fluid and the solid material.

Washout—A rapid release of constituents resulting from highly soluble species rapidly dissolving in water percolating through a material. Washout is usually indicated during Method 1314 by a decrease in leaching concentration of approximately one order of magnitude or more as the liquid to solid ratio increases from L/S = 0.2 mL/g-dry to 2.0 mL/g-dry.

Flow-around—The water contact scenario when precipitation, infiltrating water, or groundwater flows around the external surface area of a low-permeability material (e.g., cement-treated wastes, compacted material) and release occurs at the interface between the flowing water and the material.

Mass transport/diffusion-limited leaching—The release from solid material when leaching is less than equilibrium liquid-solid partitioning, typically constrained by the rate of diffusion through the material being leached.

preferential flow.[9,10] The eluant flowrate is slow so that the resulting eluant concentrations approximate liquid-solid equilibrium within the column. Samples of column eluate are collected over nine specified cumulative L/S intervals. The eluate pH and specific conductance are measured. The eluate is filtered by pressure or vacuum in preparation for constituent analysis. Analytical aliquots of the extracts are collected and preserved accordingly based on the determinative methods to be performed (U.S. EPA, 2012c).



Adapted from Kosson et al. (2014).

Up-flow percolation column to collect eluates at specified L/S values, estimating liquid-solid partitioning at percolation release conditions that approximate chemical equilibrium.

Figure 3-3. Experimental scheme of U.S. EPA Method 1314 as a percolation column test.

Measured constituent concentrations can be plotted as a function of the cumulative L/S, either as measured [mg/L] or multiplied by the incremental L/S for that sample and summed into a cumulative mass release [mg/kg-dry]. Eluate concentration and cumulative mass release can be graphed as a function of cumulative L/S. The measured pH can be plotted against the L/S to determine if early washout of soluble ions has a substantial impact on leachate pH. Figure 3-4 provides example results from Method 1314 for a contaminated smelter site soil (CFS).

Data from Method 1314 provide an estimate of pore water concentrations at low L/S (e.g., L/S of 0.2 or 0.5 mL/g-dry) and illustrate how leaching behavior changes as the cumulative L/S ratio increases. As water percolates through the material, highly soluble salts such as sodium or potassium salts, DOC, and oxyanions may be washed out, typically with a tenfold reduction in leaching concentration by cumulative L/S of 2 mL/g-dry.

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[9] Calcium chloride solution (1 mM) may be used instead of deionized water in cases where colloid formation is a concern to prevent deflocculation of clays and organic matter.

[10] The test method uses upflow through the column to minimize flow channeling. However, testing has demonstrated that use of upflow testing does not have significant impact of the results relative to field behavior (U.S. EPA, 2014c, Lopez et al, 2008)

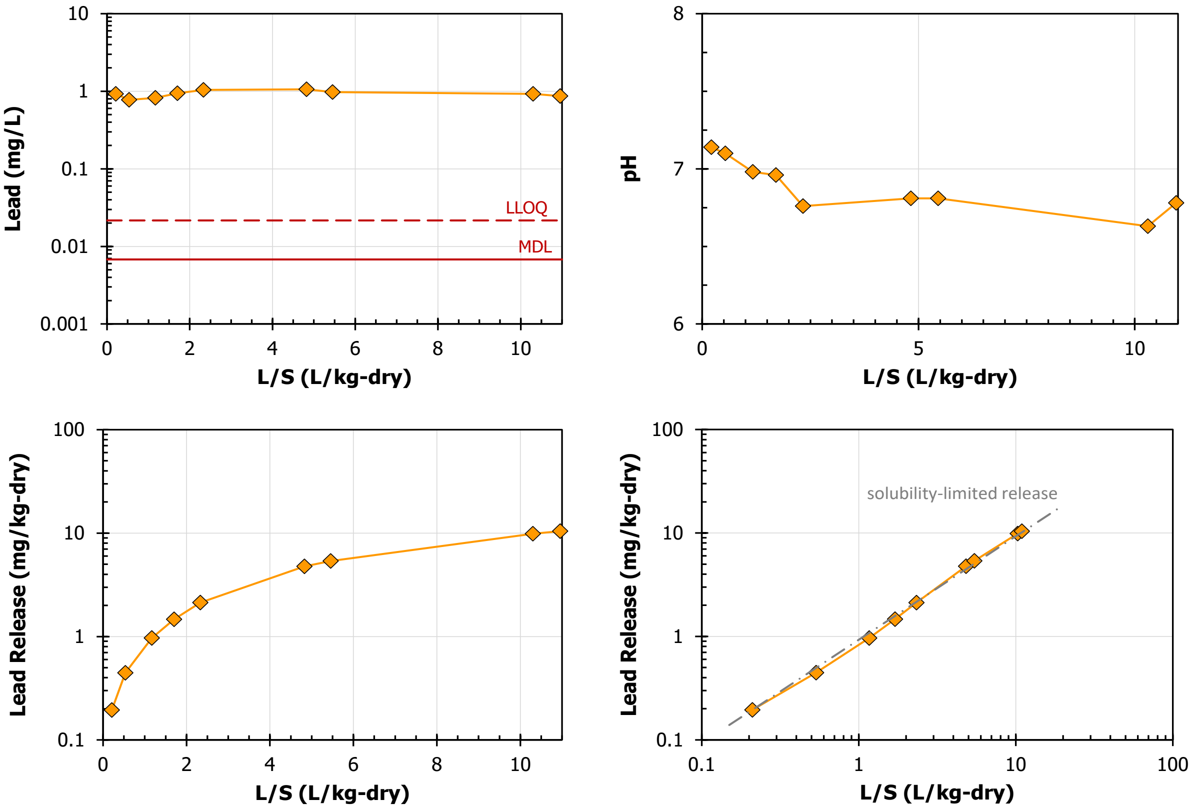


Figure 3-4. Example results from Method 1314 for lead as a function of L/S from a contaminated smelter site soil (CFS): Concentration (top, left), eluate pH (top, right) and cumulative release on Cartesian axis (lower, left) and logarithmic axis (lower, right).

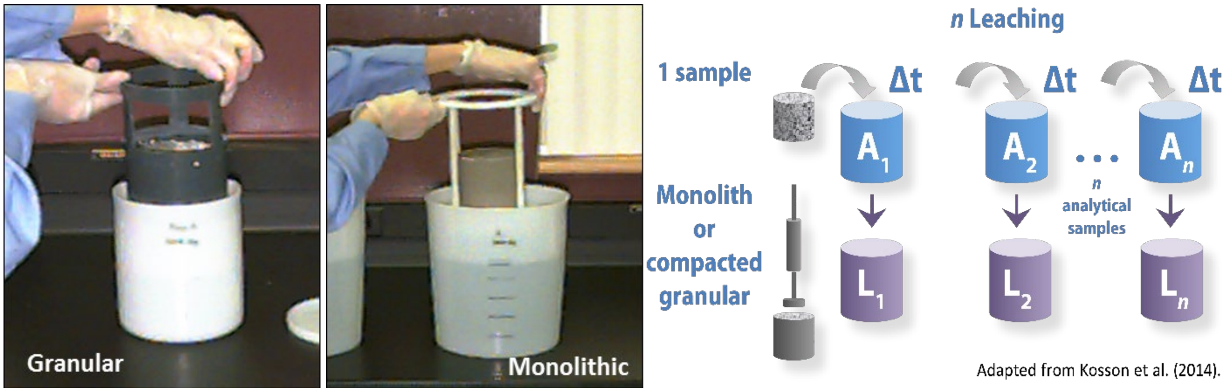
As infiltrating water percolates through a material, changes in the porewater chemistry can alter the dissolution of the more stable mineral phases, subsequent pore solutions and leaching of constituents. The data on concentrations as a function of cumulative L/S from this laboratory test can be used together with field infiltration rates to estimate leaching as a function of time. Table 3-3 presents a summary of the potential applications of Method 1314 data.

Table 3-3. Potential Applications of Method 1314 Data

Data Collected	Potential Uses
Constituent concentrations as a function of incremental and cumulative L/S	• Initial (i.e., porewater) and maximum leaching concentrations • Percolation leaching source term • Co-elution effects of COPC release (e.g., increased leaching of As after depletion of Ca; Ba and SO_4)
Eluate pH and conductivity as a function of incremental and cumulative L/S	• Estimate of porewater pH (at low L/S), ionic strength • pH relates Method 1314 results and Method 1313 results when plotted as a function of pH

3.1.3 U.S. EPA Method 1315: Rates of Mass Transfer

Method 1315 is a semi-dynamic tank leaching procedure used to determine the rate of mass transport from either monolithic materials (e.g., concrete materials, bricks, tiles) or compacted granular materials (e.g., soils, sediments, fly ash) as a function of time using deionized water as the leaching solution. The method consists of leaching of a test sample in a bath with periodic renewal of the leaching solution at specified cumulative leaching times (Figure 3-5). The volume of leachant used in the test is related to the surface area exposed to the liquid through a liquid-to-surface area ratio (L/A).



Adapted from Kosson et al. (2014).

Sequential extraction of a monolith or compacted granular specimen to determine the maximum rate of release by diffusion and dissolution processes.

Figure 3-5. Experimental scheme of U.S. EPA Method 1315 as a tank leaching test.

Monolithic samples may be cylindrical or rectangular, while granular materials are compacted into cylindrical molds to a density that approximates the peak field density on a dry basis. At nine specified time-intervals, samples are transferred to fresh reagent water and the eluate from the previous interval is analyzed for eluate properties (e.g., pH, EC) and constituent concentrations. Measured constituent concentrations in mg/L are be plotted as a function of cumulative time and along with an analogous plot of eluate pH as a function of cumulative leaching time. Eluate concentrations are presented relative to MDLs and LLOQs to indicate quantitation of measured concentrations. The interval mass flux [mg/m^2-s], or the rate of mass released over an interval, is calculated by multiplying the eluate concentration [mg/L] by the ratio of the volume of leachate to the surface area of the sample [L/m^2] and dividing by the interval-specific time in seconds [s]. Similarly, the cumulative mass release [mg/m^2] is calculated by multiplying the interval mass flux by the interval specific time and summing across all previous leaching intervals. Both interval flux and cumulative mass release are plotted as a function of cumulative leaching time. Figure 3-6 presents example results from Method 1315 for a solidified waste form (U.S. EPA, 2012c, 2012d).

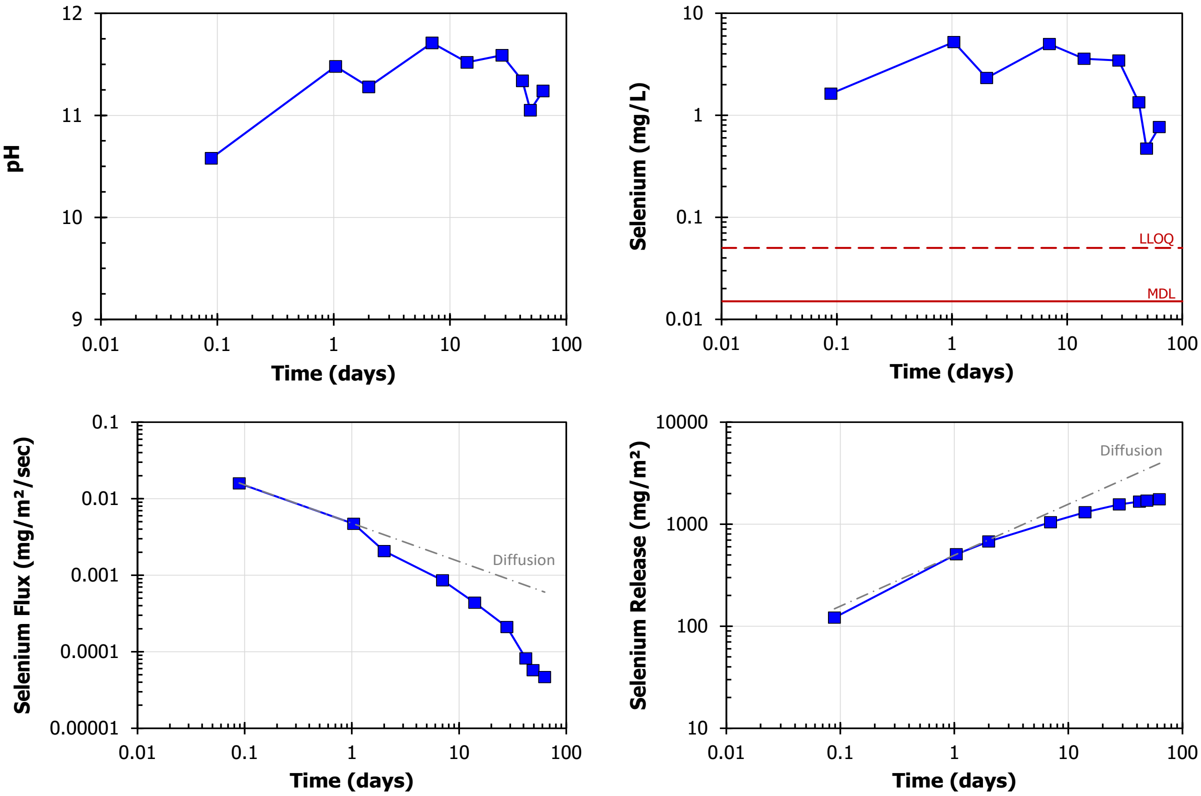


Figure 3-6. Example results from Method 1315 for selenium shown as a function of leaching time from a solidified waste form (SWA): Eluate pH (upper, left), eluate concentration (upper, right), mean interval flux (lower, left) and cumulative release (lower, right).

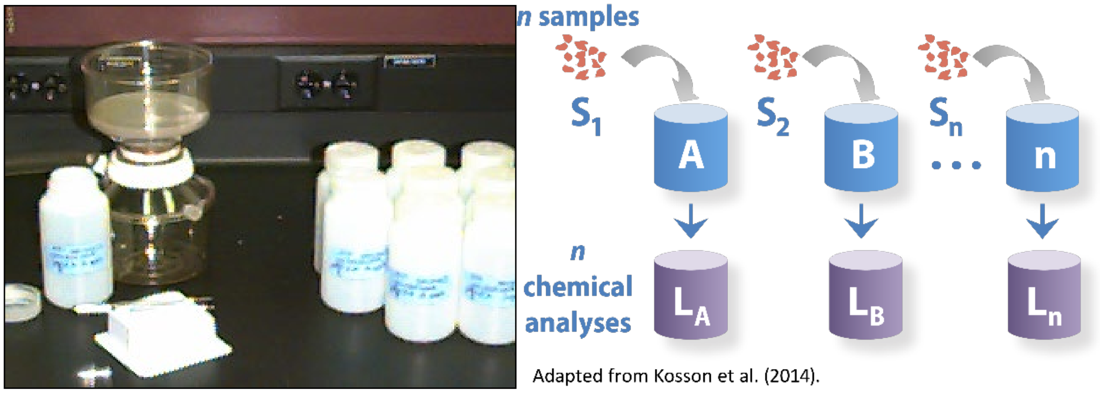
Data from Method 1315 indicate the rate of mass transport from the interior of the material to its external surface (i.e., the interface of the material with the surrounding environment). By maintaining a dilute eluate solution based on eluant refresh intervals, the boundary conditions for leaching result in a maximum release rate by diffusion for monolithic and compacted granular materials (U.S. EPA, 2010). Method 1315 is applicable for cases where water primarily flows around the material, rather than percolating through it. In the field, however, actual liquid to surface area ratios are often much less than the test conditions and leaching into the limited contacting liquid can reduce concentration gradients. Therefore, the rate of leaching in the field can be less than measured in the laboratory and Method 1315 data often are used to estimate the parameters (e.g., observed diffusivity) that control mass transfer for each constituent (Garrabants, Sanchez, Gervais, Moszkowicz, & Kosson, 2002). The data from Method 1315 may represent mass transport rates over short time durations with the mass transport parameters used to estimate rates of leaching in the field over longer time durations (U.S. EPA, 2012d). A summary of the potential applications of Method 1315 data is presented in Table 3-4.

Table 3-4. Potential Applications of Method 1315 Data

Data Collected	Potential Uses
Constituent release rates from monolithic and compacted granular materials	• Maximum leaching rates under diffusion conditions • Mass transport-based leaching source term • Tortuosity and observed diffusivity (diffusion-controlled release)
Compacted dry density (pre-test for granular materials)	• Bulk density of compacted granular materials under field compaction
Eluate pH and conductivity as a function of cumulative leaching time	• Concentrations graphed as function of pH with *Method 1313* results to verify *Method 1315* dilute boundary conditions • pH and total ionic strength domain of anticipated leaching

3.1.4 U.S. EPA Method 1316: L/S-Dependent LSP

Method 1316 is an equilibrium-based leaching test intended to provide eluate solutions over a range of L/S. This method consists of five parallel batch extractions of a particle-size-reduced solid material in reagent water over a range of L/S values from 0.5 to 10 mL/g-dry material (Figure 3-7).



Adapted from Kosson et al. (2014).

Parallel batch extractions with varying quantities of deionized water, approximating liquid-solid partitioning as a function of pH at chemical equilibrium.

Figure 3-7. Experimental scheme of U.S. EPA Method 1316 as a parallel batch extraction test.

At the end of the contact interval, the liquid and solid phases are separated by pressure or vacuum filtration in preparation for constituent analysis. Extract pH and specific conductance measurements are taken on an aliquot of the liquid phase. Analytical aliquots of the extracts are collected and preserved accordingly based on the determinative methods to be performed (U.S. EPA, 2012c). Measured eluate concentrations are plotted as a function of the L/S along with MDLs and LLOQs to indicate quantitation of measured concentrations. Method results are presented as eluate concentrations [mg/L] or as mass release [mg/kg] calculated by multiplying concentrations by the extraction-specific L/S [L/kg-dry]. Often, the measured eluate pH for each extraction is plotted against the L/S to provide content to pH-dependent

LSP concentration determined from Method 1313. Figure 3-8 provides example results from Method 1316 for a contaminated smelter site soil (U.S. EPA, 2012c, 2012d).

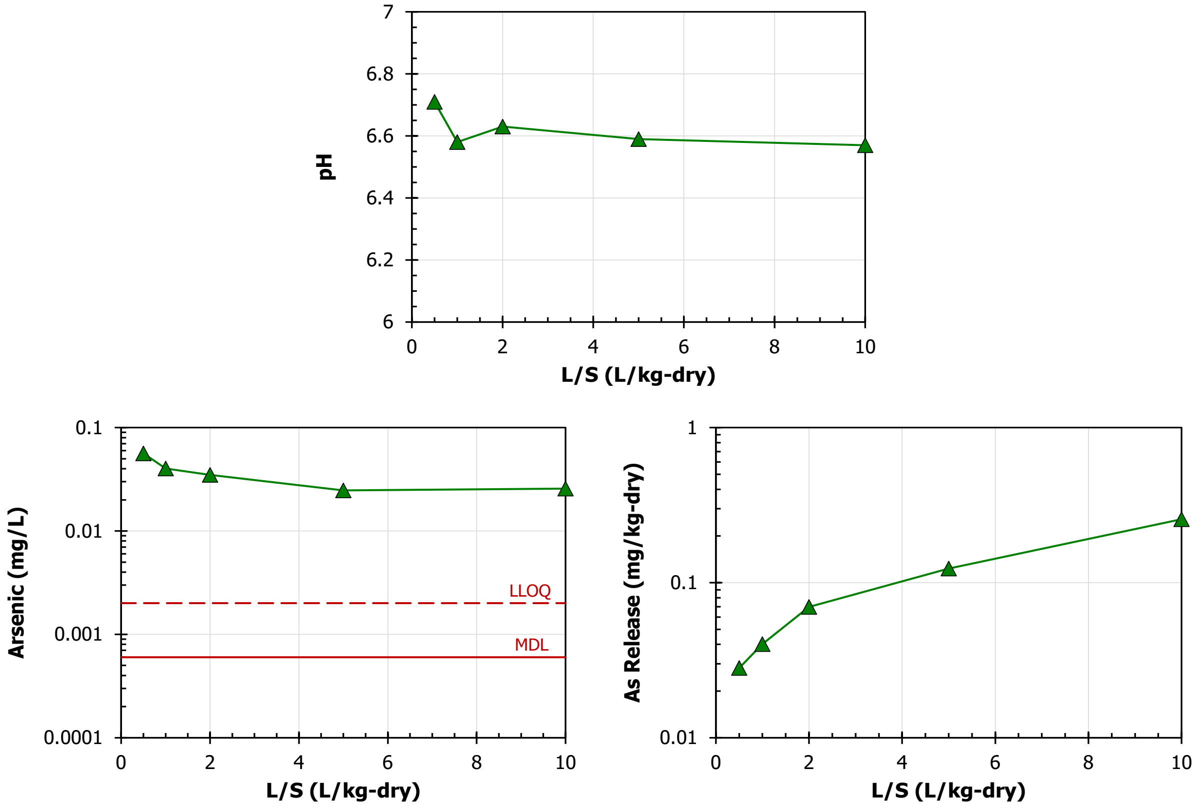


Figure 3-8. Example arsenic results for Method 1316 from a contaminated smelter site soil (CFS): Eluate pH (top), eluate concentration (lower, left) and release (lower, right).

Data from Method 1316 provides mass release information as a function of L/S similar to Method 1314 data. However, the Method 1316 eluate concentrations are often higher than Method 1314, reflecting the nature of the batch test where constituents are not sequentially removed from the system at each L/S as with a flow-through percolating column. The batch method may be useful when characterizing materials with physical properties that make flow through tests impractical (e.g., low-permeability clay soil, materials with cementitious properties). A summary of the applications of Method 1316 data is presented in Table 3-5.

Table 3-5. Potential Applications of Method 1316 Data

Data Collected	Potential Uses
COPC concentrations as a function of L/S	• Estimate porewater concentrations at low L/S
pH and conductivity as a function of L/S	• Porewater pH
COPC mass release as a function of L/S	• Constant mass release as a function of L/S is an indicator of available content limited leaching

3.1.5 Validation of LEAF Tests

Extensive method development and refinement occurred in the course of evaluating coal fly ash and other materials using the LEAF tests (U.S. EPA, 2009, 2010). LEAF has undergone multiple rounds of validation in the laboratory and in the field to ensure that the data generated is as precise, accurate, and realistic as possible (U.S. EPA, 2014c). The results of these studies indicate that the data generated by the test methods are repeatable and provide a good representation of what will occur in the field for inorganic constituents. The following text describes the results and conclusions of these different validation studies.

3.1.5.1 Interlaboratory Validation

EPA conducted interlaboratory validation studies to determine the repeatability and reproducibility of each LEAF method (U.S. EPA, 2012c, 2012d). For each method, between seven and ten laboratories participated in the study, each conducting testing in triplicate for a series of different materials types including coal fly ash, an analog of a solidified waste, a contaminated smelter site soil and a brass foundry sand. From eluate concentrations obtained from laboratory testing, method precision was calculated as the intra-laboratory repeatability relative standard deviation (RSD_r) and inter-laboratory reproducibility relative standard deviation (RSD_R). A summary of the interlaboratory validation results are presented in Table 3-6**.** For example, Method 1313 results indicate that mean lab precision was 10% of the measured value within a laboratory and 26% between laboratories. The results of interlaboratory validation provide the confidence that each method provides the characteristic leaching behavior that is intended by the LEAF leaching methods with a high degree of precision (U.S. EPA, 2012c, 2012d).

Table 3-6. Precision Data for LEAF Test Methods based on Interlaboratory Validation Studies

Method	Test Output	RSD_r	RSD_R
Method 1313	Eluate Concentration (average over pH range)	13%	28%
Method 1314	Eluate Concentration (mean at L/S 10 L/kg-dry)	12%	24%
	Mass Release (cumulative to L/S=0.5)	7%	18%
	Mass Release (cumulative to L/S=10)	5%	14%
Method 1315	Interval Flux (mean excluding wash-off)	12%	30%
	Mass Release (cumulative to 7 days)	9%	19%
	Mass Release (cumulative to 63 days)	6%	23%
Method 1316	Eluate Concentration (average over L/S range)	8%	19%

3.1.5.2 Field Validation

EPA evaluated the relationship between LEAF test results and leaching of inorganics from a broad range of materials under disposal and beneficial use scenarios. This evaluation was achieved by defining a framework for interpretation of laboratory testing results, comparison of laboratory testing on “as produced” material, laboratory testing of “field aged” material, and results from field leaching studies, and illustrating the use of chemical speciation modeling as a tool to facilitate evaluation of scenarios beyond the conditions of laboratory testing. LEAF has been shown to provide effective estimates of leaching behavior for inorganic constituents (e.g., Al, As, Sb, B, Ca, Cr, Cu, Fe, Pb, K, Mg, , Se, Si, Sr, V, Zn) for a wide range of materials (the same ones used in inter-laboratory validation) under both disposal and use conditions (U.S. EPA, 2014c).

Based on the results of this study, EPA concluded that the combined results from pH-dependent leaching tests (Method 1313) and percolation column tests (Method 1314) can provide accurate estimates of maximum field leachate concentrations, extent of leaching and expected leaching responses over time. In addition, this approach can predict or account for changes in environmental conditions under both disposal and use scenarios within reasonable bounds. Results from batch testing at low L/S (Method 1316) can be used in place of column test results when column testing is impractical. Method 1315 should be used in combination with Method 1313 for scenarios when mass transport from monolithic or compacted granular materials controls leaching. When field conditions exist that are beyond the domain of laboratory test conditions (e.g., reduction of oxidized material or introduction of DOC from external sources), consult with technical experts in geochemical speciation to develop an approach that is as technically robust as current scientific knowledge allows.

3.1.6 Relationship between LEAF and Single Point Tests (e.g., TCLP, SPLP)

Traditional single-point leaching tests use specified leaching solutions designed to simulate release under a specific set of environmental and management conditions. For example, the buffered, dilute acetic acid eluant at an L/S of 20 mL/g (wet basis) used in TCLP (Method 1311) is specified so the eluate concentrations represent leaching under a plausible mismanagement scenario of industrial waste co-disposal in a municipal solid waste landfill (U.S. EPA, 1992; U.S. Federal Register, 1986). Although procedurally analogous to TCLP, the SPLP (Method 1312) uses a blend of dilute inorganic acids to simulate near-surface exposure of solid material to acidic precipitation (U.S. EPA, 1994).

The LEAF leaching test methods are designed to measure intrinsic leaching properties over a range of environmentally relevant conditions. Eluate pH, L/S and physical form of the material (i.e., particle size) are controlled as independent variables to provide measurements of the rate and extent of constituent release into water contacting the material over a range of test conditions (Kosson et al., 2002)). For example, Method 1313 varies the final pH at targets between 2 and 14 while maintaining a constant L/S of 10 mL/g-dry, whereas Method 1316 allows the material to dictate eluate pH at five L/S levels between 0.5 and 10 mL/g-dry.

While typically not done in practice, when the endpoint pH of single point leach tests is recorded such as in TCLP test reports, the results can be compared to pH-dependent LSP results from LEAF leaching testing methods. The comparisons in Figure 3-9 illustrate that the results from single-point leaching tests typically reflect one data point on the LSP curve at equilibrium. However, due to the different L/S values used in these tests (e.g., TCLP and SPLP at L/S 20 mL/g; Method 1313 at L/S 10 mL/kg-dry), eluate concentrations from TCLP and SPLP may graph slightly below the LSP curve for Method 1313 data.

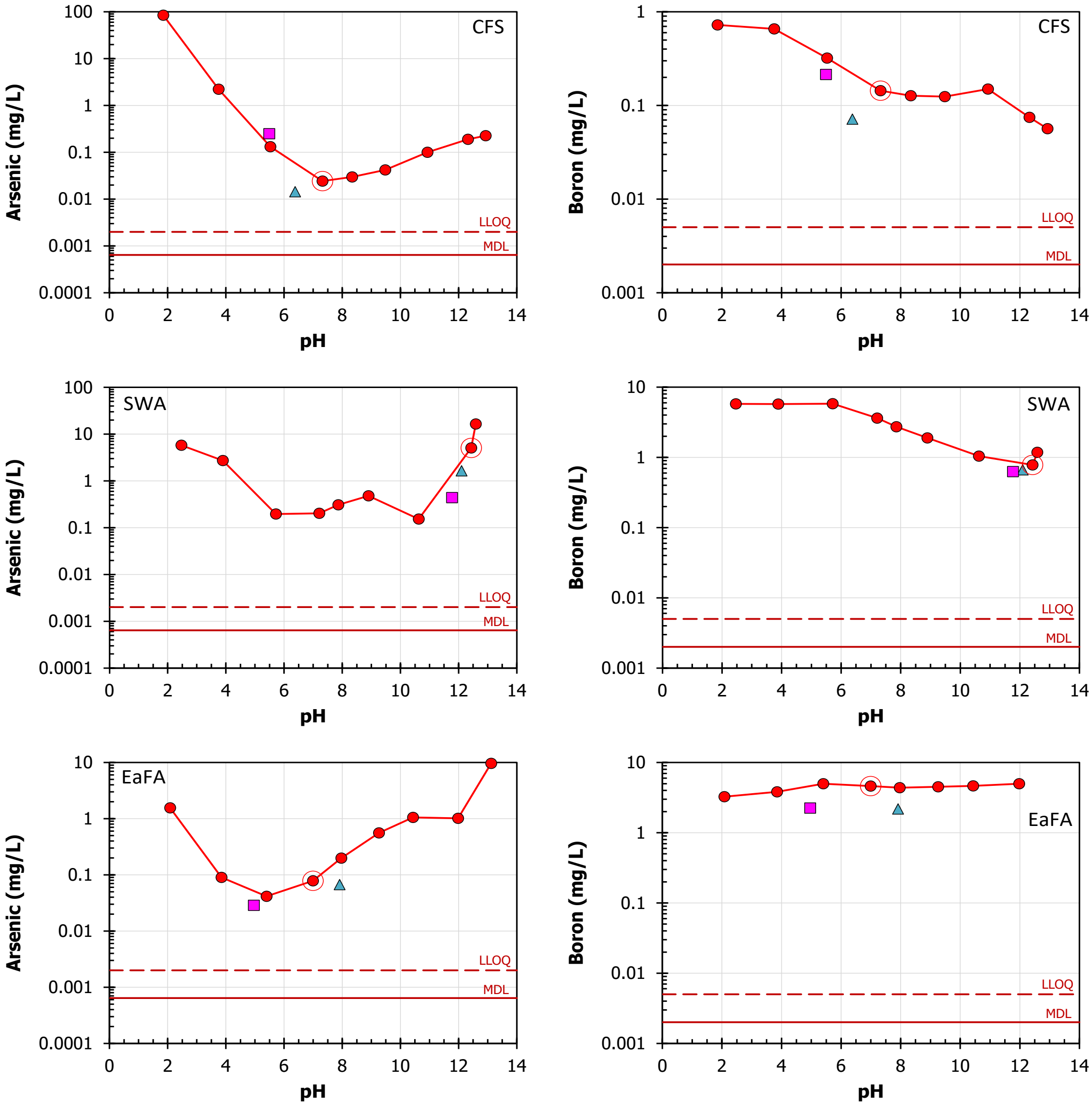


Figure 3-9. Comparison of TCLP (pink square) and SPLP (green triangle) results to pH-dependent leaching from Method 1313 for a contaminated smelter site soil (CFS; top), a solidified waste form (SWA; center) and a coal combustion fly ash (EaFA; bottom).

3.2 Building a Testing Program

Developing a testing program includes selection of appropriate leaching tests, target analytes for evaluation, and analytical methods to sufficiently detect and measure chosen analytes. The testing program should be specified in a quality assurance project plan (QAPP) that addresses the tests and conditions to be conducted as well as testing and analytical QA/QC criteria used to support the testing program. Additional information on development of analytical quality assurance can be found in chapter one of SW-846 (U.S. EPA, 2014d; available online at https://www.epa.gov/hw-sw846/quality-assurance-and-hazardous-waste-test-methods).

3.2.1 Material Collection for Leaching Tests

The goal of material sampling and subsequent material preparation should be to obtain representative samples and subsamples, or aliquots, of the materials being disposed or reused for use in the selected leaching tests. Guidance on sampling is available at *https://www.epa.gov/hw-sw846/sampling-guidance-documents-sw-846-compendium*. Initial sample collection should account for spatial and temporal variations in material characteristics through appropriate compositing of individual grab samples. For piles or accumulated quantities of (what is nominally) a single material, grab samples should be obtained from different locations and depths within the accumulated material. For a material produced over time, representative grab samples should be obtained at predefined intervals over the evaluation period. Individual grab samples should have enough mass to be spatially or temporally representative. The goal should be to have sufficient sample following preparation to meet the needs of the planned leaching testing and characterization needs of the project. The information in Table 3-1 (Section 3) includes recommended sample quantities for carrying out each LEAF leaching test. Depending upon variability in material composition, replicate testing may be needed. Often-convenient field sample sizes and containers are 2-liter wide-mouth jars, 1-gallon pails, and 5-gallon pails with tight-fitting re-sealable lids. The container materials (e.g., high-density polyethylene, glass) must be compatible with the COPCs.

Sample collection systems and subsequent handling should be designed to avoid changes in sample characteristics that may degrade the representativeness of the samples prior to analysis and can result in misleading results. For example, oxidation or carbonation of samples during collection and/or handling can result in changes in pH and constituent speciation and may significantly alter the leaching behavior of some constituents. Samples should be particle-size reduced and homogenized shortly before sub-sampling and testing to maximize the representativeness of results. Heterogeneity can result from variations in the solid material, aging of the cured materials, or by exposure of leaching solutions to the atmosphere.

3.2.2 Analytical Parameters

As specified in Methods 1313, 1314, 1315, and 1316, all eluates should be analyzed for pH and EC in the laboratory immediately after contact with the solid. For Method 1313, measurement of EC should be limited to only the natural pH eluate because of the addition of acid and base in other extractions provides an artifact in the interpretation of ionic strength. The measurement of oxidation/reduction potential (ORP) as an indicator of redox conditions is optional based on anticipated scenario conditions and material properties, but for similar reasons to EC measurements, should be limited to the natural pH test position for Method 1313 eluates (see 4.3.1 for more on interpreting ORP from LEAF testing).

The selection of COPCs and additional analytes for chemical analysis depends on the intended use of the results, with assessment-specific COPCs determined based on the requirements of the applicable regulatory agency, use of a screening list, and/or prior knowledge of the material being evaluated.

- **Screening for COPCs** – When the assessment objective to identify COPCs that have the potential to impact the environment, sufficient chemical analysis may include RCRA metals (i.e., Ag, As, Ba, Cd, Cr, Hg, Pb and Se) and/or inorganic species of the EPA Priority Pollutant List (i.e., Ag, As, Be, Cd, Cr, Cu, Hg, Pb, Ni, Sb, Se, Tl and Zn). However, additional analytes may need to be included based on consideration of the specific material being tested.

- **Understanding Basic Leaching Behavior** – In addition to the RCRA or EPA Priority Pollutant List, analyses should be conducted for constituents that can improve understanding of the LEAF test results based on the predominant chemistry of the final eluate. Because of their ability to increase eluate concentrations of COPCs, these additional constituents usually include dissolved carbon from both organic (DOC) and inorganic (e.g., dissolved inorganic carbon, carbonate) forms. Even minimal amounts of organic matter can dramatically influence the solution equilibrium chemistry of many important trace species such as copper and lead. Chloride ions can form soluble complexes with cadmium resulting in elevated measured concentrations of cadmium. In addition, analysis of dissolved iron is a useful indicator of redox state, where elevated Fe concentrations are indicative of reducing conditions.
- **Detailed Characterization** – For full characterization testing, chemical analysis is recommended to include the above analyses as well as a full suite of major and trace constituents in all leaching test eluates. Knowledge of the major constituents that control release of the trace constituents improves understanding of the factors that may affect leaching and allows for calibration of chemical speciation models. Prior knowledge from testing of analogous materials may reduce the need for, or extent of, characterization testing.

3.2.3 Suggested Best Practices for Conducting LEAF Tests

As commercial laboratories become more familiar with the LEAF leaching tests, valuable experience will be gained into the best practices for conducting these tests. Based on experience from developing, validating, and conducting the LEAF leaching methods, the following best practices are recommended:

3.2.3.1 Reagent Selection and Preparation

- For Method 1313, select a base solution (i.e., NaOH or KOH) compatible with leaching assessment objectives (i.e., potassium hydroxide should not be used if potassium is likely to be an assessment constituent). Interlaboratory validation of Method 1313 has shown that KOH may increase eluate concentrations of thallium and, therefore, NaOH should be used to raise eluate pH whenever thallium is a COPC (U.S. EPA, 2012c).
- To the extent possible, bulk reagent solutions (i.e., dilute solutions of acid or base used in Method 1313 or the deionized water used in all LEAF tests) should be prepared immediately prior to use. Storage of bulk solutions over prolonged periods between tests (e.g., > 1 week) should be avoided. Reagents should be stored in containers compatible with the reagent to avoid contamination of the solution (e.g., storing strong alkali solutions in borosilicate glass can result in contamination due to dissolution of boron; U.S. EPA, 2012c).

3.2.3.2 Measurement of Eluate pH

- Meters used for pH measurement should be calibrated with a minimum of two standard pH buffer solutions that span the range of anticipated pH values. Non-standard pH buffer solutions are available as special order for calibration of very low pH (pH < 2) and very high pH (pH > 12) as required for Method 1313. A third, mid-range standard solution (e.g., pH 7) should be used to verify the two-point calibration.
- When eluate solutions are physically separated from the solid material (e.g., after filtration), the weakly buffered liquid, especially highly alkaline solutions, may be highly susceptible to reactions

with air. Thus, eluate pH measurement should be conducted as soon as possible after collection of eluates to avoid carbonation of alkaline solutions and oxidation that could lead to precipitation of carbonate and iron species, respectively. However, care should be taken during pH measurement to ensure that a stable pH is obtained for each eluate.

3.2.3.3 Chemical Analysis

- Unlike single point extraction tests, the multipoint LEAF leaching test methods indicate "trends" in leaching behavior over a range of conditions. Therefore, eluates from a LEAF test should be considered a "set" of solutions that should be analyzed at a uniform analytical dilution whenever practical. However, the measured concentrations over the set of solutions may span several orders-of-magnitude, especially for Method 1313, and therefore analytical solutions may require various levels of dilution to complete analysis.
- Major constituents may require dilution that prevents determination of trace constituents, thus requiring analyses at more than one dilution factor to determine all specified constituents.
- Colloidal formation of DOC-bound analytes in leaching tests eluates can interfere with U.S. EPA SW-846 analytical methods (e.g., Method 6010 or 6010); however, the influence of colloids can be minimized by digestion of eluates following U.S. EPA SW-846 Method 3015A. Digestion may be necessary prior to analysis of Al, As, Be, Cd, Co, Cr, Cu, Fe, P, Pb, Sb, Ti, Tl, U, and Zn in all eluates with greater than 50 mg/L DOC.

3.2.3.4 Data Review

- Prior to the use of analytical data, the end user should review analytical QA/QC results to ensure accuracy and consistency in the evaluation of analytical blanks, spike recoveries, and analytical duplicates.
- Similarly, the results from leaching tests should be reviewed graphically for consistency in trends within and between test replicates. Abnormal jumps or discontinuities in interrelated data may indicate potential testing or analytical errors.

3.2.4 Quality Assurance/Quality Control

Preparing a detailed quality assurance project plan (QAPP) is an important first step in assuring high-quality information for subsequent decision-making. A QAPP should be tailored to the data quality needs of the project to ensure efficient use of resources. Minimum quality control for leaching tests should include use and analysis of method blanks (e.g., extractions conducted without solid material) as specified in each of the LEAF leaching test methods and appropriate quality control for the chemical analyses carried out on leaching test eluates (e.g., analytical spike recoveries, repeatability, calibration verification, etc.). Guidance on development of quality assurance project plans is provided by U.S. EPA (2002) and further information can be found at *https://www.epa.gov/quality*.

Quality assurance for leaching tests should consider the following steps:

- Obtaining representative material sample(s) for testing;
- Execution of leaching tests with test-level QA/QC evaluations;
- Chemical analysis of test eluates following accepted methods and QA/QC procedures; and

- Data management in a manner that minimizes human error and allows for validation relevant to data quality objectives.

3.2.4.1 QA/QC Samples in LEAF Leaching Tests

The procedure for each of the four LEAF leaching test methods includes steps for collecting QA/QC solutions (method blanks and eluant blanks) that are used to assess purity of the reagents and equipment surfaces used in the tests. These solutions include samples of bulk reagents or method blank eluates (i.e., extractions without solid material conducted in parallel with test extractions, using the same reagents and equipment) or samples of bulk reagents:

- **Method 1313** – method blanks conducted in deionized water (natural pH), the highest level of acid addition (pH 2.0 target), and the high level of base addition (pH 13 target);
- **Method 1314** – a sample of bulk eluant at the start of the test and when the eluant source is changed or refreshed;
- **Method 1315** – a series of method blanks conducted in parallel with test fractions; and
- **Method 1316** – a single method blank using deionized water conducted at the L/S 0.5 test fraction.

All QA/QC samples should be preserved and analyzed for COPCs in the same manner as test eluates and reviewed prior to utilization of leaching test results. Test method blanks should be less than the LLOQ or, if greater than the LLOQ, less than 20% of the minimum measured analyte concentration (U.S. EPA, 2012c, 2012d).

3.2.4.2 Analytical QA/QC

An analytical program, including identification of analytes, setting of quantitation limits and analytical quality assurance criteria, should be developed by consultation between the end user and the laboratory conducting the leaching test(s) and, if different, the laboratory conducting chemical analysis. Analytical data should be reviewed before applying LEAF assessment methodologies to ensure that quality assurance requirements have been met. Analytical QA/QC should include a selection of the solutions and evaluations shown in the sidebar to the right as appropriate to ensure adequate precision and accuracy of measurements. At a minimum, QA/QC should include establishing detection and quantitation limits for each analytical process and development of initial and continuing calibration.

Chemical analysis of leaching test eluates should include specification of reporting limits that are less than the applicable threshold values that will be used in subsequent decision-making. Management of values less than the reporting limits (e.g., less than the LLOQ or MDL) should be reported and used in calculations in a manner consistent with the relevant regulatory or other applicable evaluation program. Options for reporting and using values less than the reporting limits include using the reporting limit, one-half the reporting limit, or one-tenth the reporting limit.[11] Applicable U.S. EPA SW-846 analytical methods and example MDLs and LLOQs for a selection of COPCs are provided in Table 3-7.

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[11] Further information on the determination and use of the LLOQ and MDL can be found at *https://www.epa.gov/measurements/detection-limitquantitation-limit-summary-table*

Analytical QA/QC Solutions

Although terminology may vary between laboratories, the following is a general list of typical analytical QA/QC terms that may be used in chemical analyses.

- **Method Detection Limit (MDL)**–a statistically derived concentration of an analyte indicating that the analyte concentration is greater than zero with 99% confidence. In practical terms, the MDL represents the minimum concentration of an analyte for a given analytical technique and sample matrix.
- **Quantitation Limit** – a minimum concentration of an analyte that can be measured within specified limits of precision and accuracy. Although various forms of quantitation limits are common, the lower limit of quantitation (LLOQ) should be reported for LEAF.
- **Reporting Limit** – the level at which method, permit, regulatory and client-specific objectives are met. The reporting limit should be greater than the statistically determined MDL but may be or may not be greater than quantitation limits.
- **Calibration Standard** – a certified standard solution containing known concentration of an analyte measured to establish an initial calibration curve or to verify the validity of the calibration curve during analysis.
- **Calibration Blank** – an analyte-free quality control sample prepared in the same manner as calibration standards and used to establish reagent and system contributions to the analytical result. Calibration blanks should be less than the quantitation limit.
- **Internal Standard** – a known amount of a non-interfering substance, different from the analyte, used to adjust sample concentrations for the substance amount introduced to the instrument. Internal standards are added to each analytical solution.
- **Matrix Spike** – an aliquot of sample with known quantities of specified analytes added (spike amount) and analyzed to estimate interferences.
- **Analytical Replicate** – an analytical sample that has been split into two equal portions used to measure precision associated with handling from preparation through analysis.

Commercial analytical laboratories have internal quality assurance/quality control procedures that comply with their accreditation programs (e.g., National Environmental Laboratory Accreditation Conference). When contracting with an analytical laboratory for LEAF testing, the user of this guide is encouraged to review the QA/QC procedures, measured QA/QC solutions and evaluation frequencies with the contracted analytical laboratory. These quality assurance and quality control procedures should be considered with respect to the leaching assessment project QAPP and data quality objectives.

Table 3-7. Example Analytical Method Detection Limit (MDL) and Lower Limit of Quantitation (LLOQ) Values Compared to U.S. Drinking Water Standards

	Symbol	Drinking Water Standard [µg/L]	Analytical Method	EPA SW-846 Method	MDL [µg/L]	LLOQ [µg/L]
Aluminum	Al	50-200[N1]	ICP-OES	Method 6010	1	50
Antimony	Sb	6	ICP-MS	Method 6020	0.08	1
Arsenic*	As	10	ICP-MS	Method 6020	0.36	1
Barium	Ba	2,000	ICP-OES	Method 6010	1	10
Beryllium	Be	4	ICP-MS	Method 6020	0.6	1
Boron	B	7,000[N2]	ICP-OES	Method 6010	4.3	10
Cadmium	Cd	5	ICP-MS	Method 6020	0.08	1
Calcium	Ca	—	ICP-OES	Method 6010	2.6	10
Carbon (Inorganic)	IC	—	TOC	Method 9060A	130	500
Carbon (Organic)	OC	—	TOC	Method 9060A	170	500
Chloride	Cl	250,000[N1]	IC	Method 9056A	6.5	20
Chromium*	Cr	100	ICP-MS	Method 6020	0.44	1
Cobalt	Co		ICP-OES	Method 6010	0.26	1
Copper	Cu	1,300[N3]	ICP-OES	Method 6010	2.5	10
Iron	Fe	300[N1]	ICP-OES	Method 6010	1.3	10
Lead	Pb	15[N3]	ICP-MS	Method 6020	0.062	1
Magnesium	Mg		ICP-OES	Method 6010	1.7	10
Manganese	Mn	1,600[N2]	ICP-OES	Method 6010	1	10
Mercury	Hg	2	CVAA	Method 7470A	NR	0.025
Molybdenum	Mo	200[N2]	ICP-OES	Method 6010	0.72	1
Nitrate	NO3	10,000	IC	Method 9056A	26	100
Nitrite	NO2	1,000	IC	Method 9056A	18	50
Phosphate	PO4		IC	Method 9056A	24	100
Phosphorus	P		ICP-OES	Method 6010	4.1	10
Potassium	K		ICP-OES	Method 6010	2.3	10
Selenium	Se	50	ICP-MS	Method 6020	0.54	1
Silicon	Si		ICP-OES	Method 6010	3.1	10
Sodium	Na		ICP-OES	Method 6010	3.7	10
Sulfate	SO4	250,000[N1]	IC	Method 9056A	21	100
Sulfur	S		ICP-OES	Method 6010	4.7	10
Thallium*	Tl	2	ICP-MS	Method 6020	0.53	1
Uranium	U	30	ICP-MS	Method 6020	0.18	1
Vanadium	V		ICP-OES	Method 6010	1.9	10
Zinc	Zn	10[N2]	ICP-OES	Method 6010	1	10

COPCs indicated in **bold red** are used in subsequent example cases.
* Method detection limit (MDL) greater than minimum indicator value.

Drinking water standards are the National Primary Drinking Water Regulations (U.S. EPA, 2012a) unless noted:

[N1] National secondary drinking water regulations—non-enforceable guideline.
[N2] Drinking water equivalent level.
[N3] Treatment technique action level.

ICP-MS – Inductively coupled plasma mass spectrometry.
ICP-OES – Inductively coupled plasma optical emission spectrometry.
IC – Ion chromatography.
TOC – Total organic carbon.
CVAA – Cold vapor atomic absorption.

Typically, initial calibration is conducted at the beginning of the analytical process or as recommended by analytical process or the instrument manufacturer. Continuing calibration is recommended to be conducted periodically (e.g., every 20 analytical samples) and assessed relative to the expected value (e.g., within 15% of the standard value). For chemical analysis of LEAF eluates, it is recommended that matrix spikes and analytical replicates be carried out on the following test fractions:

- **Method 1313:** Eluates corresponding to the natural pH condition, the maximum acid condition (lowest pH target), and the maximum base condition (highest pH target);
- **Method 1314:** Eluate collected at cumulative L/S 0.5 and 10 mL/g-dry;
- **Method 1315:** Eluate from the 1-day cumulative leaching fraction; and
- **Method 1316:** Eluate conducted at L/S 0.5 mL/g-dry.

Matrix spikes are measured periodically over a set of analyses (e.g., once for each test) and are evaluated as a percent recovery of a known spike amount (e.g., within 15% of expected value). Analytical replicates are recommended at regular intervals during an analysis (e.g., once for each test) and are evaluated as a replicate percent difference between replicate analyses.

3.2.5 Testing and Analytical Costs

Estimated total analytical costs for a single test are anticipated to range from $2,000 to $5,000, which includes an extensive suite of chemical analyses. Estimated costs for laboratory services are presented in Table 3-8 through Table 3-11. The method-specific costs in these tables are estimated for single testing runs on an unknown material with a more complete suite of chemical analytes (e.g. pH, EC, ORP, metals, anions) than may be applicable for other scenarios. Costs also include the preparation of an electronic data deliverable for uploading to LeachXS™ Lite for data interpretation. Additional cost information is available in EPA's *Background Information for the Leaching Environmental Assessment Framework (LEAF) Test Methods* (US EPA, 2010). Reductions in costs to laboratories are anticipated as the methods become commercialized, equipment specific to the test methods is developed, and data interpretation becomes automated. LEAF may be more economical for significant amounts of material because the potential analytical costs may be fixed while the quantity of material is scalable. A stepwise approach to testing can be more economical for smaller material volumes and therefore more broadly feasible (Kosson, van der Sloot et al., 2002).

Table 3-8. Estimated Laboratory Costs for Method 1313

Parameters	Method	Matrix	Unit Price	Number of Analytical Samples [2]	Single Sample Cost
LEAF 1313 [1]	SW846 1313	Solid	$1,650	1	$1,650
pH	SW846 9040C	Water	$10	19	$190
Oxidation-reduction potential	SM 2580B	Water	$20	12	$240
Conductivity	SM 2510B	Water	$18	12	$216
DOC/DIC	SW846 9060A	Water	$30	12	$360
Metals (19-22)	SW846 6020A	Water	$80	12	$960
Mercury	SW846 7470A	Water	$25	12	$300
Anions (4-7)	SW846 9056A	Water	$75	12	$900
				Total:	$4,816

Source: A representative US commercial laboratory (2015)

[1] The cost for Method 1313 includes:
A) Sample air-drying to the prescribed >85% total solids.
B) Particle size reduction and sieving of the sample.
C) Nine parallel extractions at the prescribed method pH ranges.
D) Seven pretest extractions used to determine titration curve.
E) Three extraction blanks at low pH, neutral pH, and high pH.
F) A charge for an electronic data deliverable (EDD).

[2] Total number of analytical samples includes three method-prescribed blanks. Number of pH samples includes the seven pre-test samples.

Table 3-9. Estimated Laboratory Costs for Method 1314

Parameters	Method	Matrix	Unit Price	Number of Analytical Samples [2]	Single Sample Cost
LEAF 1314 [1]	SW846 1314	Solid	$1,870	1	$1,870
pH	SW846 9040C	Water	$10	10	$100
Oxidation-reduction potential	SM 2580B	Water	$20	10	$200
Conductivity	SM 2510B	Water	$18	10	$180
DOC/DIC	SW846 9060A	Water	$30	10	$300
Metals (19-22)	SW846 6020A	Water	$80	10	$800
Mercury	SW846 7470A	Water	$25	10	$250
Anions (4-7)	SW846 9056A	Water	$75	10	$750
				Total:	$4,450

Source: A representative US commercial laboratory (2015)

[1] Included in the cost for Method 1314 is the following:
A) Sample air-drying to the prescribed >85% total solids.
B) Particle size reduction and sieving of the sample.
C) One extraction blank collected at Time 1.
D) A charge for an EDD.

[2] Total number of analytical samples includes one method prescribed blank.

Table 3-10. Estimated Laboratory Costs for Method 1315

Parameters	Method	Matrix	Unit Price	Number of Analytical Samples [2]	Single Sample Cost
LEAF 1315 [1]	SW846 1315	Solid	$1,100	1	$1,100
pH	SW846 9040C	Water	$10	18	$180
Oxidation-reduction potential	SM 2580B	Water	$20	18	$360
Conductivity	SM 2510B	Water	$18	18	$324
DOC/DIC	SW846 9060A	Water	$30	18	$540
Metals (19-22)	SW846 6020A	Water	$80	18	$1,440
Mercury	SW846 7470A	Water	$25	18	$450
Anions (4-7)	SW846 9056A	Water	$75	18	$1,350
				Total:	$5,744

Source: A representative US commercial laboratory (2015)

Table 3-11. Estimated Laboratory Costs for Method 1316

Parameters	Method	Matrix	Unit Price	Number of Analytical Samples [2]	Single Sample Cost
LEAF 1316 [1]	SW846 1316	Solid	$730	1	$730
pH	SW846 9040C	Water	$10	6	$60
Conductivity	SM 2510B	Water	$18	6	$108
Oxidation-reduction potential	SM 2580B	Water	$20	6	$120
DOC/DIC	SW846 9060A	Water	$30	6	$180
Metals (19-22)	SW846 6020A	Water	$80	6	$480
Mercury	SW846 7470A	Water	$25	6	$150
Anions (4-7)	SW846 9056A	Water	$75	6	$450
				Total:	$2,278

Source: A representative US commercial laboratory (2015)

[1] Included in the cost for the Method 1316 is the following:
A) Sample air-drying to the prescribed >85% total solids.
B) Particle size reduction and sieving of the sample.
C) One extraction blank.
D) A charge for an EDD.

[2] Total number of analytical samples includes one method-prescribed blank.

3.2.6 Processing Time

Table 3-12 presents approximate processing times (in days) for conducting LEAF testing and chemical analysis of eluate after receipt of a material by the laboratory. Actual processing times would need to be negotiated with contracted laboratories. Accelerated testing may be available, though at least one week is needed for Method 1313 and 1316 and two weeks are needed for Method 1314. Method 1315 may be carried out more quickly if not all eluates are required. For a step-by-step breakdown of labor and processing time in a research laboratory, see the Background Information for the Leaching Environmental Assessment Framework (LEAF) Test Methods (US EPA, 2010).

Table 3-12. Processing Time

Method	Turnaround Time in Days from Receipt at Laboratory
Method 1313	35
Method 1314	35
Method 1315	84 (63 + 21 for analyses/reporting)
Method 1316	28

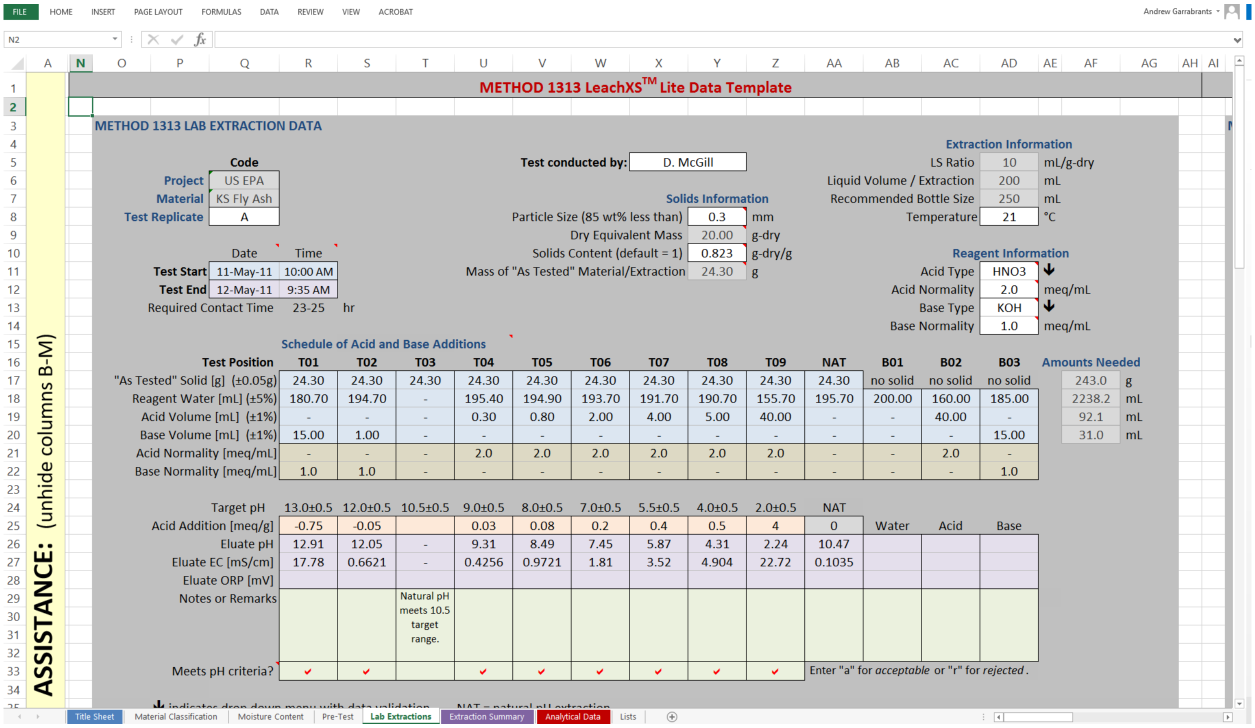
Source: US EPA (2010)

3.3 LEAF Data Management Tools

Because LEAF multi-point testing and comprehensive chemical analysis creates a considerably large data set of inter-related leaching measurements, LEAF includes tools for collecting, managing, and reporting data. Microsoft Excel® spreadsheets are provided as templates to assist laboratory personnel in preparation of tests and collection bench and analytical data. These templates import directly into LeachXS™ Lite, a desktop-based decision support software provided as a free download intended to be used as a data management tool for LEAF data (see Section 6, "Useful Resources").

3.3.1 Laboratory Data and Import Templates

LEAF and LeachXS™ Lite include a set of method-specific Excel® spreadsheet templates (available at *http://www.vanderbilt.edu/leaching/downloads/test-methods*) that laboratories can use to calculate test parameters, record and document laboratory observations, and archive analytical results. These data templates, illustrated in Figure 3-10, contain the verified calculations required to conduct each method at the bench scale. The embedded calculations and upload-ready format help assure data quality by minimizing errors in calculations and data transfer. Special care is recommended in ensuring that results are entered into the templates using the parameter units indicated (e.g., eluate concentrations in µg/L) and that the entered analytical data properly accounts for eluate dilutions for chemical analysis. These are the two most common errors in using the templates. Populated templates can be uploaded directly into all versions of the LeachXS™ data management program.



METHOD 1313 LeachXS^{TM} Lite Data Template

METHOD 1313 LAB EXTRACTION DATA

	Code
Project	US EPA
Material	KS Fly Ash
Test Replicate	A

Test conducted by: D. McGill

Solids Information

Particle Size (85 wt% less than)	0.3	mm
Dry Equivalent Mass	20.00	g-dry
Solids Content (default = 1)	0.823	g-dry/g
Mass of "As Tested" Material/Extraction	24.30	g

Extraction Information

LS Ratio	10	mL/g-dry
Liquid Volume / Extraction	200	mL
Recommended Bottle Size	250	mL
Temperature	21	°C

Reagent Information

Acid Type	HNO3	↓
Acid Normality	2.0	meq/mL
Base Type	KOH	↓
Base Normality	1.0	meq/mL

	Date	Time
Test Start	11-May-11	10:00 AM
Test End	12-May-11	9:35 AM

Required Contact Time 23-25 hr

Schedule of Acid and Base Additions

Test Position	**T01**	**T02**	**T03**	**T04**	**T05**	**T06**	**T07**	**T08**	**T09**	**NAT**	**B01**	**B02**	**B03**	**Amounts Needed**	
"As Tested" Solid [g] (±0.05g)	24.30	24.30	24.30	24.30	24.30	24.30	24.30	24.30	24.30	24.30	no solid	no solid	no solid	243.0	g
Reagent Water [mL] (±5%)	180.70	194.70	-	195.40	194.90	193.70	191.70	190.70	155.70	195.70	200.00	160.00	185.00	2238.2	mL
Acid Volume [mL] (±1%)	-	-	-	0.30	0.80	2.00	4.00	5.00	40.00	-	-	40.00	-	92.1	mL
Base Volume [mL] (±1%)	15.00	1.00	-	-	-	-	-	-	-	-	-	-	15.00	31.0	mL
Acid Normality [meq/mL]	-	-	-	2.0	2.0	2.0	2.0	2.0	2.0	-	-	2.0	-		
Base Normality [meq/mL]	1.0	1.0	-	-	-	-	-	-	-	-	-	-	1.0		

Target pH	13.0±0.5	12.0±0.5	10.5±0.5	9.0±0.5	8.0±0.5	7.0±0.5	5.5±0.5	4.0±0.5	2.0±0.5	NAT			
Acid Addition [meq/g]	-0.75	-0.05		0.03	0.08	0.2	0.4	0.5	4	0	Water	Acid	Base
Eluate pH	12.91	12.05	-	9.31	8.49	7.45	5.87	4.31	2.24	10.47			
Eluate EC [mS/cm]	17.78	0.6621	-	0.4256	0.9721	1.81	3.52	4.904	22.72	0.1035			
Eluate ORP [mV]													
Notes or Remarks			Natural pH meets 10.5 target range.										
Meets pH criteria?	✓	✓		✓	✓	✓	✓	✓	✓				

Enter "a" for *acceptable* or "r" for *rejected*.

↓ indicates drop down menu with data validation NAT = natural pH extraction

Figure 3-10. Example of a Microsoft Excel® data template for recording and archiving laboratory and analytical information from LEAF tests.

3.3.2 Data Management with LeachXS™ Lite

LeachXS™ Lite is a limited capacity version of LeachXS™[12] that provides users with a simplified tool for comparing leaching data between materials and test types and for exporting tabular and graphical leaching results. The Microsoft Excel® templates upload LEAF leaching test data directly from the LeachXS™ Lite interface and output results are exported as Microsoft Excel® workbooks for easy incorporation into reports and other documents. LeachXS™ Lite can be used to facilitate the process of compiling data from testing, compare leaching results within and between tests or material replicates and between different materials, and formulate standardized tables and graphics for data reporting. The flowchart in Figure 3-11 illustrates the general structure of the LeachXS™ program with the inputs to and outputs from LeachXS™ Lite.

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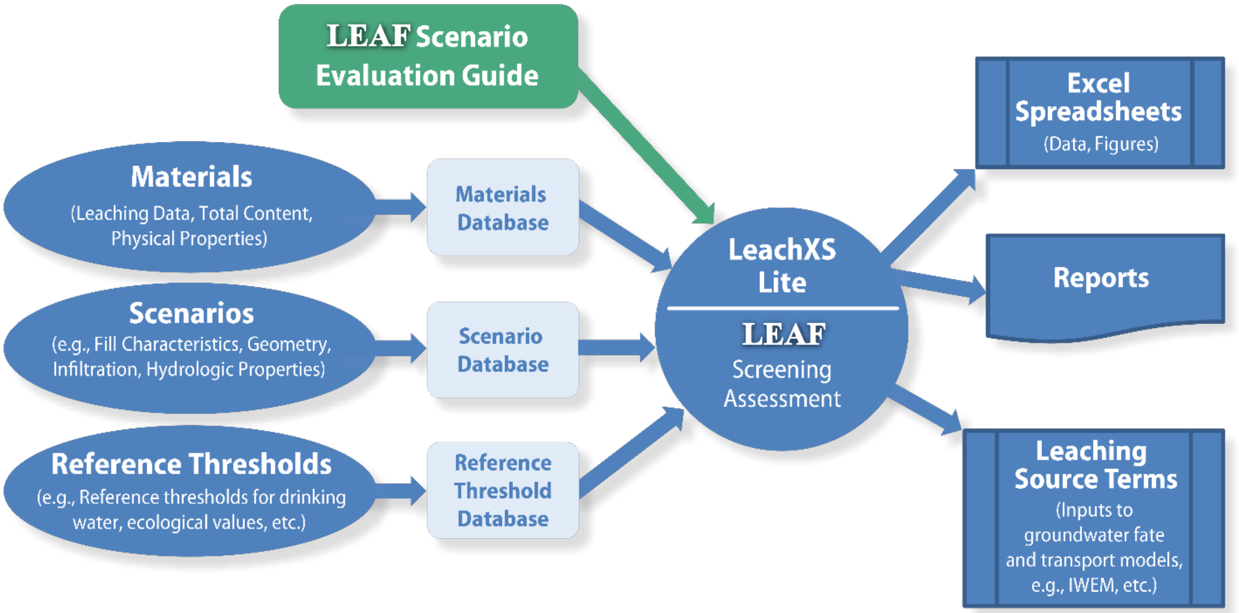
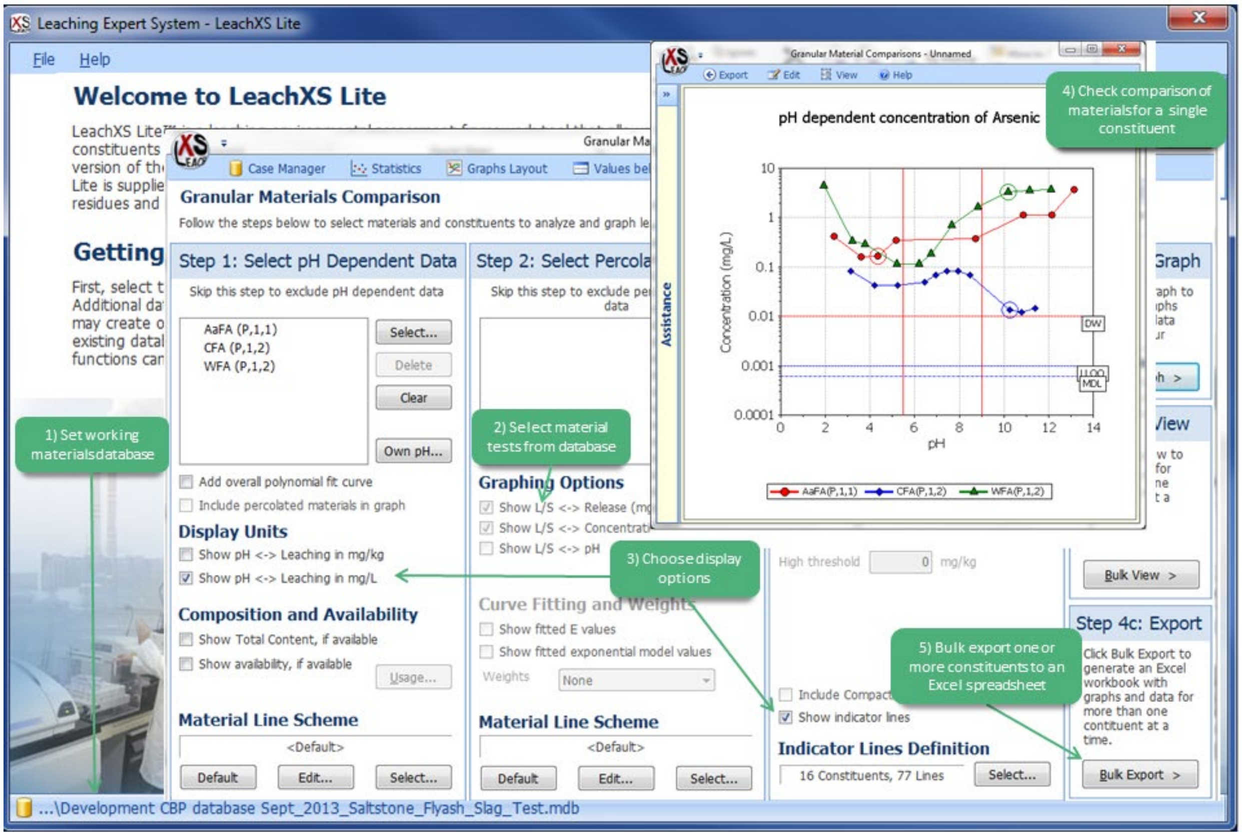
[12] LeachXS™ is licensed software whereby on-going development is supported by annual user fees. The LeachXS™ program was developed in collaboration between Vanderbilt University, the Energy Research Centre of The Netherlands and Hans van der Sloot Consultancy. Development of early versions of LeachXS™ also included participation by DHI (Denmark).



IWEM = Industrial Waste Management Evaluation Model

Figure 3-11. LeachXS™ Lite program structure showing data inputs, databases and outputs.

LeachXS™ Lite was created as a collaboration between the LeachXS™ development team and U.S. EPA with the initial purpose of facilitating data analysis and presentation of leaching potential for CCRs in U.S. EPA research (U.S. EPA, 2006a, 2008, 2009). Thus, the default materials database included in LeachXS™ Lite contains leaching data on more than 40 constituents found in 70 CCR samples and several other materials. However, like the LEAF methods, the LeachXS™ Lite program is not specific to any particular material type and can be used to evaluate any material for which LEAF leaching data has been generated. A sample screen capture of the primary interface in LeachXS™ for comparison of leaching from granular materials is presented in Figure 3-12.



Follow the steps below to select materials and constituents to analyze and graph le

1) Set working materials database

2) Select material tests from database

3) Choose display options

4) Check comparison of materials for a single constituent

5) Bulk export one or more constituents to an Excel spreadsheet

Click Bulk Export to generate an Excel workbook with graphs and data for more than one contituent at a time.

Figure 3-12. LeachXS™ Lite interface for comparison of granular materials showing the approach for comparing pH-dependent arsenic data for three CCR materials.

3.3.3 Pre-Existing Leaching Data

LeachXS™ Lite contains data on a limited number of samples analyzed through EPA support and other data that is publicly available. A wider spectrum of leach test results from data collected over several decades is available in the LeachXS™ database (available at *www.vanderbilt.edu/leaching*; accessed May 2, 2016). The comprehensive database includes LEAF test results from more than 250 waste types, secondary materials, contaminated soil, mineral processing slags, sludges, mine tailings, industrial waste streams (e.g., red mud), fertilizers, municipal solid waste and incineration residues, and construction products. In addition, users of LEAF and LeachXS™ Lite will generate additional data on materials of interest as testing continues. Such pre-existing LEAF data for a particular waste material or material type can be helpful in the understanding of a subject material and useful to inform testing schedules and possibly reduce testing costs.

For example, the material database contained within LeachXS™ Lite contains the leach test results that supported the EPA evaluations of CCRs from power plants employing different air pollution control technologies and burning different types of coal (U.S. EPA, 2006a, 2008, 2009). These materials include a number of samples of coal combustion fly ash, flue gas desulfurization (FGD) gypsum, and several combined CCR waste streams. CCR generators can compare LEAF leaching test method results for their materials to the existing LeachXS™ Lite data to put their materials into perspective of the wider range of similar materials and to better understand CCR leaching potential from the interpretation of leaching data from these EPA evaluations.

For materials that are generated and evaluated on a regular or ongoing basis, pre-existing leaching data may be helpful for optimizing the assessment process. The scope of a testing program to characterize a waste can be potentially focused to obtain missing data or to evaluate consistency with previous material characterizations. Periodic testing of continuous or near-continuous waste streams can inform the industrial process as the long-term variability of leaching performance is established through time-dependent sampling and characterization.

4. Developing Leaching Evaluations using LEAF

In general, a leaching assessment can be described as developing a leaching source term by estimating COPC release to the environment resulting from material contact with infiltrating rain or with groundwater. One or multiple LEAF tests can be used in an assessment depending on the parameters needed to represent the material when placed in the environment. The progressive nature of the LEAF framework tests allows assessment to occur in a stepwise progression with evaluation as to whether the results at each step are adequate to support a determination that the material is appropriate for the planned use or disposal. If the results at each step are not adequate, additional testing or more-detailed evaluations may be conducted to provide assessments that more fully reflect release in the anticipated placement. For example, a relatively simple screening assessment comparing the results of an individual LEAF test method directly with COPC target values (e.g., drinking water MCLs) may provide adequate support in some assessments when no COPC target values are exceeded at any pH value, or over the plausible range of pH values. However, when screening assessments cannot provide adequate supporting results, further testing (e.g., Method 1314 and/or Method 1315) and site-specific data may be required to develop a leaching source term that considers the effects of field conditions for a particular scenario and the time varying leaching behavior (referred to as a “scenario assessment”). Additionally, leaching assessments for some cases may utilize empirical or numerical modeling to describe the movement of COPCs from the source term derived from one or more LEAF test methods to a defined point-of-compliance.

Using a “source-to-compliance point” approach, the leaching test results are material specific in that they are only a function of the material leaching performance; the source term accounts for the release under the environmental conditions of the application scenario; and the source term may be used with dilution and attenuation factor(s) (DAFs) or as an input to fate and transport models to account for the location-specific point-of-compliance or source-to-receptor factors (in some cases, the POC may be treated waste prior to disposal, or the outer edge of contaminated soil that has been treated in-place, without use of groundwater transport modeling i.e., a DAF with the value 1). Results from this form of evaluation can be used to back-calculate from thresholds at the point of compliance or to develop threshold values directly comparable to leaching test results for specific scenarios. In addition, this approach allows for substantial decoupling of leaching test results, source term models, and location-specific factors to allow greater generalization of the approach and applicability of leaching test data. This approach allows users to generate “what if” model simulations to understand likely changes in release/risks for the material under hypothetical conditions.

This chapter explains how to develop a leaching evaluation utilizing the LEAF test methods. A leaching evaluation requires determining the appropriate tests and testing parameters and then understanding how laboratory scale results can be translated to field settings. The appropriate selection of leaching tests will depend upon both material properties and the anticipated environmental conditions, as well as on the environmental decision that testing is intended to support. In some cases, a simple evaluation with minimal testing will provide sufficient results that adequately support environmental decision-making. A more thorough and complex evaluation may be needed when there is large uncertainty in the leaching of a material due to possible changing environmental conditions, high waste heterogeneity, or waste generated in high volumes (where more certainty about release potential may be needed). Alternatively, a more thorough leaching evaluation may be warranted when the estimated leaching is close to a regulatory threshold, where more certainty about the release potential would also be needed.

4.1 Applications of LEAF

LEAF has been used for leaching assessment of CCRs in both disposal and reuse situations, for evaluating waste treatment effectiveness and in other assessments. These uses illustrate that it can be used to estimate constituent leaching from a wide range of inorganic materials as-is, or under environmental scenarios relevant for the beneficial use, treatment, and disposal of waste:

- Materials types for which LEAF is applicable include wastes, treated wastes (e.g., materials treated by solidification/stabilization), secondary materials potentially being re-used (e.g., blast furnace slags, bauxite residues), energy residuals (e.g., coal combustion fly ash), contaminated soils and sediments, and mining and mineral processing wastes.
- Scenarios that can be evaluated using LEAF include, but are not limited to, coal combustion residue (CCR) disposal units, large or small scale use of secondary materials in concrete or road construction, management of mining and mineral processing wastes, evaluation of soil amendments, and evaluation of treatment effectiveness for contaminated soils, sediments, and wastes.
- LEAF leaching tests provide data that can be used to address a range of assessment objectives including simple screening assessments to evaluate material acceptability for a selected disposal or use application, consistency testing during and after treatment of waste or contaminated materials, and development of detailed leaching source terms for driving more complex fate and transport models.

The factors addressed by the LEAF leaching tests include the most significant determinants of leaching for most solid materials under most disposal or use conditions, including wastes and secondary materials (U.S. EPA, 2014c). The framework recognizes that some factors (e.g., reducing conditions), may be important for certain materials and field scenarios, but are difficult to evaluate reproducibly in a laboratory setting. However, their effects on the leaching process may be evaluated using LEAF test results in conjunction with geochemical speciation modeling. Section 4.3 provides examples of additional factors, typical COPC leaching behaviors and considerations when developing leaching assessments.

4.1.1 Material Characterization

LEAF was developed for the assessment of a broad range of materials; however, the need to assess CCR leaching proved to be an opportunity to refine and validate LEAF for inorganic constituents. As a result, the initial development of LEAF was directed at evaluating and comparing leaching potential of CCRs generated by facilities burning a range of coal types and utilizing various air pollution control technologies. LEAF was used to assess the potential leaching of mercury and other metals from CCRs over the range of field conditions to which CCRs are typically exposed during land disposal and in engineering and commercial re-use applications (Thorneloe et al., 2010; U.S. EPA, 2006a, 2008, 2009). The LEAF methods also provided leaching data in support of EPA's assessment of the potential hazards from using coal fly ash as partial replacement of cement in making concrete (Garrabrants, Kosson, DeLapp, & van der Sloot, 2014; Kosson et al., 2014; U.S. EPA, 2012b, 2012d, 2014a).

4.1.2 Beneficial Use Evaluation

LEAF has also been applied to leaching assessments estimating the environmental impacts from utilization of secondary materials, primarily as construction materials. The pH-dependent and L/S-dependent leaching behavior of contaminated dredged sediments for potential replacement of sand in the manufacture of controlled low-strength material, or flowable fill, has been characterized using LEAF tests (Gardner, Tsiatsios, Melton, & Seager, 2007). The LEAF approach has been used to evaluate the reuse of coal fly ash as road base material and construction of embankments; municipal solid waste incinerator (MSWI) bottom ash as road base; and secondary materials (e.g., coal fly ash, recycled concrete aggregate, furnace slags) used as partial substitutes for Portland cement or admixtures in cement and concrete construction products (U.S. EPA, 2014c). In Europe, leaching procedures analogous to the LEAF methods (see Appendix A) have been used to evaluate materials such as coal fly ash, recycled concrete aggregate or municipal solid waste incinerator bottom ash for reuse in road bases and embankments (Engelsen et al., 2010; Engelsen, Wibetoe, van der Sloot, Lund, & Petkovic, 2012), and use of a byproduct from the aluminum industry as soil amendment (Carter, van der Sloot, & Cooling, 2009). In China, LEAF methods have been used to evaluate the environmental safety of use of sewage sludge compost as an agricultural amendment (Fang, et al., 2017, 2018). Leaching data from LEAF or other relevant leaching tests can be used in EPA's *Methodology for Evaluating Beneficial Uses of Industrial Non-Hazardous Secondary Materials,* which presents a voluntary approach for evaluating potential adverse impacts to human health and the environment from a wide range of industrial non-hazardous secondary materials and their associated beneficial uses. Prior to beneficially using secondary materials in any projects, interested individuals or organizations should consult with the relevant state and federal environmental agencies to ensure proposed uses are consistent with state and federal requirements.

4.1.3 Treatment Effectiveness

LEAF leaching test methods have also been applied to evaluate treatment effectiveness for remediation or disposal purposes for industrial wastes such as soil, sludge, and slag using stabilization/solidification technologies. In these cases, leachability is considered a primary performance parameter used to assess treatment effectiveness because it indicates the ability of a treatment material to retain or immobilize a specific set of site contaminants of concern (Pereira, Rodriguez-Pinero, & Vale, 2001). Additional examples of application of LEAF leaching test methods for treatment effectiveness include evaluation of treatment process effectiveness for contaminated soils (Sanchez et al., 2002; U.S. EPA, 2003).

4.1.4 Miscellaneous Uses

In Europe, leaching tests analogous to the LEAF methods have been used to develop regulatory criteria for construction products that may be used on the ground (BMD, 1995; SQD, 2007; Verschoor et al., 2008) and guidelines for assessment of sustainable landfill in the Netherlands (Brand et al., 2014). Additionally, leaching tests were used as the basis for evaluation of ecological toxicology (ecotox) testing of soils and wastes (Postma, van der Sloot, & van Zomeren, 2009). These applications are beyond the scope of this guide.

4.2 Developing an Assessment Framework

The goal of environmental leaching assessments is to provide an estimate of the leaching potential of constituents in a material for a plausible management scenario that is as accurate as practical or needed, but also represents an upper bound that does not underestimate the release of COPCs. LEAF leaching test methods can be used effectively to estimate the field leaching behavior of a wide range of materials under both disposal and use conditions. However, it is important to interpret the leaching test results *in the context of the controlling physical and chemical mechanisms of the field scenario* (U.S. EPA, 2014c). The application of laboratory testing results to environmental decision-making requires comparability of the laboratory data with threshold or limit values at a defined point of compliance or location. This comparison may be achieved through (i) screening assessments (i.e., comparisons of bounding leaching concentrations based directly on test results with threshold values), (ii) scenario-based assessments for percolation and/or mass transport scenarios, or (iii) subsequent analyses such as the combining of LEAF source terms with fate and transport or geochemical speciation modeling representing environmental processes not accounted for by LEAF.

The first step in developing an assessment is to define the objectives of the assessment and the parameters of the potential material use or disposal scenario. These definitions will support the subsequent selection of appropriate leaching tests and will provide the basis for interpreting and applying the resultant leaching data. The assessment scenario is described by a conceptual model of constituent leaching that considers the physical and leaching characteristics of the material when doing a screening assessment. When conducting a scenario-based assessment, details about its anticipated placement (i.e., quantity, depth or height, footprint, porosity, etc.), the net amount and mode of water contact, the water quality, would be added to the waste characteristics data.

4.2.1 A Stepwise Assessment Approach

When developing an assessment approach using multiple tests to evaluate leaching in a scenario, the assessor can consider the information provided by each test in a stepwise fashion. Starting with the simplest tests and considering the expected results before moving on to more elaborate testing schemes allows for developing the appropriate leaching evaluation tailored to the environmental scenario. The LEAF assessment approach can be viewed as a set of progressive steps, whereby each successive step becomes more accurate by more fully reflecting site conditions present in the environment. However, each successive step requires an additional level of testing and interpretation. Screening assessments can provide increasingly refined estimates of the maximum leaching concentration (considered an “infinite source”) for each COPC, while scenario assessments provide estimates of the time varying leaching concentration and the amount of each COPC that may leach (i.e., a “finite source”). LEAF provides flexibility in developing an assessment approach because the amount of testing and effort can be tailored to the assessment, depending upon the objectives of the assessment and the relevant information regarding the material and the environment. An illustration of the hierarchy in this stepwise approach to leaching assessment is provided in Figure 4-1. LEAF provides user flexibility in that an evaluation may utilize one to four methods depending on the assessment objectives and project scope. A LEAF evaluation may vary from a simple screening estimate using the results of a single test method to a comprehensive evaluation of leaching behavior of multiple COPCs that encompass the results of all four LEAF methods. The selection of an evaluation approach will result in differing amounts of material required for testing and scenario specific information that required to conduct the assessment. Table 4-1 illustrates testing plans in screening based assessments (described in section 4.2.4). Table 4-2 illustrates testing plans for use in scenario-based assessments (described in section 4.2.5)

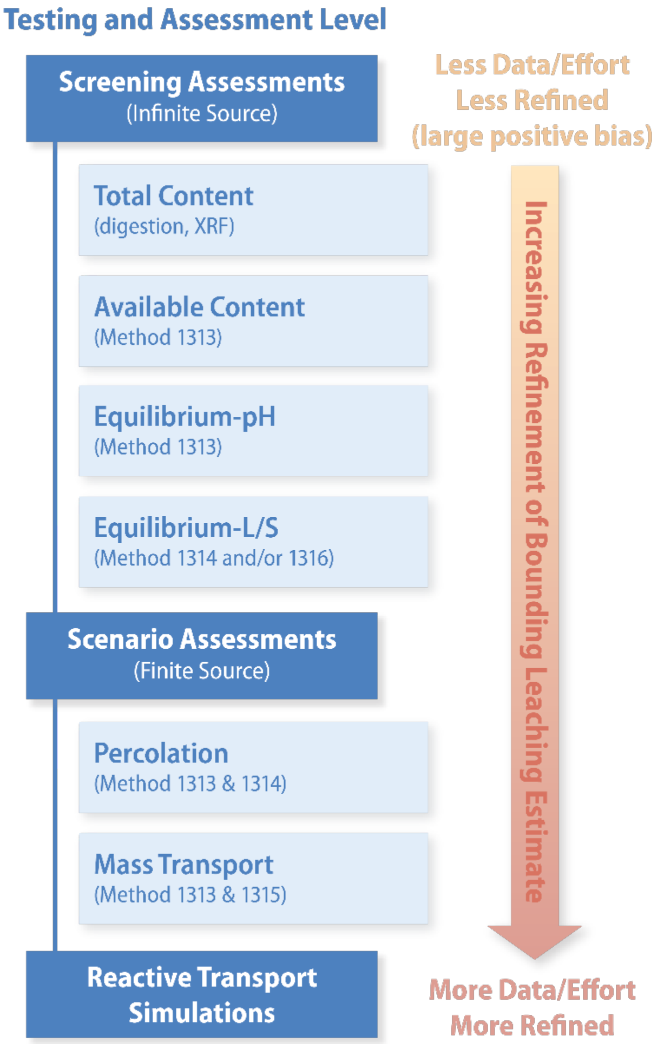


Figure adapted from Kosson and van der Sloot (2015).

Figure 4-1. Example assessment hierarchy presenting options for progressively working from more bounding assessments to less bounding assessments based on levels of leaching information.

4.2.2 Assessment Objectives

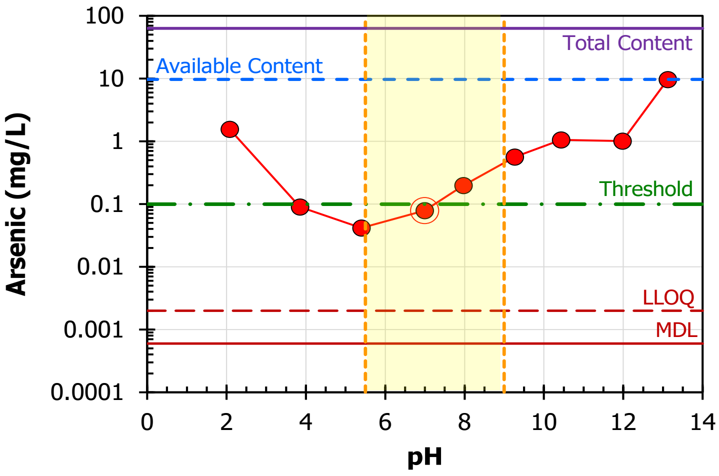
Since the LEAF approach is intended to be flexible and to follow a stepwise methodology, the objectives for conducting an assessment determine the amount of testing and data analysis required. For example, a relatively simple screening assessment typically requires less testing and interpretation than a more-complex “source-to-compliance point” assessment. The objectives of the assessment should address the decisions anticipated to be made, the nature and physical structure of materials to be tested, the potential scenarios that may be evaluated, and all applicable regulations or constraints. Definition of these objectives can follow the Agency’s data quality objectives process (U.S. EPA, 2006b) whereby the data quality objectives or questions to be answered for a specific circumstance (e.g., beneficial use of a material, site characterization) may influence the decision to use LEAF and the selection of a testing program.

One outcome of defining the assessment objectives is the identification of the appropriate leaching assessment level (e.g., screening assessment vs. detailed characterization) required to meet the assessment objectives. The extent of information needed as part of the scenario definition increases as the evaluator seeks to achieve a more detailed and refined (and potentially, site-specific) estimate of constituent leaching. For example, screening level assessments, which seek to determine the acceptability of a material for a particular management scenario based on direct comparison of leaching test data to exposure limit values, such as MCLs, may only require a single test (e.g., Method 1313 or 1314) to provide an adequate basis for making a scientifically supported decision. Detailed characterization to support a complex fate and transport model between the leaching source term and a point of compliance will require integration of leaching data from several leaching tests and incorporation of knowledge of the environmental scenario. The assumptions used when defining assessment objectives and determining information needs should be fully described so that results between assessments can be meaningfully compared.

4.2.3 Comparing Test Results to Threshold Values

4.2.3.1 Direct Comparison of Eluates to Threshold Values

Depending on the defined assessment scenario and the regulatory program, relevant benchmarks may be derived from drinking water maximum contaminant levels (MCLs), national recommended water quality criteria, or EPA regional screening levels (RSLs); however, a set of specific benchmarks should be determined on a case-by-case basis based on assessment objectives and all associate constraints and limitations. Figure 4-2 illustrates a graphical comparison of leaching results over a range of pH values to the regulatory limit for a particular constituent, and to the total content of the constituent in the material that was evaluated. When used to evaluate materials, the LEAF leaching test method results can be used as the source term for risk assessment to generate estimated risk distributions that can form the basis for environmental decision-making. This example is for illustrative purposes; users should consult with the appropriate regulatory body to select appropriate acceptance criteria.



Adapted from Kosson et al. (2002).

Figure 4-2. Method 1313 LSP results over an applicable pH domain compared to total content, available content and a reference threshold.

When leaching under a plausible range of conditions is demonstrated to be below threshold values for all COPCs, it may be possible to conclude that the proposed application of the material is acceptable provided that all regulatory requirements have been met (U.S. EPA, 2012e). However, direct comparison of eluate concentration to benchmark concentrations (e.g., as illustrated in Figure 4-2) does not always complete an evaluation. Furthermore, the threshold values used in comparison should be relevant to the type of testing results being compared. For example, eluate concentrations from Method 1315 results are used for calculating fluxes and are not reflective of expected maximum leaching concentrations. Thus, Method 1315 eluate concentrations should not be applied to comparisons with threshold concentrations; whereas, the Method 1315 COPCs flux may be used after consideration of the relative amount of contacting water to exposed surface area in the assessment scenario. When comparing Method 1313 results to benchmark concentrations, the pH of Method 1313 and the pH of the benchmark may differ. One approach is to interpolate between two endpoint pH values from Method 1313 (see Section 4.4.2.)

The screening-level assessment of leaching in a particular application can follow the stepwise approach described in Section 4.2.1. Typically, the threshold criteria against which potential leaching of COPCs is evaluated (e.g., drinking water MCLs, surface water quality concentrations, etc.) are expressed as concentrations and, therefore, estimates of COPC leaching should be derived on a similar basis as concentrations. Screening assessments utilize estimates of maximum leaching concentration, C_{leach_max}, derived from a limited dataset of COPC leaching (e.g., from total content analysis or one or more LEAF tests) which are adjusted to an initial L/S value, $(L/S)_{initial}$. The initial L/S value can be a default value of 0.5 L/kg-dry, an estimate of porewater L/S based on materials properties,[13] or an L/S estimate that reflects the maximum expected leachate concentration for the specified scenario. For illustrative purposes, the default value of 0.5 L/kg-dry will be used in all examples of this guide.

For simple screening assessments, the maximum leaching concentration may assume that the total content of a COPC is leached into an initial L/S, while more-complex screening assessments may utilize the broader range of leaching behavior (e.g., Method 1313 and Method 1316) to estimate the maximum leaching concentration over a range of scenario conditions. All screening assessment assumed an infinite source of leaching based on results obtained from testing the material or treated material[14] as it would be used or disposed.

4.2.3.2 Assessment Ratios

The comparison between the estimated maximum leaching concentration (C_{leach_max}) and threshold limit concentrations (C_{thes}) can be illustrated by a simple ratio of the leaching concentration of a COPC divided by the target threshold value. For purposes of this document, this is referred to as an assessment ratio (AR), which considers the maximum leaching estimate and threshold concentrations.

$$AR = C_{leach\_max}/C_{thres} \qquad \textbf{Equation 4-1}$$

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[13] The lower bound for the porewater L/S of a material can be estimated using the skeletal density, ρ_s [kg_{solid}/m^3_{solid}], and a bulk porosity, ε [m^3_{pore}/m^3] as ε /(1- ε)/ ρ_s *1,000 where 1,000 is a conversion factor for volume (1,000 L/m^3).

[14] Blending a material with soil or lime would be considered a treatment, and, therefore, the material should be tested "as used" considering the mixture. Separate testing and modeling can be used to predict the behavior of mixtures of materials; such testing and modeling is beyond the scope of this document.

where

AR is the assessment ratio [-];
C_{leach_max} is the estimated maximum concentration for the COPC [mg/L]; and
C_{thres} is the threshold value for the COPC [mg/L].

When the assessment ratio for a COPC is less than or equal to 1 ($AR \leq 1$), the constituent is not likely to leach at concentrations greater than the threshold limit concentration under the anticipated scenario conditions and further evaluation may not be required. An assessment ratio greater than 1 ($AR > 1$) does not necessarily indicate that a COPC will leach at a level greater than the threshold limit concentration in the field but does indicate that further evaluation is required to refine the assessment. For example, a decision-maker may choose to perform additional leach testing using other LEAF methods to develop a more refined source term for COPC leaching or may modify the planned use in some way to reduce the release potential (e.g., a change in the environmental application).[15] Additionally, LEAF test results could be used as an input to groundwater fate and transport modeling to estimate the degree of offsite migration and potential for groundwater contamination. Additional LEAF leaching test results could result in a more refined modeling of the potential release. See Section 4.4.7 for consideration of dilution and attenuation within an Assessment Ratio.

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[15] In research partially supported by U.S. EPA (e.g., use of 20 percent coal fly ash in making concrete could reduce fivefold the amount of COPC available to leach; Garrabrants et al., 2014; Kosson et al., 2014; U.S. EPA, 2012b), blending of fly ash into concrete as a replacement for Portland cement allowed for reuse of a secondary material without significant impact. The replacement ratio of 20% of the Portland cement fraction reduced the available content for some COPCs fivefold over the available content in fly ash alone; however, lowering the replacement ratio would further reduce the available content of fly ash COPCS in the concrete product.

Table 4-1. Summary of Suggested Test Methods and Analyses for Screening Assessments.

Test Methods	Eluate Analyses	Assessment Attributes
Step 1 – Total Content Screening (*if determined*)		
Total Content: digestion, XRF, etc.	COPCs	• Total content mass release [mg/kg-dry] converted to estimated maximum leaching concentration (C_{leach_max}) through division by a scenario L/S value [L/kg-dry]. • Conversion of total content [mg/kg] to dry mass basis [mg/kg-dry] is necessary using solids content or moisture content (wet basis).
Step 2 – Available Content Screening		
Method 1313: pH 2, 9, and 13	pH, EC,[1] COPCs, DOC	• Basis for infinite source term; assumes available content is maximum cumulative release under field conditions. • Available content mass release [mg/kg-dry] derived from maximum leachate concentration at Method 1313 endpoint target pH extractions at 2, 9, and 13. Target pH values in Method 1313 can be reduced to only those demonstrated to achieve maximum eluate concentration as used for available content determination. • Estimated maximum leaching concentration (C_{leach_max}); adjusted to initial L/S (default 0.5 L/kg-dry).
Step 3 – Equilibrium-pH Screening		
Method 1313: Applicable pH domain[2] and pH 2, 9, and 13	pH, EC,[1] COPCs, DOC	• Basis for infinite source term over applicable scenario pH domain; assumes equilibrium concentrations as an upper bound of leaching under field conditions. • Available content as indicated above; used to determine solubility-limited vs. available content-limited leaching. • Acid/base neutralization capacity to pH ≈ 7 relevant to evaluation of neutralization due to long-term aging processes (e.g., carbonation, acid attack). • Estimated maximum leachate concentration (C_{leach_max}) determined as the maximum eluate concentration over the applicable pH domain for solubility-limited constituents; adjusted to initial L/S (default at 0.5 L/kg-dry) for available content-limited COPCs.[3]
Step 4 – Equilibrium-L/S Screening		
Method 1313: Applicable pH domain[2] and pH 2, 9, and 13 and *Method 1314 or Method 1316:* Full set of L/S values	pH, EC,[1] COPCs, DOC	• Basis for infinite source term at low L/S; assumes eluate concentrations at low L/S are comparable to porewater. • Estimated maximum leachate concentration (C_{leach_max}) for solubility-limited and available content-limited leaching constituents determined as greater of maximum eluate concentration over the applicable pH domain or maximum eluate concentration over the L/S range.[4] • Supplemental basis for determination of solubility-limited vs. available content limited leaching when evaluated along with Method 1313 data.

[1] Electrical conductivity (EC) measurement in Method 1313 is recommended for natural pH eluate only due to interferences provided by acid/base additions.

[2] An applicable pH domain for an assessment scenario is determined by extending the default pH domain (5.5 ≤ pH ≤ 9.0) to include the natural pH of the material and adjustments required from consideration of the chemical composition of the contacting water, interfaces or commingling with other materials, and long-term changes in pH due to material aging processes.

[3] For many applications, available content-limited species include the Group IA cations (e.g., Na, K) and anions (e.g., Br^-, Cl^-, F^-, NO_3^-). In addition, oxyanions (e.g., As, B, Cr, Se, Mo, V) may display available content-limited leaching on a case-by-case basis.

[4] For some cases, the maximum concentration over the applicable pH domain from Method 1313 may be less than the maximum concentration over the L/S range from Method 1314 because of aqueous phase complexation by increased concentration of DOC or other constituents at low L/S values in Method 1314. Method 1314 results also can be used to provide a basis for narrowing the applicable pH domain for evaluation of Method 1313 results to the pH range observed during Method 1314, with 0.5 pH units added to the maximum pH observed and 0.5 pH units subtracted from the minimum pH observed during Method 1314, unless known aging processes would result in a broader pH domain (e.g., carbonation of alkali cement materials may result in observed pH values as low as pH 7).

Table 4-2. Summary of Suggested Test Methods and Analyses for Scenario-Based Assessments.

Test Methods	Eluate Analyses	Assessment Attributes
Percolation Through Permeable Material Scenario Assessment		
Method 1313: Full endpoint target pH values and *Method 1314:* Full set of L/S eluates or *Method 1316:* Full set of L/S eluates	pH, EC,[2] ORP,[3] COPCs, DOC, DIC, Major/minor constituents[4]	• Basis for infinite source term; assuming LSP with percolating water limited to available mass release. • Available content mass release [mg/kg-dry] at Method 1313 endpoint target pH values of 2, 9, and 13. • Acid/base neutralization capacity to pH ≈ 7 relevant to evaluation of neutralization due to long-term aging processes (e.g., carbonation, acid attack). • LSP as a function of pH providing a baseline understanding of leaching behavior and speciation assessment.[5] • Basis for determination of solubility-limited vs. available content-limited leaching through comparison between pH- and L/S-dependent leaching.[6] • Leachate concentration evolution as a function of L/S for source term development based on test elution curve. • Basis for verification of chemical speciation modeling at low L/S. • Supports fate and transport simulations considering sensitivity of field conditions (e.g., infiltration chemistry, preferential flow, material aging).
Mass Transport Limited Leaching Scenario (Impermeable Material) Assessment		
Method 1313: Full endpoint target pH values and *Method 1314:* Full set of L/S eluates and *Method 1315:* Full set of time intervals	pH, EC,[2] ORP,[3] COPCs, DOC, DIC, Major/minor constituents[4]	Attributes of Percolation Scenario Assessment plus: • Estimate of initial porewater concentration (Method 1314 through cumulative L/S 0.2 L/kg-dry). • Cumulative release and interval flux as a function of leaching time (Method 1315) for saturated and intermittent wetting conditions. • Basis for fate and transport model parameters (e.g., diffusivity, tortuosity) for simulation of evolving conditions (e.g., low liquid-to-surface area, external solution chemistry, carbonation, oxidation, intermittent wetting, etc.).

[1] Prior information, such as characterization information from similar materials, may reduce or supplant extent of equilibrium-based assessment for characterization.

[2] Electrical conductivity (EC) measurement in Method 1313 is recommended for natural pH eluate only due to interferences provided by acid/base additions.

[3] Oxidation reduction potential (ORP) measurement in Method 1313 is recommended for natural pH eluate only due to interferences provided by acid/base additions. ORP provides useful indications of material properties under abiotic and anoxic conditions, recognizing the sensitivity and uncertainty of ORP measurements.

[4] The list of major and minor constituents should include all constituents that are important to the mineralogy and chemical behavior of the material. At minimum, these constituents would include Al, Ba, Ca, Cl, Fe, Si, Mg, Na, P and S for many materials.

[5] Speciation assessment refers to evaluations and/or simulations that consider the effects of changes in pH, redox conditions, extent of carbonation, complexation with dissolved organic carbon, etc. on COPC release. Such assessments may be accomplished heuristically or in combination with geochemical speciation modeling.

[6] For many applications, available content-limited species include the Group IA cations (e.g., Na, K) and anions (e.g., Br^-, Cl^-, F^-, NO_3^-). In addition, oxyanions (e.g., As, B, Cr, Se, Mo, V) may display available content-limited leaching on a case-by-case basis.

4.2.4 Screening Level Assessments

One approach to a leaching assessment that offsets the level of detail obtained from testing against the increased effort to provide more refined source terms is a series of screening approaches. These screening approaches are not required but may be used to determine whether more-detailed assessments (e.g., scenario-based assessments) are necessary or whether screening test results alone adequately support environmental decision-making. In some scenarios, the leaching behavior of COPCs may be screened against threshold values based on a source term that estimates leachate concentrations for the total content, available content, and equilibrium LSP (Figure 4-3). The levels of the screening approach allow for a trade-off between progressive refinement of a bounding estimate of potential leachate concentration against increased testing and analysis effort. The intent of a screening assessment is to determine which constituents are relevant to the scenario (i.e., which COPCs are likely to leach in concentrations presenting a threat to human health and the environment). Screening assessments utilize results from limited testing and default or minimal assessment scenario information to provide upper bound estimate of leaching (i.e., “not expected to exceed” concentrations). In the most conservative estimates, a screening may be based on an “infinite source” leaching assessment[16] that can be compared to threshold values (e.g., the total concentration of a COPC may be less than a threshold value). However, screening approaches should consider finite sources when possible.

An example of how these testing schemes may estimate environmental leaching is shown below in Figure 4-3. In an example screening application, an assessor may be already aware of or test for the total content of a COPC in a material. The total content value provides an upper limit on the amount of material that can be released. A screening use of Method 1313 with pH endpoints of 2, 9 and 13 will provide the assessor with an estimate of the available content of COPCs within the material. If a more specific pH domain of the environment is known, the assessor can choose to tailor Method 1313 to provide a better estimate of equilibrium-controlled leaching. If the assessor is aware that percolation effects will control leaching, Method 1314 provides additional information on the expected leaching behavior in the environment.

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[16] An “infinite source” assumes that leaching will continue without change in COPC concentrations over infinite time (i.e., the COPC will never become depleted from the material). More advanced assessments typically assume a “finite source” whereby the COPC becomes depleted within the material once the available content has been leached.

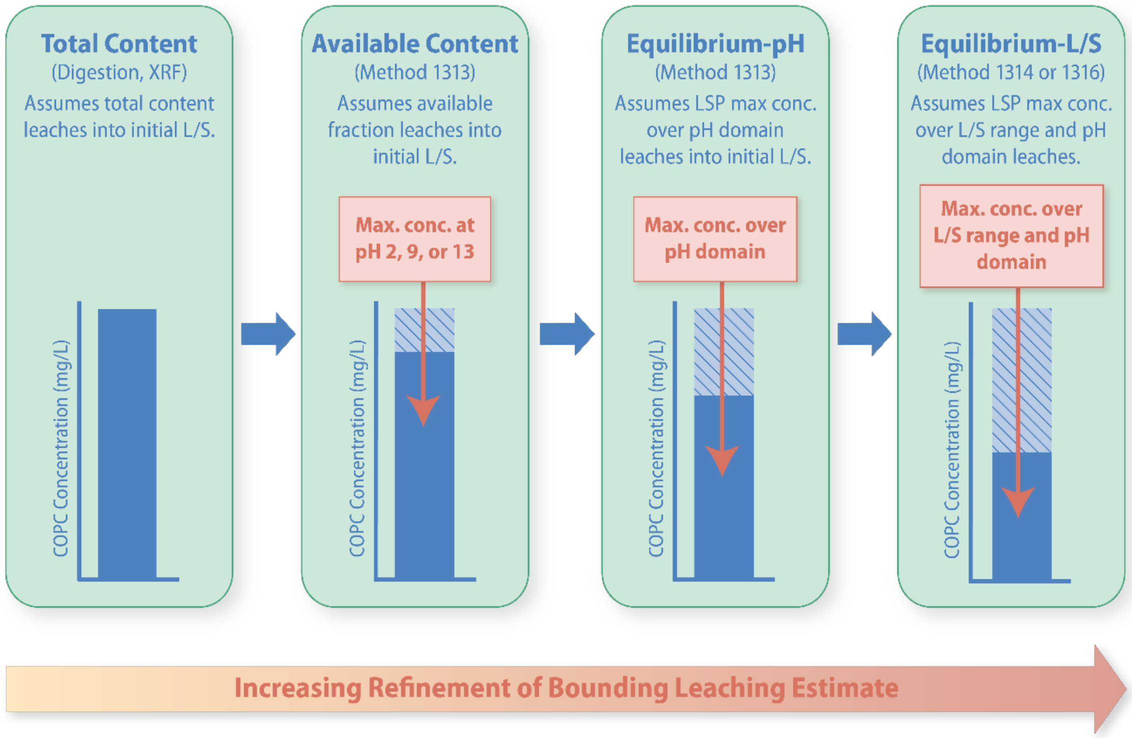

Figure 4-3. Screening level assessments, test methods and assumed leaching conditions[17].

Screening level assessments may recognize that not all COPCs are present in the material at sufficient concentration to be of concern and that not all COPCs present will leach under all scenario conditions. Therefore, the goal of the assessment is to identify and separate material constituents that may leach at less than or equal to the identified benchmark or threshold values from those COPCs that may be a concern. Constituents with upper bound leaching estimates less than benchmarks or thresholds would not require further analysis whereas an evaluation of COPCs with values that exceed benchmarks or thresholds may benefit from subsequent characterization and analysis.

A screening-based assessment generally assumes limited or partial information regarding the material and its placement into the environment when developing a leaching assessment. The more information that is available regarding the material and the environment, the more accurately a testing and analysis plan can reflect environmental conditions in the field. The flexibility provided by LEAF allows for the development of a range of assessments from a simple screening-based assessment with limited testing and limited environmental information to advanced scenario-based assessments with more elaborate testing and source term model development to evaluate anticipated environmental field conditions. A screening level assessment can be compared to relevant threshold values to identify and separate COPCs not likely to adversely impact the environment at threshold levels from COPCs for which further testing is required. Screening assessments often provide higher estimates of leaching than scenario assessments due to relying on estimates of maximum leachate concentrations or available content estimates.

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[17] The max concentrations shown are illustrative and may differ by orders of magnitude depending on the testing and material.

4.2.4.1 Total Content Screening

Total content is the concentration of a COPC within the solid material [mg/kg_{dry}] that may be derived from destructive or non-destructive total analysis of the solid material. The total content of COPCs in a material ($\mathrm{m_{total}}$) is obtained through analytical methods such as solid phase digestion (e.g., U.S. EPA Method 3052) or other total elemental analysis (e.g., X-ray fluorescence). Because this source term does not require any LEAF methods, it can serve as a useful first step when the bulk content is known from prior knowledge (e.g., available literature) or testing. This source term assumes that the entire bulk content of a material is released into the water immediately, resulting in the highest concentration that is physically possible, albeit unlikely.

The bulk content from digestion methods may be reported on a wet-mass basis [mg/kg], which will result in an incorrect estimation of releases if not converted into a dry-mass basis. Conversion between wet and dry bases requires knowledge of the moisture content of the material on a wet mass basis or, alternatively, the solids content. Equation 4-2 presents the conversion between wet and dry weight:

$$\mathrm{m_{total,dry}} = (\mathrm{m_{total,wet}})(\mathrm{SC}) = (\mathrm{m_{total,wet}})(1-\mathrm{MC_{dry}})$$ **Equation 4-2**

where

$\mathrm{m_{Total,dry}}$ is Bulk content adjusted to a dry mass [mg/kg-dry]

$\mathrm{m_{Total,wet}}$ is Bulk content reported on a wet mass [mg/kg]

$\mathrm{MC_{dry}}$ is Moisture content of the material [kg-H2O/kg]

SC is Solids content of the material [kg-dry/kg]

If total content of the COPCs in the material, m_{total}, is known from prior knowledge or obtained through a solid phase digestion method (e.g., U.S. EPA Method 3052) or other total elemental analysis (e.g., X-ray fluorescence), then the estimated maximum leaching concentration (C_{leach_max}) may be calculated by adjusting the total content on a mass basis for the initial L/S: [18]

$$\boldsymbol{C_{leach\_max} = m_{total}/(L/S)_{initial}}$$ **Equation 4-3**

where

C_{leach_max}	is the maximum concentration based on total content
m_{total}	is the total content of a COPC [mg/kg-dry]; and
$(L/S)_{initial}$	is the initial L/S [L/kg-dry].

The calculated concentration is assumed to remain constant in all releases over the timeframe relevant to the assessment. Since it is likely that only a fraction of the total content is actually available to leach, use of total content to estimate the maximum leaching concentration should be considered the upper-

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[18] Evaluation of field L/S values (i.e., Cases 5 and 8 in U.S. EPA, 2014c) demonstrated that an effective porewater L/S of 0.5 L/kg-dry is appropriate for coarse landfilled materials subject to percolation and preferential flow, resulting in a multiplier of 20 to adjust the eluate concentrations measured using Method 1313. L/S may be expressed in equivalent units of L/kg-dry that are typically used for the scenario scale or units of mL/g-dry that are typically used in laboratory testing (e.g., 10 L/kg-dry = 10 mL/g-dry).

most bound on possible concentrations. This maximum concentration is likely to overestimate the actual leaching of COPCs by a significant margin (i.e., one or more orders of magnitude). However, if total content data is obtained through either testing or prior knowledge, this initial step in the screening assessment sequence is easy to execute and may focus subsequent assessment effort on only those COPCs that have a potential to leach based on a significant presence in the material.

4.2.4.2 Available Content Screening

Following the stepwise approach, the screening assessment based on total content may be refined to consider only the fraction that is available to leach from the material. As discussed in detail in Section 4.4.1, the eluate concentration associated with available content of a COPC can be determined directly from Method 1313 extractions conducted at endpoint target pH values of 2, 9 and 13. The pH endpoint values of 2 and 13 provide a bounding estimate for the amount of leachable material over a broad pH range.

By test specifications, the available content concentration from Method 1313 data is determined at an L/S of 10 L/kg-dry. However, the concentration used in the screening assessment should be adjusted to the initial L/S by multiplying the maximum eluate concentration ($C_{1313(\max pH\ 2,9,13)}$) by the ratio of the method-specific L/S for Method 1313 [$(L/S)_{1313}$ = 10 L/kg-dry] to the initial L/S, $(L/S)_{initial}$:

$$C_{leach\_max} = C_{1313(\max pH\ 2,9,13)} \times (L/S)_{1313}/(L/S)_{initial} \qquad \textbf{Equation 4-4}$$

Based on a default initial L/S value of 0.5 L/kg-dry, the resulting multiplier for the maximum Method 1313 eluate concentration over the pH domain in the equation is 20 (i.e., 10 L/kg-dry divided by 0.5 L/kg-dry):

$$C_{leach\_max} = C_{1313(\max pH\ 2,9,13)} \times \frac{10}{0.5} = 20 \times C_{1313(\max pH\ 2,9,13)}$$

For cases where available content is known or reported as a mass release [mg/kg-dry] but the underlying concentrations [mg/L] from Method 1313 are not known, the maximum leaching concentration may be estimated in the same manner as for the total content.

$$C_{leach\_max} = m_{avail}/(L/S)_{initial} \qquad \textbf{Equation 4-5}$$

where

m_{avail} is the available content of a COPC [mg/kg-dry]; and

$(L/S)_{initial}$ is the initial L/S [L/kg-dry].

One advantage of using the available content in a screening approach is that it requires only three Method 1313 extractions at endpoint target pH values of 2, 9, and 13; however, the estimate may be overly bounding because it assumes that the entire available content is leached. For COPCs with low solubility in the near-neutral pH range (e.g., lead, cadmium, chromium, etc.), the estimate of C_{leach_max} may be refined further by considering only that leaching that may occur over the applicable pH domain through equilibrium-based screening assessment.

4.2.4.3 Equilibrium-pH Screening

An equilibrium-based leaching evaluation considers the equilibrium-based partitioning of a constituent between a liquid and solid phase, LSP, over a range of applicable scenario conditions (i.e., pH domain and L/S range) as the basis for COPC release. The estimated maximum leaching concentration, C_{leach_max}, is based on the maximum concentration from interpolated values of Method 1313 over the applicable scenario pH domain, $C_{1313(max\ pH\ domain)}$, with consideration for that estimate for available content-limited COPCs to increase as the L/S decreases to the initial L/S value.

As discussed in Section 4.2.5.1, the applicable scenario pH domain is defined as part of the assessment scenario definition based on the default pH range of 5.5 ≤ pH ≤ 9. However, the applicable scenario pH domain may be adapted for specific materials or assessment scenarios. Typically, the definition of a scenario-specific pH domain considers the natural pH of the material, any established pH values imposed by scenario conditions, and any anticipated long-term neutralization effects.[19] Figure 4-4 presents examples of Method 1313 eluate concentrations, interpolated Method 1313 data, and the maximum concentration over the pH domain for cadmium (cation) and selenium (oxyanion) in three materials matrices – a coal combustion fly ash (CaFA), a contaminated field soil (CFS) and a solidified waste form (SWA). Note that the applicable pH domain for the assessment changes from the default 5.5 ≤ pH ≤ 9.0 used for the neutral pH soil to 7 ≤ pH ≤ 13 for the cement-based solidified waste form in order to capture the natural pH of the material and anticipated environmental process (e.g., carbonation) that may occur over time.

Whether a COPC is availability-content limited or solubility-limited can determine whether the LSP leaching concentration is a strong function of L/S (see Section 4.4.5 for determining solubility-limited leaching versus available content-limited leaching). When a COPC is demonstrated to be solubility-limited over the pH domain (e.g., cadmium for all material and selenium for CFS and CaFA in Figure 4-4,), the LSP concentration is a weak function of L/S. Therefore, C_{leach_max} can be assumed bounded by the maximum concentration in Method 1313 testing of the pH domain, $C_{1313\ (max\ pH\ domain}$:

$$C_{leach\_max} = C_{1313(\max \mathrm{pH\ domain})}$$

Equation 4-6

If a COPC exhibits available content-limited leaching over the pH domain (e.g., SWA selenium in Figure 4-4), the maximum concentration measured over the applicable pH domain is likely to be a function of L/S. The estimated maximum leaching concentration, C_{leach_max}, is derived by adjusting the maximum Method 1313 concentration over the pH domain, $C_{1313(max\ pH\ domain)}$, to the initial L/S, $(L/S)_{initial}$, using Equation 4-7:

$$C_{leach\_max} = C_{1313(max\ pH\ domain)} \times (L/S)_{1313}/(L/S)_{initial}$$

Equation 4-7

Using the default value of 0.5 L/kg-dry as the initial L/S, Equation 4-6 becomes:

$$C_{leach\_max} = C_{1313(max\ pH\ domain)} \times \frac{10}{0.5} = 20 \times C_{1313(\max pH\ \mathrm{domain})}$$

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[19] Although the applicable pH domain may be a fraction of the domain covered by Method 1313, it is useful to obtain data from the entire range of endpoint pH target values to provide definition of the available content (Section 4.4.1) and identification of available content-limited and solubility-limited leaching (Section 4.4.5).

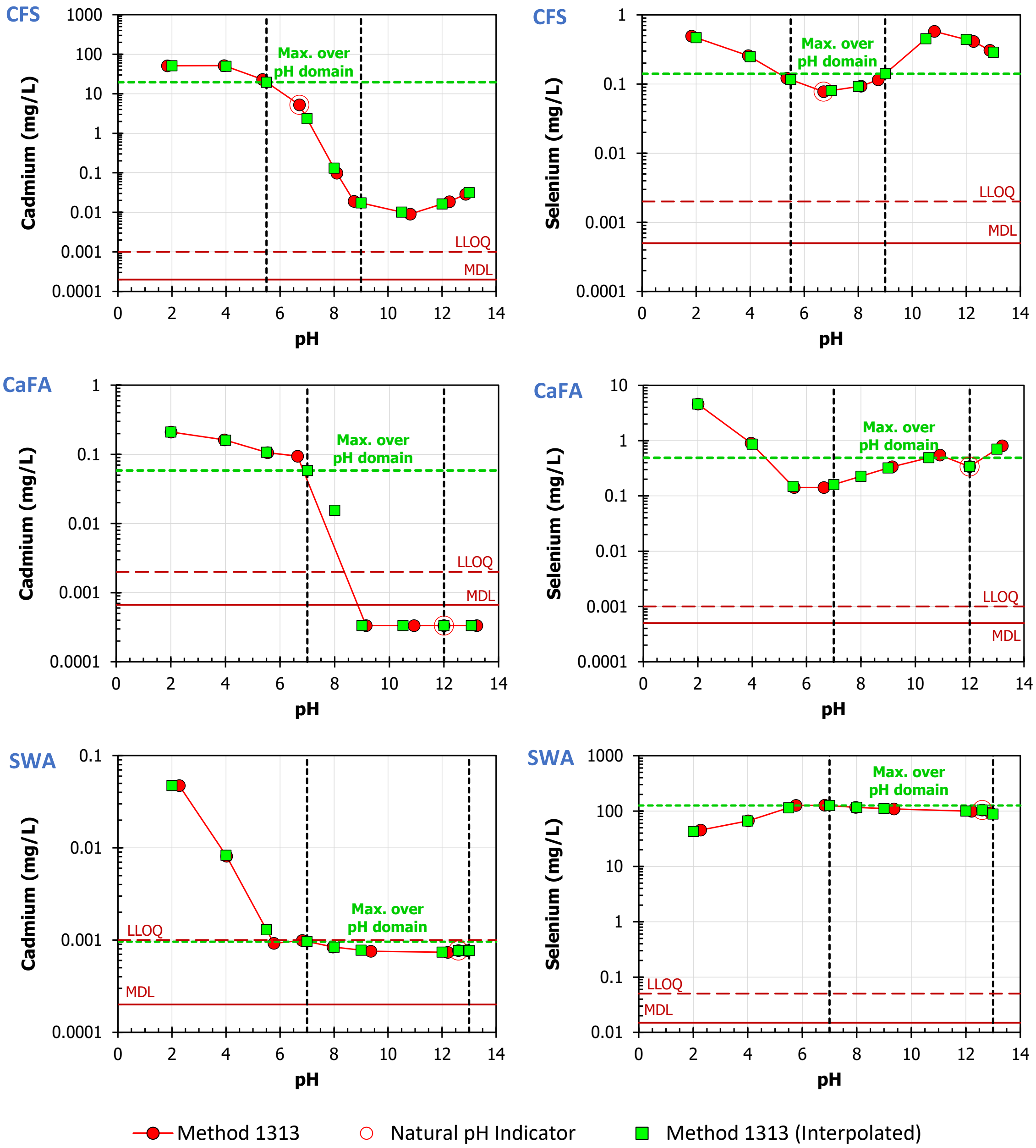

Figure 4-4. Maximum concentration over an applicable scenario pH domain for cadmium (left) and selenium (right) from Method 1313 testing of a coal combustion fly ash (CaFA), a contaminated soils (CFS) and a solidified waste form (SWA).

4.2.4.4 Full Liquid Solid Partitioning (LSP) Screening

In some evaluations, the material and environmental conditions may be uncertain or vary. LSP results from Methods 1313 and L/S results from Method 1314 or Method 1316 can be used to develop an upper estimate under the potential environmental conditions. The LSP screening level assessment builds from the equilibrium-pH assessment in that it assumes that COPCs leach at a maximum concentration associated with the greater of the pH effect over the applicable pH domain, or the L/S-dependent effect on eluate concentration. Although data from Method 1314 or Method 1316 can be used in this evaluation, the data provided by Method 1314 should be considered over that from Method 1316 in low L/S screenings due to the ability of the column test to capture concentrations at very low L/S values (e.g., < 0.5 L/kg-dry) and the nature of the Method 1316 batch test to mask the evolution of competitive dissolution with L/S (see Section 4.4.4).

The estimated maximum leaching concentration in a full LSP screening, C_{leach_max}, is the greater value between the maximum concentration over the applicable pH domain, $C_{1313(max\,pH\,domain)}$, and the maximum concentration over the L/S range, $C_{(L/S)max}$:

$$C_{leach\_max} = MAX\left[C_{1313(max\,pH\,domain)}, C_{(L/S)max}\right] \qquad \textbf{Equation 4-8}$$

Figure 4-5 presents two examples of data leading to full LSP screening. Barium in solidified waste form (SWA) shows a solubility-limited leaching in Method 1313 and a relatively weak influence of L/S in both Method 1314 and Method 1316 data. Thus, the maximum concentration of barium over the applicable scenario pH domain is significantly greater than maximum eluate concentrations from Method 1314 or Method 1316. Conversely, the LSP data for boron in the coal combustion fly ash (EaFA) shows available content-limited leaching and strong influence of L/S. The estimated maximum leaching concentration for boron used in the full LSP screening assessment would be the greatest concentration at low L/S in Method 1314 (or, alternatively, the highest concentration in Method 1316 in the absence of Method 1314 data).

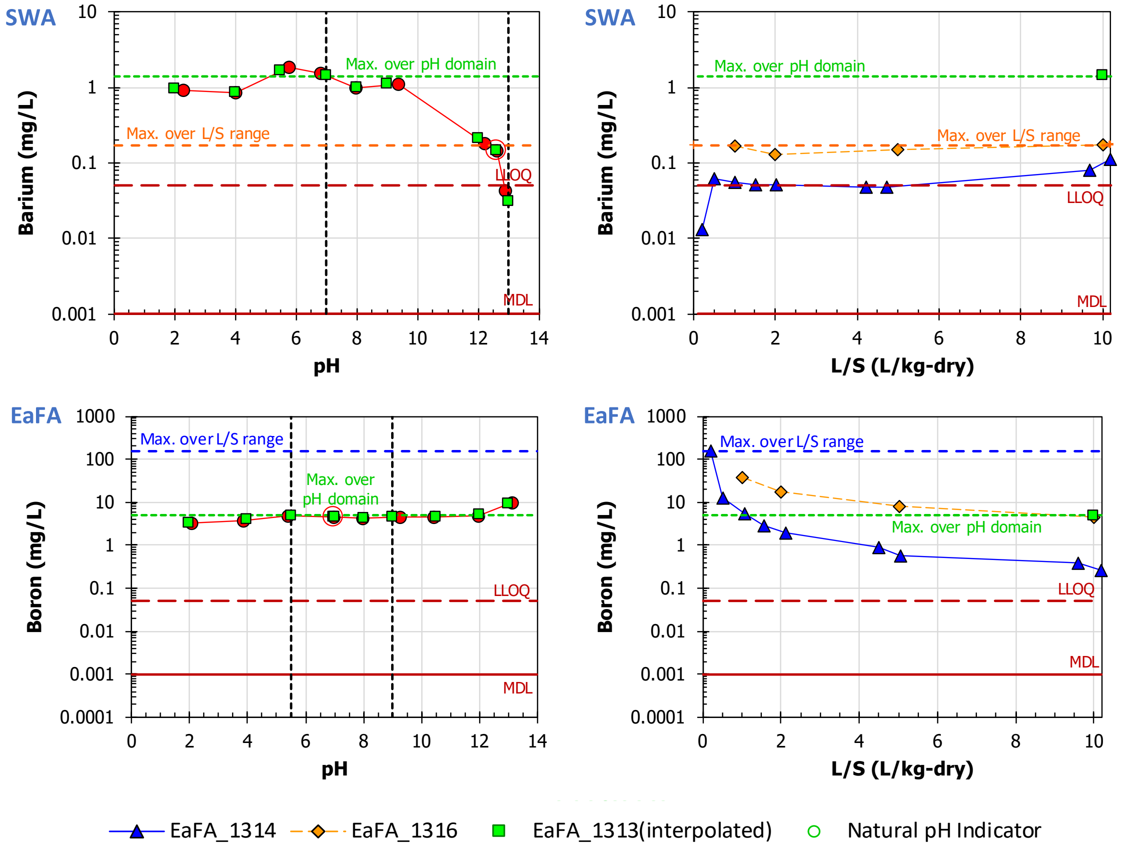

Figure 4-5. Full LSP screening data showing examples where pH effects dominate LSP (barium in solidified waste form, SWA) and where L/S-dependence influences maximum LSP concentration (boron in coal fly ash, EaFA).

4.2.5 Scenario Based Assessments

Screening assessments may provide bounding estimates of leaching in the environment. A scenario assessment may utilize information and testing that provides a more accurate estimate of leaching in the environment. Factors contributing to uncertainty in screening estimates can include use of an assumed "infinite source," reliance on only a limited amount of leaching data, or utilization of default or estimated scenario information. An assessor using LEAF may also have additional information regarding their site or material that can be used in conjunction with data from testing to refine their leaching assessment. These more-refined leaching estimates may be based on parameters derived from site-specific, generic scenario-specific[20] or national assessments of the leaching potential for a material. A site-specific assessment may include representative samples of a specific waste, with defined waste management unit designs, local environmental conditions including metrological and soil data and specific chemical interactions that may occur within the scenario. For a national assessment, LEAF results from numerous samples representative of a waste stream type are used in conjunction with the range of waste management unit designs, national meteorological data, soil types, and other information from numerous units to estimate a national probability distribution of release (U.S. EPA, 2014b). When such a probabilistic source term is used in conjunction with a groundwater fate and transport modeling, exposure pathways and toxicity estimates, a national distribution of risks from disposal or use of the material can be estimated. Similarly, regional assessments would take the same approach with inputs relevant to a region.

For the purposes of determining the applicability of a material for a scenario with respect to leaching performance, the flow chart presented in Figure 4-6 shows that the results from the appropriate LEAF leaching test methods integrate with site- or scenario-specific information to provide an estimated source term under the assumed release conditions. Scenario assessments rely on Method 1313 pH-dependent testing data used in conjunction with time or L/S-dependent data from Methods 1314, 1315 or 1316. The most appropriate method to incorporate with Method 1313 data will depend on the composition of the material, the mode of water contact, and the specifics of the assessment scenario. Method 1315 is best suited for flow-around scenarios where water is diverted around a material that is impermeable relative to the surrounding media. Method 1314 and 1316 are best suited for flow-through scenarios where the hydraulic conductivity of the material is relatively close to that of the surrounding media (within and order-of-magnitude) and water percolates through the material.

A source term developed to represent the estimated COPC release for each chemical of concern in an environmental application is based upon the testing results considered as whole. The development of the source term is dependent upon the testing and a description of the scenario chosen to represent the environmental scenario. Considered together, the results of the testing can be used to identify the bounding estimate of release as constrained by the anticipated effects of the range of pH, L/S, and mass transfer considerations.

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[20] Where a range of materials may be considered for use under a single, bounding application scenario definition.

4.2.5.1 Determining the Applicable pH Domain

Evaluating the effects of pH plays an important role in almost all leaching assessments. In most scenarios, the natural pH of the material, the prevailing pH in the proposed application, and long-term pH shifts associated with material aging or degradation processes should be considered. Inorganic constituents generally exist in aqueous solution as ionic species, the solubility of which is often dependent upon pH. As a result, an evaluation of pH dependence on the available content of a material provides important understanding to almost all leaching evaluations for inorganic constituents (see Section 4.4.1 for details on calculating available content from Method 1313). The applicable pH domain for a management scenario may be based on knowledge of material or scenario characteristics, including those anticipated to evolve over time. Evolving scenario characteristics may include self-acidification (e.g., via oxidation of sulfide reactive phases or biodegradation of organic matter), commingling of the material with more alkaline or acidic materials, and external sources of acidity or alkalinity (e.g., from adjacent materials or the chemistry of contacting water). Examples of environmental conditions, including pH domains and special considerations, for several materials and scenarios are presented in Table 4-3.

Because pH-dependent leaching will be evaluated based on the results of Method 1313, which specifies endpoint target pH values, the applicable pH domain should be based on similar defined pH values. As a default range, the target pH domain[21,22] should include 5.5 ≤ pH ≤ 9.0, but should be expanded as appropriate to include the natural pH of the material. For example:

- For an alkaline coal fly ash with a natural pH of 10, the applicable pH domain would range from pH 5.5 (the lower end of the default domain) to pH 10.5 (the upper end extended to correspond with endpoint target pH values of Method 1313).[23]
- For an acidic coal fly ash with a natural pH of 4.2, the applicable pH domain would range from pH 4.0 (the lower end extended to correspond with the endpoint target pH values of Method 1313) to pH 9.0 (the upper end of the default domain).

The applicable pH range may be further refined (expanded or narrowed) based on material-specific or site-specific scenarios and knowledge of the material's behavior. Changes to the default pH domain should be supported based on anticipated changes in pH at boundary conditions, as a result of materials aging (e.g., carbonation), or potential for acid or alkali influx in context with the acid-base neutralization capacity information from Method 1313. Definition of scenario specific pH domains should be done in consultation with the appropriate regulatory authority.

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[21] Although LEAF is applicable to materials other than CCRs, the CCR risk analysis (U.S EPA 2014b) provides useful information regarding soil pH ranges across the U.S. These results indicate a soil pH distribution of 4.8 (5th percentile), 5.0 (10th percentile), 6.2 (median/50th percentile), 7.8 (90th percentile), and 8.2 (95th percentile). For ease of use with LEAF data at the screening level, a default pH domain should correspond with Method 1313 endpoint target pH values of 2, 4, 5.5, 7, 8, 9, 10.5, 12, and 13. Thus, the default pH domain is recommended as 5.5 ≤ pH ≤ 9.0 with the pH value of 9.0 roughly corresponding to the maximum solubility pH observed for many oxyanions of regulatory concern (e.g., As[V], Cr[VI], Se[VI]).

[22] The SSURGO database contains information about soil as collected by the National Cooperative Soil Survey over the course of a century. The information can be displayed in tables or as maps and is available for most areas in the United States and the Territories, Commonwealths, and Island Nations served by the USDA-NRCS. This database is available online at: https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey

[23] Interpolation of Method 1313 test results within LeachXS™ Lite is currently limited to the target pH values of the test method. Interpolation to user-defined pH values is a capability currently available within the full version of LeachXS™.

Table 4 3. Summary of Observed pH and Redox Conditions for Field Scenarios

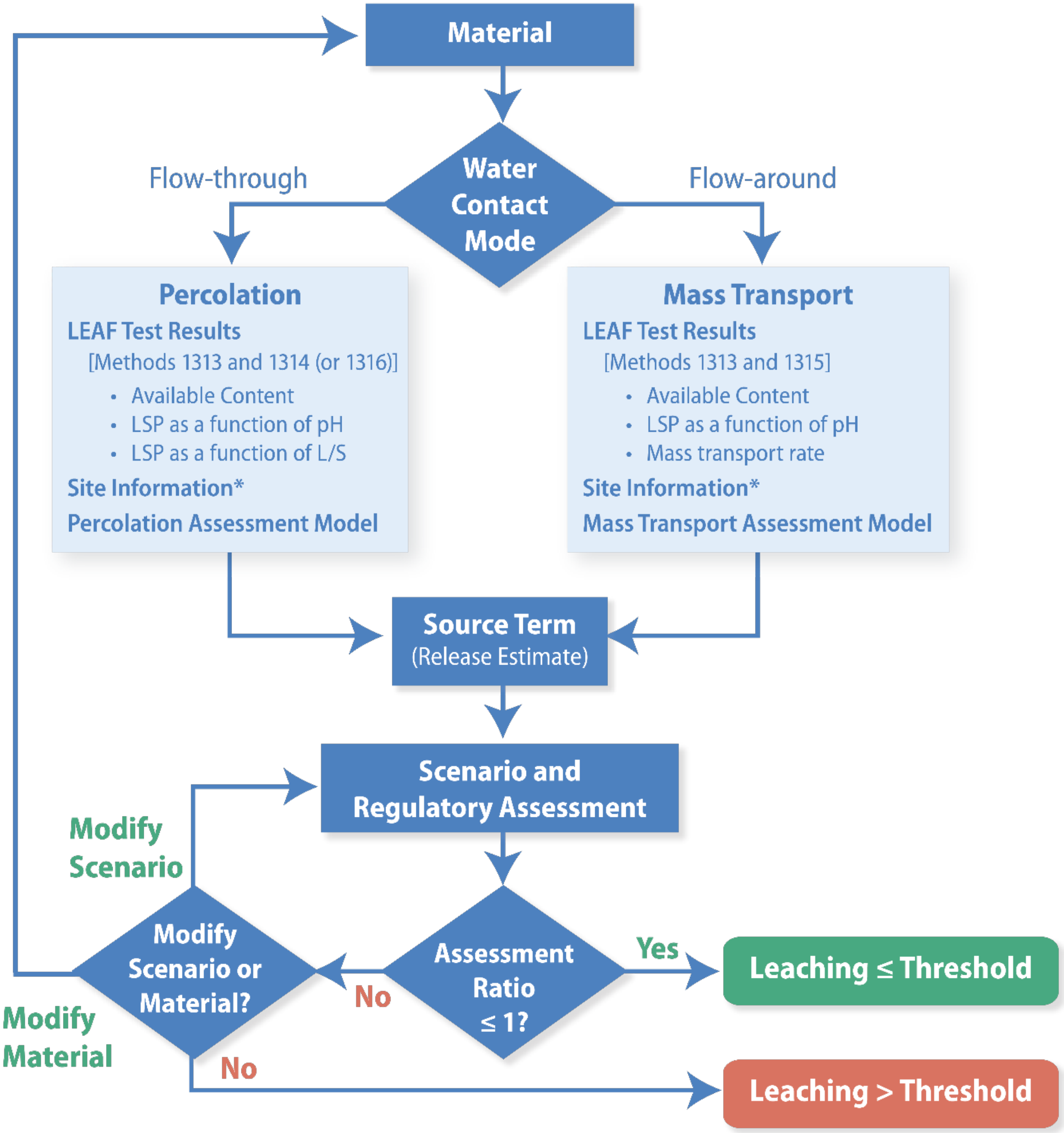
Case Name (Country)	Leachates	pH Domain	Special Conditions
Coal fly ash landfill leachate (U.S.)	multiple, landfills	6-13	oxidizing to reducing
Coal fly ash in large-scale field lysimeters (Denmark)	lysimeters	11-13	oxidizing to reducing
Landfill of coal combustion fixated scrubber sludge with lime (U.S.)	landfill	6-12	oxidizing
Coal fly ash used as roadbase and in embankments (The Netherlands)	road base, embankment	8-12	oxidizing to reducing
Municipal solid waste incinerator (MSWI) incinerator bottom ash landfill (Denmark)	landfill	7-11	reducing
MSWI bottom ash used as roadbase (Sweden)	road base test section	7-10	oxidizing to reducing
Inorganic industrial waste landfill (The Netherlands)	lysimeters, landfill	6-9	oxidizing to reducing
Municipal solid waste landfill (The Netherlands)	landfill, multiple landfills	5-9	strongly reducing, high organic carbon
Stabilized MSWI fly ash disposal (The Netherlands)	pilot test cells, landfill	8-13	oxidizing
Portland cement mortars and concrete (Germany, Norway, and The Netherlands)		8-13	oxidizing, carbonation

Source: U.S. EPA (2014c).

4.2.5.2 Water Contact and Material Placement in the Environment (Scenario Description)

The placement of material in the environment will have a significant influence on the amount of water that contacts the material and the mode through which water contacts the material. Direct contact with groundwater and intermittent rainfall can result in different leaching behavior for constituents. In addition, physical properties such as soil porosity can influence leaching of constituents. Important information that should be defined in a leaching scenario includes a description of how the material will be placed into the environment, the location of the placement relative to the water table (e.g., in the vadose or saturated zone), the physical dimensions of the placement, and the physical characteristics of the material.

Aside from the physical parameters of the placement, the most significant factor for the leaching assessment involves the mode of water contact between the material and infiltrating rainwater or groundwater. Material may be located: (i) above the ground surface where it is exposed directly to rainfall, (ii) in the vadose zone where contact is limited to that fraction of rainwater that infiltrates the subsurface, or (iii) in a saturated environment (e.g., below the water table in the groundwater or surface water sediments). The physical characteristics of a material and the environment (e.g., density, porosity, and hydraulic conductivity) may determine whether the contacting water flows through or flows around the material. When infiltration or groundwater flows through a permeable material at a relatively slow rate, equilibrium controls the extent of leaching in what is termed a "percolation scenario." However, when the flow is fast or predominantly around a material with low hydraulic conductivity or through preferential flow pathways (Kosson et al., 2002), mass transport through the material to the water boundary controls the rate of leaching. The LEAF approach defines the applicable water contact mode as either percolation for materials that are as or more permeable than the surrounding materials or flow-around if the material performs as a monolith because of significantly lower permeability than the surrounding materials. A determination that the water contact mode is percolation based allows for evaluating leaching using Method 1314, while a flow-around scenario may be better represented by Method 1315 results.



* Default values or site-specific information
Figure adapted from Kosson, Garrabrants et al. (2012).

Figure 4-6. Flowchart for using LEAF for leaching assessments based on water contact.

4.2.5.3 Percolation Scenarios (Permeable Materials)

For management scenarios where water contact is primarily through percolation, Method 1314 results can be used directly as an estimate of field leaching as a function of the L/S for the management scenario. In some cases, Method 1316 results can also be used to understand time-dependent releases. In a percolation scenario, an evaluator may be using knowledge of water infiltration rates or management timescales to determine relevant L/S for the scenario. However, studies comparing laboratory results to field leachates indicate that actual field leachate may have significantly lower COPC concentrations because of preferential flow pathways. These studies suggest that leaching may be over-predicted by direct leaching test results by an order of magnitude for available content-limited COPCs for many assessment scenarios (U.S. EPA, 2014c). Solubility limited constituents may have less dependence on preferential flow and will be less often over-predicted due to preferential flow as a result. In some cases fate and transport models may be used to examine sensitivity to scenarios beyond laboratory testing conditions (Dijkstra, Meeussen, van der Sloot, & Comans, 2008; Meima & Comans, 1998).

Materials that could be encountered in percolation scenarios include granular material used as structural fill or landfilled. These types of materials have a larger surface area that is exposed to water that can result in equilibrium conditions being reached more quickly. Methods 1314 and 1316 provide data on leachate concentrations at or near equilibrium as a function of cumulative L/S. The lower L/S provide measurements of pore water concentrations. These empirical measurements can reflect instances where only a fraction of COPC mass is limited by available content and instances where solubility limits are reached before the lowest L/S, which may result in lower concentrations than predicted based on adjusting Method 1313 data. Conversely, these methods can capture shifts in the pH at low L/S due to the quick washout of highly soluble ions. This pH shift might result in higher early leachate concentrations than predicted based on the final fixed pH used in Method 1313. Thus, Methods 1314 and 1316 concentrations may provide a more realistic source term without additional adjustment.

4.2.5.4 Mass Transport Limited Leaching Scenarios (Impermeable Materials)

When the water contact is primarily from flow-around a relatively impermeable fill or monolithic material, the Fickian diffusion model (Crank, 1975) is commonly used to estimate mass transport of COPCs. Fickian diffusion assumes that a constituent is initially present throughout the material at a uniform concentration and that mass transfer takes place in response to concentration gradients in the pore water solution of the porous material. The Fickian diffusion model is most appropriate for release scenarios for which highly soluble species are a concern or for which external stresses do not induce sharp internal chemical gradients (e.g., pH gradients, carbonation, and redox changes) that significantly influence local LSP within the material (U.S. EPA, 2014c). The amount of water contacting the material also will impact the amount of a COPC released under a diffusion-controlled scenario.

The mass transport source term for the scenario-based assessment can be bounding because the amount of a COPC released can be several orders of magnitude less than would be estimated using an infinite bath assumption in field scenarios when (i) the material is subject to intermittent wetting due to periodic infiltration (Section 4.4.6), (ii) a portion of the material surface area is obscured from contacting water due engineering controls or placement in the environment, and (iii) where the amount of water contacting the material is limited and LSP at a limited L/S controls leaching.

See Section 4.4.6 for more information on understanding and evaluating mass transport parameters. Examples of use of empirical mass transport results from Method 1315 as part of scenario assessments are provided in Section 5.2 (See also U.S. EPA, 2014, Appendix C). Mass transport testing results also may be incorporated in more detailed reactive transport scenario modeling that integrates geochemical speciation with diffusion-controlled release.

4.3 Accounting for Environmental Processes That Can Influence Leaching

When defining assessment scenarios, both environmental conditions and the presence of important environmental processes should be considered. Environmental factors can alter leachability by changing the chemistry of the material, the concentration of COPCs at equilibrium or the rate of mass transport. The LEAF leaching tests are designed such that the data reflects the response to one or more of these factors under controlled laboratory conditions. However, it is important to acknowledge that these factors do not remain constant in the field as both the environmental media and the solid material under consideration will change over time. Within the normal range of values, some factors (e.g., temperature) are unlikely to have a significant effect on leachability whereas slight changes in other factors (e.g., pH) can have substantial effects on leaching.

Environmental processes may also need to be considered because of their capability to alter leaching under field conditions from those observed in laboratory testing. The effect of some processes may be observable from careful evaluation of testing results (e.g., As-Ca interactions) or by conditioning test materials prior to testing (e.g., carbonated vs non-carbonated materials). Other processes (e.g., evolving redox conditions) may be best evaluated through geochemical speciation modeling of leaching behavior.

Examples of key phenomena that can influence leaching include:

- Chemical, physical, and biological reactions that may occur on or within the material, including the change in redox, production of carbon dioxide, organic acids or other products of biodegradation that may change pH or liquid-solid partitioning of some constituents;
- External stresses (e.g., acids, carbon dioxide, dissolved organic matter) from the surrounding liquid or gas phases that can change the scenario pH or the sorption capacity of the material;
- Physical degradation of the solid matrix due to erosion or stress-related cracking (e.g., freeze/thaw or precipitation reactions);
- Preferential flow through a material that can “short-circuit” the percolation pathway resulting in leaching concentrations less than estimated by equilibrium-based leaching tests;
- Loss of primary matrix constituents due to the leaching process itself (e.g., calcium, sulfate, hydroxide, chloride); and
- Changes in the chemistry of the surrounding media (e.g., abiotic, or biotic oxidation/reduction reactions, and dissolution of atmospheric or biogenic carbon dioxide).

The factors that affect leachability do not act independently of each other and often multiple factors can result in releases that are synergistically different than would be predicted for each factor. However, validation of the LEAF approach to field-collected and monitored cases (U.S. EPA, 2014c) indicate that combined effects either are captured by the test data or can be considered through fate and transport modeling. In addition, the effects of varying a particular factor will differ for each inorganic constituent. As a result, understanding how the variability of the different chemical and physical factors (e.g., pH, redox, dissolved organic carbon) can affect the leachability of each constituent of concern is key to understanding how the material will behave from a leaching perspective in an application scenario. Insights to these affects can be gained both through LEAF testing and geochemical speciation modeling (U.S EPA 2014c; van der Sloot et al, 2017).

4.3.1 Reducing and Oxidizing Conditions

An assessment scenario should consider the potential for the leaching behavior of COPCs to change due to anticipated changes in reducing or oxidizing conditions of the management scenario. These changes may be relevant if the assessment material contains redox-sensitive constituents that can leach more readily under reducing conditions and whether there is a possibility of oxidizing or reducing conditions under the planned management scenario. As a consequence of exposure during treatment or placement in a management scenario, changes in the redox state of a waste or secondary material can affect the speciation, solubility, and partitioning of multivalent constituents (e.g., Fe, As, Cr). For example, oxidizing conditions prevail widely in the near-surface environment due to contact with ambient oxygen; however, biological activity can deplete sources of oxygen over time, resulting in anoxic and reducing conditions. Biological activity is nearly ubiquitous at near neutral pH ($5.0 \leq pH \leq 8.5$), especially in the presence of microbial substrates such as organic carbon. Thus, a material initially managed under oxidized conditions may become reduced as is the case for some fill scenarios, municipal solid waste landfills or sediments (U.S. EPA, 2014c). The formation of reducing conditions during use or disposal may have adverse consequences with respect to leaching through the following mechanisms:

- Reduction of iron (hydr)oxides, Fe(III), which can result in increased dissolution of iron as Fe(II) and loss of sorption surfaces responsible for COPC retention (Ghosh, Mukiibi, & Ela, 2004);
- Direct reduction of multivalent species (e.g., arsenic, chromium, selenium, and molybdenum) that can change the solubility and sorption characteristics of COPCs; and
- Increased dissolution of organic matter that increase dissolved concentrations of some COPCs (e.g., lead and copper) through formation of soluble complexes with DOC.

For example, the effect of reducing conditions on arsenic is especially significant due to the conversion of As(V) to As(III) under moderately reducing conditions which may increase the total solubility of As and decrease As sorption (Dixit & Hering, 2003; Masscheleyn, Delaune, & Patrick Jr., 1991; Schwartz et al., 2016; Smedley & Kinniburgh, 2002; Vaca-Escobar, Villalobos, & Ceniceros-Gomez, 2012). However, strongly reducing conditions can result in the formation of sulfides, which can reduce the solubility of arsenic and other elements. Similarly, molybdenum and manganese exhibit increased partitioning to the aqueous phase under reducing conditions, while other COPCs exhibit decreased leaching under reducing conditions. For example, the partitioning of chromium to the aqueous phase typically is decreased under reducing conditions because of stronger adsorption and decreased solubility of Cr(III) compared to Cr(VI) at neutral pH conditions. Often, the presence of dissolved iron is an indicator of the formation or presence of reducing conditions.

Reducing conditions may be caused by commingling with other materials that are reducing such as slags or some mining wastes or the presence of significant amounts of biodegradable organic matter and barriers to exchange of atmospheric oxygen. In general, laboratory tests are always conducted under oxidizing conditions unless special precautions are taken (e.g., environmental chambers, anoxic gloveboxes). Examples of materials that are moderately oxidized include combustion residues and low-organic-content soils.[24] Oxidizing conditions for initially reduced material can be caused by exposure to air and oxygenated water (i.e., infiltration). However, materials with high reducing capacities or high levels of degradable organic matter may remain or become reducing during testing (e.g., Method 1314) or under field conditions, even if initially oxidized or oxidized only at the surface. Materials that are initially reduced, or may generate reducing conditions, typically are slags (e.g., blast furnace slag), mining wastes, and high-organic-matter soils, compost, sewage sludge and sediments. The most common reducing constituents in waste are organic matter, reduced sulfur species (e.g., sulfides), and reduced Fe(II) species. In addition, reduced tin is also often used as a reducing agent in industrially produced materials (e.g., some cements).

Systems may become more oxidized resulting from reaction with atmospheric oxygen. These processes may result in the precipitation of reduced species (the reverse of reducing conditions) or increased solubility of some species (e.g., conversion of relatively insoluble Cr(III) to relatively soluble Cr(VI), i.e., formation of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) anions. Oxidation of sulfides (e.g., pyrites [FeS_2]) may result in the release of sulfuric acid.

Within the LEAF testing methods, redox conditions are inferred by measurement of ORP in the test eluate. Depending on the natural pH of the material, ORP of Method 1313 eluates may be moderately oxidizing or reducing at mildly acidic to alkaline pH conditions. Unless the material has a high reducing capacity, oxidizing conditions tend to prevail at strongly acidic pH values because of the use of oxidizing nitric acid in the test method, along with oxygen exposure during sampling, handling, and testing. In addition, the presence of iron in solution at pH values above 5 is usually an indicator of reducing conditions because of the presence of Fe(II) which is more soluble than Fe(III) at those pH conditions. In Method 1314, oxidizing conditions usually prevail unless significant organic carbon and a near-neutral pH is present in the material being tested, in which case, reducing conditions can occur during the test. Again, the formation of reducing conditions is typically indicated by the increased leaching of iron. Establishment of reducing conditions during Method 1314 testing of some materials (e.g., compost-amended soils) has been observed at or after cumulative L/S of 5 mL/g-dry. For sensitive COPCs or environments, evaluation of material characteristics and potential changes in redox conditions is critical. Redox potential (Eh), sometimes referred to as “oxidation-reduction potential” (ORP), measured in solution using units of mV can be viewed as an electrical potential of the pool of the available free electrons (pE):

$$\boldsymbol{pE = -\log[e^-] = Eh \times F/(2.3 \times R \times T)} \qquad \textbf{Equation 4-9}$$

where

Eh is the redox potential (mV),

F is Faraday’s Constant [96.42 kJ/(V eq)],

R is the Universal Gas Constant (8.31 J/(K mol)], and

T is temperature (K).

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[24] The case studies (Section 5) are limited to oxic or oxidizing scenario conditions. Oxidizing conditions usually result in the highest extent of leaching for most COPCs. However, notable exceptions include mobilization of precipitated iron Fe(III) through reductive conversion to Fe(II), increased leaching of species (e.g., arsenic) adsorbed to dissolved hydrous iron oxides, soluble complexes for cations with dissolved organic carbon (e.g., humic, fulvic, or fatty acids), and methylation of mercury under reducing conditions that results in more toxic Hg speciation.

The equilibrium constant for redox-sensitive COPCs, K, may be expressed in terms of the concentrations of reduced species, oxidized species, H$^+$ and e$^-$ in the system:

$$K = \frac{[reduced\ species]}{[oxidized\ species] \times [e^-] \times [H^+]} \qquad \textbf{Equation 4-10}$$

Or rearranging,

$$\log K = \log[red] - \log[ox] - \log[e^-] - \log[H^+] = pH + pE \qquad \textbf{Equation 4-11}$$

Thus, the relative value of (pH + pE) represents the tendency for oxidized species at higher values (oxidizing conditions) and reduced species at lesser values (reducing conditions). The reduction potentials of redox half reactions can be compared to the pE of the system to anticipate whether constituents may oxidize or reduce. Test results may also not reflect environmental conditions if the redox capability of the leachate does not reflect the redox capabilities of the environment. Additionally, redox reactions can occur over longer timeframes than bench testing allows for. When reduction or oxidation of COPCs to more mobile forms is anticipated, the estimated environmental impact may require geochemical speciation modeling or other considerations. In some cases, oxidizing atmospheres in the laboratory may underestimate reducing conditions encountered in the field, especially when field conditions do not allow for infiltration of the atmosphere. The translation of redox behavior from the lab to the field can be seen in the case studies EPA previously evaluated (U.S. EPA, 2014c).

The concentration of iron in solution as a function of pH is often a useful indicator of the redox state of a system. Typically, iron is present as Fe(III) under oxidizing conditions (pH + pE) > 15 and is insoluble at pH > 4, with solubility increasing with decreasing pH. With progressively more reducing conditions, indicated by progressively decreasing (pH + pE) and resulting in fractional conversion of Fe^{3+} to Fe^{2+}, the transition from insoluble iron to higher iron solubility occurs at greater pH values. The data in Figure 4-7 depicts iron leaching as a function of pH from municipal solid waste (MSW) as pH-dependent and column leaching test results. The various lines in the figures show the simulated LSP of iron under different redox conditions using geochemical speciation modeling (Figure 4.69, U.S. EPA, 2014c, van der Sloot, et al., 2017). Shown at L/S 10 mL/g-dry of the pH=dependent leaching test and L/S 0.3 mL/g-dry as the lowest L/S in the column test, the values of (pH + pE) range from (pH + pE) = 13 indicating oxidizing to mildly reducing conditions to (pH + pE) = 4 indicating strongly reducing conditions. In the pH region anticipated for field applications (pH ≥ 6), the test data from MSW leachate appear to correspond with (pH + pE) values between 4 and 6, indicating strongly reducing conditions (van der Sloot et al, 2017). .

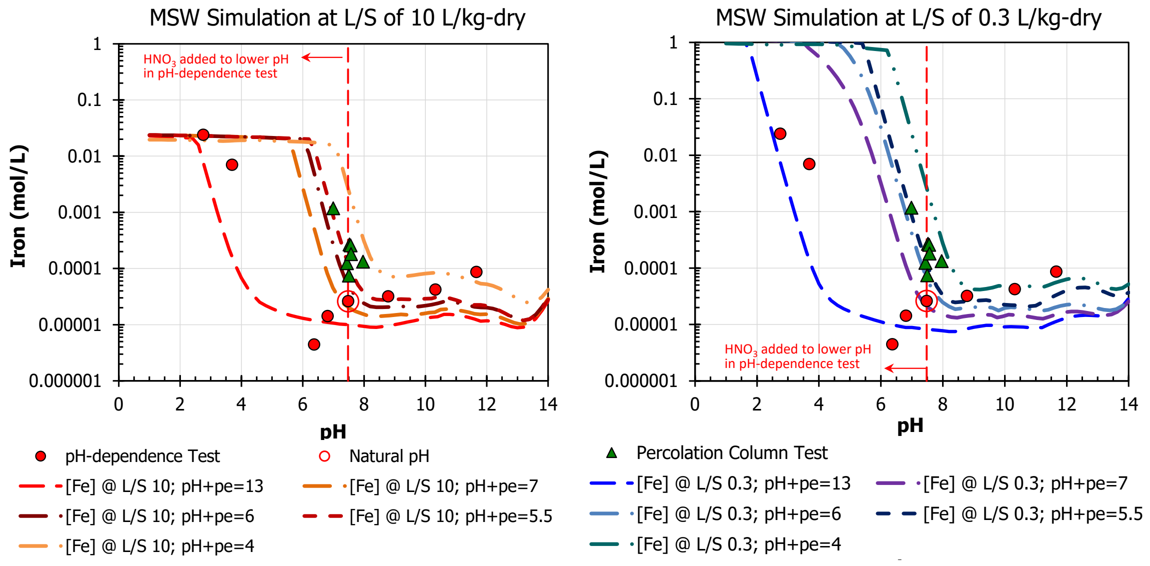


Figure 4-7. Comparison of geochemical simulation of iron leaching at various pH/redox conditions (pH + pE) to laboratory test results for mixed municipal solid waste (MSW) landfill material.

4.3.2 Carbonation of Alkaline Materials

Alkaline materials, especially those primarily composed of calcium hydroxide and calcium-aluminum-silicate minerals (e.g., lime and cement-based materials), are likely to react with carbon dioxide when placed in the environment. The results of the carbonation reaction include reduction of the alkalinity of the system (i.e., neutralization) and precipitation of relatively insoluble carbonate minerals within the pore structure of the material. Neutralization of the natural pH from pH > 10 to pH < 9 may concurrently alter the chemical speciation of COPCs [e.g., lead from soluble $Pb(OH)_4^{-2}$ may precipitate as insoluble $PbCO_3$ or result in Pb sorption to hydrated iron oxide], changes in the mineral distribution (e.g., dissolution of ettringite) or shifts in the COPC leaching concentration along the LSP curve. Exposure to carbon dioxide can result from near surface applications where the material is exposed to relatively moderate concentrations of atmospheric carbon dioxide or from exposure to elevated carbon dioxide in subsurface scenarios due to microbial respiration. Dissolved carbonates can also compete with other oxyanions for adsorption to reactive surfaces, e.g., iron (hydr)oxides, and, therefore, increase the leaching concentrations of oxyanions such as arsenates, chromates, molybdates and selenates.

4.3.3 Microbial Activity

When placed in the environment, the redox conditions of some systems may become more reducing due to microbial respiration processes that consume available oxygen, nitrate, metal oxides, sulfate, and carbonate (electron acceptors). These processes are most prevalent and important at pH between 5 and 9 and when significant concentrations of organic carbon are present as substrate (electron donors). As discussed above, reducing conditions can result in decreased leaching through formation of precipitates (e.g., sulfides) or can increase leaching through the formation of more soluble reduced species (e.g., copper, molybdenum, vanadium).

4.3.4 Complexation with Dissolved Organic Matter

Dissolved organic matter in the form of humic, fulvic or other analogous polar species as well as organic acids complex with many dissolved multivalent cations (e.g., Pb, Cu, Mn, Cr(III)), resulting in increased apparent solubility because of the presence of both uncomplexed and complexed ions in solution. The solubility of dissolved organic matter often is a strong function of pH because of protonation/deprotonation of ionic moieties and alkaline hydrolysis of more complex organic matter. In addition, organic acids are often formed because of microbial activity.

4.3.5 Co-precipitation of Arsenic with Calcium

Since a COPC may be incorporated into or sorbed onto solid mineral phases, the observed leaching behavior of a COPC in LEAF tests may be strongly influenced by the release of other constituents. In U.S. EPA (2014c), a significant increase in arsenic concentration was observed in the latter stages of the column test due to co-precipitation with calcium minerals. Figure 4-8 shows Method 1314 results for pH, calcium release and arsenic release from a low calcium fly ash (Sample ID: EaFA). Method 1313 results for each are shown on the right side of the figure. The graph in the top left shows that the eluate pH released from the column increases from an initial pH of 4.2 to a near-neutral pH by an L/S value of approximately 2 L/kg_{dry}. The titration curve to right indicates that only a small amount of acid needs be released to result in this pH increase. At an L/S of 2 L/kg_{dry}, the cumulative release of calcium has reached a plateau; however, since the LSP of calcium is not a strong function of pH between 4.2 and 7.1, the plateau in the calcium cumulative release curve must be a result of calcium depletion. The cumulative release of arsenic remains relatively low until calcium is depleted (i.e. the point at which cumulative calcium plateaus), beyond which arsenic increases significantly. Geochemical speciation modeling confirmed that arsenic is co-precipitated with calcium.

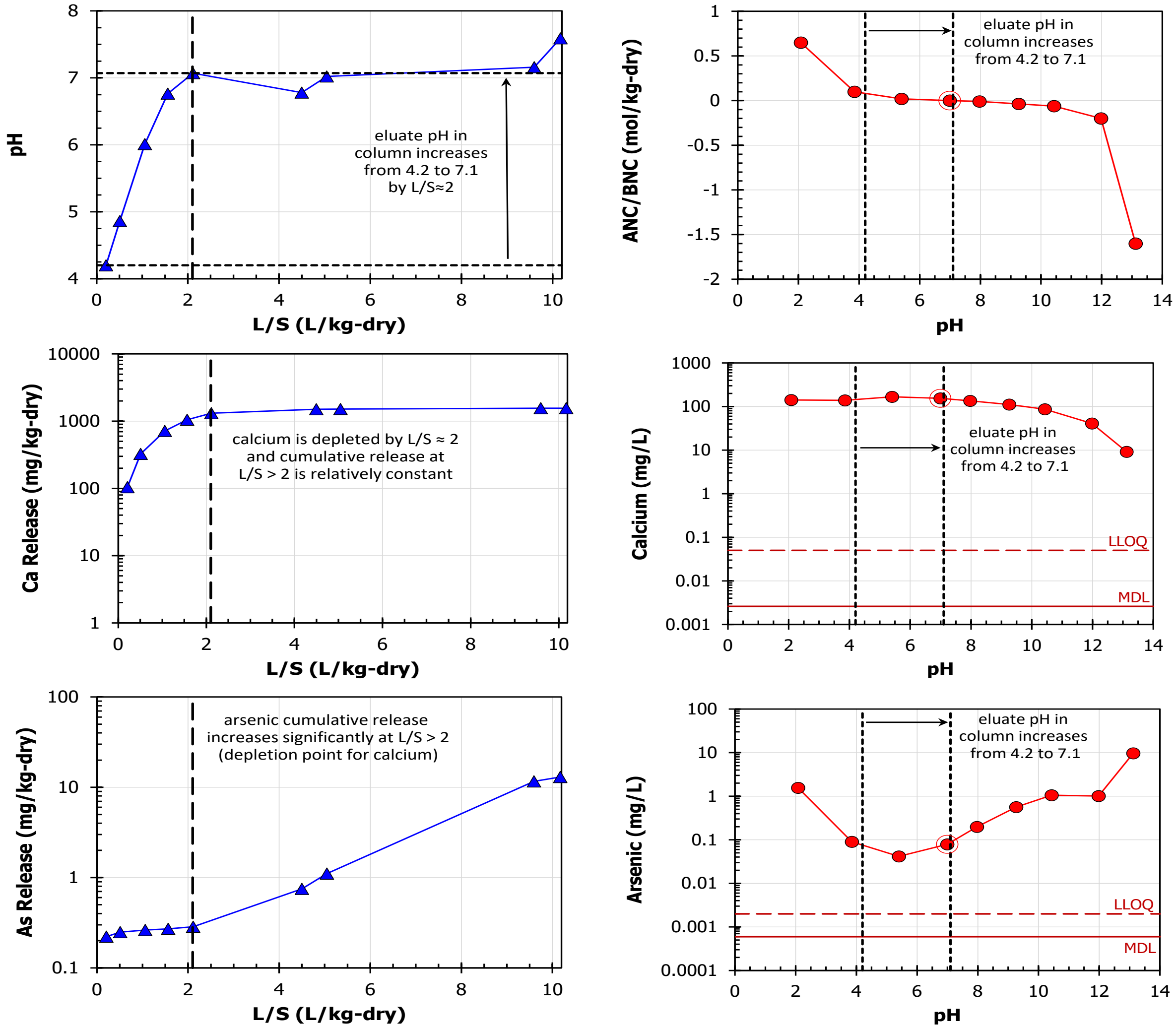


Figure 4-8. Method 1314 (left) and Method 1313 (right) for eluate pH, calcium, and arsenic.

4.3.6 Chemical Interactions

The observed leaching concentrations of specific COPCs can be a result of complex interactions, prompted, suppressed or enhanced by pH and the leaching of other constituents. For example, in the presence of calcium-bearing minerals, arsenic leaching may be minimal; however, leaching of arsenic may increase sharply when calcium concentrations decrease below approximately 100 mg/L because of the decrease in precipitation of calcium arsenate.

Figure 4-9 shows a comparison of LSP (interpolated from test data) and percolation column data for two coal combustion fly ash materials - a calcium-rich ash, CaFA, shown in red and a calcium-poor ash, EaFA, shown in gold. Panels A-H show the titration and pH behavior as well as the leaching data for calcium, arsenic and chromium. The column test data for calcium (Panel D) illustrates the depletion of calcium for EaFA prior to an L/S of 5 L/kg-dry (gold vertical line) that is not evident in the higher calcium CaFA ash. Panel F shows a corresponding increase in arsenic leaching from EaFA starting at approximately L/S 4.5 L/kg-dry, concurrent with the depletion of calcium. In CaFA, however, the leaching of arsenic remains unchanged consistent with calcium concentrations above 100 mg/L. The leaching of chromium (Panel H) may appear at first to be similar to arsenic (i.e., the shape of the column eluate data for EaFA is similar for chromium and arsenic). However, comparison of chromium pH-dependent behavior (Panel G) with column concentrations (Panel H) shows that the increase in chromium between L/S 4.5 and 10 L/kg-dry are a consequence of the change in chromium leaching as a function of pH. Note that the initial eluate pH in the EaFA column is approximately pH 4 increasing rapidly to a pH of 7 by L/S 2 L/kg-dry (Panel B), while chromium LSP goes through a minimum leaching concentration at pH 5.5 (Panel G). The observed pH shift in the column data for EaFA is a consequence of an acidic coating on the fly ash due to sulfuric acid spray injection. This analysis illustrates the importance of evaluating pH-dependent leaching test results (Method 1313) in conjunction with percolation column leaching test results (Method 1314) to provide an improved understanding of complex leaching behavior.

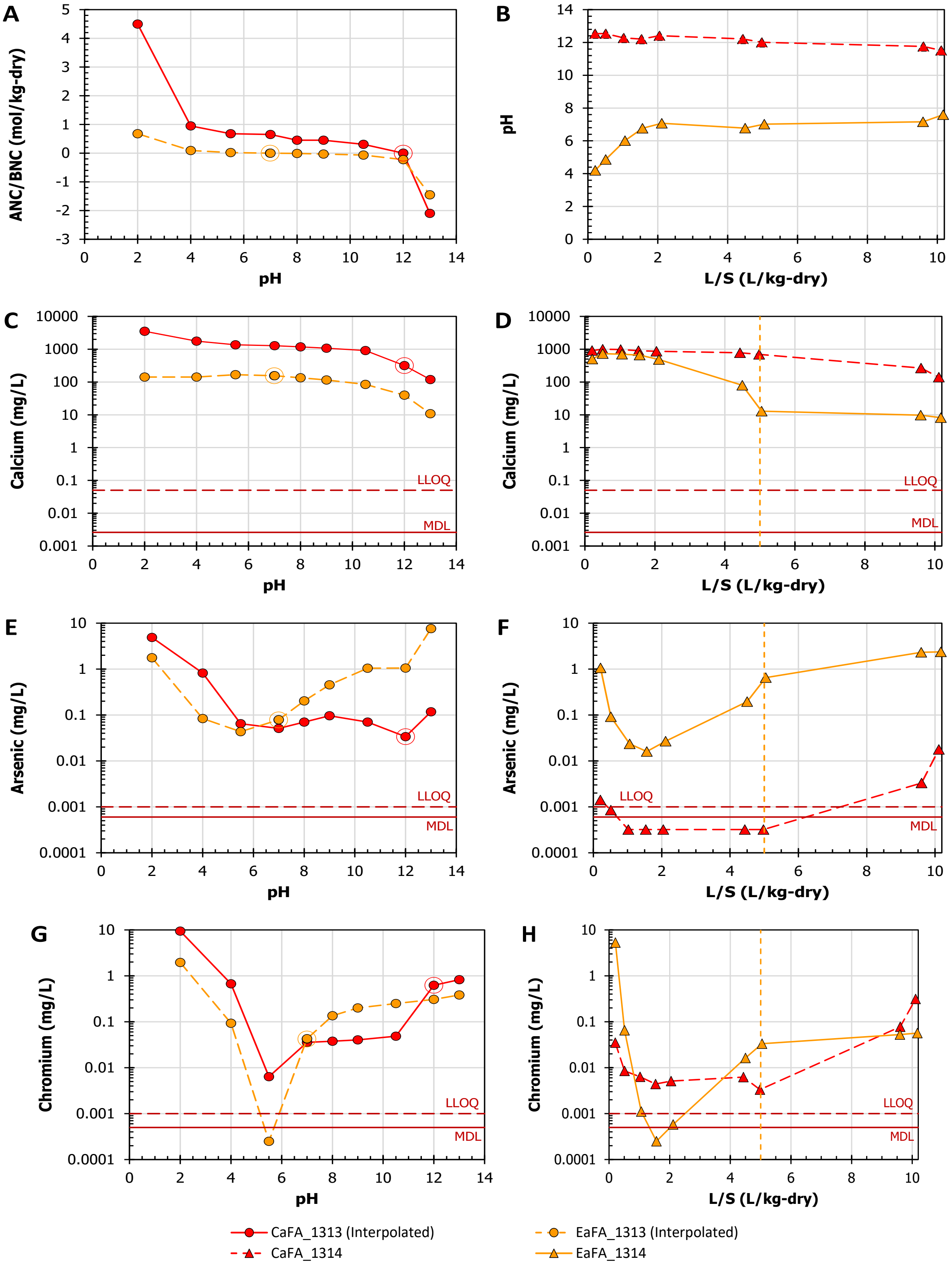


Figure 4-9. Comparison of Method 1313 and Method 1316 for calcium, arsenic and chromium leaching from low-calcium fly ash (EaFA) and high-calcium fly ash (CaFA).

4.4 Performing Common Analyses in Leaching Assessments

4.4.1 Determining the Available Content from Method 1313 Data

Within the LEAF approach, the available content is defined as the fraction of the total content that has the potential to leach under typical environmental conditions. The available content is determined as the mass release in mg/kg-dry associated with the maximum leaching concentration from Method 1313 conducted at endpoint target pH values of 2, 9, and 13:

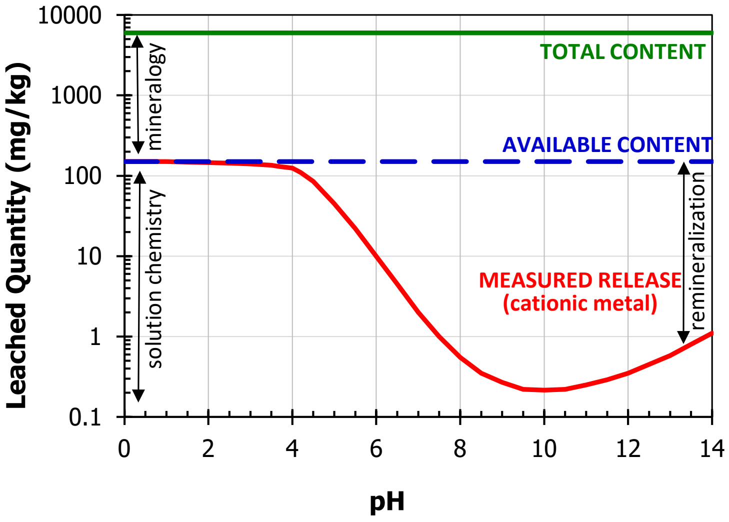
$$m_{avail} = C_{max(pH\ 2,9,13)} \times (L/S)_{1313} \qquad \textbf{Equation 4-12}$$

where

m_{avail}	is the available content on a dry mass basis [mg/kg-dry];
$C_{max(pH\ 2,9,13)}$	is the maximum eluate concentration [mg/L] at the endpoint target pH values of 2, 9, and 13, and;
$(L/S)_{1313}$	is the liquid-to-solid ratio of the Method 1313 eluate (i.e., 10 L/kg-dry).

The relationship between total and available content relative to Method 1313 data is presented Figure 4-10. The figure presents the pH-dependent cumulative mass release of a cationic metal (red solid line) in comparison to total content (green solid line) and available content (blue dashed line). The total content is a single mass release value in mg/kg-dry derived from total analysis of the solid material (e.g., from digestion techniques or non-destructive methods). The total content is comprised of a fraction that is available for leaching and a fraction that is bound within the mineralogy of the solid material. The available fraction of the total content is both constituent-dependent (i.e., boron and lead will have different fractions that are available within a material) and material-dependent (i.e., lead may be primarily leachable in one material and recalcitrant to leaching in another). Retention is based on the specific structure of material solid phases (e.g., mineralogy, amorphous/glassy phases) and the potential substitutions of COPCs within those solid phases. For example, some mineral forms such as quartz are very stable so that COPCs bound within silicate are not likely to leach. Conversely, hydroxides tend to be more soluble under environmental pH conditions and COPCs that precipitate as hydroxides are released when the hydroxide minerals dissolve. As a practical matter, for the timeframes of interest for waste disposal/use, the fraction of COPCs bound in these stable mineral forms and amorphous phases is unlikely to be available for leaching (U.S. EPA, 2014c). As the pH changes (i.e., following the LSP curve), remineralization results in COPCs present in various solid phases being released or retained depending on the solubility values of individual minerals, sorption characteristics of the solid phases and solution chemistry.

Determination of available content based on the maximum concentration at end-point eluate pH values of 2, 9 and 13 is a practical approach because solubility of specific elements is at a maximum at one of these pH conditions over the Method 1313 test, and therefore release is available-content limited for most materials. The lowest pH value, pH=2, also results in dissolution of COPCs sorbed to iron (hydr)oxide surfaces and clays.



Adapted from Heasman et al. (1997).

Figure 4-10. Relationship between total content, available content and measured pH-dependent release for a cationic metal.

The reported values for available content using Method 1313 in some cases may be greater than the reported total content because of uncertainties in the testing methodologies. These uncertainties include: (i) inherent analytical uncertainty associated with both total content and leaching test chemical analysis, especially at low extract concentrations, (ii) reliance on very small material quantities used in total content analyses that may not be representative of the material as a whole, (iii) partial digestion techniques for total content analysis where recalcitrant minerals (e.g., silicates) are not fully dissolved, and (iv) analytical dilution of total content digestions from a concentrated but near-dry state to a volume sufficient for chemical analysis.

Figure 4-11 shows the Method 1313 data for cadmium, boron, molybdenum in each of three materials including a contaminated smelter site soil (CFS; left), a coal combustion fly ash (EaFA; middle) and a solidified waste form (SWA; right). Vertical lines in each graph indicate the endpoint target pH values of 2 (blue), 9 (red) and 13 (green) where the maximum concentration values would be expected for various pH-dependent behaviors. Numerical values for measured concentrations as well as the available content calculated at the endpoint target pH values are provided in Table 4-4, along with additional COPCs for comparison. Note that the actual measured concentration for the eluate is used for the calculation of available content, not the concentration interpolated to the target pH value. In all materials, the maximum concentration of cadmium occurs at a pH of approximately 2, which is consistent with cationic pH-dependence. For boron, the pH-dependent leaching is not a strong function of pH and the maximum concentration occurs at a pH near 2 for CFS and SWA, but at an alkaline pH for EaFA. The maximum concentration of molybdenum occurs at near pH 9 (SWA) or near 13 (CFS, EaFA). Note that the graphs in Figure 4-11 show essentially constant concentration at or near the available content for molybdenum (EaFA, SWA) and boron (EaFA) at pH ≥ 9.

Table 4-3. Comparison of Method 1313 Eluate Concentrations at pH 2, 9, 13 and Reported Available Content: Contaminated smelter site soil (CFS), coal combustion fly ash (EaFA) and solidified waste form (SWA).

COPC	Material	Conc. at pH 2 Target [mg/L]	Conc. at pH 9 Target [mg/L]	Conc. at pH 13 Target [mg/L]	Available Content [mg/kg-dry]	Max. Conc. at pH
Arsenic	CFS	**85**	0.042	0.23	850	1.9
	EaFA	1.6	0.56	**9.7**	970	13.1
	SWA	5.8	0.48	**16**	160	12.6
Boron	CFS	**0.72**	0.12	0.056	7.2	1.9
	EaFA	3.3	4.5	**5.0**	50	12.0*
	SWA	**5.8**	1.9	0.78	58	2.5
Cadmium	CFS	**47**	0.006	0.009	470	1.9
	EaFA	**0.066**	0.015	0.015	0.66	2.1
	SWA	**0.029**	< 0.002	< 0.002	0.29	2.5
Molybdenum	CFS	0.11	0.57	**1.3**	13	13.1
	EaFA	0.33	3.7	**3.9**	39	13.1
	SWA	0.0067	**0.15**	0.14	1.5	8.9
Selenium	CFS	**0.51**	0.20	0.29	5.1	1.9
	EaFA	0.55	4.0	**6.9**	69	13.1
	SWA	35	**130**	98	1,300	8.9
Zinc	CFS	**170**	0.009	5.6	1,700	1.9
	EaFA	**1.6**	< 0.001	0.057	16	2.1
	SWA	**1.9**	0.021	0.017	19	2.5

"<" indicates eluate concentration presented as less than reported MDL value.

"*" pH 13 extraction was not measured for boron due to base storage in dissolution of borosilicate glass (U.S. EPA, 2012c).

Eluate concentrations in **bold** indicate maximum concentration.

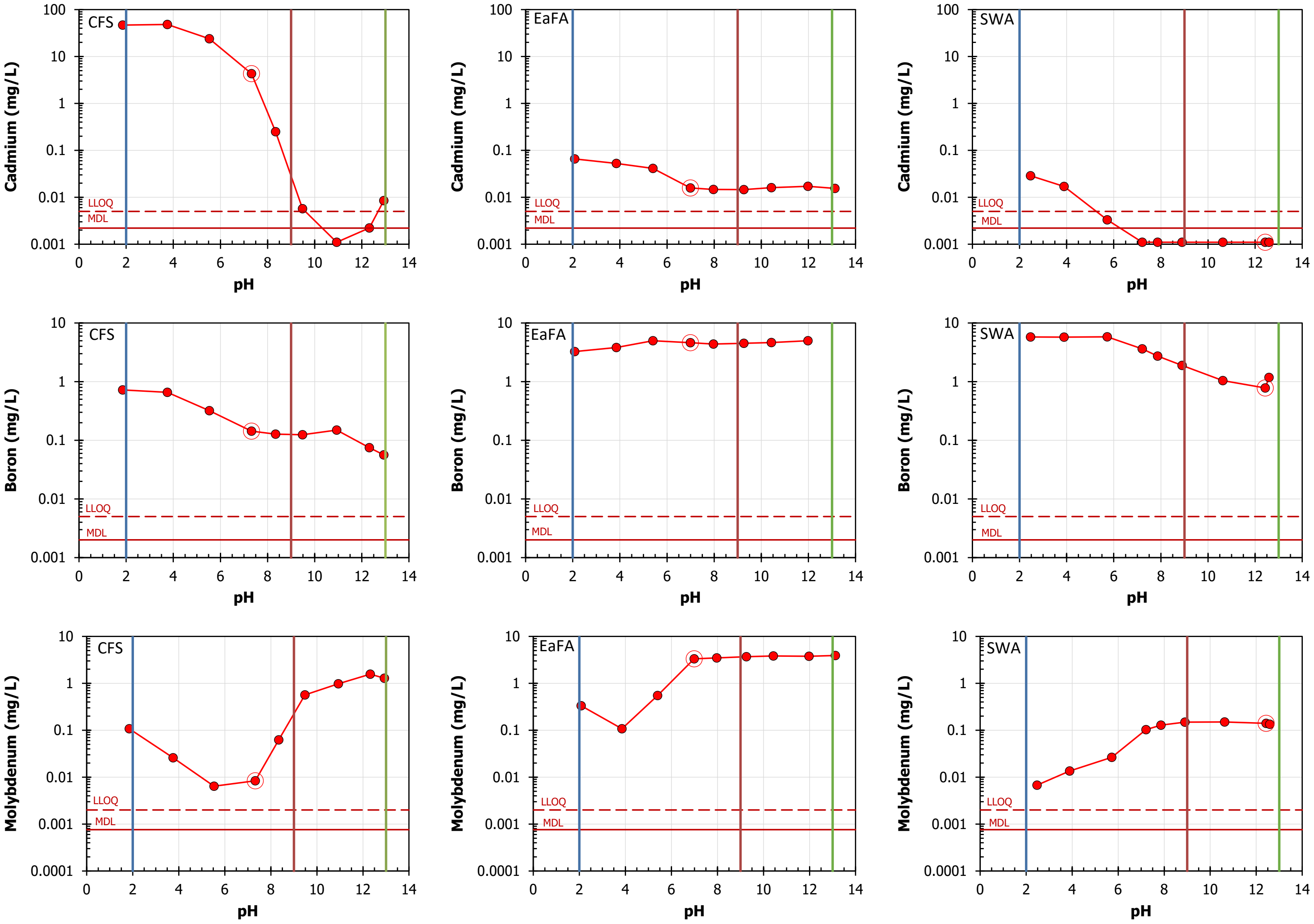


Figure 4-11. Comparison of eluate concentrations at specified pH values of 2, 9, and 13 used to determine the available content: Contaminated smelter site soil (CFS; left), coal combustion fly ash (EaFA; middle) and solidified waste form (SWA; right).

4.4.2 Interpolating Method 1313 Data to Endpoint Target pH

Since the pH-dependent leaching of many COPCs may be sensitive to minor fluctuations in eluate pH, it is necessary to interpolate Method 1313 test results to the specified endpoint target pH values to provide reproducible, comparative results to be used in conjunction with comparison the threshold or limit values. In practice, Method 1313 allows for a tolerance of ±0.5 pH unit for each target pH value recognizing the experimental error inherent to addition of acid and base and measurement of pH. However, the measured eluate concentration over the tolerance interval may result in a concentration difference as much as an order of magnitude. Thus, eluate concentration data to be used to evaluate leaching over a scenario pH domain should be interpolated to the endpoint target pH values to minimize the bias in eluate concentrations for highly pH-dependent COPCs. Interpolated eluate concentrations are obtained by standard linear interpolation of log-transformed data from two neighboring Method 1313 eluates (U.S. EPA, 2012c).[25]

$$\log C = \log C_a + (pH - pH_a) \times (\log C_b - \log C_a)/(pH_b - pH_a) \qquad \textbf{Equation 4-13}$$

where

$\log C$ is the log-transform of the eluate concentration interpolated to the endpoint target pH value of 2, 9, or 13 in log[mg/L];

pH_a is the measured pH value for eluate a;

pH_b is the measured pH value of eluate b;

$\log C_a$ is the log-transform of the measured eluate concentration at pH_a in log[mg/L], and;

$\log C_b$ is the log-transform of the measured eluate concentration at pH_b in log[mg/L].

Figure 4-12 shows that the overall result of interpolating measured concentration to Method 1313 endpoint target pH values is not significant except in pH regions where the LSP is highly sensitive (e.g., see iron near pH 4 or cadmium from pH 5-12).

Although interpolation should be considered carefully or may not be possible for data collected before the methods were standardized (e.g., Method SR002.1, the predecessor to Method 1313)[26] or from single-point leaching tests, older pH dependent data from the predecessor methods can provide a useful comparison basis (e.g., see U.S. EPA, 2012b) and be used for more detailed assessments (e.g., see U.S. EPA, 2014b). Interpolation can be carried out automatically in LeachXS™ Lite upon importing of Method 1313 test results.

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[25] Interpolation of Method 1313 results to target pH values is achieved automatically using LeachXS™ Lite (see Section 3.3.2).

[26] Interpolation is recommended for Method 1313 results within ± 0.5 pH units of endpoint target pH values. However, if interpolation is conducted at greater intervals, consistency of interpolated values with the trend of the measured eluate concentration should be evaluated.

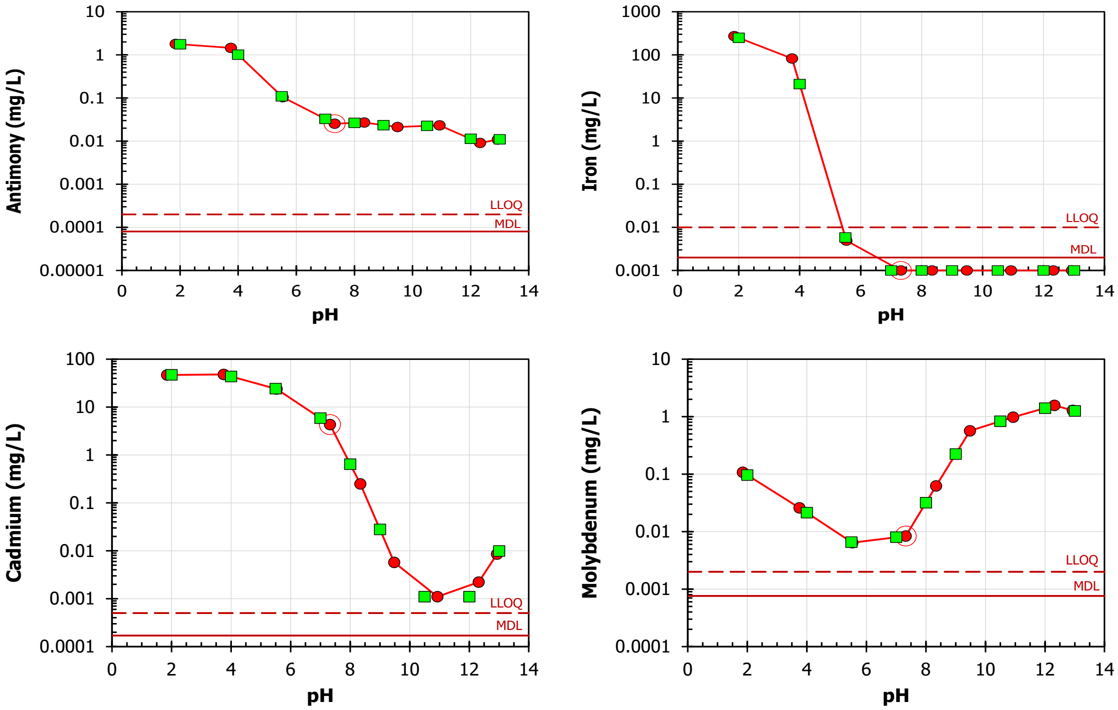


Figure 4-12. Comparison of measured Method 1313 eluate data (red dots) for a contaminated smelter site soil (CFS) with interpolated test results (green squares) using linear interpolation of log-transformed concentration data.

4.4.3 Calculating Water Contact and Assessment Time: Liquid-Solid Ratio (L/S, percolation mode) and Liquid-Area Ratio (L/A, flow around mode)

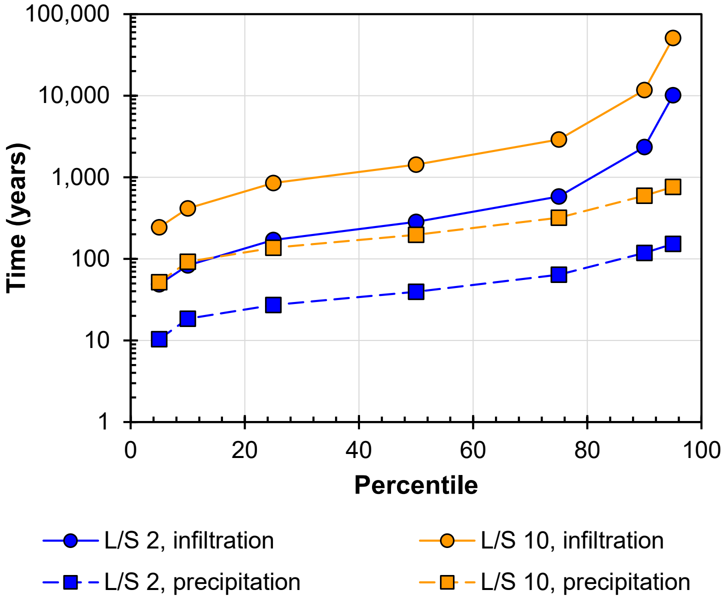
The amount of each COPC that leaches over time in a particular assessment scenario can be estimated based on the amount of contacting water. In order to evaluate a leaching assessment over time, a liquid to solid ratio (L/S) can be calculated based on the amount of material in the environment and the expected amount of water to contact that material over time. L/S is defined as the contacting water per unit mass of material (i.e., the L/S associated with the annual infiltration or groundwater flow rate) multiplied by the cumulative leaching time for the assessment. When the assessment is for a material that has a known geometry volume, per unit mass of the material in the application, LS can be calculated using Equation 4-14 (Hjelmar, 1990).

$$(L/S)_{scenario} = (Inf \times t_{yr})/(\rho \times H_{fill}) \times 1000 \qquad \textbf{Equation 4-14}$$

where

Inf	is the annual rate of infiltration or groundwater flow [m/year];
t_{yr}	is the cumulative leaching time for the scenario [years];
ρ	is the material bulk dry density [kg-dry/m^3];
H_{fill}	is the dimension of the fill in the direction of water flow [m]; and
1000	is a units conversion factor (1,000 L = m^3).

Using the above approach, Figure 4-13 illustrates the distribution of time to achieve L/S 2 and 10 L/kg-dry for a selection of U.S. CCR landfills based on site geometries, material properties and the rates of annual precipitation or infiltration. These results indicate that only a small fraction of precipitation becomes infiltration and that achieving even a modest L/S of 2 L/kg-dry can take several decades to centuries depending on site-specific factors. The time to achieve a higher L/S value like 10 L/kg-dry can take from about 200 years and up to several millennia. Based on this evaluation at the 10th percentile (i.e., 90% of the cases in the distribution take longer than the 10th percentile), the cumulative time required to reach an L/S of 2 and 10 L/kg-dry in a U.S. CCR landfill is approximately 80 and 400 years, respectively.



Data adapted from U.S. EPA (2014b).

Figure 4-13. Statistical distribution of time to reach L/S=2 L/kg-dry or L/S=10 L/kg-dry based on national distributions of precipitation and infiltration for CCR landfills.

If the material of interest is present in a saturated zone (e.g., within groundwater or surface water sediments), the amount of water flowing through the material or contacting the external geometric surface area of a monolithic material can be estimated to determine the annual L/S for percolation cases or liquid to surface area (L/A) for mass transport cases. L/A is calculated based on the geometry and resulting surface area of your material that is in contact with water.

4.4.4 Interpreting Observed Liquid Solid Partitioning (LSP) Behavior

The observed leaching behavior of a material (e.g., waste, secondary material, contaminated soil, sediment, construction material), when exposed to water in the environment, can be viewed as the combined result of constituent mass transfer and chemical equilibrium between solid, liquid and gas phases. Chemical equilibrium, often described as liquid-solid partitioning (LSP), is considered the endpoint, or limit case, for mass transfer when concentration gradients have been minimized. LSP may be achieved over relatively short duration (e.g., minutes to hours) when water is directly and uniformly in contact with a representative volume of the solid phase (e.g., in the case of uniform percolation) or over long durations (e.g., months to decades, or longer) when water contacts is limited to an external geometric surface in the case of monolithic or compacted granular materials. Additionally, the approach to chemical equilibrium is delayed when hydraulic conditions result in significant flow channeling which reduces the contact time between the liquid and the solid. In scenarios where LSP of a constituent cannot be assumed, the driving force for mass transport is the difference between the constituent concentration at equilibrium and the existing concentration in the leachate. Thus, an underlying knowledge of leaching behavior based on LSP and the rates of mass transport (due to diffusion or other processes) is crucial for the understanding of observed leaching behavior both in the laboratory and in the field.

The partitioning of constituents between solid and liquid phases at equilibrium is controlled primarily by the following factors:

- The content of the full set of constituents (COPCs and non-COPC constituents such as calcium, chloride, sulfate, phosphate and humic/fulvic substances) that can participate in partitioning,
- The system pH which acts as a master variable controlling the solubility and LSP of ionic species (e.g., most inorganic and many organic constituents),[27]
- The liquid-to-solid ratio (L/S) in the system defined as the amount of the water present relative to the equivalent dry mass of solid present in units of [mL/g-dry] at the laboratory scale and [L/kg-dry] at the field scale,
- The system redox potential which controls the oxidation state of constituents that have multiple potential valence states, such as Cr(III) versus Cr(VI), and
- The amount of reactive solid surfaces (e. g., iron (hydr)oxide, clay minerals, natural organic matter) available for constituent sorption.

Based on these factors, a COPC or other constituent may exist in the liquid phase as a combination of free and complexed chemical species either at aqueous saturation (maximum liquid concentration at the given pH, redox and system composition) or at a concentration less than aqueous saturation. The concentration at aqueous saturation also can be modified by the presence of complexing agents in the water such as dissolved humic or fulvic substances (often estimated from dissolved organic carbon) or chloride or other dissolved ionic substances.

As discussed in Section 4.2.4.2 and 4.4.1, the available content is determined as the mass release associated with the maximum eluate concentration from pH-dependent LSP. In order to provide a uniform procedure for determining available content, the maximum LSP concentrations from Method 1313 testing are evaluated at pH values of 2, 9, and 13. The available content represents the fraction of the total content of a constituent that may leach under environmental conditions. In solution, the available content may represent an endpoint conditions for leaching (available content-limited leaching) if the available content in the solid material has been leached into solution at less than aqueous saturation. In addition, a constituent that is part of the available content (i.e., is leachable under the appropriate conditions) may exist as the solid in one or more chemical species:

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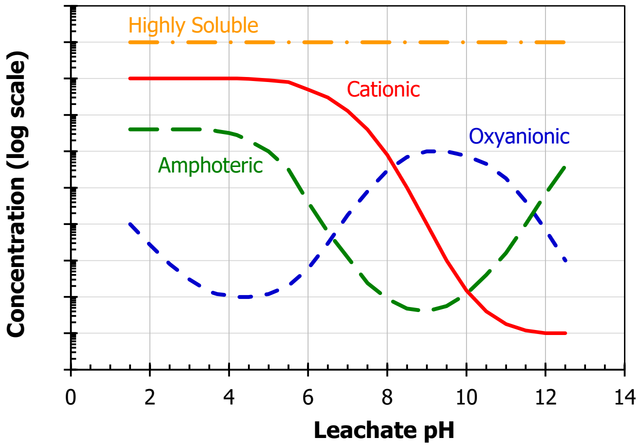
[27] The system pH can also be viewed as the available concentration of H^+ or OH^- ions in the water (i.e., $pH = -\log[H^+]$ and $pOH = 14 - pH$).

- Precipitated in one or more mineral forms based on the dissolution/precipitation reactions that may take place based on the overall system composition,
- Co-precipitated within the mineral phase as by matrix substitution (i.e., a solid solution), or
- Sorbed to a reactive surface (e.g., iron (hydr)oxide, aluminum oxide, clay minerals, natural organic matter) based on adsorption/desorption or ion exchange reactions.

Many of the above reactions that define the observed LSP may not be well quantified or even well defined. Research in geochemistry seeks to define and quantify these reactions to the extent possible or practical. However, even without detailed geochemical knowledge, the leaching behavior is empirically observed through laboratory testing and field measurements.

In pH-dependent leaching tests, the shape of the observed LSP curve (i.e., relative locations of maxima and minima) typically has four classic shapes presented schematically in Figure 4-14.



Adapted from Kosson et al. (2002), as cited in U.S. EPA (2012f).

Figure 4-14. LSP patterns for classical pH-dependence leaching behaviors.

Although the shapes in the figure are idealized and seldom are seen as clearly as presented, these trends provide a basic evaluation of how COPCs may behavior in complex natural systems. Comparing measured LSP curves obtained through Method 1313 to these idealized shapes may be useful for interpreting broad-stroke speciation of a constituent. The four classic LSP behaviors as shown in the Figure 4-14 include:

- **Highly Soluble Species** – The LSP curves for highly soluble species (e.g., B, Cl, Na, K, etc.) are usually a weak function of pH where the measured concentration may vary by up to an order of magnitude across the entire pH domain. Often, highly soluble species are considered to leach to the point of depletion of the available content (i.e., no more leachable COC exists in the solid phase) and re-mineralization due to shifts in pH are minor. Because highly soluble species release a relatively constant available mass into solution, the concentration of highly soluble species in solution is typically a strong function of L/S (e.g., halving the amount of liquid doubles the concentration).

- **Cationic Species** – The LSP curves of cationic species (e.g., Ca, Cd, Fe, etc.) show a maximum concentration in the acidic pH range and a decreasing LSP trend in the alkaline range. Within the usual alkaline range of pH ≤ 14, the LSP concentration does not increase again. The maximum concentration value associated with determination of availability content is observed as an asymptote, typically, at pH < 4.
- **Amphoteric Species** – The LSP curve for amphoteric species [e.g., Al, As(III), Pb, Cr(III), Cu, Zn, etc.] tend toward a similar shape to that of cationic species; however, concentrations pass through a minimum in the alkaline pH range and increase in highly alkaline regimes. The increase at high pH is due to the increasing solubility of hydroxide complexes (e.g., $Zn(OH)_3^{-1}$, $Zn(OH)_4^{-2}$). The pH associated with the maximum LSP concentration used to determine the available content may be observed at low pH (pH = 2) or high pH (pH = 13).
- **Oxyanionic Species** – The LSP curves for oxyanions [e.g., As(V), Cr(VI), Se(VI), Mo(VI), etc.] often show maxima in the neutral to slightly alkaline range and a decrease in concentration as pH decreases. Since many metals which make up oxyanions (e.g., Cr in Cr_2O_7) may be sensitive to changes in oxidation-reduction potential, the LSP curve also may show a local maximum at low pH where more reducing conditions are present.

A more detailed evaluation of constituent speciation may be conducted through geochemical speciation models that infer the mineral phases, adsorption reactions, and soluble complexes that control the release of the constituent using Method 1313 data.

Figure 4-15 and Figure 4-16 provide results of Method 1313 testing, as a comparison of observed leaching behavior of several COPCs for four materials:

- CFS – a lead smelter field soil (U.S. EPA, 2012c, 2012d)
- SWA – a solidified waste analog (U.S. EPA, 2012c, 2012d)
- EaFA – a low calcium coal fly ash (U.S. EPA, 2012c, 2012d)
- CaFA – a high calcium coal fly ash (U.S. EPA, 2009)

Method 1313 results are also provided for several of the key elements that influence the leaching behavior as discussed above (e.g., calcium, iron, DOC, sulfate, phosphorous).

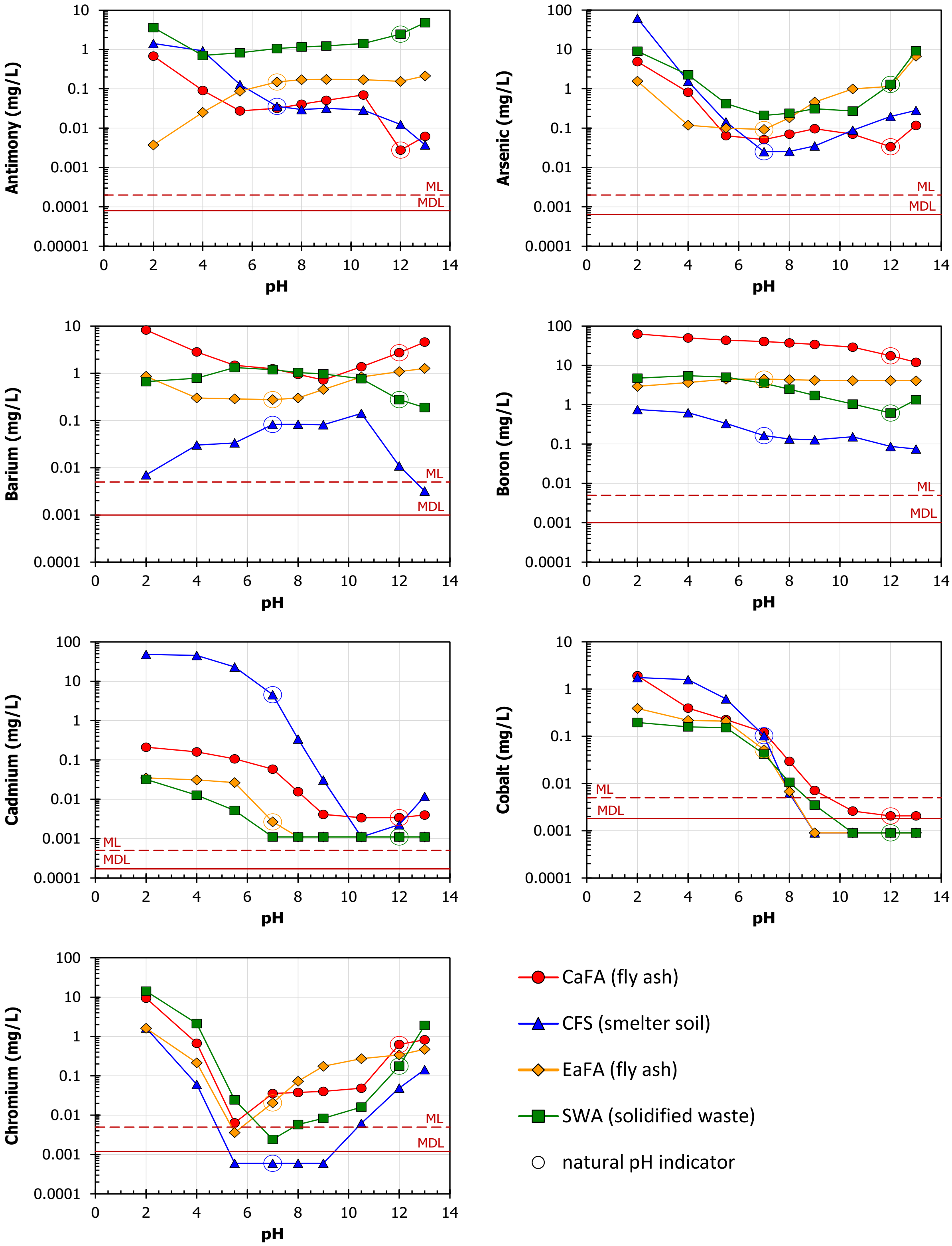


Figure 4-15. LSP behavior for different example waste forms: coal combustion fly ash (CaFA and EaFA), smelter site soil (CFS) and solidified waste (SWA).

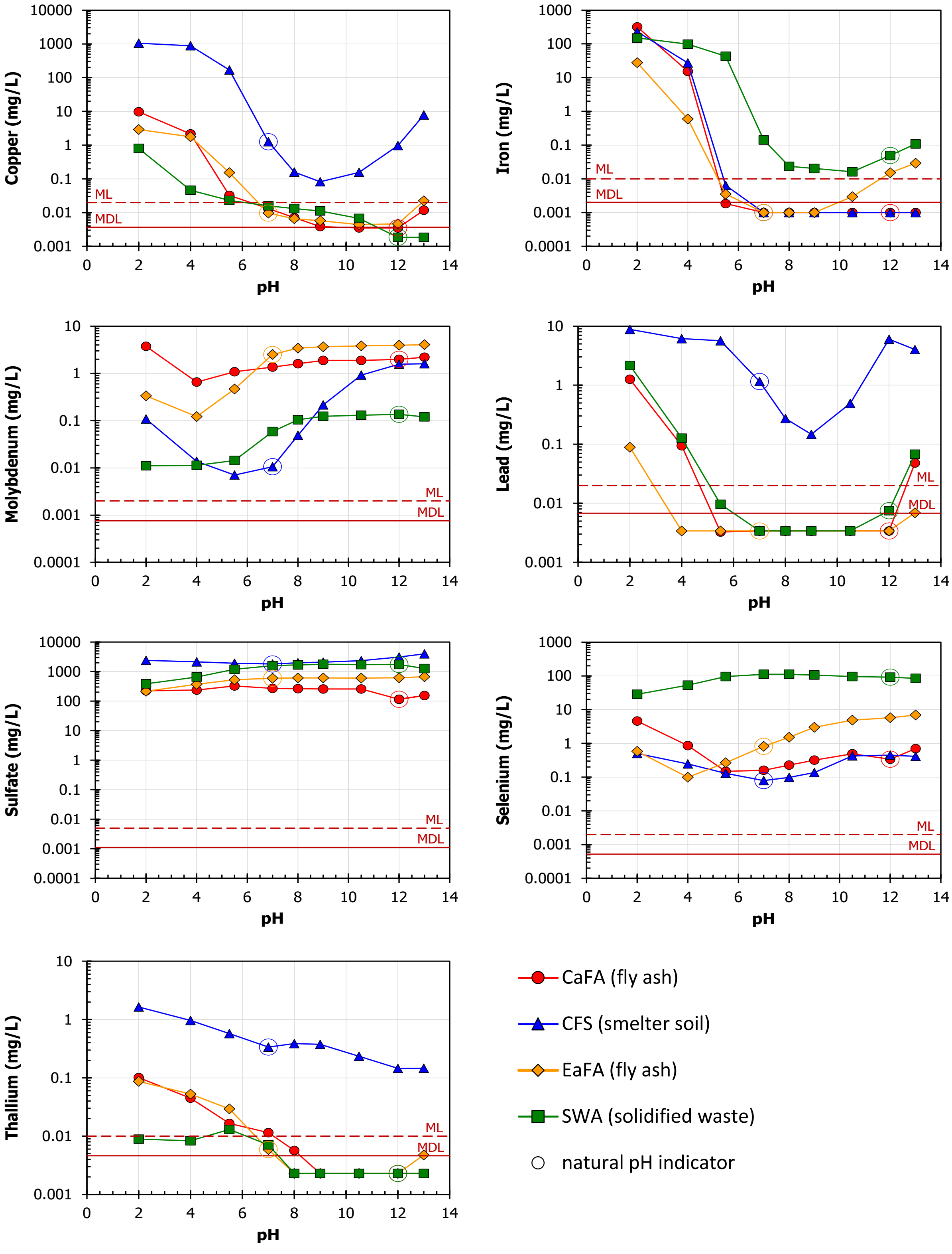


Figure 4-16. LSP behavior for different example waste forms: coal combustion fly ash (CaFA and EaFA), smelter site soil (CFS) and solidified waste (SWA).

4.4.5 Identifying Solubility- and Available Content-Limited Leaching

Screening-based assessments utilize an upper bounding estimate of the maximum expected leaching concentration of COPCs in comparisons with relevant thresholds (see Section 4.2.4). When using Method 1313 results to estimate the maximum leaching concentration, it is important to identify if the measured eluate concentration of each COPC over the scenario pH domain reflects available content-limited leaching in contrast to solubility-limited leaching.[28]

- When the LSP determined by Method 1313 reflects solubility limits or adsorption control, the eluate concentrations are a weak function of L/S and the maximum leaching concentration may be estimated at the Method 1313 test conditions.
- When LSP leaching reflects available content, however, higher leachate concentrations are expected a lower L/S values and lower leachate concentrations are expected at higher L/S values than laboratory test conditions. Thus, Method 1313 results must be adjusted from laboratory test conditions (i.e., 10 mL/g-dry) to the field scenario L/S to obtain the upper bound concentration estimate for COPCs.

The simplest way to determine if available content-limited leaching is occurring during Method 1313 is to compare the measured concentration at each targeted eluate pH to the maximum concentration used to determine the available content (Section 4.4.1). If leaching is limited by the available content, the measured concentration should be equal to the maximum concentration used to determine the available content within the uncertainty of the test method. Based on interlaboratory validation, the mean test uncertainty for Method 1313 has been determined to be 28% of the measured value shown in Table 3-6. Thus, leaching is considered available content-limited when evaluating each Method 1313 eluate if the following condition is met:

$$\frac{C_{\max(pH\ 2,9,13)} \times [1-0.28]}{C_{max(pH\ domain)} \times [1+0.28]} \leq 1 \qquad \textbf{Equation 4-15}$$

where

$C_{max(pH\ 2,9,13)}$	is the maximum eluate concentration used for determination of available content [mg/L];
$C_{max\ (pH\ domain)}$	is the maximum eluate concentration over the applicable scenario pH domain [mg/L], and;
0.28	is the reproducibility residual standard deviation (RSD_R) for concentrations from the Method 1313 interlaboratory validation study (Table 3-6).

If the fraction in Equation 4-15 is greater than 1, then the LSP behavior is dominated by solubility-limited or sorption-controlled leaching.

An alternate way to determine whether the environmental leaching is solubility (or sorption)-limited vs. available content-limited is based on evaluation of Method 1316 results. Graphical presentation of Method 1316 test results can provide insight into whether the leaching at the natural pH of a material is

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[28] For some materials, some COPCs may reflect solubility-limited leaching over part of the applicable pH domain, and available content-limited leaching over another part of the applicable pH domain for the field scenario being evaluated. When this situation occurs, the maximum concentration estimate based on the available content-limited leaching is used.

available content-limited or solubility-limited. The Method 1313 and Method 1316 results for boron and chromium leaching from a coal combustion fly ash (EaFA) are shown in Figure 4-17**.** The maximum observed concentration of boron over the applicable pH domain of 5.5 ≤ pH ≤ 9 is 4.97 mg/L is statistically 100% of the maximum concentration of 4.99 mg/L measured at pH 12 for determination of the available content. In Method 1316, the mass release of boron is a weak function of L/S at values greater than 72% of the available content and the release at high L/S (where solubility constraints would normally be less) limited by the available content value. Therefore, boron displays available content-limited leaching behavior over the pH domain shown in Method 1313 results.

Solubility-limited leaching is indicated by Method 1313 concentrations over the applicable pH domain that are significantly less than the maximum concentration used to determine the available content and that vary strongly with pH values. For solubility-limited release, the mass release Method 1316 usually is a strong function of L/S (slope of approximately 1 of concentration as a function of L/S), increasing with L/S to a value that is only a fraction of the available content under laboratory conditions. In contrast, Method 1316 concentration data is a weak function of L/S for solubility-limited release. In Figure 4-17, the maximum concentration of chromium over the 5.5≤pH≤9 domain (0.22 mg/L) is significantly less than the maximum concentration at pH 2 (1.95 mg/L), indicating solubility-limited or sorption-controlled leaching. In addition, the mass release of chromium is a strong function of L/S increasing by a factor of approximately 20 between L/S value of 1 and 10 mL/g-dry. The mass release at L/S 10 (0.42 mg/kg-dry) is only 2% of the available content (19.6 mg/kg-dry).

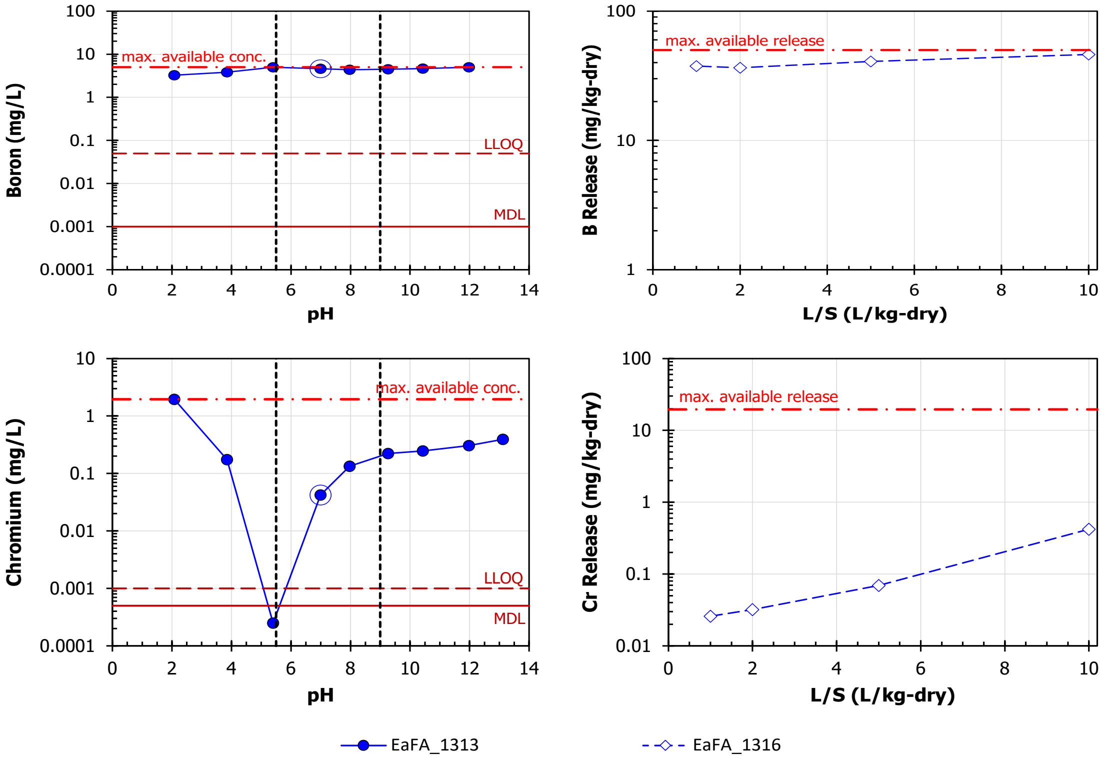

Figure 4-17. Available content-limited leaching of boron and solubility-limited leaching of chromium from a coal combustion fly ash (EaFA) based on the results of Method 1313 (left) and Method 1316 (right).

4.4.6 Understanding Mass Transport Parameters (Low Permeability Materials)

Method 1315 is most appropriate for understanding the rate of release under conditions where mass transport dominates the rate of constituent release (e.g., relatively impermeable materials). If the material will form, or be incorporated into, a solid monolithic or compacted granular form, it may be useful to perform Method 1315 to understand the degree to which the reduced surface area exposed to water contact reduces leaching. Example materials that benefit from mass transport testing include clay-like soils and sediments, or materials with low permeability due to cementitious or pozzolanic reactions. Method 1315 is applicable if water is expected to flow around the material, or if fractures in the material result in diffusion-limited release, based on exposed surface area.

Since the sample material in Method 1315 has contact with water only at the external geometric surface, COPCs must migrate from the interior of the material before partitioning into the leachate. The tortuous pathway for migration and chemical interactions with minerals and other constituents that occur along the pathway within the pore structure of the material reduce the observed rate of leaching. Field conditions associated with mass transport-controlled leaching are often different from Method 1315 laboratory test conditions:

- Method 1315 conditions are designed to maintain a dilute solution relative to aqueous solubility (e.g., an “infinite bath” boundary) through specification of a large L/A value and frequent eluant exchanges. These laboratory conditions ensure that the observed ratio of leaching is limited by transport through the material and by solubility-limited leaching in the Method 1315 leachate. The result is the Method 1315 measures a maximum rate of release for a given material. Field conditions often have a much smaller L/A that results in more cases where LSP at equilibrium limits leaching (especially for elements with low solubility). However, the range of these field conditions, which can be highly site-specific, cannot be universally represented in a standardized leaching test such as Method 1315.
- Method 1315 results represent a case of continuous mass transport over a cumulative leaching period of 63 days. The continuous liquid contact and eluant exchange intervals of Method 1315 are designed to maintain internal diffusion gradients within the material for the duration of the test. The peak interval flux measured at the beginning of Method 1315 declines rapidly because of the established concentration gradient within the material and, eventually, local depletion and low concentration gradients at the external surface of the material. However, field conditions often are variable such that a material present at the surface or in the vadose zone is likely to undergo intermittent water contact (e.g., due to a pattern of rainfall events leading to periodic infiltration). When a material is not in contact with water (i.e., during drying or storage periods), the internal concentration gradients established during the previous wetting period relax or “flatten out,” replenishing the low porewater concentration at the material surface. In the porewater at the material surface, local equilibrium may be established during a drying or storage period. Thus, the initial release in the next wetting period is greater than would be anticipated by continuous leaching due to the elevated gradient across the material surface (Garrabants, Sanchez, & Kosson, 2003; Sanchez, Garrabants, & Kosson, 2003). The greater flux observed for wetting stages after drying or storage is referred to as a “first flush” phenomena. However, the cumulative mass release under intermittent wetting conditions typically is significantly less than

the mass release under continuous leaching conditions (i.e., those imposed by Method 1315) because material only leaches for a fraction of the total evaluation time.

- Natural aging of the material, leaching of the mineral structure, and exposure to external field conditions may result in the formation of a surface layer or “rind” that has a different composition and properties than the material that was tested in the laboratory. For example, exposure to atmospheric carbon dioxide leads to pore filling and neutralization of porewater pH that may reduce the observed leaching rate in cementitious materials. Similarly, pore filling may occur after chemical reaction with constituents present in contacting water (e.g., magnesium carbonate or sulfate precipitation). Leaching of constituents can result in an increase in porosity resulting from removal of highly soluble salts when initially present as a large fraction of the material.
- When the hydraulic conductivity of a monolithic or compact granular material is relatively close (within and order-of-magnitude) of the surround materials, field conditions may allow for a fraction of the contacting water to percolate through the material such that both percolation and diffusion processes are present. For these scenarios, the results of Method 1314 (or possibly Method 1316) at the estimated L/S ratio of the percolation provide a bounding estimate of the maximum leaching concentration.

Based on the above differences between Method 1315 test conditions and field conditions, the concentration results from Method 1315 cannot be considered representative of field leachates and should not be used in comparison to threshold values. However, Method 1315 results may be used in several different ways to estimate field leaching:

- The flux of COPCs measured during first intervals of Method 1315 testing may be used as a bounding estimate of initial leaching fluxes or fluxes after drying periods associated with intermittent wetting. This approach was used in assessing leaching from concrete containing coal fly ash (U.S. EPA, 2014a).
- The observed diffusivity of COPCs estimated from Method 1315 results applied to a simple Fickian diffusion model can provide a basis for comparison of relative leaching rates between different materials potentially used or managed under the same field conditions. For example, observed diffusivities can be used as a basis of comparison of the effectiveness of different treatment process for a waste (Sanchez, Kosson, Mattus, & Morris, 2001; Westsik Jr. et al., 2013).
- Method 1315 results may be used to parameterize diffusion processes in simple diffusion models in cases when physical-chemical conditions do not change (Garrabants et al., 2002) or more detailed fate and transport model to estimate long-term constituent leaching under a range of field exposure conditions or scenarios (SRR, 2013, 2014; U.S. EPA, 2014c).

Method 1315 is often conducted in conjunction with Method 1313 to provide information on both the *rate* and *extent* of leaching (Section 2.4). Release calculated from Method 1315 provides a “best estimate” of leaching rate under mass transport conditions that may be assumed as long as the material maintains its structural integrity. Method 1313 can provide an upper bounding estimate that may be useful for understanding leaching as the solid material breaks down over time and ensuring there is not excessive release. The combined effects of leaching rate and leaching extent were used to evaluate the impact of coal combustion fly ash substitution for Portland cement in commercial concrete considering under intermittent wetting conditions based on surface application of concrete exposed to precipitation (U.S.

EPA, 2014a). Empirical data from Method 1313 estimating available content and Method 1315 estimating effective diffusivity were used to evaluate applications of MSWI bottom ash scenarios (Kosson, van der Sloot, & Eighmy, 1996). These approaches can also be used in conjunction with chemical speciation-based mass transfer models to provide insights into potential changes in leaching that may occur in response to changing conditions within or on the external surface of the material being evaluated.

Method 1315 results should be accompanied by a careful review to understand controlling mechanisms during testing and apply appropriate assumptions in extrapolation 1315 results to field scenarios. LEAF users can determine which process dominates based on comparison of Method 1313 and 1315 results. As indicated earlier, the test conditions of Method 1315 (i.e., liquid-to-surface area ratio and eluant refresh schedules) are designed to maintain a dilute eluate with respect to LSP in order to maintain the driving force for constituent mass transport (e.g., diffusion and dissolution; U.S. EPA, 2010). Thus, Method 1315 concentrations should be significantly less than the corresponding Method 1313 LSP concentration at the same pH (e.g., arsenic and cadmium in the top of Figure 4-18) for the assumed boundary condition to be valid. If Method 1315 concentrations for a constituent approach or are equal to the LSP concentrations (e.g., boron and barium in Figure 4-18), the Method 1315 dilute boundary condition assumption may not have been maintained throughout the test and the LSP as defined by Method 1313 and 1314 should be used as the basis for assessment.

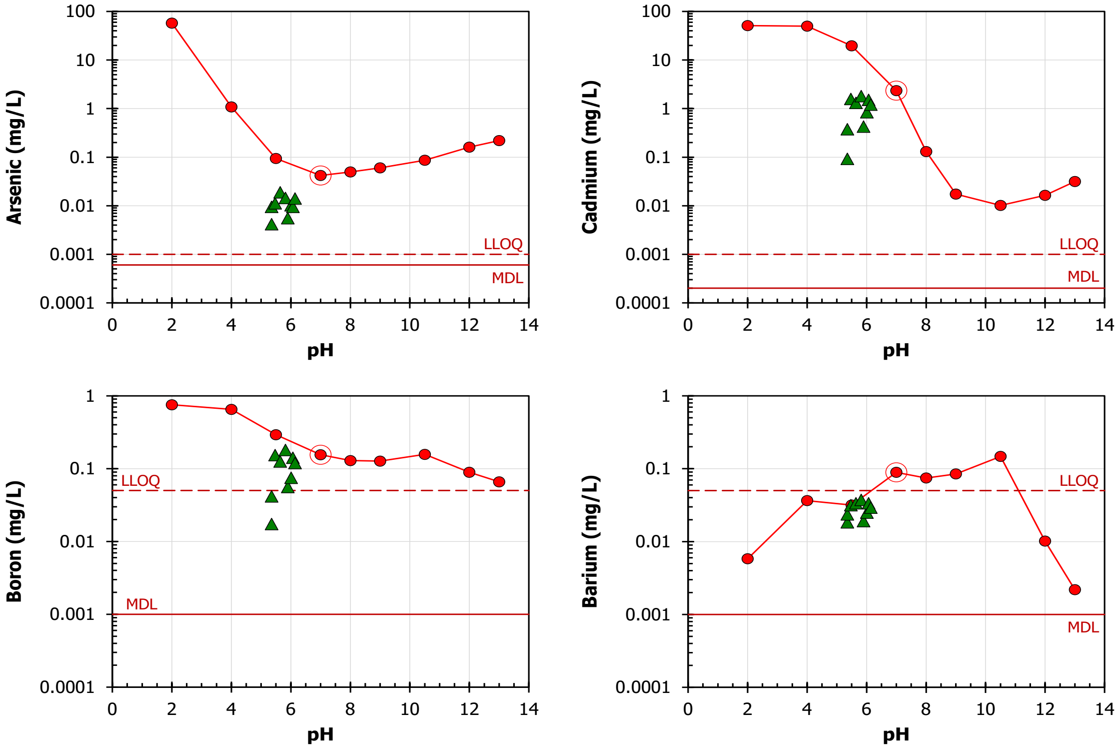

Figure 4-18. Comparison of mass transport data (green triangles, Method 1315) to equilibrium data shown as a function of pH (red circles, Method 1313) for a contaminated lead smelter soil (CFS).

In describing the leaching process (Section 2.4), mass transport was considered to continue as long as the concentration gradient was maintained which infers that when eluate concentrations approach equilibrium concentrations, Method 1315 data represents equilibrium and not mass transport. As an internal quality control check, eluate concentrations may be plotted over the LSP data from Method 1313 to verify that the “dilute” boundary condition is met for each constituent.

- Barium eluate concentrations for Method 1315 are essentially the same as the results from Method 1313. Therefore, the resulting Method 1315 eluates were saturated solutions with respect to aluminum and did not meet the “dilute” boundary condition. Thus, these barium results were not mass transfer-controlled, and should not be interpreted as diffusion-controlled release.
- Arsenic eluate concentrations in Method 1315 are significantly less than the Method 1313 results at the corresponding eluate pH and greater than the LLOQ. Therefore, Method 1315 eluates were dilute solutions with respect to arsenic and the arsenic results can be further evaluated to determine if diffusion-controlled release is a reasonable assumption.

Inspection of the cumulative release and flux as functions of leaching time indicate that release of selenium initially followed the reference line for idealized Fickian diffusion (i.e., log-linear release with a slope of ½ with respect to time for cumulative release and -½ with respect to time for flux). After approximately 14 days, release declined somewhat which may be indicative of depletion of selenium from the material. In contrast, the cumulative release and flux of aluminum follow the slopes of ½ and -½, respectively; however, aluminum is not diffusion controlled because the Method 1315 data did not meet the criteria for maintaining dilute solutions. Furthermore, pH gradients internal to the monolith being tested result in varying pore solution concentrations of aluminum that cannot be effectively represented as a constant observed diffusivity in a simple Fickian diffusion-controlled release model.

4.4.7 Considering Dilution and Attenuation in an Assessment Ratio

In some evaluations, it may be appropriate to consider the effect of a relatively small volume of leachate interacting with a larger groundwater body through use of dilution and attenuation factors. The COPC concentrations from LEAF test results represent a source term for leaching directly into contacting water. Upon leaving the source and entering the environment, COPCs may become diluted or immobilized into the environment before reaching a receptor. A dilution and attenuation factor (DAF) can sometimes be used to estimate this reduction in concentration of a COPC in the environment. A DAF is COPC specific and based on existing knowledge of fate and transport for the site of interest. DAFs have a value greater than or equal to one (DAF ≥ 1), representing the reduction in COPC concentration due to dilution of leachate from the source into a larger waterbody or the attenuation of COPCs to surrounding materials and processes, such as sorption to soil.

Constituents can interact with different media in ways that are non-linear with respect to concentration, pH and other factors. In addition, interactions between different stressors have the potential to affect fate and transport. As a result, it is important to understand and discuss the basis for a DAF to demonstrate that the magnitude of reduction identified is applicable to a specific evaluation.

In situations where it is appropriate to apply existing DAF values, the source term from LEAF tests is divided by DAF values to estimate COPC concentrations at particular points downgradient which can be compared to threshold values. Alternatively, the Assessment Ratio (see Equation 4-1) can be modified to account for dilution and attenuation (Equation 4-16).

$$AR_{DAF} = \frac{AR}{DAF} = C_{leach\_max} / (DAF \times C_{thres}) \qquad \textbf{Equation 4-16}$$

Where

AR_{DAF} is the assessment ratio considering dilution and attenuation [-];

C_{leach_max} is the estimated maximum concentration for the COPC [mg/L] (within the applicable pH domain when using Method 1313 results or L/S range when using results from either Method 1314 or Method 1316);

C_{thres} is the threshold value for the COPC [mg/L]; and

DAF is a COPC-specific dilution and attenuation factor appropriate for a given site[-].

Unless otherwise specified, the Assessment Ratio used in this guide does not consider DAFs.

4.4.8 Integrating Source Terms into Models

Source terms developed using LEAF are dependent upon the level of testing and assessment applied. Simpler testing and assessments with less information regarding material placement in the environment result in less defined source terms. The infinite source term assumes that the material will continue to leach into the future. Infinite source terms developed from LEAF are often based on screening level assessments. Increased levels of testing and assessment can result in finite-release source terms. A finite source term representing time dependent leaching will often entail Method 1313 pH dependent data suited to the scenario pH domain, combined with data from Methods 1314, 1315 or 1316 to evaluate L/S dependence in the scenario.

The source terms developed from LEAF can be used directly, in conjunction with screening DAF values or with a bounding deterministic groundwater fate and transport model (e.g., the Industrial Waste Management Evaluation Model, or IWEM). The use of source terms from LEAF paired with modeling can provide a more complete understanding of likely releases and resulting risks in contrast to the results from a single-point leaching test. Sensitivity analysis can be carried out using estimates from LEAF testing of COPC release over the anticipated pH and other conditions of the landfill or use scenario. Numerical modeling can allow for consideration of vadose zone and groundwater transport of released constituents, exposure to humans or animals via drinking water, and the toxicity of the released COPCs. In these models, leaching data expressed on a concentration basis in mg/L or mass basis in mg/kg-dry represent the source term for estimating the release of potentially hazardous substances.

Leaching data from LEAF can be used as an input to a sophisticated mass transport model to develop a more-refined estimate of release for complex environmental conditions. For example, geochemical speciation modeling software allows for simulation of LSP as a function of pH, L/S, and leachate chemistry (e.g., redox changes, ionic strength) which can be used directly to inform decision-making or applied subsequently to several different mass transport models to simulate COPC release in a range of field leaching scenarios. Tools for geochemical speciation and reactive mass transport modeling include PHREEQC *wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/*), MINTEQA2 *(www2.epa.gov/exposure-assessment-models/minteqa2*), LeachXS™ (van der Sloot & Kosson, 2012), and The Geochemist's Workbench *(www.gwb.com*).

Reactive mass transport models, including use of geochemical speciation, may be used to examine sensitivity to scenarios beyond laboratory testing conditions (Dijkstra et al., 2008; Meima & Comans, 1998). In addition, chemical speciation modeling of pH-dependent and L/S-dependent test data can be helpful to improve the understanding of the retention mechanisms that control the release of COPCs (e.g., mineral phase dissolution, sorption, and aqueous phase complexation phenomena) (van der Sloot, et al., 2017). Where data are adequate, modeling can be used to estimate the effects of factors that may modify leaching such as changes in the level of dissolved and particulate organic matter due to biological degradation, arsenic leaching in the presence of calcium, potential impacts of common ions, and the impact of constituents that can affect redox conditions (e.g., iron or sulfur), or changes in redox over time due to microbial processes (i.e., anaerobic biodegradation).

One approach to integrating field scenarios into understanding leaching behavior is to use numeric models designed to simulate specific release conditions. For example, when the water contact is primarily through flow-around a relatively impermeable fill, the Fickian diffusion model (Crank, 1975) is commonly used to estimate mass transport of COPCs. Fickian diffusion assumes that a constituent is initially present throughout the material at a uniform concentration and that mass transfer takes place in response to concentration gradients in the pore water solution of the porous material. The Fickian diffusion model is most appropriate for release scenarios for which highly soluble species are a concern or for which external stresses do not induce sharp internal chemical gradients (e.g., pH gradients, carbonation, and redox changes) that significantly influence local LSP within the material (U.S. EPA, 2014c).

The effects of physical parameters can be evaluated through coupling of the results from chemical speciation models with transport models, or reactive transport models. Chemical speciation and reactive transport models can be useful tools to evaluate: (i) conditions not practically achievable in the laboratory on material leaching behavior, (ii) the aging of materials under factors that historically control leaching in the field, and (iii) integration between laboratory and field leaching data (U.S. EPA, 2014c). ORCHESTRA can calculate chemical speciation in thermodynamic equilibrium systems using the same thermodynamic database format as other geochemical speciation programs (e.g., PHREEQC or MINTEQ) and contains state-of-the-art adsorption models for oxide and organic surfaces as well as solid solutions (U.S. EPA, 2014c).

5. Case Studies of Using LEAF for Assessments

5.1 Screening Assessment: Evaluating Coal Combustion Fly Ash for Use as Structural Fill Material

The leaching data used in this illustrative example includes the measured and interpolated results of LEAF testing conducted on the subject materials and presented in U.S. EPA reports (U.S. EPA, 2009, 2012c, 2012d). The equations cited in the example are found in Section 4.2.4. Full graphical and tabular leaching data associated with the example are provided in Appendix B. This case study is for illustrative purposes only and is not intended to be directly applicable to any evaluation. The use of LEAF is voluntary but may provide information in support of a beneficial use determination.

In this example, a coal combustion fly ash is proposed for beneficial use as construction fill material. LEAF testing may provide useful information in support of meeting one of the four criteria defined by EPA for beneficial use of CCR, the environmental demonstration criteria.[29] Laboratory leaching test results for the coal combustion fly ash, EaFA, are used as reported by the U.S. EPA (U.S. EPA, 2012c, 2012d). The determination as to whether the fly ash material may be appropriate for use from a leaching perspective is conducted in stages as described by the stepwise screening assessment approach (Section 4.2.1 and Table 4-1). This evaluation provides an example of a leaching assessment that may be used as one of several factors within an overall evaluation determining the potential for adverse impacts to human health and the environmental associated with the proposed beneficial use of a material. EPA's *Methodology for Evaluating Beneficial Uses of Industrial Non-Hazardous Secondary Materials* presents a voluntary approach for evaluating a wide range of industrial non-hazardous secondary materials and their associated beneficial uses. Prior to beneficially using secondary materials in any projects, interested individuals or organizations should consult with the relevant state and federal environmental agencies to ensure proposed uses are consistent with state and federal requirements.

The simplest stage of the screening assessment is estimated maximum leaching concentration derived from total and available content of COPCs in the material. These estimated leaching concentrations are compared directly to relevant thresholds values based on requirements for beneficial use of a material, other applicable use criteria and the regulatory program. In this example, the criteria for beneficial use is assumed the compliance of estimated leaching concentrations for all COPCs with drinking water MCLs. If all COPC release estimate concentrations fall below the applicable regulatory threshold values, the beneficial use may be considered appropriate on this basis. The comparison between estimated leachate concentrations and threshold concentrations is made through calculation of an assessment ratio using Equation 4-1:

$$AR = C_{leach\_max}/C_{thres}$$

For the screening assessment in this case study, it is assumed that the assessment is conducted at the boundary of the fly ash fill.

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[29] For coal combustion residuals (CCR), the Agency's April 2015 CCR Disposal Final Rule promulgated a definition for beneficial use (40 CFR 257.53). This definition identifies four criteria that distinguish beneficial use from disposal (21349 FR 80). Those considering beneficial use for CCR should consult both this definition and the relevant state authorities to identify all the requirements that would apply.

5.1.1 Definition of the Assessment Scenario

Following the workflow discussed in Section 4.2, the application scenario is defined as a 3-meter thick structural fill of fly ash material compacted in place to a dry density of 1,500 kg-dry/m^3 that is used as a permeable construction fill. The construction fill is covered by a layer of clean sandy loam with a natural pH of 6.0 and a permeability that allows infiltrating water to percolate through to the fill material at a rate of 25 cm per year.

The objective of this leaching assessment is to determine if the leaching of COPCs from the EaFA fly ash when used as construction fill is appropriate from a leaching perspective (i.e., to meet the environmental demonstration criteria within the definition of beneficial use of CCR material). Many of the scenario-based assumptions and parameters used in this hypothetical case study were chosen for purely illustrative purposes and were not intended to represent typical or default values to be used in similar assessments. For example, the U.S. national drinking water regulations were selected as thresholds in this hypothetical example to illustrate how LEAF leaching results may be evaluated relative to applicable benchmarks. The appropriate regulatory thresholds for actual scenarios will be dependent upon the rules and guidance of the applicable regulatory agency, but the methodology for evaluation will be essentially the same. Other potential thresholds could include site-specific performance values or surface or ambient water quality limits (e.g., U.S. EPA National Recommended Water Quality Criteria). Since this case study focuses on the leaching performance related to evaluation of coal combustion fly ash for construction applications, all other aspects of the application (e.g., geotechnical, etc.) are assumed not to preclude use of fly ash as construction fill.

Key Attributes of the Beneficial Use Case Study

Problem Statement – Will leaching concentrations of COPCs exceed or fall below the leaching thresholds designated at the point of compliance?

Assumed Field Conditions – A sandy loam soil with a natural pH of 6.0 is used as a cover over a 3-meter thick layer of construction fill. The soil offers negligible acidity to the infiltrating water that percolates through the soil at a net infiltration rate of 25 cm/year into the underlying construction fill material. The construction fill is compacted in place to a density of approximately 1,500 kg-dry/m^3.

Material Composition – The properties of a coal combustion fly ash material (EaFA) are as reported by U.S. EPA (2012c) and include total content analysis, Method 1313 and Method 1316 test results.

Assumed Threshold Values – For this hypothetical case study, it is assumed that the state environmental regulatory agency has determined the relevant COPCs to be antimony (Sb), arsenic (As), barium (Ba), boron (B), cadmium (Cd), lead (Pb), molybdenum (Mo), selenium (Se) and thallium (Tl) and that the applicable threshold values are the national drinking water regulations.

Assumed Point of Compliance – In consultation with the state environmental agency, the point of compliance is determined to be 100 m hydraulically downgradient from the proposed fill. Surface water quality threshold are not considered because the nearest surface water body is greater than 100 m from the source.

5.1.2 Testing Program and Results

Since the overlying soil is a sandy loam with a natural pH of 6.0 and an insignificant amount of acidity, the natural pH of the fly ash fill will dominate the leachate pH. Therefore, Method 1313, Method 1316 and Method 1314 are the most appropriate LEAF tests to characterize leaching for this scenario and the leaching assessment should follow the screening approach in Figure 4-1 through the equilibrium-based and percolation-based leaching steps. Table 5-1 presents the total content by digestion and LEAF leaching data that were used to support the assessments in this case study. Because Method 1314 is preferred over Method 1316 data when both are available (see Section 4.2.4.4), Method 1314 data is used in the assessment presented here. Only the LEAF results that are relevant to the various assessment stage (i.e., leaching of the available content, maximum leaching over the application pH domain, maximum over the L/S range) are presented in Table 5-1; however, all leaching data, including data from Method 1316, are presented in graphical and tabular form in Appendix B.

Table 5-1. Total Content and LEAF Testing Results for EaFA Coal Combustion Fly Ash

EaFA		LEAF Leaching Test Results						
		Method 1313					Method 1314	
COPC	Total Content [mg/kg-dry]	Max Conc. pH 2, 9, 13 Used to Calculate Available Content [mg/L]	pH of Max Conc. used for Available Content	Max Conc. pH Domain 5.5 ≤ pH ≤ 9 [mg/L]	pH at Max Conc.	LSP Limit	Max Conc. Over L/S Range [mg/L]	L/S at Max Conc. [mL/g-dry]
Antimony (Sb)	1.5	0.18	13	0.15	7	Avail. Cont.	0.38	2
Arsenic (As)	63	9.7	13	0.46	9	Solubility	2.4	10
Barium (Ba)	830	0.88	2	0.48	9	Solubility	2.2	5
Boron (B)	1,400	9.8	13	5.0	5.5	Solubility	160	0.2
Cadmium (Cd)	3.5	0.056	2	0.028	5.5	Solubility	1.4	0.2
Chromium (Cr)	120	2.0	2	0.20	9	Solubility	5.3	0.2
Lead (Pb)	39	0.26	2	0.0015	5.5	Solubility	0.028	0.2
Molybdenum (Mo)	15	3.9	13	3.7	9	Avail. Cont.	22	0.5
Selenium (Se)	24	6.9	13	3.3	9	Solubility	6.9	2
Thallium (Tl)	0.91	0.26	2	0.03	5.5	Solubility	0.51	0.2

Source: U.S. EPA (2012c, 2012d).

Reported values of total content by digestion may be less than available content by Method 1313 because of uncertainty associated with testing (see Section 4.4.1)

5.1.3 Total and Available Content Screening

Screening based on total content is an assessment level that requires testing data outside of the scope of the LEAF test methods; therefore, it may not be practical for all assessments. Typically, total content data is provided through digestion of the solid material or through non-destructive testing. When total content data is available, estimates of maximum leaching concentration (C_{leach_max}) based on total content may be calculated for the default initial L/S value of 0.5 L/kg-dry using Equation 4-3.

$$\boldsymbol{C_{leach\_max} = m_{total}/(L/S)_{initial}}$$

Using the testing and characterization data for the EaFA fly ash shown in Table 5-1, the total content for antimony is 1.5 mg/kg-dry and, therefore, Equation 4-3 becomes:

$$\boldsymbol{C_{leach\_max} = 1.5\left(\frac{mg}{kg-dry}\right)\Big|\frac{1}{0.5}\left(\frac{kg-dry}{L}\right) = 3.0\left(\frac{mg}{L}\right)}$$

The C_{leach_max} value based on the total content assumes that the full amount of a COPC in a solid material leaches into a liquid at the default initial L/S.

The available content data in Table 5-1 is reported directly from Method 1313 as the maximum eluate concentration of the three available content pH extractions at endpoint target pH values of 2, 9 and 13. Therefore, the estimated maximum leaching concentration for available content is calculated using Equation 4-4:

$$\boldsymbol{C_{leach\_max} = C_{1313(\max pH\ 2,9,13)} \times \frac{(L/S)_{1313}}{(L/S)initial} = 20 \times C_{1313(max\ pH\ 2,9,13)}}$$

Since, the L/S for Method 1313, $(L/S)_{1313}$, is defined as 10 L/kg-dry in the test method (U.S. EPA, 2012f), the multiplier for the maximum leaching concentration, $C_{1313(max\ pH\ 2,9,13)}$, is 20 (i.e., 10 L/kg-dry divided by 0.5 L/kg-dry). From Table 5-1, the available content of antimony was determined to be 0.17 mg/kg-dry measured at a pH of 13. Therefore, the estimated maximum leaching concentration for the available content assessment is:

$$C_{leach\_max} = 20 \text{ x } C_{1313(max\ pH\ 2,9,13)} = 20 \text{ x } 0.18\left(\frac{mg}{L}\right) = 3.6\left(\frac{mg}{L}\right)$$

Note that the estimated leachate concentration based on available content is greater than that estimated by total content**.** Section 4.4.1 discusses the uncertainties regarding total content analysis that may result in an available content greater than a total content.

Table 5-2 provides the threshold concentration for each COPC in EaFA, the estimated maximum leaching concentration and assessment ratio value for the total content and available content screening levels. Assessment ratio values less than or equal to one ($AR \leq 1$) indicate COPCs where the maximum leaching concentrations does not exceed threshold values and, therefore, are not likely to be a concern. For COPCs where the assessment ratio is greater than one ($AR > 1$), additional refinement of the assessment, either through further leaching evaluation or through alteration of the reuse scenario, is indicated. For all COPCs, the assessment ratios in Table 5-2 indicate that estimated leaching concentrations based on both total content and available content exceed threshold values by 1 to 4 orders of magnitude. However, this screening level approach is highly bounding in that it assumes the complete release of the total or available content of all COPCs under field conditions. Thus, this assessment alone cannot support a conclusion that the proposed use of EaFA as a construction fill is acceptable and a more-refined assessment is required to account for environmental processes not considered in this initial screening.

Table 5-2. Initial Screening Values for EaFA Fly Ash Using LEAF Leaching Estimates

EaFA COPC	Threshold Value [mg/L]	Total Content C_{leach_max} [mg/L]	Assessment Ratio (AR)	Available Content C_{leach_max} [mg/L]	Assessment Ratio (AR)
Antimony (Sb)	0.006	3.0	**500**	3.6	**600**
Arsenic (As)	0.01	130	**13,000**	190	**19,000**
Barium (Ba)	2	1700	**830**	18	**8.8**
Boron (B)	7	2800	**400**	200	**28**
Cadmium (Cd)	0.005	7.0	**1,400**	1.1	**220**
Chromium (Cr)	0.1	240	**2,400**	40	**400**
Lead (Pb)	0.015	78	**5,200**	5.2	**350**
Molybdenum (Mo)	0.2	30	**150**	78	**390**
Selenium (Se)	0.05	48	**960**	140	**2,800**
Thallium (Tl)	0.002	1.8	**910**	5.2	**2,600**

Assessment ratios shown in **bold red** indicate COPCs where the maximum estimated leaching concentration for the assessment exceeds the indicated comparative threshold.

Threshold values are the National Primary Drinking Water Regulations (U.S. EPA, 2012a) unless otherwise noted in Table 3-7.

5.1.4 Equilibrium-pH Screening (Method 1313)

In addition to available content, Method 1313 provides eluate concentration data across a broad pH range that may be focused to estimate the maximum leaching of COPCs over an applicable pH domain for the application scenario. The maximum concentration over an applicable pH domain provides a bounding estimate of potential leaching under field conditions that may be more accurate for COPCs with LSP behaviors that are a strong function of pH (e.g., heavy metals, radionuclides).

The selection and modification of an applicable scenario pH domain are discussed in Section 4.2.5.1 of the guide. For this case study, the default pH domain of 5.5 ≤ pH ≤ 9.0 was selected since the natural pH of EaFA (pH = 6.8) falls within this interval.[30] For COPCs where solubility-limited leaching dictates the concentration over the pH domain, the estimated maximum concentration is derived from the maximum concentration of the pH domain, $C_{1313(max\ pH\ domain)}$, using Equation 4-6:

$$C_{leach\_max} = C_{1313(\max pH\ domain)}$$

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[30] As discussed in Section 4.2.5.1, the pH domain applicable to many scenarios should include the natural pH of the material and should consider the prevailing pH in proposed application and the pH effects associated with any aging or degradation processes to which the material might be exposed.

If a COPC has been demonstrated to be available content-limited over the entire applicable scenario pH domain, the estimated maximum leachate concentration will be a strong function of L/S and requires adjustment to the default initial L/S value of 0.5 L/kg-dry using Equation 4-4:

$$C_{leach\_max} = C_{1313(max\,pH\,domain)} \times \frac{(L/S)_{1313}}{(L/S)_{initial}}$$

Based on the Method 1313 testing data provided in Table 5-1, the maximum concentration of antimony over the default pH domain, 5.5 ≤ pH ≤ 9.0, is 0.15 mg/L measured at the natural pH of 6.8. Since antimony was determined to be available content limited over this pH domain, Equation 4-4 is used to estimate the maximum leachate concentration at the default L/S:

$$C_{leach\_max} = 20 \times C_{1313(max\,pH\,domain)}$$

$$C_{leach\_max} = 20 \times 0.15\left(\frac{mg}{L}\right) = 3.0\left(\frac{mg}{L}\right)$$

Table 5-3 provides a summary of the test results and estimated maximum leachate concentrations for the equilibrium-pH leaching assessment of EaFA fly ash. For each COPC, Method 1313 test data includes the maximum eluate concentration measured over the applicable pH domain and the identified LSP limit (i.e., available content- or solubility-limited leaching). The assessment columns show the corresponding C_{leach_max} value and the assessment ratio value based on the equilibrium-pH assessment. The assessment ratio results show that the maximum estimated field concentration for most COPCs in the EaFA fly ash exceed threshold values for the equilibrium-based assessment. Only the leaching of barium, boron and lead are acceptable based on this leaching assessment. Therefore, a more-detailed leaching source term, such as that provided by percolation leaching assessment using Method 1314, may be used to further refine the leaching assessment.

Table 5-3. Equilibrium-pH Assessment of Fly Ash

EaFA		**Method 1313**		**Equil-pH Assessment**	
COPC	**Threshold Value** [mg/L]	**Max Conc. Over pH Domain** [mg/L]	**LSP limit**	C_{leach_max} [mg/L]	**AR**
Antimony (Sb)	0.006	0.15	Available Content	3.0	**500**
Arsenic (As)	0.01	0.46	Solubility	0.46	**46**
Barium (Ba)	2	0.48	Solubility	0.48	0.24
Boron (B)	7	5.0	Solubility	5.0	0.71
Cadmium (Cd)	0.005	0.028	Solubility	0.028	**5.6**
Chromium (Cr)	0.1	0.20	Solubility	0.2	**2.0**
Lead (Pb)	0.015	0.0015	Solubility	0.0015	0.10
Molybdenum (Mo)	0.2	3.7	Available Content	74	**370**
Selenium (Se)	0.05	3.3	Solubility	3.3	**66**
Thallium (Tl)	0.002	0.03	Solubility	0.03	**15**

Assessment ratios shown in **bold red** indicate COPCs where the maximum estimated leaching concentration for the assessment exceeds the indicated comparative threshold.

Threshold values are the National Primary Drinking Water Regulations (U.S. EPA, 2012a) unless otherwise noted in Table 3-7.

5.1.5 Full LSP Screening (Method 1313 and Method 1314)

For the scenario presented in this illustrative example, a granular material is contacted with infiltration such that the mode of water contact may be considered percolation of infiltrating water through a relative permeable bed (Section 4.2.5.3). Therefore, the inclusion of L/S-dependent leaching data (e.g., from Method 1314 or Method 1316) in the screening assessment may provide increased refinement of the bounding estimate of leaching offered through equilibrium-pH screening.

The estimated maximum leachate concentration is the greater of the maximum eluate concentration over the applicable pH domain (i.e., $C_{1313(max\ pH\ domain)}$ from the equilibrium-pH screening) and the maximum eluate concentration as a function of L/S as shown in Equation 4-8:

$$C_{leach\_max} = MAX\left[C_{1313(max\ pH\ domain)}, C_{(L/S),max}\right]$$

An illustration of the improved understanding provided by Method 1314 is presented in Figure 5-1 by comparisons of EaFA eluate pH and COPC concentrations for Method 1314 (blue triangles), Method 1316 (orange diamonds) and the natural pH from Method 1313 (red dot with indicator circle). In the column test (Method 1314), the eluate pH data from the column indicates an initial eluate pH of 4.2 with increasing pH to near-neutral values an L/S of 2 L/kg-dry. Thereafter, the eluate pH in the column remained approximately pH 7, consistent with the pH in the batch style leaching tests (Method 1313 and Method 1316). The initially acidic pH that is obvious in the Method 1314 data is not indicated by the eluate pH in Method 1316 or the natural pH in Method 1313 due to the differences between batch tests and column elution tests. For this coal combustion ash, the cause of the initially low pH is a process operation where sulfuric acid is sprayed into the effluent stream to aid in electrostatic precipitator collection of fly ash resulting in an acidic surface coating on the EaFA sample.

The full results of Method 1314 testing of EaFA fly ash presented in Appendix B show the impact of the evolution in eluate pH in the column on the LSP behavior of each COPC as a function of pH (e.g., as characterized by Method 1313). As a result of the pH increase from pH 4.2 to pH 7, COPC concentrations in column eluates initially may be high when solubility is increased under acidic conditions only to decrease as pH becomes more neutral (e.g., cadmium). Alternatively, initial concentrations of a COPC in column eluates may be low because of lower solubility at acidic pH than at neutral pH (e.g., selenium). COPCs may rapidly wash out or are depleted after the pH reaches an available content-limited domain (e.g., boron). The arsenic and chromium represent special cases where increased eluate concentration reflect solubility-limited leaching at acidic and neutral pH but pass through a minimum solubility point at approximately pH 5.

Table 5-4 presents the maximum eluate concentrations for each COPC derived from Method 1314 testing of EaFA fly ash, along with the corresponding L/S at which the maximum occurred. The table also provides assessment ratio for the equilibrium-L/S assessment calculated as the maximum for each COPC in a percolation assessment step, calculated by dividing the maximum concentration over the L/S by the threshold value. The conclusions of the percolation assessment are consistent with those in previous steps indicating that most or all of the COPCs leach at concentrations above threshold value. Therefore, the only conclusion that can be reached based on this stepwise leaching assessment is that EaFA is not appropriate for the proposed permeable construction fill scenario.

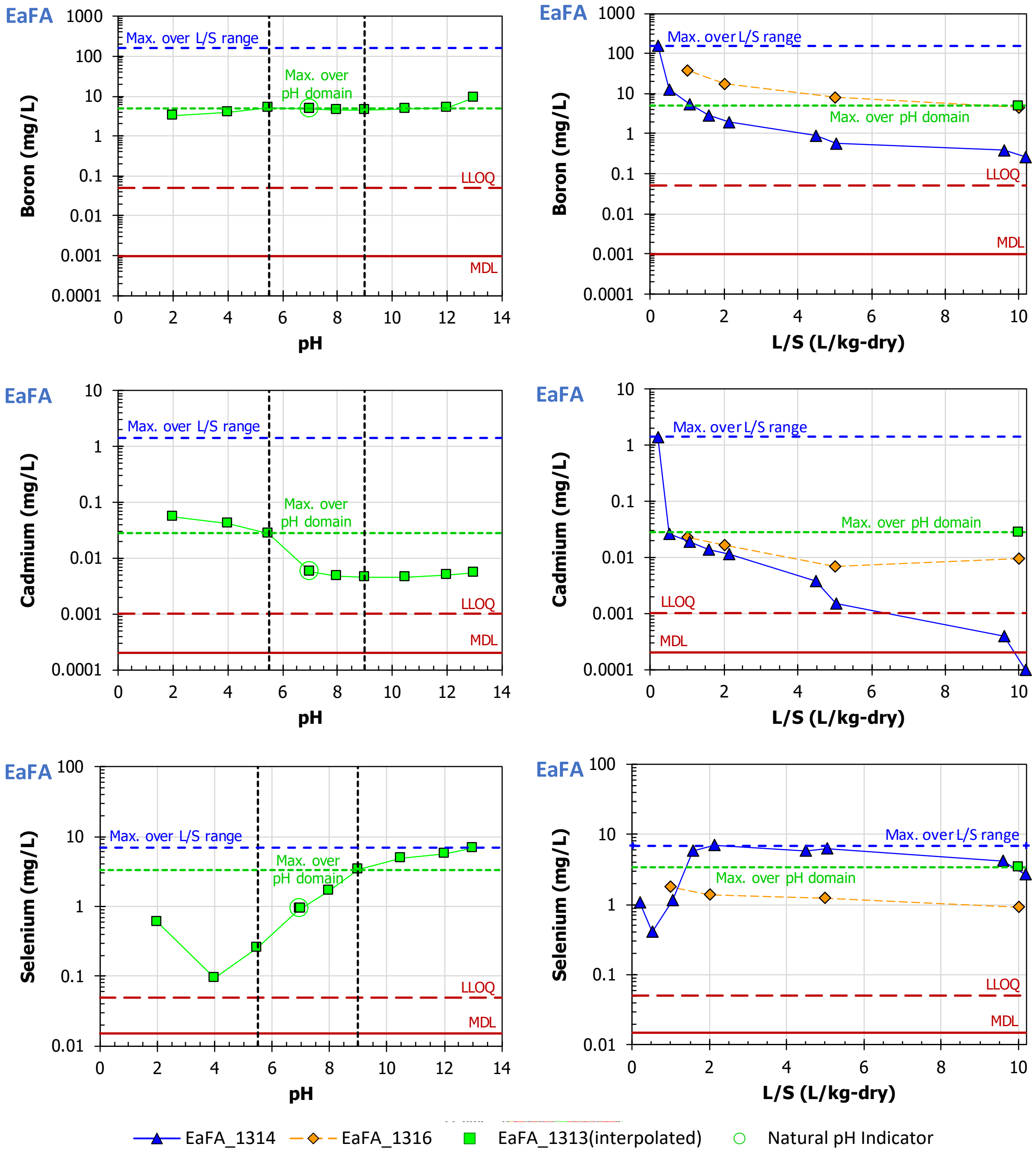

Figure 5-1. COPC concentrations as a function of pH (left) and L/S (right) for a coal combustion fly ash (EaFA) for full LSP screening assessment: Method 1313 interpolated), Method 1314, and Method 1316.

Table 5-4. Full LSP Screening Assessment of EaFA Fly Ash Fill Material

EaFA		Method 1313			Method 1314		Full LSP Assessment	
COPC	Threshold Value (mg/L)	Max Conc. pH Domain 5.5≤pH≤9 [mg/L]	pH at Max Conc.	LSP Limit	Max Conc. Over L/S [mg/L]	L/S at Max Conc. [mL/g-dry]	C_{leach_max} [mg/L]	Full LSP AR
Antimony (Sb)	0.006	0.15	7	Avail. Cont.	0.38	2	0.38	**64**
Arsenic (As)	0.01	0.46	9	Solubility	2.4	10	2.4	**240**
Barium (Ba)	2	0.48	9	Solubility	2.2	5	2.2	1.0
Boron (B)	7	5.0	5.5	Solubility	160	0.2	160	**22**
Cadmium (Cd)	0.005	0.028	5.5	Solubility	1.4	0.2	1.4	**280**
Chromium (Cr)	0.1	0.20	9	Solubility	5.3	0.2	5.3	**53**
Lead (Pb)	0.015	0.0015	5.5	Solubility	0.028	0.2	0.028	**1.8**
Molybdenum (Mo)	0.2	3.7	9	Avail. Cont.	22	0.5	22	**110**
Selenium (Se)	0.05	3.3	9	Solubility	6.9	2	6.9	**140**
Thallium (Tl)	0.002	0.03	5.5	Solubility	0.51	0.2	0.51	**260**

Assessment ratios shown in **bold red** indicate COPCs where the maximum estimated leaching concentration for the assessment exceeds the indicated comparative threshold.

Threshold values are the National Primary Drinking Water Regulations (U.S. EPA, 2012a) unless otherwise noted in Table 3-7.

5.1.6 Consideration of an Alternate Coal Combustion Fly Ash

In parallel to evaluation of EaFA, an alternate coal combustion fly ash, CaFA, was evaluated for use in the same scenario. The evaluation of this alternative material is one of many ways in which leaching assessments may vary. Results from LEAF testing of CaFA are provided in Table 5-7 while the associated assessment results are provided in Table 5-8.

The assessment for the alternative CaFA material was conducted in the same manner as described for EaFA fly ash with the exceptions that the upper bound of scenario pH domain was expanded from the default value 9.0 to a value of 12.0. Therefore, the applicable pH domain used in equilibrium-based assessment of Method 1313 data ($5.5 \leq pH \leq 12.0$) captured the natural pH of the CaFA material.

The results of the leaching assessment of CaFA provided in Table 5-8 indicate that the CaFA material is similarly not appropriate for use as a construction fill under the assumption of no dilution and attenuation. Although both CaFA and EaFa are coal combustion fly ash materials, the contrast between assessment results illustrates the importance of careful consideration of scenario parameters in accordance with existing regulatory requirements.

Table 5-5. LEAF Coal Fly Ash CaFA Total Content Analysis and LEAF Leaching Test Results

CaFA		LEAF Leaching Test Results						
		Method 1313					Method 1314	
COPC	Total Content [mg/kg-dry]	Available Content [mg/L]	pH for Available Content	Max Conc. pH Domain 7 ≤ pH ≤ 12 [mg/L]	pH at Max Conc.	Available content- or Solubility-limited	Max Conc. Over L/S Range [mg/L]	L/S at Max Conc. [mL/g-dry]
Antimony (Sb)	6.2	0.68	2	0.070	10.5	Solubility	0.039	10
Arsenic (As)	22	4.9	2	0.097	9	Solubility	0.018	10
Barium (Ba)	960	8.3	2	2.7	12	Solubility	400	0.2
Boron (B)	NA	63	2	41	7	Avail. Cont.	21	5
Cadmium (Cd)	1.7	0.21	2	0.058	7	Solubility	<0.00067	-
Chromium (Cr)	88	9.4	2	0.63	12	Solubility	0.31	10
Lead (Pb)	56	1.3	2	0.0026	7	Solubility	0.015	1
Molybdenum (Mo)	19	3.7	2	2.0	12	Solubility	4.7	9.5
Selenium (Se)	8.6	4.6	2	0.49	10.5	Solubility	0.83	2
Thallium (Tl)	1.5	0.10	2	0.0115	7	Solubility	<0.005	-

Reported values of total content by digestion may be less than available content by Method 1313 because of uncertainty associated with testing (see Section 4.4.1)

NA = boron total content not available because of metaborate addition.

"<" indicates all eluate values less than the reported MDL concentration.

Table 5-6. Leaching Assessment Ratios for Alternative Coal Combustion Fly Ash CaFA

CaFA		Assessment Ratio (AR)			
COPC	Threshold Value [mg/L]	Total Content (total content leaches)	Available Content (available content leaches)	Equil-pH (max. conc. over pH domain)	Full LSP (max. conc. over pH domain and L/S range)
Antimony (Sb)	0.006	**2,100**	**2,300**	**12**	**12**
Arsenic (As)	0.01	**4,400**	**9,800**	**10**	**10**
Barium (Ba)	2	**960**	**83**	**1.4**	**200**
Boron (B)	7	NA	**180**	**120**	**5.8**
Cadmium (Cd)	0.005	**680**	**840**	**12**	**12**
Chromium (Cr)	0.1	**1,800**	**1,900**	**6.3**	**6.3**
Lead (Pb)	0.015	**7,500**	**1,700**	0.17	1.0
Molybdenum (Mo)	0.2	**190**	**370**	**10**	**24**
Selenium (Se)	0.05	**340**	**1,800**	**10**	**17**
Thallium (Tl)	0.002	**1,500**	**1,000**	**5.8**	**5.8**

NA indicates data or assessment ratios that are “not available.”

Assessment ratios shown in **bold red** indicate COPCs where the maximum estimated leaching concentration for the assessment exceeds the indicated comparative threshold.

Assessment ratios shown as “<0.001” (see chromium and selenium) indicate values calculated at less than 0.001.

Threshold values are the National Primary Drinking Water Regulations (U.S. EPA, 2012a) unless otherwise noted in Table 3-7.

5.2 Scenario Assessment: Evaluating Treatment Effectiveness of a Cement-Based Stabilization/Solidification (SS) Process

In this example, the potential effectiveness of onsite treatment using a cement-based Stabilization/Solidification (S/S) process is evaluated for contaminated soil at a copper and lead smelter. This evaluation provides an example of a leaching assessment for determining treatment effectiveness based on data from (Garrabrants et al. Pending Publication a, b). This case study is for illustrative purposes only and is not intended to be directly applicable to any evaluation. The use of LEAF is voluntary but may provide information in support of a treatment effectiveness study. A number of other tests or criteria may also be appropriate or required when determining treatment effectiveness.

The leaching of COPCs from contaminated foundry soil subject to Stabilization/Solidification (S/S-CFS) follows a mass transport leaching scenario. Infiltrating water flows around the exposed surface area of the monolith and COPCs must diffuse toward the exposed surface to leach. The rate of diffusion is driven by the internal concentration gradient between the concentration in the porewater at the core of the material and the concentration at the monolith surface. For permanently submerged materials in the water table, COPCs that diffuse to the material surface are leached into a continuous surrounding liquid phase; however, a continuous liquid phase does not exist in the vadose zone during the interval between infiltration events. Internal concentration gradients within the material relax by diffusion and the initial conditions within the monolith are restored for the beginning of the next infiltration event.

The methodology for estimating leaching concentrations under a mass transport scenario is based on the approach used to estimate COPC release from cement pavements containing coal combustion fly ash [US

EPA 2014a]. An effective leaching concentration is calculated for both 1-day and 2-day infiltration events as the estimated COPC mass released from the monolith dissolved in the volume of contacting water. The average leaching concentration over the assessment interval is determined as the weighted average of isolated and extended infiltration events (see 2.4.1.).

5.2.1 Definition of the Assessment Scenario

It has been determined that contaminated soil surrounding a copper and lead smelter is in need of remediation. The impact is localized to a 400 m^2 plan-view area (20 m by 20 m), starting at grade level to a depth of 5 m. The total volume of impacted material is 2,000 m^3. The soil is a loamy sand with an assumed bulk porosity of 0.4 cm^3_{pores}/cm^3, density of 1,700 kg/m^3, and field capacity of 0.24 cm^3_{water}/cm^3_{pore} based on the negligible drainage flux approach of Meyer and Gee (Meyer & Gee, 1999). The water table is sufficiently deep that it is not a concern for leaching of constituents at the unit boundary of the site.

The objective of this assessment is to determine if the release of COPCs from treated soil is acceptable from a leaching perspective. Many of the scenario-based assumptions and parameters used in this hypothetical case study were chosen for purely illustrative purposes and were not intended to represent typical or default values to be used in similar assessments. For example, the U.S. national drinking water regulations were selected as thresholds in this hypothetical example to illustrate how LEAF leaching results may be evaluated relative to applicable benchmarks. The appropriate regulatory thresholds for actual scenarios will be dependent upon the rules and guidance of the applicable regulatory agency, but the methodology for evaluation will be essentially the same. Other potential thresholds could include site-specific performance values or surface or ambient water quality limits (e.g., U.S. EPA National Recommended Water Quality Criteria). Since this case study focuses on the leaching performance related to evaluation of coal combustion fly ash for construction applications, all other aspects of the application (e.g., geotechnical, etc.) are assumed not to preclude use of fly ash as construction fill.

A portion of contaminated field soil (CFS) was treated for analysis of the treatment effectiveness at the laboratory bench scale. The proposed S/S remedy called for mixing the soil with Portland cement (12% dry mass basis) to create a monolithic material (S/S-CFS). The final water/binder ratio was 2:1 which is higher than typical cement blends; however, much of the added water was absorbed by the air-dried soil so that the effective water/binder ratio was estimated to be 0.65:1. The moisture content of the S/S-CFS was 26% (wet basis). The S/S-CFS material was cast into 5-cm diameter by 10-cm long cylindrical molds and cured in a humid environment (≥95% relative humidity) for a minimum cure time of 90 days. Prior to testing using Method 1313 and 1314 (both of which use granular or particle-size reduced material), the S/S-CFS material was crushed with a hammer and fed through a parallel plate grinder until >85% of the mass passed a No. 10 (2-mm) sieve. Cast materials used for Method 1315 were dry cut in half to create 5-cm diameter by 5-cm long monolithic samples.

Key Attributes of the Treatment Effectiveness Case Study

Problem Statement – Will leaching concentrations of COPCs exceed or fall below the thresholds designated at the point of compliance?

Assumed Field Conditions – The soil contamination is across a 400 m^2 plan-view area (20 m by 20 m), starting at grade level to a depth of 5 m. The total volume of impacted material is 2,000 m^3. The soil is a loamy sand with an assumed bulk porosity of 0.4 cm^3_{pores}/cm^3, density of 1,700 kg/m^3, and field capacity of 0.24 cm^3_{water}/cm^3_{pore} based on the negligible drainage flux approach of Meyer and Gee [Meyer and Gee, 1999]. The water table is sufficiently deep that it is not a concern for leaching of constituents at the unit boundary of the site.

Material Composition – Total content analysis of soil indicate concentrations of aluminum (Al), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), and zinc (Zn) in excess of 1000 mg/kg. Other COPCs include arsenic (As), barium (Ba), beryllium (Be), chloride (Cl^-), fluoride (F^-), nitrate (NO_3), antimony (Sb), selenium (Se), sulfate (SO_4) and thallium (Tl).

Assumed Threshold Values – For this hypothetical case study, it is assumed that the state environmental regulatory agency has determined the relevant COPCs to be antimony (Sb), arsenic (As), barium (Ba), boron (B), cadmium (Cd), lead (Pb), molybdenum (Mo), selenium (Se) and thallium (Tl) and that the applicable threshold values are the national drinking water regulations.

Assumed Point of Compliance – The point of compliance is at the edge of the unit boundary of contaminated soil.

5.2.2 Testing Plan

The selection of appropriate leaching tests depends on the environmental factors that drive leaching in the field. In this scenario the use of Portland cement to solidify and stabilize the CFS material is expected to raise the pH and to limit leaching due to mass transfer. In order to estimate the effects of these two parameters, Methods 1313, 1314, and 1315 are chosen. Method 1315 is selected for this testing plan as it provides leaching data under mass transfer limited scenarios (e.g., leaching from a monolithic sample of S/S-CFS). Method 1313 is selected to serve two purposes in this testing plan. The first purpose of Method 1313 in this testing plan is to estimate the anticipated environmental pH (e.g., alkaline Portland cement will raise the pH of the material, See Figure 5-2). The second purpose of Method 1313 is to provide pH dependent equilibrium values for leaching of particle size reduced SS-CFS to compare against the mass transport limited results from Method 1315 (at L/S = 10). The use of Method 1313 is important because the test results from Method 1315 are a function of time and L/A ratio (comparable to L/S by considering sample geometry) while Method 1313 is a function of pH and fixed at an L/S of 10. The pH of the leachate in Method 1315 may change during testing and an understanding of the possible effects on equilibrium from Method 1313 data assists the evaluator in making the appropriate estimate on leachability in the field. Further characterization of potential leaching could rely on Methods 1314 or 1316. Both methods provide equilibrium leaching results for particle size reduced SS-CFR at L/S increments similar to the L/A increments used in Method 1315. In this case, Method 1314 is selected as the test method is an open system, potentially providing information on co-constituent dependent leaching behavior.

5.2.3 Material Characterization and Environmental Conditions

The total content analysis of a representative sample of contaminated soil indicated concentrations of aluminum (Al), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), and zinc (Zn) in excess of

1000 mg/kg. Other COPCs include arsenic (As), barium (Ba), beryllium (Be), chloride (Cl^-), fluoride (F^-), nitrate (NO_3), antimony (Sb), selenium (Se), sulfate (SO_4) and thallium (Tl) (See Table 5-9). This indicates the primary constituents of concern in the sample are inorganics, several of which are known to display pH dependent behavior (e.g., lead, and arsenic.)

Table 5-7. Total Content Analysis of Contaminated Field Soil (CFS) and Monolithic Material (S/S-CFS)

Material	Total Content (mg/kg)	
-	CFS	S/S-CFS
Aluminum	26,000	25,000
Antimony	460	440
Arsenic	360	250
Barium	530	520
Beryllium	0.34	0.38
Cadmium	14,000	13,000
Chloride	NA	NA
Chromium	1,200	550
Copper	15,000	16,000
Fluoride	NA	NA
Iron	17,000	49,000
Lead	3,400	3,100
Nitrate	NA	NA
Selenium	32	32
Sulfate	NA	NA
Thallium	35	24
Zinc	12,000	11,000

Note: “NA” indicates that contents Cl, F, NO_3 and SO_4 of $LiBO_2$ digests were not analyzed.

The change in pH of the CFS material due to stabilization/solidification was determined using HNO_3 and KOH additions in Method 1313 extract. Additions of KOH were used to raise the eluent pH above the natural pH of the material. Relative to the titration of CFS, the titration curve for S/S-CFS is shifted toward higher acid addition values, indicating more buffering capacity than the untreated soil (Figure 5-2). The differences in the natural pH of the materials (CFS pH_{nat} = 6.9 and S/S-CFS pH_{nat} = 12.8) and the shift in buffering capacity are a direct result of the addition of Portland cement during S/S treatment. The strong shift in pH of the material upon stabilization highlights the importance of leach testing for pH dependence as well as for testing for mass transfer limitations. The anticipated pH of the scenario needs to consider the strong shift in pH to a highly alkaline environment and whether that alkalinity is sufficiently buffered to represent environmental conditions. An anticipated environmental pH for the untreated material (pH =6.9) would be 5.9 ≤ pH ≤ 7.9. For the treated material in this scenario, a more plausible range is 8 ≤ pH ≤ 13.3.

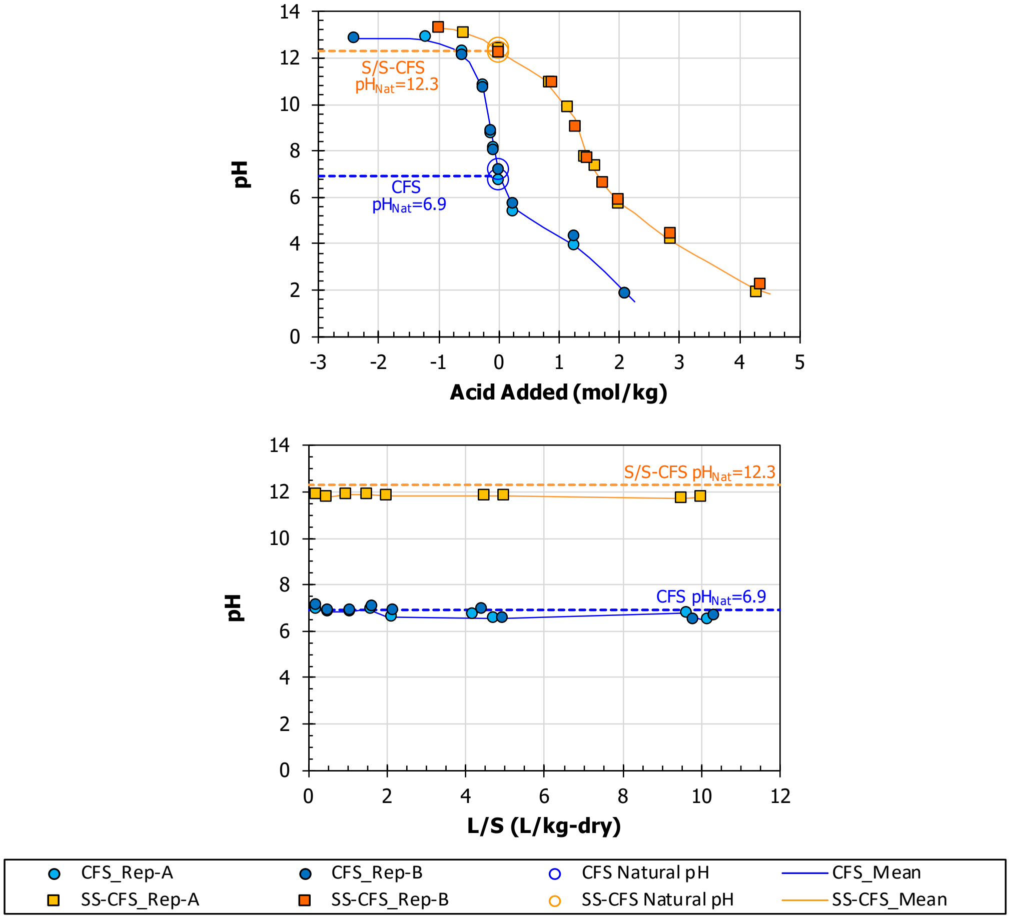

Figure 5-2. pH characterization of contaminated field soil (CFS) and monolithic material (S/S-CFS)

The volume of contacting water, or anticipated L/S, in the environment can be determined based on the infiltration rate of water. This illustrative scenario uses U.S. EPA meteorological data [14] for Nashville, TN (Table 5-8.) The EPA datasets included daily precipitation, evaporation, evapotranspiration, and other data collected over a 30-year period from 1961-1990. For days with recorded precipitation greater than zero, daily net infiltration was calculated as the balance of the daily precipitation (P), the pan evaporation (E_{PAN}), and the evapotranspiration (ET_0) data:

$$Inf = P - E_{pan} - ET_0$$

Summary statistics for the relevant precipitation data and infiltration data for this environmental setting are shown in Table 5-8.

Table 5-8. Precipitation data for Nashville, TN

	Units	Dry
City, State		Nashville, TN
Annual Precipitation	cm/y	120
Days with Precipitation	d/y	118
Annual Net Infiltration	cm/y	82
Infiltration Events ≤1-day (N1)	events/y	32
Infiltration Events >1-day (N2)	events/y	13
Net Infiltration of Events ≤1-day (P1)	cm/event	1.2
Net Infiltration of Events >1-day (P2)	cm/event	3.5
Infiltration Events >2-days	%	6.7%

After each infiltration event, soils in the subsurface drain to a relative pore saturation at field capacity [8]. The volume of water-filled pores at any saturation can be expressed in terms of L/S[31] as:

$$(L/S)_\theta = \frac{\varepsilon \cdot \theta \cdot v_{bed} \cdot 1{,}000}{m_d}$$

The capacity for water uptake (*i.e.*, volume of empty pores at the beginning of an infiltration event) is the difference between the L/S at water saturation (θ_{sat} = 1) and the L/S at field capacity (θ_f = 0.24). For the CFS bed, the L/S at water saturation and field capacity is 0.25 L/kg-dry and 0.15 L/kg-dry, respectively, indicating that the empty pore volume at the start of each infiltration event is 0.1 L/kg-dry. Converted to an L/S basis for the defined field scenarios, the annual net infiltration represents an L/S of 0.1 L/kg per year.

5.2.4 Mass Transport Assessment

In the mass transport scenario, L/S cannot be directly compared to lab results. Instead, daily infiltration events were separated into "isolated events" (≤one-day) and "extended events" (>one-day) based infiltration during consecutive days. The average duration of extended events was 2.5 days. Given that infiltration is not likely to occur over the entirety of an extended infiltration event, the mass release over a 2-day cumulative leaching interval, which can be provided directly by Method 1315, was a good approximation for release over extended infiltration events. The annual average number of infiltration events (N1 and N2) and water volumes per event (P1 and P2) over the 30-year dataset were determined and considered constant for each assessment interval. These data are used to estimate effective leaching concentrations for one- and two-day infiltration events. An average concentration for the assessment interval, I, can then be calculated based on the effective concentrations of the one- and two-day infiltration events.

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[31] Where ε is the bulk porosity, [m^3_{pore}/m^3]; θ is water saturation, v_{bed} is the volume of material, and m_d is the dry mass.

The effective concentration for a one-day event is estimated using data points on the Method 1315 cumulative release curve (Figure 5-3). From the Method 1315 interval concentration data (c_j^{1315}), the cumulative mass release per area at the end of a test interval *J* (R_J) is calculated using the volume of eluate collected (v_j^{1315}) and the exposed surface area (A_{exp}^{1315}) of the test sample as:

$$\Sigma R_J = \frac{\sum_{j=1}^{J}\left(c_j^{1315}\cdot v_j^{1315}\right)}{A_{exp}^{1315}}$$

The mass released for the one-day interval is represented by the difference in cumulative release between the first leaching interval (ΣR_1, at cumulative leaching time of 0.08 days) and second leaching interval (ΣR_2, at cumulative leaching of 1.1 days).[32] The average volume of infiltration for a 1 day event (P1) is dependent upon the ratio of the infiltrated area (A_{inf}) to the exposed surface area (A_{exp}) of the SS-CFS material. The effective concentration of a COPC for a one-day event may be estimated as:

$$C1 = \frac{M1}{V1} = \frac{(\Sigma R_2 - \Sigma R_1)\cdot A_{exp}}{P1\cdot A_{inf}\cdot 1{,}000}$$

An analogous equation for a two-day infiltration event uses $(\Sigma R_3 - \Sigma R_1)$ to represent the mass release and *P2* to represent the average volume of infiltration over a 2-day interval:

$$C2 = \frac{M2}{V2} = \frac{(\Sigma R_3 - \Sigma R_1)\cdot A_{exp}}{P2\cdot A_{inf}\cdot 1{,}000}$$

An average concentration for an assessment interval, *i*, may be calculated as a weighted average concentration over the series of one- and two-day infiltration events: This average leaching concentration is the effective leaching concentration over the assessment interval.

$$C_i^{av} = \left[\frac{N1\cdot C1 + N2\cdot C2}{N1 + N2}\right]$$

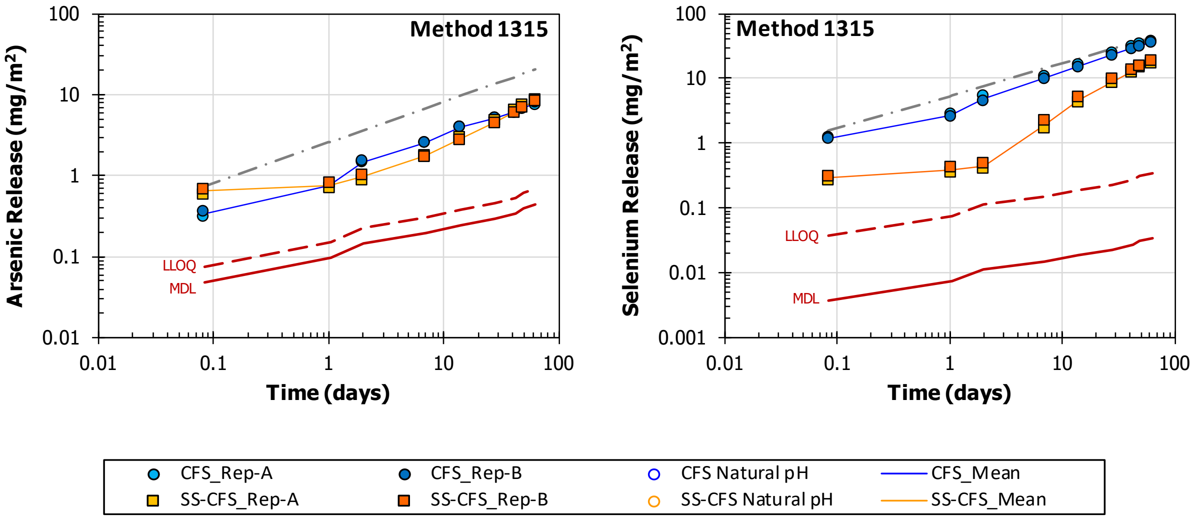

Figure 5-3. Method 1315 test results for arsenic and selenium release

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[32] The concentration measured in the first interval of Method 1315 is often biased by surface dissolution and sample preparation (*e.g.*, washing off of cutting swarf). Therefore, the mass released this first interval at 0.08 days is not used in calculations as it is not representative of the mass transport leaching behavior of the bulk material.

5.2.5 LSP Considerations

The suggested effective leaching concentrations for one and two-day infiltration events are based on Method 1315 data where a relatively small sample is exposed to a large bath of water to maintain the interval concentration gradients that drive mass transport. However, these conditions are not indicative of the majority of field conditions where, typically, a small volume of water contacts a relatively large surface area. Thus, the effective concentration calculations can numerically exceed the thermodynamic bounds of chemical equilibrium represented by the Method 1313 data. If the effective leaching concentration for any one- or two-day event is greater than the measured Method 1313 solubility-controlled eluate concentration, the effective concentration should be set to the Method 1313 maximum concentration over the pH domain:

$$\text{if } C1(or\ C2) > C^{1313}_{max\ pH\ domain}\text{; then } C1\ (or\ C2) = C^{1313}_{max\ pH\ domain}$$

The results of Method 1313 and 1314 testing for arsenic and selenium before and after treatment can be seen in Figure 5-4. Method 1313 shows that both COPCs have pH dependent solubility behavior above the regulatory thresholds and that the stabilization process (i.e., increased alkalinity) effects the leachate concentrations.

The arsenic behavior seen in Methods 1313 and 1314 (Figure 5-4) suggests that arsenic is solubility controlled as Method 1313 results show a strong dependence of solubility on pH while Method 1314 results show weak dependence on L/S. The selenium behavior appears to be available content limited as there is a strong dependence of concentration on L/S and a weak dependence on pH. In comparison, the Method 1315 test results (Figure 5-3) show an initial concentration likely representative of pore water values and surface effects before a more gradual increase in leaching with time. The grey dashed line indicates the expected Fickian diffusion that would occur if no other mass transport limitations were in place. Both arsenic and selenium show less leaching than predicted by Fickian diffusion in Method 1315.

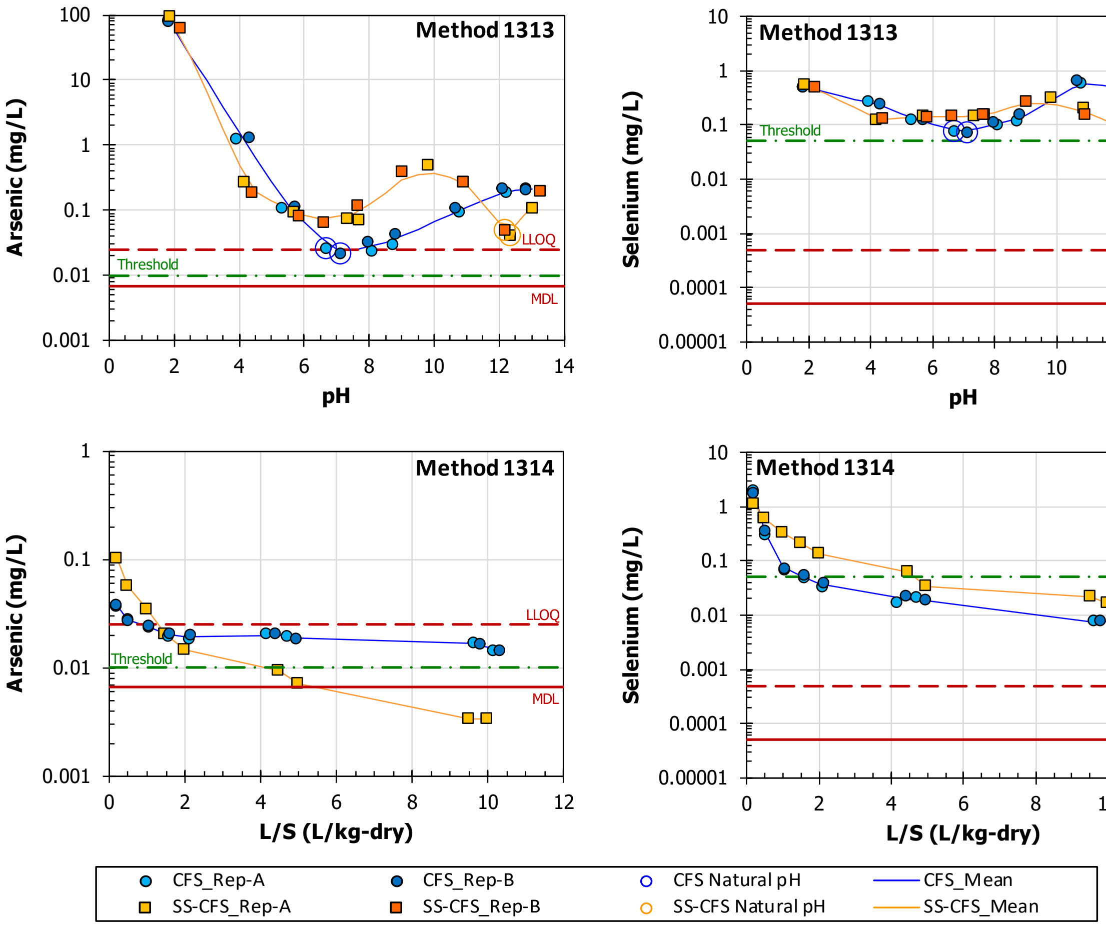


Figure 5-4. Method 1313 and 1314 test results for CFS and SS-CFS

The available content for arsenic and selenium can be determined from Method 1313 as the highest leachate concentration at a pH of 2, 9 and 13.

$$C_{leach\_max} = C_{1313(\max pH\ 2,9,13)}$$

Method 1313 also shows an increase in arsenic concentrations after treatment that directly overlaps with the scenario pH of 8 ≤ pH ≤ 13.3. The LSP limited concentration for arsenic is the maximum concentration within the pH range (including interpolation to endpoints of the pH range if necessary):

$$C_{leach\_max} = C_{1313(\ 8 \le pH \le 13.3)}$$

The mass transport scenario has the restriction that the total mass released cannot exceed the available content for a COPC. The interval mass release for an assessment interval *i* is calculated as:

$$M_i = \mathrm{M1} + \mathrm{M2} = \frac{(\mathrm{N1 \cdot C1 \cdot P1 \cdot A}_{inf} \cdot 1000)}{m_d} + \frac{(\mathrm{N2 \cdot C2 \cdot P2 \cdot A}_{inf} \cdot 1000)}{m_d}$$

The available content at the end of an assessment interval is estimated as previous available content minus the mass released over the assessment interval. If the available content for any assessment interval is less than zero, the COPC has depleted and the interval mass release is limited to the previous available content:

$$\text{if } (AC)_i < 0\text{; then } (AC)_i = 0 \text{ and } M_i = (AC)_{i-1}$$

The average leaching concentration should be adjusted to match the mass released over the assessment interval. ARs may be calculated for the mass transport scenario based on the estimated leaching concentration for an assessment interval or an averaged value for an assessment period.

5.2.6 Treatment Effectiveness

The cumulative release of selected COPCs for untreated CFS and cement-treated S/S-CFS over a 30-year timescale is shown in Figure 5-5. In each figure, the available content is the upper limit of mass release and the CFS mass release was normalized to the exposed surface area of S/S-CFS monolith. The comparison between the original material and the treated material illustrates the effectiveness of treatment for different constituents. In this case, treatment of the S/S-CFS material would be expected to significantly reduce the rate of leaching for cadmium, selenium, and lead. Arsenic leaching was reduced to a lesser amount while chloride and nitrate releases were only significantly reduced by treatment over shorter timescales than 30 years.

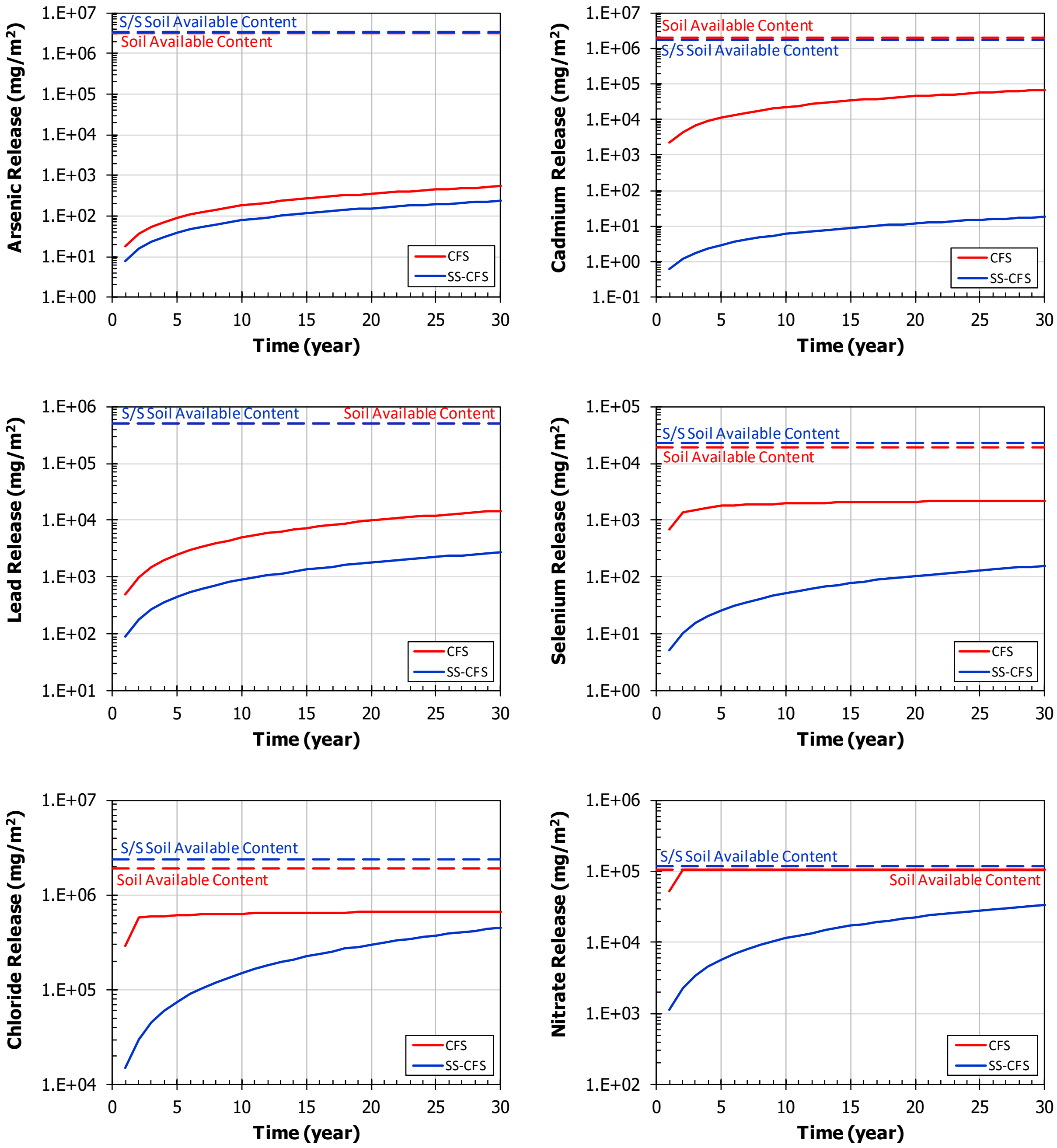


Figure 5-5. Mass transport limited leaching of arsenic, cadmium, lead, selenium, chloride, and nitrate.

5.2.7 Comparison to Reference Thresholds

The assessment ratio for COPCs can be calculated using the average concentrations for an assessment interval and the threshold values for this example, the U.S. EPA National Primary Drinking Water Regulations. In this scenario the point of compliance is at the unit boundary of the contaminated soil, meaning the leachate concentrations are directly compared to the threshold values with no consideration of dilution or attenuation. Table 5-9 below shows assessment ratios for 1, 5, and 30 year assessments. While the stabilization process was effective at reducing the mobility of the majority of the COPCs, Arsenic, lead and thallium remain above the threshold values. The proposed remedy for this site of in-situ stabilization with Portland cement is not appropriate based on LEAF testing results and the assumptions made in the assessment to estimate leaching in the field.

All leaching assessments make simplifying assumptions when developing estimates of leaching. This example provided estimates of leaching in the field assuming that LEAF test results from short timescales can represent long term behavior, and also relied on net infiltration parameters derived from 30 years of meteorological data to anticipate field conditions. In cases where leaching of COPCs exhibits time dependent behavior (e.g., one or more constituents becomes depleted), an average value for an assessment interval may not appropriately reflect the environmental conditions. Users of LEAF testing should work closely with the appropriate regulatory body when developing a leaching evaluation to meet regulatory requirements.

Table 5-9. Comparison of leaching assessment results to reference thresholds

COPC	Threshold (mg/L)	1-Year Assessment		5-Year Assessment		30-Year Assessment	
		C_{av} (mg/L)	AR (-)	C_{av} (mg/L)	AR (-)	C_{av} (mg/L)	AR (-)
Antimony	0.006	0.0022	*0.4*	0.0022	*0.4*	0.0022	*0.4*
Arsenic	0.01	0.018	1.8	0.018	1.8	0.018	1.8
Cadmium	0.005	0.0014	*0.3*	0.0014	*0.3*	0.0014	*0.3*
Chloride	250*	36	*0.1*	36	*0.1*	36	*0.1*
Chromium	0.1	0.014	*0.1*	0.014	*0.1*	0.014	*0.1*
Copper	1.3	0.070	*0.05*	0.070	*0.05*	0.070	*0.05*
Fluoride	4	0.019	*<0.01*	0.019	*<0.01*	0.019	*<0.01*
Lead	0.015	0.20	14	0.20	14	0.20	14
Nitrate	44	2.7	*0.06*	2.7	*0.06*	2.7	*0.06*
Selenium	0.05	0.014	*0.3*	0.014	*0.3*	0.014	*0.3*
Sulfate	250*	140	*0.6*	140	*0.6*	140	*0.6*
Thallium	0.002	0.17	87	0.17	87	0.17	87
Zinc	5*	0.018	*<0.01*	0.018	*<0.01*	0.018	*<0.01*

Notes: Orange italic text indicates ARs ≤1 (*i.e.*, no further assessment is required).

Threshold values based on U.S. EPA National Primary Drinking Water Regulations (U.S. EPA 2009) with * indicating secondary drinking water criteria.

6. Test Your Knowledge

The below exercises are based on the data used in the screening assessment case study above in Section 5.1. The calculations and concepts used below are explained in Section 4. This example is for illustrative purposes and is not intended to be directly applied to an evaluation. The actual use of LEAF testing must be tailored to a given purpose and site-specific conditions that may occur.

6.1 Paula's First Assignment

Paula the program manager is a new employee at a state environmental agency. Paula is working on a team to determine whether fly ash can be used as structural fill in a local project. The team assigns Paula to study the potential effects of the fly ash material on groundwater. The potential for leaching of constituents of concern to groundwater had been overlooked to this point by the team and Paula is starting from the beginning. Paula is eager to impress her new supervisor and coworkers, and she knows that she needs to start with a good testing plan to characterize the material. After talking to the analytical chemist in the Agency's testing lab, Paula realizes that she needs to understand her material and the environment to choose the right leaching tests.

Question 1: What does Paula need to know about her material and the environment before she can develop a leaching evaluation?

(See next page for answer)

Answer 1: What does Paula need to know about her material and the environment before she can develop a leaching evaluation?

- Paula needs to know the composition of her material and which constituents of concern are present.
- Paula also needs to know what the anticipated field conditions (now and over time) are in order to estimate leaching under the right conditions. For example, many inorganic constituents have pH dependent leaching behavior. Additionally, the amount, frequency, and mode of water contacting the material needs to be understood or estimated. Testing of soil at a site or consultation with databases for rainfall or soil data can provide valuable information.
- Paula will also need threshold values to compare her leaching estimates to. In some cases, the total content of constituents of concern may be so high or so low, testing will not provide value. For example, if leaching tests (or total content) show that leaching values will not exceed the relevant thresholds, then no further analysis may be needed. If there is uncertainty in the estimated leaching, further testing may determine a material is or is not appropriate for use.

6.2 Characterizing the Fly Ash

Paula checks back in with her analytical lab and learns that she is in luck. The total content analysis of a representative sample of fly ash has already been completed using acid digestion (EPA Method 3052) followed by ICP-OES (EPA Method 6010). The total content testing (shown below) indicates that the constituents of concern are primarily inorganic. The pH of the fly ash material is 6.8 and the pH of the soil the fly ash will be adjacent to is 6.0. Paula expects the fly ash material pH to control the pH of the leachate as the soil has no significant buffering capacity. Paula decides the default pH range suggested in the LEAF How-To Guide (Section 4.2.5.1) of $5.5 \leq pH \leq 9.0$ could be used here to estimate the anticipated pH of the fly ash and to estimate behavior if the pH were to change over time. Paula checks her notes from the team meeting to remind herself that the infiltration rate is expected to be 25 cm per year and the fly ash material will be compacted to 1,500 kg-dry/m^3. Before investing resources into testing, Paula compares the total content of her material against standards set by EPA drinking water regulations. She notes that the total concentrations of arsenic, chromium, and other inorganics appear high and warrant further testing before a decision is made on the appropriateness of the fly ash as structural fill.

COPC	**Total Content** [mg/kg-dry]	**Drinking Water Standard** [mg/L
Antimony (Sb)	1.5	0.006[N1]
Arsenic (As)	63	0.01
Barium (Ba)	830	2
Boron (B)	1,400	7[N2]
Cadmium (Cd)	3.5	0.005
Chromium (Cr)	120	0.1
Lead (Pb)	39	0.015[N3]
Molybdenum (Mo)	15	0.2[N2]
Selenium (Se)	24	0.05
Thallium (Tl)	0.91	0.002

Source: U.S. EPA (2012c, 2012d)

Drinking water standards are the National Primary Drinking Water Regulations (U.S. EPA, 2012a) unless noted:

[N1] National secondary drinking water regulations—non-enforceable guideline.

[N2] Drinking water equivalent level.

[N3] Treatment technique action level.

Question 2: Which constituents listed in the table above are of potential concern to Paula based on total content analysis?

(See next page for answer)

Answer 2: Which constituents are of potential concern to Paula based on total content analysis?

In this scenario Paula is comparing constituents against drinking water standards. All of the constituents listed in the table are above the drinking water standards and therefore are of concern to Paula.

In real applications, the standards against which a constituent is compared should be carefully considered. Consultation with the appropriate regulatory body may be needed.

Part 3: Paula's Proposed Testing Plan

Armed with knowledge of the material and the anticipated environmental conditions, Paula knows she needs to determine what tests are appropriate to estimate leaching from the fly ash. She knows that there are a variety of tests that may help her predict leaching in the environment, but she is specifically looking for testing that applies to inorganic constituents such as lead, arsenic, and chromium. This helps her narrow down the list, removing tests focused on organics or designed to simulate specific scenarios that do not adequately represent structural fill. She decides to then check with her coworkers, and the state's analytical laboratory to see what existing testing capabilities are available. Finally, before spending time and resources on testing, Paula checks in with technical consultant hired onto the project, who just happens to be you.

Question 3: What leaching tests should Paula employ in her evaluation?

(See next page for answer)

Answer 3: What leaching tests should Paula employ in her evaluation?

- Paula knows there are a variety of leaching tests available for inorganics, such as the EPA Methods; TCLP, SPLP, or LEAF Methods 1313, 1314, 1315, or 1316; ASTM Standards D-3897 or D-4874; and European methods such as EN 14429, NEN 7373, or EN 15863.
- The TCLP (EPA Method 1311) employs buffered solutions of acetic acid (either pH of 4.93 or 2.88) to simulate conditions in municipal solid waste landfills. TCLP is likely not the best choice for Paula as there is no acetic acid in her anticipated environment or in the waste and Paula is interested in evaluating pH dependent leaching closer to a pH of 6.
- The SPLP (EPA Method 1312) is designed to simulate leaching of organic or inorganic constituents in soils and employs a leachant consisting of a mixture of sulfuric and nitric acid with a pH of 4.2 or 5 depending on whether the soil is east or west of the Mississippi River. SPLP is not likely to be the most appropriate test for Paula's anticipated environmental conditions.
- EPA Method 1313 will allow Paula to estimate leaching in the field within a window of pH endpoints. Equilibrium data from this test alone will provide an estimate of the upper bound, or available content, that a constituent that may leach at a given pH. EPA Method 1313 is generally applicable to most scenarios with inorganics that have pH dependent solubility.
- EPA Method 1314 or EPA Method 1316 will allow Paula to estimate L/S dependent leaching behavior of the fly ash. The L/S dependent leaching results from either test will provide information on whether the material is solubility or availability controlled. EPA Method 1314 estimates percolation-based leaching in an open system, which may also provide insight into percolation-based effects or preferential flow. Method 1316 estimates equilibrium results from batch testing. In some cases, both tests may provide useful and complimentary results. However, testing from one of these two methods is often sufficient.
- EPA Method 1315 estimates mass transport limited leaching from densely compacted or stabilized material. The fly ash is not solidified into a bound matrix or otherwise densely compacted. As a result, this test method will provide minimal value to Paula's evaluation.

Note: This question does not have one right answer. A variety of other tests to estimate leaching are available that may or may not be suitable. LEAF testing is chosen for the purposes of this guide. See the Appendix for a comparison of LEAF testing to analogous European standards.

6.3 Preliminary Available Content Evaluation

Paula knows that she is interested in evaluating pH dependent behavior of her fly ash and selects EPA Method 1313 to do so. She also knows that L/S can be used as a surrogate for leaching over time and elects to choose EPA Method 1314 to evaluate this parameter (Note: Paula could have also chosen Method 1316 to evaluate L/S and it is not necessarily wrong to choose one or both methods for this purpose.) The analytical lab completes Method 1313 and 1314 testing and sends the test results to Paula. Paula is particularly worried about the high concentrations of arsenic in the leachate. Before proceeding to evaluate the solubility within the pH range of interest, Paula checks the available content for arsenic using Method 1313 results.

Question 4: Can you determine the available content for arsenic from the Method 1313 lab results (next page)? Hint: Paula recalls from reading the LEAF How-To Guide that available content is calculated from the highest concentrations in the leachate at pH 2, 9 or 13 (see Section 4.4.1).

Concentration in mg/L

Fraction	*9*	*8*	*7*	*6*	*5*	*4*	*3*	*2*	*1*
pH	*2.08*	*3.85*	*5.40*	*6.99*	*7.97*	*9.26*	*10.4*	*12.0*	*13.1*
Al	128	32.0	0.335	0.202	1.21	17.7	27.1	33.8	37.0
As	1.55	0.0900	0.0417	0.0784	0.199	0.560	1.05	1.01	9.69
B	3.25	3.82	4.98	4.62	4.38	4.50	4.64	4.99	9.77
Ba	0.876	0.220	0.281	0.260	0.256	0.562	0.903	0.921	0.659
Be	0.441	0.142	0.00258	(0.000320)	(0.000320)	(0.000320)	(0.000320)	(0.000320)	(0.000320)
Br^-	(0.00871)	0.668	0.687	0.515	0.598	0.700	0.652	0.722	0.827
Ca	141	140	167	155	135	111	87.3	40.9	9.20
Cd	0.0555	0.0427	0.0311	0.00580	0.00470	0.00460	0.00461	0.00505	0.00540
Cl^-	1.64	1.57	1.25	1.30	1.28	1.30	1.26	1.30	4.19
Co	0.419	0.214	0.252	0.0261	0.00430	0.00140	0.00118	0.000726	(0.000207)
Cr	1.96	0.175	(0.000249)	0.0422	0.134	0.223	0.248	0.306	0.392
Cs	0.0642	0.0239	0.0172	0.0130	0.0148	0.0188	0.0218	0.0282	0.0336
Cu	3.16	1.91	0.0894	0.000900	(0.000351)	(0.000351)	0.000900	0.00192	0.0179
DIC	0.138	0.150	0.154	(0.0650)	(0.0650)	0.653	1.93	7.95	29.2
DOC	1.69	1.04	1.06	1.15	1.21	1.83	3.19	9.66	142
F^-	0.0945	3.34	0.409	1.70	2.05	3.13	3.62	3.91	9.38
Fe	33.9	0.419	(0.00100)	(0.00100)	(0.00100)	(0.00100)	(0.00100)	0.0202	0.0339
K	22.1	18.6	26.1	25.0	55.3	135	190	441	1719
Li	1.51	2.12	3.26	3.24	2.97	2.70	2.56	2.23	1.56
Mg	14.0	7.69	8.90	7.49	5.10	2.86	0.111	(0.000500)	(0.000500)
Mn	1.84	1.17	0.982	0.268	0.0324	(0.000171)	(0.000171)	(0.000171)	(0.000171)
Mo	0.334	0.108	0.552	3.32	3.49	3.70	3.83	3.77	3.92

See next page for answer

Answer 4: Can you determine the available content for arsenic from the lab results?

Paula knows that the available content will be determined by the highest leaching concentration at a pH of 2, 9, or 13. For arsenic, the highest concentration in the leachate is 9.69 mg/L at a pH of 13.1. However, Paula needs to interpolate to estimate the concentration of arsenic at a pH of 13. In this case the pH endpoints of 13.1 and 12.0 are used to interpolate. Using Equation 4-13 from section 4.4.2, the concentration of arsenic in the leachate is found to be 7.9 mg/L at a pH of 13.

$$logC_{As} = logC_a + (pH - pH_a) \times (logC_b - logC_a)/(pH_b - pH_a)$$

$$logC_{As} = log(9.69) + (13 - 13.1) \times (log(1.01) - log(9.69))/(12 - 13.1)$$

$$\mathrm{C_{As}} = 7.9\,\frac{\mathrm{mg}}{\mathrm{L}}$$

Now that Paula has the concentration of arsenic in the leachate at a pH of 13, she needs to account for the liquid to solid ratio in Method 1313 using Equation 4-12 (See section 4.4.1)

$$m_{avail} = C_{max(pH\ 2,9,13)} \times (L/S)_{1313}$$

$$m_{avail} = 7.9\,\frac{mg}{L} \times 10\,\frac{L}{Kg - dry}$$

$$m_{avail} = 79\,\frac{mg}{kg - dry}$$

Available content can be reported as mg/kg-dry, however, Paula wants to be able to compare the available content to a leachate concentration that may represent her environmental scenario. Paula uses the initial L/S value of 0.5 to estimate the maximum potential for leaching when the material is initially placed as structural fill, based on available content.

$$C_{leach\_max} = m_{avail}/(L/S)_{initial}$$

$$\mathrm{m_{avail}} = 79\,\frac{\mathrm{mg}}{\mathrm{LKg - dry}}/0.5\,\frac{\mathrm{L}}{\mathrm{Kg - dry}}$$

$$\mathrm{m_{avail}} = 158\,\frac{\mathrm{mg}}{\mathrm{L}}$$

6.4 Paula's Plausible Range of pH Dependent Leaching

Paula is not relieved to see her available content estimate for arsenic is considerably higher than the regulatory thresholds for drinking water. However, Paula knows that her anticipated environment considers a pH between 5.5 and 9. Using the same data from Method 1313, Paula can calculate the maximum concentration of arsenic in the leachate within her anticipated conditions. What concentrations of arsenic can Paula expect to see in her leachate when she considers the applicable pH range?

Question 5: What is the maximum concentration of arsenic in the anticipated pH range? (Hint: Use the Method 1313 data from the table provided in Question 4.)

See next page for answer

Answer 5: What is the maximum concentration of arsenic in the anticipated pH range?

The maximum concentration of arsenic in the anticipated pH range is 0.46 mg/L. The Method 1313 data shows an arsenic concentration of 0.56 mg/L at a pH of 9.26 and 0.199mg/L at a pH of 7.97. The arsenic solubility is increasing with increasing pH and the highest pH in the anticipated pH range is 9. Paula therefore needs to interpolate an arsenic concentration value at pH 9 using the data at a pH of 9.26 and a pH of 7.97.

$$\boldsymbol{logC_{As} = logC_a + (pH - pH_a) \times (logC_b - logC_a)/(pH_b - pH_a)}$$

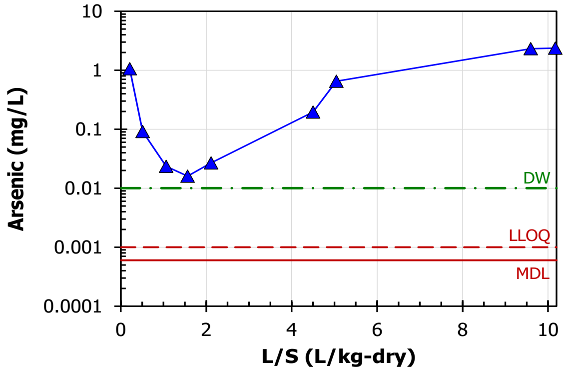
$$\boldsymbol{logC_{As} = log(0.56) + (9 - 9.26) \times (log(0.199) - log(0.56))/(7.97 - 9.26)}$$

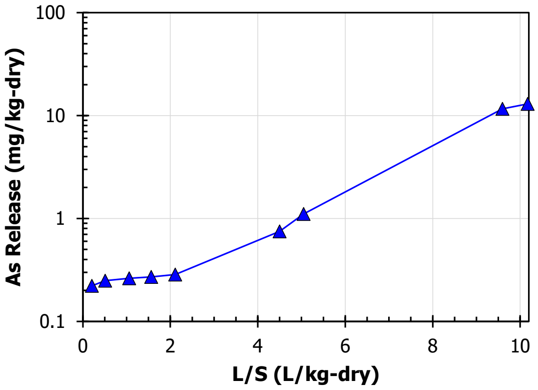
$$\mathbf{C_{As} = 0.46\ \frac{mg}{L}}$$

6.5 Confirming Solubility Limited Leaching

Paula reviewed the Method 1313 results and suspects that the leaching behavior of arsenic in her anticipated environment is solubility limited. She noticed that the leachate concentration controlling her available content, 7.9 mg/L at pH 12, is significantly higher than the maximum leaching concentrations within the anticipated environmental window, 5.5 ≤ pH ≤ 9.0, of 0.46 mg/L at pH 9. Paula would like to confirm the solubility limited behavior with the Method 1314 results.

Question 6: How can Paula confirm that arsenic is solubility limited using her Method 1314 data below? Hint: Paula realizes in reviewing her data that the L/S behavior of arsenic below an L/S ratio of 2 is controlled by interactions between calcium and arsenic. The calcium has washed out of the column at an L/S ratio greater than 2.





See next page for answer

Answer 6: How can Paula confirm that arsenic is solubility-limited using the 1314 data below?

- Paula can tell that the arsenic leaching is solubility controlled because the cumulative release of arsenic is a strong function of L/S (right figure).
- The method 1314 data in the left figure shows the concentration of arsenic is dependent on L/S below an L/S of 2 (L/Kg-dry). Solubility controlled leaching does not often show a strong dependence of concentration on L/S. However, Paula realized from looking at her other constituents that the solubility of arsenic at low L/S values was likely controlled by calcium, which washed out of the system at an L/S close to 2 (L/kg-dry).
- Paula can also compare the cumulative arsenic release at an L/S of 10 (mg/kg-dry) to the available content of 79 (mg/kg-dry). The release of only 14% of the available arsenic by an L/S ratio of 10 indicates the leaching is limited by solubility. Available-content limited leaching would have been expected to leach almost all of the available arsenic by or before L/S 10.
- A slope close to 1 on a logarithmic plot of cumulative constituent release versus L/S is often an indicator of solubility-limited leaching. Available-content limited leaching will often show a more rapid release of the constituent (e.g., an exponential curve).

6.6 Conclusions on Use for Structural Fill

While Paula has learned a great deal about the potential behavior of the arsenic in the fly ash, her analysis has not concluded that the fly ash is suitable for use as a structural fill. The estimated leaching concentration from Method 1313 results within the anticipated pH range of 0.46 mg/L is above Paula's threshold of the 0.01 mg/L drinking water standard. In addition, analysis of the 1314 data indicates that arsenic levels will reach 2.4 mg/L at an L/S of 10. The higher concentrations of arsenic at high L/S are a result of the initially acidic nature of the fly ash (likely from acid washing) changing over time to a more alkaline pH that better solubilizes (and therefore mobilizes) arsenic. At the same time, constituents such as calcium lower arsenic solubility while present but eventually wash out of the method 1314 column test. Paula returns to her supervisor with her results and to discuss considering alternative materials for structural fill in the project.

7. Useful Resources

Resource	Available Online[1]
LeachXS and LeachXS Lite	*www.vanderbilt.edu/leaching/leach-xs-lite/* *www.leachxs.com/lxsdll.html*
LeachXS Lite data templates	*www.vanderbilt.edu/leaching/downloads/test-methods/*
LEAF leaching test methods	*https://www.epa.gov/hw-sw846/validated-test-methods-recommended-waste-testing*
TCLP leaching test method	*https://www.epa.gov/hw-sw846/sw-846-test-method-1311-toxicity-characteristic-leaching-procedure*
SPLP leaching test method	*https://www.epa.gov/hw-sw846/sw-846-test-method-1312-synthetic-precipitation-leaching-procedure*
EPA test methods: frequently asked questions	*https://www.epa.gov/hw-sw846/frequent-questions-about-sw-846-compendium-and-related-documents*
ORCHESTRA: geochemical speciation and reactive transport code	*http://orchestra.meeussen.nl/*
PHREEQC: computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations	*wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc*
MINTEQA2: geochemical equilibrium speciation model	*www2.epa.gov/exposure-assessment-models/minteqa2*
The Geochemist's Workbench: geochemical modeling software	*www.gwb.com*
IWEM: deterministic groundwater fate and transport model	*https://www.epa.gov/smm/industrial-waste-management-evaluation-model-version-31*
EPA's Leaching Test Relationships, Laboratory-to-Field Comparisons and Recommendations for Leaching Evaluation using the Leaching Environmental Assessment Framework (EPA/600/R-14/061)	*www.vanderbilt.edu/leaching/wordpress/wp-content/uploads/600r14061-Lab-to-Field-LEAF1.pdf*
EPA's Background Information for the Leaching Environmental Assessment Framework (LEAF) Test Methods (EPA/600/R-10/170)	*https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryID=231332*
EPA's Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Method 1313 and Method 1316 (EPA/600/R/12/623)	*https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryID=307273*
EPA's Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Method 1314 and Method 1315 (EPA 600/R-12/624)	*nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100FAFC.TXT*
EPA's Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control (EPA/600/R-06/008)	*https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryID=147063*
EPA's Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control (EPA/600/R-08/077)	*nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100EEGL.txt*
EPA's Characterization of Coal Combustion Residues from Electric Utilities—Leaching and Characterization Data (EPA/600/R-09/151)	*nepis.epa.gov/Adobe/PDF/P1007JBD.pdf*
EPA's Leaching Behavior of "AGREMAX" Collected from a Coal-Fired Power Plant in Puerto Rico (EPA/600/R-12/724)	*nepis.epa.gov/Adobe/PDF/P100G02B.pdf*
EPA's The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on the Leaching Constituents from Cements and Concretes (EPA/600/R-12/704)	*nepis.epa.gov/Adobe/PDF/P100FBS5.pdf*
EPA's Final Report for Sampling and Analysis Project—Beneficial Use of Red and Brown Mud and Phosphogypsum as Alternative Construction Materials	*nepis.epa.gov/Adobe/PDF/P100BMWU.pdf*
EPA's Composite Model for Leachate Migration with Transformation Products (EPACMTP)	*www.epa.gov/epawaste/nonhaz/industrial/tools/cmtp/index.htm*

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