

**Application of New Leaching Protocols for
Assessing Beneficial Use of Solid Wastes in Florida**

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
ABM	Abrasive Blasting Media
AES	Atomic Emission Spectrometry
ASTM	American Society for Testing and Materials
Avg.	Average
BDAT	Best Demonstrated Available Technology
BDL	Below Detection Limit
C&D	Construction and Demolition
CCA	Chromated Copper Arsenate
COD	Chemical Oxygen Demand
COPC	Constituents of Potential Concern
DAF	Dilution Attenuation Factor
DI	Deionized
EP-TOX	Extraction Procedure for Toxicity
FDEP	Florida Department of Environmental Protection
GCTL	Groundwater Cleanup Target Levels
HDPE	High Density Polyethylene
ICP	Inductively Coupled Plasma
LBP	Lead-Based Paint
L/S	Liquid-to-Solid Ratio
LDR	Land Disposal Restriction
MEP	Multiple Extraction Procedure
MSW	Municipal Solid Waste
NPOC	Non-Purgeable Organic Carbon
ORP	Oxidation Reduction Potential
QA/QC	Quality Assurance / Quality Control
RCRA	Resource Conservation and Recovery Act
SCTL	Soil Cleanup Target Level
SPLP	Synthetic Precipitation Leaching Procedure
Std. Dev.	Standard Deviation
TC	Toxicity Characteristic
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total Dissolved Solids
US EPA	United States Environmental Protection Agency
WET	Waste Extraction Test

UNITS OF MEASURE

cm	Centimeter
cm ²	Square centimeters
cm ³	Cubic centimeters
ft ³	Cubic feet
g	Gram
kg	Kilogram
L	Liter
lb/ft ³	Pounds per cubic foot
mg	Milligrams
mg/kg	Milligrams per kilogram
mL	Milliliter
mL/g	Milliliter per gram
mg/L	Milligram per liter
pH	Measurement of the hydrogen ion activity or acidity of water
μg	Microgram
μg/L	Microgram per liter
μm	Micrometer

KEYWORDS

Batch Test

Beneficial Use

Column Test

Groundwater Cleanup Target Levels (GCTLs)

Leaching

Liquid-to-Solid Ratio (L/S Ratio)

Lysimeter

Risk

Soil Cleanup Target Levels (SCTLs)

Synthetic Precipitation Leaching Procedure (SPLP)

Toxicity

Toxicity Characteristic Leaching Procedure (TCLP)

Wood and Tire Ash

ABSTRACT

The US EPA has supported the development of a new suite of leaching procedures (Leaching Environmental Assessment Framework, LEAF) that can provide a greater amount of information on chemical leaching from a waste under different environmental conditions. The intent and procedures of these leaching tests as well as other tests which have been used for characterization are discussed. Previous beneficial use assessments for a number of waste materials in Florida are summarized. The characterization tests and resulting guidance based on the previously employed leaching/ risk assessment test results are summarized along with the impact that the implementation of additional leach testing could have had on these decisions. In order to conduct a case study to demonstrate the potential for the impact of the LEAF methods lab testing was conducted on three waste materials: wood-tire ash, coal combustion residue, and waste-to-energy ash. The three case study results and interpretation are provided and demonstrate how LEAF can be used in conjunction with established leaching tests in a beneficial use risk assessment. A Guidance Document was drafted to accompany this report and is contained in the Appendix. This document can serve as a standalone resource which provides a simple tool for regulatory agencies, landfill operators, and waste generators to understand the different leaching tests that are available, how they are performed, and how to interpret the results from these tests.

EXECUTIVE SUMMARY

(Dates: 09/01/14 to 06/01/16)

PROJECT TITLE: Application of New Leaching Protocols for Assessing Beneficial Use of Solid Wastes in Florida

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PROJECT WEB SITE: <http://www.essie.ufl.edu/home/townsend/research/leaching-tests-for-characterizing-wastes/hc14/>

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PROJECT SUMMARY:

The Leaching Environmental Assessment Framework, or LEAF, was released by the US EPA in 2010. The introduction of these tests raised questions on their utility and how the data would compare to historically used tests such as the Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure (SPLP). Questions were raised regarding whether the LEAF tests would change the results of a beneficial use assessment and what utility they would provide.

As a part of this project the utility of each of the leaching tests is outlined. TCLP testing is designed for toxicity characteristic hazardous waste characterization and has little applicability for beneficial use. The SPLP is the test which historically has been used to examine beneficial use and serves as a good screening level test with a large volume of historical data. The LEAF suite of tests is composed of four methods. Method 1313 examines leaching as a function of pH and can be used to evaluate the impact of waste treatment or behavior in a beneficial use scenario where the pH would not be representative of the natural pore water conditions. Methods 1314 and 1316 serve to examine leaching as a function of liquid to solid ratio and can illustrate whether pollutant concentrations remain constant or are depleted over time. Method 1315 tests a waste material in a monolithic or compacted granular form and can serve to provide both a more realistic evaluation of waste leaching in the as-used condition as well as allow for the calculation different sources terms for use in transport modeling.

A review of previous beneficial use assessments and leach testing on three case study wastes demonstrated that for many of the assessments conducted the application of LEAF tests would not have dramatically altered the final outcome. Scenarios where pH conditions were different than the natural pH encountered in SPLP would perhaps be the most significant example of where results of previous and current tests could have differed. A guidance document was developed and is contained in the report's Appendix which provides a user friendly guide on leach tests, their utility, and appropriate use.

METRICS

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1.0 Relevant Background and Prior Efforts

1.1 Solid Waste Management Decision Making

The ability to appropriately and consistently quantify environmental risk is an essential component in solid waste management decision making and policy development. With additional tools such as pollutant transport modeling and a wide variety of leaching tests, the process for conducting an appropriate risk assessment can become convoluted. Presently, these types of assessments have been used at the federal level to evaluate risk for coal combustion residuals, and at the state level for waste products such as recovered screened material, recycled concrete, and waste to energy ash. As beneficial use becomes a topic of increased focus, due in part to the desire to increase recycling rates and reduce greenhouse gas emissions (through a reduction in the use of virgin construction materials), the use of these types of methodologies will become more common place. Therefore, it is essential that the utility of the available leaching test be well understood. The EPA released a new suite of leaching tests in 2010, referred to as the LEAF (Leaching Environmental Assessment Framework) methods which are rapidly being adopted and used in risk assessment processes. This documents outlines leaching tests which are currently used and provides a description of historically employed leaching procedures and their intent.

As the currently employed leaching procedures differ from those previously used in risk assessments, the natural question is whether the outcome of these evaluations would have differed based on the test employed. As the second component of this study the researchers examined past risk assessments conducted for waste materials in the state of Florida and evaluated how the introduction of new test measures could have influenced the results. While leaching tests provide a mechanism for the quantification of the concentration of constituents of potential concern (COPC) released from a waste material, these values must be compared to a set standard or threshold to allow for a judgement on the risk posed by the proposed application. Often times a pollutant fate and transport model, such as the US EPA's IWEM (Industrial Waste Management Evaluation Model), is used to account for a degree of pollutant dilution and attenuation before the results are compared to a threshold value.

In the State of Florida, two different exposure pathways are typically considered when evaluating environmental risk: direct human exposure and leaching to water supplies. Direct human exposure is commonly evaluated by conducting a refereed laboratory procedure to determine the total environmentally available element concentration, calculating a statistical confidence interval of the data set and comparing this value to a risk thresholds, such as standard for contaminated soil at a contaminated site cleanup. As there are no consistent clean soil standards at the federal level, there is a variance from state to state; in the state of Florida, the Soil Cleanup Target Levels (SCTLs) are commonly used as the clean soil standard when evaluating beneficial use, and are typically reported in units of mg-COPC/kg-dry mass soil. These standards reflect a 1 in 1,000,000 health risk and exposure assumptions relating to either a commercial or residential site.

Unlike soil screening levels, drinking water standards have been set at the federal level for a large number of COPC. These standards are typically adopted as the risk thresholds used to evaluate the contamination of water bodies (typically after an environmental model is employed); for COPC where explicit standards have not been set at the federal level the majority of states adopt a risk threshold based on a relative health risk and exposure assumptions. In Florida, the Groundwater Cleanup Target Levels (GCTLs) are commonly used as the thresholds for evaluating leaching risk in beneficial use applications. These are reported in units of mg-COPC/L-leachate. Many of these standards are reflective of U.S. primary drinking water standards while others are derived using the health risk approach discussed above.

1.2 Leaching Test Application in Florida

In recent years, the investigators have conducted the LEAF testing on several waste streams relevant to the Florida solid waste community as a part of other research efforts. While the LEAF tests provide additional data, questions have been raised with regard to their application as well as differences between the currently utilized tests. This was illustrated in previous Hinkley Center research by the investigators. A recently completed project, *Exploring Pathways and Limitations to Recycling Combustion Residuals in Florida*, brought professionals together from both the industry and the regulatory community to discuss the recycling of fuel combustion residuals in Florida. Members of the working group raised concerns that LEAF protocols were being suggested as a requirement for future testing of coal combustion products. Specific issues related to the cost associated with the testing and how the test results could be used or interpreted.

One such example of how testing data could be inappropriately interpreted are results from LEAF Method 1313 testing. In Method 1313 wastes are tested at a range of static pH's including a highly acidic test at a pH 2. While this data point certainly could provide utility by acting as an indicator of the total amount of an element in a waste, waste leaching at a pH of 2 is a scenario not typically encountered in a beneficial use application. These results would typically be elevated with respect to data at other pH values, as many metals are highly soluble at this pH and concerns were raised that this data could be used incorrectly.

Dialogue by the project's working group also included a discussion focused on the recycling of waste products in applications such as roads and uncertainties regarding the interpretation of leaching test results with respect to regulated points of compliance. Consider Figure 1, for example, which illustrates potential points of compliance for a beneficially used waste material. Discussion centered on the issue that the leaching test data represented the concentration of the pore water leaving the waste material and that an appropriate methodology was needed to predict concentrations some distance away from the intended use. Further discussion centered on the most appropriate mechanisms for such an assessment and what additional data would need to be collected in order for it to be completed.

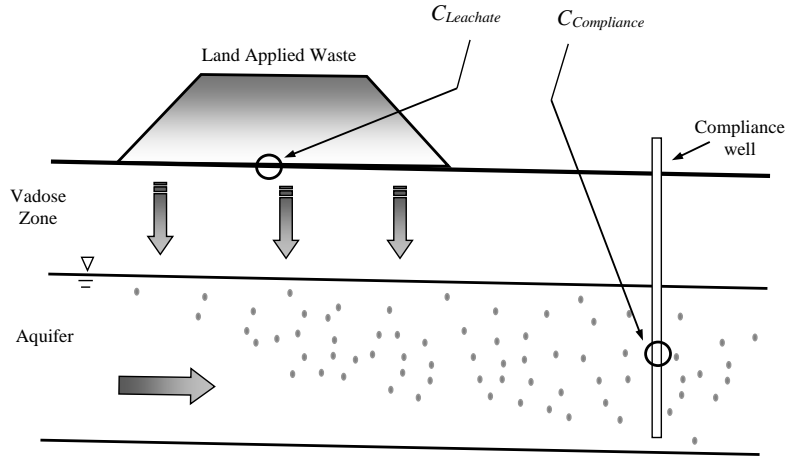


Figure 1. Conceptual Illustration Of Points of Compliance

1.3 Approach

The intent of this work was to examine the LEAF methods in the context of historic and current beneficial use assessments (in Florida), and develop guidance for the Florida solid waste industry and regulatory community on the appropriate use of leaching protocols for solid waste management risk assessment and decision making. Specific objectives included:

- Fully documenting the LEAF leaching procedures and developing a simple guidance document which provides an overview of the different methods and their utility
- The examination of previous beneficial use assessments and an evaluation on how their outcome could have been impacted by the incorporation of LEAF testing
- Additional leach testing on three wastes identified by the project's TAG, evaluation of the dataset and observation of differences between LEAF and other leaching methods

1.4 Document Organization

This report is separated into five chapters as well as the leaching guidance document which is contained in the Appendix. This guidance document has been developed to serve as a standalone reference. Chapter Two provides a description of the method and its intent for a variety of established and newly adopted leaching procedures. Chapter Three summarizes previous beneficial use assessments for waste materials in Florida, discussing the characterization tests used and the regulatory guidance provided based on the leaching test and risk assessment results. This chapter also discusses how the newly adopted LEAF tests may have contributed to or changed the beneficial use decision for these materials. Chapter Four describes the results of the additional leach testing on the selected waste products. A report summary and conclusions are provided in Chapter Five.

2.0 Review of Leaching Methods

This section provides a description of leaching tests and their utility. A number of these procedures were outlined in *Leaching Tests for Evaluating Risk in Solid Waste Management Decision Making* a previous Hinkley Center project which examined similar issues (Townsend et al., 2003). The LEAF methods are discussed in addition to the previously outlined leaching tests. A list of available leaching tests and a number of conceptual diagrams describing them are also presented in the Guidance Document that accompanies this report.

2.1 Overview of Leaching Methods

Leaching tests can be divided into four major categories: batch extraction tests, lysimeter or column tests, tank tests, and the field-scale leaching experiments. Over the past several decades a large assortment of leaching tests have been developed and conducted. This document focuses on describing tests which either were or are frequently employed in waste characterization and decision making.

Batch tests involve the introduction of a waste material (typically sized reduced to some degree) to a bottle or other closed vessel, the waste is then introduced to an extraction solution (such as deionized water) and agitated (typically through rotation); the dissolved concentrations of COPCs are then measured. Tank tests are a subset of batch leaching tests that involve immersing a monolithic or compacted granular waste sample in to a tank, unlike the majority of batch leaching tests, the tank test do not rotate the leaching vessel but allow chemicals to diffuse out from the material over time. Tank leaching tests are similar to column tests with respect to the increased time and costs in comparison to more traditional batch leaching tests. Tank tests typically evaluate pollutant release from the material in its monolithic form or as a compacted granular specimen (in order to represent physical conditions that would occur in actual applications), these tests can provide valuable data on the elemental mass release from a waste product as a function of time and help to identify the mechanisms of contaminant release present.

Column tests (often called a “lysimeter test” when the column size is relatively large or it is placed in the field for testing) are another type of leaching test used to study the leaching processes from a waste material. The test involves a continuous flow of a leaching solution through waste material placed in a column. Unlike laboratory batch leaching tests, which are performed under controlled conditions (e.g., pH, liquid to solid ratio, contact time), the column test is designed to simulate actual field conditions. Column leaching experiments have been widely used to examine the fate and movement of pesticides, salts, nutrients, tracers, and heavy metals in the environment. A column test is often used to verify laboratory batch leaching tests and to better predict contaminant release in the environment. Column leaching tests are typically more expensive than traditional batch leaching tests and the experimental conditions can be difficult to control. The field-scale leaching tests (such as lysimeters) are the most expensive, time-consuming, and labor-intensive leaching experiment, although they more accurately simulate leaching from waste in the environment

2.2 Batch Leaching Procedures

Common batch leaching tests that are or have been used in the United States include the: Toxicity Characteristic Leaching Procedure (TCLP US EPA Method 1311), Synthetic Precipitation Leaching Procedure (SPLP US EPA Method 1312), California Waste Extraction Test (WET, California, 1985), Multiple Extraction Procedure (MEP, US EPA Method 1320), Liquid-Solid Partitioning as a Function Of Extract pH (EPA LEAF Method 1313), and Liquid-Solid Partitioning as a Function of Liquid-to-Solid Ratio (EPA LEAF Method 1314). Batch leaching test are typically employed for one of two purposes: regulatory hazardous waste classification and treatment, or beneficial use or land disposal assessment. The specific methodology and intent of these tests are discussed in the subsequent sections.

2.2.1 Toxicity Characteristic Leaching Procedure (TCLP) (EPA Method 1311)

The TCLP is a batch test that involves leaching a size-reduced mass (< 3/8" or 9.5 mm) of waste material with an acetic acid solution. A 20:1 liquid to solid (L/S) ratio is employed, and the mixture is rotated for 18 hours. TCLP pollutant concentrations are also used to determine whether a waste will be classified as a Toxicity Characteristic (TC) hazardous waste under RCRA as well as to determine if it specific treatment requirements as a hazardous waste. The TCLP test replaced the EP-TOX test, which was included in the first promulgation of the RCRA regulations. The TCLP is also used as a tool for site cleanup demonstration and to evaluate metal leachability in municipal solid waste (MSW) landfills. The extraction fluid simulates a worst-case scenario in which a potentially hazardous waste is co-disposed with MSW, the acetic acid solutions used in the test are designed to simulate the leachate produced from decomposing MSW. (Francis et al. 1984).

The TCLP test procedure involves extracting contaminants from a size-reduced mass of waste material using an acetic acid solution. Depending on the alkalinity of the waste, the TCLP requires one of two extraction fluids. This is determined using a pre-test titration and a small subsample (5 grams) of the waste; this can create issues for wastes which are heterogeneous as both fluids can be obtained during the classification. Extraction fluid one is prepared by diluting a mixture of 11.4 mL acetic acid (CH₃COOH) and 128.6 mL of 1N sodium hydroxide (NaOH) to two liters using reagent water. The final pH of the solution is 4.93 ± 0.05; this is the less aggressive of the two extraction fluids. For more alkaline materials such as wood ash, extraction fluid two is used. This extraction solution is prepared by diluting 11.4 mL acetic acid (CH₃COOH) to two liters using reagent water, the sodium hydroxide is not added decreasing the final pH of the solution to a value of 2.80 ± 0.05. The appropriate extraction solution is added to 100 grams of sample (not accounting for moisture content) to achieve an L/S of 20:1, and this mixture is rotated for 18 ± 2 hours. After rotation, the final pH is measured, and the slurry is filtered using a 0.7 µm glass fiber filter. (US EPA 1996b).

2.2.2 Waste Extraction Test (WET)

While the TCLP is the test used at the federal level to characterize hazardous wastes, California has developed an additional batch test used regulatory characterization. In the State of California a waste must be deemed non-hazardous under WET in addition to TCLP. Like the TCLP, this test uses a buffered organic acid solution as the extraction fluid. The main difference lies in the choice of the acid; the TCLP uses an acetic acid mixture, whereas the WET uses a buffered citric acid solution. The WET extraction solution is prepared by titrating a 0.2 M citric acid solution with 4.0 N NaOH to a pH of 5.0 ± 0.1 . One liter of this fluid is added to a 100-g sample and rotated for a period of 48 hours. After rotation, the final pH is measured, and samples are filtered through a 0.45- μ m membrane filter. (CCR 1985).

2.2.3 Synthetic Precipitation Leaching Procedure (EPA Method 1312)

The US EPA developed the SPLP with the intent of creating a test that better simulated leaching in the environment, where water infiltration would be the primary concern. The SPLP is performed in the same manner as the TCLP (size reduction, L/S, extraction time), except a simulated acid rain solution is used instead of the acetic acid based fluid in the TCLP (US EPA, 1996). The SPLP has historically been the test that has been used to evaluate the potential for COPC release from beneficial used waste to impact water supplies and there is a large amount of available leaching data on wastes tested with SPLP since the tests inception in 1994 (Brantley and Townsend 1999; Hageman et al. 2000; Jang and Townsend 2001; Townsend et al. 2002).

Conditions in which this test might apply include the disposal of an inorganic waste in a mono-fill or waste pile and land application of a recycled waste material such as ash or compost. US-EPA illustrated its interpretation of the different applications of these two tests in its recent proposed lead-based paint (LBP) debris rule. Since test results indicated that LBP debris leached at a greater amount in the TCLP than in the SPLP, allowing LBP debris to be disposed in construction and demolition (C&D) landfills but not MSW landfills was proposed. Because of the high alkalinity of some solid wastes like incinerator ash, synthetic acid rain water extraction tests do not differ substantially from DI water based extractions (Wiles 1996). To prepare the SPLP extraction fluid a 60% (nitric) and 40% (sulfuric) acid solution is added to reagent grade water in order to reach a desired pH of 4.20 ± 0.05 . A 100 g sample of as-received material and 2 L of the prepared solution are combined (L/S of 20:1) in a closed 2 L HDPE bottle and rotated for 18 hours at 30 rpm. Leachate is then filtered using 0.7 micron glass fiber filters.

2.2.4 Multiple Extraction Procedure (EPA Method 1320)

The Multiple Extraction Procedure (MEP) was developed prior to the SPLP, in 1984 and was designed “to simulate the leaching that a waste will undergo from repetitive precipitation of acid rain on an improperly designed sanitary landfill”. The extraction fluids used in the MEP consist of both an organic acid (acetic acid) to simulate MSW leachate and an inorganic acid mixture (nitric and sulfuric acids) designed to simulate acid rain. The repetitiveness of the extraction procedure allows for maximum leaching of chemical constituents. This extraction method has therefore been used to predict the maximum leachable fraction of a COPC from a waste. The extraction is initially performed on a 60 gram sample using the acetic acid solution from the EP-Tox test (similar to TCLP). After the 24-hour rotation period and filtration of the leachate, seven additional extractions are performed on the solids captured on the filter. The solvent used for these extractions is a sulfuric acid/nitric acid solution which is prepared in the same way as the SPLP leaching fluid except that the pH of the MEP fluid is fixed at 3.0 ± 0.2 . During each subsequent extraction, the synthetic rain extraction fluid is added to the waste at a 20:1 L/S, and the samples are rotated for 24 hours. After rotation, the final pH is measured, and the leachate is then filtered through a 0.45 um membrane filter.

2.2.5 Liquid-Solid Partitioning As A Function Of Extract pH Using a Parallel Batch Extraction Procedure (EPA Method 1313)

U.S. EPA Method 1313 evaluates leaching as a function of pH, a factor known to significantly affect leaching and metal mobility. This allows for examination of COPC release from wastes in situations where the natural pH of the material (SPLP) or its pH when co-disposed with MSW (TCLP) would not be representative of its use. An example of this would be the reuse of a waste in contact with a water body, where the pH of the reuse scenario would be more adequately represented by the natural pH of the water than the pH found in an SPLP. Other beneficial use applications, such as the land application of a waste as a soil amendment, would also produce leaching conditions differing from SPLP.

Method 1313 is conducted at a L/S of 10 mL per gram of dry sample, moisture content of the waste is accounted for unlike SPLP. The required sample mass and extraction time is the same as EPA LEAF Method 1316 and is dependent on the particle size of the waste material. The leaching solution is prepared using reagent water, and an appropriate amount of nitric acid or potassium hydroxide to reach nine desired final leachate pH values (2, 3, 4, 5.5, 7, 8, 9, 10.5, 12, and 13).

2.2.6 Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials Using an Up-Flow Percolation Column Procedure (EPA Method 1316)

EPA Method 1316 is a batch test that is designed to evaluate constituent release from waste materials as a function of liquid to solid ratio. This allows practitioners to evaluate whether wastes will continuously release an element over time (solubility control) or if concentrations will be reduced with a loss of the available COPC (depletion). The

intent of this test is similar to that of LEAF Method 1314, however because column testing can be time consuming and cost intensive to run, a batch test method was developed that was designed to produce a similar outcome in a shorter time period. Waste samples are tested at 5 different L/S (0.5, 1.0, 2.0, 5.0, and 10) using de-ionized water as the extraction solution.

2.2.7 LEAF Batch Leaching Tests

EPA Methods 1313 and 1316 base their extraction time and sample mass on the nominal maximum (85% passing) particle size of the material; there are three particle size classifications for these tests. Method 1313 (which operates at a L/S of 10) requires either a 0.3 mm (U.S. #50 sieve), 2.0 mm (U.S. #10 sieve), or a 5.0 mm (U.S. #4 sieve) nominal maximum particle size; rotation times are 24, 48, and 72 hours increasing from the smallest to the largest particle size. For Method 1316 the sample mass for each of the three particle sizes is used at a L/S of 10, after which the L/S is increased through the addition of more sample. For example, a 1316 test where the finest size was used would utilize 20 g in the L/S 10 extraction and increase the sample mass (to 40 g) for the L/S 5 extraction while keeping the volume of water added fixed. All extractions are rotated at 30 rpm and all the leachates are using 0.45 micron polypropylene filter.

2.2.8 Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Procedure (EPA Method 1315)

Method 1315 is a tank leaching test assessing contaminant mass transfer from a monolithic or compacted granular waste into the surrounding water. In many beneficial use applications, wastes are compacted or integrated into a solidified product. Since SPLP requires size reduction, Method 1315 may provide a more realistic assessment of mass release. Because 1315 is conducted over a longer duration (63 days) it allows for the measurement of mass flux and the analysis of trace element mobility, helping to predict a waste's long term leaching behavior.

This test is commonly used on materials which have a naturally low permeability or will be compacted into a form where the majority of the liquid in contact with the system will be flowing around the outside edge of the media. Candidate waste materials include waste-amended concrete products, granular materials employed as a roadway base or sub-base course, and hazardous materials treated through stabilization and solidification (S/S). In addition to quantifying the leachate concentration of elements from the waste material in the tank test the cumulative mass release (mg-COPC/kg-waste), mass flux (mg-COPC/m²-waste), and observed diffusivity of a particular COPC (m²/sec) can be calculated as a function of time; these parameters can serve as inputs in a fate and transport modeling evaluation.

Granular materials are compacted using the modified proctor procedure at a moisture content that corresponds to 90% of the optimum density. The compacted sample is contained in an inert sample holder where only the top face of the compacted specimen is exposed. The sample is placed in a leaching vessel where the distance between the outer

diameter of the sample holder and the inner diameter of the leaching vessel is less than 0.5 cm. The monolith or compacted granular material is immersed into the leaching vessel containing a volume of reagent water corresponding to a liquid-to-sample surface area ratio of 9 mL/cm². At nine time intervals (0.08, 1.0, 2.0, 7.0, 14.0, 28.0, 42.0, 49.0, 63.0 days), the eluate in the leaching vessel is collected for analysis and the required volume of reagent water is renewed. Collected eluate is filtered using 0.45 micron polypropylene filter.

2.3 Flow-Through Column Leaching Procedures

Method 1314 is an up-flow percolation column leaching test under saturated conditions that allows for an examination of chemical leaching as a function of liquid to solid ratio. A potential limitation of the SPLP is that it is conducted at a fixed liquid to solid ratio (20:1), which may not be representative of the conditions a waste is subjected to when beneficially used. Leachate concentrations at low liquid to solid ratios may be more representative of pore water concentrations of granular wastes placed in a beneficial use scenario (e.g. use as an embankment fill material). Method 1314 provides information on the mobility of elements from a solid waste including an indication of which elements are washed from the surface of the material and quickly depleted and which elements diffuse at a constant rate.

In the Method 1314 test the material is crushed until its nominal maximum particle size is less 1/20 of the column diameter, in order to limit channeling; this size is equivalent to 2.5 mm or a U.S. No. 8 sieve. A minimum of 300 grams of dry mass equivalent of material is packed into a 5 cm diameter, 30 cm long PVC column. Reagent water is pumped through the column in an up-flow fashion using a peristaltic pump. A flow rate that corresponds to a L/S of 0.75 per day is used. Leachate exiting the column is collected in nine discreet L/S intervals (0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5, 10.0 mL/g-dry); this corresponds to a test duration of approximately fourteen days. Following collection leachates are filtered using 0.45 micron polypropylene filters.

Lysimeter experiments can be used to verify laboratory batch tests and to better predict contaminant release in the environment. In a lysimeter test, a column apparatus is packed with the waste material of interest. Different depths of material can be loaded into the column to better reflect intended reuse conditions in the field. Water is introduced at the top of the column at a controlled rate and allowed to percolate downward through the material. Periodically, the leachate exiting the bottom of the column is collected and analyzed. These tests can be performed over a time period of months or years, and are intended to capture the leaching behavior of the material over longer periods of time and under fluctuating geochemical conditions that might be expected to occur in the environment.

2.4 Application of Leaching Test Results

Most often, an established batch leaching test (such as the SPLP or a DI water extraction – 1316 at an L/S of 10) is conducted on the waste material proposed for beneficial use. These tests are relatively simple to perform and provide an effective screening level determination of which COPC may pose a leaching risk. In a more refined risk assessment, additional leaching procedures such as LEAF tests can be employed to better assess the changes in constituent release with L/S (Method 1314 or 1316) or with changes in geochemical parameters such pH (Method 1313).

The primary objective of these leaching tests are to develop an initial leachate concentration (C_{leachate}) to be used in an environmental model. Constituents in the leachate are then expected to travel through the vadose zone to the saturated zone and move in the groundwater to a given point of interest or compliance. Consequently, it is not only the leachate concentrations that should be considered, but also the groundwater concentrations at a point of compliance some distance away from the beneficial use site ($C_{\text{compliance}}$). Computational tools for modeling constituent fate and transport and estimating point-of-compliance concentrations have been developed for use in beneficial use decision making. These tools incorporate initial leachate concentrations, hydrological data, soil parameters, and groundwater properties to estimate the concentration of certain COPCs at a receptor location (EPA, 2015).

In EPA's *Human and Ecological Risk Assessment of Coal Combustion Residuals* report (US EPA, 2014), the use of the newly adopted LEAF methods to determine leachate concentrations as a source term for subsequent transport modeling was discussed. Method 1313 was used to determine the total leachable mass of each constituent by taking the maximum observed leachate concentration over the pH range prescribed by the method and converting it to a mass concentration through the use of the L/S (10 L/kg). Leaching behavior was determined using Methods 1314 and 1316 to evaluate leaching as a function of L/S. This dataset revealed whether elements from a specific waste material exhibited either solubility or washout controlled behavior. Solubility controlled elements maintain a relatively constant leachate concentration across all of the test L/S. For these elements, the initial leachate concentration input was held constant until the available mass, determined by Method 1313, was depleted. In contrast, an element with washout behavior would be released at high concentrations initially but would become depleted at subsequent L/S. In this risk assessment approach, the initial pulse of higher concentrations seen with these elements was not modeled as an exponential decay function but as a constant concentration (as with solubility controlled elements) except that the concentration was multiplied by 20 to avoid underestimating the initial risk. The methodology employed above serves as one example of how leaching test results can be incorporated into a transport model. A guidance documents was published by the EPA and a team of researchers in 2014 which provided additional scenarios for how the results of LEAF tests could be integrated into such an assessment. This document is entitled *Leaching Test Relationships, Laboratory to Field Comparisons and Recommendations for Leaching Evaluation using the Leaching Environmental Assessment Framework* and is available freely online. (USEPA, 2014)

3.0 Leaching Methods in Florida Beneficial Use Decisions

3.1 Florida's Experience

FDEP has used leaching tests as tools for beneficial use determinations (BUDs) of different types of wastes. Wastes that have been previously proposed for beneficial use include wood and tire ash, recovered screen material (RSM) from C&D recycling, and water treatment residues. The following subsections describe the research done on these and other wastes used in Florida, including the total metal concentrations observed, leaching tests performed, mobilized concentrations of elements and a comparison to applicable soil or water standards.

3.2 Recovered Screen Material (RSM) from C&D Debris Recycling

Construction and demolition debris recycling facilities use screening equipment to separate fine material from larger pieces that are sorted for recycling and disposal. The soil-like fine material separated at the recycling facilities is known as recovered screen material (RSM). There have been a number of beneficial uses which have been proposed for RSM. However, the most commonly proposed applications include use as a landfill cover or as a fill material for grading. In 1998, the DEP commissioned a study on the total and leachable concentrations of organic and inorganic compounds in RSM. This ultimately resulted in Department issued guidance (FDEP, 1998), which was subsequently updated in 2011 (FDEP, 2011). This Department guidance was updated in 2011 to include the recently promulgated statutory definition of RSM: "Recovered screen material means the fines fraction, consisting of soil and other small materials, derived from the processing or recycling of construction and demolition debris which passes through a final screen size no greater than 3/4 of an inch." (62-701.200(73) F.A.C.). At present, the most common beneficial use for RSM is as landfill cover.

The 1998 RSM characterization study (Townsend et al., 1998) focused on examining the total concentrations of organic compounds (VOCs, SVOCs and Pesticides) as well as heavy metals. The leachable concentrations of the organic compounds, heavy metals, and inorganic anions (most importantly sulfate) were evaluated using the SPLP test. RSM samples were collected over 18 months at 13 different C&D recycling facilities throughout the state of Florida (although the majority of the facilities tested were located in South Florida). In all but one instance, all of the organic compounds tested were found in concentrations below the Departments residential SCTLs. RSM samples from one facility did have total concentrations of indeno[1,2,3-cd]pyrene and benzo(a)pyrene elevated above the residential SCTLs in one sample. Leaching of organic compounds in the SPLP test were found to yield concentrations below GCTLs in all instances.

Leaching of metals from this material was assessed in a 2004 study (Townsend et al., 2004) and leached concentrations were found not to exceed GCTLs in the RSM samples. The total concentration of As, along with its 95% upper confidence limit (UCL) of 3.2 mg/kg was found to exceed the residential SCTL for As (0.8 mg/kg, subsequently revised to 2.1 mg/kg in 2005). Additionally, several of the samples were found to exceed

the commercial-industrial SCTL of 3.7 mg/kg (subsequently revised to 12 mg/kg in 2005). None of the other heavy metals evaluated were found to exceed residential SCTLs when the 95% UCL of all of the samples was examined.

Inorganic anion release from RSM was also evaluated. In a 2001 study (Jang et al., 2001), sulfate (SO_4^{2-}) was found to leach from the RSM, in both batch (SPLP) and column leaching tests in quantities (890-1,600 mg/L) which were elevated with respect to its secondary drinking water standard of 250 mg/L. Many RSM streams contain appreciable quantities of gypsum (CaSO_4) drywall, and this was cited as the source of the sulfate release. It is important to note, however, that secondary drinking water standards are designated as “non-enforceable” by the US EPA and represent concentration thresholds which were developed to be indicative of aesthetic considerations (e.g. taste and odor) and are not related to health effects.

Based in large part on the results of the 1998 study, the Department issued guidance related to the beneficial use of RSM. This guidance outlined a characterization methodology to apply for a beneficial use determination involving an initial examination of the total and leachable concentrations of the constituents evaluated in the previous studies (organics and RCRA trace metals) along with continued monitoring (most frequently to measure the total concentration of As in the material). Continued monitoring requirements were allowed to be waived if the RSM generated by the C&D recycler was used either as landfill cover or in an encapsulated use (such as in asphalt or concrete). Approved beneficial use in a residential setting would require a demonstration that the 95% UCL of the mean for each COPC is below its respective residential SCTL, and that leaching test results do not indicate that the use of RSM will result in groundwater impacts.

At the time of this 1998 study, the SPLP was one of the few standardized EPA tests utilized for evaluating leaching to groundwater. LEAF testing of RSM would provide more detailed characterization information which could help to illustrate other potential options for the beneficial use of RSM.

3.3 Street Sweepings, Catch Basin Sediments, Storm Water System Sediments

A characterization study on catch basin sediments, storm water pond sediments, and street sweepings was conducted between 2001 and 2003 (Townsend et al., 2003). Results and interpretation of the catch basin/storm water residuals and street sweepings characterization study were also more recently discussed in Jang et al., 2010 and 2009 respectively.

Catch basin and storm water pond sediments may contain a number of pollutants including metals, hydrocarbons, and pesticides. Sediments accumulate in storm water systems and are routinely removed. Therefore, characterization of these sediment residuals is important for assessing risk and selecting best management practices. In this study, more than 150 residual samples were taken from catch basins and storm water ponds through the state of Florida over a 15 month period. Total concentrations (mg/kg) of metals and metalloids (arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, selenium,

silver, and zinc), and 290 trace organics were measured and compared to corresponding risk – based guidelines for Florida (SCTLs). In addition, the SPLP was conducted to evaluate the leachable concentrations of these constituents of concern. Leached 95% UCL concentrations were compared to respective GCTLs. Arsenic, barium, chromium, copper, nickel, lead, and zinc were consistently detected in the analyzed samples, but were generally found in concentrations below the respective SCTLs. No leachable metal concentrations exceeded corresponding GCTLs. A small group of organochlorine compounds, such as 4,4'-DDE, 4,4'-DDT, were detected in less than 10% of the samples. Leaching of these organic constituents above respective GCTLs was rare. The results suggest that the characterized residuals do not pose a significant risk. Based on the characterization study, the FDEP developed a guidance document outlining acceptable disposal and beneficial use practices for these residuals in Florida (FDEP, 2004). Guidelines allow adequately dewatered residuals to be disposed of in both lined and unlined permitted landfills. Other uses such as land application require that the residuals undergo site specific testing, as some constituents did exceed risk-based thresholds for select samples (Jang et al., 2010).

Street sweepings are comprised mainly of soil, sediment, small pieces of pavement, leaves, and trash. Approximately 200 samples of street sweepings were collected from 20 municipalities across the state of Florida. Total concentrations (mg/kg) and leachable concentrations (evaluated with the SPLP) of metals and trace organic pollutants were measured. The same suite of metals and organic pollutants analyzed in (Jang et al., 2010) were also examined here. No total or leachable 95% UCL concentration of any of the constituents analyzed were found to exceed the respective risk-based thresholds (SCTL and GCTL, respectively). The results suggest that street sweepings will not pose a significant direct exposure or groundwater contamination risk. Based on this characterization study, the FDEP developed a guidance document for the regulatory community on the disposal and beneficial use of street sweepings (FDEP, 2004). According to the issued guidance, double screened material (for trash removal) can be beneficially reused in road applications and non-residential construction fill or as a soil amendment. Unrestricted use is not permitted in residential areas as some of the COPC (e.g. Benzo(a)pyrene) had laboratory detection limits greater than the respective SCTL for direct exposure (Jang et al., 2009).

3.4 Water Treatment Sludge

The beneficial use of water treatment residues (WTR) have been explored by the state in two instances. Water treatment processes generate WTR from both water softening (lime WTR) and coagulation (alum or ferric WTR) processes. The first study conducted by the Hinkley Center in 2001 collected WTR from 26 facilities throughout the state. These were a mixture of both lime WTR and Ferric and Alum WTR. The intent of this study was to evaluate the potential for the beneficial use of these WTR most commonly used in land application. Samples were analyzed for their total environmentally available element content as well as for their potential to impact surrounding water supplies using the SPLP. Metals, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and a number of pesticides were evaluated as constituents of potential concern.

An update to this 2001 study was conducted by the Hinkley Center in 2013. The goal of this 2013 study was two-fold: first, its intent was to evaluate whether the characteristics of lime WTR had changed due to the inclusion of small amounts of other treatment additives including ferric chloride and aluminum sulfate (referred to as mixed WTR). The second goal of the study was to examine element release from the WTR when placed as fill in low oxygen conditions either in a surface water body or as a subsurface fill below the groundwater table. This study is also outlined in Blaisi et al., (2015) and Cheng et al., (2014). The first phase of the 2013 study utilized the methodology employed in the 2001 testing. SPLP and total element concentrations were evaluated for 18 different WTR samples. These samples were collected from throughout the state; however, the majority of the samples tested were from South Florida where the majority of the beneficial uses were proposed. The next phase of testing involved the addition of a chemical reducing agent (sodium dithionite) to the SPLP solution. This was designed to lower the oxidation reduction potential of the SPLP and produce conditions which would conservatively estimate element release in a low oxygen environment; this testing was conducted on all 18 samples. To further examine leaching from WTR a sub – set of five samples, including samples which represented mixed WTR, were tested with a more detailed suite of leaching tests. This testing included the natural water leaching test where WTR samples were leached with different surface waters to evaluate the impacts of organic matter on element release. Additional tests were also conducted to examine WTR leaching in low oxygen environments which included EPA Method 1315, a compacted granular tank leaching test, and column tests conducted in an anaerobic environment.

3.4.1 Lime WTR

The results of the initial characterization study indicated that no constituents of concern were observed to leach from lime WTR in quantities that would exceed GCTLs. The results of the 2013 study supported the findings from the 2001 tests with the exception that leached concentrations of Al were elevated above its GCTL by less than 10% in some instances. When evaluating direct exposure risk, the first study did find certain facilities where Ba and As exceeded their respective residential SCTLs. An analysis of the data showed that when the 95% upper confidence limit was calculated using the total element concentration from all of the facilities sampled Ba (77.7 mg/kg) and As (2.04 mg/kg) were found to be below their respective residential SCTLs (120 mg/kg and 2.1 mg/kg). The results of this study were supported by the analysis conducted in 2013. The 2013 study did not reveal facilities where As or Ba were evaluated above SCTLs. Organic compounds were not measured in significant total or leachable concentrations. Based on the results of the 2001 characterization, the Department concluded that the beneficial use of lime WTR (through land application) was not expected to create any significant threat to public health or the environment and that no additional regulation or approval by the FDEP was required prior to its use. The Department developed a guidance which suggests that WTR be applied at a rate no greater than 9 dry tons per acre per year in order to minimize movement of metals into the environment.

With respect to use of lime WTR in low oxygen environments, the results of the chemical reducing agent and anaerobic column testing demonstrated that concentrations of Fe, Mn, and Al could increase (in comparison to aerobic test results) when placed in these types of conditions, and that in some instances these results were elevated above GCTLs. Furthermore, several of the natural water solutions tested showed an increase in leached Fe concentrations (in comparison to SPLP), which, in some instances, exceeded GCTLs (a secondary aesthetic based drinking water standard). Based on the characterization results for the other proposed beneficial uses, the Department has maintained that these must be approved on a case by case basis.

3.4.2 Alum WTR

Alum and Ferric WTR were only evaluated during the first study. The SPLP results from the 2001 testing indicated that Al, Pb, and Mn leached from alum WTR in quantities above their respective GCTLs. The results of the total elemental analysis showed that Al, Ba, and As were observed to exceed their respective direct exposure criteria. In the five samples analyzed, Al and As were found above the residential SCTLs in all cases, while Ba was found above residential SCTL in one case. Mean total concentrations of As and Al were 16.89 mg/kg and 142,000 mg/kg, respectively. The results suggest that the unlimited land application of alum WTRs could pose a threat to public health and the environment and such use would require site- and material-specific risk analysis in addition to a land application proposal.

3.4.3 Ferric WTR

The SPLP results from the characterization study indicated that Al, Fe, and Mn leached from ferric WTR in quantities above respective GCTLs. The results for total analyses indicated that As, Cu, and Fe were observed to exceed their respective direct exposure criteria. In the five samples analyzed, Al and As were found above the residential soil CTLs in all cases, while Ba was found above residential soil CTLs in one case. Mean total concentrations of As and Al were 7.04 mg/kg and 4,400 mg/kg, respectively. These results suggest that the unlimited land application of ferric WTRs could pose a threat to public health and the environment and such use would require site- and material-specific risk analysis in addition to a land application proposal.

3.4.4 Mixed Lime WTR

The results of the 2013 WTR characterization study demonstrate that mixed WTR were most appropriately characterized as lime WTR with respect to total element content and leachability and thus could be managed as such. Leach testing on the mixed lime WTR did not indicate substantial leaching of any elements due to the inclusion of other treatment additives. Total concentrations of mixed lime WTR were slightly enriched in either Fe (for Ferric WTR) or Al (for Alum WTR) when compared to lime WTR. However, the concentrations of Al and Fe were still orders of magnitudes lower than the comparable concentrations of Al and Fe in Alum and Ferric WTR, respectively, and fell below SCTLs.

3.5 Wood and Tire Ash

Tolaymat et al. (2008) investigated the direct exposure risk of land applied wood and tire (WT) ash, taken from a Florida waste-to-energy facility. Totals analysis was conducted on this material and results were compared to respective Florida SCTLs. SPLP was also conducted on the material to assess leaching and risk to groundwater and results were compared to respective Florida GCTLs. From this analysis, only arsenic exceeded both its corresponding residential and commercial SCTLs and copper exceeded only its corresponding residential criteria. All other elements analyzed in this study were present in lower concentrations than their respective target levels. When comparing the WT ash SPLP results to their respective GCTL criteria, lead was the only element with a primary drinking water standard that exceeded its GCTL. SPLP leachate concentration of arsenic, cadmium, cobalt, copper, and vanadium were consistently below their detection limits.

Following the beneficial use assessment methodology for Florida, this material could not be used in a manner that would result in direct contact exposure. These results suggest that alternative assessments be incorporated into a beneficial use determination. It is important to note the SCTLs were developed on the assumption that a land applied waste would be replacing native soil. In the case of agricultural amendment, the material is being mixed with the existing soil and so exposure is also a function of background soil concentrations and rate of material application (Tolaymat, 2008).

3.6 Summary of Florida's Leaching Experience

Table 1. Materials Previously Evaluated for Beneficial Use in Florida

<u>Material</u>	<u>Leaching Observation</u>	<u>Additional Information</u>
Wood and Tire Ash	<p>Mid 2000's: SPLP Pb = 52 ug/L SPLP As = < 5 ug/L</p> <p>2015 (Current project): SPLP Pb = 240 ug/L SPLP As = < 4 ug/L</p>	<p>1314 and 1316 results similar to SPLP. Method 1313 (pH stat) results corresponding to expected pH regime can provide better understanding of Co input for fate and transport modeling.</p>
Recovered Screen Material	<p>Metals < GCTL Sulfate 4-6 times GCTL</p>	<p>Method 1314 or 1316 could evaluate if sulfate leaching would decrease over time and factored in transport modeling efforts.</p>
Street Sweepings, Catch Basin Sediments, Stormwater Sediments	<p>Metal < GCTL</p>	<p>Method 1313 evaluates if leaching can pose a risk under expected pH conditions in beneficial use scenario</p>
Lime WTR	<p>Metal < GCTL</p>	<p>Method 1313 evaluates if leaching can pose a risk under expected pH conditions in beneficial use scenario</p>
Alum WTR	<p>Al, Pb, Mn > GCTL</p>	<p>Method 1314 or 1316 could be used from more accurate Co input for fate and transport model.</p>
Ferric WTR	<p>Al, Fe, Mn > GCTL</p>	<p>Hybrid approaches could be used to assess potential leachability when waste is blended with soil.</p>

4.0 Case Studies of LEAF Testing

4.1 Approach

In order to demonstrate how the LEAF tests can be applied and to provide a comparison with the more traditional TCLP and SPLP, three solid waste streams were characterized and analyzed. Wood and tire ash, a coal combustion air pollution control residue, and waste to energy bottom ash were obtained from facilities in Florida. Table 2 below provides a more detailed description of the three wastes used, while Table 3 provides a brief summary of the leaching tests performed on each waste. Subsections 4.2 to 4.4 provide the results of the leaching test performed on these materials.

Table 2. Wastes Tests for Case Study

<u>Waste Stream Analyzed</u>	<u>Description</u>
Wood and tire ash	Combined ash from the combustion of waste wood and tires for energy generation
Coal combustion by-product	Coal fired power plant scrubber product, mixture of calcium sulfite/sulfate sludge and fly ash
WTE Combined Ash	Ash resulting from the combustion of municipal solid waste for energy generation

Table 3. Leaching Tests Conducted as Part of Case Study

<u>Analytical Method</u>	<u>Description</u>
Synthetic Precipitation Leaching Procedure (EPA Method 1312)	Batch leaching test at liquid-solid ratio of 20 using solution of dilute nitric and sulfuric acid to simulate acid rainfall.
Leaching as a function of pH (EPA Method 1313)	Evaluates leaching as a function of pH involving a series of parallel batch leaching tests at liquid-solid ratio of 10 where an appropriate amount of acid or base is initially added to the leaching solution to yield a desired final extract pH. Target pH values range from 2 to 13.
Leaching as a Function of L/S Ratio using Percolation Column (EPA Method 1314)	Examines leaching as function of liquid to solid ratio through a continuous up-flow percolation column packed with the material of interest. Reagent grade water is advanced thorough the material at a rate of 0.5 to 1 LS/day and extract is collected at the prescribed L/S intervals
Monolithic Tank Leaching (EPA Method 1315)	Examines release rates of constituents from monolithic or compacted granular material submerged in a tank of reagent grade water over a period of 63 days. Extract is collected and new reagent grade water replaced at prescribed intervals. Mass fluxes (mass/area-time) can also be determined.
Leaching as a Function of L/S Ratio using Batch Testing (EPA Method 1316)	Examines leaching as function of liquid to solid ratio through a series of parallel batch tests. The appropriate mass of dry waste and reagent water to achieve the target liquid-solid ratios are combined in separate leaching vessels as a parallel batch extraction.
Environmentally Available Element Analysis (EPA Method 3050B)	Acid digestion involving concentrated nitric acid, hydrochloric acid, and hydrogen peroxide to determine the total environmentally available concentration of contaminants

4.2 Wood and Tire Ash

Table 4 presents the total environmentally available concentration of elements as obtained from EPA Method 3050B. These values are typically used to determine the risk to human health by direct exposure and were compared to the FL SCTLs, both residential and commercial/industrial.

Table 4. Results of EPA Method 3050B Digestion on Wood and Tire Ash

<u>Element</u>	<u>Mean ± STD</u> <u>(mg/kg)</u>	<u>UCL₉₅ (mg/kg)</u>	<u>SCTL^R (mg/kg)</u>	<u>SCTL^{CI} (mg/kg)</u>
Al	3,540 ± 774	4,100	80,000	-
As	68.0 ± 7.22	73.2	2.1	12
B	72.6 ± 6.00	76.9	17,000	430,000
Ba	84.1 ± 17.8	96.8	120	130,000
Be	0.164 ± 0.026	0.182	120	1,400
Ca	131,000 ± 14,900	141,000	-	-
Cd	3.79 ± 0.417	4.09	82	1,700
Cr	48.1 ± 11.9	56.6	210	470
Cu	186 ± 75.4	240	110	76,000
Fe	18,900 ± 8630	25,100	53,000	-
Mg	4,900 ± 434	5,200	-	-
Mn	237 ± 33.6	261	1,600	22,000
Mo	3.18 ± 0.405	3.47	440	11,000
Na	1,990 ± 200	2130	-	-
Ni	11.5 ± 3.22	13.8	340	28,000
Pb	126 ± 24.2	144	400	1400
Sb	12.1 ± 2.54	13.9	27	370
Se	0.836 ± 1.28	1.75	440	11,000
Sn	15.9 ± 11.4	24.0	47,000	880,000
Sr	349 ± 48.7	384	52,000	-
V	5.68 ± 2.13	7.2	67	10,000
Zn	7,160 ± 912	7810	26,000	630,000

From the total environmentally available element analysis results for wood and tire ash (Figure 2), arsenic (As) was present in concentrations that exceeded both the respective residential and industrial soil cleanup target level. Copper concentrations were found to exceed only the residential SCTL. These exceedance indicate reuse options for wood-tire ash would need to limit direct human exposure risk through additional controls. Results for SPLP and L/S 10 fraction of Method 1316 are presented in Table 5. Since these tests aim to determine the risk to water contamination, the results were compared to GCTLs.

Table 5. Results of Leach Testing on Wood and Tire Ash

<u>Element</u>	<u>SPLP (mg/L)</u>	<u>UCL₉₅ (mg/L)</u>	<u>Method 1316</u>	<u>GCTL (mg/L)</u>
	<u>Mean ± STD</u>		<u>L:S 10 (mg/L)</u>	
Al	0.078 ± 0.013	0.090	0.108	0.2
As	0.004 ± 0.0003	0.005	0.005	0.01
B	0.052 ± 0.013	0.064	0.052	1.4
Ba	0.285 ± 0.072	0.350	0.216	2
Be	< 0.012	0.012	<0.0121	0.004
Ca	946 ± 121	1050	1320	-
Cd	0.00047 ± 0.0002	0.001	0.001	0.005
Cr	0.013 ± 0.006	0.018	0.034	0.1
Cu	0.003 ± 0.0006	0.004	0.009	1
Fe	0.006 ± 0.004	0.009	0.003	0.3
Mg	< 0.00048	0.000	0.013	-
Mn	0.00037 ± 0.00031	0.001	0.002	0.05
Mo	0.027 ± 0.002	0.028	0.060	0.035
Na	51.5 ± 8.94	59.5	147	160
Ni	< 0.00071	0.001	0.002	0.1
Pb	0.241 ± 0.101	0.332	0.17	0.015
Sb	< 0.0042	0.004	<0.0042	0.006
Se	0.009 ± 0.0004	0.009	<0.0084	0.05
Sn	< 0.0011	0.001	<0.0011	4.2
Sr	2.02 ± 0.37	2.36	4.50	4.2
V	0.00045 ± 0.0003	0.001	0.002	0.049
Zn	2.06 ± 0.184	2.23	2.02	5

Based on these results, lead (Pb) was the only element that was measured at concentrations higher than its respective target level and might pose a leaching risk if beneficially used. This assessment provides information on the leaching risk at conditions governed by the natural pH of the materials. Additional information on maximum leaching potential or leaching under different pH conditions that might be expected in a field

scenario can be obtained from Method 1313 data. Figures 2 and 3 present leaching as a function of pH for both As and Pb from the wood-tire ash. At the natural pH conditions of the wood-tire ash (11-12), arsenic and lead mobility reflect that observed with the SPLP. However, if pH conditions were to change under a reuse scenario (e.g. 6-8) As may then pose a leaching risk while Pb leaching may decrease.

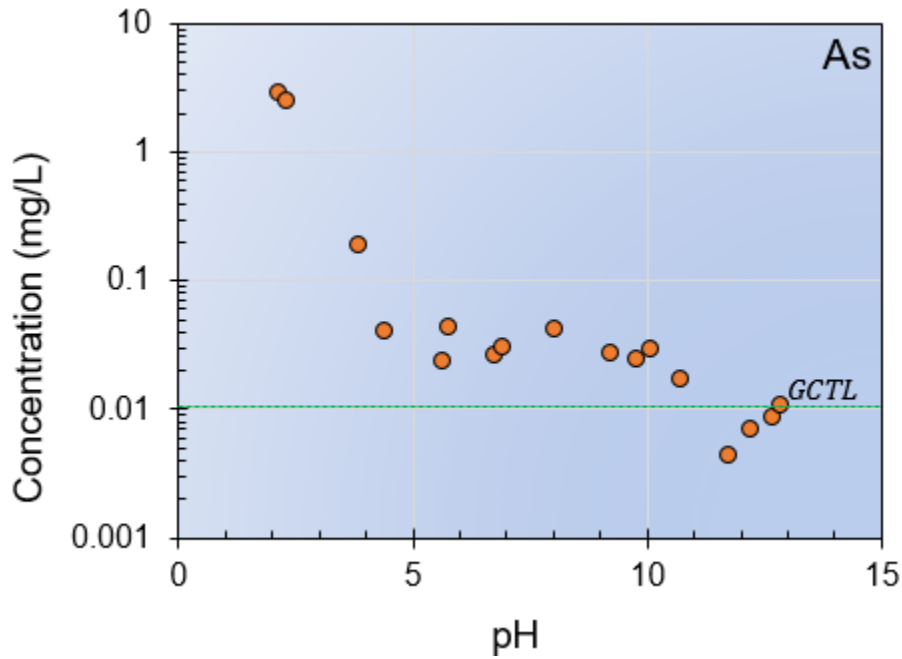


Figure 2. Arsenic Leaching as a Function of pH (Method 1313) WT-Ash

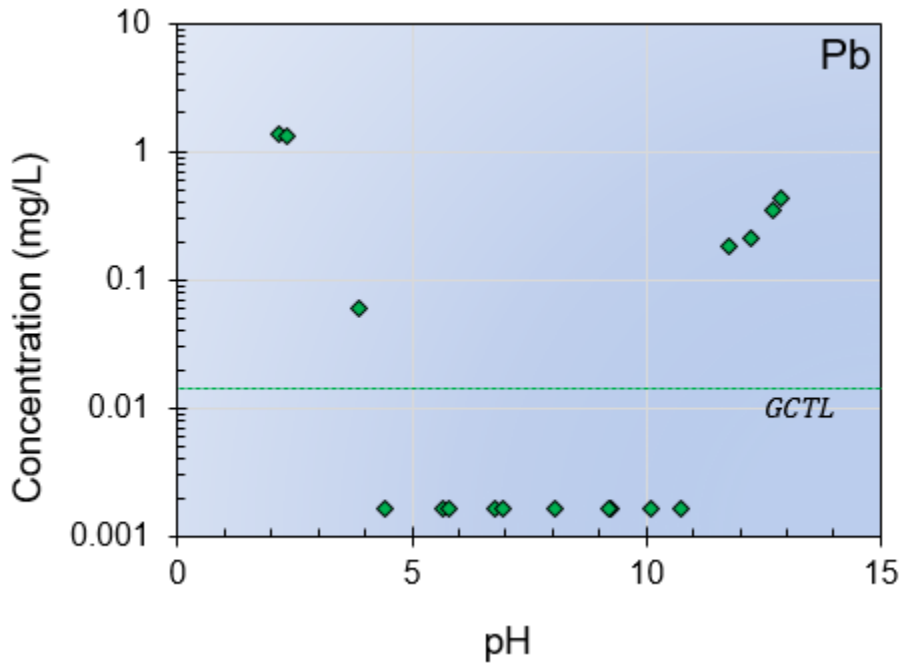


Figure 3. Lead Leaching as a Function of pH (Method 1313) WT-Ash

4.3 Coal Combustion Product

Table 6 below includes the total environmentally available concentrations of elements in the coal combustion product analyzed, and it provides a comparison to the SCTLs; while Table 7 shows the results for SPLP and the L/S 10 fraction of Method 1316 and compares them against the GCTLs.

Table 6. Results of EPA Method 3050B Digestion on Coal Combustion Product

<u>Element</u>	<u>Mean ± STD</u> <u>(mg/kg)</u>	<u>UCL₉₅ (mg/kg)</u>	<u>SCTL^R (mg/kg)</u>	<u>SCTL^{CI} (mg/kg)</u>
Al	11,200 ± 3.00	11,190	80,000	-
As	53.9 ± 0.02	53.9	2.1	12
B	91.8 ± 0.02	91.8	17000	430,000
Ba	149 ± 0.12	149	120	130,000
Be	3.26 ± 0.001	3.26	120	1,400
Ca	52,000 ± 47.2	52,000	-	-
Cd	1.14 ± 0.001	1.14	82	1,700
Cr	27.3 ± 0.005	27.3	210	470
Cu	41.5 ± 0.006	41.5	110	76,000
Fe	14,800 ± 2.46	14,800	53,000	-
Mg	1,880 ± 0.595	1,880	-	-
Mn	66.1 ± 0.01	66.1	1,600	22,000
Mo	10.2 ± 0.004	10.2	440	11,000
Na	263 ± 0.165	264	-	-
Ni	35.7 ± 0.014	35.7	340	28,000
Pb	14.2 ± 0.007	14.2	400	1,400
Sb	0.92 ± 0.001	0.921	27	370
Se	11.7 ± 0.007	11.7	440	11,000
Sn	2.01 ± 0.001	2.0	47,000	880,000
Sr	278 ± 0.078	278	52,000	-
V	106 ± 0.062	106	67	10,000
Zn	44.9 ± 0.016	44.9	26,000	630,000

From these results, barium (Ba) and vanadium (V) were present in concentrations that exceeded their respective residential soil cleanup target level. These exceedances indicate reuse options for the coal combustion product would need to limit direct exposure risk through additional controls such as cover or encapsulation.

Table 7. Results of Leach Testing on Coal Combustion Product

<u>Element</u>	<u>SPLP (mg/L)</u> <u>Mean ± STD</u>	<u>UCL₉₅ (mg/L)</u>	<u>EPA Method</u> <u>1316 L:S10</u> <u>(mg/L)</u>	<u>GCTL (mg/L)</u>
Al	0.325 ± 0.018	0.341	0.364	0.2
As	0.043 ± 0.002	0.046	0.050	0.01
B	2.15 ± 0.060	2.20	4.07	1.4
Ba	0.071 ± 0.003	0.074	0.047	2
Be	< 0.012	0.012	<0.012	0.004
Ca	653 ± 11.8	664	657	-
Cd	< 0.0004	-	<0.0004	0.005
Cr	0.003 ± 0.0002	0.004	0.006	0.1
Cu	< 0.00093	0.001	0.005	1
Fe	0.009 ± 0.004	0.013	0.028	0.3
Mg	4.08 ± 0.127	4.20	7.12	-
Mn	0.006 ± 0.001	0.007	0.007	0.05
Mo	0.278 ± 0.026	0.301	0.531	0.035
Na	5.67 ± 0.182	5.83	11.0	160
Ni	0.001 ± 0.001	0.001	0.001	0.1
Pb	< 0.0033	-	<0.0033	0.015
Sb	0.007 ± 0.0005	0.007	0.009	0.006
Se	0.111 ± 0.004	0.114	0.179	0.05
Sn	< 0.0011	-	<0.0011	4.2
Sr	1.66 ± 0.025	1.69	2.10	4.2
V	0.130 ± 0.005	0.134	0.153	0.049
Zn	0.021 ± 0.005	0.026	0.003	5

Based on the results of the SPLP and a L/S 10, aluminum (Al), arsenic (As), barium (Ba), molybdenum (Mo), antimony (Sb), selenium (Se), and vanadium (V) were measured at concentrations higher than their respective target level. A fate and transport modeling assessment would need to be conducted to determine if these elements would be sufficiently diluted and attenuated at a set point of compliance. Figure 4 and 5 show the behavior of As and Mo leaching from the coal combustion product as a function of pH (EPA Method 1313). As it can be seen, over the neutral and alkaline pH range, their mobility is relatively independent of the pH of the system.

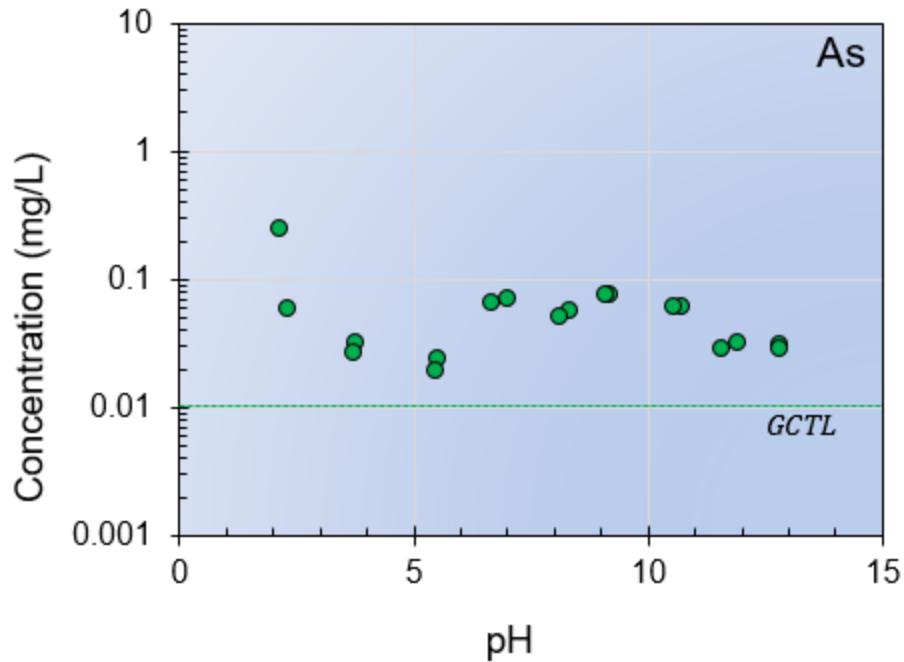


Figure 4. Arsenic Leaching as a Function of pH (Method 1313) CCP

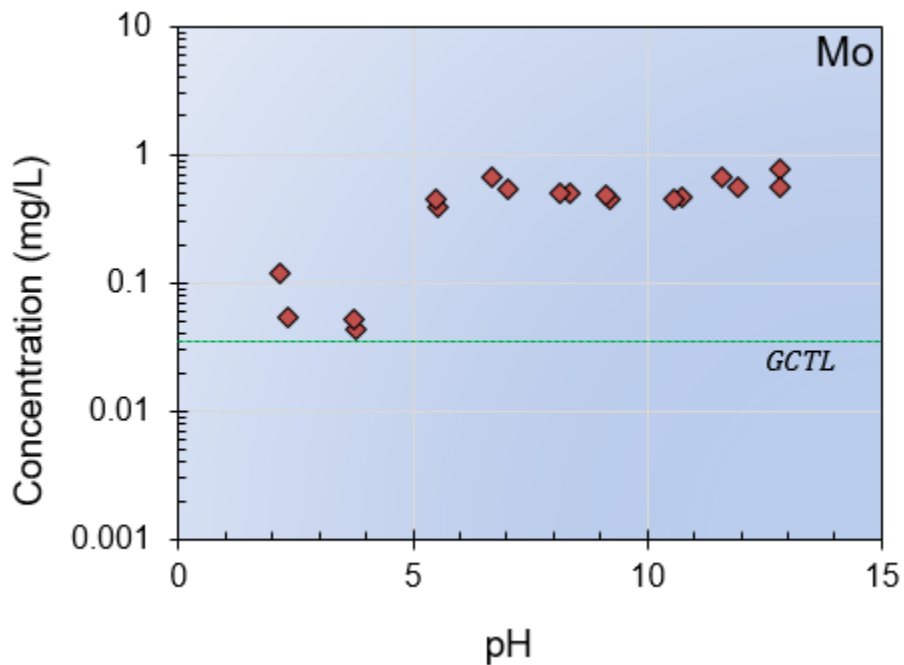


Figure 5. Molybdenum Leaching as a Function of pH (Method 1313) CCP

Results for Method 1316 for As and Mo are presented in Figures 6 and 7 below. As shown in Figures 6 and 7 it is observed that the mobilization of arsenic is independent of the L/S of the system, while Mo shows a higher dependence on L/S. For this element, the released concentration is high at lower L/S and it decreases with increasing L/S the washout trend seen for Mo indicates that the leaching risk of this element to water supplies would be depleted with increasing water concentration.

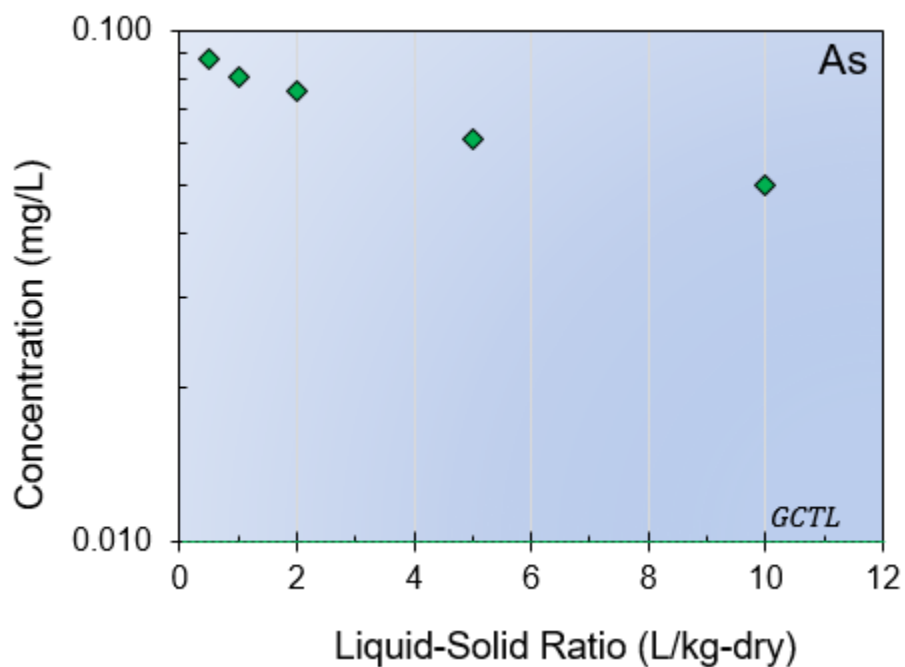


Figure 6. Arsenic Leaching as a Function of L/S (Method 1316) CCP

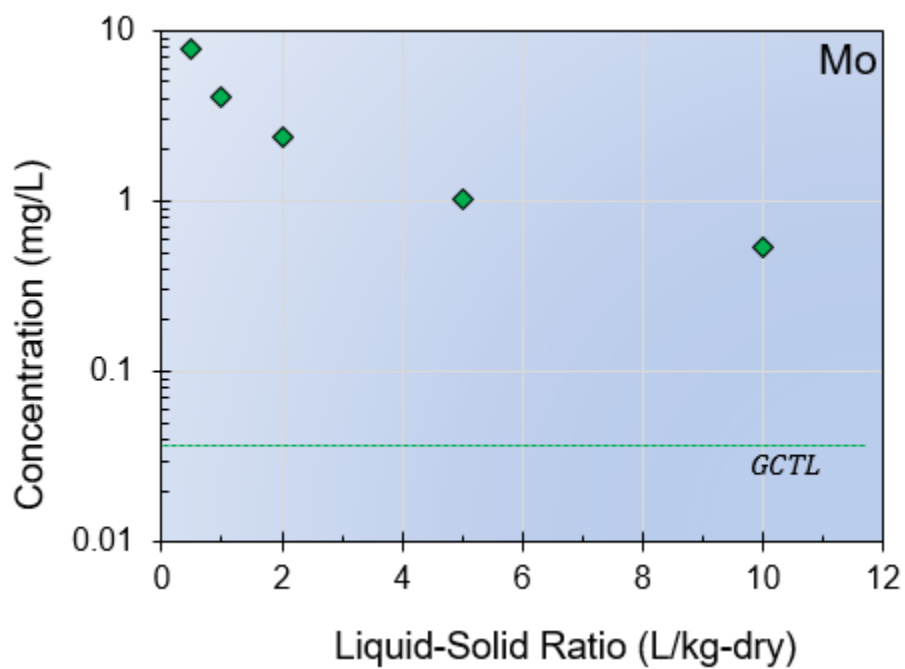


Figure 7. Molybdenum Leaching as a Function of L/S (Method 1316) CCP

Method 1315 data on monolithic or compacted granular materials can be presented as cumulative mass release per unit area of exposed surface area. These data can be used as an input term in groundwater fate and transport modeling to estimate groundwater concentrations at a receptor location downgradient. Figure 8 presents Method 1315 data on a compacted mixture of coal combustion residuals and reclaimed asphalt pavement. These data can better estimate release of constituents from a compacted base course made from these materials where water is not percolating throughout the base layer but is instead accumulating around the outer surface area. Constituents like arsenic in Figure 6 may exhibit more sustained release, while other elements like molybdenum may show more rapid decrease in element release over time. These data can be incorporated into modeling assessments as source terms to provide a more realistic assessment of COPC release in the in-place environment.

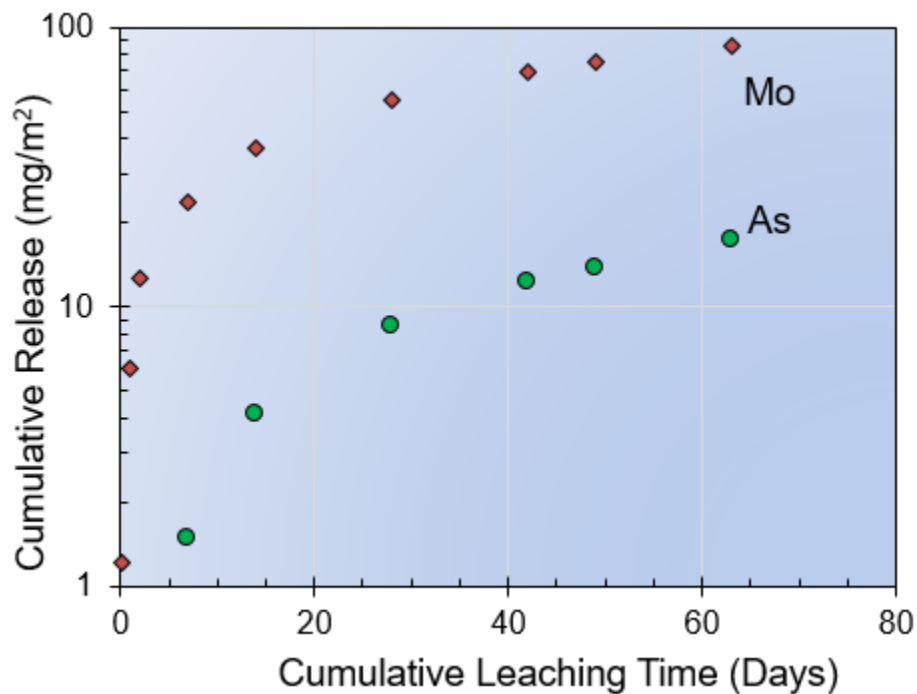


Figure 8. Cumulative Flux (mg/m^2) as a Function of Leaching Time (Method 1315) CCP

4.4 Combined Waste-to-Energy Ash

The results of total concentration testing on combined WTE ash are presented in Table 8. These data are compared to the soil cleanup target levels. From the total environmentally available element analysis results for WTE ash, arsenic, barium, copper, lead and antimony were present in concentrations that exceeded their respective residential soil cleanup target levels. These exceedances indicate reuse options for WTE ash would need to limit direct exposure risk through additional controls such as cover or encapsulation.

Table 8. Results of EPA Method 3050B Digestion on Waste to Energy Ash

<u>Element</u>	<u>Mean ± STD</u> <u>(mg/kg)</u>	<u>UCL₉₅ (mg/kg)</u>	<u>SCTL^R (mg/kg)</u>	<u>SCTL^{CI} (mg/kg)</u>
Al	17,500 ± 1,420	18,800	80,000	-
As	9.84 ± 2.00	11.7	2.1	12
B	207 ± 13.7	217	17,000	430,000
Ba	178 ± 24.8	200	120	130,000
Be	0.254 ± .0347	0.284	120	1,400
Ca	86,300 ± 4,550	89,000	-	-
Cd	38.2 ± 3.07	40.5	82	1,700
Cr	168 ± 45.9	213	210	470
Cu	1400 ± 557	2140	110	76,000
Fe	36,600 ± 5940	40,400	53,000	-
Mg	7,370 ± 1740	9,040	-	-
Mn	638 ± 182	817	1600	22,000
Mo	9.67 ± 1.87	11.4	440	11,000
Na	9,160 ± 349	9,310	-	-
Ni	162 ± 30.8	190	340	28,000
Pb	976 ± 99.7	1,060	400	1,400
Sb	43.0 ± 3.71	45.9	27	370
Se	1.08 ± 0.00	1.05	440	11,000
Sn	139 ± 63.7	204	47,000	880,000
Sr	211 ± 20.9	228	52,000	-
V	15.9 ± 1.71	17.3	67	10,000
Zn	4,020 ± 558	4,520	26,000	630,000

SPLP and Method 1316 at a L/S of 10 were conducted on the WTE ash this data are presented in Table 9. Al, Ba, Mo, Na, Pb, Sb, and V were measured at concentrations higher than their respective target level. It is important to note that the ash tested was fresh and was not allowed to age, which is known to reduce the pH of the material and subsequently decrease leaching.

Table 9. Results of Leach Testing on Waste to Energy Ash

<u>Element</u>	<u>SPLP (mg/L)</u> <u>Mean ± STD</u>	<u>UCL₉₅ (mg/L)</u>	<u>EPA Method</u> <u>1316 L:S10</u> <u>(mg/L)</u>	<u>GCTL (mg/L)</u>
Al	33.7 ± 8.03	40.3	4.77	0.2
As	< 0.0042	-	<0.0042	0.01
B	0.005 ± 0.003	0.007	0.005	1.4
Ba	2.51 ± 0.78	2.74	7.63	2
Be	< 0.0121	-	< 0.0121	0.004
Ca	400 ± 28.9	424	<0.0004	-
Cd	< 0.0004	-	0.003	0.005
Cr	<0.00083	-	0.498	0.1
Cu	0.170 ± 0.011	0.180	0.159	1
Fe	0.00455 ± 0.0027	0.007	0.006	0.3
Mg	0.012 ± 0.0025	0.014	0.079	-
Mn	0.000633 ± 0.0002	0.001	0.006	0.05
Mo	0.0369 ± 0.004	0.039	0.570	0.035
Na	240 ± 20.8	257	0.014	160
Ni	0.00242 ± 0.0004	0.003	0.0084	0.1
Pb	0.103 ± 0.023	0.122	0.0022	0.015
Sb	0.0158 ± 0.004	0.019	7.57	0.006
Se	< 0.084	-	< 0.0084	0.05
Sn	0.0016 ± 0.004	0.005	0.001	4.2
Sr	2.50 ± 0.223	2.682	0.326	4.2
V	0.00567 ± 0.001	0.007	11.5	0.049
Zn	0.202 ± 0.023	0.221	4.77	5

Figures 9 and 10 show the behavior of lead and antimony mobilized from a samples of WTE bottom ash as a function of pH. In both cases, the elements show an amphoteric behavior: with increased mobility in the acidic and alkaline pH range, but low mobility around 8 – 10. For both elements, the lower mobility region is also below the corresponding GCTLs, this is one example of how Method 1313 can be used to provide information on practices which can be used to reduce leaching.

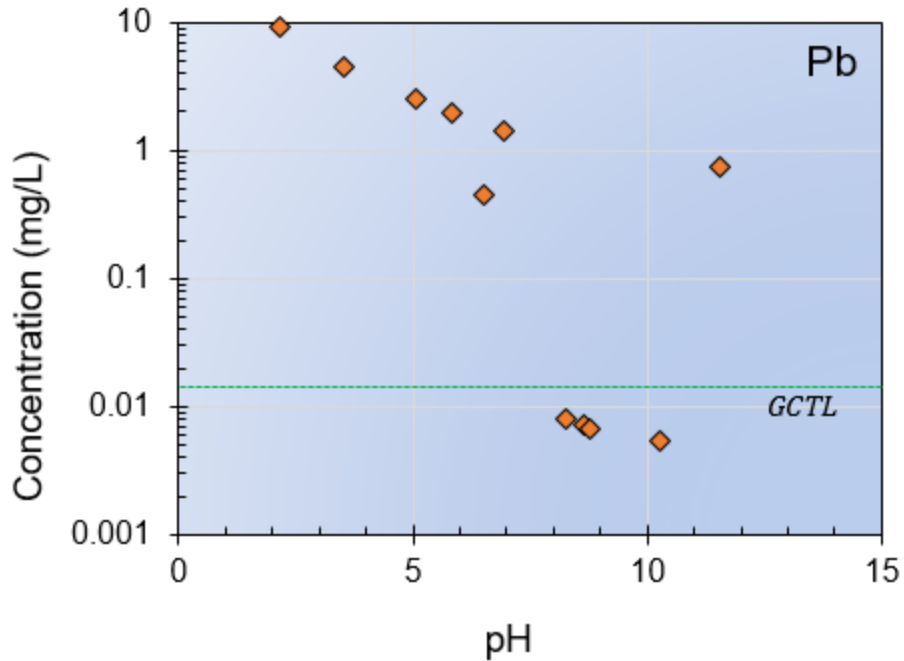


Figure 9. Lead Leaching as a Function of pH (Method 1313) WTE Ash

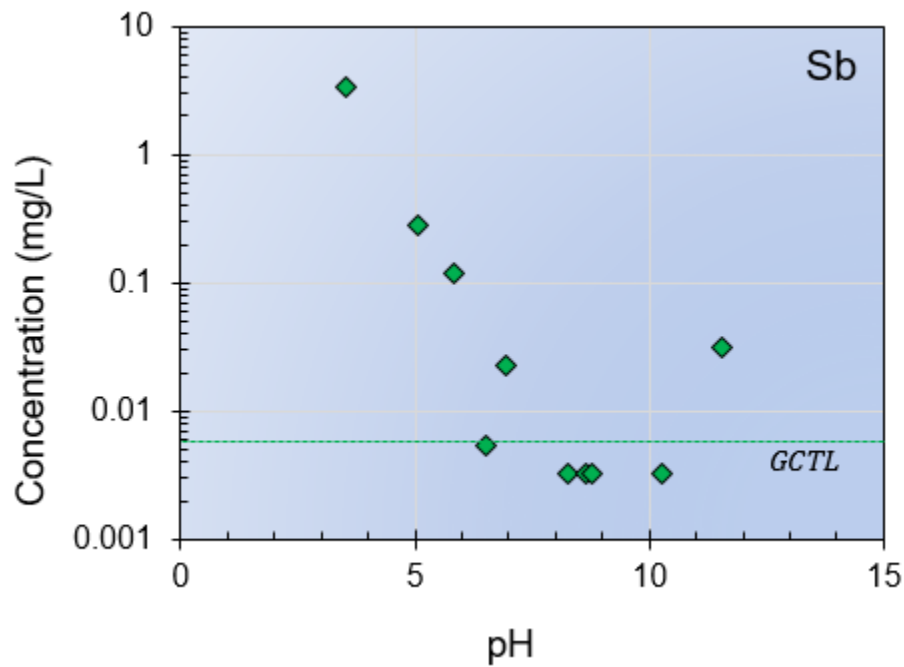


Figure 10. Antimony Leaching as a Function of pH (Method 1313) WTE Ash

Results for Method 1316 are shown in Figures 11 and 12 for Pb and Sb. For Sb, at natural pH conditions of the fresh ash, the release in solution is relatively constant at any L/S, however it is close to the GCTL for this element. In the case of Pb, at natural pH of the fresh ash, this elements may continue to pose a risk. The reduction of the pH of the ash through carbonation or aging, for example, can reduce the release of this element based on the Method 1313 data shown above.

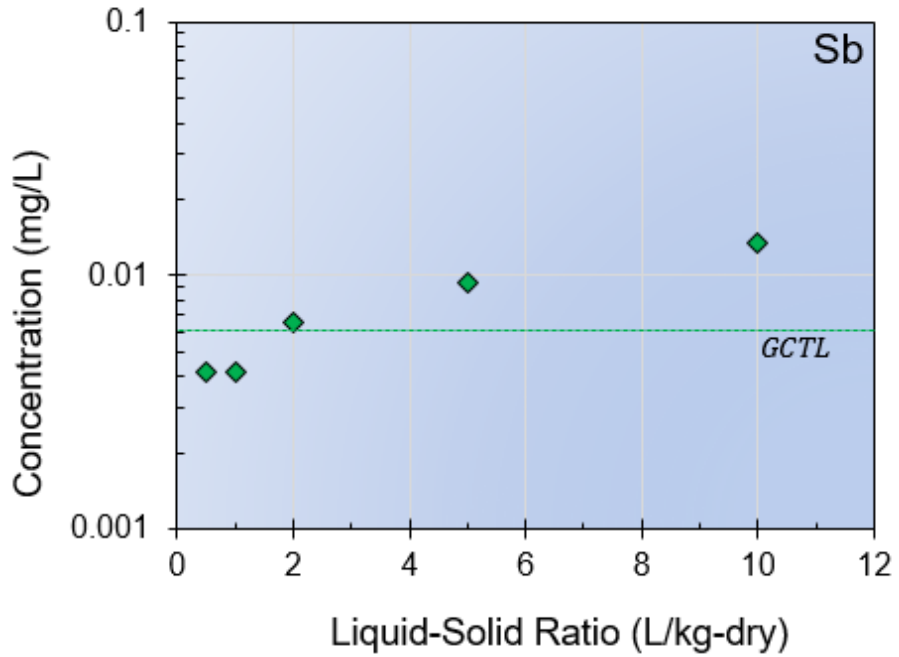


Figure 11. Antimony Leaching as a Function of L:S (Method 1316) WTE Ash

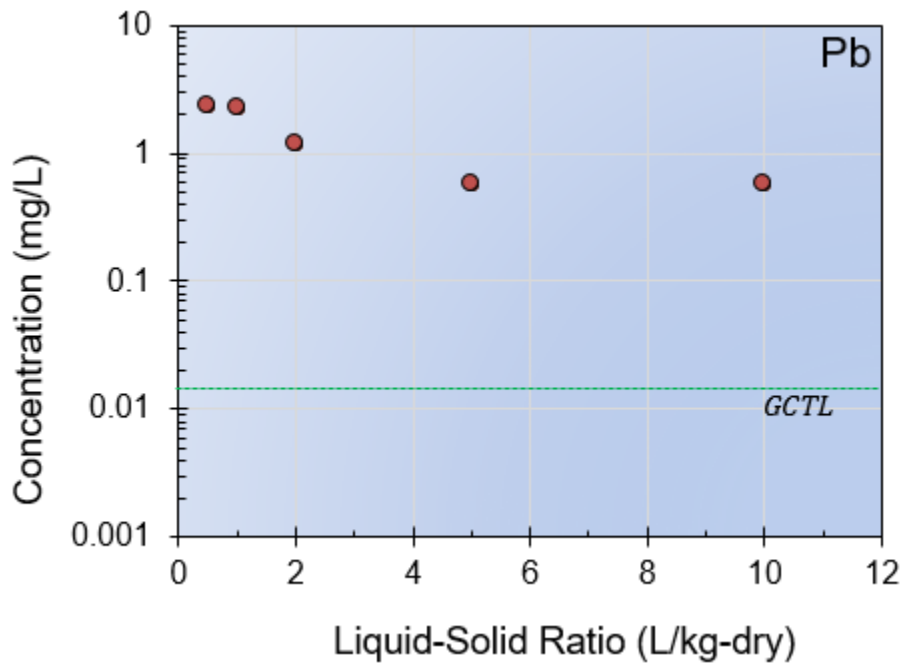


Figure 12. Lead Leaching as a Function of L:S (Method 1316) CCP

5.0 Summary and Conclusions

This document presents the intent and description of both the historically used and recently adopted leaching tests. A review of beneficial use assessments previously performed for a variety of wastes generated in Florida are included. As part of this project, the characterization tests on three different wastes are included and the results are discussed from a risk assessment point of view. Finally, a guidance document describing different leaching procedures was developed as a tool for regulatory agencies, landfill operators and waste generators to understand the tests and the meaning of the information they provide.

The new suite of leaching tests provide an expanded set of tools for use in beneficial use decision-making. Leaching tests are just one component in a larger risk evaluation which likely will include fate and transport modeling. In order to appropriately predict environmental risk it is essential that both the leached concentration and other geochemical parameters (such as the hydrology of the surrounding groundwater) be well understood. Unlike the most traditional leaching tests such as TCLP and SPLP, the use of the LEAF procedures sheds light on why some elements behave the way they do, and allow a more detailed risk assessment to be conducted. However, for the majority of wastes and scenarios encountered in Florida, the use of LEAF data as an input to pollutant fate and transport models does not alter risk assessment outcomes dramatically compared to using SPLP. Therefore it is important to understand that these new leach tests are tools and that they should be used when appropriate.

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APPENDIX

Guidance Document Development

The purpose of the guidance document is to provide a simple tool for regulatory agencies, landfill operators, and waste generators to understand the different leaching tests that are available, how they are performed, and how to interpret the results from these tests. This guide includes a brief description of commonly used leaching procedures, examples of data obtained for different materials, and comparisons between the tests to allow a better understanding of the applicability of these methods.