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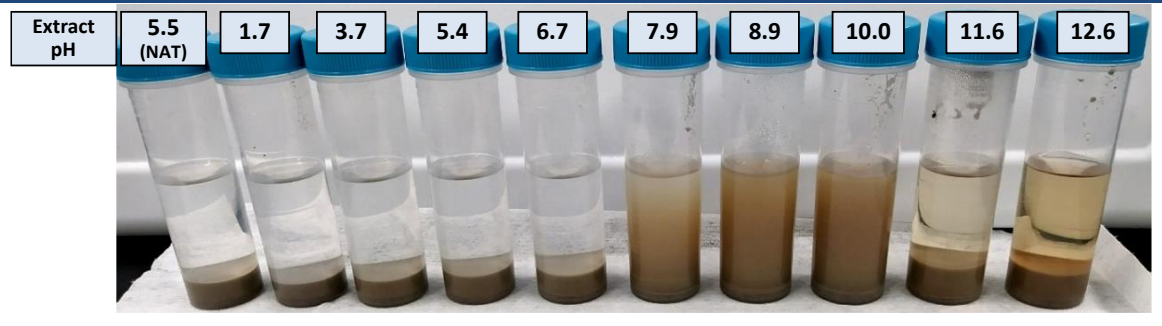
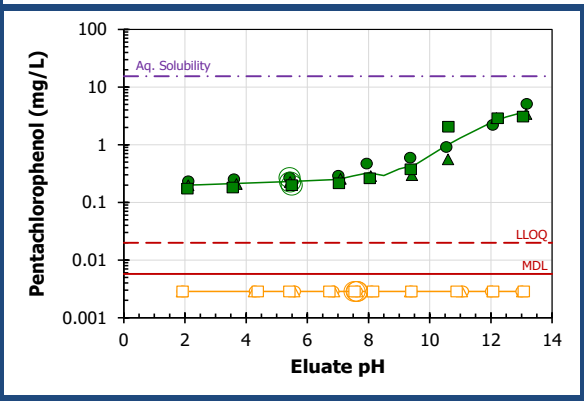
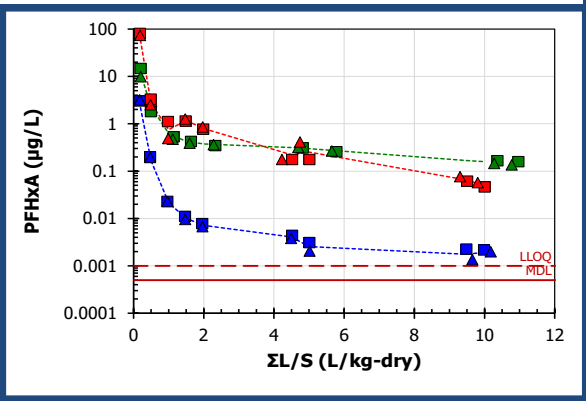
Development of Leaching Tests for Materials Containing SVOCs and PFAS

Background Information Document







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Development of Leaching Tests for Materials Containing SVOCs and PFAS

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Disclaimers

The United States Environmental Protection Agency (U.S. EPA, or the Agency) through its Office of Research and Development, directed and managed this research through Contract No. EP C-15-008 with Jacobs Technology, Inc and subcontract to Vanderbilt University. This document has been subjected to the Agency's review and has been approved for publication. Note that approval does not signify that the contents necessarily reflect the views of the Agency. Mention of trade names, products, or services does not convey official U.S. EPA approval, endorsement, or recommendation.

Foreword

The United States Environmental Protection Agency (U.S. EPA, or the Agency) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The Center for Environmental Solutions and Emergency Response (CESER) within the Office of Research and Development (ORD) conducts applied, stakeholder-driven research and provides responsive technical support to help solve the Nation’s environmental challenges. CESER develops technologies and decision-support tools to help safeguard public water systems and groundwater, guide sustainable materials management, remediate sites from traditional contamination sources and emerging environmental stressors, and address potential threats from terrorism and natural disasters. The Center collaborates with both public and private sector partners to foster technologies that improve the effectiveness and reduce the cost of compliance, while anticipating emerging problems. CESER also provides technical support to EPA regions and programs, states, tribal nations, and federal partners.

The Leaching Environmental Assessment Framework (LEAF) methods, as incorporated into the SW-846 compendium, exemplify applied stakeholder-driven research to develop methods that provide data required to evaluate treatment options for contaminated soil, assess beneficial use of industrial by-products such as coal fly ash, slag, and flue-gas desulfurization gypsum, and support land application of waste and materials such as biosolids. In 2012, the original methods (Methods 1313, 1314, 1315, and 1316) were validated for inorganic constituents of potential concern (COPCs). The methods were published in SW-846 in 2019 and are considered to provide a comprehensive characterization of how COPCs in wastes and other materials interact with water under various environmental conditions, thereby providing the ability to predict the mobility of COPCs (including concentrations and cumulative release) over time in response to changing environmental conditions. Recognizing the evolving landscape of environmental contaminants, the EPA has taken a significant step forward by extending the LEAF methods to include materials containing semi-volatile organic compounds (SVOCs) and per- and polyfluoroalkyl substances (PFAS). This background information document (BID) describes the adaptation and update of LEAF methods for SVOCs and PFAS, addressing knowledge gaps, especially the need for changes in materials of construction and eluate handling. The revised draft test methods (Draft Methods 1313A, 1314A, 1315A, and 1316A) are included in the appendices as was done for the BID compiled for the LEAF methods for inorganic COPCs.

Gregory Sayles, Director

Center for Environmental Solutions and Emergency Response

Table of Contents

List of Tables

List of Figures

Acknowledgments

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The LEAF methods as published in U.S. EPA's SW-846, are widely used in the U.S. and internationally, including as integral part of DOE's Consortium for Risk Evaluation with Stakeholder Participation (CRESP) program. However, where LEAF is used to evaluate the release of organic COPCs, the updated methods developed through this study are needed to establish uncertainties in method execution that can ensure accuracy of results. With release of this report, the updated "to-be-validated" methods will be available although some changes are likely to occur in response to lessons learned from the validation. The validated final methods will be available through publication in SW-846 EPA's compendium of test methods.

The authors appreciate those that served as peer reviewers of this document for their help towards developing the updated methods. Specifically, the authors thank Troy Strock for his extensive comments that led to improved leaching methods ensuring more accurate liquid-solid separation, colloid management, and other challenges associated with working with waste streams that contains inorganic and organic constituents of potential concern (COPCs). The authors also thank Dahman Touati who served as the Jacobs Technology, Inc. Task Order Manager to document updating LEAF methods for organics in this report including the updated methods in the appendices.

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Abbreviations

AAS	atomic absorption spectrometry
AC	activated carbon
ACS	American Chemical Society
ADM	advective dispersion model
AFFF	aqueous film-forming foam
ANC	acid neutralization capacity (mol/kg-dry)
ANOVA	analysis of variance
AOM	anthropogenic organic matter
ASLP	Australian standard leaching procedure
BID	background information document
BNC	base neutralization capacity (mol/kg-dry)
B.S.	Bachelor of Science degree
BTEX	benzene, toluene, ethylbenzene, and xylenes
CAS	Chemical Abstracts Service
CCV(s)	continuing calibration verification(s)
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CESER	Center for Environmental Solutions and Emergency Response
CMC	critical micelle concentration
COC	chain of custody
COPC(s)	constituent(s) of potential concern
DCA	dissolved carbon analysis
DIC	dissolved inorganic carbon
DIW	deionized water
diPAP	two-tailed polyfluoroalkyl phosphate esters
DOC	dissolved organic carbon
DQO(s)	data quality objective(s)
EAF	electric arc furnace
EC	electrical conductivity
EPRI	Electric Power Research Institute (Palo Alto, CA)
ESI-	electrospray ionization negative
ESP	electrostatic precipitator
FGD	flue gas desulfurization
f_{clay}	mass fraction of clay (unitless)
f_{oc}	mass fraction of organic matter (unitless)

GAC	granular activated carbon
GC-MS	gas chromatography-mass spectrometry
HDPE	high-density polyethylene
HPLC	high performance liquid chromatography
IC	ion chromatography
ICAL	initial calibration
ICP-MS	inductively coupled plasma-mass spectrometry
ICP-OES	inductively coupled plasma-optical emission spectrometry
ICV(s)	initial calibration verification(s)
ID	internal diameter
ISS	in-situ stabilization
ISTD(s)	internal standard(s)
K	effective permeability (m^2)
K_d	linear partitioning coefficient
K_{soil}	permeability of surrounding soils (m^2)
K_{mat}	permeability of a study material in the subsurface (m^2)
LC-MS/MS	liquid chromatography-tandem mass spectrometry
LCS(s)	laboratory control sample(s)
LDPE	low-density polyethylene
LEA	local equilibration assumption
LEAF	Leaching Environmental Assessment Framework
LLOQ(s)	lower limit(s) of quantitation
LOD(s)	limit(s) of detection
log(K_{ow})	n-octanol-water partitioning coefficient
L/S	liquid-to-solid ratio (mL/g-dry solid or L/kg-dry solid)
L/S_i	interval liquid-to-solid ratio (mg/L-dry solid or L/kg-dry solid)
LSP	liquid-solid partitioning
MB(s)	method blank(s)
MC	moisture content
MCL(s)	maximum contaminant level(s)
MDL(s)	method detection limit(s)
meq	milli-equivalent
MGP	manufactured gas plant
MRMHR	high-resolution multiple reaction monitoring
M.S.	Master of Science degree
NAPL(s)	nonaqueous phase liquid(s)

NIOSH	National Institute of Occupational Safety and Health (Washington, DC)
NIST	National Institute of Science and Technology (Gaithersburg, VA)
NOM	natural organic matter
NTU(s)	nephelometric turbidity unit(s)
NPOC	non-purgeable organic carbon
NVOC(s)	non-volatile organic compound(s)
OD	outer diameter
OECD	Organization of Economic Cooperation and Development (Paris, France)
OLEM	Office of Land and Emergency Management (U.S. EPA)
ORD	Office of Research and Development (U.S. EPA)
PAH(s)	polycyclic aromatic hydrocarbon(s)
PCB(s)	polychlorinated biphenyl(s)
PCTFE	polychlorotrifluoroethylene
PDMS	polydimethylsiloxane
PFAS	per-and polyfluoroalkyl substances
PFCA(s)	perfluoroalkyl carboxylic acid(s)
PFSA(s)	perfluoroalkyl sulfonic acid(s)
Ph.D.	Doctor of Philosophy degree
pKa(s)	dissociation constant(s)
PP	polypropylene
PTFE	polytetrafluoroethylene (e.g., Teflon®)
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
PVF	polyvinyl fluoride
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
QToF	quadrupole time-of-flight
R^2	coefficient of determination
RCF	relative centrifugal force (g-force)
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
rpm	revolutions per minute
RSD_r	relative standard deviation associated with intra-laboratory repeatability
RSD_R	relative standard deviation associated with inter-laboratory reproducibility
RT(s)	retention time(s)
SAB	Science Advisory Board (of the U.S. EPA)

SAR	sodium adsorption ratio
SERDP	Strategic Environmental Research and Development Program (U.S. DOE)
SOP(s)	standard operating procedure(s)
SPE	solid phase extraction
SVOC(s)	semi-volatile organic compound(s)
SW-846	*Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*
TEC	total elemental carbon
TOC	total organic carbon
TOP	total oxidizable precursor (assay)
TTU	Texas Tech University (Lubbock, TX)
U.S. EPA	United States Environmental Protection Agency
UV	ultraviolet
VOA	volatile organic analysis
VOC(s)	volatile organic compound(s)
VU	Vanderbilt University (Nashville, TN)
wt%	percent by mass or weight percent
ΣL/S	cumulative liquid-to-solid ratio
%Diff	percentage difference
%R	percentage (mass) recovery

Chemicals and Reagents

$Al_2(SO_4)_3$•$18H_2O$	aluminum sulfate octadecahydrate or alum
$KC_8H_5KO_4$	potassium hydrogen phthalate
CsCl	cesium chloride
HCl	hydrochloric acid
HNO_3	nitric acid
H_2SO_4	sulfuric acid
KOH	potassium hydroxide
MeCl	methylene chloride
$NaHCO_3$	sodium bicarbonate
NaN_3	sodium azide (biocide)
Na_2SO_4	sodium sulfate

Study and Demonstration Material IDs

CS	creosote soil containing phenols and PAHs

EaFA	coal fly ash cited in various EPA reports
MS	manufactured gas plant soil containing phenols and PAHs
Site 1 Soil	AFFF-impacted soil from a military site containing PFAS
Site 2 Soil	AFFF-impacted soil from a military site containing PFAS
Site 3 Soil	AFFF-impacted soil from a military site containing PFAS
Site 4 Soil	AFFF-impacted soil from a military site containing PFAS

Executive Summary

In 2019, the United States Environmental Protection Agency (U.S. EPA, or the Agency) published the Leaching Environmental Assessment Framework (LEAF) methods into U.S. EPA's compendium of laboratory tests, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846 (U.S. EPA, 2020). The four, LEAF test methods represent part of a comprehensive approach to evaluate the mobility of constituents from solid or granular materials (e.g., soils, wastes, industrial by-products) that when in contact with water or aqueous solutions can become more mobile based on pH, the ratio of liquid volume to solid mass, and diffusion rates from concentration gradients. These conditions are changing more rapidly considering climate change with extreme precipitation events occurring more frequently. Past leaching tests have not considered environmental conditions affecting mobility and are not able to provide mass and time-dependent source terms for evaluating leaching from waste management that can impact surface and ground-water bodies.

The LEAF methods were developed to determine the intrinsic leaching characteristics of COPC leaching from a subject material over a broad range of test conditions and management options. Testing is used to evaluate how COPCs in a material respond to a range of environmental conditions that occur and can change over time. In contrast to LEAF, other leaching assessment approaches define a release scenario and design a testing method (e.g., the U.S. EPA Toxicity Characteristic Leaching Procedure, or TCLP) to provide an aqueous eluate considered to simulate a field leachate under that defined scenario. The LEAF methods, however, are not intended to yield eluates representative of leachates under defined field conditions but to characterize the leaching behavior of COPCs intrinsic to the material over a range of testing conditions. Thus, the results of the LEAF methods, in conjunction with scenario information (e.g., fill geometry and local precipitation), can be used to estimate field performance of a wide range of waste materials (e.g., contaminated soils, contaminated sediments, and industrial by-products subject to beneficial use, treatment, land application, or disposal) for multiple environmental scenarios (Garrabrants et al., 2021a; 2021b; U.S. EPA, 2019a). The LEAF test methods also provide a uniform basis for comparison of leaching properties from a broad range of materials.

Prior to publication in SW-846, the U.S. EPA assembled a complete set of documentation for the LEAF methods applicable for inorganic COPCs as support for the validation of the LEAF tests for inorganic COPCs. This documentation included: (i) a background information document (BID) that reviewed the current state of leaching tests, identified information gaps, and provided analysis to fill those gaps (Garrabrants et al., 2010), (ii) draft leaching methods used for interlaboratory validation, (iii) reports documenting the results of the interlaboratory validation studies documenting the statistical repeatability (interlaboratory variance) and reproducibility (intra-laboratory variance) of the methods (Garrabrants et al., 2012a; 2012b), and (iv) a report that reviewed how the results of laboratory evaluations using the LEAF methods, or analogous methods standardized in the European Union, compare to observed field leaching cases for inorganic waste matrices (Kosson et al., 2014a).

Since many environmental samples contain blends of organic compounds and inorganic COPCs, the U.S. EPA currently is supporting the adaption and validation of the LEAF methods for common and emerging organic COPCs, such as semi-volatile organic compounds (SVOCs) and per- and polyfluoroalkyl substances (PFAS). This document provides the analogous BID as the inorganic BID but for use of the LEAF tests applied to materials containing SVOCs and PFAS. The BID: (i) reviews the state-of-the-art in the understanding of leaching for organic compounds from solid matrices, (ii) describes an experimental program used to address

knowledge gaps in the current understanding of organic COPC leaching, and (iii) applies practical modifications to the current LEAF test methods to facilitate determination of leaching characteristics of both inorganic and organic COPCs and other constituents from solid materials.

Literature Review

The existing body of SVOC literature indicates that several leaching strategies have been developed to address the chemical and physical characteristics of some SVOCs, primarily polycyclic aromatic hydrocarbons (PAHs); however, little research has been specifically focused on phenolic compounds. The major concerns of these leaching test approaches include the low aqueous solubility of many PAHs in leaching approaches designed to measure rates of release and the association of PAHs with dissolved organic carbon (DOC) which may enhance the apparent leaching of some SVOCs. Several of these studies were used as a foundation for adaptation of the LEAF methods for SVOCs.

The literature on the emerging pollutant family of PFAS continues to evolve. In many published studies, standardized leaching tests (e.g., TCLP) were heavily modified for use with PFAS-contaminated materials; however, the extent of the reported modifications may compromise the applicability of the test results or the comparability of test results with the those of the cited standardized methods. Thus, many of the reported testing approaches for PFAS may not be appropriate for generation of a leaching source-term (i.e., release of constituents of interest from a solid material over time or under variable field conditions) in support of environmental decision-making.

Based on review of the available literature, the identified gaps in the knowledge base for SVOCs and PFAS primarily focused on three topics:

- Materials of Construction regarding the sorption of COPCs to the labware and vessels used in the leaching procedure,
- Colloid Matter including the formation of colloidal matter, especially during agitated batch leaching tests, and approaches to reduce the impact of colloid formation and to screen samples for high turbidity prior to eluate processing, and
- Eluate Processing such as methodologies for processing a leaching test eluate to maximize the recovery of COPCs, especially when combinations of SVOCs, PFAS, and inorganic COPCs are to be evaluated.

Development and Modification of SW-846 Methods

Materials of Construction

In the SW-846 methods (i.e., SW-846 Method 1313 through Method 1316), high-density polyethylene (HDPE), polypropylene (PP), or other polymer-based materials were recommended for extraction and storage of solutions containing inorganic COPCs. However, research indicates that phenolic compounds and PAHs may sorb significantly to plastics such that measured eluate concentrations may be underpredicted. Therefore, when SVOCs are to be analyzed, Type I (borosilicate) or Type III (soda-lime glass) are recommended for as materials of construction for test method apparatus that contact solid test materials or leaching test eluates. When glass apparatus components are impractical (e.g., column transfer lines or fabricated centrifugation vessels), corrosion-resistant 316L stainless steel is recommended. However, research conducted for this background information document (BID) indicated that Cr,

Fe, and Mn may leach from stainless steel under acidic conditions at concentrations greater than 10 µg/L, which may impact the determinative analysis for these inorganic COPCs. Conversely, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, and Ti were demonstrated to partition under alkaline pH from a 100 µg/L standard solution onto the inner surface of stainless-steel columns which may impact interpretation of leaching test results at low concentration levels. Therefore, when PFAS and/or inorganic COPCs are the only constituents of interest, contact surfaces made of HDPE or nonfluorinated polymers are recommended.

Whenever PFAS are to be analyzed, fluorinated polymers, such as polytetrafluoroethylene (PTFE, commonly Teflon®) and fluoride-finished polymers (e.g., some HDPE and PP vessels) should be avoided due to the potential for PFAS release. It is recommended that, prior to use of vessels from a new manufacturer or a new model of containers, containers be checked for contaminant sources.

Colloidal Matter

The presence of colloidal matter (i.e., suspended organic and inorganic particles, typically with a diameter less than 1 µm) is common in the environment. During batch leaching tests, however, agitation (i.e., tumbling or shaking) can facilitate the dissolution or dispersion of organic matter and deflocculation of clay minerals, leading to colloid formation above which would be expected in the environment (Bergendahl and Grasso, 1998; Yasutaka et al., 2017; Gu et al., 2019). Since both PFAS and SVOCs have been associated with organic carbon in leaching test eluates (Bergendahl, 2005; Roskam and Comans, 2009), the management of colloids in agitated leaching tests may be a concern. To address these concerns, the default leaching solution in the modified draft leaching methods has been changed from deionized water (which may promote colloid formation) to 1-mM $CaCl_2$ to provide Ca^{+2} bridging ions and reduce the deflocculation of clay minerals and natural organic matter. However, even with this change to 1-mM $CaCl_2$, colloidal matter was observed in alkaline eluates of pH-dependent leaching tests as evidenced by cloudiness associated with turbidity readings greater than 50 nephelometric turbidity units (NTUs). Therefore, Draft Method 1313A and Draft Method 1316A (both batch extraction methods) include centrifugation steps to clarify eluates and minimize turbidity.

Eluate Processing

When the leaching assessment plan includes multiple types of COPC groups (i.e., inorganic COPCs, SVOCs, and PFAS), the procedures for test method eluate processing prior to chemical analysis should address the requirements for representative eluate sampling for the COPC type. For example, PFAS are known to sorb to bottle surfaces and accumulate at the air-water interface (Brusseau and Van Glubt, 2019) such that eluate subsampling for PFAS requires proper mixing to homogenize PFAS in the eluate collection bottle and yield a representative analytical sample. Experimentation and management of practical concerns showed that sonication of the eluate collection bottle prior to subsampling, rather than methanol rinsing after subsampling, was the preferred methodology to maximize recovery of PFAS. In eluate fraction targeted for SVOC analysis, the mixture of solids and liquids in batch leaching tests should not be filtered due to sorption of SVOCs to filtration membranes (Lath et al., 2019). Batch test eluates for SVOC analysis should be centrifuged at 9,500-G relative centrifugation force (RCF) to separate eluates from test solids. For extractions at low liquid-to-solid ratio (L/S), the amount of eluate collected from bottle centrifugation may not be sufficient to complete a full suite of analytical determinations; therefore, a stainless-steel apparatus was developed to allow centrifuged eluates to pass through the solid material and be collected at the bottom of the apparatus. This optional low L/S extraction apparatus improved the separation efficiency of centrifugation at low L/S.

Document Organization

This BID reviews the critical literature regarding leaching of SVOCs and PFAS, addresses identified gaps in research through experimentation and presents draft leaching methods adapted from the SW-846 LEAF methods specifically for SVOC and PFAS leaching concurrent with evaluation of inorganic COPCs. **Section 1** of this document discusses the role of the LEAF leaching methods as incorporated into SW-846 for leaching assessment of inorganic COPCs, and the primary issues associated with adapting these methods for SVOCs and PFAS is reviewed. **Section 2** provides basic characteristic information about SVOC and PFAS, specifically relative to how chemical and physical properties could impact leaching test development. The method development and demonstration for SVOCs (**Section 3** and **Section 4**, respectively) are separated from those for PFAS (**Section 5** and **Section 6**, respectively) due to the differences in the intrinsic behavior of these COPC groups. **Section 7** addresses method development adaptations required when combinations of SVOC, PFAS, and inorganic COPCs are to be analyzed. A summary of this BID is presented in **Section 8** including recommendations for generation of repeatability and reproducibility data for the draft methods using interlaboratory validation. **Section 9** reviews the quality assurance/quality control (QA/QC) protocols taken for the research presented in this BID.

The appendices provide supporting information on organic compounds in terms of physical and chemical data (**Appendix A**) and current EPA regulatory thresholds (**Appendix B**). Detailed results for the experiments used to support leaching test modifications are provided in the **Appendix C**. **Appendix D** presents the finalized Draft Methods 1313A, 1314A, and 1316A that reflect the results reported in this document. A summary of anticipated equipment and supplies needed to conduct each of the draft leaching tests along with estimates of the required personnel time is provided in **Appendix E**. Lastly, **Appendix F** provides a presentation by Hans A. van der Sloot, Ph.D., presented to Vanderbilt University (VU) regarding interlaboratory validation of leaching tests conducted in the European Union.

Recommendations

To ensure the reliability of the draft leaching methods, an interlaboratory validation program in accordance with Agency recommendations should be conducted to develop repeatability (intra-laboratory variance) and reproducibility (inter-laboratory variance) for the extraction methods. A program for this validation has been developed under a quality assurance project plan (QAPP) to guide this validation (U.S. EPA, 2023a). The study plan includes four participating laboratories each conducting the leaching tests in triplicate using at least two solid materials containing SVOCs and two materials containing PFAS and a reference laboratory. To the extent possible, each material should include inorganic COPCs so that repeatability and reproducibility can be compared to the previous LEAF method interlaboratory studies (Garrabrants et al., 2012a; 2012b). The interlaboratory study findings will be documented and the draft leaching methods updated prior to publication in SW-846.

1 Introduction

LEAF was designed to evaluate environmental release of constituents from solid matrices to runoff, groundwater, or surface water bodies. This approach is applicable for waste materials, contaminated soils, contaminated sediments, or industrial by-products that may be subject to beneficial use, treatment, land application or disposal. Unlike other assessment methodologies that define a set of release conditions, the LEAF methods consider that the mobility of COPCs in different solid matrices is controlled over time by inherent leaching behaviors and environmental parameters. LEAF tests can be used as standard methods where results can be directly compared between different material samples or matrices using default or site-specific environmental conditions to inform decisions ensuring that materials are managed in a way that is protective of human health and the environment.

In 2019, the LEAF methods were published by the U.S. EPA for evaluation of materials containing inorganic COPCs, non-volatile organic compounds (NVOCs), and radionuclides in low-activity wastes. Leaching tests analogous to the LEAF methods currently are standardized for use in Europe, Asia, Australia, and North America for a range of environmental media, including coal fly ash (Kosson et al., 2009; Sanchez et al., 2006; 2008; Thorneloe et al., 2010; X. Wang et al., 2022a; 2022b; 2023), flue-gas desulfurization (FGD) gypsum (U.S. EPA, 2023b; Kosson et al., 2009), electric arc furnace (EAF) slag (Garrabrants et al., 2022; Loncnar et al., 2022), wastewater biosolids (Fang et al., 2016; 2018), cementitious materials and wasteforms (Branch et al., 2016; Chen et al., 2021; Garrabrants et al., 2014; Gruber et al., 2022; Kosson et al., 2014b; Van Gerven et al., 2005; Zhang et al., 2022), and other waste streams (Engelsen et al., 2010; van der Sloot et al., 2017). However, since many environmental media contain a range of inorganic and organic constituents, the LEAF methods should be adapted and validated for application to common and emerging organic COPCs, such as SVOCs and PFAS.

This document focuses on adapting established leaching tests for inorganic COPCs to also address the specific characteristics of SVOCs and PFAS. The goal is to develop methods applicable to all three contaminant types. Details on the selection and use of leaching tests for to estimate source terms for leaching under field conditions are available through the EPA LEAF How-To Guide (U.S. EPA, 2019a) and the EPA LEAF website (https://www.epa.gov/hw-sw846/leaching-environmental-assessment-framework-leaf-methods-and-guidance).

The updated LEAF methods presented in this BID reflect the state-of-the-art in the understanding of leaching for organic compounds from solid matrices, experimental evaluation used to fill in knowledge gaps, and practical modifications to the current LEAF laboratory protocols. Primary modifications reflected in these updated methods address: (i) materials of construction, as sorption of organic COPCs to container walls and test apparatus is likely to provide results that understate the leaching potential, and (ii) subsampling of leaching test ***eluates*** to ensure representative aliquots for determinative analyses. Further modifications were implemented to minimize formation of colloids during testing and to provide compatibility with determinative methods for chemical analysis. This document provides an overview of the work conducted in establishing methods that can be solid used for both

Eluate is the solution collected *from a leaching test* after contact with the solid phase. Eluates typically contain the eluent plus leached species.

Eluent is the solution placed into contact with the solid material *in a leaching test*. Eluents are usually free of COPCs.

Leachate is the solution resulting from contact of a solid with a leachant *in the environment.*

Leachant is the solution (e.g., infiltration or groundwater) that contacts the solid in the environment.

organic and inorganic COPCs.

1.1 Leaching Test Goals, Selection, and General Usage

The goal of leaching assessment should be to provide a foundation for evaluating the release of COPCs from solid materials to waterborne environmental exposure pathways. In this context, solid materials may encompass wastes (e.g., from energy production, industrial manufacturing, water, and wastewater treatment), contaminated soil or sediment, demolition debris, construction materials derived from recycled or secondary materials, and treated contaminated materials (e.g., wastes or contaminated soils treated by stabilization or solidification processes). Relevant waterborne pathways may include precipitation runoff, net infiltration, surface water, or groundwater in contact with the solid material. Leaching assessment often is derived from the results of one or more leaching tests that measure either the equilibrium between the solid and liquid under specified conditions or the rate of mass transport through the solid material to the contacting liquid phase.

1.1.1 Leaching Test Conditions and Laboratory-to-Field Relationships

From the beginning of the LEAF development approximately 20 years ago, the intent has been to provide a flexible framework that allows for a leaching characterization that is applicable to a wide range of field conditions and release scenarios (Garrabrants et al., 2021a; 2021b; 2022) rather than mimicking a single field condition. The leaching characterization approach was in direct response to the U.S. EPA Science Advisory Board (U.S. EPA, 1991; 1999) criticisms of the Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedures (SPLP). Thus, the LEAF methods for SVOCs and PFAS, like the methods for inorganic COPCs, the LEAF methods are not designed to simulate the conditions of any release scenario. Thus, LEAF defines equilibrium and time-dependent leaching behavior over a range of values for release controlling parameters (e.g., pH, liquid-to-solid ratio, time, etc.) and the tests are designed to encompass the likely conditions seen in the environment, but not to simulate any single scenario. The results of the LEAF test methos can be used in conjunction with site- or scenario-specific to generate a leaching source term, including expected peak concentrations and mass of COPCs released over time as was done for the coal combustion residual rulemaking (U.S. EPA, 2015 and 2024) and explained in the LEAF guide (U.S. EPA, 2019). The only release controlling parameter that cannot be controlled sufficiently for a standardized test is reduction-oxidation potential (redox) as most laboratory testing is conducted under, at best, mildly oxic conditions (Kosson et al., 2014; Wang et al., 2022a). However, to evaluate the impact of reducing conditions for redox-sensitive COPCs (e.g., chromium, arsenic, selenium), it is recommended that users perform geochemical speciation modeling at various pe conditions (Chen et al., 2021; Wang, 2022b; 2023).

1.1.2 Selection of Leaching Tests

The U.S. EPA publishes a compendium of leaching tests applicable for solid wastes containing either inorganic COPCs and/or organic COPCs as part of *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846 (U.S. EPA, 2020). To be most broadly applicable, leaching test methods used in an assessment should consider: (i) the physical properties of the solid material (e.g., a granular or monolithic material), (ii) the types of COPCs to be evaluated (e.g., metals, hydrophilic and hydrophobic organics), and (iii) the range of release conditions likely to be encountered in the anticipated disposal or use scenario (e.g., pH, redox and water contact).

A fundamental step in the leaching assessment process is to define the ***mode of water contact*** for a solid material in the environment. The mode of water contact supports the selection of appropriate leaching tests to support the leaching assessment. The LEAF "How-To" Guide published by U.S. EPA (2019) provides a discussion of the mode of water contact with respect to leaching test selection.

> ***Mode of water contact*** refers to how precipitation, infiltration, or groundwater contacts the solid material primarily with two modalities: (i) percolation through a permeable granular material or (ii) flow around a relatively impermeable monolithic material (U.S. EPA, 2019a).

Figure 1-1 provides an example of how the hydraulic conductivity of a contaminated material relative to that of the surrounding media can be used to determine the mode of water contact (ITRC, 2011) and, hence, the leaching data required to determine a source term for leaching. In this example, the hydraulic conductivity is defined as the ease at which water can pass through a porous solid material (e.g., soil, waste, clay, concrete, etc.). In the subsurface, the heterogeneity of soil layers or of waste materials buried within soil can lead to combinations of (i) continued percolation through the contaminated material and (ii) diversion of groundwater around the contaminated material.

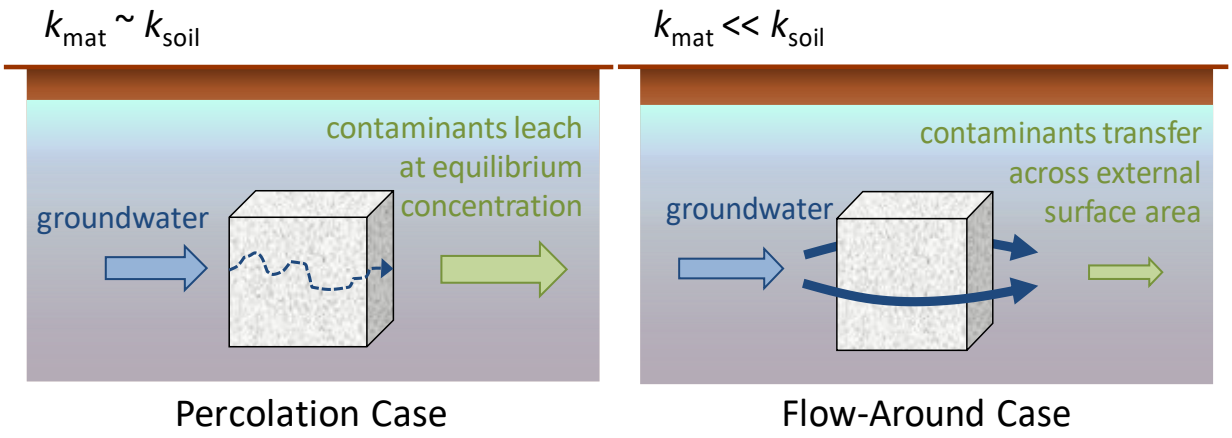

Figure 1-1. Water contact mode for a subsurface waste material based on permeability of the contaminated material (k_{mat}) relative to the permeability of surrounding soils (k_{soil}).

- When the hydraulic conductivity of the contaminated porous material is approximately the same as the hydraulic conductivity of surrounding soils ($k_{mat} \approx k_{soil}$), most of the infiltration will continue along a porous network pathway from the surround soils into and through the contaminated material. Due to the high contact area and long liquid-solid contact time, COPCs in the percolating liquid are assumed to be in local equilibrium with COPCs in the solid. This scenario is most likely to occur with granular materials like soils, loose sediments, and certain process wastes.

  Using the local equilibrium assumption (LEA) as a bounding case, the concentration of COPCs can be estimated by various equilibrium-based batch extraction tests, for example Method 1311 (SW-846, 1992), Method 1312 (SW-846, 1994), Method 1313 (SW-846, 2017a), or Method 1316 (SW-846, 2017d). However, test conditions such as eluant composition, eluate pH, and liquid-to-solid ratio (L/S) under which the equilibrium

concentration is estimated often greatly impact the measured COPC concentrations. Therefore, selection of the appropriate leaching test conditions is critical. As leaching continues and minerals are dissolved from the solid material, the concentration under the LEA may change, for example, because of a pH shift due to leaching of alkaline minerals. When the material buffering capacity is low (e.g., some soils or neutral pH wastes), the eluate pH can be influenced by the acidity/alkalinity of the infiltrating water. Alternatively, the leaching of some constituents may influence the subsequent release of other constituents. In these cases, percolation-based column tests, such as Method 1314 (SW-846, 2017b), most accurately represent the change in equilibrium that may occur with progressive infiltration.

- When the hydraulic conductivity of the contaminated material is approximately 5x less than the hydraulic conductivity of the surrounding soil ($k_{mat} * 5 < k_{soil}$), most of the groundwater will not penetrate the less permeable material and will be forced around the exterior of the contaminated material. Therefore, the contact area for leaching into the groundwater will be limited to external geometric area of the contaminated material and diffusion through the material to the groundwater will be the dominant leaching mechanism. This scenario occurs most often when cements, concretes, or clay lenses are surrounded by more permeable soils.

For these flow-around cases, diffusion-based tank leaching tests measure the rate at which a COPC may be released when diffusion through the solid material controls the rate of leaching. Consistent use of leaching test results, within a proper interpretive framework, also will allow for evaluation of treatment process effectiveness and comparisons of potential impacts under multiple use, treatment, and disposal scenarios.

1.1.3 Uses of LEAF Data in Leaching Assessments

The characterization of COPC release via leaching, i.e., leaching assessment, may be used to support waste and material management decisions concerning the disposal and reuse of secondary and waste materials. For example, leaching assessment is useful for evaluating the impact of wastes (e.g., biosolids, industrial process gypsums, etc.) that may be applied to soils for agricultural purposes. In a regulatory context, the results of leaching tests may be used as input to quantitative models that estimate leachate concentrations and extent of leaching from a solid material under the specific default of site-specific field conditions, for example, remediation, reuse, or disposal scenarios (U.S. EPA, 2019a; Garrabrants et al., 2021a).

Alternatively, leaching test results may be used to screen a wide range of COPCs for only those constituents relevant to a particular scenario (U.S. EPA, 2019a; Garrabrants et al., 2021b). The estimates of release should be as detailed as necessary for the decision process under which the estimates are intended to be used. At the same time, estimates should be considered ***bounding with respect to uncertainties.*** As part of the LEAF approach***,*** leaching assessment estimates are intended to be as accurate as needed or practical while not underestimating the concentrations and amounts of COPCs that may leach. Using this approach, a leaching assessment can be considered an upper bounding estimate to maintain protection of human health and the environment, considering the uncertainties and assumptions (U.S. EPA, 2019a). In general, the interpretive framework for leaching test results may range from: (i) direct comparison of test results from

> ***Bounding with respect to uncertainties*** means that the accuracy of leaching estimates is consistent with the uncertainties associated with the leaching method, analytical methods, reporting limits, etc., and uses assumptions that are biased toward providing the maximum reasonably anticipated leaching concentrations and extent.

single-point leaching tests (e.g., Method 1311 or Method 1312) to threshold values for screening assessments, to (ii) integration of results from multiple leaching tests along with site- or scenario-specific information to provide a detailed scenario assessment for subsequent fate and transport and risk assessment.

In cases where soils or disposed materials are recovered from field settings, the disturbance of material will change the structure and compaction of the material. Although there are methodologies to minimize disturbances, some modification of the compacted structure is inevitable whenever laboratory leach testing is the goal. The extent to which this disturbance impacts retention mechanisms or leaching behavior has not been quantified. These effects are universal regardless of the testing method, and the same precautions recommended in this document should be taken for all such cases. Within the leaching tests, the impact of physical disruptions is minimized for batch and column tests by selection of test conditions that support LEA. However, for chemical species that are susceptible to changes in redox conditions, sampling and testing under laboratory conditions may impact testing outcomes. For example, materials recovered from chemically reducing field conditions may be exposed to oxidation during sampling, leading to changes in arsenic leaching (X. Wang et al., 2022a). In such cases, care should be taken to minimize redox changes during sampling and testing, and test results should be interpreted in the context of potential impacts of redox changes.

1.2 The Leaching Environmental Assessment Framework

The U.S. EPA has published a series of leaching tests which forms a part of the LEAF. Currently, these leaching tests are published as SW-846 Methods 1313 through 1316 (U.S. EPA, 2020). LEAF is a comprehensive leaching assessment approach in which the results of leaching characterization tests are combined with default or scenario-specific leaching parameters to provide a ***leaching source term*** for COPC release from solid materials. The LEAF methods were developed, in part, to address concerns of the U.S. EPA's Science Advisory Board (SAB) that the traditional leaching test approaches using single extraction conditions could not adequately cover the range of leaching conditions present in the field (U.S. EPA 1991; 1999). Documentation of LEAF test development for inorganic COPCs included: (i) a BID (Garrabrants et al., 2010) that supported the development of draft methods, (ii) Draft Methods 1313 through 1316 to be validated, (iii) the results of two interlaboratory validation studies (Garrabrants et al., 2012a; 2012b) that established uncertainties in the draft test methods, and (iv) a comparison between field leaching observations and laboratory test results (Kosson et al., 2014a). At that time, the supported application of LEAF tests was limited to inorganic COPCs and non-volatile organic carbon. Insofar as most radionuclides behave chemically as inorganic compounds, the LEAF tests are considered applicable to radionuclides as well.

> In environmental assessment, a ***leaching source term*** is a description of the concentration (mg/L), mass release (mg/kg), or flux (mg/m^{2}s) for COPCs from a subject material in contact with precipitation, infiltration, or groundwater (U.S. EPA, 2019a). Source terms may provide a measurement of leaching at a point in time under specified conditions or may be used as an input to models for predicting fate and transport of COPC to a point of compliance.

LEAF establishes a standardized framework for estimating leaching from solid wastes, secondary materials and contaminated soils and sediments using test method results along with screening or scenario-based models. Although LEAF was developed and validated primarily for inorganic COPCs under disposal, remediation, and beneficial use in construction applications (Garrabrants et al., 2014; 2020a; 2020b; X. Wang et al., 2022a; 2022b; 2023; Chen et al., 2021;

Gruber et al., 2022; Zhang et al., 2022), applicability has been extended to evaluation of agricultural use of secondary materials (Fang et al., 2016; 2017; 2018; Moshe, 2018). The fundamental principles of the LEAF approach include the:

- Leaching assessment is used as one of several inputs to support the decision whether a proposed management scenario for a material containing COPCs is adequately protective of human health and the environment. Leaching assessment provides useful information regarding the contaminant source term for fate and transport through the waterborne pathway by providing the aqueous COPC concentration, maximum amount, and/or mass flux at the boundary of the contaminated material in natural or engineered systems (i.e., COPC source term). For other applications, such as for differentiating among various COPC sorption mechanisms, additional data and different approaches to augment leaching assessment may be needed.

- Leaching test methods measure the intrinsic properties of materials that control the leaching of COPCs. These leaching properties include:

    - the maximum mass of a COPC that can leach under environmental conditions determined using Method 1313 (SW-846, 2017a). This parameter often is referred to as ***the available content*** *(U.S. EPA, 2019a).*

    - the concentration of COPCs at near-equilibrium conditions controlled by solution pH, such as during Method 1313 (SW-846, 2017a), and liquid-to-solid ratio (L/S) as in Method 1316 (SW-846, 2017d). These concentrations represent the liquid-solid partitioning (LSP) between the solid material and an aqueous phase which is considered to approximate the distribution of COPCs between the solid and contacting water at chemical equilibrium.

    - the rate at which leaching occurs under percolation conditions (Method 1314 (SW-846, 2017b)) and monolithic dissolution-diffusion controlled mass transport conditions (Method 1315 (SW-846, 2017c)).

The ***available content*** is the maximum mass of a COPC that can leach under environmental conditions. For inorganic COPCs, available content can be obtained from Method 1313 as the maximum over the full pH domain or estimated from the maximum release at pH 2, 9, or 13 (U.S. EPA, 2019a). Frequently, the available content is significantly less than the total content; however, the available content and the total content may be the same for some organic COPCs.

Through the LEAF approach, COPC leaching can be estimated as a function of time for a specific disposal or use scenario, given the mechanism and the amount and frequency of water in contact with the material can be defined or estimated. In the absence of detailed information regarding water contact in the disposal or use scenario, the maximum COPC leaching concentration under assumed conditions can be derived directly from the test results.

- Leaching assessment is designed to provide estimates of ***peak COPC leaching concentrations*** and available content, as well as the concentration, flux, or mass release of COPCs over time. These estimates should be as accurate as practical given consideration of uncertainties and practical implementation; therefore, COPC leaching estimates are upper-bounding estimates whereby predicted leaching concentrations or release would be greater than or equal to the actual values in the context of uncertainties and simplifying assumptions.

> ***Peak leaching concentrations*** are often estimated under near equilibrium conditions and compared to decision thresholds to ensure that most of the actual leaching concentrations (assumed to be below an estimated peak value) are compliant with project criteria.

- A graded, or tiered, approach is used for leaching assessment (U.S. EPA, 2019a), whereby the amount of information needed to complete the assessment (e.g., leaching test results and field or scenario parameters) is tailored to the decision needs. For relatively simple comparisons to regulatory or decision thresholds (e.g., to determine which contaminants may be of potential concern), screening approaches using peak COPC concentrations over limited test conditions (i.e., maximum COPC concentration over an applicable pH range) may be directly compared to thresholds. Integration of results from multiple LEAF tests and additional scenario details allow for leaching assessment to be more accurate with a reduced margin (likelihood and extent of over-estimation). This graded approach allows the end-users (e.g., responsible parties and regulators) to decide on the extent of testing and evaluation needed and, thus, the time and cost resources required for evaluation that may influence the decision outcome.

1.3 Background Information Document for Semi-volatile Organic Compounds and Per- and Polyfluoroalkyl Substances

The U.S. EPA Office of Research and Development (ORD) and Office of Land and Emergency Management (OLEM) have supported VU and Texas Tech University (TTU) with the development of this BID which reviews previous knowledge on the release of SVOCs and PFAS from waste and soil materials. Due to the large number of chemical compounds in each of these broad chemical groups, this document focuses on the 8 phenols (e.g., chlorophenols, nitrophenols, etc.) and 16 PAHs (e.g., naphthalene, anthracene, benzo(a)pyrene, etc.) designated as U.S. EPA priority pollutants under the Clean Water Act (Appendix A of 40 CFR Part 423) as well as approximately 25 PFAS consisting of two homologous series of perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), and select polyfluoroalkyl substances, e.g., fluorotelomer-based PFAS.

This document extends the documentation of LEAF test development to provide background information and critical considerations used to adapt the current batch characterization methods (Methods 1313 and 1316) and percolation column test (Method 1314) for wastes and materials containing SVOCs and/or PFAS. Adaptation of the mass transport test (Method 1315) for SVOCs and PFAS will be addressed separately. The structure of the current document addresses the development of batch and percolation methods for SVOCs first, followed by the same for PFAS. For each of these COPC groups, the sections of the BID include:

- the description of a framework for estimating release due to leaching from solid wastes and contaminated environmental media (e.g., soils and sediments) which may include a review of prior related work providing a basis for development of draft leaching test methods for interlaboratory validation.

- a summary of the experimental results filling the identified information gaps (appropriate supporting data in appendices).
- a single-laboratory demonstration in triplicate of the draft test methods conducted on two different materials containing COPCs. When applicable, the demonstration includes a presentation of the performance of the method for inorganic COPCs in comparison to the SW-846 version of the LEAF test.

In addition, this BID discusses how the tests may be integrated to address materials containing a combination of SVOCs, PFAS, and inorganic COPCs. Throughout, the underlying concepts and integrated approach provided in the earlier documentation of LEAF test development BID for inorganic COPCs (Garrabrants et al., 2010) remain applicable and are, thus, extended here.

2 Organic COPCs in the Environment

SVOCs are a subclass of organic compounds with volatility between volatile organic compounds (VOCs) and water. A search of the available literature revealed no universal definition of the term “SVOCs”; however, the following definitions have been applied:

- organic compounds with a boiling point range between 240/260 °C and 380/400 °C (U.S. EPA, 2022a; Lucattini et al., 2018) based on the World Health Organization definition of SVOCs relative to indoor air quality,
- organic compounds with saturated vapor pressures between 10^{-2} and 10^{-8} kPa at 25 °C (Liu, 2022), and
- organic compounds with Henry’s Law Constants from 10^{-5} to $3x10^{-7}$ atm m^3/mol and higher boiling points than water with correspondingly lower vapor pressure from 10^{-4} to 10^{-14} atm or 10^{-1} to 10^{-11} kPa (Thermo-Fisher Scientific, 2022).

Compound families that are traditionally considered SVOCs include PAHs, polychlorinated biphenyls (PCBs), brominated and organophosphate flame retardants, phthalates, chlorinated paraffins, siloxanes, musk/fragrances, and pesticides (Liu, 2022; Lucattini et al., 2018). Some researchers consider PFAS as SVOCs based on the above definitions (Eichler and Little, 2020; Eichler et al., 2022); however, due to their unique surfactant properties and analytical techniques, PFAS were considered separately from SVOCs in this BID.

2.1 Workshop on Leaching of Organic Compounds

In 2015, the U.S. EPA convened a workshop in Arlington, VA, to discuss the development of leaching tests for semi- and non-volatile organic COPCs at contaminated sites where sub-surface treatment approaches have been applied to control migration, and from waste that is disposed or reused (U.S. EPA, 2016). The workshop also considered how best to predict sub-surface leaching potential at the outer edge of treated media (i.e., near-field release) such as used in some Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) programs, while allowing for prediction of COPC concentration or release at a unit or application boundary for disposal or material reuse situations (i.e., down-gradient impacts at a point of compliance) such as in the Resource Conservation and Recovery Act (RCRA) program. Key parameters were identified that are expected to govern leaching potential of semi- and non-volatile COPCs from subsurface treated media or disposed wastes. Additionally, a general interpretive framework for organic COPCs was provided, based on organic COPC environmental chemistry and mass transport principles.

The workshop also presented some observations that would be useful in the development of leaching test methods for organic COPCs:

- Organic COPCs span multiple classes of compounds, including VOCs, SVOCs, and NVOCs. The wide range of physical-chemical properties of these COPCs, including volatility, hydrophobicity, and aqueous solubility, can affect the efficacy of test methods. The workshop concluded that ***the primary focus of test method development should be on SVOCs and NVOCs*** as the high probability for loss of VOCs during field sampling, material processing, and leach testing may not be easily minimized or accounted.
- The leaching capacity of solid wastes, contaminated soils, and contaminated sediments

depends on solid material properties and chemical properties. Soils, sediments, and treatment process amendments (e.g., char, activated charcoal) can sorb large amounts of organic compounds and slowly release them over extended periods of time.

- Leaching of organic COPCs, and test methods for evaluating this leaching, can be complicated by the presence of nonaqueous phase liquids (NAPLs, e.g., liquid petroleum hydrocarbons) present in the solid material which serve as a reservoir of organic COPCs. In addition, NAPLs complicate the leaching test processing by coating test apparatuses or by forming a separate organic phase in leaching test extracts.

- The ***materials of construction for experimental apparatuses can have a significant effect on outcome of partitioning and transport experiments***, especially for organic COPCs at low concentrations. Apparatus and test methods need to be evaluated for unintended sinks or losses for organic and inorganic contaminants. Examples of sinks or losses would include sorption of COPCs to container walls or seals/valve seats, exposure to light leading to photodegradation of organic COPCs, or biodegradation of organic COPCs during extended testing time intervals or storage of test method eluates.

The workshop concluded that the leaching of organics is controlled by the capacity of the different solid phases (e.g., soil particles, particulate organic matter, oils, and greases) to sorb or partition the organic COPCs and the mass transfer rate of COPCs from each of these phases. As water contacts or moves through a material, the solute is transported through advection, dispersion, and diffusion; each phase of the material (e.g., water, NAPL, and solid) holds some of the solute. Solutes can preferentially accumulate in specific phases (e.g., solid natural organic matter) based on adsorption and multiphase partitioning processes.

Primary phenomena that either retard or enhance leaching of SVOCs and NVOCs are: (i) the mode and amount of water contact, (ii) adsorption/desorption, (iii) multiphase partitioning (e.g., between solid, aqueous, and organic phases), and (iv) equilibrium vs diffusion-controlled release. The same fundamental premises are applicable for inorganic COPCs, and thus the LEAF concepts and approaches remain valid and useful for organic COPCs. However, leach testing to measure specific parameters requires some modifications to adapt to the physical-chemical characteristics and analytical methods for organic COPCs. This report describes the specific test method modifications needed to address leaching of SVOCs and PFAS. In addition, this report documents the approach and results from adapting and demonstrating LEAF test methods.

2.2 COPCs in this BID

The COPCs chosen as the focus of this BID for leaching test development include a suite of phenolic compounds and PAHs which can be analyzed by gas chromatography-mass spectrometry (GC-MS) following Method 8270E (SW-846, 2018b) as well as a list of carboxylic, sulfonic acid, and telomer PFAS typical of aqueous film-forming foam (AFFF) which is extensively used in firefighting training and activities.

2.2.1 Phenolic Compounds

Phenols are a family of organic compounds characterized by a single aromatic (benzene) ring with an attached hydroxyl (-OH) group (Min et al., 2015; Wade, 2023). The term “phenol” describes the simplest form of a phenolic compound; however, most phenols are methyl-, chloro-, or nitro-substituted compounds of the basic phenol compound. The U.S. EPA priority pollutant list (U.S. EPA, 2023c) contains 8 phenolic compounds including phenol (PHL), 2-

chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4-dimethylphenol (2,4-DMP), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), and pentachlorophenol (PCP). The method development and demonstration in this BID includes these priority pollutants as well as 2,4,6-trichlorophenol (2,4,6-TCP), 2-methyl-4,6-dinitrophenol (DNOC), and 4-chloro-3-methylphenol (4C-3MP) which are commonly analyzed with the above. Often, phenolic compounds in the environment are derived from anthropogenic sources, such as production of phenolic resins, chemical reagents, or by-products from fertilizer production (Sądej et al., 2016) and textile processing. Natural sources of phenolic compounds include naturally occurring flavonoids, tannins, and lignans (El Gharris, 2009; Oluwole et al., 2022) or the products of soil organic matter biodegradation (Min et al., 2015; Akomeng and Adusei, 2021).

2.2.2 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons are a class of organic compounds consisting of two or more fused aromatic rings (Yan et al., 2019; Pathak et al., 2022). The 16 PAHs on the U.S. EPA priority pollutant list (U.S. EPA, 2023c) range from the two ringed naphthalene (NAP) to the six ringed, high molecular weight indeno(c,d)pyrene (IND) and benzo(g,h,i)perylene (BGP). Sources of significant PAHs in soils results from incomplete combustion of crude oil, coal, gasoline, and wood (Dat and Chang, 2017) as well as natural sources, such as degradation and transformation of organic carbon by plants and microorganisms (Liu et al., 2019).

2.2.3 Per- and Polyfluoroalkyl Substances

PFAS are a family of anthropogenic fluorinated compounds that have emerged as pollutants of interest across multiple media because of their ubiquity, persistence, and toxicity at ppt concentration (Dat and Chang, 2017). The U.S. EPA Contaminant Candidate List 5 contains over 10,000 compounds identified as PFAS (U.S EPA, 2022b). PFAS are often characterized by an alkyl tail of the structure $CF_3(CF_2)_n$ attached to one or more charged functional groups such that the molecular charges are pH dependent as anionic, cationic, or **zwitterionic** (Backe et al., 2013; Maizel et al., 2021). In general, there is no common, universal definition of PFAS (Buck et al., 2011, Wang et al., 2021; U.S. EPA, 2022b) which can lead to different estimates of the overall number of PFAS.

Zwitterions are molecules comprised of at least two functional groups – one having a negative charge and one having a positive charge. The overall molecular charge would be zero (Davis, 2023).

The term PFAS is intended to recognize that there exist perfluorinated substances where all alkyl carbons are fully fluorinated as well as polyfluorinated substances that have some alkyl carbons bound to hydrogen. Since C-F bonds are strong, most PFAS are chemically stable and persistent in the environment (Goss, 2008; Kookana and Navarro, 2023). The most studied PFAS are PFCAs with a carboxylic acid (R-COOH) functional group and PFSAs with a sulfonic acid (R-S(=O)2OH) functional group. However, other functional groups, such as perfluoroalkyl sulfonamides (FASAs) and fluorotelomers are possible (Guelfo et al., 2018; ITRC, 2022). Another common convention is to subdivide PFAS into short-chain or long-chain PFAS based on the length of the carbon chain, $CF_3(CF_2)_n$ (Buck et al., 2011). The prevalent convention is that short-chain PFAS include C ≤6 while long-chain PFAS include C >6; however, this terminology should be interpreted with caution as universal definitions of short- and long-chain have not been adopted.

Per- and polyfluoroalkyl tails are both hydro- and lipophobic, and when the tail is bound to a charged functional group, PFAS are surface active at air-water interfaces (Alves et al., 2020; Guelfo et al., 2021; ITRC, 2022). The hydro- and lipophobicity along with surfactant properties are primary drivers for use of PFAS for stain- and water-resistant coatings, lubrication, and film-

forming applications. Due to their surfactant nature, some PFAS may form self-assemblages such as micelles or lamella (Guelfo et al., 2021), partition to air-water interfaces (Brusseau et al., 2021; 2022; Costanza et al., 2019; Guo et al., 2020; Lyu and Brusseau, 2020; Schaefer et al., 2019; Schaefer et al., 2022b), and sorb to soil mineral surfaces or soil organic matter (Guelfo and Higgins, 2013).

Primary sources of PFAS in the environment include fluoropolymer and other manufacturing facilities and use of aqueous film-forming foams used in Class B firefighting activities (Guelfo et al., 2018, Barton et al., 2006; D'Ambro et al., 2021; Davis et al., 2007). Manufacturing, use, and disposal of PFAS has led to secondary sources of PFAS in the environment. These sources include contaminated soil and concrete (Høisæter et al., 2019; ITRC, 2022; Thai et al., 2022; Wang, 2023), water treatment residuals and biosolids (Arhens et al., 2011; Schaefer et al., 2022a; Schultz et al., 2006; Sepulvado et al., 2011; Silva et al., 2022) which may be applied as agricultural soil amendments (ITRC, 2022; Pepper et al., 2021; 2023), and landfills (Huang et al., 2022, Liu et al., 2022). A significant secondary source is the release of PFAS from various consumer goods that enter municipal water systems (Crone et al., 2019; USGS, 2023), landfills (Malovanyy et al., 2023), and waste-to-energy facilities (Solo-Gabriele et al., 2020), eventually contributing to PFAS contamination.

2.3 Physical and Chemical Properties of Organic COPCs

The physical and chemical properties of the target phenols, PAHs, and PFAS for this BID are provided in **Table 2-1**. The table includes aqueous solubility, Henry's Law constant, vapor pressure, *n*-octanol-water partition coefficient [log(K_{ow})], and dissociation constants (pKa values). An expanded table, encompassing a wider range of organic compounds, is provided in **Appendix A** as a reference for selecting representative indicator compounds for test method development.

All data were experimentally determined with the exceptions that some of the PFAS data were estimated from experimental data (e), extrapolated from experimental data (x), or modeled (m) using the OPEn (q)saR app (Mansouri et al., 2018). Most data are reported at 25 °C or at other temperatures as noted. The selection of parameter values, from what is often a broad range of values, was prioritized toward measured experimental data over extrapolated or modeled data using the least number of data sources over the range of compounds.

For PFAS, modeled properties often applied to the neutral or protonated form of the acid; however, PFCAs and PFSAs are charged at all environmentally relevant pH levels. Since properties such as solubility, vapor pressure, and Henry's Law constant are different for protonated vs deprotonated acids, use of PFAS properties should be interpreted with caution.

2.3.1 Aqueous Solubility

In **Table 2-1**, COPCs are placed in order of aqueous solubility at neutral pH. The solubility data span nearly eight orders of magnitude and show that phenols, in general, are significantly more soluble in water than PAHs. The aqueous solubility of PFAS compounds spans the range between that of phenolic compounds and PAHs. However, what is not evident by the ranking of aqueous solubility tabulated for neutral pH is the effect of pH and DOC on the solubility of individual compounds. The measured concentration of organic compounds is increased by association with DOC and suspended particulate matter while reduced by sorption onto solid surfaces. In turn, these phenomena are dependent on solution pH, as the solubility of DOC is pH-dependent, and some SVOCs dissociate or deprotonate as a function of pH.

Table 2-1. Properties of Selected Volatile Organics (blue highlight), Phenols (green highlight), PAHs (orange highlight), and PFAS (purple highlight) in Order of Decreasing Aqueous Solubility.

Compound	Abbrev.	Chemical Group	CAS #	Molar Mass (g/mol)	Aqueous Solubility at 25 °C* (mg/L)	Henry's Law Constant at 25 °C (atm-m^3/mol)	Vapor Press. at 25 °C (kPa)	*n*-Octanol-Water Partitioning [log(Kow)]	pKa (-)
phenol	PHL	phenolics	108-95-2	94.11	82,800	3.33E-07	0.047	1.46	9.99
perfluorobutane sulfonic acid	PFBS	PFAS	375-73-5	300.1	26,000 [70]	0.26 (e) [20]	0.067 [70]	-0.34 [70]	0.3 (e) [60]
perfluorohexanoic acid	PFHxA	PFAS	307-24-4	314.05	25,000 [70]	2.4E-10 [70]	0.044 [70]	1.5 [70]	0.28 [80]
4-nitrophenol	4-NP	phenolics	100-02-7	139.11	15,600	1.28E-08	6.67E-05 (x)	1.91	7.15
2-chlorophenol	2-CP	phenolics	95-57-8	128.55	11,300 [10]	1.12E-05	0.337	2.15	8.56
perfluoropentanoic acid	PFPeA	PFAS	2706-90-3	264.05	9,812 (x) [20]	0.18 (e) [20]	0.151 [20]	--	0.34 [80]
perfluorooctanoic acid	PFOA	PFAS	335-67-1	414.06	9,500 [70]	9.1 (e) [20]	0.0022 [90]	4.81 (e) [20]	0.30 [80]
2,4-dimethylphenol	2,4-DMP	phenolics	105-67-9	122.16	7,870	1.70E-05	0.014	2.3	10.6
perfluorobutanoic acid	PFBA	PFAS	375-22-4	214.04	4,600 [70]	1.2E-4 [70]	2.0 [70]	2.4 [70]	0.43 [80]
2,4-dichlorophenol	2,4-DCP	phenolics	120-83-2	163.0	4,500	4.29E-06	0.012	3.06	7.89
4-chloro-3-methylphenol	4C-3MP	phenolics	59-50-7	142.58	3,830	2.45E-06	0.0067	3.1	9.55
2,4-dinitrophenol	2,4-DNP	phenolics	51-28-5	184.11	2,790	8.60E-08	5.20E-05	1.67	4.09
2-nitrophenol	2-NP	phenolics	88-75-5	139.11	2,500	1.63E-05	0.015	1.79	7.23
benzene	BEN	BTEX	71-43-2	78.11	1,790	0.0056	12.6	2.13	--
perfluorononanoic acid	PFNA	PFAS	375-95-1	464.07	1,300 [70]	33.8 (e) [20]	0.00067 [90]	2.6 [70]	0.32 [80]
perfluoropentane sulfonic acid	PFPeS	PFAS	2706-91-4	350.1	823 (m) [30]	--	--	--	--
perfluorooctane sulfonic acid	PFOS	PFAS	1763-23-1	500.1	680 [70]	4.3E-7 [70]	8.7E-5 [70]	-1.1 [70]	0.3 (e) [60]
toluene	TOL	BTEX	108-88-3	92.14	526	0.00664	3.79	2.73	--
2,4,6-trichlorophenol	2,4,6-TCP	phenolics	88-06-2	197.4	500	4.20E-06	0.001	3.69	6.23
perfluoroheptane sulfonic acid	PFHpS	PFAS	375-92-8	450.1	464 (m) [30]	--	--	--	--
perfluorononane sulfonic acid	PFNS	PFAS	68259-12-1	550.1	384 (m) [30]	--	--	--	--
perfluoroheptanoic acid	PFHpA	PFAS	375-85-9	364.06	365 (x) [20]	2.4 (e) [20]	0.055 [20]	4.15 (e) [20]	0.31 [80]
2-methyl-4,6-dinitrophenol	DNOC	phenolics	534-52-1	198.13	198	1.40E-06	1.60E-05	2.13	4.31
perfluorodecane sulfonic acid	PFDS	PFAS	335-77-3	600.1	194 (m) [30]	--	--	--	--
o-xylene	*o*-XYL	BTEX	95-47-6	106.16	178	0.00518	0.88 (x)	3.12	--
ethylbenzene	EBZ	BTEX	100-41-4	106.16	169	0.00788	1.28	3.15	--
perfluoroundecanoic acid	PFUnA	PFAS	2058-94-8	564.1	92 [70]	3.3E-10 [70]	1.8E-5 [90]	4.0 [70]	2.6 (e) [50]
naphthalene	NAP	PAHs	91-20-3	128.17	31	0.00044	0.011	3.3	--
perfluorotridecanoic acid	PFTrDA	PFAS	72629-94-8	664.1	28 (m) [30]	--	--	--	--
pentachlorophenol	PCP	phenolics	87-86-5	266.3	14	2.45E-08	1.47E-05	5.12	4.7
acenaphthylene	ACY	PAHs	208-96-8	152.19	3.93	0.000125	0.00064	3.93	--
acenaphthene	ACE	PAHs	83-32-9	154.21	3.9	0.000184	0.00029	3.92	--
perfluorohexane sulfonic acid	PFHxS	PFAS	355-46-4	400.1	2.4 [70]	3.5 (e) [20]	0.0479 [20]	2.2 [70]	0.3 (e) [60]
perfluorodecanoic acid	PFDA	PFAS	335-76-2	514.1	2.1 (x) [20]	120 (e) [20]	1.0E-4 [90]	--	0.31 [80]
fluorene	FLU	PAHs	86-73-7	166.22	1.69	9.62E-05	8.00E-05	4.18	--
phenanthrene	PHE	PAHs	85-01-8	178.23	1.15	4.23E-05	1.61E-05	4.46	--
perfluorotetradecanoic acid	PFTeDA	PFAS	376-06-7	714.1	0.30 [70]	3.6E-10 [70]	5.6E-5 [70]	5.1 [70]	--
fluoranthene	FLA	PAHs	206-44-0	202.25	0.26	9.45E-06	1.23E-06	5.16	--
pyrene	PYR	PAHs	129-00-0	202.25	0.135	1.19E-05	6.00E-07	4.88	--
perfluorododecanoic acid	PFDoA	PFAS	307-55-1	614.1	0.07 (x) [40]	400 (e) [20]	0.00417 [20]	--	3.1 (e) [50]

Compound	Abbrev.	Chemical Group	CAS #	Molar Mass (g/mol)	Aqueous Solubility at 25 °C* (mg/L)	Henry's Law Constant at 25 °C (atm-m^3/mol)	Vapor Press. at 25 °C (kPa)	*n*-Octanol-Water Partitioning [log(Kow)]	pKa (-)
anthracene	ANT	PAHs	120-12-7	178.23	0.0434	4.88E-05	8.75E-07	4.45	--
benz(a)anthracene	BAA	PAHs	56-55-3	228.3	0.0094	1.20E-05	2.80E-08	5.76	--
dibenz(a,h)anthracene	DHA	PAHs	53-70-3	278.3	0.00249	1.40E-07	1.27E-10	6.5	--
chrysene	CHR	PAHs	218-01-9	228.3	0.002	5.23E-06	8.31E-10	5.73	--
benzo(a)pyrene	BAP	PAHs	50-32-8	252.3	0.00162	4.57E-07	7.32E-10 (x)	6.13	--
benzo(b)fluoranthene	BBF	PAHs	205-99-2	252.3	0.0015	6.57E-07	6.67E-08	5.78	--
benzo(k)fluoranthene	BKF	PAHs	207-08-9	252.3	0.0008	5.84E-07	1.29E-10	6.11	--
benzo(g,h,i)perylene	BGP	PAHs	191-24-2	276.3	0.00026	2.66E-07	1.33E-11	6.63	--
indeno(1,2,3-cd)pyrene	IND	PAHs	193-39-5	276.3	0.00019	3.48E-07	1.67E-11	6.7	--

Notes:

* Aqueous solubility is a function of pH for ionizable compounds.

All data determined at 25 °C unless otherwise noted in parantheses.

(e) indicates estimated data

(x) indicates data extrapolated from experimental data

(m) indicated data modeled using OPERA – OPEn (q)saR App

-- indicates no value available

Sources:

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2.3.2 Impact of Solution pH

The pH of the leaching solution is an important controlling parameter for inorganic COPCs that significantly affects the constituent speciation and the measured concentration in aqueous solution. For SVOCs and PFAS, however, solution pH has less of a direct effect on constituent solubility but may affect the charge on functional groups of the constituent and material surfaces which can impact surface sorption. In addition, solution pH has a direct effect on the solubility of DOC which can influence the amount of colloidal material available for complexation with organic COPCs.

2.3.2.1 Protonation of Primary COPCs

The phenols and PFAS shown in **Table 2-1** deprotonate (i.e., lose a hydrogen atom) at their functional end member groups at pH values above their pKa values. However, there is some uncertainty in the parameter values in **Table 2-1** depending on if the properties were determined by experiments, extrapolated from experimental data, or modeled.

The data in **Table 2-1** show that pKa values of SVOCs generally range from just under pH 4 to over pH 11, meaning that these compounds may be protonated or deprotonated under environmental conditions. Therefore, ***the pH value of aqueous eluates for SVOCs should be adjusted with acid to a pH <2 prior to microextraction into solvent to ensure transfer to the solvent phase and minimize sorption of SVOCs to container surfaces.***

In contrast, PFAS pKa values typically are less than 2, with only PFDA, PFUdA, and PFDoA having modeled pKa values between 2 and 4 (**Table 2-1**). Generally, long-chain PFAS with greater than 7 fluoroalkyl carbons (C >7) are reported to have higher pKa values than shorter-chain PFAS. The pKa data implies that many PFAS in **Table 2-1** will always be detected in their ionic form (Goss, 2008; Guelfo et al., 2021; Nguyen et al., 2020; Wu et al., 2020) while longer-chain PFAS may be either protonated or deprotonated under the wide range of leaching test conditions. Deprotonated compounds are negatively charged in solution and, therefore, are more susceptible to sorption to positively charged surfaces. When protonated, however, these neutral compounds tend to be less polar and less prone to sorption to positively charged surfaces. As neutral compounds, these protonated PFAS may be more prone to sorption driven by hydrophobic interactions.

Although the names of PFAS groups such as PFCAs and PFSAs are a convenient approach for discussing groups of compounds, the acid forms of the species are rarely observed in the environment (Goss, 2008; Guelfo et al., 2021; Nguyen et al., 2020; Wu et al., 2020). Under most environmental conditions, PFAS exist as deprotonated partially ionic species with attraction to oppositely charged surfaces including soil minerals and vessel walls, as well as hydrophobic surfaces including air-water interfaces due to surfactant properties.

2.3.2.2 Release of DOC and Impact to COPC Concentrations

Solution pH can also impact SVOC and PFAS concentration by controlling the dissolution of DOC because protonation and deprotonation of acidic DOC moieties influences DOC water solubility. Hence, associations between DOC and organic COPCs as a means of COPC partitioning into solution may be enhanced depending on pH. **Figure 2-1** presents an example of the importance of DOC on measured concentration of PAHs. This figure shows that PAH concentration is closely associated with DOC concentrations in batch extractions of soils contaminated with PAHs (red and green lines, respectively). However, when DOC is removed from the eluate by flocculation, the measured PAH concentrations decrease significantly.

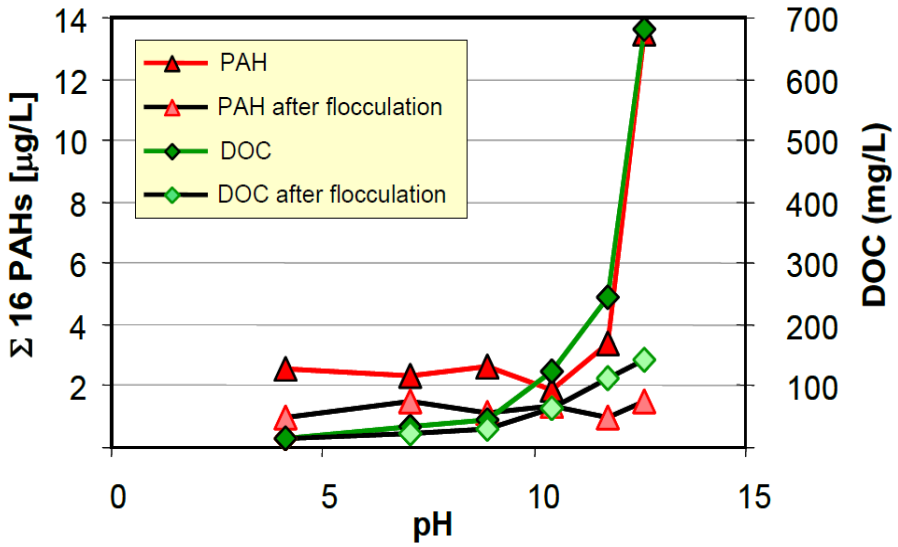

Figure 2-1. Measured sum of the 16 U.S. EPA PAHs in pH-dependent leaching eluate before and after flocculation to remove dissolved organic carbon (modified from Roskam and Comans, 2009).

Similar associations with DOC are expected for some PFAS and some SVOCs. Thus, conditions that cause DOC to form suspended ***colloidal matter*** may increase the measured concentration of organic COPCs in eluate solution.

> ***Colloidal matter*** consists of particles (as opposed to solid bulk material or dissolved phase) with an equivalent spherical diameter between approximately 1 and 1000 nm dispersed in a liquid phase (Goldberg et al., 2000, Kretzschmar, 2005). In this document, colloids are particles of solid material (minerals, agglomerates of organic particles, etc.) that are less than approximately 1 µm in diameter that cannot be separated from eluates by settling but contribute to the turbidity of the solution. Colloidal matter includes dispersed aggregates of organic matter (e.g., humic acids), metal oxyhydroxides (e.g., Fe and Al) or clay minerals.

Agitated batch testing (e.g., SW-846 Methods 1311, 1312, 1313, and 1316) can artificially increase the dissolution of organic matter and suspension of colloids beyond that which would occur without agitation (Bergendahl and Grasso, 1998; Bergendahl, 2005; Yasutaka et al., 2017; Gu et al., 2019). The association of organic COPCs with DOC could impact leaching test results by overpredicting the partitioning COPCs into test eluates (Bergendahl and Grasso, 1998; Bergendahl, 2005). ***If colloids are generated from agitation of batch leaching tests, steps (e.g., centrifugation, filtration, treatment) should be taken to prevent and reduce the amount of eluate colloidal matter prior to analysis.*** Prevention of colloid formation is best achieved through use of a 1-mM $CaCl_2$ eluant. Removal of colloids after agitated batch extractions can be carried out through the addition of alum (discussed further in **Section 2.6.2.4** and **Section 3.3.2**). Addition of alum to eluate after testing is recommended when turbidity is greater than 1 NTU when colloids can constitute an additional sink for SVOCs (see **Section 4.4.2**). Addition of alum is not recommended for removing colloids when subsequently measuring ionic species (inorganic COPCs and PFAS) in solution.

2.3.2.3 Sorption to Material Surfaces

Solution pH also can alter the surface charge of soil minerals and dispersion of soil organic matter and clays, affecting adsorption of charged COPCs to solid surfaces (ITRC, 2022). Most often, these effects are discussed from a retention mechanism for COPCs from soils and waste matrices, although the same principles apply to contact surfaces in vessels used for testing and storage of aqueous solution containing SVOCs and PFAS. Sorption phenomena are pH-dependent such that the loss of PFAS, for example, to test apparatus materials may be greater under a wide range of pH conditions such as in Draft Method 1313A.

Lath et al. (2019) have found that filter membranes, different types of plastic, and glass bottles sorb perfluorooctanoic acid (PFOA). Thus, filtration is not recommended for clarification of leaching tests for PFAS, especially for measurements at low concentrations (Lath et al., 2019). Therefore, the sorption of organic COPCs to materials of construction needs to be quantified so that a material type compatible with the intended use may be chosen for PFAS leach testing and eluate processing.

2.3.3 Hydrophobicity

The log(K_{ow}) value is a measure of the hydrophobicity of a chemical compound. Some organic compounds are nonpolar (e.g., benzene rings do not have functional groups with high electron density or the ability to become deprotonated to form charged ions) such that they are less soluble in polar solutions like water. For environmental purposes, the log(K_{ow}) value represents the relationship between lipophilic (fat soluble) and hydrophilic (water soluble) substances.

> ***Hydrophobicity*** is the physical property of a chemical compound that describes its tendency to be repelled by water (Verlicchi, et al., 2013). Hydrophobic compounds typically are characterized by log(K_{ow}) values >4 (Rogers, 1996), poor water solubility, and the potential to sorb to nonpolar surfaces (Piwoni and Keeley, 1990; Chen et al., 2021).

Phenols tend to be less hydrophobic than PAHs with log(K_{ow}) increasing with substitution on the benzene ring. However, nitrophenols, including the more substituted 2,4-dinitrophenol, tend to be less hydrophobic than chlorinated or methylated phenols. In general, the log(K_{ow}) values in **Table 2-1** inversely correlate with aqueous solubility for these SVOC compounds (i.e., compounds with greater log(K_{ow}) have lower aqueous solubility).

For leaching evaluation, the practical implication of hydrophobicity is the potential for loss in aqueous eluates to materials of construction (less polar surfaces), especially for hydrophobic organic compounds with log(K_{ow}) >4-5 (Rogers, 1996). ***Highly hydrophobic compounds (e.g., most PAHs) may require a hydrophobic sink, such as a solid phase extraction (SPE) medium, to capture the mass released into the aqueous leachate, avoiding aqueous saturation.*** However, in ionizable organic compounds (e.g., phenols), the measured log(K_{ow}) may be pH-dependent since protonated and unprotonated compounds may have different properties.

2.3.4 Vapor Pressure

> ***Volatility*** is the tendency of an organic compound to vaporize or the speed at which it vaporizes. VOCs demonstrate higher vapor pressures than SVOCs or NVOCs at a given temperature (U.S. EPA, 2022a).

Vapor pressure is a chemical parameter representing the potential of a pure phase organic compound to ***volatilize*** under standard temperature (20 °C) and pressure (1 atm). If the data in **Table 2-1** are reordered based on vapor pressure (not shown), benzene, toluene, ethylbenzene and xylenes (BTEX) chemicals would have the greatest vapor pressures with phenols and most neutral PFAS more volatile than PAHs. The most volatile PAH (i.e., NAP) is generally less volatile than five of the phenolic compounds in the BID COPC list (i.e., 2-CP, PHL, 2-NP, 2,4-DMP, and 2.4-DCP). As noted earlier (**Section 2.2.3**), acidic PFAS are predominantly dissociated at environmentally relevant pH values.

Volatilization of COPCs is a loss mechanism to be minimized during field sampling and laboratory handling. ***Solid materials for testing should be collected in containers constructed of materials compatible with the primary solid matrix, the contacting liquid phase, and the COPCs***. In the field, solid samples should be directly placed into sampling containers with effort to completely fill containers and minimize headspace. Wide-mouth glass containers with polychlorotrifluoroethylene (PCTFE)-lined lid seals are recommended for SVOCs (see SW-846, Chapter 4, Table 4-1), and 1-L containers are suggested here for collecting solids for leaching tests. Sample containers should be tightly sealed and be refrigerated to 0-6 °C as rapidly as possible. Prior to and during homogenization and/or sub-sampling, solid materials should be chilled to 0-6 °C and maintained as chilled as practical, with transfers and handling occurring with a minimum amount of air contact.

2.4 Analytical Methods

For the LEAF methods, inorganic chemical analyses are carried out by direct injection of aqueous eluates onto an analytical instrument. Analysis of inorganic COPCs, including cations (e.g., As, Sb, Cr, Pb) and anions (e.g., Cl^-, F^-, SO_4^{2-}) in aqueous solution, are typically conducted using a range of aqueous-based analytical techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma-optical emissions spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), ion chromatography (IC), and dissolved carbon analysis (DCA), that each may require a specific sample preservation approach. For inorganic COPCs, pressure or vacuum filtration of eluate through a 0.45-µm PP filtration membrane is common; however, membrane filtration is not compatible with analyses for PFAS and SVOCs due to sorption to the filtration media. Samples for AAS, ICP-OES, and ICP-MS are acidified to pH <2 with nitric acid (HNO_3) for preservation (SW-846, Chapter 3, Table 3-2).

In contrast, chemical analysis for organic COPCs is most often carried out by injection of a solvent-based sample onto an analytical instrument. For example, the guidance provided in SW-846 (U.S. EPA, 2020), recommends analysis of SVOCs by GC-MS. To obtain a solvent-based analytical sample, organic COPCs in aqueous test eluates must be quantitatively exchanged into an organic solvent such as hexane or methylene chloride (MeCl), either by direct liquid-liquid extraction, for example following Method 3511 (SW-846, 2015c) or using a SPE following Method 3535A (SW-846, 2007). During development of the draft leaching tests, Method 3511 (SW-846, 2015c) was used to prepare solvent-based analytical solutions from aqueous eluates. Alternative SW-846 methods for solvent exchange, such as Method 3510C (SW-846, 1996b), Method 3520C (SW-846, 2015d), or Method 3535A (SW-846, 2007), also can be acceptable.

Aqueous eluates were acidified to pH <2 (less than the lowest pKa of phenol COPCs) with sulfuric acid to maximize solvent extraction of phenols. Furthermore, there are concerns regarding losses of organic COPCs from aqueous solution to filters or filter housings (Lath et al., 2019) or at air-water interfaces (Brusseau et al., 2021; 2022), so eluate separation from extracted solids and eluate transfers or aliquoting required different approaches than used for inorganic COPCs. Thus, centrifugation is preferred for solid-liquid separation when PFAS are to be analyzed while settling for up to 2 hours was preferred for solid-liquid separation in SVOC extracts.

2.5 Regulatory Thresholds

A table of regulatory concentration thresholds as maximum contaminant levels (MCLs) for organic compounds currently regulated by U.S. EPA under the RCRA program is presented in **Appendix B**. Leaching test methods are assumed to be required to provide accurate measurements of extract COPC concentrations at concentration levels less than the MCL. Although PCP and benzo(a)pyrene (BAP) have regulatory limits at 1.0 and 0.2 µg/L, respectively, most phenolics and PAHs do not have regulatory limits.

On April 2024, the U.S. EPA promulgated individual national drinking water limits for five PFAS including PFOA, perfluorooctane sulfonic acid (PFOS), perfluorononanoic acid (PFNA), perfluorohexane sulfonic acid (PFHxS), and hexafluoropropylene oxide dimer acid (HFPO-DA) as shown in **Table 2-2** (U.S. EPA, 2024). In addition, aqueous mixtures of two or more PFAS – PFHxS, PFNA, HFPO-DA, and perfluorobutane sulfonate (PFBS) – cannot have a total Hazard Index (HI) greater than 1:

$$\text{where HI} = \left(\frac{[PFHxS]}{[10\ ng/L]}\right) + \left(\frac{[PFNA]}{[10\ ng/L]}\right) + \left(\frac{[HFPO\text{-}DA]}{[10\ ng/L]}\right) + \left(\frac{[PFBS]}{[2{,}000\ ng/L]}\right)$$

Table 2-2. Promulgated PFAS Regulations (U.S. EPA, 2024) as of April 10, 2024.

PFAS Compound	MCL (ng/L)	MCL Goal (ng/L)
PFOA	4	0
PFOS	4	0
PFNA	10	10
PFHxS	10	10
HFPO-DA	10	10

2.6 Specific Phenomena and Needs for LEAF Methods Development

The understanding of the phenomena and specific parameters measured by characterization-based leaching tests (e.g., LEAF) is central for the development of leaching test methods for target COPCs. This section discusses the essential phenomena that need to be considered for reliable leaching assessment of a solid material and recommends approaches for addressing these phenomena within the draft test methods.

2.6.1 Available Content

The available content is defined as the maximum amount of a COPC that may potentially leach under relevant environmental conditions (U.S. EPA, 2019a). For inorganic COPCs, the available

content may be considerably less than the total content of the specific inorganic COPC in the material because inorganic COPCs may be incorporated into or sequestered within essentially insoluble mineral phases (e.g., lead incorporation into insoluble glassy phases). However, organic COPCs are not typically substantially incorporated into insoluble mineral phases such that ***the maximum amount of an organic COPC that can potentially leach is assumed to be the total content of the COPC in the material being evaluated***. The rationale is that the mechanisms commonly known for the long-term sequestration of inorganic constituents from leaching are not typically associated with the major fraction of an organic COPC present in a material being tested. However, some mechanisms, such as partitioning into recalcitrant natural organic matter (NOM), NAPLs, or anthropogenic organic matter (AOM; e.g., grease, plastics) may significantly retard the rate of leaching (Brusseau et al., 2019; Brusseau, 2019a; Zhu et al., 2021; Schaefer et al., 2022c) while some larger or ionically excluded molecules may be physically entrapped (Zhu et al., 2021).

2.6.2 Multiphase Partitioning

For organic COPCs, partitioning under field conditions and under leaching test conditions must consider the potential for partitioning between the vapor (air) phase, aqueous and nonaqueous liquid phases, and various solid phases (inorganic, NOM, AOM).

2.6.2.1 Vapor Phase Partitioning

Partitioning into the vapor phase and associated potential losses of SVOCs should be minimized during: (i) material sampling and collection, (ii) homogenization and preparation of leaching samples for testing, (iii) the leaching test process, and (iv) handling of leaching test eluates in preparation for chemical analysis. Common approaches to minimizing volatility losses include: (i) minimizing the volume of contacting air (e.g., minimal vessel headspace, solid material homogenization within enclosed environments), (ii) maintaining samples at sub-ambient temperature (e.g., 0-6 °C) during handling and storage, and (iii) selection of containers constructed with primary and seal materials that prevent or minimize COPC uptake and diffusion (e.g., nonporous metal, glass). The adapted leaching methods offer precautions that should be taken to minimize losses of COPCs to the atmosphere during sample preparation and testing. However, the focus of leach testing is the partitioning of COPCs with the aqueous phase.

2.6.2.2 Solid Phase Partitioning

Figure 2-2 illustrates a theoretical network of partitioning pathways between a solid material containing SVOCs and contacting phases (liquid and vapor). The figure shows the LSP from a solid matrix containing an inorganic (mineral) phase, a natural organic phase, and a tar of NAPL phase into a leachate.

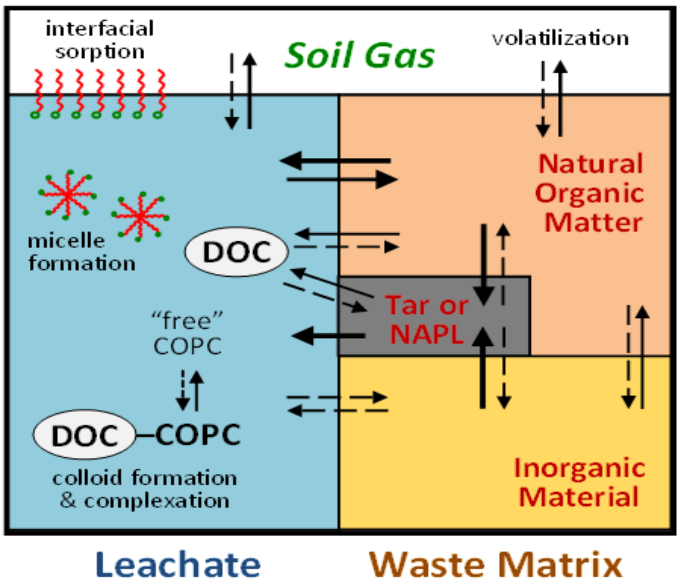

Figure 2-2. Theoretical framework for liquid-solid partitioning (LSP) of organic COPCs showing partitioning from a soil waste matrix containing an inorganic phase, a natural organic phase, and a tar or NAPL phase into a leachate containing DOC that may be complexed with organic COPCs (adapted from EPRI, 2009). The thickness of an arrow indicates the relative importance of SVOC partitioning between phases within the system.

In addition, the solid and liquid phases are in contact with a vapor or soil gas phase. Arrows between phases indicate the prevailing direction of partitioning with the arrow thickness indicating the relative importance of partitioning. The phenomena of multiphase partitioning are the same for inorganic and organic COPCs; however, the mechanisms of retention in the solid phase, which influence the distribution of COPCs between the solid and aqueous phase, may differ, and consideration of additional phases (NAPL, vapor) may be necessary for specific COPCs and contaminated materials.

For inorganic COPCs, the dominant mechanisms of retention in the solid phase include: (i) precipitation including coprecipitation and formation of solid solutions, (ii) adsorption onto metal oxide surfaces (e.g., iron, manganese, and aluminum hydroxides) and clay mineral surfaces, and (iii) adsorption onto NOM (e.g., humic substances). These mechanisms are strongly influenced by the pH of the leachate.

For organic COPCs, the dominant mechanisms of retention in the solid phase include: (i) imbibition into pores of inorganic or NOM solids by capillary retention, (ii) partitioning into NOM, AOM, or NAPLs, and (iii) adsorption onto organophilic surfaces. For PFAS, pH-dependent sorption to mineral surfaces such as metal oxides (Higgins et al., 2006; Johnson et al., 2007; Campos-Pereira et al., 2023) and ionic bridging sorption in dielectric solutions (You et al., 2010; Du et al., 2014; W. Wang et al., 2022) have been observed. ***In general, the mechanisms of retention for organic COPCs are less dependent on eluate pH than the mechanisms for inorganic COPC retention***. ***However, complexation of organic COPCs with organic matter can significantly increase measured COPC concentrations, especially at high pH where DOC release is increased*** (Roskam and Comans, 2009).

2.6.2.3 Sorption of PFAS to the Air-Water Interface

Due to their surfactant properties, many PFAS may accumulate at fluid-fluid interfaces (Brusseau and Van Glubt, 2019). This accumulation at the interface, frequently referred to as sorption at the air-water interface, decreases the surface tension, allowing for the formation of PFAS films with the hydrophilic head dissolved in water and the hydrophobic C-F tails oriented toward the more hydrophobic phase (Krafft and Riess, 2015). Lyu et al. (2018) have estimated that the air-water interface can contribute as much as 50-70% of retained PFOA in unsaturated sand/water systems; however, sorption to the air-water interface may be a function of several factors including the amount of air-water interface (Wallis et al., 2022; Brusseau, 2023), the degree of saturation (Brusseau et al., 2019; Brusseau, 2019a; 2019b; Lyu et al., 2020; Wallis et al., 2022; Brusseau, 2023), ionic and chemical composition of the liquid phase (Silva et al., 2021; Guo et al., 2023, Brusseau and Van Glubt, 2019; Le et al., 2022), and the roughness of particle surfaces (Brusseau, 2023). PFAS sorption to the NAPL-water interface has been reported to increased retention of PFAS (Brusseau, 2018; Brusseau et al., 2019; Van Glubt and Brusseau, 2021).

The primary parameters impacting sorption at the air-water interface are the amount of air-water interface available, which is a function of soil texture and water saturation (Anderson et al., 2019; Guo et al., 2020) and the PFAS chain length and molecular structure (Silva et al., 2019; Schaefer et al., 2019; Brusseau, 2021). In addition, increases in ionic strength have been shown to enhance PFAS retention at the interface (Lyu and Brusseau, 2020; Brusseau and Van Glubt, 2021). The effects of co-solutes such as ethanol, humic acid, and trichloroethene, and the influence of PFAS mixtures have been examined (Costanza et al., 2019; 2021; Silva et al., 2019; 2021; Schaefer et al., 2019; Brusseau and Van Glubt, 2019); however, the degree to which these factors impact PFAS sorption is unclear (Brusseau and Van Glubt, 2019).

Sorption of PFAS at air-water interfaces has been identified as a potentially significant source of PFAS retention in unsaturated media (Brusseau, 2018; Brusseau, 2019a; 2019b; Brusseau et al., 2019; Lyu et al., 2018). Thus, consideration of sorption to air-water interfaces may play a significant role in site characterization, leaching source term assessments, and remediation approaches. The impact of PFAS sorption at the air-water interface may range from negligible to significant and needs to be evaluated in the context of the specific PFAS compound, soil type and degree of saturation. However, most standardized leaching tests are conducted under saturated conditions where the amount of air-water interface is negligible and the primary air-water interfaces are associated with aqueous eluates collected over time (e.g., Draft Method 1314A). Therefore, the potential to accurately quantify the impact of PFAS sorption at the air-water interface on PFAS release using a standardized leaching test is likely limited as the conditions in unsaturated column tests are highly variable based on soil type and infiltration rates. ***Therefore, standardized leaching tests are unlikely to obtain an eluate representative of the amount of PFAS released under unsaturated conditions, and the interpretation of laboratory leaching tests need to consider the context of field source terms, such as by estimating the case-specific potential contribution of the air-water interface based on published findings***.

2.6.2.4 Aqueous Phase Partitioning

The mechanisms of partitioning into the aqueous phase also may differ between inorganic and organic COPCs. For inorganic COPCs, the dominant mechanisms of incorporation into the aqueous phase are solubilization, solution complexation with inorganic moieties (e.g., OH^-) and DOC (dissolved NOM), and association with colloids (colloidal NOM). Usually, COPC association with aqueous phase by solution complexation is not differentiated from association

with colloids sized smaller than the filtration pore size used in aqueous phase preparation for chemical analysis.

For organic COPCs (both SVOCs and PFAS), the dominant mechanisms for partitioning into the aqueous phase are solubilization ("free" COPCs), formation of ***micelles***, and association with organic colloids (e.g., NOM or NAPL colloids) usually considered to be associated with DOC. The formation of micelles is expected when free COPC concentrations exceed a critical micelle concentration (CMC). The CMCs for selected PFAS have been experimentally determined to range from 160,000 mg/L for PFBA to approximately 500 mg/L for PFDA or PFOS (ITRC, 2022; Bhhatarai and Gramatica, 2011). Micelles, ***hemi-micelles,*** and ***admicelles*** may form within pores blocking access to sorption cites or trapping COPCs with the pore (Dong et al., 2021). However, CMCs are significantly greater concentrations than typically seen in leaching tests, the formation of micelles within leachates is unlikely.

The practical implications for leaching of organic COPCs in comparison to inorganic COPCs include: (i) LSP of organic COPCs will behave closer to ideal liquid-liquid partitioning when an NAPL is present (e.g., Raoult's Law partitioning with NAPL), (ii) organic COPCs are more susceptible to association with colloids and micelles, and (iii) COPC solubilization will not be a function of pH unless specific organic COPCs protonate (e.g., phenols and PFAS) or sorption is influenced by pH-dependent changes in surface charge, e.g., PFAS. However, organic COPC LSP will be a function of pH to the extent that NOM partitions to the aqueous phase as a function of pH. Thus, the utility of understanding pH effects on LSP of organic COPCs is limited to the pH domain of the anticipated disposal or use field scenario. In addition, ***formation of colloids induced solely by test methods should be minimized because of the potential for overestimation of COPC partitioning to the aqueous phase***.

Micelles are loosely bound aggregates of atoms, ions, or molecules forming a colloidal particle (Britannica, 2022) when solution concentrations exceed a critica micelle concentration (CMC). For organic COPCs, micelles form to minimize the effect of hydrophobic molecular moieties in aqueous solutions (e.g., leaching test eluates). The hydrophilic ends of organic molecules form an interface with the aqueous solution sequestering the hydrophobic ends within the micelle.

Hemi-micelles are monolayer aggregates that form at solid-liquid interfaces for the same reasons as micelles with the surfactant headgroup oriented toward the surface. The critical concentration for formation of hemi-micelles (HAC) is 0.25-0.50 of the CMC (Kalam et al., 2021).

Admicelles, or adsorbed micelles, original at the surface, forming a linear bilayer structure with tails oriented toward each other. The concentration for admicelle formation is little lower than the CMC (Kalam et al., 2021).

2.6.3 Leaching Rate under Percolation Conditions

Under field conditions, leaching by percolation occurs at solid-liquid equilibrium according to the LEA due to slow pore water velocities and long residence times of the aqueous phase in the contaminated material. In most cases, the LEA is achieved rapidly for inorganic COPCs due to surface dissolution or desorption processes that occur quickly at an aqueous interface. For organic COPCs, mass transfer to the aqueous phase is likely rate limited by pore diffusion through either a capillary retained NAPL phase or solid phase NOM; therefore, the conditions that satisfy the LEA are likely to be attained more slowly than for inorganic COPCs. From a practical test method perspective, ***longer contact times (for batch tests) and longer residence times (for percolation column tests) may be necessary for organic COPCs*** compared to inorganic COPCs.

3 Development of Leaching Tests for SVOCs

The approach for test method development considers that the most robust leaching tests are those that, to the greatest extent practical, can be applied to both inorganic and organic COPCs, such that both groups of COPCs can be measured simultaneously from the same test conditions. This dual approach implies that conditions necessary for evaluation of organic COPCs, or different groups thereof, e.g., SVOCs and PFAS, must not interfere with the evaluation of other COPCs that are concurrently present. As noted earlier, the test method conditions validated for inorganic COPCs are assumed to be valid for organic COPCs except for cases where the specific properties of organic COPCs necessitate a change in the leaching method. We assume that the primary distinctions to be made regarding leaching tests for inorganic and organic COPCs are: (i) minimizing losses during preparation of materials for leaching tests, (ii) materials of construction for the test apparatus and sample handling, (iii) minimizing volatilization or other loss mechanisms during testing (e.g., photodegradation); (iv) minimizing colloid formation as a consequence of batch testing, and (vi) sample preparation for chemical analysis, including subsampling of leaching test eluates for multiple determinative analyses with different requirements. Experiments supporting the development of LEAF leaching tests for SVOCs are described in detail in **Appendix C**.

3.1 State-of-the-Art in Leaching Characterization for SVOCs

The following summarizes the most relevant studies that have focused on the development of leaching characterization methods, specifically for materials containing organic COPCs. These studies form the basis of understanding taken as the foundation for adaptation of the LEAF test methods for SVOCs.

3.1.1 Impact of NOM on Solubility of PAHs (Roskam and Comans, 2009)

Roskam and Comans (2009) compared two test methods designed to determine the available content of PAHs within a manufactured gas plant (MGP) soil and a granulated asphalt. One method consisted of a two-step sequential batch extraction in deionized water (DIW) in the presence of humic acid or Tenax® beads used to enhance release to the aqueous phase at an L/S of 2 and 8 mL/g (i.e., a cumulative L/S of 10 mL/g). The other method was a percolation column test conducted in a 5-cm internal diameter (ID) by 20-cm long cylinder filled with material of 95% of the particles less than 4 mm. The percolation test was conducted through a cumulative L/S (ΣL/S) of 10 mL/g to match the cumulative release of the sequential batch method. The column eluant was DIW with the addition of 1 g/L sodium azide (NaN_3) as a biocide introduced at a flow rate of 13 to 14 mL/h (0.5 L/S per day). In this study, the potential of the materials of construction for the column system for losses or hysteresis associated with materials of construction were not noted.

The sequential batch extraction test resulted in approximately ten times greater leaching of PAHs with five or more rings than was observed in the column test; however, the leaching results for PAHs with fewer rings were similar between tests. The higher level of PAH leaching in batch tests was attributed to the affinity of more hydrophobic PAHs to the colloids formed from dispersion of NOM from the solid. Notably, because DIW was used as the eluent, NOM was likely to be heavily released from the material and enhanced the measured release of PAH. In addition, biodegradation was observed to occur during an initial series of column tests lasting approximately one year, but biodegradation was not observed when NaN_3 was added to the influent.

3.1.2 Nordtest Project Characterization Tests for Organic COPCs

A Nordtest project (Hjelmar et al., 2000) focused on the development of leaching tests for organic COPCs in contaminated soils and waste products. Classes of COPCs of interest were chlorinated solvents, BTEX, PAHs, PCBs, and chlorinated phenols. The initial leaching test methods considered were Nordtest methods, originally targeted for inorganic COPCs. The Nordtest approach is similar and analogous to the LEAF testing approach.

The Nordtest project is analogous to the development of the LEAF leaching tests because the primary assumptions and leaching approaches are analogous to LEAF. The NordTest project results and conclusions, which were considered during LEAF development, are summarized as follows:

- The equipment should be made of materials which minimize the sorption of organic compounds.
- The leaching system should be designed to avoid photodegradation.
- Centrifugation was effective at reducing colloids in suspension and, therefore, also decreased the measured PAH concentrations in leaching test eluates because colloid-associated PAHs were not measured.
- Biodegradation should be minimized during sample handling, leach testing and during analytical sample preparation.
- Leaching test methods developed for inorganic constituents are applicable for chlorophenols. Leaching of chlorophenols was maximized in batch tests at pH 8 and 10 (equivalent results were obtained at both extraction endpoint pH values).
- Longer extraction contact intervals of at least 2 days were recommended for batch leaching tests, as PAH concentrations in batch extraction eluates were higher at 5 days than at 2 days of contact.

3.1.2.1 Availability Test (NT ENVIR 003, 1995)

The Nordtest availability test consists of sequential batch extractions of a particle size-reduced sample at high L/S conditions so that solubility limits within the eluant are not reached and at controlled pH conditions for extraction of neutral and acidic COPCs. The eluates are combined for analysis and the COPC availability is determined by the mass release (mg/kg) from the initial test sample. A subsample of test material is crushed and milled to a small particle size (<0.125 mm) considered small enough to eliminate rate-limiting diffusion through larger particles. In the first extraction step, the sample is mixed with water at a high L/S ratio (L/S=100 L/kg), and the mixture is maintained for 3 hours at pH 7 by addition of HNO_3. If the natural pH of the mixture is below 7, no acid is added. The eluate is separated from the mixture by filtration and stored. The filter containing the waste material is mixed with fresh water at an L/S of 100 L/kg, and the pH of the mixture is maintained for 18 hours at pH=4 by addition of nitric acid. If the pH of the mixture is below 4, no acid is added. The eluate is separated from the solids by filtration.

3.1.2.2 Column Test (NT ENVIR 002, 1995).

A column is filled with sample material consisting of particles of the matrix to be tested. Water is pumped from the bottom up to the top of the column, where the eluate fractions are collected based on the L/S. In the column, a local equilibrium or near-equilibrium is assumed to be

achieved between the liquid and solid phase during the test period. Achievement of equilibrium in a column is dependent on the water flow rate in the column and the kinetics of release of COPCs. The optimal flow rate is dependent on the material particle size and packing orientation. The leaching mechanism is assumed to be governed by the equilibrium LSP of the constituents. In the column test, the waste material dictates the pH and the redox potential. The properties of the eluates are measured using methods developed for water analysis adapted to meet the criteria for analysis of eluates. The test lasts until eluate fractions corresponding to an accumulated L/S = 2 L/kg or more (up to 10 L/kg) have been collected. The influent water is de-mineralized water. The column has an ID of at least 5 cm and a height of at least 20 cm. Membrane filters are placed inside at both the top and the bottom of the column.

3.1.2.3 Compliance Batch Leaching Test (NT ENVIR 005, 1998).

This test is intended to provide information on the leaching properties of waste over a wide range of L/Ss. The test contains two procedures: one is a single batch leaching test (at L/S 2.0 L/kg), and the other is a two-stage serial batch leaching test (at L/S 2.0 L/kg and at 10 L/kg). These tests are applicable to granular solids, particularly inorganic mineral waste types and have been developed for the investigations of the leaching of inorganic constituents from largely inorganic wastes. In the first procedure, the waste is brought into contact with the leaching fluid in a closed vessel at L/S 2.0 L/kg and agitated for 24 hours. The eluate is separated from the solid phase and analyzed/stored for subsequent analysis. In the second procedure, the waste is brought into contact with the leachant in a closed vessel at L/S 2 L/kg and agitated for 6 hours. The eluate is separated from the solid phase which is subsequently brought into contact with fresh leachant at L/S 8 L/kg (ΣL/S 10 L/kg) in a closed vessel and agitated for 18 hours. The eluate is again separated from the solid phase and both eluates are analyzed/stored for subsequent analysis. The leachant in this test is demineralized water. The eluates are separated from the solids by filtration.

3.1.3 Methodology for Evaluation of BTEX and PAH Leaching from Stabilized Materials

In 2009, the Electric Power Research Institute (EPRI) published a methodology to evaluate the environmental performance for in-situ stabilized (ISS) soils containing BTEX and PAHs (EPRI, 2009). The methodology was based on the LEAF test methods, at that time under development at VU for inorganic COPCs. In this study, the LEAF methods were adapted to address the specific properties of VOCs and SVOCs at former MGP sites. The purpose of this research was to provide a more comprehensive approach for evaluation of leaching potential compared to the approach provided by single-batch regulatory tests, such as Method 1311 (SW-846, 1992) or Method 1312 (SW-846, 1994). The study utilized 6.4-cm outer diameter (OD) core samples retrieved by EPRI from MGP sites where ISS has been previously utilized as a remedy to manage plume migration. Most ISS remedies had been in place for approximately 10 years.

The evaluation methodology included integration and interpretation of the results from a suite of modified leaching tests and proposed approaches for use of leaching test results in hydraulic flow and transport modeling. The suite of test methods included: (i) measurement of LSP in ground ISS core samples using a modification of Method 1314, and (ii) determination of mass transport parameters for release of SVOCs and BTEX compounds from monolithic samples of ISS cores using a modified Method 1315. The modified methods as used in this EPRI study are described below.

3.1.3.1 Modified Method 1314

The Method 1314 (SW-846, 2017b) was conducted with modification to the materials of construction intended to minimize the sorption of PAHs to column walls and transfer lines. A shortened 5-cm ID by 30-cm long column was constructed of 316L stainless steel and the polyvinyl chloride (PVC) transfer lines were replaced with rigid stainless-steel tubing. Class 3 environmental storage jars (I-Chem Brand, Chase Scientific, Inc., Rockwood, TN) made of clear borosilicate glass bottles, of volumes coordinated with the expected volume of each eluate fraction, were designed with stainless-steel drop tubes to deliver eluate to the bottom of the collection vessel. The column setup is presented in **Figure 3-1**. The clear glass collection bottles were lined with a thin layer of polydimethylsiloxane (PDMS), intended to act as a sink for PAHs in solution as eluate entered the collection vessel. The bottles were lined by adding 40 g of two-part PDMS gels (Dow Silicones Corporation, Midland, MI) into the jars with subsequent rolling of the jars on their sides overnight, approximately 18 hours, at 30 °C to facilitate curing of the PDMS. These clear glass collection bottles were covered in aluminum foil to minimize photodegradation of VOCs and SVOCs. The column tests were conducted at room temperature (22±2 °C). At the end of each leaching interval, samples of the aqueous eluate were preserved and shipped to a commercial laboratory for analysis by GC-MS. PAHs that had sorbed to PDMS liners were extracted with acetonitrile for analysis by high-performance liquid chromatography (HPLC). All other procedures and data analysis specified in Method 1314 were followed.

Figure 3-1. EPRI-modified Method 1314 column apparatus (EPRI, 2009).

3.2 Representative Materials Used for SVOC Methods Development

In response to prior testing and method development as discussed above and input from the RCRA and CERCLA program offices at the U.S. EPA, development efforts for SVOCs were focused on PAHs and phenols as representative COPCs. Furthermore, contaminated soils from a former MGP site and a creosote wood treating site were selected to serve as the basis for method development and demonstration. Bulk soil samples were collected at one site with each type of contamination as facilitated by U.S. EPA-ORD. Descriptions of sample collection, homogenization, and storage are presented in **Section 3.1**.

3.3 Summary of Method Development Experiments for SVOCs

A series of experiments was carried out to support the adaptation of the LEAF methods for SVOCs. These experiments focused on: (i) the selection of materials of construction for leaching test apparatus used for leaching evaluation of SVOCs, (ii) the management of colloids in leaching test eluates and the minimization of colloid formation due to agitation in batch experiments, and (iii) the development of approaches to process eluates containing SVOCs.

3.3.1 Selection of Materials of Construction for Leaching Test Apparatus

The primary criterion for selection of materials of construction was to find apparatus components (e.g., extraction vessels, eluate collection bottles, columns) made of materials demonstrated to have minimal losses of COPCs by sorption to or permeation through the material. To the extent possible, commercially available components were preferred over fabricated components. The sorption of SVOCs to common laboratory component materials was tested. Materials included Type I (borosilicate) glass,[1] PTFE (e.g., Teflon), PCTFE (e.g., Kel-F® or Neoflon®), 316L stainless steel (selected for availability and corrosion resistance). In addition, sorption to polyvinyl fluoride (PVF; e.g., Tedlar®) or polyvinylidene fluoride (PVDF; e.g., Kynar®) gas sampling bags was tested. An overview of experiments supporting the selection of materials of construction for SVOCs in draft methods is presented in **Table 3-1**. These experiments aimed to evaluate the potential for losses of SVOCs under conditions representative of anticipated leaching tests (e.g., temperature, duration). The intent of these experiments is to inform leaching test users about the potential for interferences in the measured eluate concentrations due to sorption or contamination from the materials of construction so that appropriate labware for each application may be selected.

3.3.1.1 Borosilicate Glass, PTFE Cap Seals, and PCTFE Cap Liners

The impact of SVOC sorption to borosilicate glass volatile organic analysis (VOA) vials, PTFE-lined silicon cap seals, and PCTFE liners used as an interface between the VOA vial and the cap seal was studied using low-concentration SVOC standards (**Appendix C-2.1**). The experiment looked at contact: (i) limited to just the glass bottle surface without tumbling versus (ii) contact with the bottle and the PTFE cap seal or PCTFE cap seal liner by tumbling the bottle. The results showed that the mean (n=5) mass recovery of six (6) selected phenols and six (6) selected PAHs for all tests was within 30% of the estimated total mass initially in the system. There was slightly less sorption to borosilicate glass without agitation than when the bottle was tumbled so that liquid was in contact with the PTFE cap seal or the PCTFE cap seal liner. However, no difference in sorption was seen when PCTFE or PTFE was used as a contact surface between the cap seal and the liquid. Extraction of rinsed bottles showed that the mass sorbed to the bottle surfaces was not, in general, recoverable, and did not make a significant difference in the total recovered mass in the system.

3.3.1.2 316L Stainless Steel

Experiments conducted on 316L stainless steel included: (i) leaching of inorganic COPCs from stainless-steel coupons (**Appendix C-2.2**), (ii) leaching of inorganic COPCs from stainless-steel

[1] Common laboratory glass is grouped by glass composition. Borosilicate glass (Type I) is preferred for its natural transparency (although amber glass is also available) and resistance to thermal shock (Scientific Glass Services, 2023). Soda-lime glass (Type III) is an affordable alternative to borosilicate glass that is chemically stable and highly inert. Due to its affordability, soda-lime glass is used for larger glassware that does not need the thermal stability of borosilicate glass (Westlab, 2023).

columns (**Appendix C-2.3**), and (iii) sorption of inorganic COPCs to stainless-steel columns (**Appendix C-2.4**). The results of these experiments indicate that several inorganic constituents (i.e., Fe, Cr, Ni, Cu, Mn, and Zn) may leach from stainless-steel apparatus at concentrations between 1 and 100 µg/L which could potentially interfere with low concentration evaluation of these specific inorganic COPCs. These results depended on the pH of the leaching test, with acidic conditions leading to greater concentrations of Fe. The sorption experiment indicated that some constituents (i.e., Al, Cr, Cu, Fe, Pb, Ti, and V) can sorb to the surfaces of stainless-steel columns and transfer lines from an eluate solution of 100 ug/L.

These experiments suggest that stainless steel is not the best material of construction when a low concentration assessment of inorganic COPCs is required. For assessment that involves only inorganic COPCs, the recommended materials of construction remain HDPE, acrylic, and PTFE. However, when inorganic and SVOC COPCs are to be evaluated simultaneously, stainless steel would be the recommended choice for materials of construction for columns and transfer lines, in part because these pieces are not practical to construct from borosilicate glass without polymer-based seals and gaskets. The experimental data presented in these appendices, however, suggest that the user should be aware of the tradeoffs between sorption losses of SVOCs to plastics and generation of low-level concentration of some inorganic COPCs with stainless steel. Parallel testing for inorganic COPCs and SVOCs may be required if the project specifications require low-concentration recovery of all COPCs.

3.3.1.3 Tedlar and Kynar Gas Sampling Bags

Gas sampling bags made of PVF (Tedlar) and PVDF (Kynar) were considered as a potential alternative for collection of column test eluates because they minimize the headspace, and hence SVOC volatility losses to headspace during collection in rigid wall glass bottles. Similar gas sampling bags have been used for low headspace sampling of aqueous samples from column tests (Claffey, 1994; Gulgule, 1997). Preliminary experiments to evaluate the losses of phenols and PAHs in Tedlar and Kynar bags were conducted (**Appendix C-2.5**) by storing a solution of SVOCs in 1-mM $CaCl_2$ for 24 and 48 hours in bags made of Tedlar and Kynar. The mean (n=3) percentage recovery (%R) was calculated and compared to an acceptance range of 70-130% of the estimated concentration in the initial concentration. The %R for 6 of the 8 analyzed phenols was reported between 100% and 70%; however, the %R of phenol and pentachlorophenol were less than 60%. The differences in mean %R with contact time and material type were insignificant relative to the uncertainty associated with phenols analysis. The recovery of all 8 analyzed PAHs was significantly below 70%, with larger, more hydrophobic PAHs reporting less than 50% recovery. For PAHs, the %R in Tedlar bags was notably higher than in Kynar bags; however, the sorption of PAHs was significant enough that neither type of gas sampling bags is recommended for column test eluate collection. These results are consistent with the results for PAH sorption to Tedlar bags from other studies (Hseih et al., 2003; Wang et al., 1996).

Table 3-1. Outline of Experiments on Materials of Construction for SVOCs and PFAS (Appendix C-2)

App #	Experiment Title	Test Description	Variables and Replication	Solutions	Eluate Processing
C-2.1	Sorption of SVOCs onto Borosilicate Glass Vials, PTFE Cap Seals, and PCTFE Cap Seal Liners	Batch storage of SVOC aqueous standard in borosilicate glass vials with three (3) different surface exposures followed by vial extraction with MeCl	• No agitation x 5 replicates (sorption to bottle) • End-over-end tumbling x 5 reps (sorption to vial and PTFE cap seal) • End-over-end tumbling with PCTFE cap liner x 5 replicates (sorption to vial and PCTFE liner)	• 1-mM $CaCl_2$ + 500 µg/L phenols + 200 µg/L PAHs • Back-extraction with MeCl	• 30 mL eluate for microextraction into MeCl and GC-MS • 20 mL MeCl from back extraction for GC-MS
C-2.2	Inorganics Leaching from 316L Stainless-steel Coupons Representative of Low L/S Extractors used in Draft Method 1316A	Batch extraction of stainless-steel coupons for two (2) contact times nested with three (3) pH conditions and two (2) types of acid	• Contact times of 4-days and 14-days at: ○ Acidic (pH 3-4): • With HNO_3 x 2 replicates + blank • With HCl x 2 replicates + blank ○ Natural pH with no acid/base x 2 replicates + blank ○ Alkaline (pH 11-12) with KOH x 2 replicates + blank	• 1-mM $CaCl_2$ + acid or base to target pH	• 5 mL for pH and EC • 10 mL eluate filtered and preserved for ICP-OES
C-2.3	Leaching of Inorganics from Draft Method 1314A Stainless-steel Columns	Fill, hold, and drain test with 1-mM $CaCl_2$ at acidic and neutral pH conditions	• 72-hour hold time at: ○ Acidic (pH 3-4) with HCl x 1 column ○ Neutral (pH ≈ 7) with KOH x 1 column	• 1-mM $CaCl_2$ + 100 µg/L Cs^+ (tracer) + acid or base to target pH	• 5 mL for pH and EC • 10 mL eluate filtered and preserved for ICP
C-2.4	Sorption of Inorganics to Draft Method 1314A 316L Stainless-steel Columns	Fill, hold, and drain test with spiked aqueous solution at neutral and alkaline pH conditions	• 72-hour hold time at: ○ Neutral (pH ≈ 7) with KOH x 1 column ○ Alkaline (pH 11-12) with KOH x 1 column	• 1-mM $CaCl_2$ + 100 µg/L inorganics + 100 µg/L Cs^+ (tracer)	• 5 mL for pH and electrical conductivity (EC) • 10 mL aqueous eluate filtered and preserved for ICP-OES
C-2.5	Sorption of SVOCs to Tedlar and Kynar Gas Collection Bags	Fill, hold, and drain test with spiked aqueous solution at two hold times with extraction of bags with MeCl	• 24-hour and 48 hour hold times ○ x 3 replicates with Tedlar bags ○ x 3 replicates with Kynar bags	• 1-mM $CaCl_2$ + 333 µg/L phenols + 40 µg/L PAHs • Back-extraction with MeCl	• 30 mL eluate for microextraction into MeCl and GC-MS • 20 mL MeCl from back-extraction for GC-MS
C-2.6	Sorption of SVOCs to Quartz Sand Used as Supplemental Column Packing	Batch adsorption experiment at two (2) L/S values and three (3) conditions	• L/S of 2 and 5 L/kg-dry, each at: ○ Acidic (pH 3-4) with HCl x 2 replicates ○ Neutral (pH ≈ 7) with KOH x 2 replicates • Alkaline (pH 11-12) with KOH x 2 replicates • One NC + one PC for each condition	• 1-mM $CaCl_2$ + 1,000 µg/L phenols + 40 µg/L PAHs + 100 µg/L Cs^+ (tracer)	• 5 mL for pH and EC • 10 mL eluate filtered and preserved for ICP-OES • 30 mL aqueous eluate for microextraction into MeCl and GC-MS
C-2.7	Sorption of PFAS to Acrylic, Stainless Steel, Tygon®, and Ottawa Sand used in Column Test Apparatus	Batch adsorption experiment at natural pH with three (3) PFAS concentrations	• One acrylic coupon (8.9-cm x 2.5-cm x 0.64-cm) • One stainless-steel coupon (8.9-cm x 2.5-cm x 0.16-cm) • Five Tygon tubing segments (5-cm x 0.64-cm OD and 0.32-cm ID) • Ottawa sand (600-800 µm ϕ; 100 g)	• 1-mM $CaCl_2$ + 50 ng/L PFAS • 1-mM $CaCl_2$ + 100 ng/L PFAS • 1-mM $CaCl_2$ + 150 ng/L PFAS	• 5 mL for pH and EC • 25 mL aqueous eluate for PFAS analysis by LC-MS/MS

3.3.1.4 Sorption of SVOCs to Quartz Sand

Batch sorption experiments were conducted to determine the potential for sorption of SVOCs to the clean quartz sand used as supplemental column packing (**Appendix C-2.6**). Sorption was determined from parallel batch adsorption experiments conducted using a single SVOC solution of 1,000 µg/L phenols and 40 µg/L PAHs at two loading levels of L/S 2 and L/S 5 L/kg-dry and three pH conditions of pH 3-4, pH~7, and pH 11-12. Analysis included SVOCs and inorganic COPCs and were compared to positive controls conducted without quartz sand. The SVOC results showed limited or no sorption of phenols and PAHs to quartz sand with %R well within the acceptance range of 70-130% of the positive control concentration. However, under alkaline conditions, the solution was not sufficiently acidified to protonate phenols prior to microextraction such that recoveries relative to the positive control were quite low. The inorganic COPCs released from the batch extractions (e.g., Al, Mg, K, Si, and Na) were consistent with the composition of quartz sand and the Type III soda-lime glass bottles.

3.3.2 Management of Colloids in Leaching Test Eluates

Colloids are comprised of a combination of mineral-based particles (e.g., clays, metal oxyhydroxides, etc.) and organic matter. There are naturally occurring colloids and colloids formed due to ion imbalances or agitation. Chemical analysis of some COPCs can be significantly affected by the presence of colloids in some turbid eluates. Therefore, to minimize the artificial generation of colloids, the development of leaching tests explored steps (i) to minimize the deflocculation of clays using multivalent cations in solution, and (ii) to remove colloids from agitated batch leaching test eluates through filtration, centrifugation, or agglomeration of colloid particles with alum.

3.3.2.1 Eluate Selection to Reduce Colloid Formation during Leaching Tests

The formation of colloids can result either as an artifact of the test method or as a natural phenomenon under field conditions. Colloid formation, as an artifact of testing methodology, is a concern because colloids can result in higher SVOC eluate concentrations than might be expected in the field. Colloid formation is a particular concern for agitated batch tests like Draft Methods 1313A and 1316A (Bergendahl and Grasso, 1998; Bergendahl, 2005; Yasutaka et al., 2017) and often is used as a rationale for selection of a percolation column testing (e.g., Draft Method 1314A) over batch procedures. In contrast to agitated batch tests, although colloids can form during percolation column testing, colloids flowing through a packed bed may be filtered by the pore structure of the test material or, alternatively, colloids may wash out from the system depending on the chemical and physical properties of the material tested.

Gu et al. (2019) showed that release of DOC is decreased when calcium solutions are utilized as opposed to sodium solutions. One chemical explanation for colloid formation due to deflocculation and dispersion of clays and natural organic matter can be an imbalance of monovalent and multivalent cations in solution (Skene and Oades, 1995). In soil chemistry, this imbalance is evaluated based on the sodium adsorption ratio (SAR), defined as:

$$SAR = \frac{[Na^+]}{([Ca^{2+}]+[Mg^{2+}])^{1/2}} \qquad \text{Equation 3-1}$$

where $[Na^+]$ is the concentration of sodium (M),

$[Ca^{2+}]$ is the concentration of calcium (M), and

$[Mg^{2+}]$ is the concentration of magnesium (M).

Dispersion of clays and organic particles can be minimized by maintaining the SAR <2 (Skene and Oades, 1995). Thus, eluents with elevated calcium or magnesium decrease the SAR and reduce dispersion of organic matter and clay particles, which can form colloidal matter.

Several test method design elements are incorporated into the LEAF methods design to minimize colloid formation. The 1-mM $CaCl_2$ is used as the eluant for Draft Methods 1313A, 1314A, and 1316A to limit colloid formation due to cation imbalance. Additionally, for Draft Method 1314A:

- a 1-cm thick layer of fine (20-30 mesh; 600-800 µm) quartz sand between the test material and the outlet of the column is used to filter eluates and prevent solid material washout; and
- The flowrate of the eluant pump is decreased to minimize disruption of organic matter with the column bed during testing, which also increases the mean fluid residence time in the columns from 1 day to approximately 2 days, further facilitating approximation of local equilibrium.

Preliminary testing of the use of 1-mM $CaCl_2$ to maintain the SAR in soil batch extractions (e.g., Draft Method 1313A) also was successful in greatly reducing colloid formation.

3.3.2.2 Alum Addition for Colloid Removal

An outline of the experiments on the management of colloidal matter in leaching test eluates is presented in **Table 3-2.** In the demonstration cases where 1-mM $CaCl_2$ alone was insufficient to prevent observed colloid formation (i.e., cloudy solutions that do not immediately settle), 20 mg alum was added to each 40 mL of eluate after the extraction to reduce colloids in the analytical solutions. The use of alum as a coagulant in water treatment and desalination is common (Van Benschoten and Edzwald, 1990a; 1990b; Duan et al., 2002) and can be appropriate for colloid removal for solutions containing nonionic organic COPCs (e.g., PAHs, phenols).

Alum treatment was pursued as an approach to minimize colloids from batch test eluates because the availability of glass or stainless-steel vessels for centrifugation which would be required for SVOC analysis is limited. Initial testing with alum as a coagulant for colloidal matter indicated that observed turbidity in preliminary Draft Method 1313A eluate could be effectively cleared with the addition of 30 mg of alum per each 40 mL aliquot of eluant (**Appendix C-3.1**). Subsequent evaluations showed that 20 mg of alum per 40 mL of eluate did not interfere with free SVOCs in solution (**Appendix C-3.2**); however, comparison between Draft Method 1313A and Draft Method 1314A eluates with and without alum addition infer that alum may release SVOCs that are associated with colloidal matter, including leached DOC, back into solution as free species. This effectively increasing the measured concentration after alum treatment (**Appendix C-3.3**). Alum may not be appropriate for solutions containing ionic COPCs, e.g., metals, some PFAS, because the cationic bridging effect of aluminum in solution can result in removal of dissolved ionic species. However, solutions containing ionic COPCs can be filtered prior to chemical analysis to remove some colloids. ***For the draft method demonstrations in this document, eluates were settled for up to 2 hours prior to dividing the eluate into fractions for (i) filtering of eluate samples saved for inorganic analysis, (ii) centrifuging of eluate samples collected for PFAS analysis, or (iii) alum treating eluate samples for SVOC analysis.***

3.3.2.3 Centrifugation

Further experimentation with alum treatment for clayey soils showed that the recommended addition of 0.5 mg of alum for each mL of eluate did not adequately reduce turbidity, especially at pH > 10.5. In addition, extensive settling time was required to clarify some clayey extracts which may lead to potentially losses of more volatile COPCs. The obvious alternative was to centrifuge all eluates in glass vessels. While less interruptive of the chemical equilibrium, centrifugation is procedurally more complex because of liquid transfers and inefficiencies with larger centrifuge vessel. However, the efficiency of centrifugation for colloid removal and clarification of muddy eluates was superior to that of alum treatment when considering the full pH domain. Therefore, in the draft method presented in this document, centrifugation was recommended for clarifying eluates and reducing colloidal matter that may have been generated by ionic imbalances or agitation. In Draft Method 1314A, centrifugation of eluates is recommended only when the impact of naturally occurring colloids upon leaching concentrations is to be studied. In general, Draft Method 1314A eluate are not centrifuged for filtered.

3.3.3 Eluate Processing Experiments

A series of experiments to optimize eluate processing and to develop integrated leaching test systems was conducted as outlined in

Table 3-3. For the column test, an experiment to evaluate the potential for in-situ microextraction of aqueous eluates into MeCl within the Draft Method 1314A collection bottle was abandoned when it was determined that (i) the dissolution of MeCl into the aqueous phase interfered with the analysis of inorganic COPCs, and (ii) the reactivity of MeCl in contact with aqueous solution was unavoidable (**Appendix C-4.1**).

Table 3-2. Outline of Experiments on Colloid Management (Appendix C-3)

Exp #	Experiment Title	Test Type	Independent Variables and Replication	Aqueous Solutions	Eluate Processing

C-3.1	Alum Addition for Management of Colloids in Batch Extraction	Batch extraction following Draft Method 1313A with addition of alum to decrease visual turbidity	• pH at nine targets + natural pH
			• Two materials x 1 run each:
			  ○ MGP Soil (MS)
			  ○ Creosote Soil (CS)
				1-mM $CaCl_2$
				+ HCl or KOH to target pH
					• 5 mL for pH and EC
					• Visual turbidity

C-3.2	Impact of Alum Addition on Soluble SVOC Concentrations in Leaching Test Eluates	Standard aqueous solution concentrations before and after alum addition	• Extracts without alum x 5 replicates • Extracts with alum x 5 replicates ○ 20 mg alum per 40 mL of eluate • NC x 5 replicates for each case	1-mM $CaCl_2$ + 800 µg/L phenols + 80 µg/L PAHs	• 5 mL for pH & EC • 30 mL aqueous eluate for microextraction into MeCl and GC-MS analysis
C-3.3	Impact of Alum Addition on Eluate Ionic Strength and Activity Coefficient	Comparison of EC before and after alum addition with analysis of activity coefficient impacts.	• Draft Method 1313A at pH 2 through 13 • Alum treatment at 20 mg/40 mL of eluate (0.5 mg/mL or 500 mg/L)	1-mM $CaCl_2$ + HCl or KOH to target pH	• EC

C-3.4	Potential Colloid Formation in Column Eluates of Draft Method 1314A	Trial Draft Method 1314A on two materials with emphasis on colloid analysis through split eluates with and without alum addition	• Two materials x 2 replicates each:
			  ○ MGP Soil (MS)
			  ○ Creosote Soil (CS)
			• 1 MB sample
			• Eluate processing without alum
			• Eluate processing with alum
			  ○ 20 mg alum per 40 mL of eluate
				1-mM $CaCl_2$	• 5 mL for pH and EC
					• 10 mL aqueous eluate filtered and preserved for ICP-OES analysis
					• 30 mL aqueous eluate for microextraction into MeCl and GC-MS analysis

C-3.5	Colloid Management through Centrifugation vs Alum Treatment	Comparison of eluate processing step using alum and centrifugation	• Method 1313A eluates at pH 9 • Alum treatment at 20 mg/mL • Centrifugation at 7,500-G for up to 20 mins	1-mM $CaCl_2$ + HCl or KOH to target pH	• Turbidity before and after treatment

Table 3-3. Outline of Experiments on Eluate Processing for SVOCs (Appendix C-4)

App #	Experiment Title	Test Type	Independent Variables and Replication	Aqueous Solutions	Eluate Processing
C-4.1	Collection and Processing of Aqueous Eluates from Draft Method 1314A Column Tests for SVOCs	Draft Method 1314A with in-situ SVOC microextraction vs ex-situ microextraction	• 2 materials: MGP Soil and Creosote Soil • Percolation ΣL/S following Draft Method 1314A • SVOC analysis with and without alum treatment of aqueous eluates	1-mM $CaCl_2$	• 5 mL for pH and EC • 10 mL aqueous eluate filtered and preserved for ICP analysis • 40 mL aqueous eluate for alum addition (20 mg/40 mL of eluate) prior to microextraction into MeCl and GC-MS analysis • 30 mL aqueous eluate for microextraction into MeCl and GC-MS analysis
C-4.2	Potential for Volatilization of SVOCs in Draft Method 1314A Eluate Collection Bottles	Vapor capture of headspace in Draft Method 1314A eluate collection bottles	• ΣL/S at 10 fractions	1-mM $CaCl_2$	• 5 mL for pH and EC • 30 mL for SVOC analysis by GC-MS after microextraction into MeCl • 5 mL of SVOCs in MeCl from headspace displacement

C-4.3	Loss of PFAS from Batch Extraction During Separation of Solid and Liquid Phases by Centrifugation	Recovery of PFAS from standard solution stored in HDPE bottles for 48 hours after centrifugation in 50-mL PP vials or 200-mL PP bottles.	• Standard PFAS solution
			  ○ 100 ng/L
			• Centrifugation vessels
			  ○ 50-mL PP vials
			  ○ 200-mL PP bottles
				Standard PFAS solutions in 1-mM $CaCl_2$	• Eluate PFAS
					• Eluate PFAS after centrifugation

C-4.4	Recovery of PFAS from Eluate Collection Bottles using Basic Methanol Rinse	Comparison of basic methanol rinse to maximize recovery of PFAS from PP and glass eluate collection bottles	• Standard PFAS solutions
			  ○ 50 ng/L
			  ○ 100 ng/L
			  ○ 150 ng/L
			• Collection vessels
			  ○ 250-mL PP bottles
			  ○ 1,000-mL PP bottles
			  ○ 250-mL glass bottles
			  ○ 1,250-mL glass bottles
				Standard PFAS solutions in 1-mM $CaCl_2$
				Rinse empty bottle with 1% NH_2OH in MeOH
				Portion of rinse goes into eluate
					• Eluate PFAS
					• MeOH rinse PFAS
					• Eluate-MeOH PFAS

C-4.5	Sonication as an Approach to Recover PFAS from Column Eluate Collection Bottles	Storage of standard PFAS solutions in PP bottles with and without sonication for 30 minutes prior to sampling	• Standard PFAS solutions
			  ○ 20 ng/L
			  ○ 40 ng/L
			• Parallel bottles for sonication and no sonication
				Deionized water	• PFAS analysis

4 Demonstration of Draft Leaching Methods for SVOCs

In this section, Draft Methods 1313A, 1314A, and 1316A were demonstrated in triplicate on two test materials to evaluate the usability of the test method and to demonstrate typical leaching test results for each method. These demonstrations are intended to illustrate the repeatability of the experiments on well-homogenized materials as well as the comparison of the modified draft methods to the U.S. EPA methods when possible. Therefore, the release of inorganic COPCs using the draft methods was compared to the release of inorganic COPCs using the corresponding published U.S. EPA method to assess if changes in the draft method needed to evaluate leaching of SVOCs impacted the leaching assessment of inorganic COPCs.

4.1 Materials Used in Demonstration

The demonstration of the modified draft methods for SVOCs was conducted using an MGP soil and a soil from a wood preservation facility that used creosote. Both soils were contaminated with phenolic compounds and PAHs. This section describes the collection, handling, preparation of these materials for testing.

4.1.1 Manufactured Gas Plant Soil

A soil collected at a former MGP was known to have been impacted by coal tar released as a by-product of town gas generation. In June 2017, approximately 19 kg of material was collected by local site personnel and shipped to VU for testing under chain-of-custody (COC) protocols in four 1-gallon steel paint cans which were stored at 0-6 °C upon receipt. The chilled “as received” material was sieved without drying through an 8-mm sieve to remove most rocks and detritus. The remaining <8 mm fraction was homogenized by cycles of passing the material through a 2-mm stainless-steel sieve, followed by cone-and-quartering to split the sample into subsamples (Schumacher, 1990). During the sieving process, the receiving pan was covered except for an opening directly below the sieve to minimize air contact and volatilization. After homogenization, 6.7 kg of MGP soil (MS) was returned to three paint cans and stored at 0-6 °C until the soil was used in testing. The homogenization process was conducted quickly (e.g., within 10-20 minutes) under a fume hood to minimize personal exposure to SVOCs. The mass of the detritus and oversized material >2 mm was measured to be 64% of the collected material due to the presence of large rocks that were not considered for further testing.

4.1.2 Creosote Soil

Approximately 8.5 kg of soil from a site contaminated with wood-preserving creosote was sampled in February 2018 by site personnel and was shipped to VU under COC for use in the development of leaching methods. The creosote soil was contained in four 1-gallon steel paint cans which were stored at 0-6 °C upon receipt. The material was homogenized in the same manner as the MGP Soil material with an initial screening through an 8-mm sieve, and two passes through a 2-mm sieve with cone-and-quartering between passes. Because the material was somewhat clayey, the completion of the homogenization process took significantly longer (e.g., 45 minutes) than the MGP Soil material. Homogenization was conducted under a fume hood to minimize exposure of laboratory personnel and approximately 8.3 kg of homogenized creosote soil (CS) was stored in 1-L borosilicate glass bottles. The oversized material was measured to be 0.2 kg or 2.5% of the collected material and consisted of small rock and plant detritus.

4.2 Analytical Methods

4.2.1 Eluate Parameter Measurements

For all aqueous eluates, eluate pH and electrical conductivity (EC) were measured by ion-specific probe following Method 9040C (SW-846, 2004a) and Method 9050A (SW-846, 1996a), respectively using an aliquot of aqueous eluate (~5 mL) removed from extraction/collection vessels with a pipette and placed into a 10-mL low- density polyethylene (LDPE) test tube.

The eluate pH was measured using a combined pH electrode connected to a pH meter, accurate and reproducible to 0.02 pH units with a range of 0 to 14. The pH meter was calibrated with a minimum 3-point calibration using National Institute of Science and Technology (NIST) traceable pH buffer solutions. Prior to measurement of eluate pH, the pH of an initial calibration verification (ICV) standard was measured with the acceptance criterion that the measured pH value be within 0.02 pH units of the certified value. The pH measurement of all aqueous samples was recorded to 0.01 pH units.

EC is a measure of the ability of an aqueous solution to carry an electric current. The measured EC value is dependent on: (i) the presence of ions; (ii) total concentration, mobility, and valence of ions in solution; and (iii) the temperature of the measurement. The EC for all aqueous eluates was determined using a standard conductivity probe calibrated to an appropriate standard conductivity solution for the conductivity range of concern. An EC meter with an accuracy and precision of ±1% and demonstrated ICV within 1 mS/cm of the certified value was used to measure EC.

4.2.2 GC-MS Sample Preparation and Analysis

After separation of solids and eluates, aqueous solutions for SVOC analysis were processed by liquid-liquid microextraction into MeCl using a modification of the approach in Method 3511 (SW-846, 2015c). Method 3511 is a microextraction procedure where a 35-mL aliquot of aqueous sample is extracted with 2 mL of MeCl (aqueous/solvent ratio of 17.5/1). Stable isotope surrogates are added to aqueous sample before MeCl is added. In addition, 12 grams of anhydrous sodium chloride (NaCl) is added directly to the extraction to increase ionic strength which is considered to improve the efficiency of the microextraction. For solvent microextraction in this BID, several modifications to Method 3511 included:

- the aqueous/solvent ratio was reduced to 3/1 so that COPCs could be extracted a single exchange and to minimize the need to perform analytical dilutions of over-range solvent concentrations,
- the concentration of surrogates and the volume of solution added to the microextraction varied as described within the **Appendix C** procedures,
- all microextractions were tumbled end-over-end for 2 hours rather than hand shaken for 5 minutes, and
- the recovered solvent phase was dried by passing the solvent through Biotage ISOLUTE® sodium sulfate (Na_2SO_4) cartridges.

No formal comparison between the modified Method 3511 and the SW-846 Method 3511 was conducted as the above modification were considered minor. A concern regarding the potential losses of COPCs during liquid-liquid microextraction from aqueous eluates to MeCl extracts was assessed through experiments that showed COPC recoveries during sample processing (i.e.,

aqueous-solvent microextraction and solvent drying) were, in general, between 80% and 120% of the estimated initial aqueous concentration.

The concentrations of PAHs and phenols in MeCl-based eluates were measured following Method 8270E (SW-846, 2018b) using an Agilent 7890B GC with an Agilent 5977B mass spectrometer detector (Agilent 7890B/5977B). A 1-µL aliquot of MeCl-based analytical solution containing target compounds was injected into the GC column. Target compounds were separated by retention on a fused silica capillary column (0.25 mm ID x 30 m long, Agilent #122-9732) where elution rates are controlled by a temperature program within the GC-MS software. Compounds eluted from the capillary column were identified by comparing their mass spectra and retention times (RTs) to known standards from an initial calibration (ICAL) curve and the NIST mass spectral library database (NIST, 2022). Quality assurance and quality control (QA/QC) acceptance limits for GC-MS analysis included that: (i) calibration curves should have a minimum coefficient of determination (R^2) of 0.98, (ii) the measured value of ICVs and continuing calibration verifications (CCVs) should be within ±30% of the expected value, and (iii) analytical blanks should be either nondetectable or less than 10% of the minimum concentration value of detected samples within the GC-MS sequence. Quantitation was based on instrument response to known quantities of ISTDs and the ICAL curve, typically from 10 to 2000 µg/L in MeCl. Method detection limits (MDLs) and lower limits of quantitation (LLOQs) for phenols and PAHs are shown in **Table 4-1**.[2]

[2] For all analytical instruments, MDL and LLOQ limits were measured periodically (e.g., every 3-6 months) over the same time as method development. Therefore, the MDLs and LLOQs are presented as examples of analytical capabilities and do not necessarily relate directly to the limits used in these method demonstrations.

Table 4-1. Example MDLs and LLOQs (in Aqueous Eluates) for GC-MS Analysis

Analyte	Symbol	MDL (µg/L)	LLOQ (µg/L)
phenol	PHL	4.60	20
2-chlorophenol	2-CP	3.6	10
2-nitrophenol	2-NP	5.9	20
2,4-dimethylphenol	2,4-DMP	3.1	10
2,4-dichlorophenol	2,4-DCP	5.5	20
4-chloro-3-methylphenol	4C-3MP	6.1	20
2,4,6-trichlorophenol	2,4,6-TCP	4.4	20
2,4-dinitrophenol	2,4-DNP	5.7	20
4-nitrophenol	4-NP	3.0	20
2-methyl-4,6-dinitrophenol	DNOC	5.4	20
pentachlorophenol	PCP	6.5	20
naphthalene	NAP	10	50
acenaphthylene	ACY	7.3	10
acenaphthene	ACE	6.3	5
fluorene	FLU	5.9	5
phenanthrene	PHE	5.5	5
anthracene	ANT	4.9	10
fluoranthene	FLA	6.0	20
pyrene	PYR	0.42	20
benz(a)anthracene	BAA	9.0	20
chrysene	CHR	5.3	5
benzo(b)fluoranthene	BBF	11	5
benzo(k)fluoranthene	BKF	8.9	10
benzo(a)pyrene	BAP	8.6	20
indeno(1,2,3-cd)pyrene	IND	12	50
dibenz(a,h)anthracene	DAA	6.1	20
benzo(g,h,i)perylene	BGP	9.9	20

Note: The aqueous phase MDL and LLOQ values indicated assume a microextraction with 30 mL of aqueous eluate and 10 mL of MeCl. Therefore, solvent-based MDLs and LLOQs used for GC-MS analysis are approximately 3x higher than the aqueous concentrations shown in the table.

4.2.3 Inorganic COPC Analysis

The concentrations of inorganic COPCs in test method eluates were determined by a combination of ICP-OES following Method 6010C (SW-846, 2018a) and ICP-MS following Method 6020A (SW-846, 2014). All eluates were initially analyzed by ICP-OES, which typically measures eluates at full strength and has faster throughput, although MDLs and LLOQs are higher than ICP-MS. Following ICP-OES, eluate samples are checked on ICP-MS to determine the low concentrations of COPCs below ICP-OES quantitation.

4.2.3.1 Inductively Coupled Plasma – Optical Emissions Spectrometry

A Varian ICP Model 720-ES (Agilent Technologies, Santa Clara, CA) was calibrated to a five-point standard curve, over a typical analytical range of 25-25,000 µg/L for most constituents and 25-500,000 µg/L for major constituents (i.e., Al, Ca, K, Mg, Na, S, and Si). **Table 4-2** provides example MDLs and LLOQs for the ICP-OES analysis used in this study. CCV standards at approximately 500 µg/L and calibration check blanks were measured every 10 to 20 samples with the acceptance requirements that check standards were within 15% of the specified value

and blanks were less than the quantification limits. Based on the U.S. EPA methods, no digestions were required as matrix spikes demonstrated good recoveries.

Table 4-2. Example MDLs and LLOQs for ICP-OES Analysis

Analyte	Symbol	MDL (µg/L)	LLOQ (µg/L)
Aluminum	Al	3.4	25
Antimony	Sb	8.4	25
Arsenic	As	6.7	25
Barium	Ba	1.6	25
Beryllium	Be	4.4	25
Boron	B	2.3	25
Cadmium	Cd	4.2	25
Calcium	Ca	6.5	25
Chromium	Cr	2.8	25
Cobalt	Co	2.4	25
Copper	Cu	4.6	25
Iron	Fe	2.2	25
Lead	Pb	5.7	25
Lithium	Li	4.7	25
Magnesium	Mg	3.5	25
Manganese	Mn	2.4	25
Molybdenum	Mo	1.8	25
Nickel	Ni	2.1	25
Potassium	K	3.2	25
Phosphorus	P	6.8	25
Selenium	Se	12	25
Silicon	Si	3.8	25
Silver	Ag	16	25
Sodium	Na	5.6	25
Strontium	Sr	3.7	25
Sulfur	S	5.8	25
Thallium	Tl	4.6	25
Tin	Sn	10	25
Titanium	Ti	2.3	25
Vanadium	V	1.2	25
Zinc	GC-MS	2.4	25

4.2.3.2 Inductively Coupled Plasma – Mass Spectrometry

A PerkinElmer NexION 2000B (PerkinElmer Inc., Waltham, MA) was calibrated to a five-point standard curve over an analytical range between approximately 0.5 and 100 µg/L while the standard curve was extended to 500 µg/L with a seven-point standard curve when needed for some elements (e.g., B, and Fe). **Table 4-3** provides MDLs and LLOQs typical for ICP-MS analysis of leaching test solutions used in this study. This table provides detection and quantitation information for a much wider range of inorganic COPCs than measured for this project but are part of a standard analysis list. ICV and CCV standards at 10 µg/L were measured every 10 to 20 samples with the acceptance requirements that check standards were within ±20% of the specified value and that calibration check blanks were below the LLOQ.

Table 4-3. Example MDLs and LLOQs for ICP-MS Analysis

Analyte	Symbol	MDL (µg/L)	LLOQ (µg/L)
Aluminum	Al	0.39	0.5
Antimony	Sb	0.013	0.5
Arsenic	As	0.036	0.5
Barium	Ba	0.071	0.5
Beryllium	Be	0.035	0.5
Boron	B	0.62	1
Cadmium	Cd	0.018	0.5
Chromium	Cr	0.053	0.5
Cobalt	Co	0.023	0.5
Copper	Cu	0.040	0.5
Iron	Fe	0.73	1
Lead	Pb	0.027	0.5
Lithium	Li	0.13	0.5
Manganese	Mn	0.032	0.5
Molybdenum	Mo	0.033	0.5
Nickel	Ni	0.032	0.5
Selenium	Se	0.062	0.5
Silver	Ag	0.042	0.5
Strontium	Sr	0.35	0.5
Thallium	Tl	0.019	0.5
Tin	Sn	0.059	0.5
Titanium	Ti	0.046	0.5
Vanadium	V	0.026	0.5
Zinc	GC-MS	0.091	0.5

4.2.4 Ion Chromatography

Anion concentrations were determined by IC following Method 300.0 (U.S. EPA, 1993) using a Metrohm 881 Compact IC Pro (Metrohm AG, Riverview, FL) with a conductivity detector. The instrument was calibrated using a bulk seven-anion standard at five calibration levels over a typical range that differs with the concentration of each anion in the bulk standard. Calibration ranges were from a low of 20-20,000 µg/L for F^- to a high of 150-150,000 µg/L for PO_4^{3-} and SO_4^{2-}. The ICAL was checked every ten samples using a 10x dilution of bulk standard with the acceptance requirement that the measured concentration be within ±15% of the specified value and that calibration check blanks be below quantification limits. The MDLs and LLOQs for IC analysis are shown in **Table 4-4**.

Table 4-4. Example MDLs and LLOQs for IC Analysis

Analyte	Symbol	MDL (µg/L)	LLOQ (µg/L)
Chloride	Cl^-	10	50
Fluoride	F^-	6.3	20
Nitrate	NO_3^-	11	100
Phosphate	PO_4^{-3}	25	150
Sulfate	SO_4^{-2}	25	150

4.2.5 Dissolved Carbon Analysis

Analyses of DOC and DIC were carried out following Method 9060A (SW-846, 2004b) on a Shimadzu model LCPH (Shimadzu Scientific Instruments, Inc., Columbia, MD) combustion catalytic oxidation non-direct infrared analyzer. The analyzer was used to measure inorganic carbon prior to organic carbon from a single analytical sample and was calibrated with a five-point calibration curve for both inorganic carbon and non-purgeable organic carbon (NPOC) with an analytical range between 500 and 100,000 µg/L. Reagent grade $C_8H_5KO_4$ was used as the NPOC standard while $NaHCO_3$ was used as the inorganic carbon standard. Calibration check standards at 10 ppm and calibration blanks were measured every 10 samples with the requirement that check standards be within ±15% of the specified value and blanks less than quantifiable limits. The detection and quantifiable limits for carbon analysis are shown in **Table 4-5** in terms of the MDLs and LLOQs.

Table 4-5. Example MDLs and LLOQs for Carbon Analysis

Analyte	Symbol	MDL (µg/L)	LLOQ (µg/L)
Dissolved Inorganic Carbon	DIC	79	500
Dissolved Organic Carbon	DOC	96	500

4.3 Data Analysis and Reporting

All test data (e.g., masses used, testing conditions) were recorded in Microsoft Excel® templates designed for each leaching test. Following analytical measurement, eluate concentration data were entered into the templates along with laboratory data. Excel® templates served as an input tool for LeachXS (VU, 2022), a database-driven data management and reporting software, specifically developed to handle the large amount of data generated with LEAF tests. LeachXS was used to create and output all the figures used in the demonstration of each leaching test. In these figures, COPC concentrations measured at less than the MDL were reported in tables as <MDL and graphed at one-half the MDL value to indicate that the measurement was conducted. Analytical results that measured less than the LLOQ but greater than the MDL are reported as "estimated values."

4.4 Demonstration of Draft Method 1313A for SVOCs

Method 1313A (SW-846, 2017a) is a parallel batch extraction test in which multiple subsamples of test material are extracted at pH endpoint values ranging from less than 2.0 to 13.0. The pH for each parallel extraction is adjusted using initial additions of dilute acid or base. The objective of Draft Method 1313A is to determine the LSP of COPCs at near-equilibrium conditions and to show how the LSP concentrations shift when the eluate pH changes (e.g., due to external sources of acidity or alkalinity). Each of the nine extractions is processed individually so that losses due to volatility are minimized. However, eluate concentration data for all 9-10 extracts in a method replicate should be considered a single analytical set such that the same instruments, technicians, and conditions are employed, thus reducing the analytical variability between test positions.

Use of the full pH range specified for Draft Method 1313A is recommended for assessment of inorganic COPCs due to the strong dependence of eluate concentrations on end-point pH for

metals and the maximum release over the pH domain is used as the available content. In contrast, most organic COPCs do not exhibit a strong direct pH dependence on leaching unless the specific organic COPC is subject to protonation or deprotonation over the pH range tested (see **Table 2-1**). However, leaching of organic COPCs can exhibit an indirect dependence on pH through complexation with DOC from NOM (e.g., humic substances) because DOC often exhibits pH dependence, typically increasing with increasingly alkaline pH. Thus, for assessment of organic COPCs, we recommend that DOC be measured in all eluates and that testing may be limited to extractions over the pH domain applicable for assessment scenarios which may be a fraction of the testing domain.

4.4.1 Summary of Modifications to Develop Draft Method 1313A for SVOCs

Method 1313 was validated for inorganic COPCs using HDPE bottles as extraction vessels (Garrabrants et al., 2012a). The leaching solution is pH-adjusted with HNO_3 or potassium hydroxide (KOH) to titrate the extraction final solution over a pH range from <2 to 13. Extractions are tumbled end-over-end at 28 revolutions-per-minute (rpm) for a contact time based on the maximum particle size of the test material. For example, a contact time of 48 hours is required for granular material with 80 percent by mass (wt%) particle size <2 mm, typical of most soils. The solid is separated from the eluate using a combination of settling and filtration through 0.45-µm PP membranes and the pH and EC of the eluate are measured prior to preserving analytical samples for inorganic constituent analysis.

The following modifications to Method 1313 were made to develop Draft Method 1313A:

- Leaching vessels were changed from 250-mL HDPE bottles to amber borosilicate glass VOA vials with PCTFE lid liners to minimize the losses of SVOCs to photodegradation, sorption, and volatility.

- 1-mM $CaCl_2$ replaced DIW as the primary eluant to reduce the formation of colloidal matter that might be induced by chemical imbalance and agitation (see **Section 3.3.2**). DIW remains an option for cases where colloidal formation is not a concern (e.g., cement stabilized materials).

- The acid used to lower the pH of eluates below the natural pH was switched from HNO_3 to nonoxidizing hydrochloric acid (HCl). HNO_3 remains an option when only inorganic COPCs are being evaluated and when increased solubilization of cadmium by chloride complexation is a concern.

- Settling was used for solid-liquid (eluate) separation rather than vacuum filtration for aliquots of eluates to be analyzed for SVOCs to reduce volatility losses during eluate processing.

- An additional larger particle size fraction, along with an associated longer contact time, was added to the test specification to minimize the pretest material handling which could result in volatilization of some SVOCs.

- Alum addition was incorporated into the method as an optional step to remove suspended colloidal matter from aqueous eluates or aliquots thereof prior to analysis for SVOCs. Although alum addition represents a modification to the test method, this step does not influence the measured concentration of inorganic COPCs because the eluate aliquot for inorganic analysis is collected prior to alum addition (**Appendix C-3.2**).

- Options in the pretest were added to allow for determination whether: (i) larger material

aggregates behaved as smaller particles during testing to reduce the sieving of solids prior to testing (e.g., if <9.5 mm sieved soils disaggregated during tumbling to a particle size <2 mm), and (ii) turbidity of settled or centrifuged liquid-solid mixtures after tumbling decided whether alum addition was needed to clarify aliquots of eluate to be analyzed for nonionic SVOCs.

4.4.2 Mitigation of the Impact of Colloids

Agitation by end-over-end tumbling as specified in Method 1313 can enhance the formation of colloidal particles during testing. These colloids may influence partitioning behavior of COPCs, potentially biasing the measured eluate concentrations toward overestimation of organic COPC leaching. The potential effects of colloids on measured leaching were mitigated by suppression of colloid formation through: (i) use of 1-mM $CaCl_2$ as the leaching solution, and (ii) use of HCl, a nonoxidizing acid, rather than the specified HNO_3 when pH conditions are more acidic than the natural pH. In cases where colloidal matter was visibly present in eluates after settling, the addition of 30 mg of alum was demonstrated to clear the visual turbidity under most pH conditions through formation of insoluble agglomerates (**Appendix C-3.1**). A follow-on experiment showed that the concentrations of free SVOCs in solution would not be impacted by the addition of alum (**Appendix C-3.2**). Although the addition of alum was seen to decrease the pH of the solution slightly, thermodynamic calculation of the impact of alum addition on ionic strength indicated no significant changes relative to the 1-mM $CaCl_2$ (**Appendix C-3.2**).

4.4.3 Leaching Apparatus

Sorption of organic COPCs to contact surfaces of leaching test apparatus is a concern as sorption will decrease the measured concentration of SVOCs in the test. In addition, losses of COPCs due to photodegradation during collection or processing of aqueous eluates is a concern. Many of these losses may be mitigated by a judicial selection of appropriate materials of construction. Sorption of PAHs and phenols onto borosilicate glass (**Appendix C-2.1**) and 316L stainless steel (**Appendix C-2.2**) was evaluated for batch extractions. In addition, secondary contact surfaces made of PCTFE were used to limit the sorption to vial and lid liners.

4.4.4 Solid Material Particle Size

The Method 1313 contact time for an extraction is commensurate with the maximum particle size of the solid material so that diffusion within the particle does not limit the rate of leaching and the approach to equilibrium (U.S. EPA, 2019a). In addition, the particle size of the solid material has implications on the minimum mass of sample considered representative of the material, with small particles requiring less material and, hence, smaller leaching vessels. **Table 4-6** shows a schedule of contact times, minimum sample masses, and minimum vessel size, from Method 1313.

Table 4-6. Extraction Contact Time Associated with Particle Size

Particle Size; 85 wt% less than (mm)	Contact Time (hours)	Minimum Sample Mass (g-dry)	Suggested Sample Mass* (g-dry)	Suggested Vessel Size (mL)
0.3	24±2	4.0	4.0	40
2.0	48±2	10	12.0	120
5.0	72±2	20	25.0	250
9.5	96±2	45	50.0	500

* Suggested equivalent dry mass of sample to be used with suggested vessel size to minimize headspace.

For the Draft Method 1313A demonstration, soil samples were sieved in a damp state to a particle size of 85 wt% less than 2 mm; therefore, the contact time used in the demonstration was 48 hours. **Table 4-6** has been amended to include a larger particle size specification of 85 wt% less than 9.5 mm, reflecting the greater challenges associated with test material homogenization while minimizing volatility losses of SVOCs. Subsequently, we recognized that larger soil aggregates are likely to disaggregate during the tumbling interval with eluent, thus behaving like smaller aggregates. Therefore, an optional pretest was developed to evaluate whether aggregates that pass larger sieve size (e.g., <9.5-mm particles) could be treated as small aggregates (e.g., <2 mm particles) due to disaggregation during testing. The pretest allows for selection of the minimum sample mass and contact time based on an effective particle size to minimize handling of materials containing SVOCs. When solid materials other than soils are tests, disaggregation is less likely and the information in **Table 4-6** would hold.

As a practical consideration, multiple determinative analytical methods, for example, ICP-OES for inorganic COPCs, GC-MS for SVOCs, and liquid chromatography tandem mass spectrometry (LC-MS/MS) for PFAS, have different eluate sample volume requirements and preservation methods. When inorganics, SVOCs, and PFAS are all COPCs, a 250-mL extraction vessel with a 22-g dry sample mass and approximately 220 mL of eluent (volume adjusted to achieve L/S = 10 mL/g-dry to account for the water inherent in the “as-tested” material) is suggested to minimize headspace in the extraction vessel while affording sufficient eluate volume for ICP analysis, carbon analysis, GC-MS, and LC-MS/MS. However, the inorganic COPCs eluate samples may need to be minimally diluted.

4.4.5 Test Procedure

The procedure for Draft Method 1313A as used in the method demonstration is illustrated in **Figure 4-1** for a single extraction. In the extraction step (Step 1), a subsample of test material equivalent to 4 g-dry was placed into a 40-mL amber VOA vial equipped with a PCTFE lined cap. The solid was contacted with 40 mL of 1-mM $CaCl_2$ solution with a measured addition of HCl or KOH. The volume of acid or base added is based on either a pretest titration curve of the material or other prior knowledge of the material titration. The L/S of the extraction, i.e., the ratio of the total liquid volume ($CaCl_2$ solution, acid or base addition, and inherent moisture in the solid sample) to the dry equivalent mass of the solid, was 10 mL/g-dry. The extraction vessels were tumbled in an end-over-end fashion at 30±2 rpm for 48 hours.

4.4.6 Eluate Collection and Processing

After the 48-hour contact time, the samples for the Draft Method 1313A demonstration were removed from tumbling and solid materials were allowed to settle prior to processing the aqueous eluate for parameter measurement and chemical analysis. **Figure 4-1** shows the eluate volumes collected and prepared for analysis in this demonstration:

- a 2-mL aliquot of aqueous eluate pipetted into a clean PP test tube for measurement of pH and EC by ion-specific probe (Step 2),
- a 5-mL aliquot of aqueous eluate (diluted to 50 mL with DIW) and filtered through 0.45-µm membrane and split for analysis of (i) inorganic COPCs (10 mL) preserved by acidification with HNO_3 to pH <2 and (ii) DOC (Step 3), and
- a 30-mL aliquot of aqueous eluate pipetted into a clean 40-mL glass vial for microextraction into 10 mL of MeCl followed by solvent drying in preparation for SVOC analysis of solvent-based samples by GC-MS (Steps 4-6).

All aliquots were taken directly from the 40-mL VOA vial after allowing solid particles to settle. After measurement of eluate parameters and preservation of aqueous eluate for inorganic analyses, the remaining eluate was used to process a sample for SVOC measurement. If visual colloidal matter in the aqueous eluate was observed,[3] the aliquot for SVOC analysis was treatment with alum prior to microextraction. The volume of the aliquot was increased to the extent possible (30+ mL) and alum was added at a rate of 0.5 mg per mL of aqueous eluate. The eluate + alum mixture was shaken by hand, and the alum was allowed to settle for 2 hours (Step 7). From the clarified aqueous eluate, a 30-mL aliquot of eluate was removed from the extraction vial by pipette and placed into a clean 40-mL VOA vial for microextraction with MeCl (Step 8). Prior to addition of MeCl, the pH of the eluate was adjusted to pH <2 with approximately three drops of H_2SO_4 to protonate phenolic endmember groups. Surrogate SVOCs were added from a bulk standard in acetone to evaluate microextraction efficiency.

The microextraction was initiated with the addition of 10 mL of MeCl solvent followed by end-over-end tumbling of the microextraction at 30±2 rpm for 2 hours after which the extraction was allowed to settle for a minimum of up to 2 hours. A majority of the aqueous phase was removed by pipette and discarded. Approximately 5 mL of MeCl solvent containing target SVOCs and surrogates was removed by pipette and dried by passing through a Biotage ISOLUTE® Na_2SO_4 cartridge (Step 9). Analytical samples for GC-MS were prepared by pipetting 1 mL of dried solvent into 2-mL GC-MS vials and addition of ISTDs (Step 10). Prior to analysis by GC-MS, the vials were stored at 0-6 °C.

A series of experiments was carried out to evaluate the recovery of COPCs, and losses of COPCs by difference, during each of the SVOC analytical sample steps indicated above. However, because assessment of each of the above steps required chemical analysis by GC-MS, evaluation started with quantifying COPC recoveries using well-defined solutions with selected COPCs, during drying of solvent extracts and during processing in the selected leaching apparatus. An integrated evaluation was carried out using a limited set of leaching test conditions for the Draft Method 1313A using contaminated materials collected from the two field sites focusing on the impact of alum use on SVOC concentrations in eluates (**Appendix C-3.2**). In addition, use of 1-mM $CaCl_2$ as the primary eluent was evaluated to minimize colloid formation in comparison to use of reagent water as the primary eluent.

[3] Due to the uncertainty associated with visual observation, the Draft Method 1313A includes a turbidity measurement step as a criterion (1 NTU threshold) for further eluate clarification prior to chemical analysis.

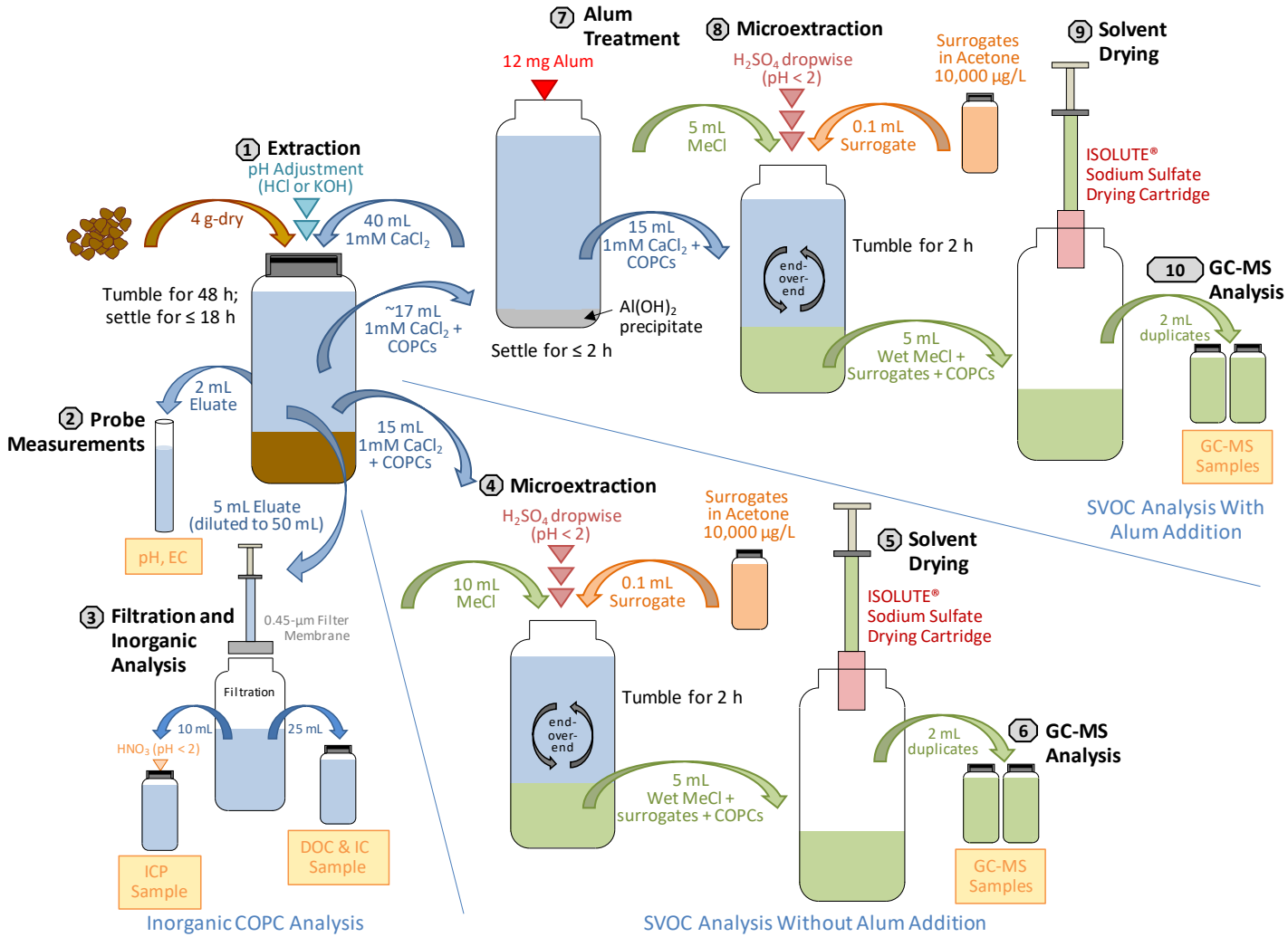

Figure 4-1. Example procedure used for demonstration of Draft Method 1313A showing extraction (Step 1), measurement of eluate parameters (Step 2), filtration for inorganic COPCs (Step 3), and parallel processing of aqueous eluates into a solvent analytical SVOC sample with (Steps 4-6) and without (Steps 7-10) alum treatment to minimize colloid impacts.

4.4.7 Demonstration Results

A comprehensive demonstration of Draft Method 1313A was conducted in triplicate for two field-contaminated soils (i.e., Creosote Soil and MGP Soil). The results of the Draft Method 1313A demonstration are shown in **Figure 4-2** through **Figure 4-4**.

Figure 4-2 shows the demonstration results for the material titration and for measured eluate parameters in Draft Method 1313A. The titration curve presents the acid neutralization capacity (ANC) or base neutralization capacity (BNC) of each material in terms of the eluate pH response to the amount of acid added to each extraction.[4] The mean natural pH of the test materials was 5.45±0.04 (mean ± standard deviation, *n*=3) for the creosote soil and 7.59±0.05 for the MGP soil. The eluate EC data were dominated by the addition of acid and base as the eluate pH moved away from the natural pH value. The EC at natural pH was 0.29±0.01 mS/cm for the creosote soil and 1.1±0.02 mS/cm for the MGP soil.

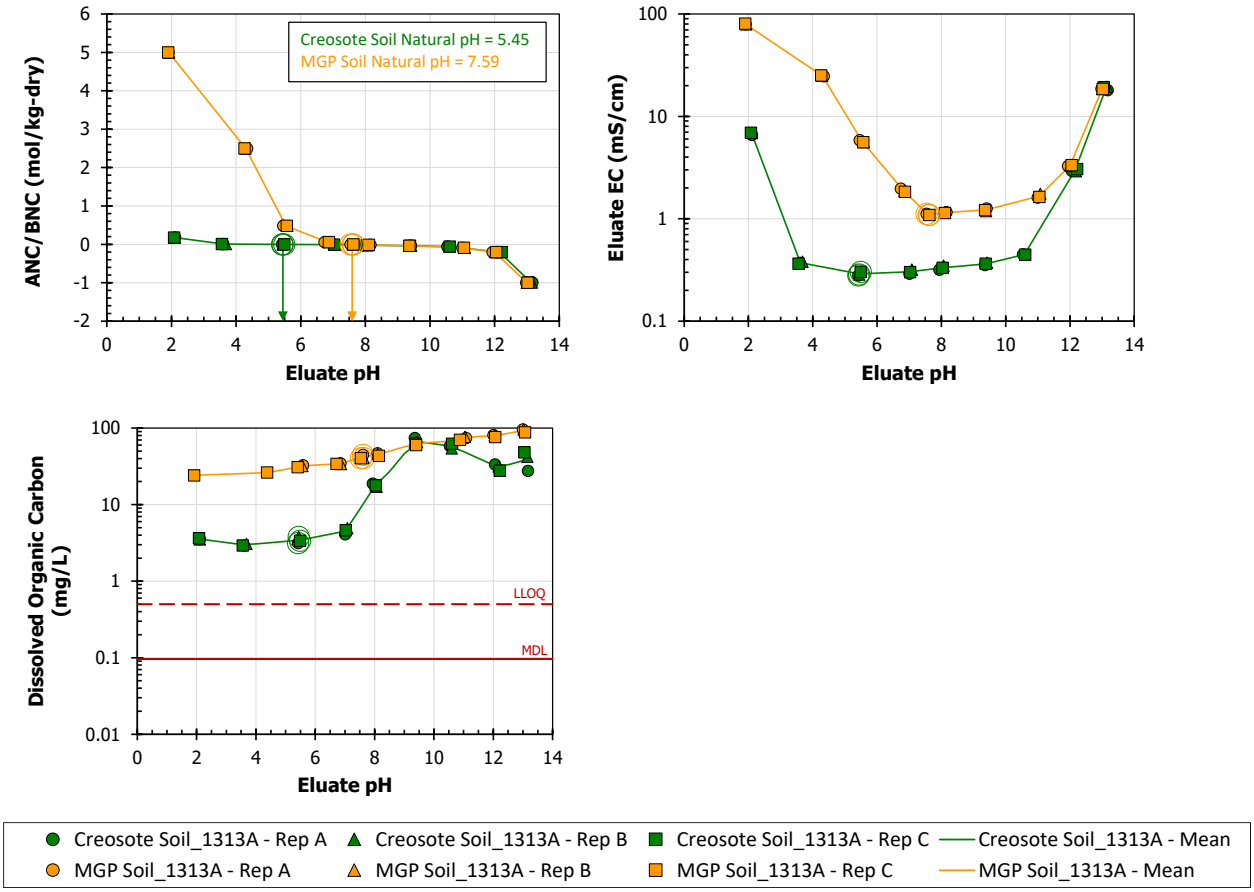

Figure 4-2. Demonstration results of Draft Method 1313A showing material titration curve shown as ANC/BNC, eluate EC, and DOC.

[4] In this representation of the titration curve, additions of base to raise the eluate pH are shown as negative acid additions.

The Draft Method 1313A demonstration results for selected phenols and PAHs are presented in **Figure 4-3** and **Figure 4-4**, respectively. In these graphs, replicate test eluate concentrations are presented as separate geometric data points while the line represents the mean eluate concentration at each of the target pH points. The mean line for the three replicates was calculated using LeachXS based on the mean of eluate concentrations interpolated to the method target pH values. The methodology for these calculations is described in the previous interlaboratory validation report for Method 1313 (SW-846, 2012a).

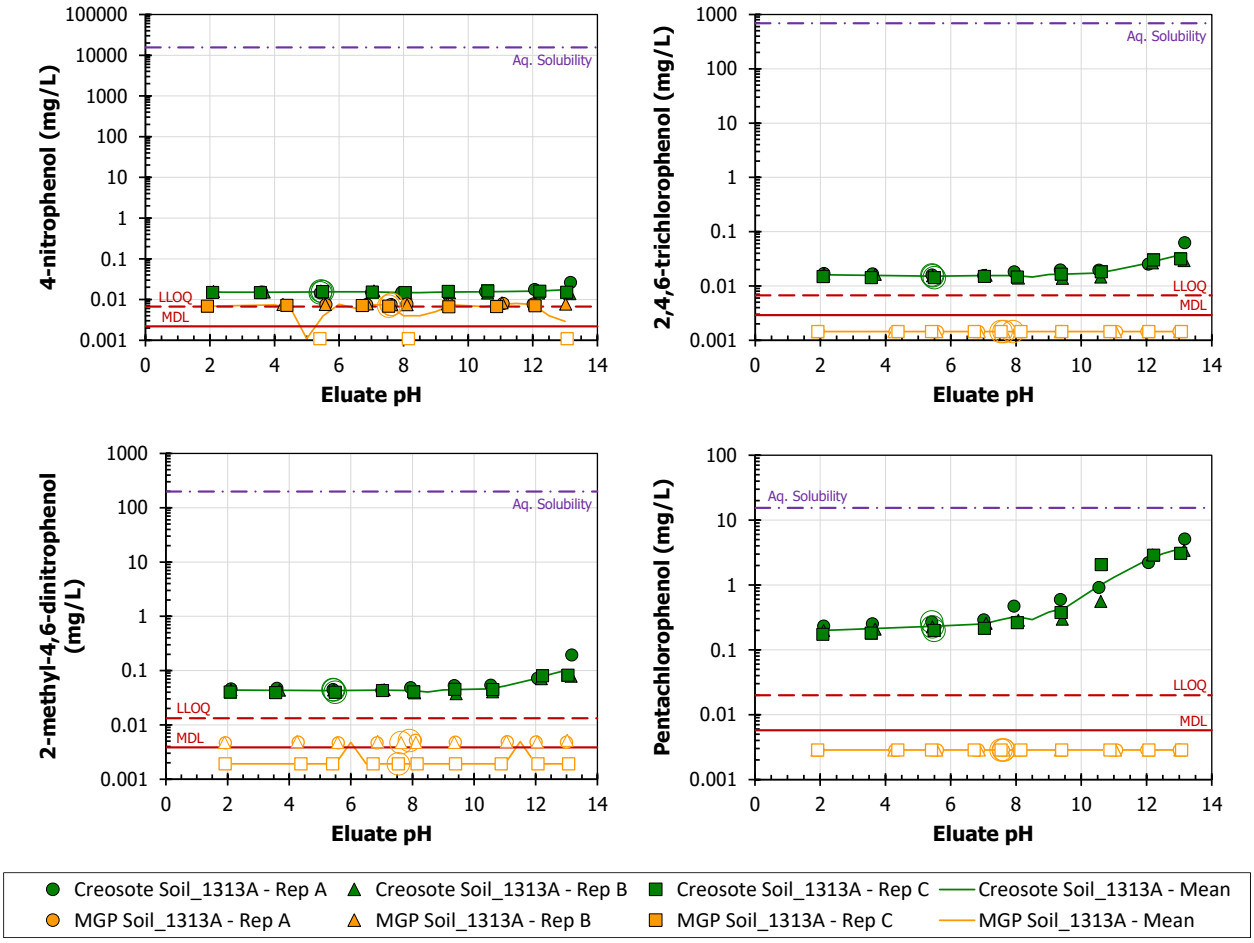

Figure 4-3. Demonstration results of Draft Method 1313A showing pH-dependent concentrations of 4-nitrophenol, 2,4,6-trichlorophenol, 2-methyl-4,6-dinitrophenol, and pentachlorophenol. Estimated and non-detected data shown as open symbols.

For phenols (**Figure 4-3**), the concentration of most phenols in the MGP Soil material were not detected or were close to the quantitation limit. For the Creosote Soil material, the concentration of phenols increased with increasing pH, likely due to the increase in DOC (**Figure 4-2**). The replication about each pH target point was good except when concentrations approached the MDL, which is expected for analytical data.

The concentrations of PAHs (**Figure 4-4**) appear to be less influenced by DOC concentrations

with the concentrations of NAP in CS, acenaphthene (ACE) and fluorene (FLU) showing no pH-dependence. In the MGP Soil material, the dip in NAP concentration at pH 7-8 was reproducible, although no mechanistic explanation was apparent, in both this demonstration as well as in method development tests on Draft Method 1313A.

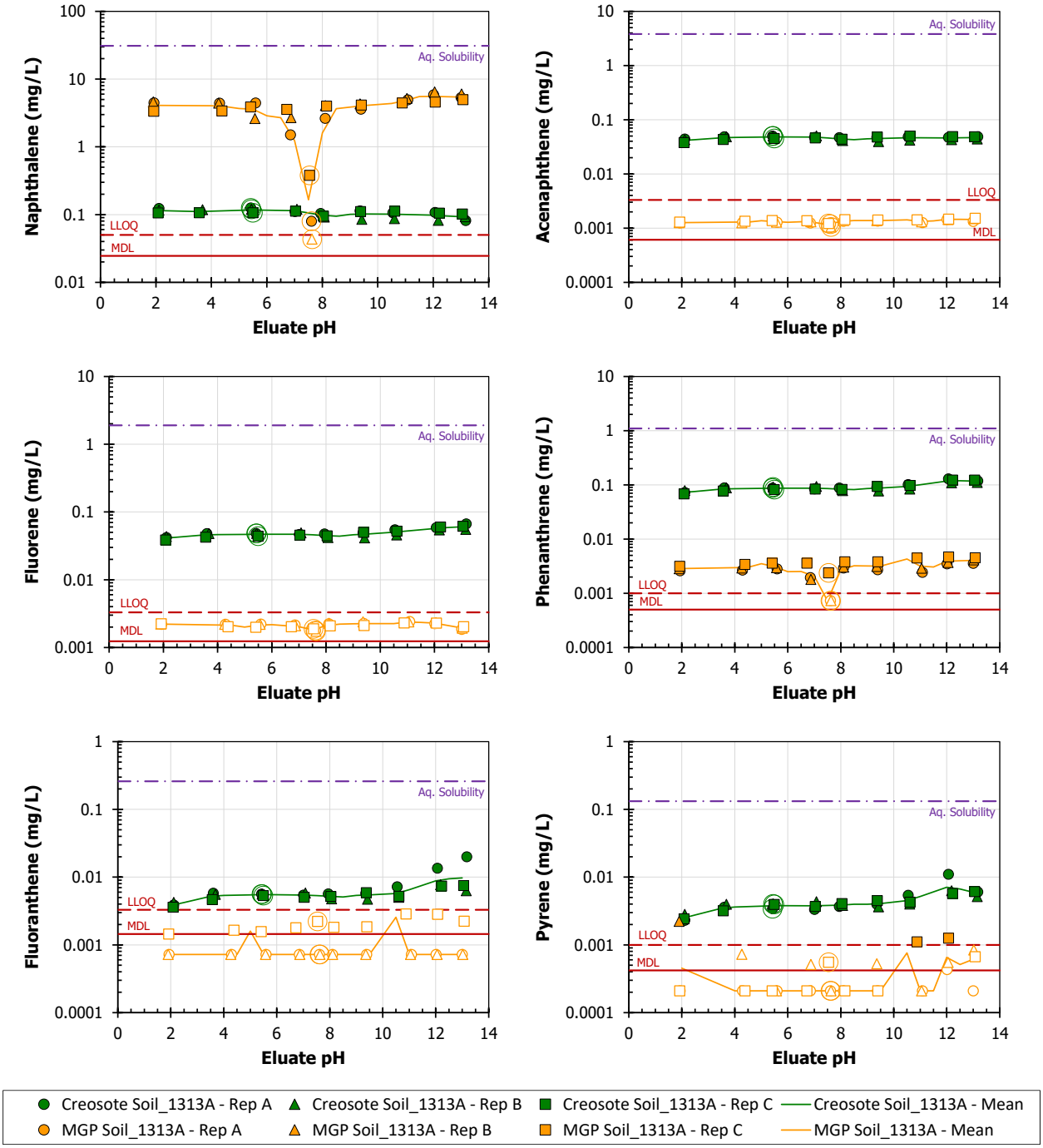

Figure 4-4. Demonstration results of Draft Method 1313A showing pH-dependent concentrations of naphthalene, acenaphthene, fluorene, phenanthrene, fluoranthene, and pyrene. Estimated and non-detected data are presented as open symbols.

4.4.8 Comparison of Method 1313 and Draft Method 1313A Results

Method 1313 is intended to provide a test method that can be used to generate an aqueous eluate in cases where constituents of interest include both organic and inorganic species. Therefore, the results of inorganic analysis from eluates of Draft Method 1313A should align with the results derived from the validated Method 1313. Draft Method 1313A and Method 1313 were conducted in parallel on the same material to demonstrate the impact of the draft test method modifications, made to optimize testing for organic and inorganic COPCs, on the leaching of inorganic COPCs. The comparison was carried out using MGP Soil and Creosote Soil because both test materials contained sufficient inorganic COPCs for this comparison.

The eluate concentrations from Method 1313 and Draft Method 1313A test results are compared for major inorganic constituents (**Figure 4-5** and **Figure 4-6**), oxyanion-forming species (**Figure 4-7**) and trace metals (**Figure 4-8**). In each figure, Method 1313 test results are shown as red diamonds or blue diamonds for Creosote Soil and MGP Soil, respectively. The SW-846 method results are shown overlaying the demonstration test results from Draft Method 1313A. The primary anticipated impacts were: (i) a decrease in the leaching of specific inorganic COPCs associated with organic colloid formation (e.g., copper) due to the switch to 1-mM $CaCl_2$ eluent, and (ii) the potential increase in cadmium leaching due to complexation with chloride ions from the $CaCl_2$ solution.

The acid and base additions for Method 1313 were determined from the demonstration titration curve for Draft Method 1313A. The comparison of pH results revealed minor shifts in final eluate pH values between HCl (Draft Method 1313A) and HNO_3 (Method 1313); however, these pH shifts are consistent with the test method tolerance about the target pH values (±0.5 pH units). The concentrations of COPCs indicated only negligible variations between the results of the draft method and the validated method, even for copper (**Figure 4-6**) and cadmium (**Figure 4-8**). Therefore, Draft Method 1313A may be considered applicable for both organic COPCs and inorganic COPCs. In a broader application, this comparison demonstrates that leaching testing for inorganic and organic COPCs can be conducted from a single extraction sample.

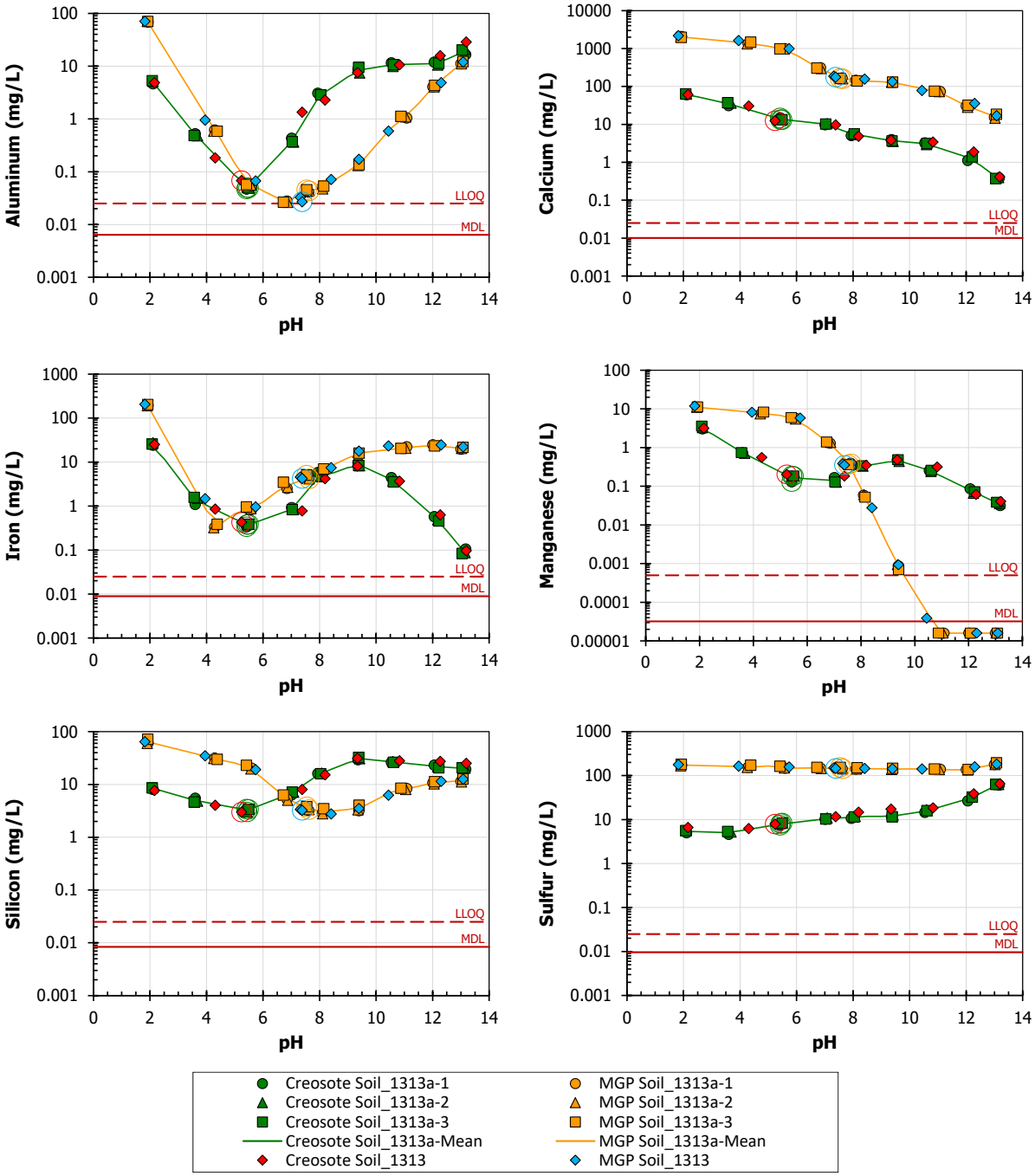

Figure 4-5. Comparison of eluate concentrations from Method 1313 and Draft Method 1313A for major constituents: aluminum, calcium, iron, manganese, silicon, and sulfur.

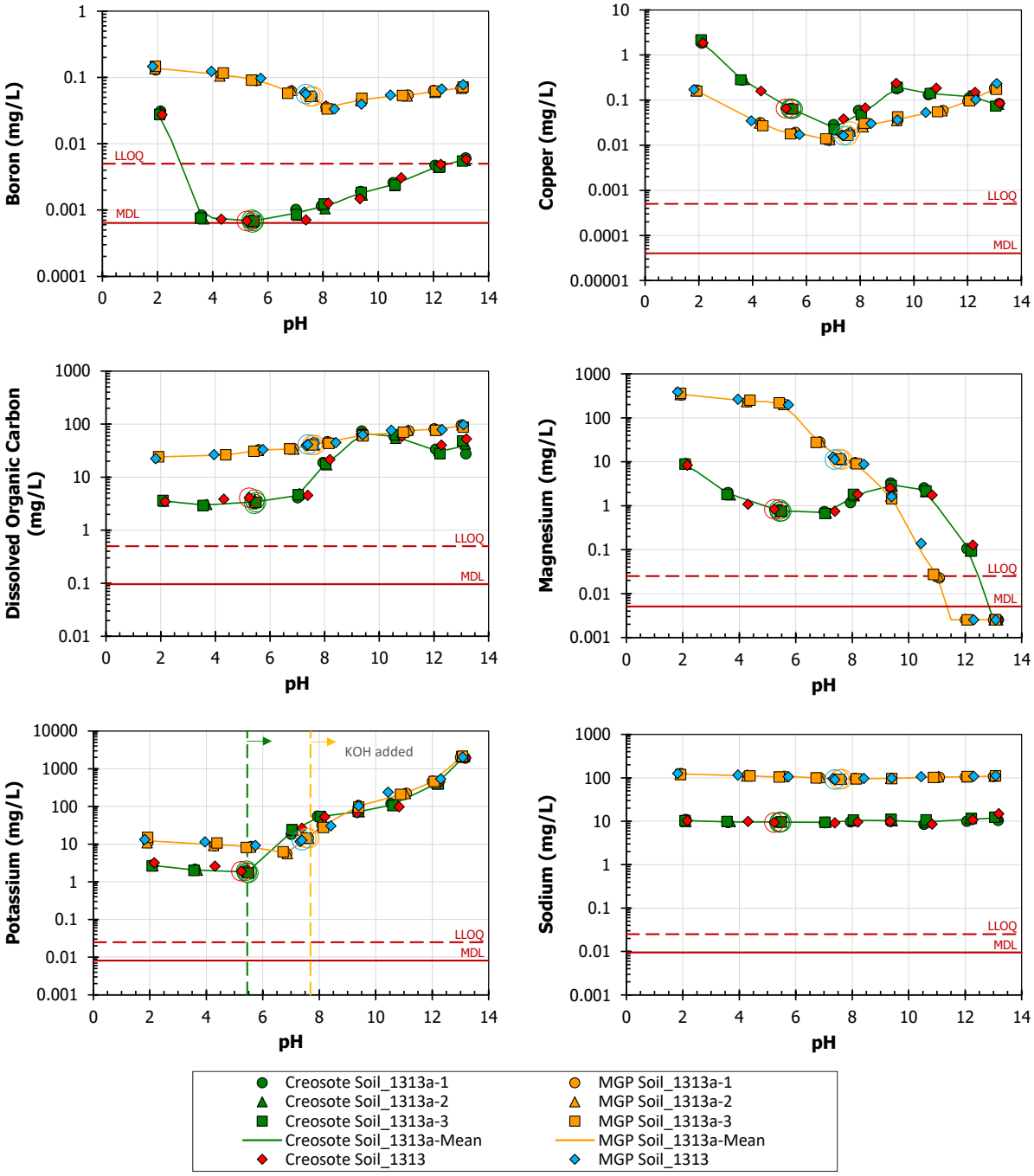

Figure 4-6. Comparison of eluate concentrations from Method 1313 and Draft Method 1313A for major constituents: boron, copper, dissolved organic carbon, magnesium, potassium, and sodium.

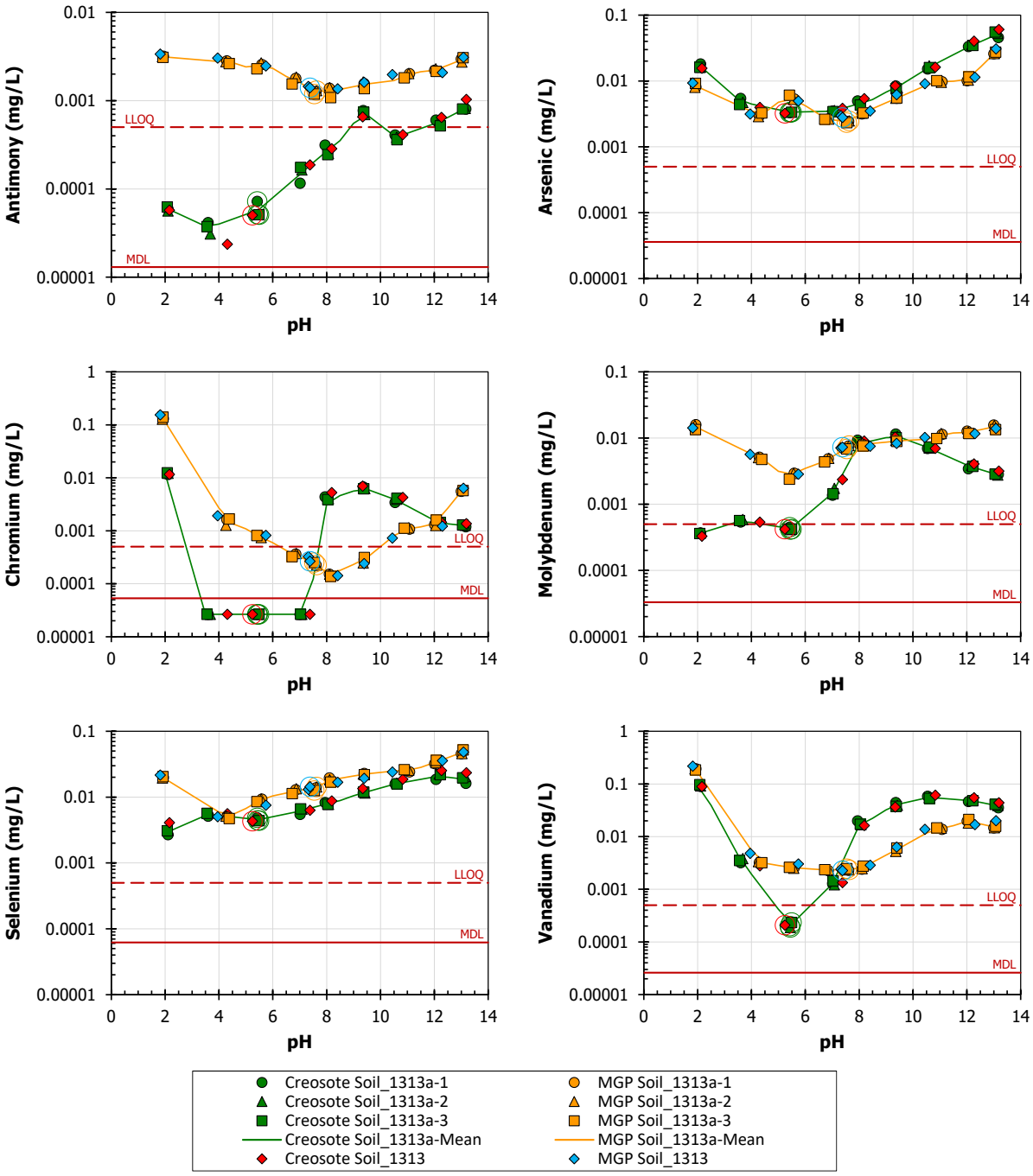

Figure 4-7. Comparison of eluate concentrations from Method 1313 and Draft Method 1313A for oxyanion-forming constituents: antimony, arsenic, chromium, molybdenum, selenium, and vanadium.

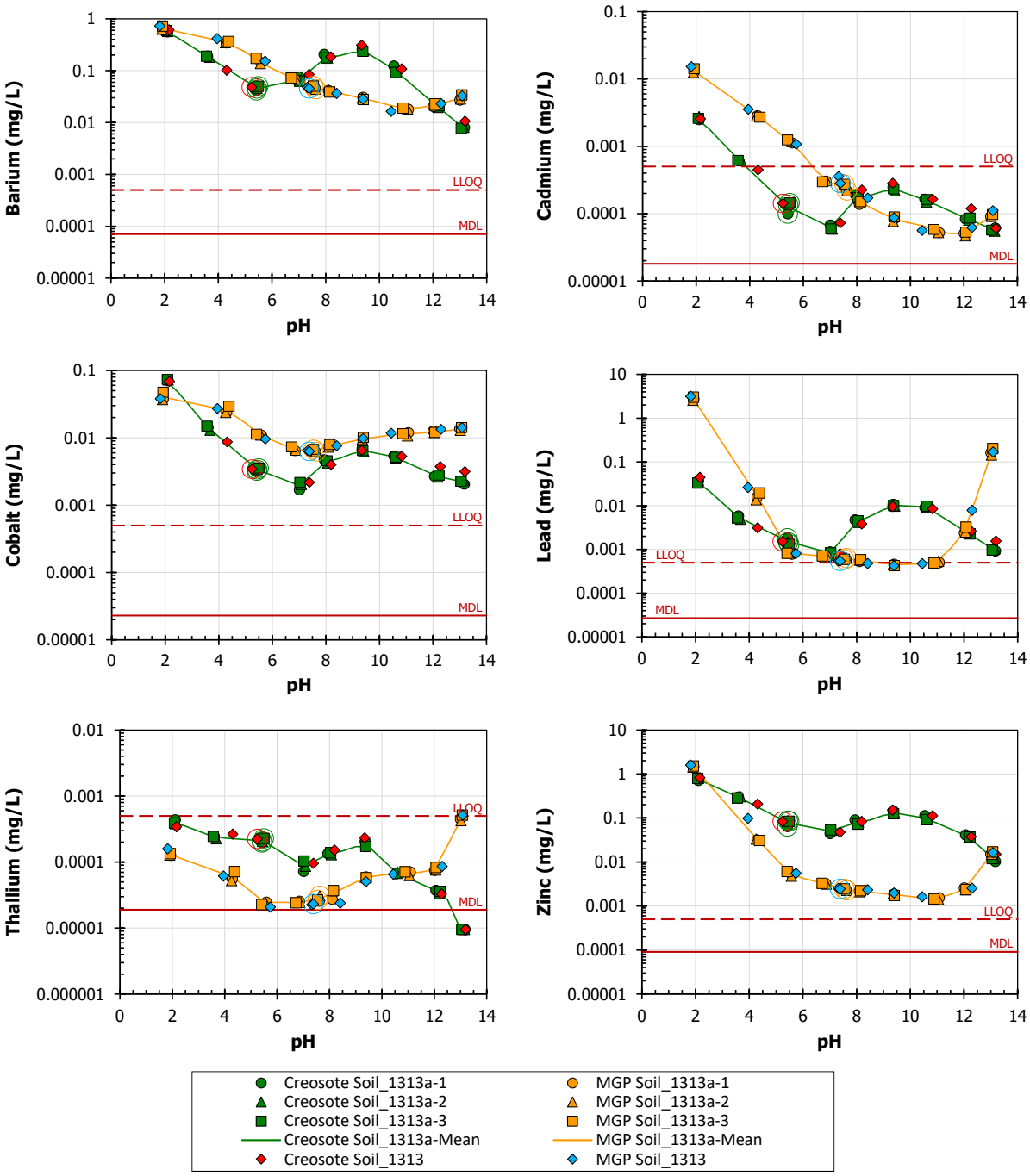

Figure 4-8. Comparison of eluate concentrations from Method 1313 and Draft Method 1313A for trace constituents: barium, cadmium, cobalt, lead, thallium, and zinc.

4.5 Demonstration of Draft Method 1314A for SVOCs

Method 1314 (SW-846, 2017b) is an up-flow percolation column procedure designed to measure the release of COPCs as water passes through a bed of granular material. An eluent solution is pumped in an upward direction to maintain a saturated state while minimizing edge effects and flow channeling in a moderately packed bed of test material. At specific elution interval L/S [$(L/S)_i$] values, eluate samples are collected as continuous fractions of a ΣL/S curve. The concentrations of COPCs in the eluate fractions are plotted as a function of ΣL/S passing through the column or alternatively as a function of pore volume. The demonstration of Draft Method 1314A was conducted in triplicate for each of MGP Soil and Creosote Soil.

4.5.1 Summary of Modifications to Develop Draft Method 1314A for SVOCs

Method 1314 is an up-flow percolation column procedure during which a clean eluent (e.g., DIW or 1 mM $CaCl_2$) is pumped through a bed of moderately compacted granular test material. The eluate is collected as a function of the L/S, given as the volume of water passing through the column relative to the dry equivalent mass of test material within the column (mL/g-dry). The collection vessels for Method 1314 are PP screw-lid jars equipped with a vapor lock that allows the vapor space of the empty bottle to be displaced without allowing external air into the vessel. Method 1314 was adapted to include assessment of SVOCs, where the modified method is currently denoted as Draft Method 1314A.

The following modifications were made to Method 1314 for Draft Method 1314A:

- The column and effluent transfer lines were changed from acrylic and PVC materials, respectively, to 316L stainless steel to minimize sorption of SVOCs. However, an evaluation of leaching from stainless-steel columns (**Appendix C-2.3**) indicated that constituents of stainless steel (e.g., Fe, Mn, Ni, and Zn) may leach into column eluates at concentrations between 10 and 500 µg/L which may interfere with low-level inorganic COPC analysis. Additionally, when sorption of inorganic constituents to stainless-steel columns from an aqueous solution at 100 µg/L was evaluated (**Appendix C-2.4**), a potential for sorption of Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, and Ti to 316L stainless-steel surfaces was observed. The impact of leaching and sorption, however, is likely to be minor if these inorganic species leach from the test material at significant concentrations.

- Column seal gaskets and shutoff valve seats on the outlet side of the column were constructed of PCTFE to minimize sorption of SVOCs to these connecting materials.

- The dimensions of the column were reduced from 4.8-cm ID by 30-cm long to 4.8-cm ID by 20.4-cm long to reduce the maximum sample volume so that replicate testing could be conducted from a limited quantity of test material.

- Amber soda-lime glass collection bottles replaced the HDPE bottles to minimize photodegradation and sorption to HDPE. Collection bottles were fitted with PCTFE lid liners to minimize sorption of SVOCs to vessel lids.

- Column material was packed at its “as received” moisture content (MC) and 0-6 °C to minimize evaporative losses due to air-drying of sample material, which is still recommended when SVOCs are not being analyzed.

- The leaching fluid was changed from DIW to 1-mM $CaCl_2$ to limit formation of colloids due to a cation imbalance.

- The eluent flow rate was reduced from 0.75 L/S per day to 0.5 L/S per day to minimize formation of colloids, as well as to allow a longer time for intraparticle mass transport and approach to local equilibrium.

A remaining question is the potential for significant volatility loss of the more-volatile SVOCs, such as naphthalene (Henry's Law Constant of 4.4 x 10^{-4} atm-m^3/mol), within the headspace of the eluate collection bottle. During collection, small volumes of eluate are deposited into an empty bottle, potentially leading to volatilization of SVOCs into the relatively large volume of headspace. As the collection bottle is filled, the headspace is displaced and any volatilized SVOCs are lost through the vapor trap which allows vapors to be released but prevents the backflow of air into the bottle.

Potential modifications to minimize volatility losses into collection bottle headspace during collection of column eluates included:

- increased frequency of eluate collections so that smaller bottles may be used in the eluate collection, and overall headspace is minimized;
- routine use of headspace vapor traps with SVOC capture into solvent so that volatilized COPCs may be quantified;
- inline or in-situ SPE collection of organic COPCs prior to volatilization into headspace;
- eluate collection into Tedlar or Kynar gas collection bags to minimize headspace; and,
- addition of a small volume of water-miscible solvent to empty eluate collection bottles so that the first few drops of eluate are not exposed to a large volume of headspace.

Preliminary evaluations on increasing the frequency of eluate collection yields additional analytical costs, which tend to drive testing costs, and potential eluate collection scheduling issues. Vapor traps and inline SPEs indicated that these options are cumbersome for a standardized method, create additional processing steps, and results in additional solutions for analysis. The results of trial recovery tests for Tedlar and Kynar bags (**Appendix C-2.5**) indicated significant losses (>30% of initial concentration) of all PAHs; therefore, aqueous eluate collection into gas sampling bags is not considered a viable option to minimize headspace losses.

Experiments were conducted to determine the potential for losses of a naphthalene standard in the headspace of Draft Method 1314A eluate collection bottles (**Appendix C-4.2**). The results of these experiments were inconsistent between duplicates indicating that small leakages in the parallel setup of the Draft Method 1314A apparatus could lead to significant (50% concentration) losses of volatile compounds. Investigation into the source of volatilization losses of naphthalene indicated that collection bottle screw cap integrity is important and difficult to manage. New collection bottles with vapor leak-tight caps result in naphthalene recoveries greater than 75-80%, which are consistent with estimated losses based on Henry's Law and within analytical uncertainty for naphthalene. However, repeated cycling of screw caps (e.g., to change collection bottles) can lead to microcracking and misalignment of the screw caps. Alternative collection bottle lid designs are currently being evaluated. This redesign only impacts SVOC testing for the most volatile SVOCs.

4.5.2 1314A-Leaching Apparatus

Pictures of a prototype column apparatus for Draft Method 1314A, with modifications specific to

the leaching of SVOCs, are presented in **Figure 4-9**. The material of construction for the column and inlet/outlet tubing of the column apparatus is 316L stainless steel, which is considered corrosion-resistant and compatible with the target SVOCs. In addition, the plastic jar collection vessels of Method 1314 have been replaced with amber or foil-covered borosilicate glass jars to minimize the sorption of SVOCs to jar surfaces and prevent photodegradation. The silicon cap seals of the collection bottles were lined with 0.25-mm thick PCTFE sheet to minimize absorption into the polymer seal of the jar.

Figure 4-9. Prototype column apparatus for Draft Method 1314A: front and side views showing eluate collection in 250-mL and 1250-mL amber glass bottles.

An expanded view of the flow path through the column apparatus is presented in **Figure 4-10**, including the dimensions and volumes for each component of the column apparatus. This figure does not show the second flow path from the 3-way valve at the top of the column, extending to the right, where the valve can be used to switch the eluate flow path from one collection bottle to the other. Because of the small-bore tubing between the pump and the collection bottle, the dead volume between the 3-way valve and the end of the tube extending to the bottom of the collection bottle is approximately 0.5 mL. Relative to the volume of eluate collected for each interval, this volume was considered negligible.

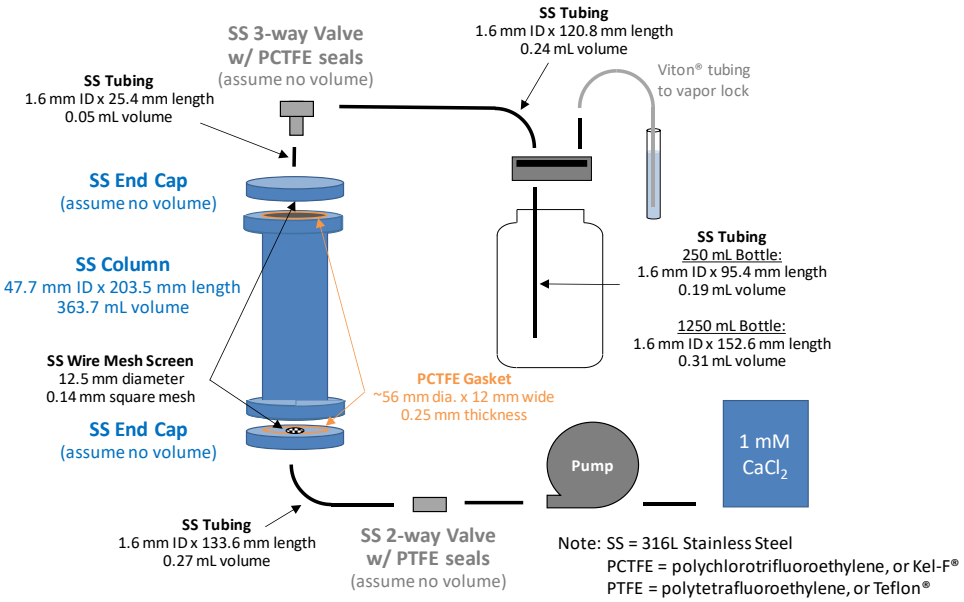

Figure 4-10. Expanded schematic of the flow path for the Draft Method 1314A column with segment dimensions and volumes.

The column contains the test material confined by layers of clean quartz sand that at the bottom distribute the flow of eluent through the column and at the top act as a coarse filter for column eluates. The packing strategy and column orientation during packing and testing is presented in Figure 4-11. The column is packed in an inverted orientation so that the 1-cm sand bed that filters column eluates is consistent between column replicates. Prior to testing, the column is reoriented so that eluent flows through a layer of clean quartz sand, through the packed test material bed, and is coarsely filtered through the 1-cm layer of clean sand before passing on to the collection vessels.

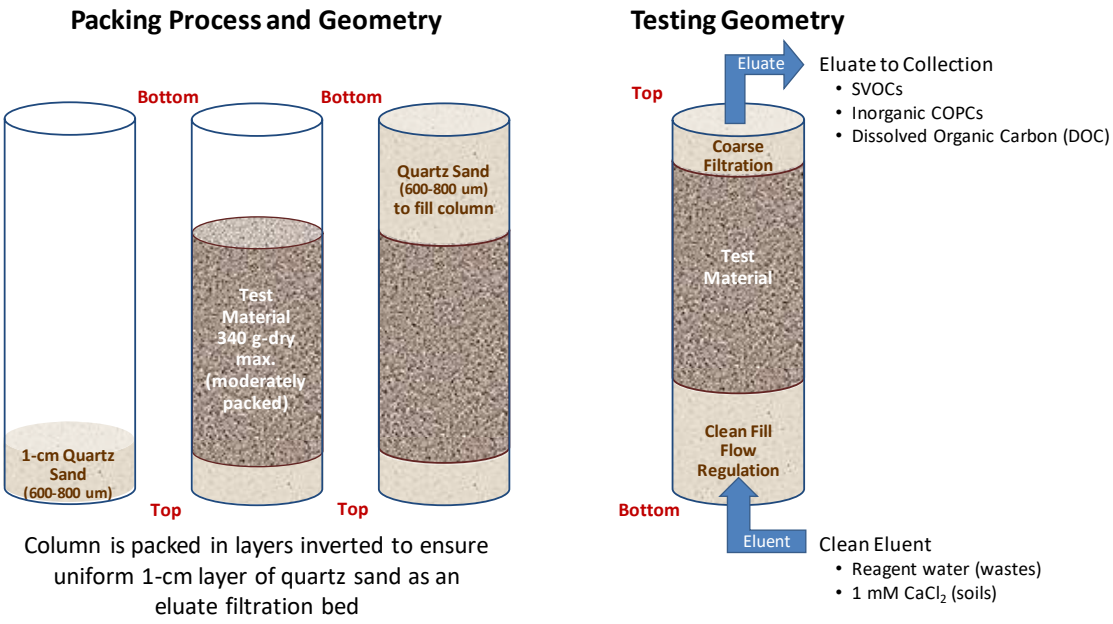

Figure 4-11. Column geometry and packing sequence (left) and geometry during percolation column duration (right).

During packing of the column in the inverted position, a 1-cm layer of sand is the first layer added to the column by mass and lightly compacted by vibrating the column to form a relatively uniform layer. The middle layer is a subsample of test material equivalent to 350 g-dry mass, which is moderately packed into the column using a tamping rod. Due to the potential for loss of SVOCs during drying, the test material is added to the column "as received" so the subsample will contain inherent moisture. If the MC at the time of column packing is known (as should be by measuring the MC on a subsample of the material), the mass of as-received material to be packed into the column may be calculated as:

$$M_{as-received} = \frac{M_{dry\ equiv}}{(1-MC)} \qquad \text{Equation 4-1.}$$

where $M_{as\text{-}received}$ is the mass of "as received" material equivalent to $M_{dry\text{-}equiv}$ (g),
$M_{dry\text{-}equiv}$ is the mass of dry equivalents (340 g-dry maximum), and
MC is the moisture content ($g\text{-}_{H2O}/g$).

The amount of sample packed into the column should be confirmed by the change in mass of the column during packing or by the mass change associated with the material source.

The third layer added to the column is a layer of clean quartz sand that is used to fill the remaining volume of the column to the top (in the packing orientation). When the column is reoriented for testing, this layer becomes an eluent flow-distribution layer that only contacts clean eluent pumped into the bottom of the column.

4.5.3 Test Procedure

A stainless-steel column with effluent transfer lines was prepared as shown in the expanded

schematic in **Figure 4-10**. Where possible, transfer line connections are Swage-lok® or similar pressure fittings and the connection between stainless steel and plastic tubing (e.g., pump output to lower valve assembly and collection bottle vapor lock) are hose-barb fittings secured with hose clamps.

The column was removed from the apparatus and moderately packed with test material and clean quartz sand (600-800 µm) used to condition incoming eluent and coarse filter outgoing eluate. The column is packed in an inverted orientation (see **Figure 4-11**) to ensure that the lower sand bed, used as an eluate filtration layer, remains consistent between replicates. The packing operation includes tamping down a 1-cm quartz sand, adding and tamping test material equivalent to 340 g-dry in 1-5 layers or lifts, and filling the column with quartz sand used for eluent flow regulation. For testing, the column is inverted so that the 1-cm filtration layer is at the top of the column.

During testing, an eluent solution of 1-mM $CaCl_2$ was introduced to the bottom of the column through a peristaltic pump at a pump speed providing an eluent flow rate of 0.5±0.1 L/S per day. Eluate leaving the top of the column was collected into a series of amber, borosilicate glass bottles with water-based air locks that keep outside air from entering the collection vessel. Eluate fractions were collected at nine ΣL/S values following an eluate collection schedule based on the flowrate of the column and the collected L/S (see example schedule in **Table 4-7**).

Table 4-7. Example Method 1314 Eluate Collection Schedule for a Column with 340 g-dry of Material and a Flowrate of 0.5 L/S per day (170 mL/day)

Fraction #	ΣL/S (L/kg-dry)	Cumulative Time (days)	$(L/S)_i$ (L/kg-dry)	Eluate Volume (mL)
1	0.2	0.4	0.2	68
2	0.5	1	0.3	100
3	1.0	2	0.5	170
4	1.5	3	0.5	170
5	2.0	4	0.5	170
6	4.5	9	2.5	850
7	5.0	10	0.5	170
8	9.5	19	4.5	1,500
9	10.0	20	0.5	170

4.5.4 Eluate Processing

Collection of column eluates in Draft Method 1314A includes: (i) the measurement of eluate parameters, such as pH, EC, and, optionally, oxidation-reduction potential (ORP), (ii) the preservation of analysis solutions for inorganic COPC analysis, and (iii) the preparation of analytical samples for GC-MS analysis for SVOCs. This process was designed to allow for enough eluate volume to compare SVOC concentrations directly from eluates before and after alum addition for colloid control. **Figure 4-12** shows the sequence of steps used to process aqueous eluates for the Draft Method 1314A demonstration including measurement of eluate parameters (Step 1), preparation of analytical samples for inorganic chemical analysis (Steps 2 and 3) and processing aqueous eluates into solvent-based analytical samples for SVOC analysis after and without alum treatment (Steps 4 and 5). The following volumes were removed from the eluate collection bottle and prepared for analysis:

- a 5-mL aliquot of aqueous eluate pipetted into a clean PP test tube for measurement of pH and EC by ion-specific probe (Step 1). Note: no ORP on first eluate due to volume constraints;

- a 20-mL aliquot of aqueous eluate (diluted to 50 mL with DIW) and filtered through 0.45-µm membrane and split for analysis of (i) inorganic COPCs (10 mL) preserved by acidification with HNO_3 to pH <2 and (ii) DOC (10 mL) unpreserved (Steps 2 and 3); and,

- a 30-mL aliquot of aqueous eluate (a 15-mL aliquot for first and second eluates) pipetted into a clean 40-mL glass vial for microextraction into 10 mL of MeCl followed by solvent drying in preparation for SVOC analysis of solvent-based samples by GC-MS (Steps 4-6).

The aliquot volumes for the first and second column eluates were modified to allow for analytical sample collection with the limited volume of column eluate collected at ΣL/S 0.2 and 0.5 mL/g-dry. All aliquots were taken directly from the collection bottles without stirring.

In parallel to the above samples, a 40-mL aliquot of aqueous eluate (a 15-mL aliquot for first and second eluates) pipetted into a clean 40-mL glass vial for alum treatment for colloid management prior to microextraction into 10 mL of MeCl followed by solvent drying in preparation for SVOC analysis of solvent-based samples by GC-MS (Steps 7-10). Colloidal matter was removed from the remaining eluate in the collection vessel by adding 20 mg of alum for each 40 mL of remaining eluate in the collection vessel. The alum was blended with the solution by swirling until visually dissolved, then allowed to settle from solution overnight (~18 hours) at 0-6 °C (Step 5). From the alum-treated eluate, a 30-mL aliquot of eluate was removed from the extraction vial (15 mL for the first and second eluate with lesser volume collected) and placed into a clean 40-mL VOA vial for microextraction with MeCl (Step 6). The microextraction and analytical solution process was conducted as described above. From this dried solvent, samples for SVOC analysis were pipetted into GC-MS vials and refrigerated prior to GC-MS preparation by addition of ISTDs and analysis (Step 7).

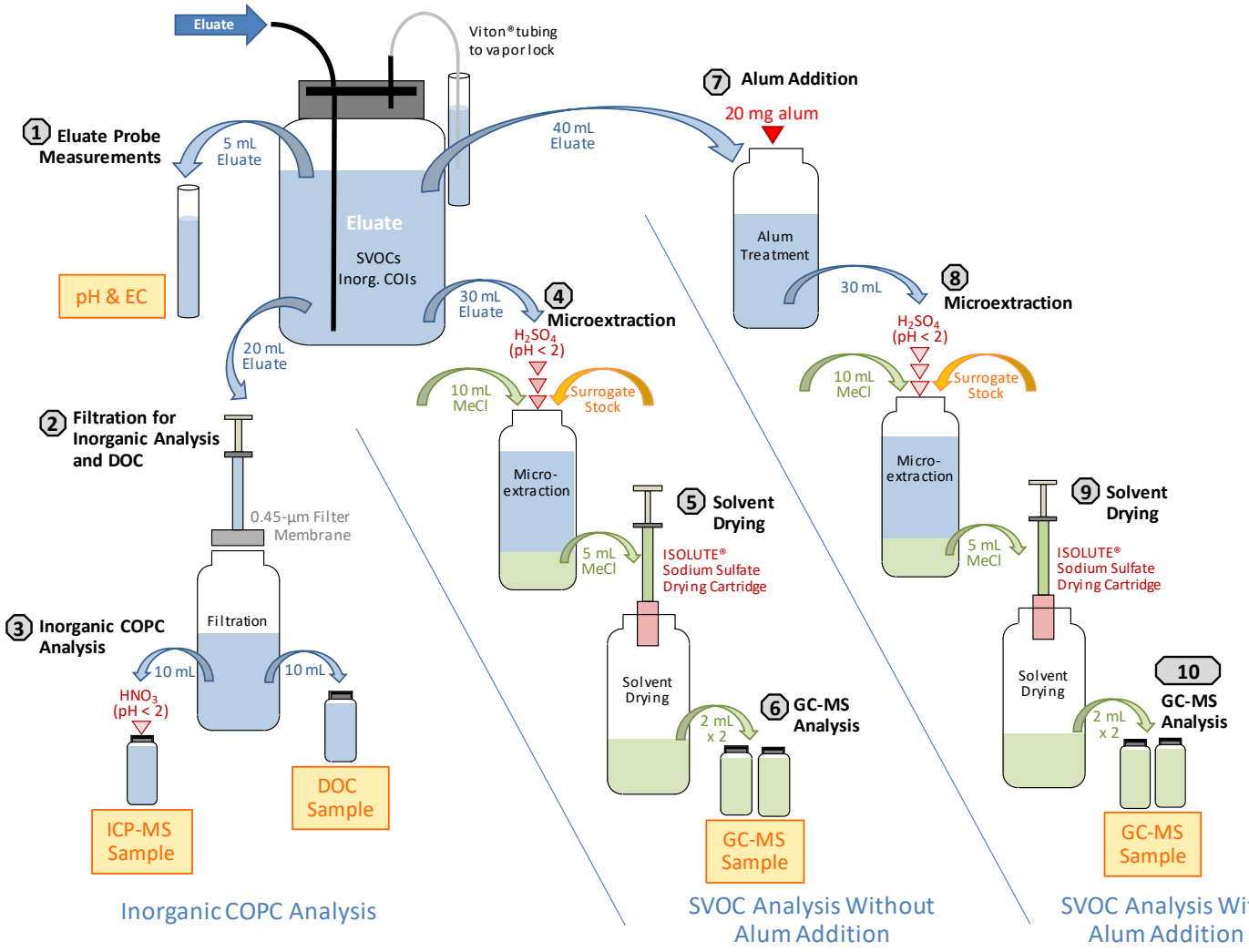

Figure 4-12. Eluate processing for the demonstration of Draft Method 1314A for inorganics and SVOCs with and without alum addition from collection vessels. Steps include measurement of eluate parameters (Step 1), preparation of analysis samples for inorganic analysis (Steps 2 and 3), and preparation of aqueous eluates for SVOC analysis (Steps 4-6) and with alum treatment for management of colloids (Steps 7-10).

4.5.5 Demonstration Results

The results of Draft Method 1314A demonstration for Creosote Soil and MGP Soil are presented in **Figure 4-13** and **Figure 4-14**. In these figures, individual data points for the three replicates are represented by solid symbols, and a mean line indicating the replicate mean at each eluate collection ΣL/S value is shown. The closeness of the data points is an indication of the intra-laboratory precision of the test extraction method; however, statistical evaluation of repeatability and reproducibility would be conducted during any interlaboratory validation study.

Figure 4-13 illustrates the demonstration results of Draft Method 1314A indicating trends in eluate pH, EC, and DOC as 1 mM $CaCl_2$ solution is pumped through the column. The initial eluate pH of the MGP Soil is approximately pH 8 while the initial pH of the Creosote Soil is approximately 6. During Draft Method 1314A, the eluate pH for the MGP Soil decreases to pH 7 after a ΣL/S of 4 L/kg-dry while the eluate pH of the Creosote Soil decreases approximately to pH 4.5 after a ΣL/S 2 L/kg-dry. Similarly, the EC and DOC of the Draft Method 1314A eluates decreases significantly during the experiment up to a ΣL/S of 2 L/kg-dry.

The eluate concentrations from Draft Method 1314A demonstration for phenols and PAHs are shown in **Figure 4-14**. PCP in the Creosote Soil was the only phenol with an eluate response which is consistent with the demonstration results from Draft Method 1313A where phenol concentrations were mostly below the quantitation limit. For PAHs, only NAP and PHE in the Creosote Soil and NAP in the MGP Soil provided eluate concentrations greater than the quantitation limit. Consistent with the pH-dependent data, the concentrations of NAP in the Creosote Soil are higher than they are for the MGP Soil. Where replicates are above quantitation limits, the replication appears to be good for the percolation column test data for SVOCs.

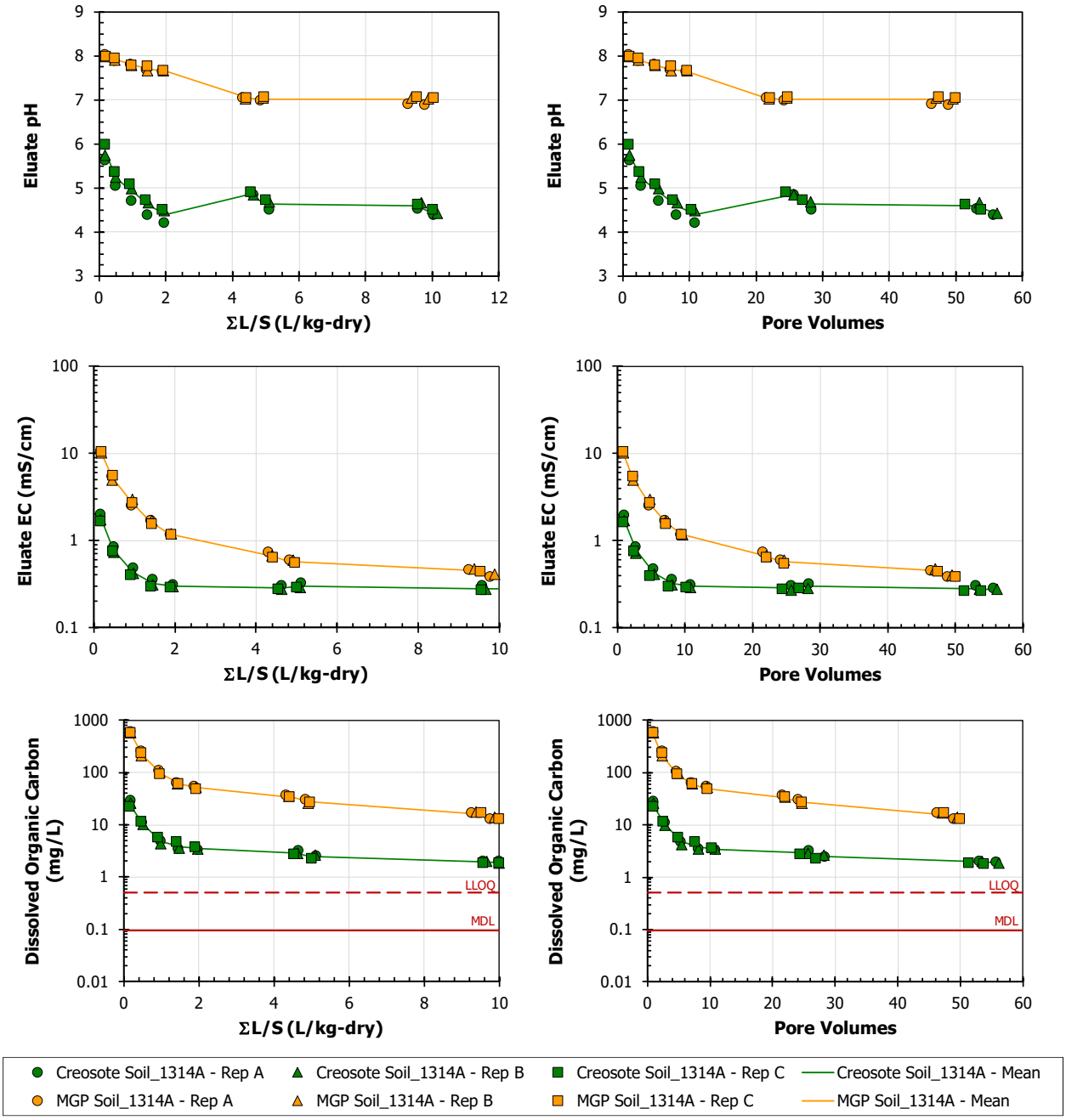

Figure 4-13. Demonstration results of Draft Method 1314A as a function of ΣL/S (left) and pore volume (right), showing material pH evolution during the column test, eluate electrical conductivity, and dissolved organic content.

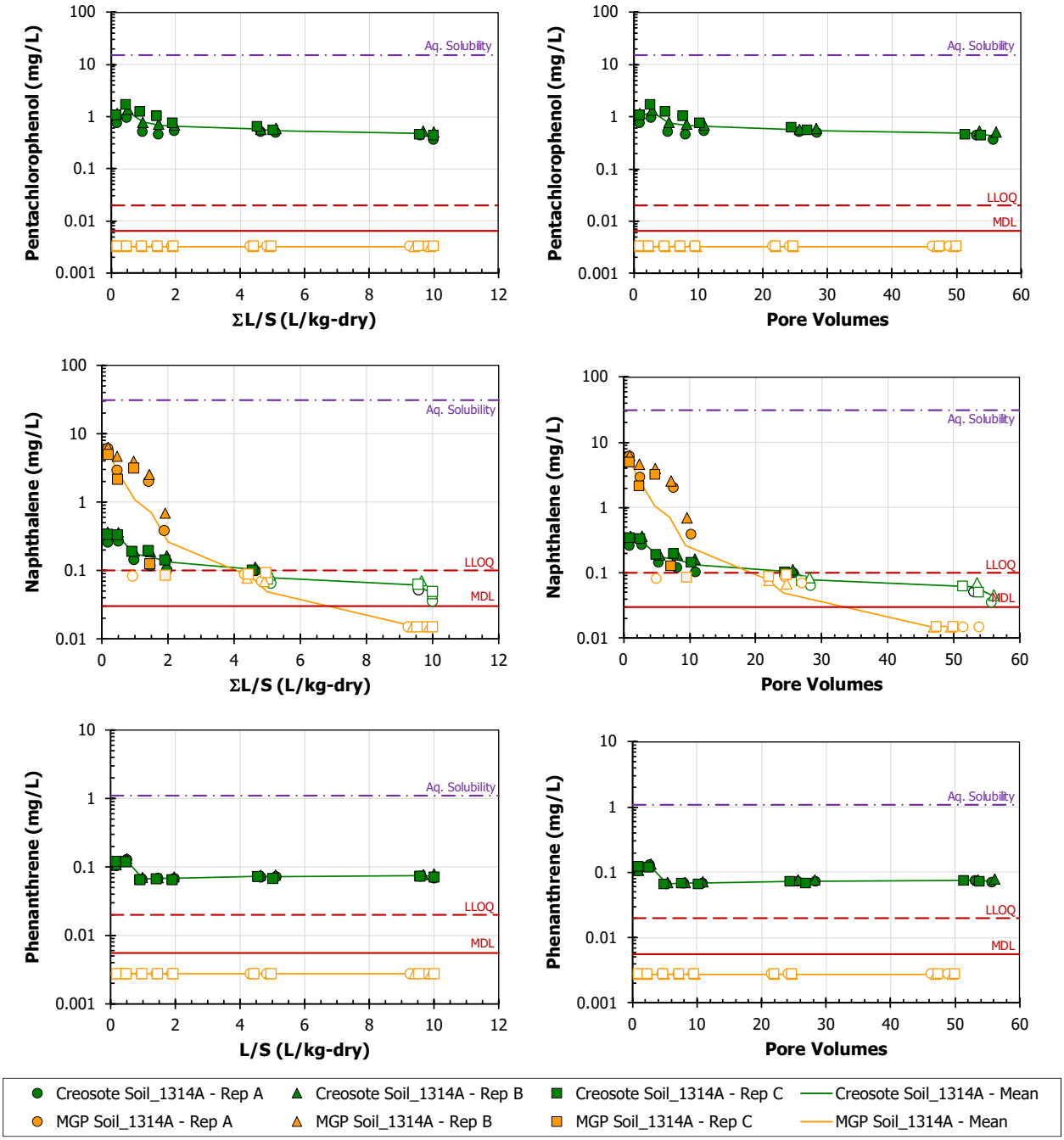

Figure 4-14. Demonstration results of Draft Method 1314A as a function of SL/S (left) and pore volume (right), showing L/S-dependent concentrations of pentachlorophenol, naphthalene, and phenanthrene. Estimated and non-detected data shown as open symbols.

4.5.6 Comparison of Draft Method 1314A and SW-846 (Inorganic COPCs and DOC)

The intent of Draft Method 1314A is to provide a leaching method that is applicable for the parallel assessment of SVOCs and inorganic COPCs. Therefore, it is important that any

modifications to address SVOC evaluation do not interfere with the ability of the draft method to provide reliable results for inorganic COPCs consistent with the validated Method 1314.

The material used for the comparison between Draft Method 1314A and Method 1314 is a coal fly ash (material ID: EaFA) which was tested extensively with Method 1314 during the method interlaboratory validation study (Garrabrants et al., 2012b). Sulfuric acid was used to increase the efficiency of the electrostatic precipitator (ESP), therefore, the EaFA ash had an acidic coating that had been neutralized since the LEAF interlaboratory study. Therefore, the results of Draft Method 1314A carried out on EaFA ash are compared to the results of Method 1314 when carried out in parallel. Aqueous eluates were analyzed by ICP-OES and ICP-MS for 32 inorganic constituents (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, U, V, and Zn).

The results of Method 1314 and Draft Method 1314A for the EaFA fly ash are shown in **Figure 4-15**, **Figure 4-16**, and **Figure 4-17**. In these figures, eluate concentrations are shown in green for two replicates plus a mean trendline for Draft Method 1314A while the same representation is shown in red for the validated method. The results of parallel testing using Method 1314 and Draft Method 1314A are summarized as follows:

- The concentrations of three (3) constituents (Be, Pb, and Sn) were reported below MDLs for all eluates (data not shown).
- The eluate concentrations of 15 inorganic constituents (B, Ba, Ca, Co, Cr, Cs, K, Li, Mg, Mo, Na, S, Se, Si, and U) show little to no difference in eluate concentrations. Selected examples are presented in **Figure 4-15**.
- The results for seven (7) constituents (Cu, Fe, Mn, Ni, Ti, Tl, and Zn) show a similar pattern of leaching where the Draft Method 1314A results are either the same or approximately 2x greater at low L/S. The eluate concentrations for these constituents quickly decrease to less than MDL by L/S of 2 mL/g-dry (See Examples in **Figure 4-16**). These constituents were identified as those inorganic COPCs expected to have interferences with the 316L stainless-steel columns and transfer lines (**Appendix C-2.3** and **Appendix C-2.4**); therefore, the leaching behavior is expected to be variable depending on pH and sorption/desorption phenomena.
- The concentrations for the remaining seven (7) constituents (Al, As, Cd, P, Sb, Sr, and V) show minor differences between the Draft Method 1314A and Method 1314 eluate concentrations which are consistent with the minor changes in eluate pH due to 316L stainless-steel columns and transfer lines. Select elements are shown in **Figure 4-17**.

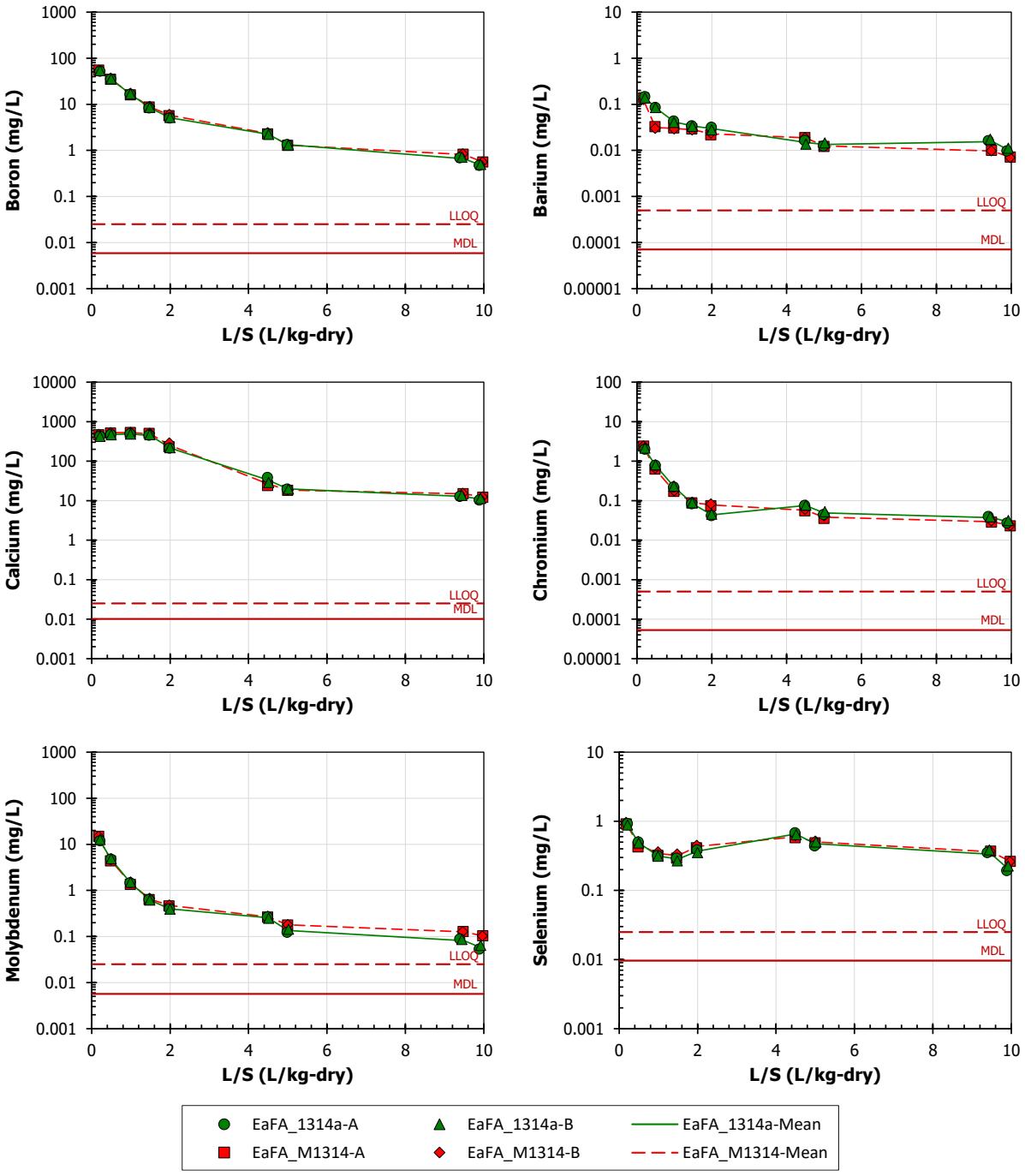

Figure 4-15. Results of Draft Method 1314A (green data) conducted in 316L stainless-steel columns and Method 1314 (red data) conducted in acrylic columns from EaFA fly ash for select inorganic COPCs.

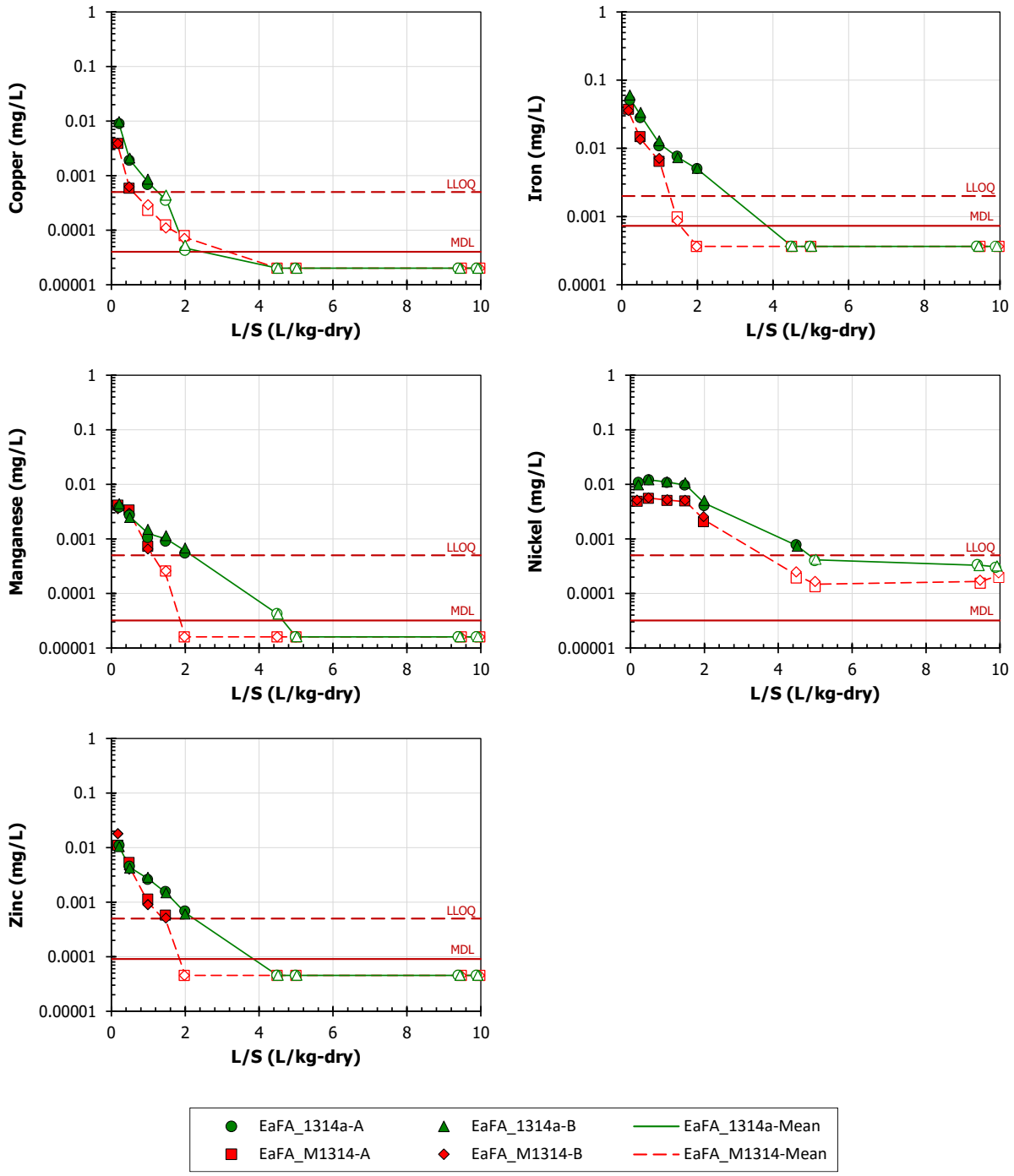

Figure 4-16. Results of Draft Method 1314A (green data) conducted in 316L stainless-steel columns and Method 1314 (red data) conducted in acrylic columns from EaFA fly ash for constituents previously known to leach from 316L stainless-steel columns (see Appendix C-2.3). Data points below the quantitation limit are shown with a white fill.

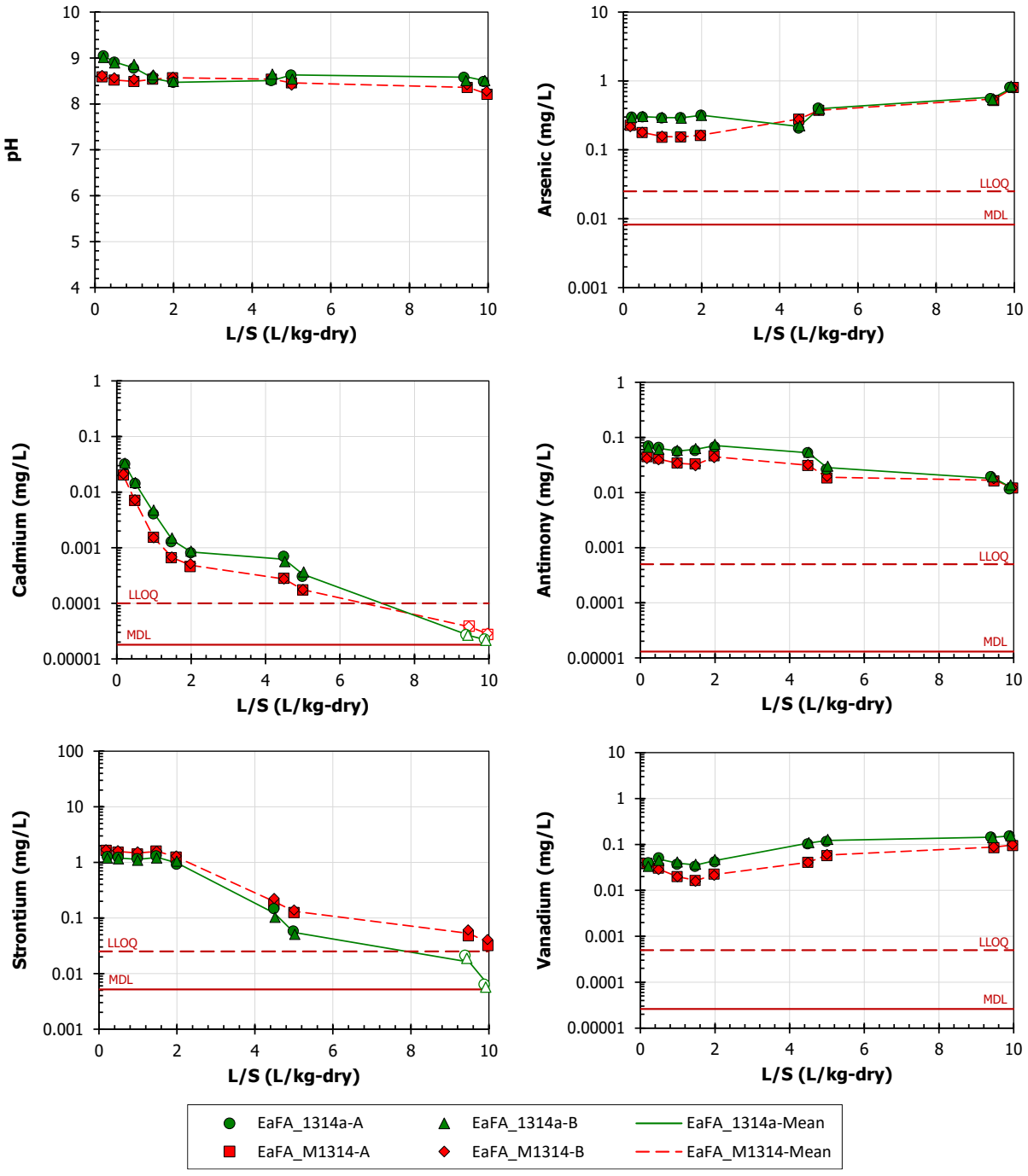

Figure 4-17. Results of Draft Method 1314A (green data) conducted in 316L stainless-steel columns and Method 1314 (red data) conducted in acrylic columns from EaFA fly ash for constituents where the initial pH increase from stainless-steel columns appears to influence the COPC concentration. Data points below the quantitation limit are shown with a white fill.

4.6 Demonstration of Draft Method 1316A for SVOCs

Method 1316 (SW-846, 2017d) is a parallel batch test that involves extraction of multiple subsamples of test material at different L/S ranging from 0.5 to 10 L/kg-dry. The extractions are performed without acid or base addition to allow the natural buffering capacity of the test material to dictate the final pH. Each of five (5) extractions is set up and processed individually so that losses due to volatility are minimized as opposed to leaving container lids open while setting up five extractions at one time. The eluate concentration data for these five extracts in a test replicate should be considered a single analytical set such that the same instruments, technicians, and conditions are used to minimize analytical variability between test positions.

The purpose of this method is to determine near-equilibrium concentrations of constituents released from a solid material and how these concentrations change as the amount of contact liquid is varied. The results obtained from Draft Method 1316A at low L/S (e.g., 0.5 mL/g-dry) can provide an approximation of porewater concentrations for constituents where COPC partitioning is not sensitive to changes in redox conditions. This approximation is valid if care is taken during sample preparation and testing to avoid redox changes. Furthermore, the results of Draft Method 1316A can be used to estimate a linear partition coefficient (K_d) for constituents and materials where adsorption/desorption is the controlling mechanism for LSP. However, an estimated K_d value would be inappropriate when LSP is limited by constituent aqueous solubility or by the available content in the solid material.

In the following demonstration of Draft Method 1316A, the test was conducted on MGP Soil and Creosote Soil. For inorganic COPCs, eluate samples were collected immediately after settling of particulate solid matter and filtered prior to analysis. From the remaining eluate, eluate samples for SVOC analysis were taken before and after treatment with alum to show the effect of minimizing the impact of solution analysis with colloids.

4.6.1 Summary of Modifications to Develop Draft Method 1316A

The general modifications to this batch extraction method to address SVOCs are essentially the same as for Draft Method 1313A (see **Section 4.4.1**). These modifications include the use of: (i) borosilicate glass extraction vials to minimize sorption to materials of construction, (ii) 1-mM $CaCl_2$ solution as the eluant to minimize deflocculation of clays and organic matter, and (iii) alum to minimize colloid formation resulting from agitation during the extraction. One significant modification incorporated into Draft Method 1316A that deviates from the Method 1316 procedure is the inclusion of low L/S centrifuge extractors used to separate solids and liquids at low L/S. For batch extractions of materials with SVOCs, sorption of SVOCs to filtration membranes and apparatus is a concern. The centrifugation extractors can be used to separate eluate from the test solid while avoiding filtration.

4.6.2 Test Procedure

The Draft Method 1316A procedure for a single extraction at an L/S of 10 mL/g-dry is illustrated in **Figure 4-18** as conducted for this demonstration. The process for extractions at other L/S values is the same, however, the ratio of test material and added leaching solution varies to meet specified L/S target values. Therefore, the aqueous eluate volumes collected for analysis were adjusted for the available total eluate volume. At low L/S (e.g., L/S <1), it is often difficult to separate enough liquid from the solid-liquid slurry to support determinative analysis of SVOCs and other COPCs. In these cases, eluates may be combined from multiple parallel extractions of subsamples of the same material at the same test condition to produce large eluate volume if needed for determinative analysis.

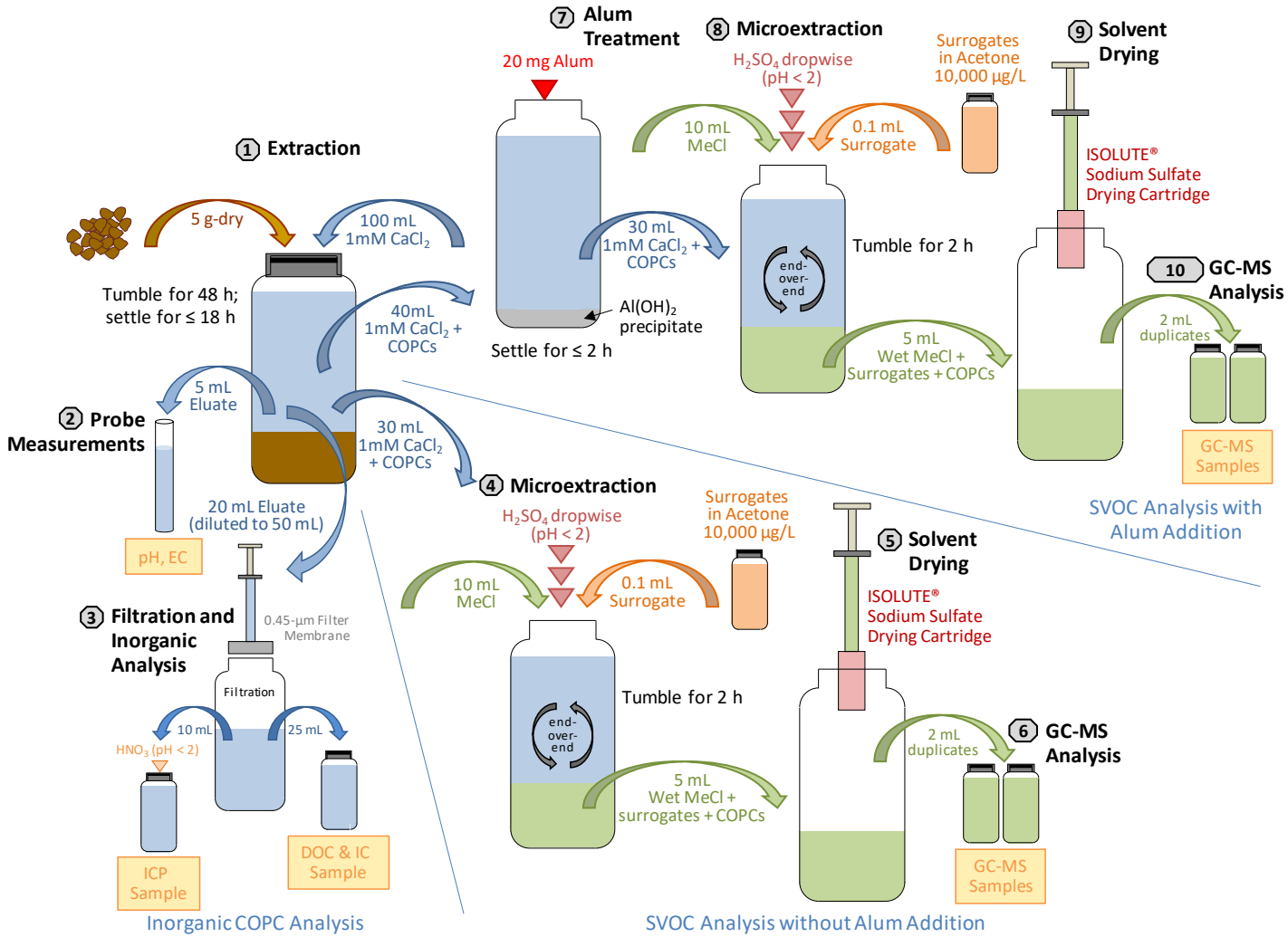

Figure 4-18. Example procedure used for demonstration of Draft Method 1316A showing extraction at L/S = 5 mL/g-dry (Step 1), measurement of eluate parameters (Step 2), filtration for inorganic COPCs (Step 3), and parallel processing of aqueous eluates into solvent based analytical SVOC sample with (Steps 4-6) and without (Steps 7-10) alum treatment.

In the extraction setup (Step 1), a subsample of test material was placed in a 250-mL amber bottle equipped with a PCTFE cap liner. The solid was contacted with the appropriate amount of 1-mM $CaCl_2$ solution at the volume associated with the specific L/S. The target L/S ratio for the extraction includes the amount liquid of inherent within the solid material (i.e., the sample mass multiplied by the MC) and the added 1-mM $CaCl_2$ leaching solution. **Table 4-8** and **Table 4-9** indicate the amounts of test material and leaching solution volume used to achieve the target L/S extractions for MGP Soil and Creosote Soil, respectively.

Table 4-8. Test Material and Eluate Quantities for Desired L/S for VOA Vial Extraction Vessels shown for the MGP Soil (Solids Content >0.99)

Test Position #	L/S (mL/g-dry)	Dry Equivalent Mass (g-dry)	Eluate Volume (mL)	As-tesWhted Mass (g)	1-mM $CaCl_2$ Added (mL)	Bottle Size (mL)
T01	10.0	10	100	10	100	125
T02	5.0	20	100	20	100	125
T03	2.0	80	160	81	160	250
T04	1.0	120	120	120	120	250
T05	0.5	160	80	160	79	250

Total mass of MGP Soil used = 392.75 g

The extraction scheme balances the use of a significant amount of test material with the production of enough eluate to perform analytical testing (i.e., in this case, parallel analysis for inorganics and SVOCs with and without alum treatment was expected to require approximately 100 mL of aqueous eluate). The extraction bottles were tumbled end-over-end at 30±2 rpm for a contact time of 48 hours. The demonstration of Draft Method 1313A (see **Section 4.4**) discusses the implications of particle size and contact time.

Table 4-9. Test Material and Eluate Quantities for Desired L/S for VOA Vial Extraction Vessels Shown for the Creosote Soil (Solids Content = 0.80)

Test Position #	L/S (mL/g-dry)	Dry Equivalent Mass (g-dry)	Eluate Volume (mL)	As-tested Mass (g)	1-mM $CaCl_2$ Added (mL)	Bottle Size (mL)
T01	10.0	10	100	12.50	97.5	125
T02	5.0	20	100	25.00	95.0	125
T03	2.0	80	160	100.00	140.0	250
T04	1.0	120	120	150.00	90.0	250
T05	0.5	160	80	200.00	40.0	250

Total mass of Creosote Soil used = 487.5 g

4.6.3 Eluate Processing

Figure 4-18 shows three distinct eluate processing pathways for Draft Method 1316A: (i) measurement of eluate parameters and preparation of eluates for inorganic COPC analysis (lower pathway), (ii) preparation of SVOC eluates without alum treatment (middle pathway), and (iii) alum treatment and preparation of SVOC eluates after alum treatment (upper pathway). In the figure, these pathways are separated by blue lines. The following eluate aliquots were collected and prepared for analysis from Draft Method 1316A extractions:

- a 5 mL aliquot placed into a clean PP test tube for measurement of eluate pH and EC using ion-specific probes (Step 2),
- a 20-mL aliquot (diluted to 50 mL with DIW) filtered through 0.45-um PP membrane prior to splitting the aliquot for analysis of inorganic COPCs (10 mL) that was preserved with HNO_3 to pH <2 and DOC (25 mL) preserved by refrigeration (Step 3),
- a 30-mL aliquot placed into a clean 40-mL glass vial for microextraction with 10 mL of MeCl prior to solvent drying in preparation for GC-MS analysis of SVOCs (Step 4), and
- a 40-mL aliquot placed into a clean 40-mL glass vial for alum treatment followed by microextraction of 30 mL of the treated eluate with 10 mL of MeCl prior to solvent drying in preparation for GC-MS analysis of SVOCs after alum treatment (Step 7).

All aliquots were removed from the extraction bottle by pipette after allowing solid particles to settle at room temperature (20±2 °C) for 2 hours.

Alum treatment was accomplished by addition of 20 mg of alum to the 40-mL aliquot of eluate to remove the colloidal matter from suspension. The eluate + alum solution was blended on a vortex mixer for 20 seconds and allowed to settle for 18 hours to separate colloids from eluate. From that vial, a 30-mL aliquot of the clarified eluate was removed from the VOA vial and placed into a clean 40-mL VOA vial for microextraction with MeCl. An additional 5 mL of the alum-treated eluate was filtered through 0.45-µm PP membrane and diluted to 20 mL with DIW in preparation for DOC determination after alum treatment. Lastly, a 30-mL aliquot of the extraction eluate is removed from the extraction bottle and placed into a clean 40-mL VOA vial for microextraction without alum treatment (Step 8).

Two aqueous eluates (i.e., 30 mL of aqueous eluates with and without alum treatment) were extracted into MeCl following the same procedure (Steps 5 and 6). The pH of each eluate was adjusted to pH <2 with three (3) drops of concentrated H_2SO_4 to protonate phenol endmember groups. Surrogate SVOCs were added from a bulk standard in acetone to evaluate microextraction efficiency. Finally, 10 mL of MeCl solvent was added and the extraction was tumbled end-over-end at 30±2 rpm for 2 hours after which the extraction was allowed to settle overnight. A large fraction of the aqueous phase was removed by pipette and discarded. Approximately 5 mL of MeCl solvent containing target SVOCs and surrogates was removed by syringe and dried by passing through a Biotage ISOLUTE® Na_2SO_4 cartridge (Steps 7 and 8). From this dried solvent, samples for SVOC analysis were pipetted into GC-MS vials, ISTDs were added, and refrigerated prior to GC-MS analysis (Steps 9 and 10).

For extractions where insufficient eluate can be recovered from the extraction after settling, eluate may be expressed from the solid slurry using low-speed centrifugation (5,000 rpm for 5 minutes) with a centrifuge separation device. **Figure 4-19** shows a schematic of the device and the process for using this centrifugation device.

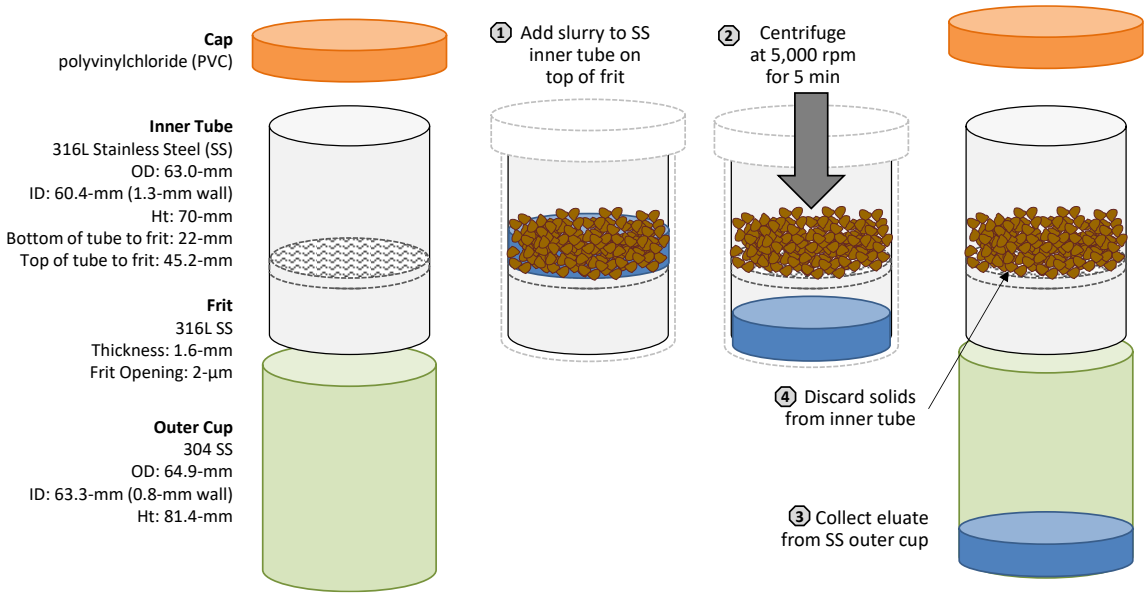

Figure 4-19. Low L/S centrifuge apparatus and description of its operation to separate eluates from solid phases at low L/S.

In cases where centrifugation did not recover enough aqueous eluate for the above analytical scheme (e.g., L/S 0.5 mL/g-dry), the sampling scheme was modified to the following eluate volumes:

- 5 mL for pH, EC measurement using an ion-specific probe.
- 10 mL (diluted to 50 mL with DIW), filtered through 0.45-µm membrane and preserved separately for analysis of inorganic COPCs and DOC.
- 15 mL for microextraction and drying in preparation for GC-MS analysis of SVOCs.
- 20 mL for alum treatment with 15 mL for microextraction and drying in preparation for GC-MS analysis of SVOCs. No DOC sample was taken for this sample.

In this demonstration, only samples at L/S 0.5 and 1 mL/g-dry required the modified sampling scheme.

4.6.4 Demonstration Results

The results of triplicate demonstration of Draft Method 1316A conducted on MGP Soil and Creosote Soil are shown in **Figure 4-20** (pH and organic carbon) and **Figure 4-21** (phenols and PAHs). In each of these figures, the results for three replicates (circles, triangles, and squares) are shown along with a mean line derived from the replicate data. Therefore, the tightness of the data groupings is a qualitative indication of the repeatability of the test data. Where applicable, a dot-dashed line, representing the aqueous solubility of the SVOC, is shown on each graph.

The natural pH of MGP Soil at L/S 10 L/kg-dry is significantly higher at pH 7.2 than the natural pH of Creosote Soil at L/S 10 L/kg-dry at pH 4 (**Figure 4-20**). However, the pH at low L/S between the two soils is somewhat closer – pH 7.5 for MGP Soil and pH 5.6 for Creosote Soil. Likewise, the organic carbon of MGP Soil is an order of magnitude higher than the organic

carbon in Creosote Soil, potentially leading to the release of colloidal matter in agitated batch extractions (**Appendix C-3.5**).

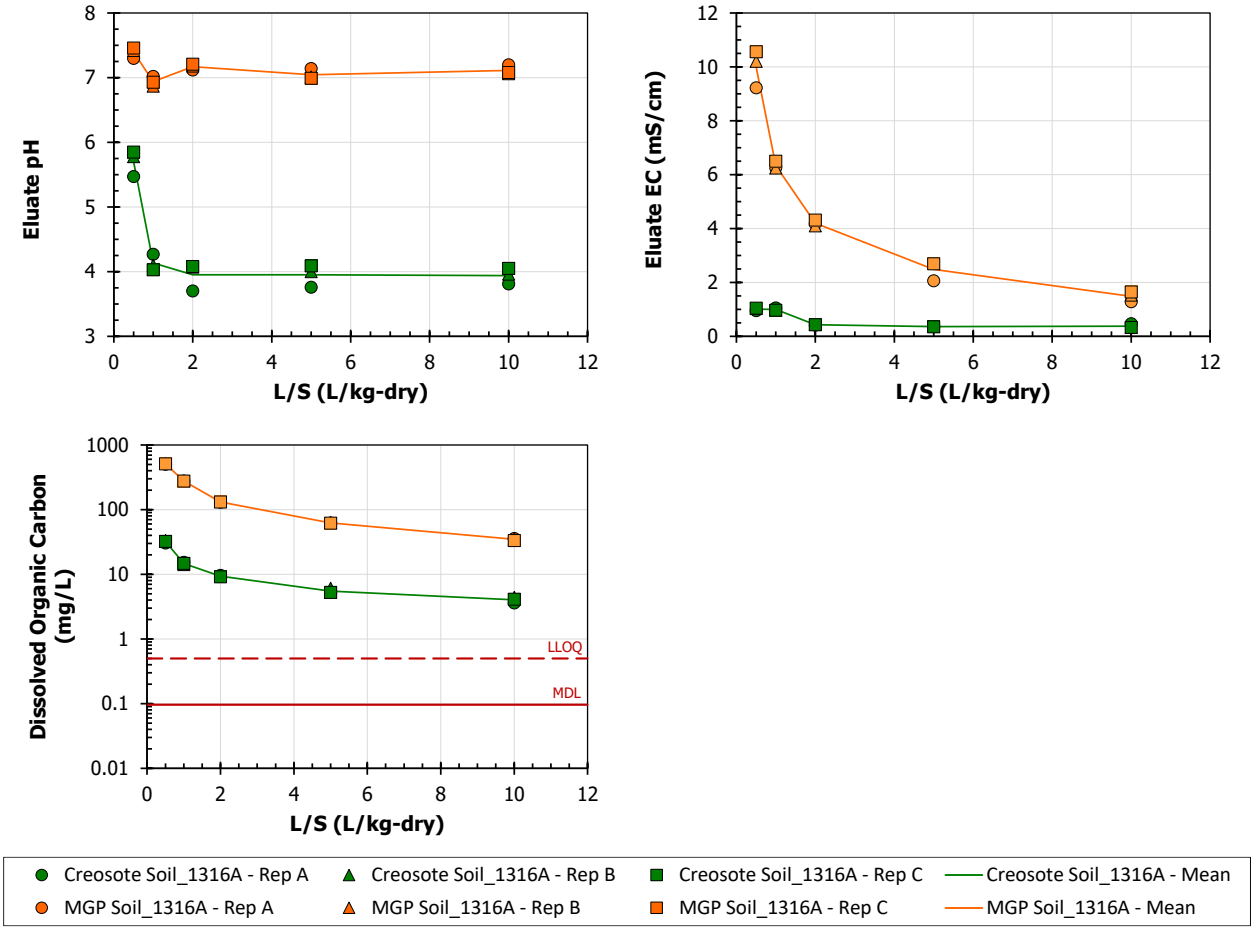

Figure 4-20. Demonstration results of Draft Method 1316A showing L/S-dependent batch data for eluate pH, eluate electrical conductivity, and dissolved organic content.

The eluate concentration data for phenols (**Figure 4-21**) were below detection limits for all phenols except PCP in the Creosote Soil. However, based on these limited data, the repeatability of Draft Method 1316A for phenols shows a high degree of precision, especially at higher L/S values. The releases of PAHs from Creosote Soil and MGP Soil are shown in **Figure 4-20** for NAP, ACE, FLU, phenanthrene (PHE), fluoranthene (FLA), and pyrene (PYR). For many of the PAHs, there is some scatter in the replication of leaching concentrations, especially at low L/S. However, these extractions are inherently more likely to develop uncertainties due to handling and inefficiencies associated with the use of low L/S extractors and centrifugation.

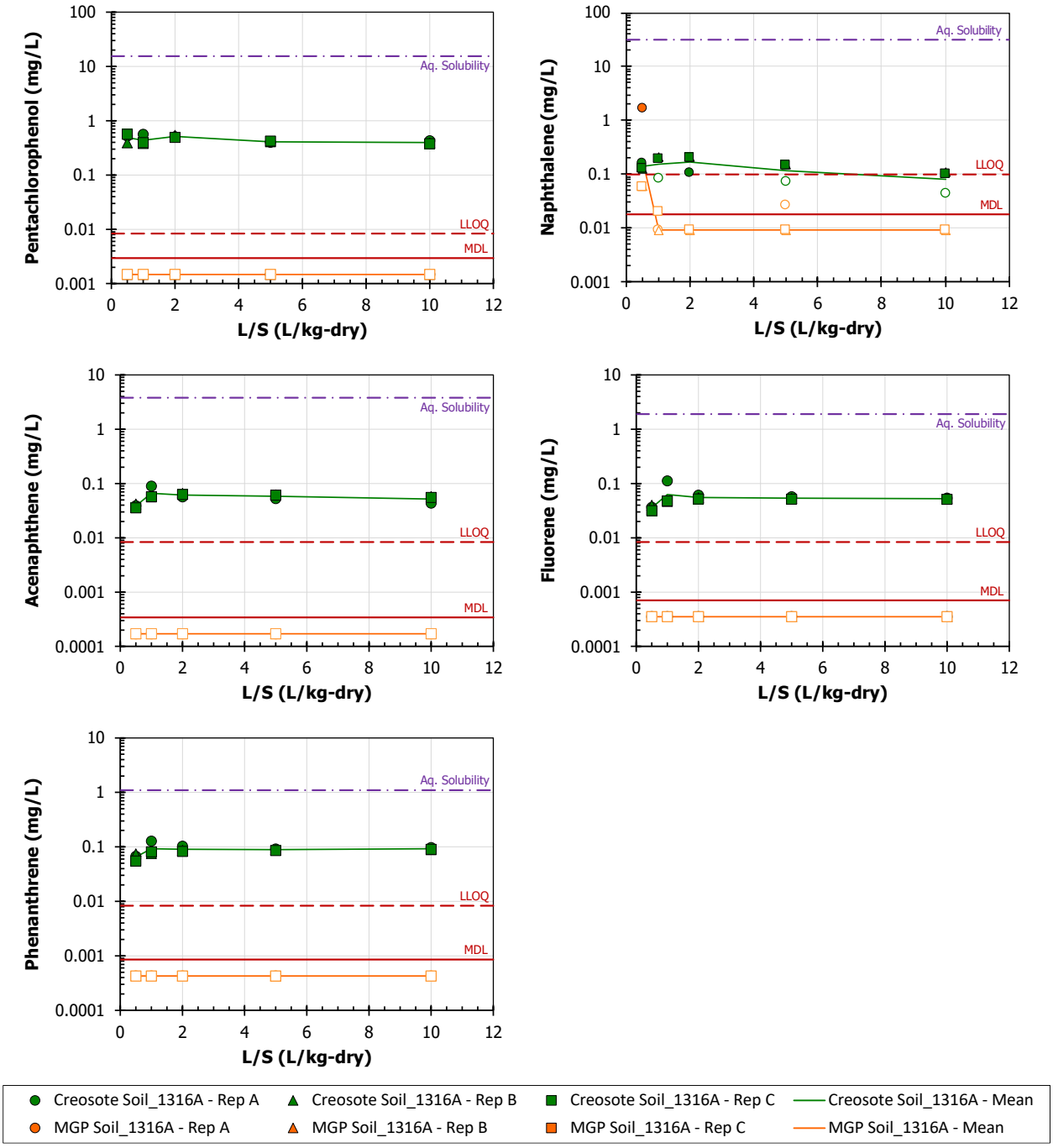

Figure 4-21. Example demonstration results for SVOCs from Draft Method 1316A for pentachlorophenol, naphthalene, acenaphthene, fluorene, and phenanthrene. Data points below the quantitation limit are shown with a white fill.

4.6.5 Effect of Alum Addition on Method 1316A Results

The addition of 20 mg of alum for each 40 mL of aqueous eluate was found to remove visual turbidity from Draft Method 1313A extracts (**Appendix C-3.1**) while not interfering with free SVOCs in solution (**Appendix C-3.2**). Comparison of Draft Method 1316A demonstration data with and without alum addition to remove colloids from the eluate is shown in **Figure 4-22**. When alum is added to eluates from the Draft Method 1316A demonstration prior to microextraction into MeCl, the measured concentrations of organic carbon and select SVOCs were comparable to eluate concentrations without alum addition. At low L/S, the addition of alum might increase the uncertainty of the measurement; however, it is likely that the differences in eluates with and without alum addition are within the uncertainty associated with the GC-MS analysis of SVOCs.

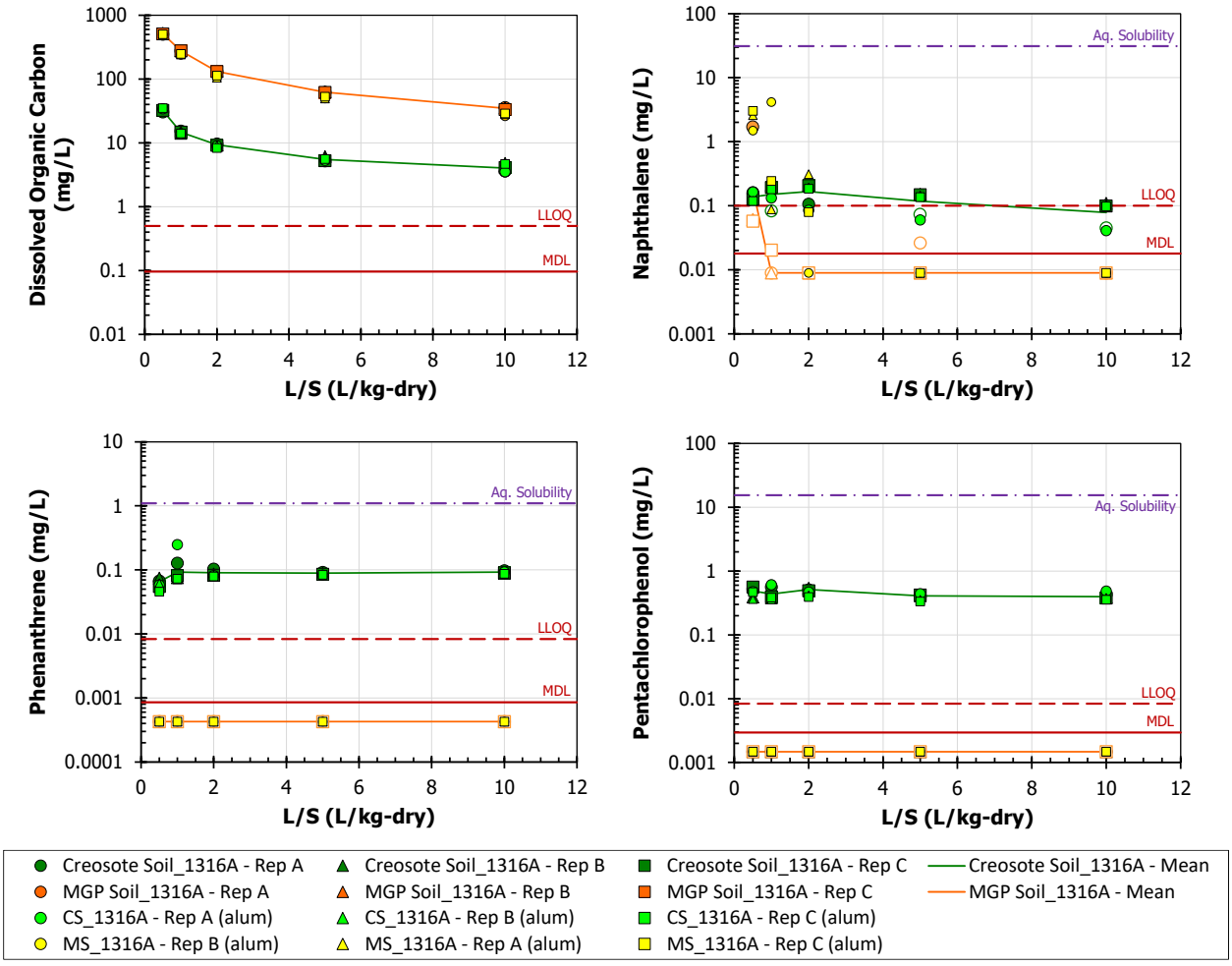

Figure 4-22. Comparison of Draft Method 1316A demonstration data with and without alum addition for removal of eluate colloids for dissolved organic carbon, naphthalene, phenanthrene, and pentachlorophenol. Data points below the quantitation limit are shown with a white fill.

4.6.6 Comparison of Draft Method 1316A and Method 1316 (inorganic COPCs and DOC)

Draft Method 1316A is intended to provide a leaching method that can be used in cases where constituents of interest include both organic and inorganic species. Therefore, the results of Draft Method 1316A for inorganic COPCs should be the same as those derived from Method 1316. However, since the procedure is essentially the same as other batch extraction tests, a direct comparison of results between Draft Method 1316A and Method 1316 was not conducted in lieu of the data comparing Draft Method 1313A and Method 1313 results (see **Section 4.4.8**).

5 Development of Leaching Tests for PFAS

The underlying phenomena of PFAS leaching, are largely controlled by phenomena that are present for inorganic COPCs and SVOCs. Therefore, the testing approaches developed in Methods 1313 through 1316 should extend to PFAS with minor modifications. In the environment, most PFAS are ionic species in solution (just like inorganic COPCs) that can partition by ionic attraction but can also have a nonpolar region that can facilitate LSP analogous to nonionic SVOCs. Relative to the SVOCs, the physical and chemical properties that make PFAS unique (see **Section 2.2.3**) are strong C-F bonds, surfactant properties, and accumulation at interfaces. The development of LEAF tests for PFAS follows the consistent leaching assessment approach applicable for a wider range of material types (e.g., soils, sediments, wastes, concretes, etc.) as well as a unified approach for materials with both inorganic and organic constituents.

5.1 State-of-the-Art in Leaching Characterization for PFAS

Due, in part, to the designation of PFAS as a family of emerging pollutants (U.S. EPA, 2023c), extensive research has been conducted on PFAS, resulting in numerous published works in the past five years. Several studies offer a general overview of PFAS in environmental systems (Guelfo et al., 2021; Lei et al., 2023; Lyu et al., 2022; Sharifan et al., 2021; Sima and Jaffé, 2021; Simon et al., 2019; Travar et al., 2021; Van Glubt, 2020; Wang et al., 2023). The reviewed PFAS research focused primarily on:

- the characterization of contaminated sites regarding site-specific information that impacts PFAS (Baduel et al., 2015; Brusseau et al., 2020; D'Ambro et al., 2021; Borthakur et al., 2021; Høisæter et al., 2019; Nickerson et al., 2023)
- the understanding of PFAS retention with environmental media through use or calculation of partitioning coefficients to various media (Adamson et al., 2022; Anderson, 2021; Helmer et al., 2022; Huang et al., 2022; Schaefer et al., 2022a)
- the evaluation of solid phase sorbents for use as retardation agents to minimize leaching of PFAS into the subsurface (Brusseau et al., 2019; Cai et al., 2022; Compos-Pereira et al., 2018; 2022; Das et al., 2013; Li et al., 2018; Navarro et al., 2023; Newell et al., 2020, Khan et al., 2021; Niarchos et al., 2022; Oliver et al., 2020; Zhao et al., 2014),
- the development of basic information to describe/predict the transport of PFAS through the saturated and unsaturated subsurface (Bratton, 2022; Brusseau and Guo, 2021; 2022; Guo et al., 2020; Mahinroosta et al., 2021; Nguyen et al., 2020; Silva et al., 2020; Schaefer et al., 2021; Van Glubt et al., 2021, Zeng et al., 2021).

Only a small fraction of research has focused on characterizing the release of PFAS from source materials (Bräunig et al., 2019; 2021; Röher et al., 2021; Borthakur et al., 2021; Høisæter and Breedveld, 2022; Silva et al., 2022; Weidemann et al., 2022) along with a few attempts to define a methodology for leaching assessment of PFAS-impacted materials (Bierbaum et al., 2023; Høisæter and Breedveld, 2022; Kabiri and McLaughlin, 2021; Kabiri et al., 2021; 2022; Lange et al., 2021; Rayner et al., 2022). The following is a brief overview of laboratory methods used to describe the release of PFAS from contaminated materials.

5.1.1 Batch Leaching Tests

Batch extractions are used in the PFAS literature as a predictor of eluate concentrations from PFAS-contaminated media, most often intended to develop linear partitioning coefficients (K_d) from experimental data (Hale et al., 2017; Oliver et al., 2020; Sørmo et al., 2021; Van Glubt et al., 2021). In general, batch extractions are characterized by a mass of granular test material contacted by a leaching fluid at a prescribed L/S for a time considered long enough to approach equilibrium between the solid and liquid phases. Many of the standardized leaching protocols call for contact times on the order of 1-2 days (e.g., Method 1311 calls for 18-h extraction of <9.5 mm particles while Method 1313 specifies a particle size-dependent contact time up to 3 days for the same particle size); however, batch extractions used for PFAS include cases of extending the contact time up to 14 days (Silvani et al., 2019; Sørmo et al., 2021). After extraction, solid and liquid phases have been separated by settling, filtration (Hale et al., 2017; Silvani et al., 2019; Sørmo et al., 2021), or centrifugation (Barth et al., 2021; Bräunig et al., 2019; 2021; Kabiri, Centner, and McLaughlin, 2021; Kabiri et al., 2021; Kabiri and McLaughlin, 2021; Lange et al., 2021; Rayner et al., 2022, Sörengård et al., 2019; Wang et al., 2021; Zhang et al., 2022).

The composition of the leaching solution can be adjusted to investigate the impact of factors such as eluate pH or ionic strength (Cai et al., 2022; Campos-Pereira et al., 2018; 2022; Kabiri, Centner, and McLaughlin, 2021; Kabiri and McLaughlin, 2021; Li et al., 2018; Nguyen et al., 2020; Oliver et al., 2020) or ionic composition (Brusseau and Van Glubt, 2019; Cai et al., 2022; Campos-Pereira et al., 2018) on PFAS partitioning. The following are brief summaries of select research where batch leaching is used as a methodology to evaluate the release of PFAS from soils and sediments.

5.1.1.1 Batch Extractions in DIW

- Hale et al. (2017) used a batch leaching test slightly modified from EN 12457-2 (CEN, 2002) to determine K_d values for PFOS in 24 AFFF-impacted soils before and after the addition of montmorillonite, compost, or activated carbon (AC). The authors stated that this was the first study that looked at release from AFFF-impacted soils as opposed to sorption to clean soils taken adjacent to AFFF-impacted areas. The batch test comprised DIW extraction of 4-mm solid at an L/S 10 mL/g over 10 days which included 8 days of extraction plus 2 days of settling. The results were considered to represent a “theoretical maximum leached concentration” due to the large amount of leaching fluid utilized in batch tests compared to field environments. The leached results were 23% and 601% of the total PFOS determined by methanol extractions. The variation in recovered PFOS was attributed to analytical method artifacts (e.g., solvent extraction being less exhaustive compared to water extracts), poor homogenization of the soil samples, or other components of AFFF (e.g., glycols and ethoxylates) impacting PFOS binding to soils.

- Silvani et al. (2019) and Sørmo et al. (2021) used a modified version of EN 12457 (CEN, 2002) to assess the ability of biochar additions to immobilize PFAS in contaminated industrial soils. Samples of AFFF-impacted soil with and without biochar amendments were extracted with DIW at L/S 10 mL/g for 16 days which included 14 days of extraction at room temperature and 2 days of settling at 4 °C followed by filtration through 1.2-µm glass microfiber filters. While most PFAS were detected in eluates from unamended soils with low levels of total organic carbon (TOC), the leaching of PFAS with carbon chains >6 from unamended soils was much less from soils with high TOC. The observation that the retention of long chain PFAS is strongly associated with the amount

of solid-phase organic matter is consistent with the observations of other researchers (Higgins and Luthy, 2006; Campos-Pereira et al., 2018). The general outcomes of these studies suggest hydrophobic interactions of PFAS with NOM and support the use of carbon-based amendments to reduce the leaching of some PFAS, particularly with C ≥6.

- Lange et al. (2021) investigated the impact of sample drying on PFAS leaching concentrations using a German batch leaching test, DIN 19529 (DIN 2015; extraction with DIW at L/S 2 mL/g for 24 h with centrifugation). This research is a retrospective review of a sampling and monitoring campaign conducted in 2015-2019 by the German state environmental protection agency. The data were grouped by soil pretreatment as: (i) sieved (5 mm) fresh samples, (ii) frozen at -18 °C and sieved (5 mm) after thawing, (iii) air-dried and ground to 2 mm, and (iv) dried at 40 °C and sieved (5 mm). The results showed that the median PFAS eluate concentrations in dried samples were greater than PFAS eluate concentrations from fresh and frozen samples. The differences were attributed to sorption of PFAS at the air-water interface in that PFAS in moist samples may be sequestered from leaching within aqueous films and air bubbles. As the MC is decreased by drying, PFAS sorbed to the air-water interface are deposited onto soil surfaces, becoming accessible for leaching. The authors considered drying a crucial sample preparation step; however, the motivation for this statement is unclear if the intent of the leaching test is to evaluate leaching that would occur in the field where samples are moist. It is also unclear why rewetting soil for leaching tests would not result in the same retention phenomena.

- Sörengård et al. (2019) used batch leaching tests (extraction in DIW at L/S=7 for 7 days with eluate centrifugation at 3,000-rpm for 15 minutes) to evaluate the release of PFAS from contaminated soils (n=20) with and without addition of colloidal activated carbon (AC) used as a PFAS sorbent. From these leaching test results, treatment efficiencies were calculated, and K_d values were evaluated in terms of fractional organic matter (f_{oc}) and fractional clay content (f_{clay}). The treatment effectiveness of colloidal AC depended on perfluorocarbon chain length with PFOA treatment efficiency at 81% compared to untreated soils. However, the treatment effect was less with shorter and longer chain lengths. The treatment efficiency increased with soil clay content and decreased organic carbon content.

- A simple batch extraction with initial pH adjustment was conducted on AFFF-impacted soils to determine leaching potential of PFAS (Bräunig et al., 2019; 2021). Relatively small 2 g subsamples of two different contaminated soils that had been passed through a 1.18-mm mesh prior to extraction with DIW at L/S of 20 mL/g for 24 hours. The leaching fluid pH was preadjusted to pH 7 using KOH to represent environmental conditions. After tumbling, the solution pH was measured, and the samples were centrifuged for 20 min at 1,455-G to separate solid and liquid phases. The relative standard deviation among the three test replicates was less than 10% for almost all analyzed PFAS. Nearly 100% of all short-chain PFAS in the soil leached into the liquid phase while 82% longer-chain PFAS (e.g., PFOS) in the soil leached.

5.1.1.2 Single-batch Extraction Tests

TCLP (Method 1311) and the Synthetic Precipitation Leaching Procedure (SPLP; Method 1312) are two single-batch extraction tests frequently used to predict leaching concentrations from contaminated media. These methods extract a solid material at an L/S of 20 L/g (wet mass) using either a buffered acetic acid solution (TCLP) or a dilute sulfuric/nitric acid solution (SPLP). The following are studies where Methods 1311 and 1312 have been used to evaluate leaching

from PFAS-contaminated media; however, there has been a lack of consistency in application of specific test methods.

- Barth et al., 2021 used a slightly modified SPLP (L/S 20; dilute 60/40 H_2SO_4/HNO_3 at an initial pH 4.2±0.5; 18±2 h) as the basis for evaluating the immobilization of PFAS from soils with and without sorbent/binders. Modifications to the standardized method included (i) smaller solid samples (25 g instead of 100 g) to save solid while still obtaining the volume of eluate required for analysis (ii) shaking at 80 rpm rather than end-over-end tumbling at 30 rpm, and (iii) phase separation by centrifugation rather than filtration to avoid sorption of PFAS to filter membranes.

- A modified SPLP test was conducted by Zhang et al. (2022) as part of an approach to investigate the treatment of PFAS-contaminated sewage sludge with and without sorbent amendments. In this case, approximately 6 g of sludge was first extracted in DIW using hand agitation and centrifugation (10,000 rpm for 20 min) in PP centrifuge tubes (water extractable PFAS). Subsequently, the sludge residue was extracted by SPLP (extractable PFAS). Modifications to SPLP included the use of a rather small mass of sewage sludge (6 g vs. 100 g), water washing prior to testing, and centrifugation (10,000 rpm for 20 min) instead of filtration.

- Wang et al. (2021) cited using TCLP as a batch leaching test to evaluate the impact of bentonite clay soil amendments on the mobility of PFAS from AFFF-impacted soils. However, the batch test used in the study was considerably different than TCLP with modifications including extraction at L/S 10 mL/g (rather than L/S 20 for TCLP) in DIW (rather than acetic acid for TCLP) for 8 days (rather than 18 h for TCLP). Eluates were centrifuged at 20,000 g for 10 min prior to PFAS analysis (rather than filtered through 0.7-um glass membranes for TCLP).

5.1.2 Column Leaching Tests

Column tests are traditionally conducted using saturated conditions where an eluent is pump upward through a bed of test material to minimize air-entrainment and preferential flow pathways. However, the PFAS literature indicates a widespread concern that PFAS sorb significantly to the air-water interface formed in unsaturated soils (Brusseau, 2018; 2019a; 2019b; Brusseau et al., 2022; Yan et al., 2020) and, thus, saturated column experiments do not capture the true rate of PFAS release in vadose zone soils because no air-water interface is formed under fully saturated conditions. of the accumulation at the air-water interface. Therefore, PFAS literature includes several unsaturated column approaches assumed to demonstrate the potential differences between column tests under saturated and unsaturated flow conditions.

5.1.2.1 Saturated Conditions

Column leaching tests were carried out on soil which had been pre-adsorbed with a solution containing PFOA (Borthakur, Olsen, et al., 2021). The soil was packed into PP columns (2.54 cm ID, 30.5 cm length) to simulate aquifer soil following the method in Borthakur, Cranmer, et al. (2021). A 6 mM NaCl solution, considered to represent synthetic groundwater, was pumped into the system from the top of the column at a rate of 6.1 cm/h over a 4-h interval with the eluate collected every 30 min. Analysis of eluate samples with and without colloids were showed that up to 36% of the leached PFOA was associated with soil colloids, indicating the importance of including PFAS adsorbed to the colloids for eluate collection and analysis. However, the SAR equation (Equation 4-1) indicates the introduction of a NaCl solution would

increase the SAR, promoting deflocculation of soil clay matter and enhancing the production of colloids. Therefore, the research of Borthakur, Olsen, et al. (2021) may overstate the importance of colloid formation for groundwater scenarios where the concentration of sodium is much less than 6 mM.

Method 1314 column leaching tests were performed on PFAS-contaminated soil (Kabiri and McLaughlin, 2021; Kabiri, et al., 2021). The soil was packed into polyethylene drying tube (1.5-cm ID x 15-cm length), with acid-washed glass wool set up at both ends. 1-mM $CaCl_2$ solution was introduced into the column from the bottom with the flow rate at about 0.027 mL/min for 7 to 21 days, and a fraction collector was used to collect fixed number of samples each day. The sample fractions were then pooled into 18 to 30 eluate samples to be analyzed for PFAS. The breakthrough curve and accumulative release showed that short-chain PFAS leached near completely after the first few pore volumes while long-chain PFAS were released gradually with greater cumulative elution pore volumes.

Column leaching tests were conducted on PFAS-contaminated soil under DIN 19528 and compared to long-term (>12 years) leaching data from a field site (Röhler et al., 2021). The soils were packed in columns with 25-cm height (5.5-cm ID x 30-cm length), with about 2 cm quartz sand layer at both ends. The water was introduced bottom-up, the flow rate being adjusted to ensure a contact time of at least 10 h for equilibration. Eluates were collected at L/S of 0.1, 0.5, 1, 2, 3, 4, 4.5, 5, 6, and 7 mL/g, and then were analyzed for PFOA and PFOS. The column leaching test results were consistent with long-term field leaching data under the advection dispersion model (ADM) in general. However, the column results that indicated rapid flush-out did not match the long tailing of PFOA and PFOS measured at the field site over the 12 years. Röhler et al. attributed the difference in the column results to ongoing transformation of PFAS precursors in the field over the years.

5.1.2.2 Unsaturated Conditions

Several column leaching studies have been conducted under unsaturated conditions (i.e., where air, liquid, and solid phase co-exist) to capture the impact of sorption at the air-water interface on leaching in the vadose zone.

- Høisæter et al. (2019) simulated AFFF infiltration into near-surface soils using intermittently wetted columns. Acrylic columns (14-cm ID x 100-cm height) were packed with uncontaminated soil from a Norwegian firefighting training facility and a dilute AFFF-water solution (1:100 dilution) was introduced to the top of the column through a reservoir at the top of the column. The dilute AFFF solution, containing multiple PFAS, was introduced either at a slow flow rate of 4.9 mm per day for 14 weeks or at a fast flow rate of 9.7 mm per day for 7 weeks. For both cases, a mass of water was weighed and added to a reservoir at the top of the column with a flow distribution network of 25 needles used to disperse the infiltration. A total of 477 mm of water was used. Eluates were collected from the bottom of the column which was open to the atmosphere. All eluates were analyzed for a range of PFAS with the results indicating increased retention of long-chain PFAS over short-chain PFAS. PFOS was not detected in the low flow rate columns which was attributed to accumulation at the air-water interface. At the higher infiltration rate, PFOS was mobilized in column leachates at concentrations up to 2,200 ng/L. These results indicate that when the air-water interface is maintained (i.e., when the infiltrating water does not saturate the cross section of the column) longer-chain PFAS may be retained in the soil column to a greater extent than for saturated conditions.

- Wiedemann et al. (2022) evaluated sorption behavior of PFAS and the impact of the transformation of two-tailed polyfluoroalkyl phosphate esters (diPAPs) on measured concentrations of PFAS in unsaturated columns. The fluoroalkyl chain length of transformation products for 6:2 and 8:2 diPAPs is limited by the length of the n:2 diPAP. Each diPAP can form 2 terminal endpoints: one from each of the two fluoroalkyl moieties on a sing n:2 diPAP. For example, a single 6:2 diPAP contains two two 6:2 alkyl tails [$CF_3(CF_2)_5(CH_2)_2$], so a single precursor can form 2 terminal PFHpA molecules each with a formula of $CF_3(CF_2)_5$-COOH. Samples of PFAS-contaminated topsoil along with uncontaminated soils spiked with 6:2 or 8:2 diPAP (<2 mm) were packed in polyethylene columns (4.6-cm ID x 25-cm bed length). A polyester net was installed at the bottom of each column as a filter but, otherwise, the columns were open to the atmosphere. Demineralized water was pipetted onto the top of the column three to five times a week (35 mL/week) for 105 weeks (2 years). Eluates were collected from the bottom of the column through a funnel and frozen at -18 °C prior to analysis for targeted PFAS and targeted diPAP precursors. To quantify the amount of PFAS precursors, total oxidizable precursor (TOP) assay was conducted on eluate samples. Column soils were extracted for total PFAS content before and after testing. The results showed that the PFAS-contaminated soils generated a wide range of shorter-chain PFCAs and PFSAs over the 2-year experiment while the diPAP spiked soils generated PFCAs up to PFHpA (6:2 diPAP) and PFOA (8:2 diPAP). However, n:2 diPAP were not detected in any percolate due to sorption within the column. These results demonstrate the importance of non-leachable PFAS precursors that transform into leachable intermediate and terminal PFAS products as a long-term source of PFAS contamination.

Another methodology to assess PFAS leaching under unsaturated conditions is field lysimeter studies. As an example, Schaefer et al. (2022a) used porous cup suction lysimeters to collect porewater from contaminated soils at an AFFF-manufacturing facility. PVC lysimeters (4.8-cm ID and various lengths) housed a 3.8-cm diameter ceramic porous cup with a 2-bar bubbling pressure. Three sets of samples from each of 11 lysimeters were collected over a 49-day period and analyzed for pH, EC, TOC, and a range of PFAS. The results of these lysimeters showed that PFOS (up to 10,000 ng/L) and PFHxS (up to 25,000 ng/L) as the PFAS with highest porewater concentrations. The lysimeter data were used to compare with batch testing K_d estimates with and without corrections for the retention of PFAS at the air-water interface.

5.1.3 Comparison of Methods

Most studies on leaching tests for PFAS were conducted under the assumption that the tests are designed to simulate release of PFAS from soil or sediment under field conditions. Therefore, many PFAS studies select a single leaching methodology to determine the release of PFAS from soils or sediments without consideration of the limitations or limited applicability of the test method. Few studies compare the results of multiple types of leaching tests as part of an attempt to develop a uniform testing approach.

- Bierbaum et al. (2023) compared the results of three leaching approaches: (i) a multiple batch extraction test, (ii) a saturated column test, and (iii) an unsaturated lysimeter test evaluate leaching of PFAS at difference scales, flows, and saturation conditions. These tests were used to determine the impact of AC and cement/bentonite retardation agents on PFAS release. Two subsamples of a PFAS-contaminated agricultural soil (compost/paper-fiber biosolids amendment) were treated with powdered AC or AC with clay minerals and aluminum hydroxide while a third subsample was treated with cement, bentonite, and powdered AC.

- Infinite Sink Batch Method. This multiple stage batch method was designed by Wege and Klaas (2005) as a simple approach to continuous batch leaching of PAHs in soils. The method uses a small amount of granular activated carbon (GAC) added to a demineralized water extraction of a soil sample at an L/S of 5 mL/g. The concept is that PFAS leaching into the demineralized water are immediately taken up by the GAC such that equilibrium does not take place. Although not specified in the test description, the GAC is likely added as a packet because it is said to be replaced periodically (e.g., after day 1, 3, 7, 14, and monthly thereafter), resulting in the multiple stages of the batch test. The recovered GAC is extracted by a 4-fold extraction in a solution of 0.1 wt% ammonia in methanol at 105 °C to extract sorbed PFAS and the mass recovered from the GAC is presented as a cumulative release curve with leaching time.

  The results from of the infinite sink batch tests were presented as a cumulative mass release curve, like a graph generated from a column test. Duplicate tests showed consistent results between replicate tests for each study material. For some PFAS (PFOA, PFDA, PFOS, and N-EtFOSAA), the total contents were not extracted by the leaching test even after 100 days of leaching. The authors attributed the lack of complete recovery with the strong sorption interactions of long-chain PFAS with the soil. However, for PFAS with C <8, insignificant rates of leaching were observed in the last batch extractions, indicating that the leaching process was complete. For some PFCAs, the authors considered that linger leaching rates was ab indication of transformation of PFAS precursors to PFCAs, especially when cumulative mass exceeded the extractable total content.

- Column Method. This method generally follows the approach of DIN 19528 (DIN, 2009). Glass columns (9-cm ID x 55-cm length) were packed with soil and a 7-8 cm layer of quartz sand was added to both ends. Packing was conducted under water-saturated conditions. Demineralized water was pumped into the column from the bottom using a peristaltic pump with polyurethane tubes and the eluate was collected for PFAS analysis at different intervals (in the beginning, 2 to 3 days, then incrementally increased to 2 weeks). The general residence time within the column was 11 hours; however, the flow rate was varied in some columns to achieve residence times of 5 hours and 40 hours so that the role of flow rate may be evaluated. The collection of column eluates was extended to an ΣL/S greater than 40 mL/g to evaluate long-term leaching.

  For three of the four study materials, the column tests showed good replication between four replicates conducted at the various residence times, indicating that flow rate does not affect the leaching behavior of PFAS significantly. Shorter-chain PFAS were flushed out by approximately ΣL/S = 5 mL/g, while long-chain PFAS reached a “quasi-steady state”, where PFAS slowly leached out as ΣL/S increased. However, the authors also suspected the influence of biodegradation after L/S at 20 mL/g.

- Laboratory Lysimeters. Glass lysimeters (60-cm ID) were installed on a perforated stainless-steel sheet to allow for drainage. Demineralized water was added to the top of each lysimeter once a day using a drip hose. The discharges varied from 410-450 mL/day for the treated soils to 850 L/day for the untreated soil depending on the hydraulic permeability in each lysimeter. These experiments were operated for 30 months (2.5 years).

The results of the lysimeter experiments showed high temporal resolution of the leaching process was gained due to the relatively slow water infiltration and the free drainage. Ongoing leaching at low concentrations (<1 µg/L) was attributed to biotransformation of precursors.

The authors noted that the infinite sink batch tests provided higher desorption mass (up to 3x higher) than the column experiment, which was associated with accelerated desorption due to mixing in the batch test and irreversible sorption and non-extractable residues in the column. However, the potential for enhanced release in the infinite sink where direct contact of the GAC with the solid material occurs was not discussed. Leaching under the variably saturated lysimeter was retarded relative to the column test. The authors noted that although the infinite sink experiments led to greater desorption than columns, they require less time and analytical effort. Therefore, this approach may be more practical for screening efforts such as comparing the effect of multiple amendments.

- Rayner et al. (2022) conducted a series of batch leaching tests on intact and dried/sieved soil samples to highlight the differences in test results. Intact soil cores were immersed as cores (420-g average mass, 40-mm ID x 150-200 mm length) in DIW for up to 6 weeks and eluates were directly subsampled from the container for PFAS analysis. This method was considered representative of in-situ soil leaching in the field. Batch testing was chosen to explore which experimental conditions (i.e., L/S, agitation, eluate pH) yield results that are representative of field leaching. Batch tests included the following test conditions:
    - Single Batch #1 (L/S = 3 mL/g; DIW for 8 h; no agitation; centrifugation at 10,000 rpm for 10 min).
    - Single Batch #2 (L/S = 3 mL/g; DIW for 8 h; tumbled at 30 rpm; centrifugation at 10,000 rpm for 10 min).
    - Australian Standard Leaching Procedure (ASLP) (L/S = 20 mL/g; dilute acetic acid for 18 h; tumbled at 30 rpm).
    - Method 1313 (pH 2 to 12, L/S = 10 mL/g; DIW for 2 h; tumbled at 30 rpm).

  The percentage of PFAS release was used to compare results across all experimental conditions. The greatest release was provided by ASLP (90%) and Method 1313 at pH of 10 (88%) while the release decreased with Method 1313 pH (65% release at pH 5), L/S = 3 mL/g with tumbling (30%) or L/S = 3 mL/g without tumbling (30%). The percentage release was lowest during leaching of intact soil cores (27%) which is reasonable for release under diffusion controlled leaching conditions. The authors concluded that the leaching test at L/S = 3 mL/g without tumbling provided leaching concentrations closest to soil core leaching because it best simulated the leaching from intact cores. Thus, may indicate the in-situ soil leaching on the sites, while ASLP and 1313 may be more beneficial to evaluate leaching for landfill and material reuse.

5.1.4 Comments on Previous PFAS Leaching Research

In summary, no uniform approach for leaching of PFAS from soils and other environmental media has been developed and the published literature provides conflicting observations in some cases. Most research is focused on describing the sorption or release of a broader

subclass of PFAS (e.g., short-chain PFCAs or long-term PFAS) from Soils or on trying to simulate field observations from laboratory leaching tests. ***The literature implies that the results of a leaching test are considered to provide a measure of leaching that directly applicable to the field scenario.*** Therefore, some research concluded that the LEAF tests, or analogous European tests, are not appropriate for PFAS because the resultant concentration doesn't match the concentration measured in the field. ***However, the intent of the LEAF methods is not to simulate field concentrations but to measure intrinsic leaching characteristics that can be used to develop estimates of leaching under field scenarios***. In addition, the interpretation of Method 1313 as individual extractions negates the intended use of the test as providing a trend of how LSP changes with eluate pH.

Many authors have utilized minor or major modifications to standardized tests to adopt the test for PFAS; however, in the extreme, these modifications result in leaching tests that are far removed from the standardized test method (e.g., the "TCLP" method used by Wang et al. (2021) can no longer be considered TCLP). In addition, the variations in modified methods and evaluation approaches make comparisons of leaching results difficult as it is unclear if differences in test results, often attributed to analytical uncertainties or variations in the representativeness of soils samples and soil properties, are associated with different leach testing approaches and analytical method limitations.

5.2 Summary of Experiments Supporting Method Development for PFAS

As part of the process of developing the LEAF methods for PFAS, a series of experiments were implemented using PFAS-impacted soils to (i) evaluate the potential for sorption to materials of construction (**Appendix C-2.7**, **Appendix C-4.3**), (ii) identify eluate process approaches for maximize the recovery of PFAS (**Appendix C-4.4**, **Appendix C-4.5**), and (iii) verify contact times specified in U.S. EPA batch extraction methods are applicable for PFAS (**Appendix C-5.1**). The following is a summary of these experiments, including important conclusions and recommendations.

5.2.1 Selection of Materials of Construction for PFAS

5.2.1.1 Acrylic, Tygon®, Stainless Steel, Quartz Sand and HDPE (Appendix C-2.7)

During methods development for PFAS, sorption experiments were carried out in HDPE bottles containing known PFAS standard mixtures at 50, 100, and 150 ng/L in contact with (i) acrylic coupons (column material), (ii) Tygon tubing (eluate transfer lines), (iii) 316L stainless-steel coupons (alternative column and transfer line material), and (iv) quartz sand (flow regulation layers within a packed column). HDPE bottles with no test material were used as positive controls to evaluate PFAS sorption to the bottles. All experiments were carried out in triplicate. The percentage recovery (%R) was calculated as the mean mass (n=3) recovered in the sorption tests divided by the mass in the initial solution. For presentation, the results were grouped into PFCAs, PFSAs, sulfonamides, and fluorotelomers with %R compared to an acceptance interval of 70 to 130% recovery. Sorption of a wide range PFAS onto acrylic, 316L stainless steel, and Tygon tubing was considered low.

The results of the positive controls showed limited to negligible sorption of PFAS onto HDPE. For acrylic coupons, Tygon tubing, and stainless-steel coupons, the %R of fluorotelomers and PFCAs/PFSAs (C ≤8) were within the acceptance interval; however, the %R of longer PFCAs and PFSA homologues and sulfonamides were below 70% indicating significant losses. Recoveries of most PFAS suggest sorption onto quartz sand when the mass recovered per gram of sand was compared between 50, 100, and 150 ng/L PFAS solutions. The sorption onto

quartz sand could be explained by one of three behaviors: (i) limited sorption that reaches a plateau at higher PFAS concentrations (PFOS, PFNA, PFNS, PFDoA, and N-EtFOSAA), (ii) sorption that did not plateau within the 50-150 µg/L concentration range (PFDA, PFDS, PFUdA, PFOSA, N-MeFOSAA, and 8:2 FTS) and, (iii) negligible sorption values within the uncertainty of the experiment (all remaining PFAS). Estimations of the impact of sorption to the Ottawa sand used as a coarse filter within the column packing indicated that loss of mass from the column to sorption occurs within the collected column eluate where concentrations are highest. This infers that sorption to a limited amount of Ottawa sand coarse filtration is should not impact column test results.

5.2.1.2 PP Centrifuge Bottles (Appendix C-4.3)

Lath et al. (2019) indicated that PFAS have a significant potential to sorb to filtration apparatus and membranes. Therefore, batch extractions (i.e., Draft Method 1313A and Draft Method 1316A) were modified to include centrifugation for the separation of solid and liquid phases whenever PFAS are to be analyzed. The method development experiments include a study to assess the sorption of PFAS onto PP centrifuge bottles in support of the use of centrifugation to separate solid and liquid phases and to remove colloid from solution on eluates with a turbidity ≥1 NTU.

Sorption experiments were conducted in triplicate by subsampling a 100 ng/L stock PFAS solution from a 250-mL HDPE bottle (representing an extraction vessel) into either three 50-mL PP tubes or three 250-mL PP bottles for centrifugation. The stock solution was pH-adjusted using dilute HCl or KOH and experiments at five pH values (pH 2, 5, 7, 9, and 13) were carried out in parallel. After subsampling, batch testing eluates were centrifuged at an RCF of 9,700-G (50-mL PP tubes) or 16,800-G (250-mL PP bottles) for 10 minutes prior to preparation of PFAS analytical samples. The results were presented as %R (i.e., the mass recovered in each centrifuge bottle or tube relative to the mass in the initial stock solution). Results indicated that %R for PFAS (C ≤8) were generally 70-130% whereas losses of some PFAS (C >8) may be significant with %R less than 70%. The cause of the lower %R of longer-chain PFAS was unclear. Eluate pH, the RCF used during centrifugation, and size of the centrifuge vessel did not impact the %R.

5.2.1.3 Summary of Materials of Construction Experiments

Overall, these materials of construction experiments indicated that PFAS sorption onto most non-fluorinated polymers, such as HDPE and PP (**Appendix C-4.3**) as well as acrylic and 316L stainless steel (**Appendix C-2.7**), and Type III soda-lime glass (**Appendix C-4.4**) are negligible for PFCAs and PFSAs (C ≤9) and the 4:2, 6:2 and 8:2 fluorotelomer sulfonates.

5.2.2 Eluate Processing to Maximize PFAS Recovery

Based on batch extraction testing, some sorption of longer-chain PFAS onto Type III (soda-lime) glass and HDPE containers was expected; however, the sorbed mass was considered negligible due to the limited contact times and surface areas for 250-mL containers. However, the percolation column test uses larger volume bottles to collect eluates over longer collection times. Therefore, losses of PFAS onto Draft Method 1314A eluate collection bottles (PP or Type III glass and sizes up to 1,250-mL) have the potential to bias the column leaching testing results. Experiments to evaluate how sorbed PFAS may be recovered in column test eluates were carried out.

5.2.2.1 Basic Methanol Rinse Eluate Collection Bottles (Appendix C4.4)

The recovery of PFAS from PP and Type III glass eluate collection bottles, typical of Draft Method 1314A, was evaluated to understand the impact of rinsing the eluate bottle with basic (alkaline) methanol as an approach to capture sorbed PFAS. Eluate collection bottles (250-mL PP and glass, 1000-mL PP, and 1250-mL glass bottles) were filled with stock PFAS solution at concentration levels of 50, 100, or 150 ng/L and stored at room temperature for 48 h. Three bottles at each concentration, bottle type, and bottle size were used to provide triplicate results. After storage, two 25-mL analytical samples were decanted into sample analysis tubes for (i) direct eluate analysis of aqueous eluate or (ii) combined analysis of an eluate + rinsate sample. The remainder of the eluate was discarded prior to rinsing the bottle an aliquot of basic methanol (1% ammonia hydroxide in methanol) equivalent to 2% of the bottle volume (i.e., 5-mL basic methanol for a 250-mL bottle). A fraction of the methanol ***rinsate*** was added to the 25-mL aqueous eluate tube and the remaining rinsate was saved for direct rinsate analysis.

> ***Rinsate*** is the solution that results from rinsing, typically comprised of the solvent used for rinsing (e.g., MeCl, HCl in DIW) plus trace COPCs.

The comparison of the mass in the original stock solution versus the mass recovered in the aqueous eluate and the mass recovered in the eluate + rinsate sample indicated that, in general, recovery of the original mass was good (%R >80%) with and without methanol rinsate for both glass and PP bottles. Value of %R for eluate + rinsate samples were closer to 100% than samples of eluate alone, especially for longer-chain PFAS which tend to adsorb the container surfaces. The improvement in %R in the eluate + rinsate samples indicates that rinsing eluate collection bottles with the basic methanol captures PFAS that would otherwise sorb to the bottle surface. However, inclusion of the methanol rinsate into the aqueous eluate subsample lowered the measured concentration of PFAS after analysis for some of the more soluble PFAS (e.g., PFBA, PFBS, PFPeA, and FBSA), perhaps through dilution.

5.2.2.2 Sonication of Eluate Collection Bottles (Appendix C-4.5)

Recovery of sorbed PFAS from large PP bottles was evaluated by comparing the measured PFAS concentrations from a stock solution stored in PP bottles of various sizes with sonication as an eluate processing step prior to subsampling for analysis. PP bottles typical of the material and size used for column eluate collection (i.e., 250-mL, 500-mL, 2 L, and 3L) were filled with a stock PFAS solution at two concentrations (20 and 40 ng/L). The bottles were stored at 4 °C overnight prior to subsampling for PFAS analysis. The bottles were sonicated at 40 °C for 30 minutes and allowed to cool to room temperature before sampling. Values of %R in eluate concentrations relative to the target stock solution concentration were generally between 70% and 100% of the target concentration. At the lower stock concentration of 20 ng/L, the recovery of PFAS with C ≥10 was generally around 70% and sometimes lower (e.g., PFDoA, PFTeDA, and N-MeFOSAA), especially in the larger 2-L and 3-L bottles. However, the decrease was thought to be caused by the level of the eluate in the bottle being higher than the sonication bath levels. Changing the orientation of the bottle in the sonication bath moved the eluate level to just below the sonication bath level; however, the recoveries did not improve. In the horizontal orientation, the seal on the eluate collection bottles were suspect such that sonication bath water may have leaked into the eluate.

The focus of these experiments was on representative subsampling and recovery of a specific set of PFAS target analytes, and there's some uncertainty as to whether other more labile PFAS precursors could be subject to loss and/or transformation during sonication (Woudneh et al., 2019). Overall, this experiment confirmed that sonication of eluate samples prior to subsampling

for PFAS analysis results in improved recovery of eluate concentrations.

5.2.2.3 Summary of Eluate Processing Experiments

The test results showed that the recovery of PFAS from eluate collection bottles using methanol rinsing and sonication were similar. Basic methanol rinsing increases recovery of PFAS sorbed to glass bottles over PP bottles. Also, the analytical costs associated with an additional methanol rinsate with each eluate sample may be cost-prohibitive. For sonication, the results showed high (≥80%) recovery for almost all PFAS, indicating that sonication can serve as a routine procedure for subsampling. However, an important parameter is the location of the air-water interface in the eluate collection bottle relative to the level of the sonication bath and caution should be taken that eluate bottles are well-sealed prior to sonication in a horizontal orientation.

5.2.3 Contact Time for Batch Extraction of Materials Containing PFAS (Appendix C-5.1)

In part because of the wide range of PFAS chemistries and competitive effects, the extraction of PFAS has been described as a kinetically controlled process (Schaefer et al., 2021). Therefore, an experiment was carried out to confirm the recommended contact time for batch extraction of soils containing PFAS. The experiment consisted of parallel batch extractions of four materials (i.e., four PFAS-impacted soils) in 1-mM $CaCl_2$ solution at L/S of 10 mL/g with contact times of 2 days (specified in Method 1313 and Method 1316), as well as 4-day and 10-day contact times. The mean eluate concentrations (n=3) and 95% confidence intervals were plotted to evaluate the impact of contact time on test results. In general, contact time was not a significant parameter for most cases. By including the 95% confidence interval in the evaluation, it was determined that even when mean eluate concentrations appeared to increase with contact time, overlapping confidence intervals indicated that there was no difference in the mean values. As a result, the contact times, recommended in the SW-846 methods and adopted for SVOCs are also appropriate for PFAS.

6 Demonstration of Draft Methods for PFAS

In this section, each of the draft methods adapted for use on material containing PFAS were demonstrated in triplicate using two test materials. This intent of the demonstration is to evaluate the usability of the test method, to illustrate the repeatability of the experiments on well-homogenized materials, and to provide typical leaching test results for each draft method. In **Section 4**, the draft methods were compared to the U.S. EPA SW-846 procedures relative to the leaching of inorganic COPC; therefore, that exercise is not repeated here.

6.1 Materials Used in Demonstrations

A significant source of PFAS in the environment comes from firefighting training and activities, especially at military airfields where AFFF usage was common and surface runoff moves contaminants into surrounding soils (Borthakur, Wang, et al., 2021; Dauchy et al., 2019). For the demonstration of Draft Method 1313A, AFFF-impacted soils from four different military airfields were collected, air-dried, and homogenized prior to testing. These four soils are referred to as Site 1 Soil through Site 4 Soil for the demonstration. Homogenization consisted of four cycles of sieving through a 2-mm mesh followed by cone-and-quartering, all conducted within a large PP glove bag. The characteristics of the four demonstration soils are presented in **Table 6-1**.

Table 6-1. Soil Characteristics of AFFF-impacted Materials used in Draft Method Demonstrations

Material	Soil pH	% Sand	% Silt	% Clay	BET SA (m^2/g)	CEC (meq/100g)	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Foc (%)
Site 1 Soil	5.6	87	5	8	1.3	2.4	290	13	32	0.81
Site 2 Soil	5.6	73	9	18	10	3.9	500	21	50	0.69
Site 3 Soil	5.2	77	11	12	3.3	5.2	560	42	48	1.2
Site 4 Soil	7.8	69	5	26	27	28	5,400	140	84	1.4

Note: Site 1 Soil is classified as a sand, Site 2 Soil as a sandy loam, Site 3 Soil as a loamy sand, and Site 4 Soil as a sandy clay loam.

SA = specific surface area
CEC = cation exchange capacity
meq = milli-equivalents
BET SA = Brunauer-Emmett-Teller Surface Area
Foc = Fraction of organic carbon

The total PFAS concentrations in each soil were determined by triplicate extraction of a 1-g soil subsample in basic methanol (**Table 6-2**). While total content is not indicative of leachability, these values provide a context to the eluate concentrations shown for the demonstration of draft methods.

Table 6-2. Total Content of PFAS in AFFF-impacted Soils used in Draft Method Demonstrations

	Total Content by Basic Methanol Extraction			
PFAS	Site 1 Soil (µg/kg)	Site 2 Soil (µg/kg)	Site 3 Soil (µg/kg)	Site 4 Soil (µg/kg)
PFBA	0.58	1.9	0.33	3.2
PFPeA	3.2	8.2	0.91	6.4
PFHxA	11	13	0.57	5.8
PFHpA	4.5	8.0	0.26	2.9
PFOA	35	23	0.87	7.0
PFNA	2.1	33	0.38	4.2
PFDA	0.38	6.2	0.24	4.1
PFUdA	0.32	1.4	0.32	5.8
PFDoA	0.27	1.1	0.12	1.7
PFTrDA	0.10	0.064	0.12	0.97
PFTeDA	0.11	0.13	ND	0.07
PFBS	25	5.2	0.10	2.1
PFPeS	53	6.2	0.14	2.4
PFHxS	62	200	2.9	37
PFHpS	13	120	0.15	3.4
PFOS	480	2,900	37	2,300
PFNS	88	15	0.43	29
PFDS	8.8	14	ND	63
4:2 FTS	0.69	1.1	ND	ND
6:2 FTS	55	200	0.26	12
8:2 FTS	22	230	0.25	23
PFOSA	14	290	0.82	12
N-EtFOSAA	ND	1.4	ND	ND
N-MeFOSAA	ND	0.56	ND	ND

Notes: ND = not detected

6.2 Eluate Analytical Methods

As with the demonstration of draft methods for SVOCs (**Section 4**), the pH and EC of all test eluates were measured directly after separation of solid and liquid phases (see **Section 4.2.1**). In addition, chemical analysis included determination of DOC and DIC using Method 9060A (see **Section 4.2.5**).

6.2.1 Targeted PFAS Analysis by LC-MS/MS

Analytical samples were typically shipped to TTU for analysis under chain-of-custody (COC) in 50-mL SCP Science Digitube® (#NC9739574, Fisher, Waltham, MA) with each tube containing at least 10-mL of solution. Preparation of aqueous analytical samples included sonication at 40 °C for 30 minutes to desorb PFAS from bottle surfaces, transfer of 1,260 µL of aqueous solution into a 2-mL autosampler vial with 537 µL of HPLC-grade MeOH and 3 µL of a solution containing 0.36 ng of each targeted PFAS as an internal standard.

The concentration of a targeted list of PFAS (see **Table 2-1**) in aqueous solutions was analyzed by LC-MS/MS. Chromatography to separate COPCs peaks was performed on a dual pump Shimadzu (manufactured for SCIEX) HPLC using aqueous ammonium acetate (20 mM) and

MeOH as a liquid phase at 60 µL/min. Analytical sample aliquots (0.5-1 mL) were injected from an autosampler onto a 3-mm ID x 100-mm long Gemini C18 column (Phenomenex, Torrance, CA). The profile of the MeOH fraction in the liquid phase was ramped from 5% to 65% for 1.5 mins, held at 65% for 6.5 mins, ramped up to 99% over 1.5 min, and held at 99% for 4.4 min. The profile was then ramped down to 5% over 0.5 min. The output of the HPLC was pumped into a SCIEX X500R quadrupole time-of-flight (QToF) (AB SCIEX, Framingham, MA) operating in electrospray ionization negative (ESI-), high resolution multiple reaction monitoring (MRMHR) mode. The SCIEX X500R QToF was calibrated using the instrument's calibrant delivery system which introduces a calibration solution directly into the source. During calibration, a mass was considered to pass if each precursor and fragment mass errors were within 5 ppm with a minimum peak resolution of 10,000.

Analytical datasets included method blanks, laboratory control samples (LCSs), and matrix duplicate samples as well as internal standards for each analytical sample. Method blanks were expected to have analytes <1/2 the LOQ while LCSs were expected to return concentrations within 30% of the anticipated concentration. Matrix duplicate samples were expected to have replicate percent difference (RPD) of ≤30% between samples. Internal standards were considered acceptable if the recovery was 50-150% of the midpoint of the calibration curve.

6.3 Data Analysis and Reporting

All laboratory test data (e.g., masses used, testing conditions) were recorded in Microsoft Excel® templates designed for each leaching test. These templates which serve as an import tool for LeachXS™ (VU, 2022) were modified to include all targeted PFAS compounds with the abbreviations included in the PFAS list in **Table 2-1**. The LeachXS software was used to create and output the figures in the demonstration of each leaching test. In these figures, COPC concentrations measured at less than the MDL are reported in tables as <MDL and graphed at one-half the MDL value to indicate that the measurement was conducted. Analytical results that measured less than the LLOQ but greater than the MDL are reported as "estimated values." All data below the LLOQ are displayed as white symbols with color-coded outlines to indicate that these data are below analytical quantitation limits.

6.4 Demonstration of Draft Method 1313A for PFAS

The development of Draft Method 1313A, including recommended materials of construction, test procedure, and eluate handling is described in **Section 4.4**. For PFAS, the following modifications to Method 1313 were made:

- All sources of leaching vessels and apparatus were checked for PFAS contamination prior to use by exposing samples of the materials to 1-mM $CaCl_2$ overnight and collecting aliquots of the eluate for PFAS analysis. On a regular basis (i.e., with every set of test replicates), method blanks were monitored to ensure that apparatus materials of construction did not leach PFAS.

- The leaching vessels from Method 1313 (i.e., 250-mL HDPE bottles) were retained as they did not show significant leaching or sorption of PFAS (**Appendix C-2.7**). Alternatively, the amber borosilicate glass VOA vials with PCTFE lid liners (i.e., the recommended apparatus for leaching vessels in Draft Method 1313A) may be used to test materials containing PFAS; however, matrix blanks should be examined prior to conducting the test to assess the potential for PFAS release from PCTFE lid liners.

- The primary eluant was changed from DIW to 1-mM $CaCl_2$ to minimize the formation of colloidal matter from soil samples due to charge imbalances.[5]
- The acid used to decrease the pH of eluates to less than the natural pH was changed to non-oxidizing HCl rather than HNO_3.
- Solid-eluate separation by initial settling followed by centrifugation was used to replace the vacuum filtration steps to minimize loss of PFAS to filtration membranes.
- An additional, larger particle size, along with an associated longer contact time, was added to the test specification to minimize the extent of pre-testing material handling.

6.4.1 Extraction Procedure

The overall test procedure for Draft Method 1313A is presented in **Figure 6-1**. For each of the nine target pH values of Draft Method 1313A, three parallel extractions of 15 g-dry of test material with 150-mL of 1-mM $CaCl_2$ were carried out in 250-mL HDPE bottles (Step 1). The acid or base addition to each bottle was adjusted to obtain the target pH in the final eluate, within the specified pH tolerance, according to a pre-test titration curve of the material. In addition, triplicate natural pH extractions were conducted without addition of acid or base. In total, 30 extractions (nine target pH values + natural pH, all in triplicate) plus three QA/QC blanks (i.e., acid, neutral, and base) were created and tumbled end-over-end at 28±2 rpm for 48 hours.

6.4.2 Eluate Collection and Processing

After tumbling, a 40 mL aliquot of each solid-liquid slurry was decanted into 200 mL PP centrifuge bottles. These bottles were centrifuged at 9,700-G for 10 minutes to separate the solid phase from the liquid eluate (Step 2). From the extraction bottle, a 5-mL aliquot was collected for measurement of pH and EC (Step 3). An additional 40 mL aliquot of the solid-liquid slurry was filtered through 0.45-um filtration membranes and split into a 10-mL analytical sample for ICP analysis of inorganic COPCs and a 25-mL analytical sample for DOC analysis (Step 4). A 25-mL aliquot of the clarified eluate after centrifugation was decanted into a clean 50-mL PP SCP Science Digitube® for PFAS analysis (Steps 5 & 6). Samples were overnight shipped under COC to TTU for analysis on ice. All analysis samples at TTU were sonicated prior to subsampling for analysis.

[5] While addition of Ca^{+2} ions in solution may reduce the deflocculation of clay minerals and dissolution of DOC, divalent cations can bridge negative PFAS ions to negative mineral surfaces (Cai et al., 2022). Therefore, the sorption of PFAS to soils at pH values above the pKa of the mineral surface may be enhanced when leaching is conducted in 1-mM $CaCl_2$ solution.

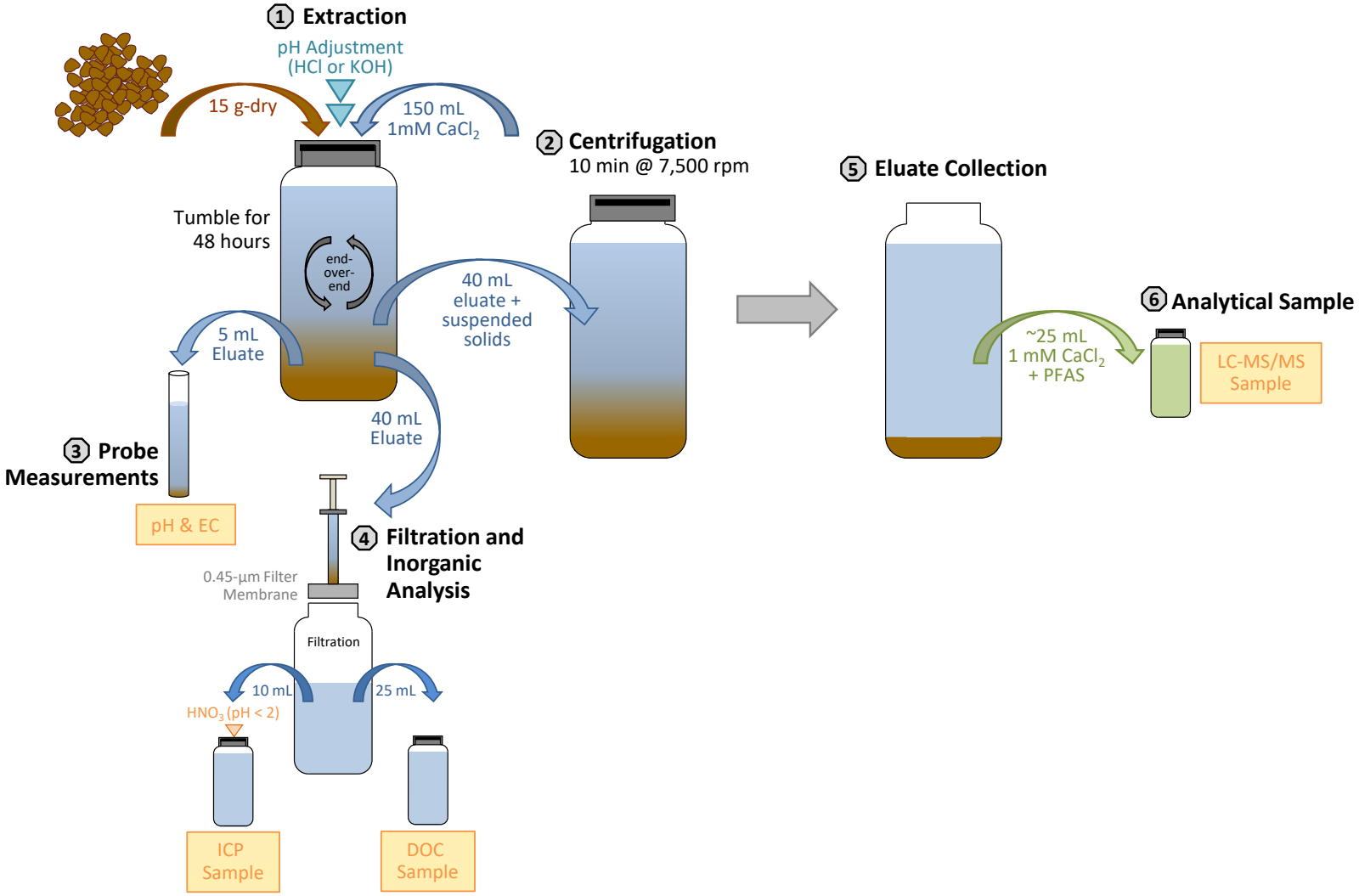

Figure 6-1. Example procedure for demonstration of Draft Method 1313A for PFAS. The full demonstration scope was carried out in triplicate for nine target pH values plus the natural pH.

6.4.3 Demonstration Results

The results of the demonstration of Draft Method 1313A for four AFFF-impacted soils are presented in **Figure 6-2** through **Figure 6-5**. These results include the titration curve of each material and the eluate DOC (**Figure 6-2**) due to the influence of these measurements on the solubility of COPCs. In addition, demonstration of Draft Method 1313A includes the results of PFAS analysis in triplicate for PFCAs (**Figure 6-3**), PFSAs (**Figure 6-4**), and fluorotelomers and other PFAS (**Figure 6-5**).

6.4.3.1 pH and Dissolved Organic Carbon

The titration curve of a material shows the amount of acid or base required to change the eluate pH at an L/S of 10 mL/g-dry from the natural pH (i.e., eluate pH when no acid or base is added to the extraction) to another pH value. In **Figure 6-2** (left), the titration curves for the four AFFF-impacted soils show that the Site 4 Soil has a significantly greater acid/bass neutralization capacity than the other three soils. The same material composition that yields a higher buffering capacity in Site 4 Soil also results in a greater natural pH (8.8) relative to the natural pH range of 5.1-5.6 for the other three soils.

The pH-dependent concentration of DOC in **Figure 6-2** (right) shows similar behavior for the four soils within a band of an order-of-magnitude. DOC concentrations display a minimum around pH 5, which corresponds to the approximate natural pH for three of the four soils, with an increasing trend to a maximum as pH increases. This is typical for DOC as high pH dissolves some organic matter (see **Figure 2-1**). For those PFAS that strongly sorb to organic matter, it is likely that pH-dependent concentrations would increase along with the increasing DOC measurements.

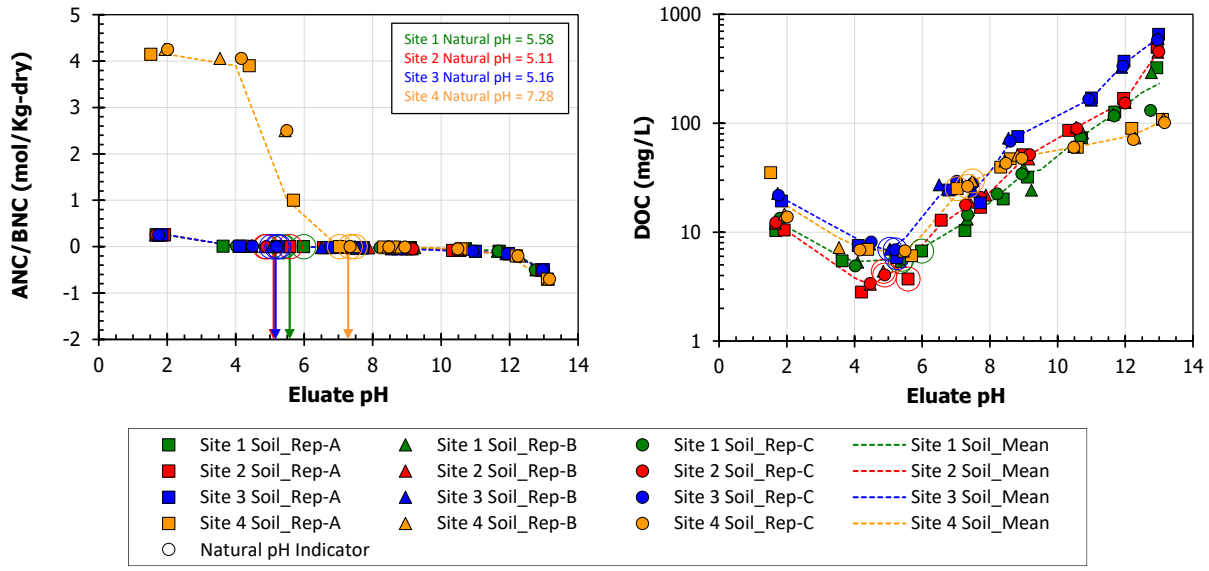

Figure 6-2. Demonstration of Draft Method 1313A showing a material specific titration curve (left) and pH-dependent leaching of dissolved organic carbon (DOC) from four AFFF-impacted soils. All data shown as triplicates with a calculated mean line.

6.4.3.2 pH-dependent PFAS Concentrations

The pH-dependent concentrations of individual targeted PFAS are shown in **Figure 6-3** for PFCAs, **Figure 6-4** for PFSAs, and **Figure 6-5** for fluorotelomers and other PFAS. In these figures, the results of Draft Method 1313A are presented in triplicate. The variability in these replicate data indicates the potential variance in measured pH (horizontal uncertainty) and the combined potential test method and analytical variance (vertical uncertainty). Also shown in these figures are representative mean lines for each triplicate calculated by LeachXS based on replicate leaching data linearly interpolated to the Method 1313 target pH points.[6] Data shown as white solid symbols with color-coded outlines represent data less than the LLOQ. These data are considered estimated data between the LLOQ and the MDL while data less than the MDL are plotted at ½ MDL to indicated data that were analyzed, but not detected.

In general, the triplicate test results show a high degree of repeatability with the calculated mean line in line with the replicate data. PFAS with shorter fluoroalkyl chains PFAS (C ≤8) appear to have better repeatability than longer chain PFAS (C >8). For example, the data in **Figure 6-3** show that the replicate groupings for PFBA, PFPeA, PFHpA, and PFOA, in general, are better than the replicate groupings for PFNA and PFDoA. In addition, the eluate concentrations of shorter chain PFAS (e.g., PFBA in **Figure 6-3** and PFBS in **Figure 6-4**) do not show a strong pH-dependence whereas longer chain PFAS concentration (e.g., PFDS in **Figure 6-4** or 4:4 FTS and PFOSA in **Figure 6-5**) increase in correlation with increased in DOC (**Figure 6-2**).

[6] COPC concentrations may be a strong function of pH so that minor differences in measured eluate pH within the target value tolerance of ±0.5 pH units can create significant variance in the mean value. Therefore, LeachXS interpolates replicate data to the Method 1313 target pH points prior to calculation of the replicate mean.

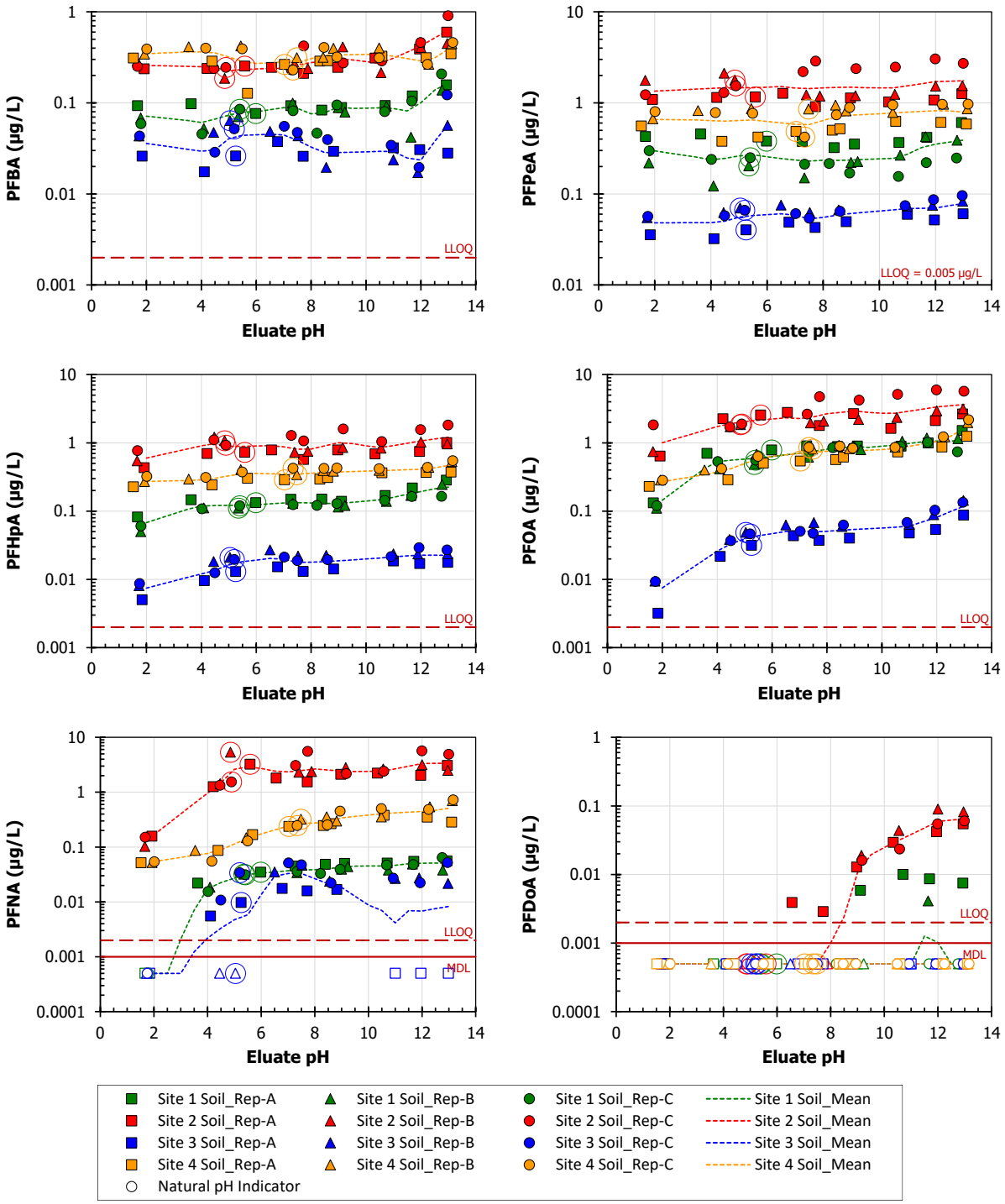

Figure 6-3. Demonstration of Draft Method 1313A showing pH-dependent leaching of perfluoroalkyl carboxylic acids (PFCAs) from four AFFF-impacted soils showing triplicate test results with a mean line. All data are shown as test method triplicates with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

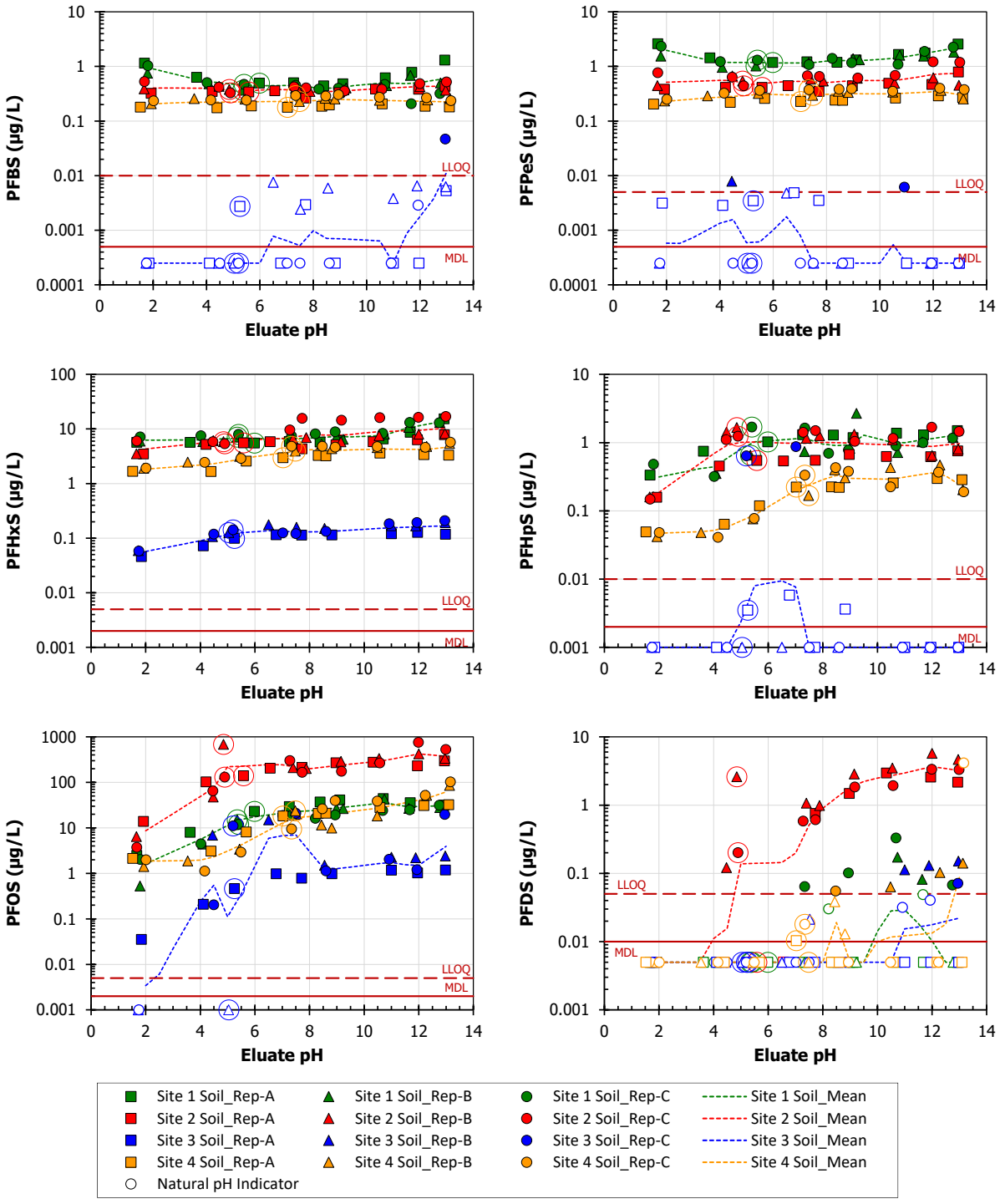

Figure 6-4. Demonstration of Draft Method 1313A showing pH-dependent leaching of perfluoroalkyl sulfonic acids (PFSAs) from four AFFF-impacted soils showing triplicate test results with a mean line. All data are shown as test method triplicates with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

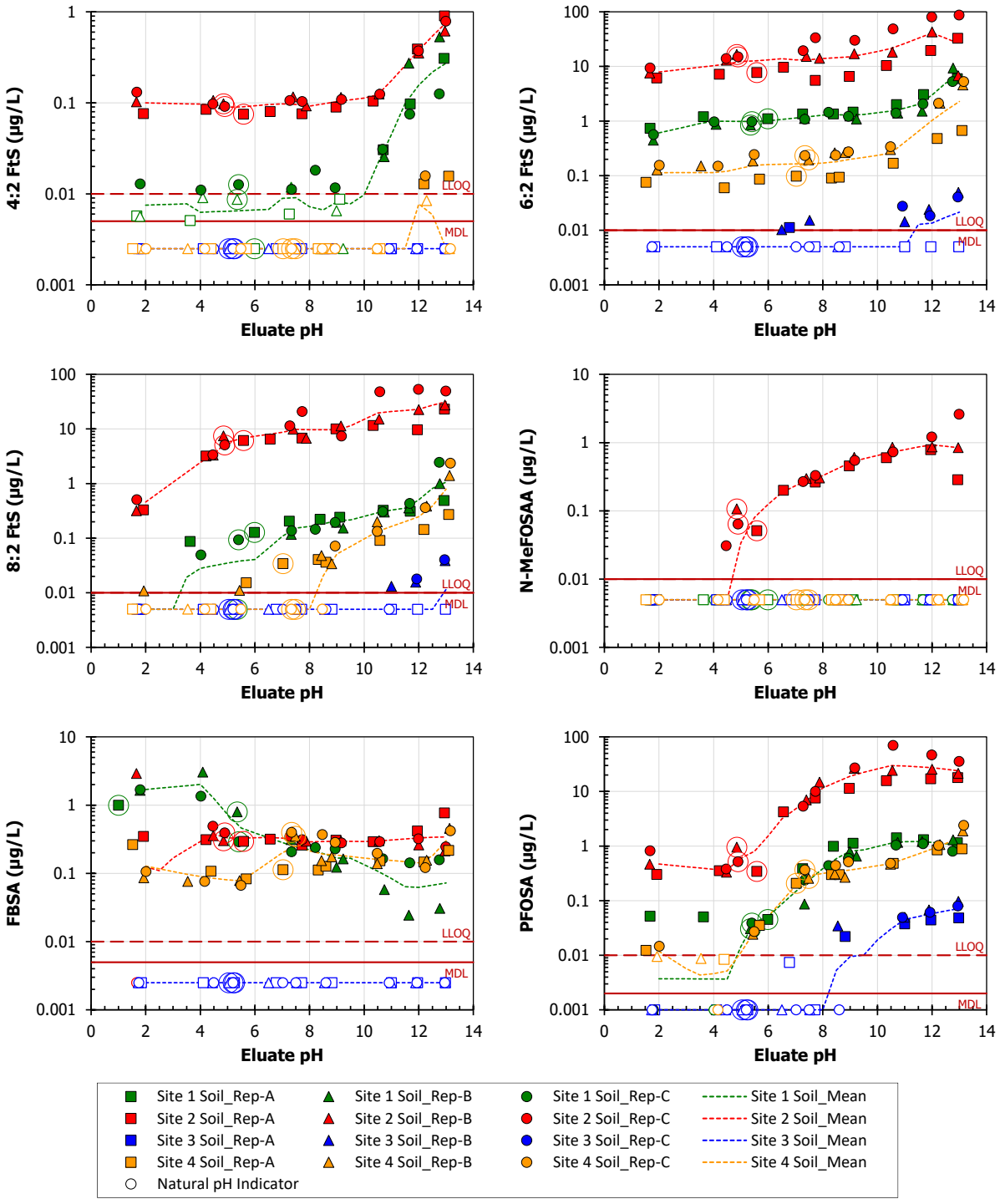

Figure 6-5. Demonstration of Draft Method 1313A showing pH-dependent leaching of fluorotelomers and sulfonamide PFAS from four AFFF-impacted soils showing triplicate test results with a mean line. All data are shown as test method triplicates with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

6.5 Demonstration of Draft Method 1314A for PFAS

Section 4.5 presents a description of the Method 1314 as validated for inorganic COPCs. Changes to the Method 1314 apparatus and procedure were made to address PFAS leaching:

- The leaching fluid was changed from DIW to 1-mM $CaCl_2$ to limit formation of colloids due to a cation imbalance.
- The quartz sand used for material support, flow regulation, and eluate coarse filtration was initially found to be a minimal source of PFAS (~10 ng/L). Therefore, all quartz sand used for PFAS experiments was triple rinsed in MeOH, triple rinsed in DIW and air-dried prior to use.
- Eluates were not filtered prior to saving analytical samples for PFAS.
- Subsampling for PFAS analysis was conducted after sonication of the eluate collection bottle for 30 mins at 40 °C to desorb PFAS from the collection bottle walls (**Appendix C-4.5**).

Furthermore, the flow rate for the Draft Method 1314A leaching test columns was reduced to 0.5 L/S per day, the low end of the 0.75±0.25 L/S per day range, to provide longer residence times for eluates within the column packing.

6.5.1 Test Procedure

The apparatus used in the demonstration of Draft Method 1314A for PFAS was the same apparatus used for Method 1314 (**Figure 6-6**). An acrylic column (5-cm ID x 30-cm long) was connected to PP eluate collection bottles using 0.32-cm ID Tygon tubing. In addition, the bottom of the column was connected via 0.32-cm ID Tygon tubing to a Masterflex® multi-channel peristaltic pump (Cole Parmer, Vernon Hills, IL) and a 10-L HDPE reservoir of 1-mM $CaCl_2$. The demonstration was conducted with the column in up-flow mode to minimize channel and preferential flow pathways. Each of the collection bottles was equipped with a vapor lock that allows the vapor space of the empty bottle to be displaced without allowing external air into the vessel.

A comparison between the demonstration data shown below and Draft Method 1314A conducted in the stainless-steel apparatus using the Draft Method 1314A demonstration for SVOCs is presented in **Section 7.1.2**.

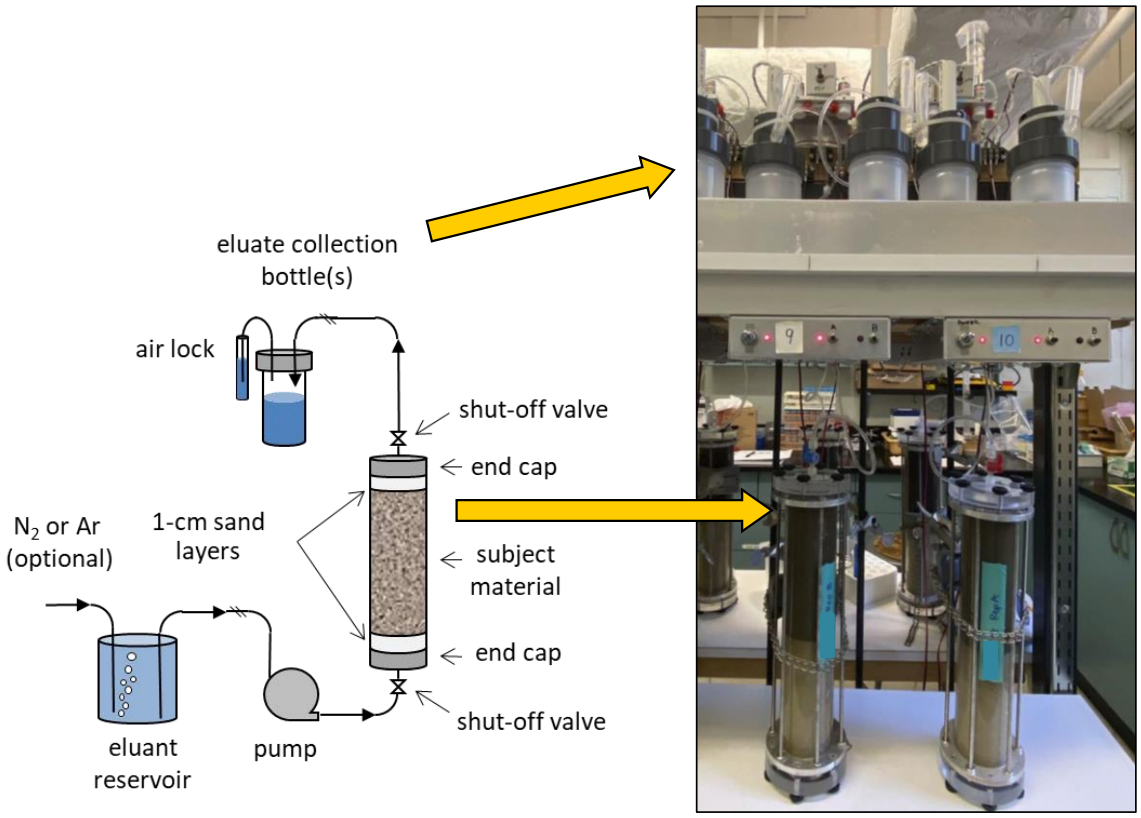

Figure 6-6. Schematic of the column apparatus for PFAS testing (left) and picture of Site 1 Soil demonstration of Draft Method 1314A for PFAS (right).

The column was removed from the apparatus and moderately packed with test material. Clean quartz sand (600-800 µm), triple-rinsed with DIW and air dried, was used at the bottom of the column to condition incoming eluent (≥1-cm layer) and at the top of the column as a coarse filter for the outgoing eluate (1-cm layer). The column was packed in an inverted orientation (see **Figure 4-11**) to ensure that the eluate filtration sand bed remains consistent between replicates. The packing operation includes tamping down a 1-cm quartz sand, adding and tamping test material equivalent to 340 g-dry in approximately 5 layers or lifts, and filling the column with quartz sand used for eluent flow regulation. For testing, the column is inverted so that the 1-cm filtration layer is at the top of the column.

During testing, an eluent solution of 1-mM $CaCl_2$ was pumped from the bottom of the column at an eluent flow rate of 0.75±0.25 L/S per day. Eluate leaving the top of the column was collected into a series of PP collection bottles with water-based air locks that keep outside air from entering the collection vessel. Eluate fractions were collected at nine ΣL/S values following an eluate collection schedule based on the flowrate of the column and the collected L/S (see example schedule in **Table 4-7**.

6.5.2 Eluate Collection and Processing

The procedure for processing eluates used in the demonstration of Draft Method 1314A for PFAS is shown in **Figure 6-7**. Following the process for method development experiments on eluate subsampling (**Appendix C-2.7**), the entire eluate collection bottle was sonicated for 30

min at 40 °C (Step 1) to minimize sorption of PFAS to the bottle surfaces. An aliquot between 25 and 50 mL of eluate was saved for PFAS analysis in a 50-mL PP Digitube (Step 2). For measurement of eluate parameters, a 5-mL aliquot of the well-mixed eluate was removed for pH and EC determination (Step 3). Finally, an additional 40 mL aliquot of eluate was filtered through 0.45-µm filtration membranes and preserved for inorganic COPC chemical analysis (Step 4). The following volumes were removed from the eluate collection bottle and prepared for analysis:

- 5 mL for pH and EC by ion-specific probe,
- 20-50 mL for PFAS analysis, and
- 40 mL for inorganic COPC analysis; filtered through 0.45-µm membranes with 10 mL saved for DOC analysis and 10 mL preserved with HNO_3 to pH <2 for ICP-OES.

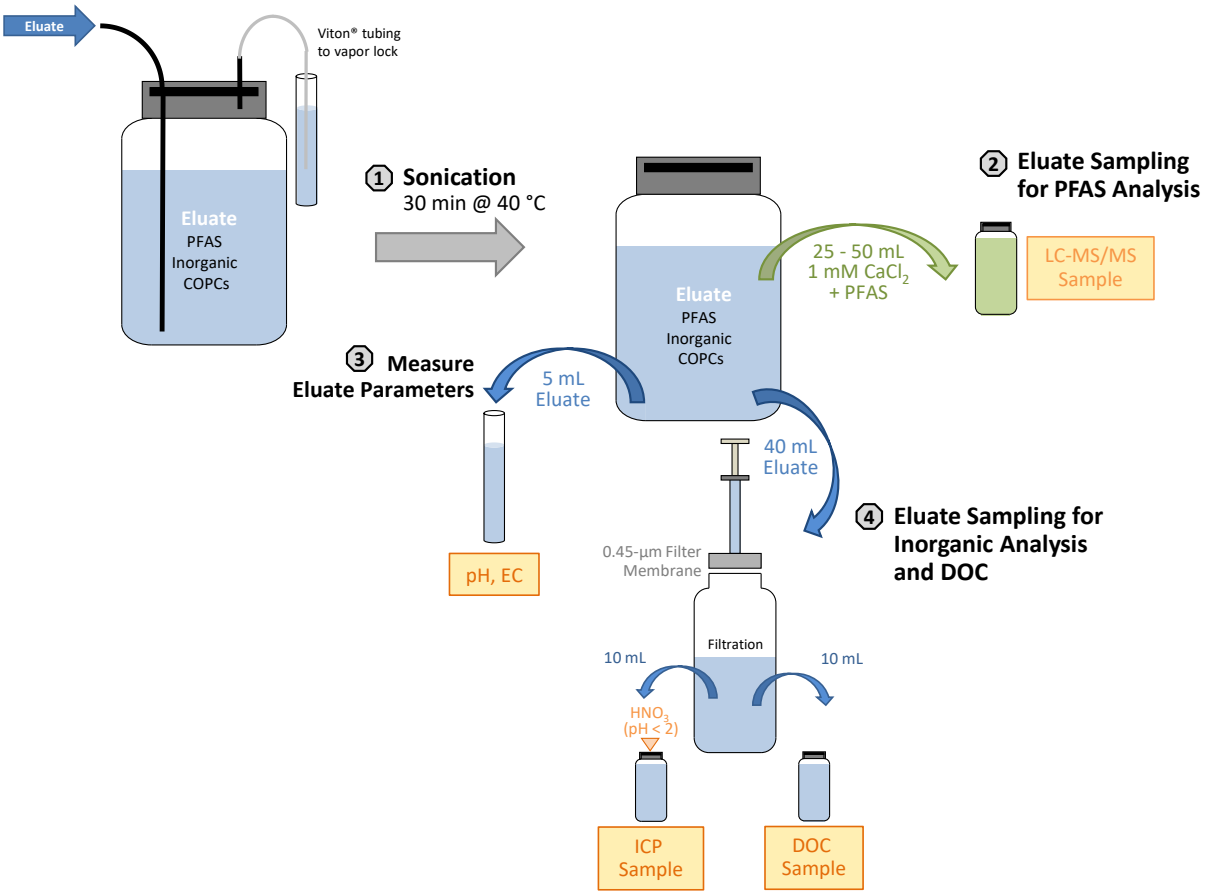

Figure 6-7. Eluate processing for demonstration of Draft Method 1314A for PFAS.

6.5.3 Demonstration Results

The results of the demonstration of Draft Method 1314A for four AFFF-impacted soils are presented in **Figure 6-8** through **Figure 6-14**. These results include the L/S-dependence of pH

and DOC (**Figure 6-8**) due to the influence of these eluate parameters on the solubility of COPCs. In addition, demonstration of Draft Method 1314A includes the results of PFAS analysis in triplicate for PFCAs (**Figure 6-10**), PFSAs (**Figure 6-12**), and fluorotelomers and other PFAS (**Figure 6-14**).

pH and Organic Carbon Concentrations

The eluate pH and DOC concentrations are shown in **Figure 6-8** for the three soils used in the demonstration of Draft Method 1314A for PFAS. Also shown in the figure is the eluate iron concentration with ΣL/S. For Site 1 Soil, the eluate pH remains constant over the ΣL/S range; however, a marked shift in pH for Site 2 and Site 3 soils is shown at ΣL/S of 10 mL/g-dry. The increase in pH for these soils is accompanied by an increase in DOC and Fe at that same ΣL/S. These observations are consistent with a shift in reduction-oxidation within the column toward reducing conditions after an ΣL/S of 9, which most likely a consequence of the onset of iron reducing microbial activity.

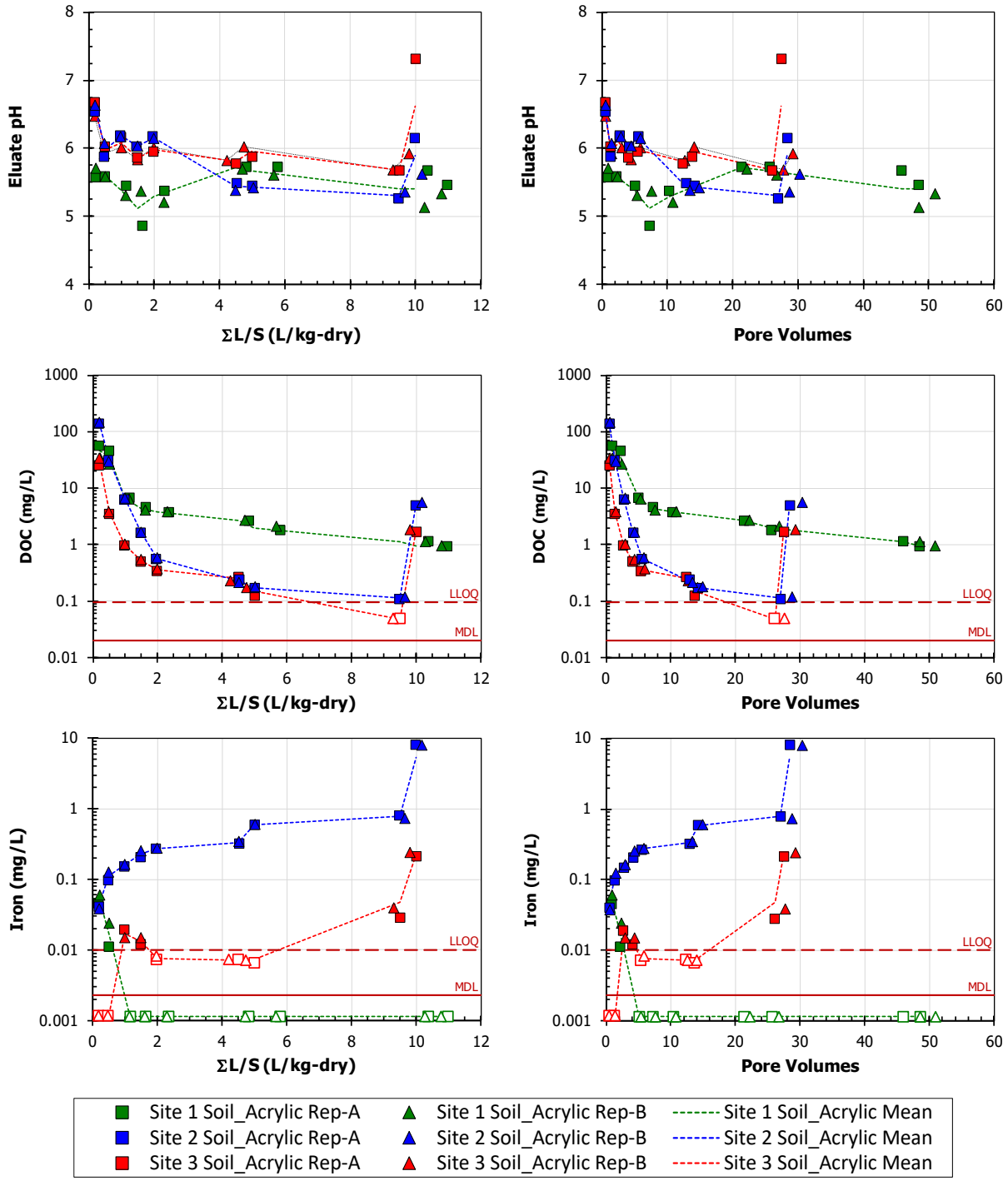

Figure 6-8. Demonstration of Draft Method 1314A showing eluate pH, dissolved organic carbon and iron from three AFFF-impacted soils. All data from duplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

Percolation Column Concentrations

The method demonstration results for select PFCAs is shown in **Figure 6-9** through **Figure 6-14** for three AFFF-impacted soils. Individual data points show duplicate test results while the line represents the replicate mean calculated by LeachXS. The replication of these results is quite good indicating that repeatability for the percolation column test is high for most PFCAs. In addition, the data indicate that shorter-chain PFCAs (C ≤7) tend to have initially high eluate concentrations that drop quickly by ΣL/S 2 to lower concentrations. The LEAF guide (U.S. EPA 2019) describes this behavior as a “wash-off” of more soluble species; however, the PFAS literature speaks of this phenomenon as a dual regime release with fast and slow desorption (Brusseau et al., 2019). The release curve for longer chain PFCAs (C >7) is flatter, either relatively constant (PFDA) or monotonically falling (PFNA), indicative of sorption-controlled release.

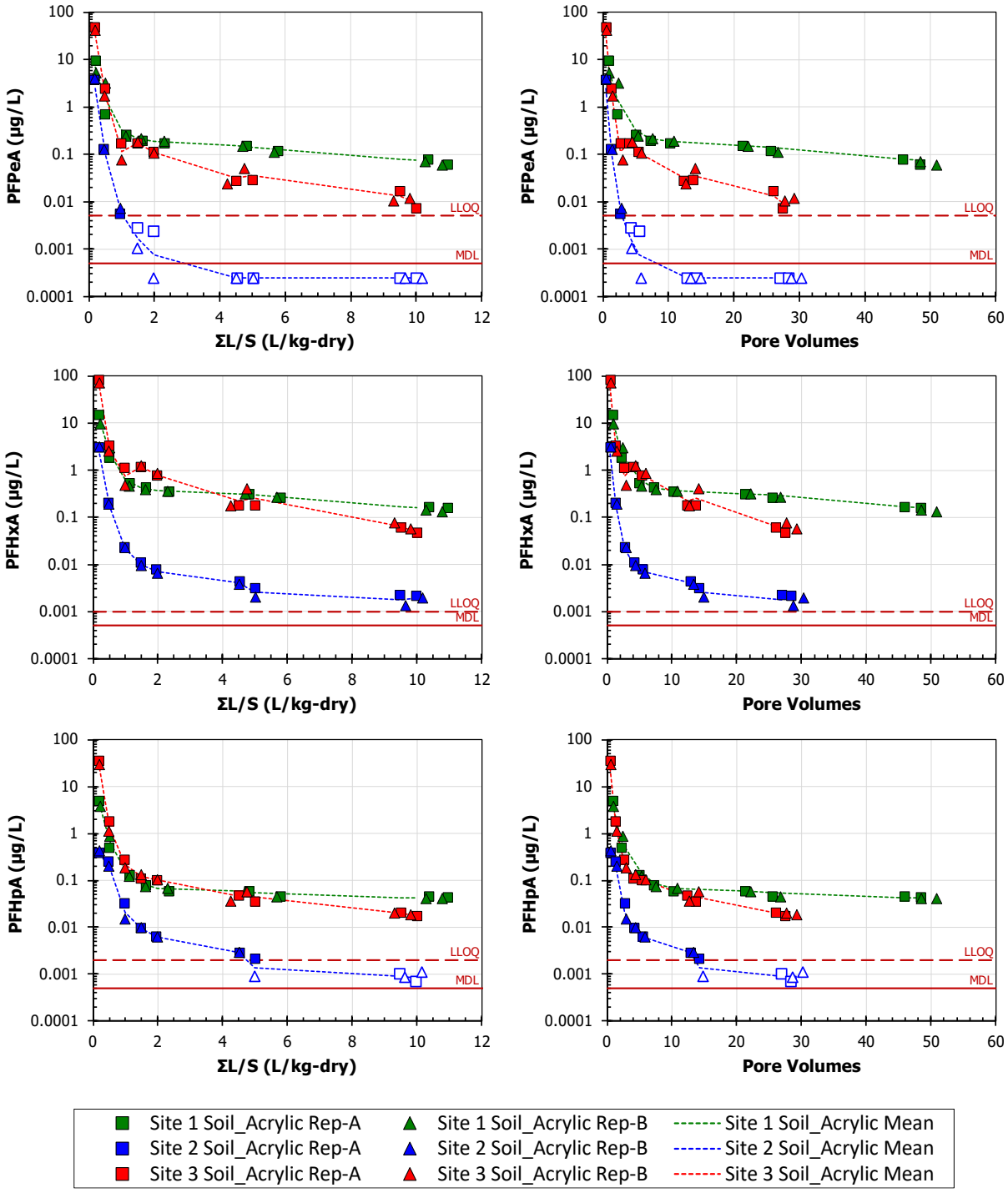

Figure 6-9. Demonstration of Draft Method 1314A showing percolation column leaching of perfluoroalkyl carboxylic acids (PFCAs) from three AFFF-impacted soils. All data from duplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

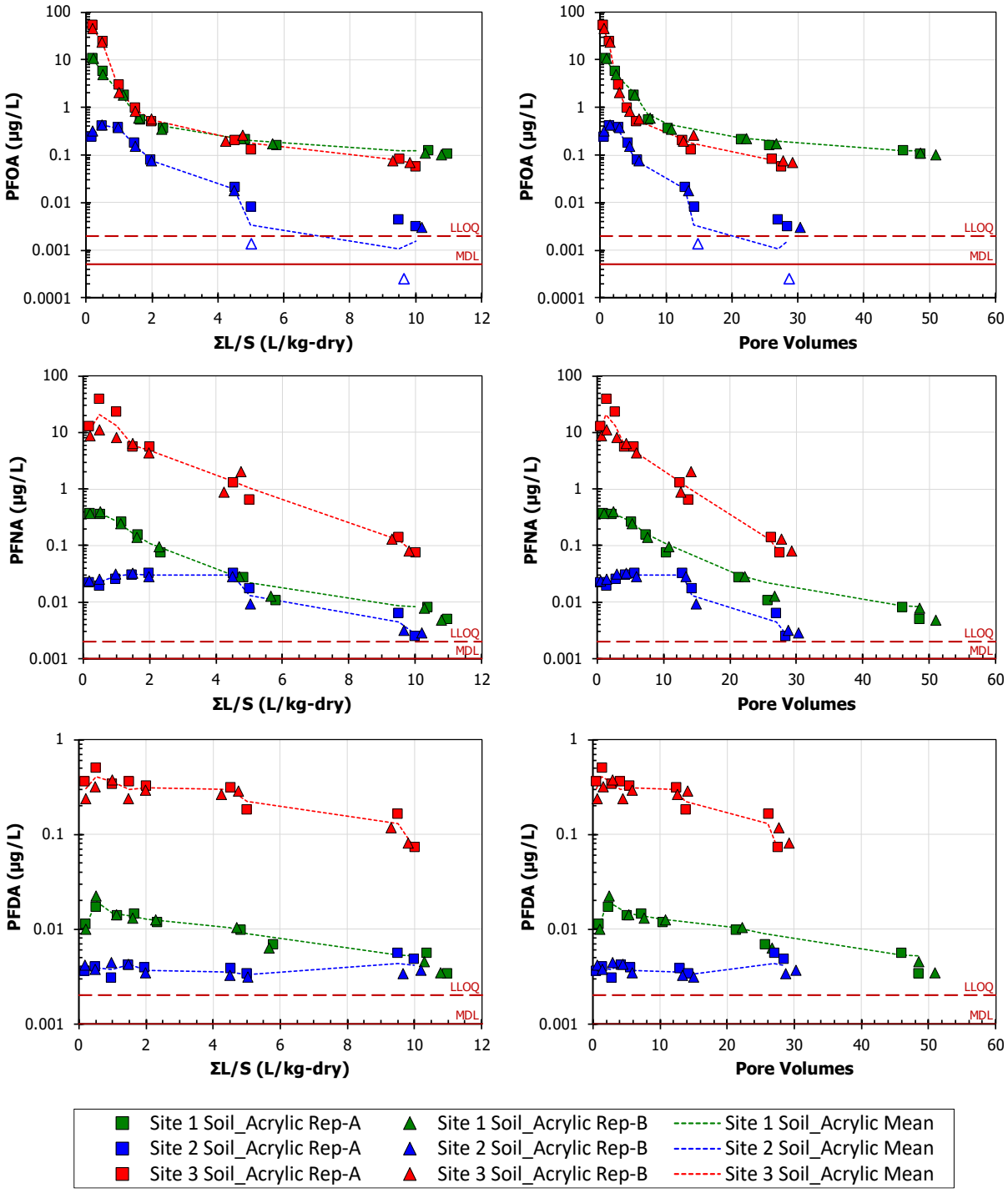

Figure 6-10. Demonstration of Draft Method 1314A showing percolation column leaching of perfluoroalkyl carboxylic acids (PFCAs) from three AFFF-impacted soils. All data from duplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

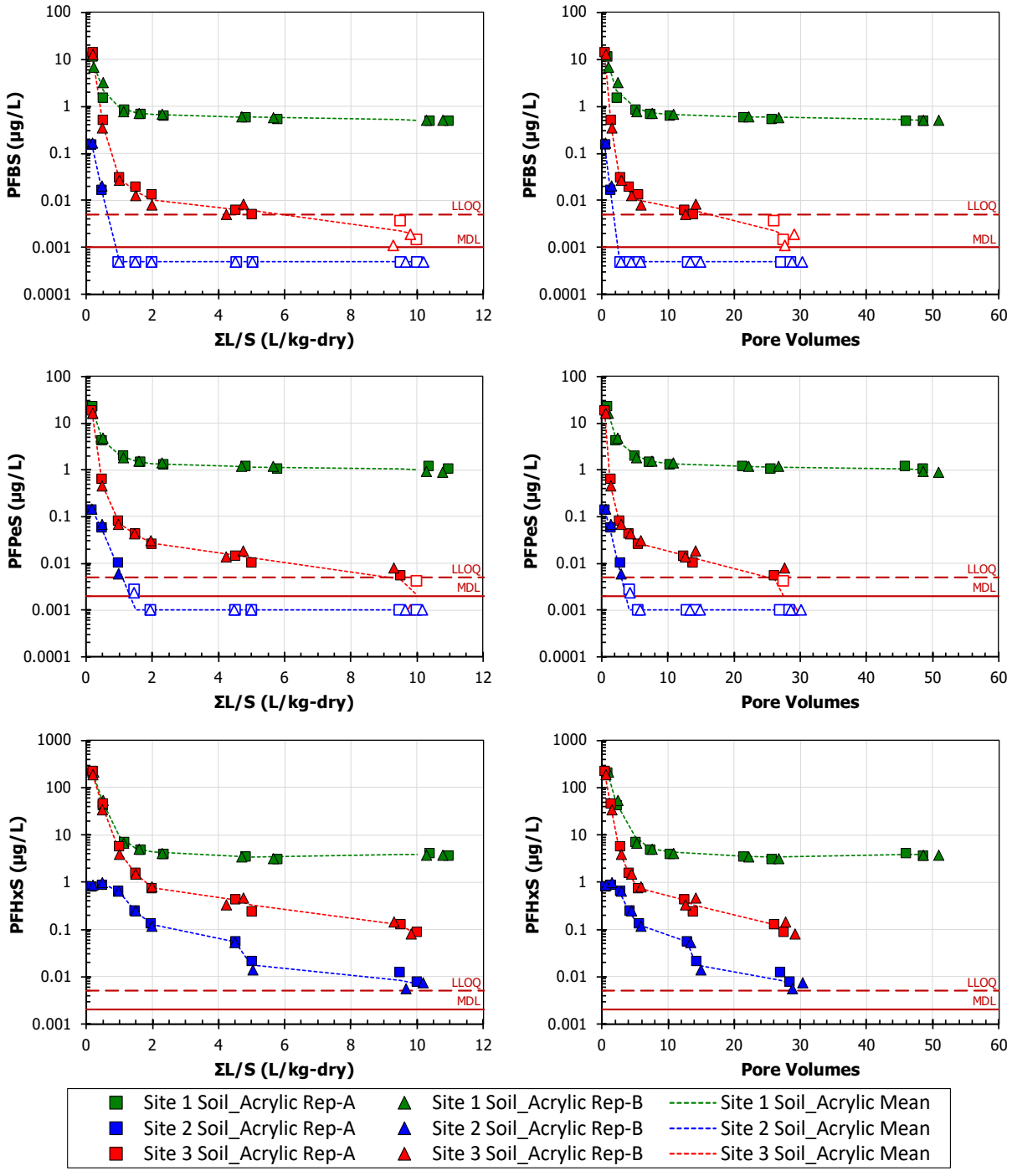

Figure 6-11. Demonstration of Draft Method 1314A showing percolation column leaching of perfluoroalkyl sulfonic acids (PFSAs) from three AFFF-impacted soils. All data from duplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

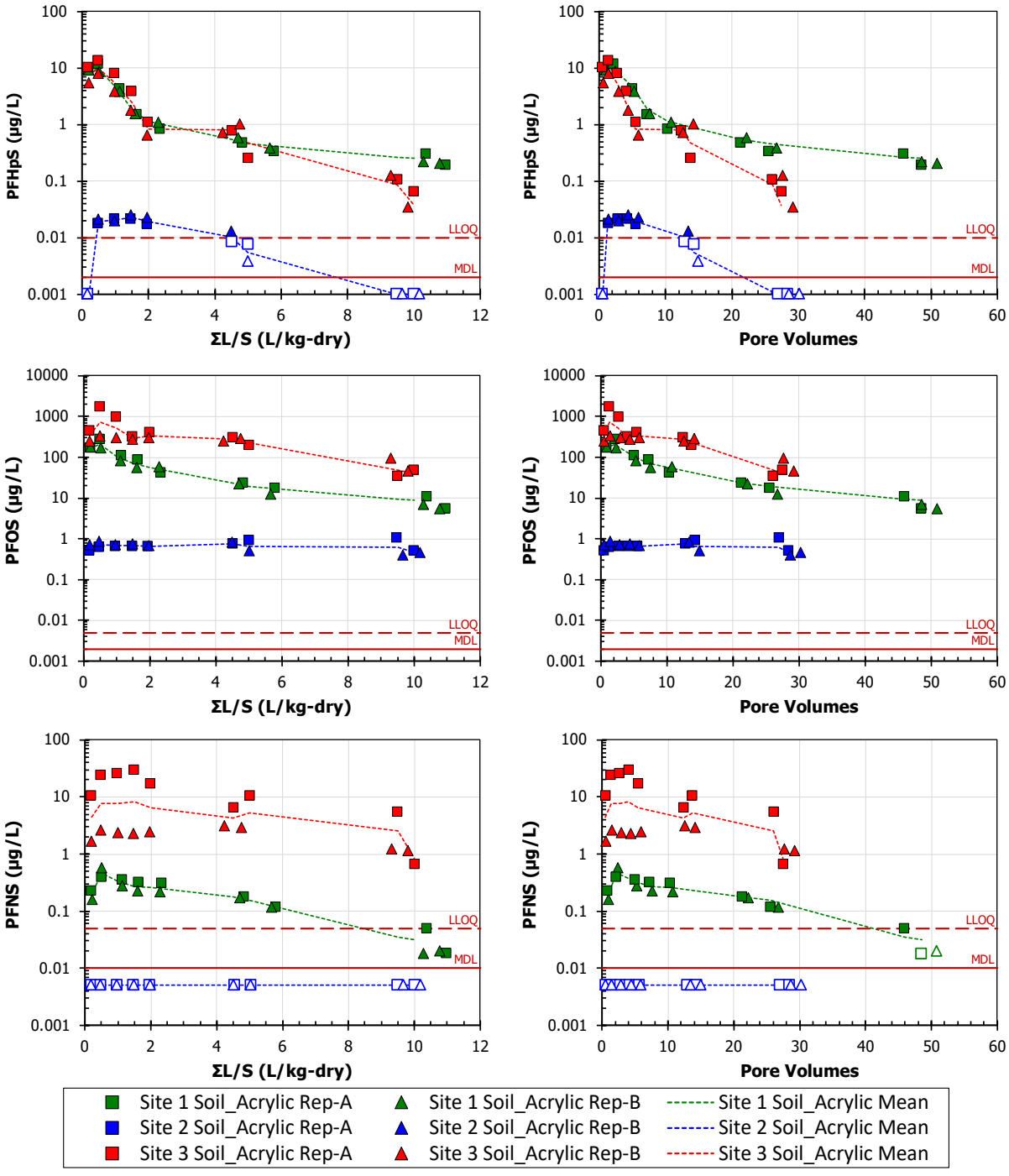

Figure 6-12. Demonstration of Draft Method 1314A showing percolation column leaching of perfluoroalkyl sulfonic acids (PFSAs) from three AFFF-impacted soils. All data from duplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

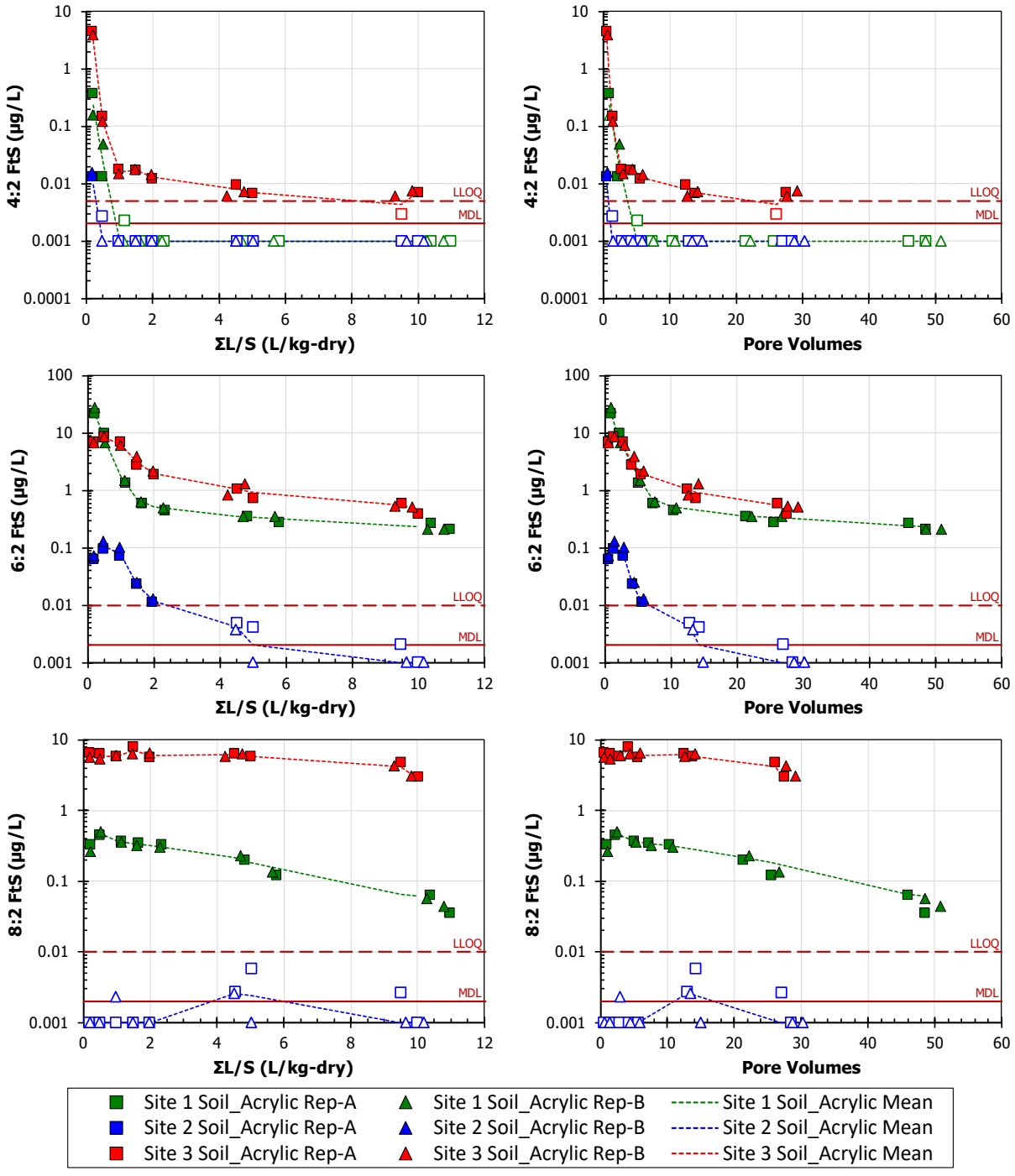

Figure 6-13. Demonstration of Draft Method 1314A showing percolation column leaching of fluorotelomers and sulfonamide PFAS from three AFFF-impacted soils. All data from duplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

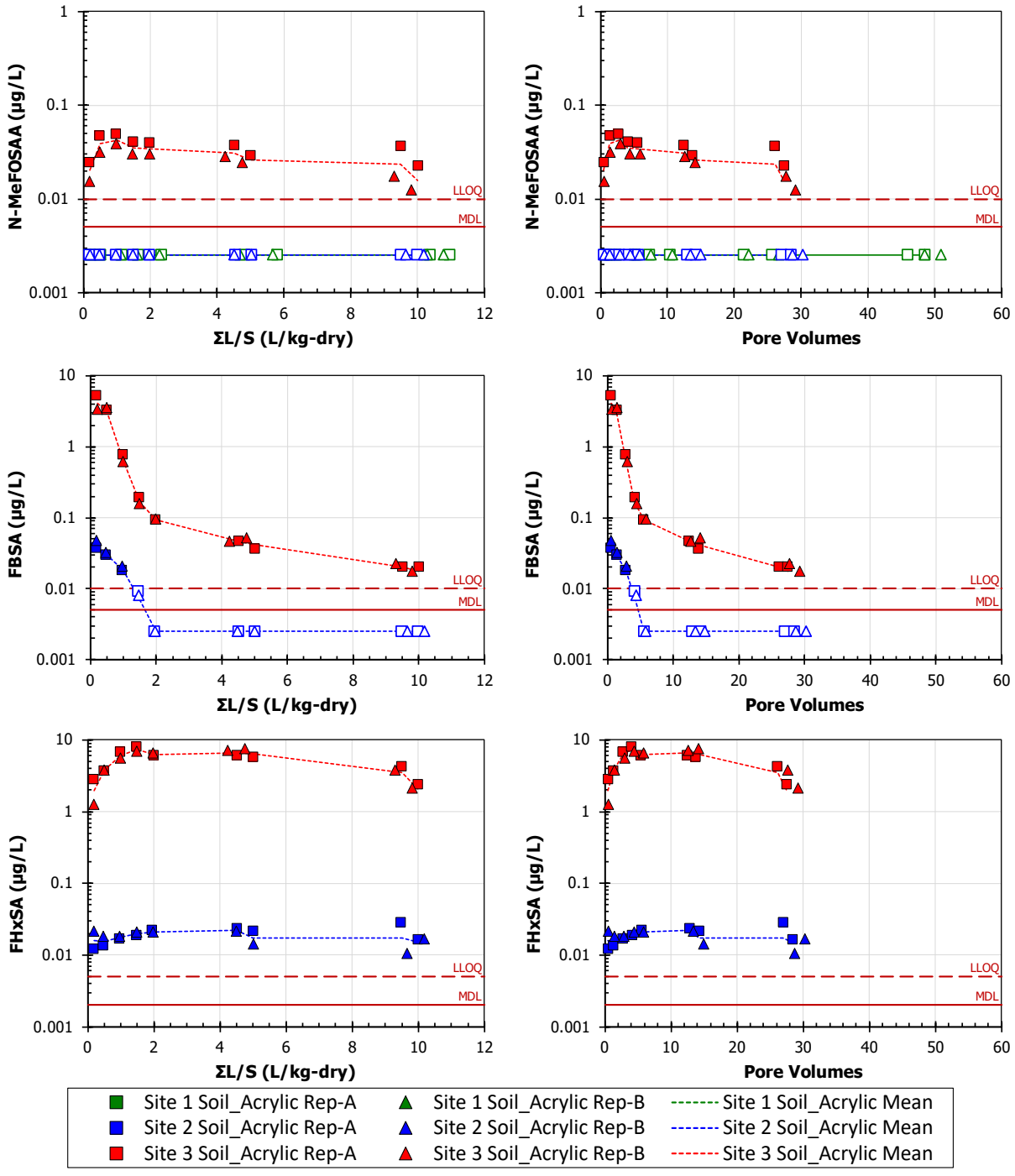

Figure 6-14. Demonstration of Draft Method 1314A showing percolation column leaching of fluorotelomers and sulfonamide PFAS from three AFFF-impacted soils. All data from duplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

6.6 Demonstration of Draft Method 1316A for PFAS

The demonstration of Draft Method 1316A was carried out on four AFFF-impacted soils (i.e., Site 1 Soil, Site 2 Soil, Site 3 Soil, and Site 4 Soil) in triplicate. The concentration of PFAS in each replicate eluate were measured by LC-MS/MS and graphed as a function of L/S. Based on similarities to the Draft Method 1313A procedure, the modifications made to Method 1316 to address L/S-dependent PFAS leaching are the same as those made to Method 1313 to address pH-dependent PFAS leaching (**Section 6.4.1**). To facilitate the separation of eluates from solid materials at low L/S (L/S ≤1 mL/g-dry), the low L/S centrifuge devices were used for this demonstration (see **Appendix C-2.2**).

6.6.1 Test Procedure

The procedure for Draft Method 1316A for PFAS follows the procedure for the SW-846 as presented in **Figure 6-15**. No changes were made to the test method procedure except as indicated for Draft Method 1313A. Centrifugation of solid and liquid slurries in PP centrifugation bottles (**Appendix C-4.3**) was used in lieu of filtration through PP membranes and the low L/S centrifuge devices were used for separating eluate at L/S of 0.5 and 1.0 mL/g-dry.

After tumbling, a 40 mL aliquot of the solid-liquid slurry was decanted into 200 mL PP centrifuge bottles. These bottles were centrifuged at 9,700-G for 10 minutes to separate the solid phase from the liquid eluate (Step 2). From the extraction bottle, a 5-mL aliquot was collected for measurement of pH and EC (Step 3). An additional 40 mL aliquot of the solid-liquid slurry was filtered through 0.45-um filtration membranes and split into a 10-mL analytical sample for ICP analysis of inorganic COPCs and a 25-mL analytical sample for DOC analysis (Step 4). A 25-mL aliquot of the clarified eluate after centrifugation was decanted into a clean 50-mL PP SCP Science Digitube® (#NC9739574, Fisher, Waltham, MA) for PFAS analysis (Steps 5 & 6).

6.6.2 Demonstration Results

The results of the demonstration of Draft Method 1316A for four AFFF-impacted soils are presented in **Figure 6-16** through **Figure 6-19**. These results include the L/S-dependence of pH and DOC (**Figure 6-16**) due to the influence of these eluate parameters on the solubility of COPCs. In addition, demonstration of Draft Method 1316A includes the results of PFAS analysis in triplicate for PFCAs (**Figure 6-17**), PFSAs (**Figure 6-18**), and fluorotelomers and other PFAS (**Figure 6-19**).

6.6.2.1 pH and Organic Carbon Concentrations

Although the equilibrium concentration of most short-chain PFAS has been reported as not significantly influenced by pH (Campos-Pereira et al., 2018; Kabiri, Centner, and McLaughlin, 2021; Li et al., 2018; Nguyen, et al., 2020; Oliver et al., 2020), the retention of longer chain PFAS has been associated with particulate organic carbon (Compos-Pereira et al., 2022; Kabiri et al., 2022; Zhao et al., 2014). Therefore, eluate pH and DOC (representing the soluble fraction of TOC) are important parameters for interpretation of the leaching behavior of PFAS as a function of L/S. **Figure 6-16** shows the eluate pH and DOC measured in eluates of Draft Method 1316A for four AFFF-impact soils.

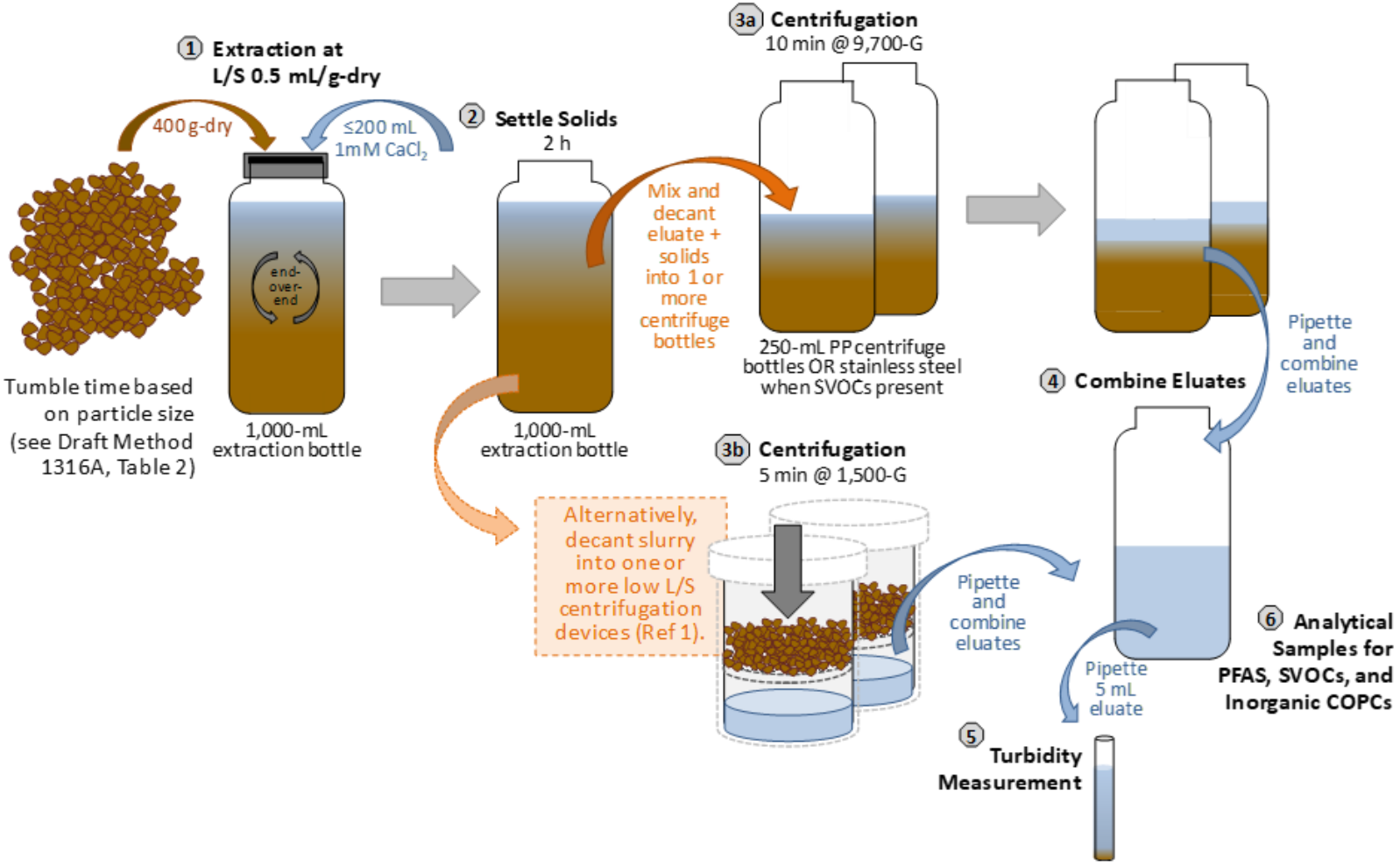

Figure 6-15. Example procedure for demonstration of Draft Method 1316A (L/S = 0.5 mL/g-dry) showing eluate processing for inorganic COPCs and PFAS.

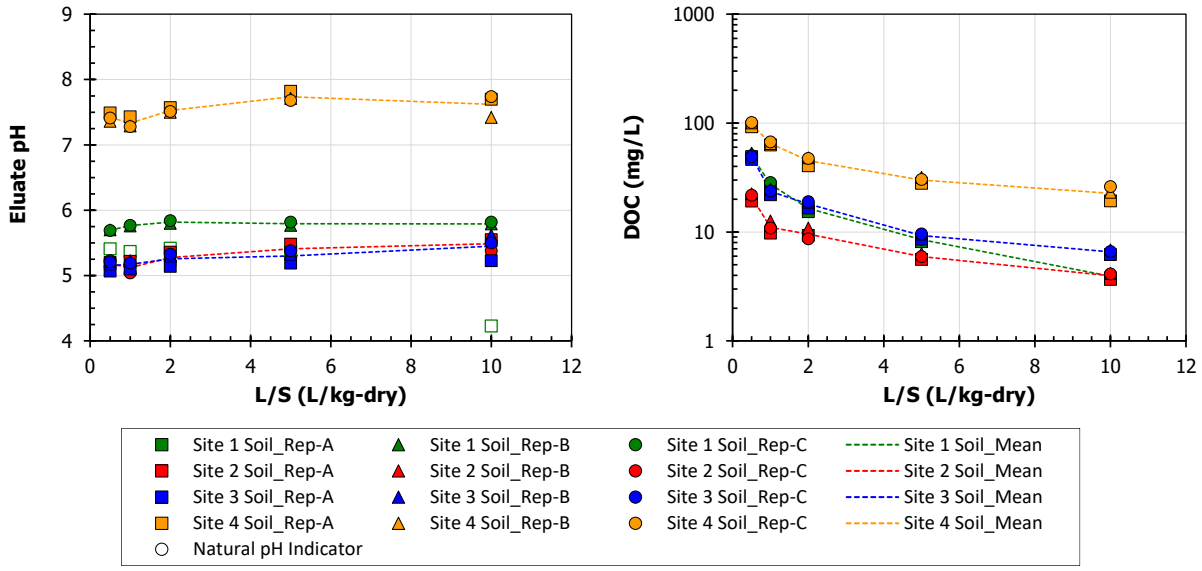

Figure 6-16. Eluate pH and dissolved organic carbon (DOC) from demonstration of Draft Method 1316A. All data from triplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

6.6.2.2 L/S-dependent PFAS Concentrations

The demonstration results for Draft Method 1316A carried out on the four AFFF-impacted soils are presented in **Figure 6-17** for PFCAs, **Figure 6-18** for PFSAs, and **Figure 6-19** for fluorotelomers and other PFAS. All tests were conducted in triplicate and are shown as individual replicate data with a replicate mean line calculated in LeachXS.

The results of the Draft Method 1316A demonstration illustrate similar results as provided by Draft Method 1314A. Shorter chain PFCAs and PFSAs (C ≤8) show a more rapid reduction in PFAS concentration with increasing L/S whereas longer chain PFAS (C >8) tend to have essentially constant (PFOS, 8:2 FTS) or minor decreases (PFDA, FHxSA) in PFAS concentrations with increasing L/S.

In general, replication for the demonstration of Draft Method 1316A is good; however, a few sets of replicate data exhibit significant variability. The best replication was observed for shorter chain PFAS rather than longer chain PFAS. Also, when eluate concentrations approach the quantitation limit, the variability of the data increases (e.g., Site 3 Soil for PFPeA and 6:2 FTS). Since this behavior is typical of analytical uncertainty, it is likely that the variability of demonstration results near the quantitation limit is driven by analytical uncertainty.

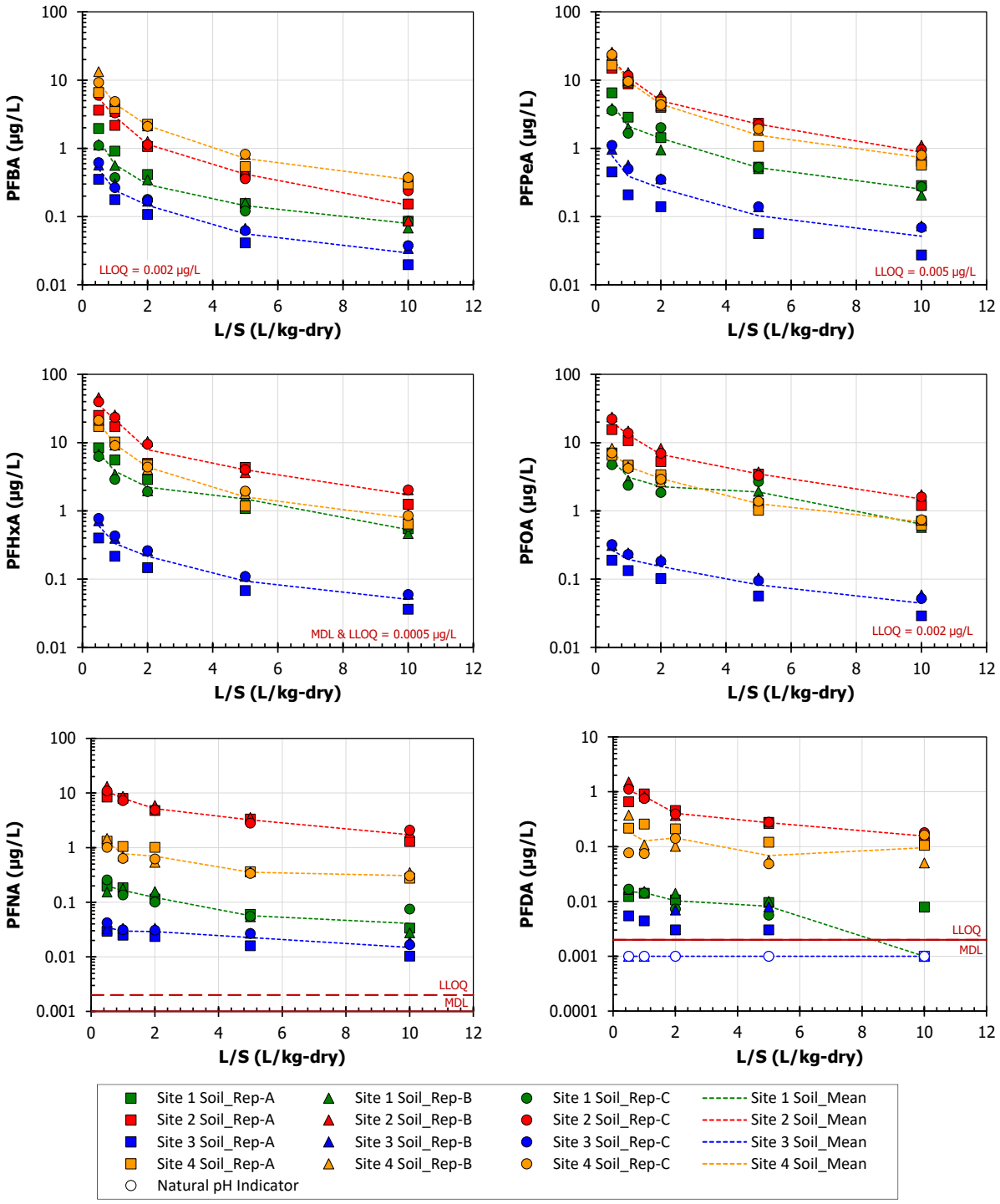

Figure 6-17. Demonstration of Draft Method 1316A showing L/S-dependent leaching of perfluoroalkyl carboxylic acids (PFCAs) from four AFFF-impacted soils. All data from triplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

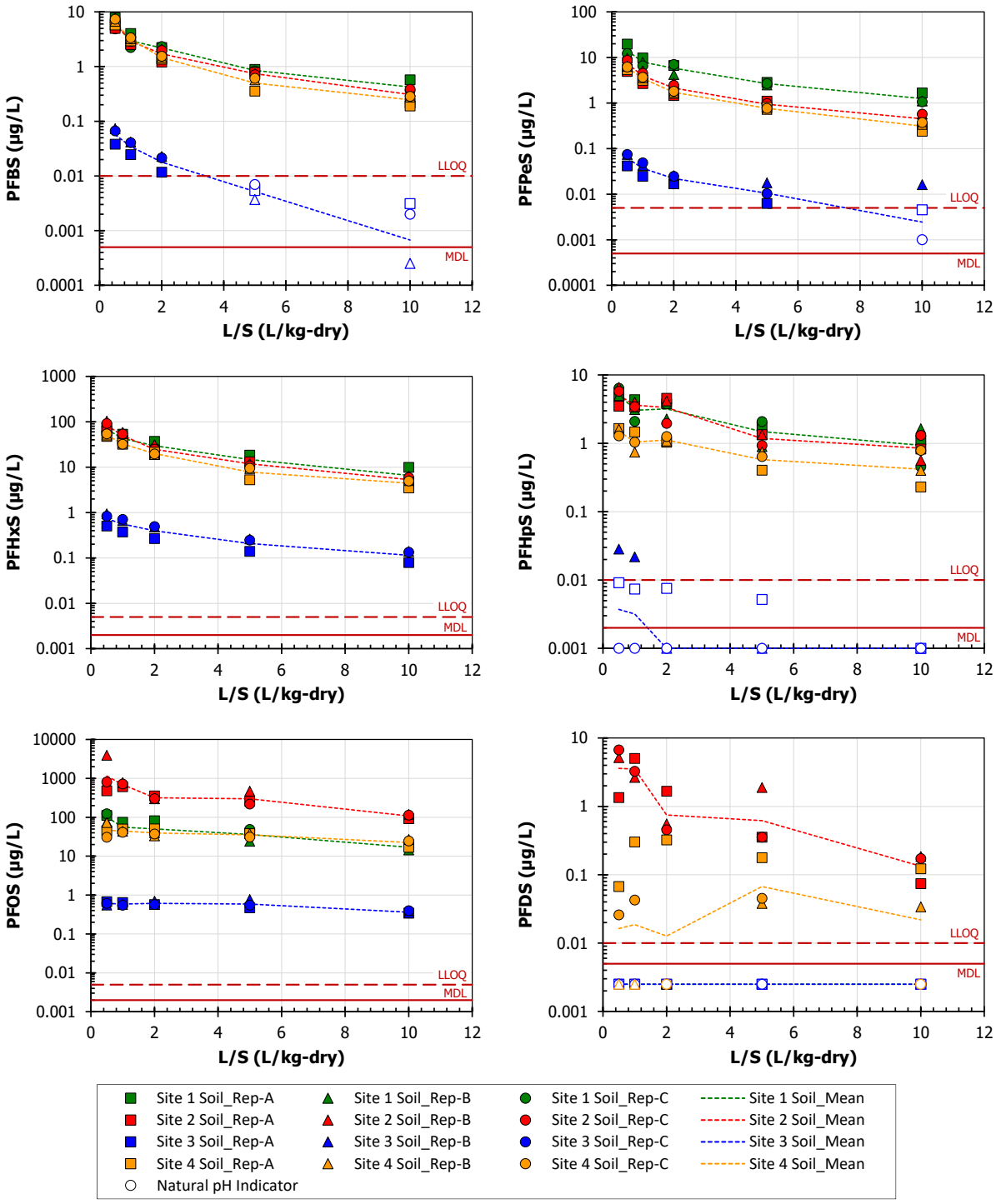

Figure 6-18. Demonstration of Draft Method 1316A showing L/S-dependent leaching of perfluoroalkyl sulfonic acids (PFSAs) from four AFFF-impacted soils. All data from triplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

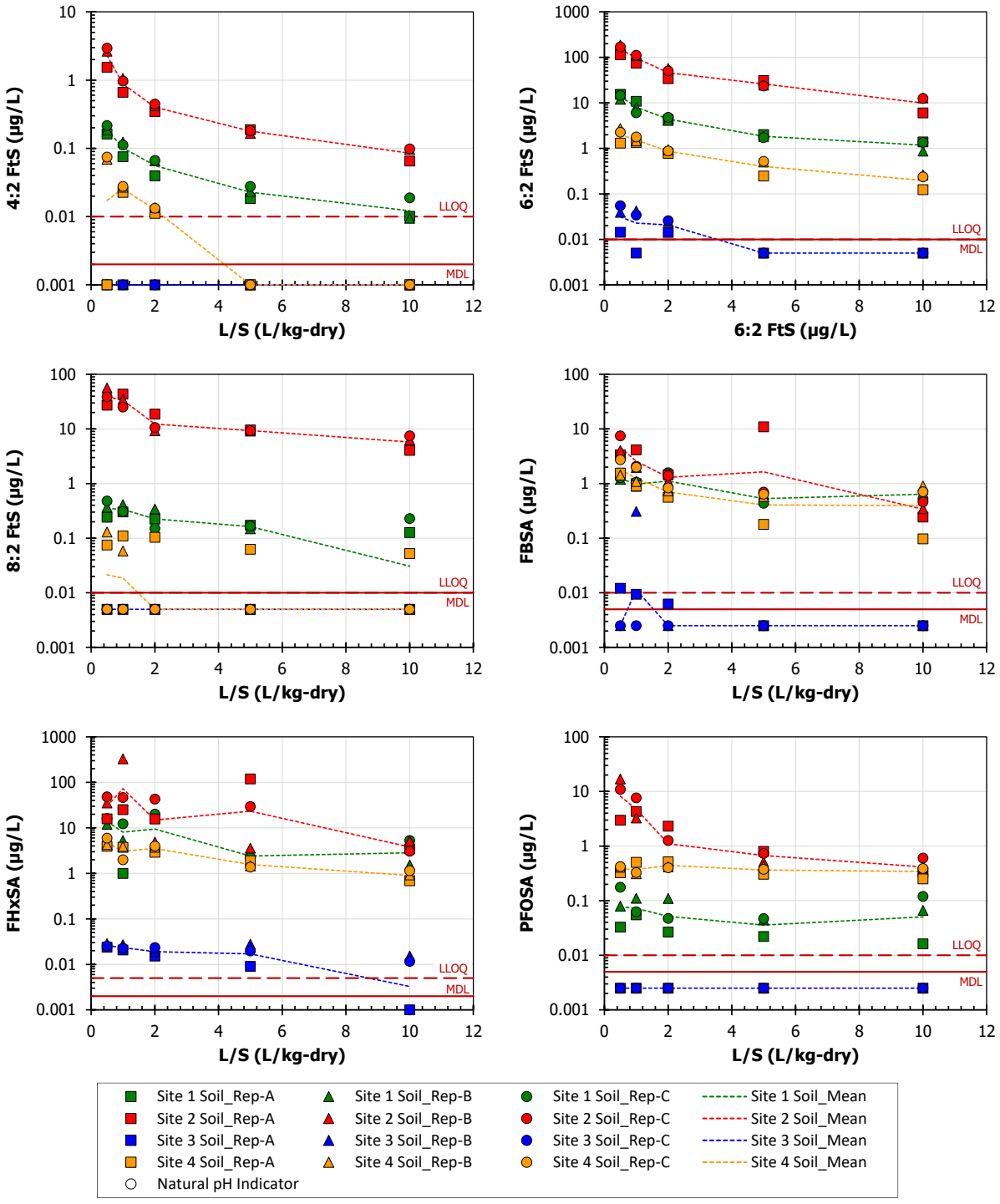

Figure 6-19. Demonstration of Draft Method 1316A showing L/S-dependent leaching of fluorotelomers and sulfonamide PFAS from four AFFF-impacted soils. All data from triplicate analyses are shown with a calculated mean line. Data points below the quantitation limit are shown with a white fill.

7 Integration of Test Methods for Inorganic COPCs, SVOCs, and PFAS Compounds

7.1 Materials of Construction

Within the method development experiments in this BID (**Appendix C**), the sorption of SVOC and PFAS was evaluated relative to several types of plastic (e.g., HDPE, PP, acrylic), Type I borosilicate glass and Type III soda-lime glass, 316L stainless steel, and quartz sand. The results of these experiments show that sorption losses may be minimized by proper selection of materials of construction for primary components (e.g., extraction vessels, eluate collection and storage vessels, columns, transfer lines) and secondary components (e.g., valve seals, vessel cap liners, etc.).

7.1.1 Recommended Materials of Construction by COPC Type

In general, the selection of appropriate materials of construction is one of the most important aspects of methods development in this BID. Poor selection may lead to losses of SVOCs to HDPE materials or release of PFAS from fluorinated polymers. **Table 7-1** presents the recommended materials of construction based on the methods development experiments carried out for this project.

Table 7-1. Recommended Materials of Construction for Various COPCs

	Class of Constituents of Potential Concern			
	Inorganics/ Metals	Hg	SVOCs	PFAS
Glass[1] (Type I and Type III)	nr	P	P	P
Acrylic	P	Nr	nr	P
HDPE	P	Nr	nr	P, S
PP	S	Nr	nr	P, S
PCTFE	P	S[2]	S[2]	S[2]
PTFE	P	P	P, S	nr
Stainless Steel[3] (316L)	nr	nr	P[2]	P[2]

NOTE: P = recommended as a material for primary components (e.g., vessels, tubing, etc.)
S = recommended as a material for secondary components only (e.g., valve seals, lid liners)
nr = not recommended as a material for primary or secondary components

[1] Amber glass is preferred to minimize exposure of eluate solutions to UV light.
[2] PCTFE should be limited to seals and lid liners (minimum exposure).
[3] 316L stainless steel may cause interferences via release or absorption of chromium, copper, iron, manganese, and molybdenum.

NVOCs = non-volatile organic compounds
SVOCs = semi-volatile organic compounds
PFAS = per- and polyfluorinated alkyl substances
HDPE = high-density polyethylene
PP = polypropylene
PC = polycarbonate
PCTFE = polychlorotrifluoroethylene
PTFE = polytetrafluoroethylene

Selection of materials of construction are based on studies designed to minimize losses of mercury during batch extractions (Kelley et al., 2024). These studies explored extraction materials of construction and eluate preservation techniques. The results indicated that sorption to vessel surfaces is minimized when extractions are conducted in PTFE or Type I (borosilicate) glass. Preservation of eluate solutions containing mercury should include (i) minimization of headspace in storage/collection vessels, (ii) pH adjustment to <2 using Optima grade HNO_3 at a final concentration of 1%, (iii) inclusion of a gold(III) standard at a final concentration of 200 µg/L, and (iv) refrigeration at <6 °C prior to analysis.

These results indicate that, while there is no perfect material for all cases, overlaps in the recommended materials of construction exist such that combined evaluation of inorganic COPCs, SVOCs, and PFAS may be carried out from the same test apparatus with some limitations. For example, although **Table 7-1** shows that stainless steel is not recommended for inorganics/metals, it can be used to evaluate leaching from all three COPC types providing that the project quality objectives allow for the expected low-concentration release of metals from stainless steel vessels (see **Appendix C-2.2**). For cases where no single material can be accepted, parallel testing of a well-homogenized material may be necessary.

7.1.2 Comparison of Draft Method 1314A Results for PFAS from Acrylic and Stainless-steel Columns

The comparability in recommended materials of construction is demonstrated in **Figure 7-1** for Draft Method 1314A carried out in parallel using acrylic columns and 316L stainless-steel columns. The column apparatus used in the demonstration of Draft Method 1314A (see **Section 6.5**), included acrylic columns (5-cm ID x 30-cm long), Tygon transfer lines (0.32-cm ID), and PP collection bottles ranging from 250-cm to 1,000-mL in volume. Method development experiments were conducted that support use of these materials relative to PFAS sorption (**Appendix C-2.7**).

The demonstration results (darker colors) are compared to the PFAS results when 316L stainless-steel columns (5-cm ID x 20-cm long) are used along with stainless-steel transfer lines (0.32-cm ID) and Type III soda-lime glass collection bottles of 250-mL and 1,250-mL. This apparatus is the same as the one used in the demonstration of Draft Method 1314A for SVOCs and which showed that sorption of SVOCs to these materials (**Appendix C-2.1** through **Appendix C-2.6**) was minimal and indicated that these materials would be recommended for SVOC leaching assessment; however, minor leaching (e.g., <100 µg/L) of Cr, Fe, and Mn from the column and initial sorption of Co, Cr, Fe, Mn, Ni, and Zn to the column could interfere with quantitation of some inorganic COPCs at low-level (**Appendix C-2.3**).

The comparison in **Figure 7-1** shows that the results of acrylic and stainless-steel column apparatus are essentially the same. Although the concentration of PFAS in acrylic and steel columns (**Figure 7-1**, left) vary 2-3 µg/L in general, these differences are within experimental uncertainty. In addition, the cumulative release is not sensitive to these small variations (**Figure 7-1**, right). Therefore, either the apparatus in Method 1314, recommended for inorganic COPCs and PFAS, or the apparatus demonstrated in Draft Method 1314A for SVOCs could be appropriate for use when PFAS and SVOCs are COPCs.

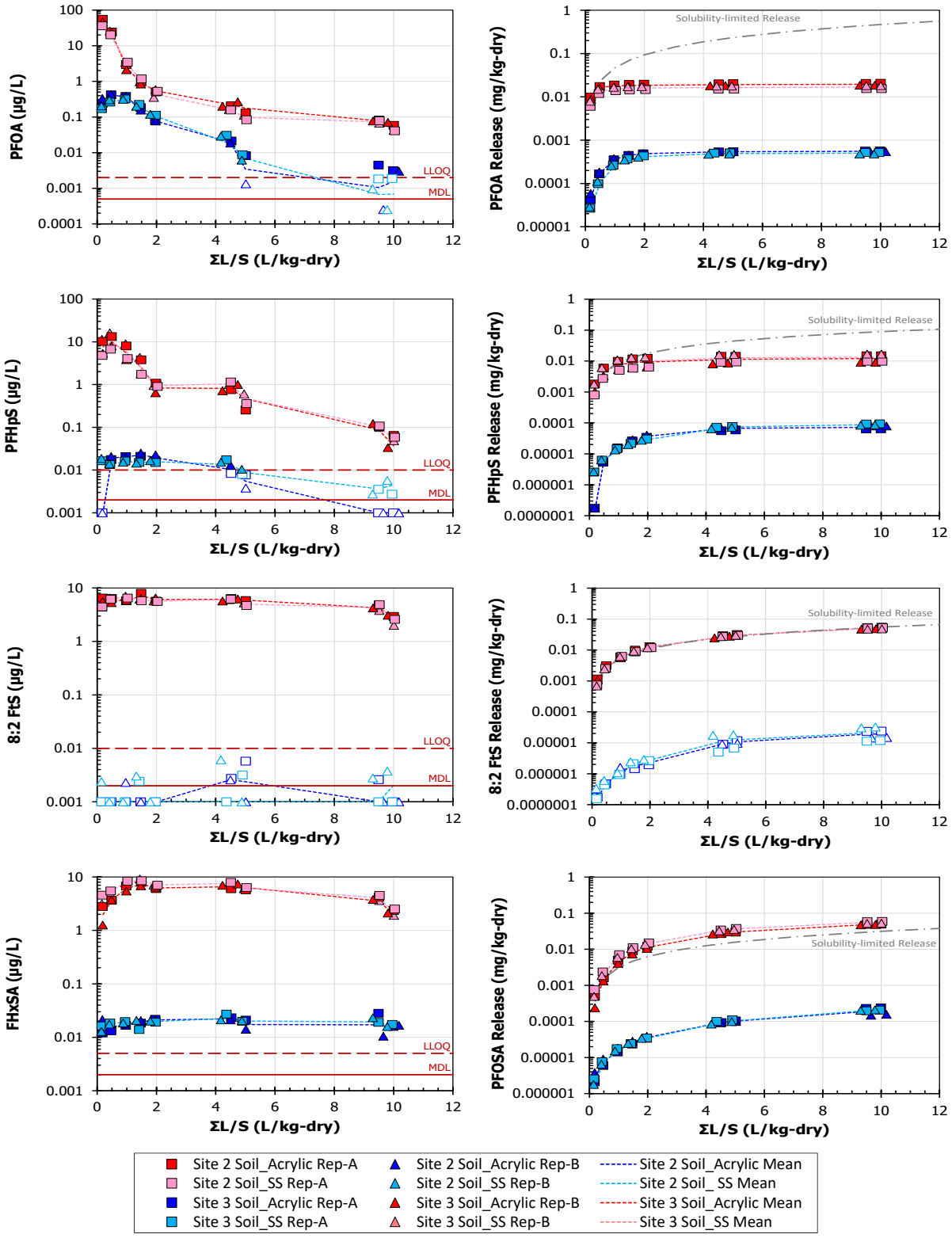

Figure 7-1. Comparison of Draft Method 1314A demonstration results conducted in acrylic columns with Tygon transfer lines (dark data) and in stainless-steel columns with stainless-steel transfer lines (light data). Results presented as PFAS concentration (left) and PFAS cumulative mass release (right).

7.2 Colloid Management for Batch Extraction Procedures

In batch equilibrium leaching tests (e.g., Draft Method 1313A and 1316A), enhanced colloid formation may occur due to deflocculation of clays and dissolution of organic matter caused by ion imbalances and/or agitation of the solid and liquid. Ion imbalances are management through use of 1 mM $CaCl_2$ solution to maintain a low SAR values (see Section 3.3.2.1); however, agitation, required to ensure solid-liquid contact during leaching, is likely to result in eluate colloidal matter above that expected in non-agitated systems. For the results shown in this document, the addition of alum at 0.5 mg/mL of eluate was used for SVOC eluates while PFAS eluate received centrifugation and eluates for inorganic COPCs were filtered. These three methods for three COPC types were considered importance due to the various materials of construction required for eluate handling (e.g., glass for SVOCs, stainless steel for PFAS, and plastics for inorganic COPCs) and the fact that glass centrifuge tubes for centrifugation of SVOC eluate were not widely available.

Following the generation of the Draft Method 1313A and 1316A demonstration data, the threshold of 1 NTU was found to be impractical, especially for clayey samples containing SVOCs treated with alum. Therefore, a pathway was determined to coordinate eluate processing across COPC types and that minimized enhanced colloids remaining in analytical samples using centrifugation. Centrifugation of all COPC types was found to be more efficient at colloid removal than alum treatment (**Appendix C-3.5**).

Changes to Draft Method 1313A and Draft Method 1316A provided in **Appendix D** reflect the switch to centrifugation for all eluates that do not visually clear after two hours of settling. Eluates are still split into fractions for SVOC, PFAS, and inorganic COPC handing due to the different materials of construction required for centrifugation. However, in the revised methods, aliquots for SVOC analysis are centrifuged up to 2,800-G for 5 minutes in small volume glass centrifuge tubes while aliquots for PFAS and inorganic COPCs analysis are centrifuged at 7,500-G for 10 minutes in large stainless steel or HDPE centrifuge vessels. The turbidity of all clarified solutions is measured and recorded. Although a target of 1 NTU may not be achievable for all tested solid materials under all conditions, the experiment in **Appendix C-3.5** indicates that a solution turbidity after centrifugation of 50 NTUs or less is achievable even for difficult clayey extractions. The use of centrifugation for all eluate regardless of COPC type provides a uniform methodology consistent with the intent of all batch extraction leaching methods. However, the final turbidity of all samples should be measured and reported prior to collection for chemical analysis.

7.3 Eluate Sampling Procedure

Although the validity and reliability of a leaching procedure are not dependent on the method of chemical analysis, the processing of leaching test eluates needs to be compatible with subsequent chemical analyses. Eluate processing should ensure that sufficient eluate volumes are available and that the processing sequence minimizes interferences. Some method development was required for measurement of eluate concentrations of organic COPCs. A guiding objective of the LEAF methods developed in this BID was to minimize the number of separate leaching tests that need to be carried out to evaluate multiple COPC classes (e.g., inorganic and SVOC COPCs); however, some duplication of effort is likely to be required when a wide range of COPCs are to be evaluated.

Assuming the need to collect and preserve samples for analysis of inorganic COPCs, SVOCs, and PFAS, a recommended eluate processing procedure is presented in **Figure 7-2**. This figure assumes a batch extraction at an L/S of 10 mL/g-dry, consistent with Draft Method 1313A or

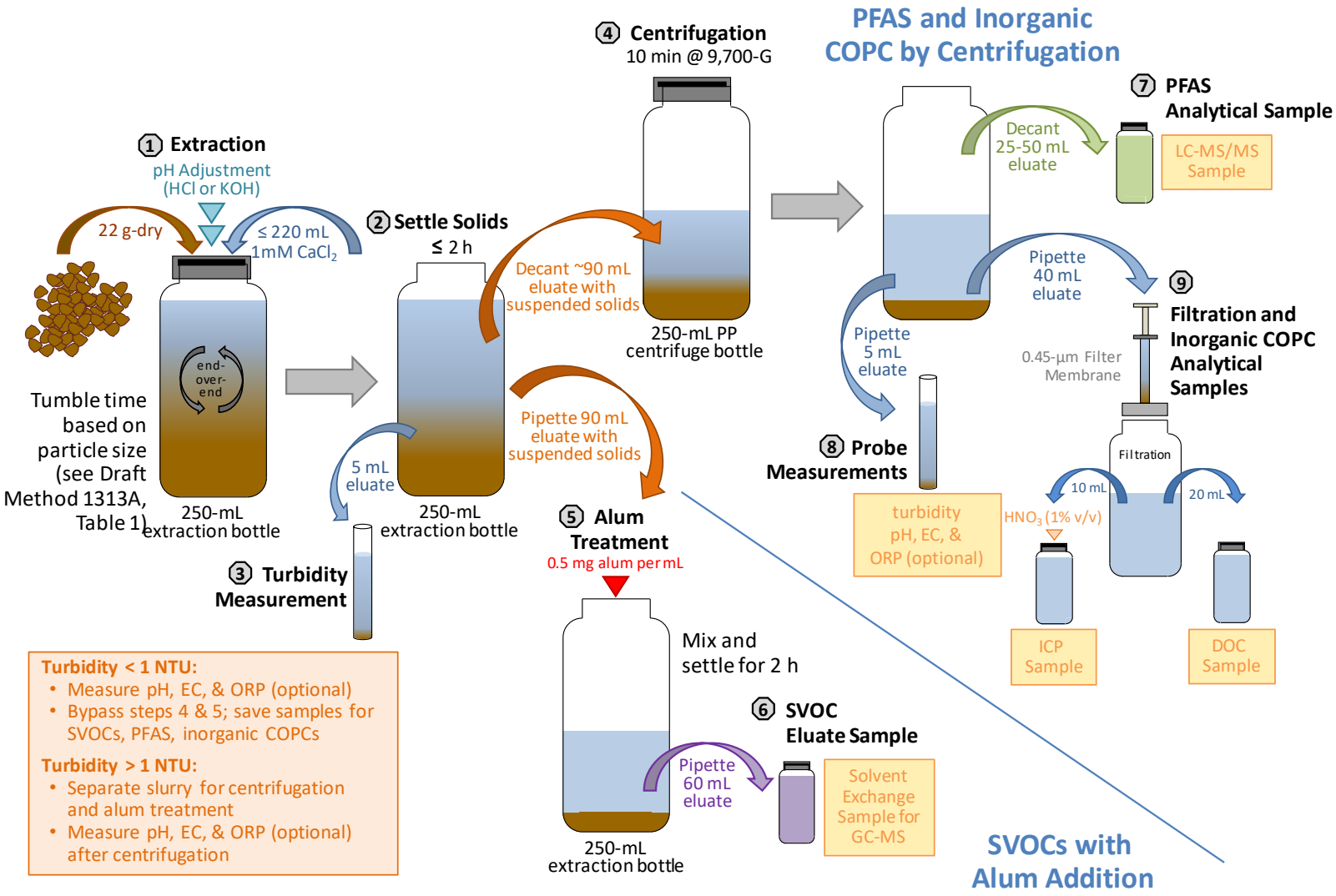

Figure 7-2. Example eluate processing procedure for a batch extraction at L/S of 10 mL/g-dry with analytical sampling for SVOCs, PFAS, and inorganic COPCs.

Draft Method 1316A. The presumed sequence for collecting and preserving analytical samples from leaching test eluates is:

1. Separate of leaching test eluates from sample solids within the extraction vessel by settling for 2 hours.

2. Pipette a nominal 5-mL aliquot of settled eluate and measure and record the turbidity of the unpreserved eluate.

    a. If the turbidity of the aliquot is less than 1 NTU, measure and record the eluate pH, EC, and ORP (optional). The pH measurement should be completed within 15 minutes of settling to minimize the absorption of carbon dioxide from the atmosphere. If ORP is to be measured, eluate separation and ORP measurement, ideally, should be carried out in an inert atmosphere (e.g., under N_2 or Ar). Skip to steps 5, 6, and 8 for collection of analytical samples for SVOCs, PFAS, and inorganic COPCs, respectively.

    b. If the turbidity of the eluate aliquot is greater than or equal to 1 NTU, further clarification to remove colloidal matter is required following the remaining steps in the procedure.

3. Decant approximately half of the settled eluate (~90 mL in the figure) to a clean HDPE or PP centrifuge bottle and centrifuge the bottle for 10 minutes at 9,700-G to further separate suspended solids from the test eluate. Decanting the settled eluate is preferred when PFAS are COPCs due to the tendency of PFAS to accumulate at the air-water interface (Brusseau and Guo, 2021; Constanza et al., 2019; and Schaefer et al., 2019).

4. Pipette the remaining half of the settled eluate into a clean Type I glass bottle for alum treatment by addition of 0.5 mg of alum per mL of eluate. Vortex mix the suspension and allow the alum to settle for 2 hours.

5. Collect a 60-mL aliquot of alum-treated eluate for microextraction into 10-mL of MeCl in preparation of SVOC analysis by GC-MS following Method 3511 (SW-846, 1996c) and Method 8270E (SW-846, 2018b). MeCl-based samples should be preserved by refrigeration to 0-6 °C. The ratio of eluate to solvent may be increased if the mass of SVOC in eluates is below analysis detection limits. In any case, the ratio of eluate to solvent, alternatively the volumes of eluate and solvent, should be recorded.

6. From the centrifuged eluate, collect a 25-50 mL aliquot of clarified eluate in HDPE or PP bottles for PFAS analysis by SW-846 methods 3512 and 8327 (modified using isotope dilution quantification instead of internal-standard corrected external calibration), preserved by refrigeration 0-6 °C. Pipette approximately 5-mL aliquot of the centrifuged eluate. Measure and record the eluate pH, EC, and ORP (optional). The pH measurement should be completed within 15 minutes of settling to minimize the absorption of carbon dioxide from the atmosphere.

7. If ORP is to be measured, eluate separation and ORP measurement, ideally, should be carried out in an inert atmosphere (e.g., under N_2 or Ar). Skip to steps 5, 6, and 8 for collection of analytical samples for SVOCs, PFAS, and inorganic COPCs, respectively.

8. Pipette approximately 50 mL of centrifuged eluate for filtration through 0.45-µm membrane for collection of analytical samples for inorganic COPCs and DIC/DOC measurements

    a. Collect at least 10 mL of filtered eluate for measurement of inorganics by Method 6010D (SW-846, 2018a) and/or Method 6020B (SW-846, 2014), preserved by addition of 1% (v/v) of Optima grade nitric acid.

    b. Collect a 10-mL aliquot of filtered eluate for measurement of anions by Method 300.0 (U.S. EPA, 1993), preserved by refrigeration 0-6 °C (not shown in the **Figure 7-2**).

    c. Collect a 20 mL aliquot of filtered eluate for measurement of DIC and DOC by Method 9060A (SW-846, 2004b), preserved by refrigeration 0-6 °C.

In the above sequence, it is assumed that the scale of the leaching test is designed to provide at least 200 mL (total) of eluate (e.g., Draft Method 1313A and Draft Method 1316A) and the eluate volumes discussed in the sequence represent minimum volumes required for analysis. There are some cases (e.g., first two eluate collections of the Draft Method 1314A), where dilution of analytical samples may be necessary given the limitations of the leaching test parameters. Analytical solutions for all COPC types should be refrigerated at 0-6 °C between collection and analysis.

7.4 Summary of Method Costs and Effort

The BID for the development of LEAF leaching methods for inorganic COPCs included a detailed analysis of the consumables, supplies, and equipment required to conduct each leaching test as well as review of the estimated time to carry out each test. Tables of laboratory supplies and equipment for Draft Method 1313A, Draft Method 1314A, and Draft Method 1316A for SVOCs and PFAS are shown **Appendix E**. Time estimates for each leaching also are presented in the same appendix. **Table 7-2** provides a summary of the supplies and equipment costs and estimated testing times.

Table 7-2. Estimated Supply/Equipment Costs and Technician Time Required to Carry Out Draft Methods 1313A, 1314A, and 1316A

Test Name	Description	Supplies Costs	Equipment Cost	Technician Time (hr)	Testing Time (days)
Draft Method 1313A	pH-dependent batch test	$540	-	4.2	3-4
Draft Method 1314A	Percolation column test	$650	$7,800	4.8	21
Draft Method 1316A	L/S-dependent batch test	$350	$1,500	3.3	2

7.5 Validation of Leaching Test Methods

Prior to incorporation into SW-846 as accepted leaching procedures, the SW-846 LEAF methods were validated for inorganic COPCs through an interlaboratory validation study (Garrabrants et al., 2012a; 2012b). At that time, the program was limited to inorganic COPCs; however, these LEAF tests, primarily European analogs or modified SW-846 tests, have been used for leaching assessment of PAHs (EPRI, 2009; Mougnol et al., 2022; Zand et al., 2010).

7.5.1 International Studies Related to Leaching Test Methods for SVOCs

Over the past decade, European interlaboratory validation studies have been carried out for total content analysis, leaching test eluate analysis, and leaching test methods in the context of several standardization committees (van der Sloot, 2022; **Appendix F**). Materials of interest have been construction products, recycled materials, soils, wastes, and stabilized waste. Constituents of interest have been inorganic elements, PAHs, PCBs, and polychlorinated dioxins/furans. **Table 7-3** presents the median standard deviations for intra-laboratory repeatability (RSD_r) and interlaboratory reproducibility (RSD_R) from several studies for total content analysis, leaching test eluate analysis (multiple analyses of the same eluates), and leaching test methods.

Table 7-3. Median Percent Relative Standard Deviation for Repeatability (RSD_r) and Reproducibility (RSD_R) Associated with Total Content, Eluate Analysis, and Leaching Test Performance from European Interlaboratory Validation Studies for Inorganic and Organic Constituents

	Total Content		Eluate Analysis		Leaching Tests	
Constituents	RSD_r	RSD_R	RSD_r	RSD_R	RSD_r	RSD_R
Inorganic Elements	5-11%	10-31%	<5%	12-15%	5-28%	14-37%
PAHs	7-11%	25-36%	31%	48%	7-51%	52-67%
PCB	6-11%	19-63%	-	-	13%	42%

For inorganic elemental evaluation, the median RSD_r and RSD_R were generally less than 20% for total content, less than 30% for leaching test eluate analysis, and less than 40% for leaching tests performance. The RSD_r values increases considerably when measured concentrations approach the method limits of detection (LODs) as shown in **Figure 7-3** and **Figure 7-4**; however, the increase in RSD_r may not be problematic if the applicable regulatory threshold is substantially greater than the LOD.

For PAHs, the median RSD_r and RSD_R have been generally less than 40%, while eluate analysis is generally less than 50%, and leaching test results greater than 50%. However, leaching test eluates from construction products typically had very low PAH concentrations (90^{th} percentile <5 µg/L) resulting in more variability in the reproducibility value.

For many of these studies, it is difficult to separate the RSD_r and RSD_R associated with eluate analysis from the RSD_r and RSD_R for the leaching test for which eluate analysis is an integral part. Therefore, it is unlikely that the RSD_r and RSD_R for leaching tests would be considerably less than that RSD_r and RSD_R for eluate analysis.

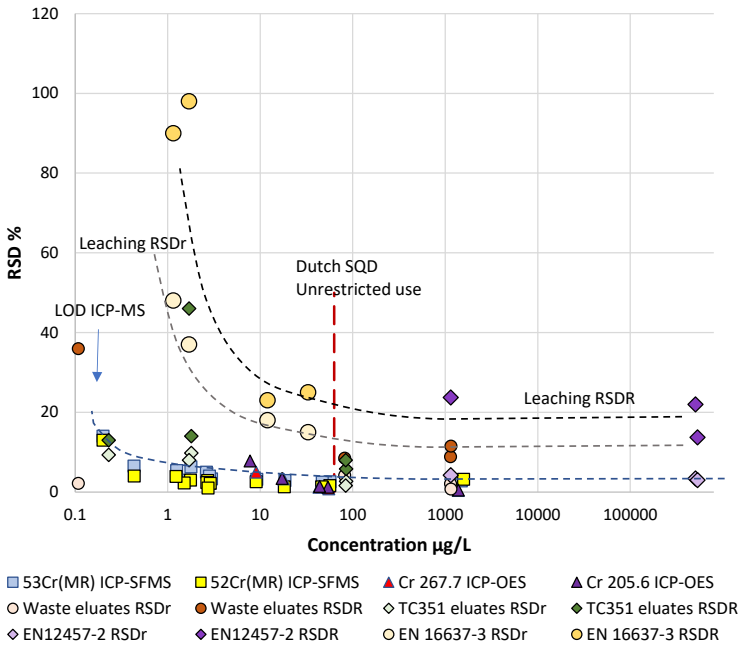

Figure 7-3. Relationship between chromium concentration level, analytical performance, leaching test performance, and regulatory criteria.

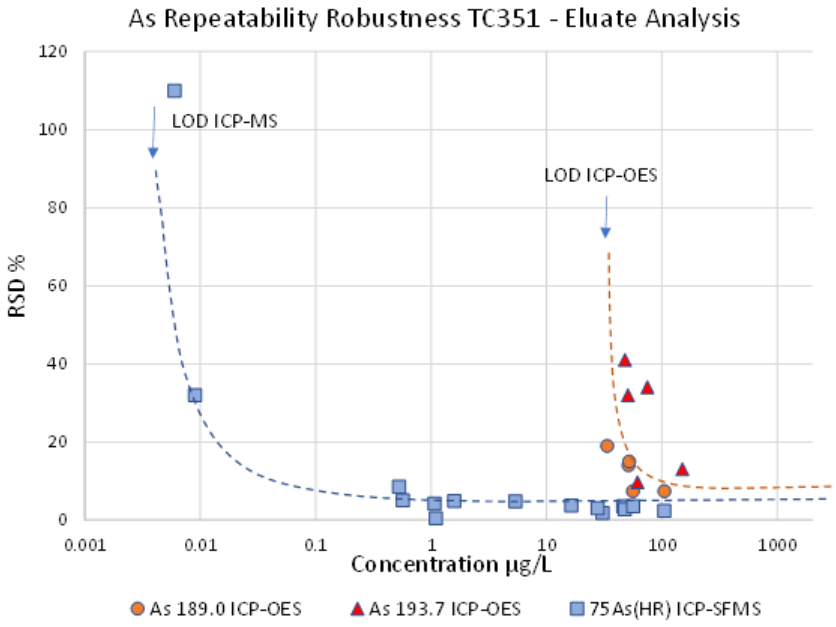

Figure 7-4. Mean repeatability standard deviation (*n*=10) for eluate analysis of arsenic in construction products by ICP-OES and ICP-MS (robustness study TC351) in comparison to method limits of detection (LODs).

8 BID Conclusions

This BID provides a review of the state-of-the-science for leaching tests applied to SVOCs (e.g., phenolic compounds and PAHs) and PFAS. The gaps in the literature were identified and investigated through a series of targeted experiments that support the method development of the LEAF methods for parallel assessment of SVOCs, PFAS and inorganic COPCs. The LEAF leaching methods, as published in SW-846 and validated for inorganic COPCs and non-volatile organic compounds like DOC, were adapted to address the specific characteristics of the target analytes.

The method development was supported by a series of experiments that explored (i) sorption and release COPCs to various materials of construction (**Appendix C-2**), (ii) management of colloids which may be enhanced when agitation is used to mix batch leaching tests (**Appendix C-3**), and (iii) procedures for optimizing the processing of eluates after leaching tests for parallel evaluation of SVOCs, PFAS, and inorganic COPCs (**Appendix C-4** and **Appendix C-5**). To the extent possible, these experiments used commonly available laboratory materials and a combination of standard COPC solutions and contaminated solid materials containing COPCs. Evaluation for these studies included analysis of surrogate COPCs (SVOCs) and negative/positive controls.

8.1 Modifications to SW-846 Methods

In general, more modifications were made to address SVOCs than PFAS. This was because the materials of construction for PFAS did not need to be changed from the HDPE bottles used with inorganic COPCs. Changes to the published methods for SVOCs centered around materials of construction (i.e., avoiding the use of PP, HDPE, LDPE, and other plastics as SVOCs are likely to sorb to contact surfaces) and minimizing volatility losses (i.e., use of VOA vials and bottles in batch extraction tests and a leak tight eluate transfer and collection system for the column test).

8.1.1 General Leaching Test Recommendations

Laboratory leaching test procedures should be carried out with minimal headspace, especially when SVOCs or other potentially volatile species are of concern. All apparatus should be constructed of materials for primary and secondary components (e.g., liners and seals) that avoid or minimize adsorption of COPCs (**Table 7-1**). Eluate transfers and air contact should be minimized throughout all handling. For SVOCs, samples are recommended to be tested within 14 days of receipt, complete the extraction of aqueous eluates into solvents within 7 days of eluate production, and analyze the solvent extracts within 40 days (see SW-846, Chapter 4, Table 4-1). All aqueous and solvent extracts should be stored at 0-6 °C.

One modification applied throughout the draft methods is that the default eluent was changed from reagent water to 1-mM $CaCl_2$ solution to minimize the deflocculation of clay minerals and dissolution of solid organic matter leading to enhanced colloid formation. Other test-specific modification made to address SVOC leaching included:

8.1.2 Changes to Leaching Methods for SVOCs

Draft Method 1313A for SVOCs

- SVOCs should be tested in Type I or Type III glass vessels, preferably VOA vials, to minimize the loss of SVOCs that would occur in PP, HDPE, LDPE, or other plastic vessels. While stainless-steel vessels were shown to be acceptable relative to SVOC sorption, the release of Cr, Fe, and Mn to stainless steel, as well as the low-

concentration sorption of Cu, Cr, Fe, Ni, Mn, and Zn to stainless steel surfaces, may interfere with parallel assessment of SVOCs and inorganic COPCs.

- HCl is recommended to lower eluate pH as it is less oxidizing than HNO_3; however, HNO_3 may be used if chloride from acid addition is expected to interfere with the test results (e.g., increase complexation of inorganic COPCs).

- Settling for up to 2 hours at room temperature is the primary method for gross separation of solids and liquids after which further clarification via centrifugation is required. For eluate fractions for SVOC analysis, low-G centrifugation in glass vessels is possible; however, smaller vessels appear to be more efficient at clarification than larger vessels. Therefore, it may be necessary to centrifuge multiple smaller glass vessels in order to obtain sufficient sample for SVOC analysis.

- During test sample preparation of aggregate materials (e.g., soils), options were included to use larger particle sizes which require less material handling and to decrease potential losses via volatilization. Soil aggregates may disaggregate during tumbling, effectively behaving like small particles.

Draft Method 1314A for SVOCs

- For SVOCs, a revised column apparatus was developed from 316L stainless steel columns, valves, and transfer lines that feed into Type III glass eluate collection vessels. Secondary materials such as valve seats and gaskets should be made of a compatible material for SVOCs and the contact time for eluates and secondary materials should be minimized.

- Columns are packed with “as received” material with minimal or no particle size reduction which minimizes the loss of SVOCs during sample preparation.

- The eluate flow rate was reduced to 0.5±0.15 L/S per day, relative to the published flow rate of 0.75±0.25 L/S per day, increases the residence time of eluent within a shorter bed of test material while allowing for more practical working day collection intervals.

Draft Method 1316A for SVOCs

- Apparatus and method changes follow those made for SVOC analysis using Draft Method 1313A.

- Use of 316L stainless-steel low L/S centrifugation devices to enhance the separation of liquid eluates from solid materials provides a higher yield of eluate from batch extractions at L/S ≤1 mL/g-dry.

8.1.3 Changes to Leaching Methods for PFAS

Relative to changes made to address SVOC leaching, changes for PFAS leaching methods were minimal but include some of the same changes. Since many PFAS are non-volatile and showed little sorption to the same materials of construction recommended in the current LEAF methods. However, PFAS may be released from polyethylene that has been fluorinated as a finishing technique (Vitale et al., 2022). All sources of leaching vessels and apparatus should be tested for PFAS contamination prior to use. Testing may be carried out by exposing samples of the materials to 1-mM $CaCl_2$ overnight and collecting aliquots of the eluate for PFAS analysis. On a regular basis (i.e., with every set of test replicates), method blanks should be monitored to

ensure that apparatus materials of construction did not leach PFAS or the presence of spurious contamination.

Draft Method 1313A and 1316A for PFAS

- Materials impacted by PFAS should be testing in HDPE bottles, or alternatively, in amber borosilicate glass vials. Fluorinated polymers (e.g., PTFE or PCTFE) should be avoided due to the potential for PFAS release.
- HCl is used to decrease the pH of eluates less than the natural pH to minimize the potential for oxidation.
- Gross separation of solids and eluates is conducted by initial settling followed by centrifugation. It is not recommended to use filtration to separate solid and liquid phases when PFAS are COPCs due to PFAS loss to filtration membranes.
- Use of 316L stainless-steel low L/S centrifugation devices to enhance the separation of liquid eluates from solid materials provides a higher yield of eluate from batch extractions at L/S ≤1 mL/g-dry.

Draft Method 1314A for PFAS

- The quartz sand used for material support, flow regulation, and eluate coarse filtration has been shown to sorb PFAS (**Appendix C-2.7**). Therefore, all quartz sand used for PFAS experiments should be triple rinsed in MeOH, triple rinsed in DIW, and air-dried prior to testing and use.
- Eluates collection bottles should be sonicated 30 mins at 40 °C prior to subsampling to dissolve sorbed PFAS from contact surfaces. Filtration is not recommended due to adsorption of PFAS for filtration apparatus.

8.2 Demonstration of Leaching Methods

The developed leaching methods were demonstrated by conducting each method for at least two waste materials. For SVOCs, the study materials included a coal-tar impacted soil from a former MGP site and a creosote-impacted soil from a remediation project. The demonstration of the methods for PFAS was carried out on four AFFF-impacted soils collected from military firefighting activity facilities. Since these are field materials and not certified materials, the full range of COPCs was not available for each material. The repeatability of triplicate demonstration results was considered good, with tight replication given the estimated uncertainty of the analytical methods for SVOCs (±20% for GC-MS) and PFAS (±30% for LC-MS/MS).

In addition, the response of the draft methods for inorganic COPCs was considered important as the draft methods should not reduce the test response for inorganic COPCs. The results of each draft method were compared to the results of the SW-846 methods. The comparison indicated that differences between the two leaching methods were within the uncertainties of the analytical method. Therefore, it is expected that the repeatability and reproducibility of the draft methods would be comparable to that of the validated SW-846 methods.

For PFAS, the results of the Draft Method 1314A using an apparatus made of stainless steel with eluate collection in Type III glass containers (i.e., as recommended for evaluation of SVOCs) was found to show no difference in the test results compared to the acrylic column with

HDPE collection bottles (i.e., recommended for evaluation of inorganic COPCs). Therefore, the simultaneous determination of SVOCs and PFAS from a single eluate is possible but may require a specified eluate processing procedure described in the draft methods.

8.3 Ongoing and Future Research

The research conducted in support of this BID adds to the background on the use of leaching tests for SVOC and PFAS. Some of this information should be developed into peer-reviewed manuscripts (e.g., the materials of construction experiments). Similar studies are not readily available.

The draft leaching methods should undergo interlaboratory validation in accordance with Agency recommendations to develop repeatability (intra-laboratory variance) and reproducibility (inter-laboratory variance) for the extraction methods. A program for this validation has been developed under a quality assurance project plan (U.S. EPA, 2023a). The validation study would target four participating laboratories conducting each leaching test in triplicate on at least two solid materials containing SVOCs and two materials containing PFAS. To the extent possible, each material should include inorganic COPCs so that repeatability and reproducibility can be compared to the LEAF method interlaboratory studies (Garrabrants et al., 2012a, 2012b). Ideally, the materials would contain all three contaminant types, although this is unlikely.

9 Quality Assurance/Quality Control

This section outlines the QA/QC protocols performed according to the approved Quality Assurance Project Plan (QAPP) K-HSMMD-0030117-QP-1-2 (U.S. EPA, 2019b; approved 16-Jan-2020) which focuses on ensuring the accuracy and reliability of leaching methods for materials containing semi-volatile organic constituents. The QAPP encompasses experimental design, general laboratory equipment calibration and monitoring, standardized and customized analytical methods, material property determinations, total carbon analysis, and specific chemical analysis methods for SVOCs and PFAS.

9.1 Personnel Training and Qualifications

VU has entrusted a team of highly qualified personnel to implement this project. Their expertise in developing leaching methods and executing test procedures aligns with the stringent guidelines of the QAPP approved by the EPA. This ensures that all chemical analyses are conducted with precision and accuracy reflective of the department's commitment to excellence.

The project PI and co-PI each hold a doctorate (Ph.D.) in chemical engineering and have more than 35 and 20 years, respectively, in development and use of leaching test methods and environmental assessments. Graduate students working on the project are focused on development and use of leaching test methods for specific applications as part of Master of Science (M.S.) or Ph.D. research in environmental engineering. Students are required to review relevant agency reports and peer-reviewed literature, both from the U.S. and internationally, as part of their training. Laboratory staff members typically have completed a Bachelor of Science (B.S.) or equivalent degree, and more than half of the laboratory staff have an advanced degree in chemistry, environmental science, or engineering. All graduate students and staff are initially trained on specific procedures under the tutelage and supervision of senior staff members (i.e., with either a relevant M.S. or Ph.D. and 5 or more years of experience). Training of all personnel includes laboratory experience in carrying out basic procedures (e.g., pipetting, weighing) and leaching tests according to standard procedures, data management and analysis, and quality assurance/quality control. Periodic reviews of all staff and student performance occurs along with data quality reviews, typically in conjunction with each set of experiments (e.g., weekly to monthly).

9.2 General Laboratory Equipment Calibration and Monitoring

Calibration and maintenance of laboratory equipment are critical to ensure that each piece of equipment adheres to established standards and procedures, which is fundamental for the generation of accurate and reliable data. Adherence to a calibration and operation protocol is a key component of maintaining the integrity and quality of the environmental analyses conducted in the project. VU has verified that all the equipment has been certified calibrated or having the calibration validated at the time of use.

Table 9-1 provides a non-exhaustive list of primary laboratory equipment used in this project and their calibration procedures. Specific recalibrations and corrective actions were taken if tolerances were not met, including the replacement of the equipment.

Table 9-1. General Laboratory Equipment Calibration and Monitoring

Item	Capabilities	Model Manufacturer	Calibration Procedure and Frequency
Heavy Duty Tumbler	28±2 rpm Holds minimum of twelve 250-mL VOA vials	EW-35208-00 Environmental Express	Followed equipment manual for specific maintenance procedures and safety checks.
Centrifuge	Capable of 7,500 rpm for 10 minutes Swinging bucket rotor for 250-mL bottles	Sorvall Lynx 4000 ThermoFisher Scientific	Followed equipment manual for specific maintenance procedures and safety checks.
Refrigerator	Cold storage at 0-6 °C	Fisher TSX2305SA	Monthly temperature monitoring for sample and standard storage; system alarms if temperature deviates out of specified range.
Pan Balance 1	2,200 g x 0.01 g	Scout SPX2202 Ohaus Corporation	Semi-annually certified calibration and checked prior to each use with a certified check weight for accuracy.
Pan Balance 2	15,000 g x 0.5 g	Ranger R31P15 Ohaus Corporation	Semi-annually certified calibration and checked prior to each use with a certified check weight for accuracy.
Analytical Balance	220 g x 0.0001 g	NewClassic ME Mettler Toledo	Semi-annually certified calibration and checked prior to each use with a certified check weight for accuracy.
pH/Conductivity Meter	pH: -2 to 20 EC: 0 to 500 mS mV: ±2,000 mV	Accumet XL200 ThermoFisher Scientific	External calibration certification semi-annually; calibration verified before each use with certified calibration standards.
pH Probe	pH: 1 to 14	Accumet pH/ATC electrode ThermoFisher Scientific	External calibration certification semi-annually; calibration verified before each use with certified calibration standards.
Conductivity Probe	EC: 0 to 500 mS	Accumet 2-cell probe ThermoFisher Scientific	External calibration certification semi-annually; calibration verified before each use with certified calibration standards.
Turbidity Meter	1,000 - 0.1 NTU	Orion AQUAfast AQ3010	External calibration certification semi-annually; calibration verified before each use with certified calibration standards.
Pipette Controllers and Disposable PP Pipette Tips	10, 5, 1, and 0.25-mL	Finnpipette FBE1000 ThermoFisher Scientific	Annual calibration and regular gravimetric checks ensure precise volume delivery. Users must demonstration accuracy and precision at least annually based on gravimetric verification of volume delivered by pipette.

9.3 QA/QC in Experimental Design

During the development of the leaching methods in this BID, all experimental designs included the following QA/QC samples and checks:

- Method Blanks – Experiments conducted with the same reagents and processes, but without solid materials designed to check that leaching vessels and reagents to not contain COPCs. These QA/QC extractions are sometimes referred to as negative controls. All negative controls are checked to ensure that COPC concentrations are less that quantitation limits or are <10% of the median COPC concentration.
- Positive Controls – Experiments conducted with the same reagents and processes with a known amount of COPCs included at the start of the experiment. Thus, the expected concentration of COPCs in the final analytical solution is known or calculatable. Depending on the experiment, the experiment may be conducted without a solid matrix.
- Replication – All experiments were conducted with at least 2, and sometimes up to 5, replicates so that trends and conclusions may be based on average impacts rather than single values.

The specific application of these QA/QC samples depends on the structure and nature of the specific experiment to be conducted. Details of these experiments, including the experimental design and replication, are presented in **Appendix C** of this BID.

9.4 Material Preparation and Characterization

This section includes specific QA/QC procedures applied for sample preparation including sample characterization, homogenization, preservation, holding times, and analytical method criteria.

9.4.1 Study Materials

In this study, soil samples contaminated in the field were sent to VU for analysis under COC in 5-gallon HDPE buckets. These samples were initially sieved through a 6-mm mesh to remove larger inert materials like rocks, sticks, roots, etc. The mass and type of discarded materials were documented with photographs and noted in the lab notebook. Post-sieving, the samples were systematically quartered and re-sieved through a 2-mm mesh multiple times, ensuring thorough homogenization. Particles not passing through the mesh were recorded to quantify oversized rejects. Homogenized samples were stored in 1-L HDPE jars for subsequent testing and analysis.

The homogeneity of field source materials was evaluated following sieving and quartering by extraction a minimum of four 10-g samples of solid sample using a solvent designed to quantitative extract the total elemental content (TEC) of SVOCs or PFAS, depending on the contaminants in each material. Homogenization was considered acceptable if the following RSD values were met after solvent extraction followed by chemical analysis:

- RSD ≤20% for major COPCs (TEC >1% by mass),
- RSD ≤30% for minor COPCs (0.1% ≤ TEC ≤ 1% by mass), and
- RSD ≤50% for trace COPCs (TEC <0.1% by mass).

9.4.2 Study Material Property Determinations

As part of basic characterization of demonstration materials, VU conducted physical and chemical testing as described below. Whenever possible, standard methods as cited were used to perform required measurements; however, where standard methods were not available, operating procedures were written to describe the associated activities.

9.4.2.1 Moisture Content

MC was determined for each study material using ASTM D2216 (ASTM, 2019). The process involved comparing the mass of wet samples against that of the samples once oven dried. Notably, for materials with hydrated minerals like gypsum, a reduced drying temperature of 60 °C was employed, instead of the standard 110 °C, to prevent mineral dehydration and unintended formation of calcium sulfate hemihydrates. This adjustment allowed for accurate moisture assessments without altering the mineralogical composition of the samples.

9.4.2.2 Total Elemental/Organic Carbon Analysis

TEC and TOC were determined on the solids by VU using a Shimadzu model TOC-LCPH (Shimadzu Scientific instruments, Inc., Columbia, MD) equipped with a Total Carbon Analyzer following a method defined in National Institute of Occupational Safety and Health (NIOSH) Standard Method 5040 (NIOSH, 2018). This equipment uses a furnace to heat the sample and combust carbon to carbon dioxide. The carbon dioxide is reduced to methane and flame ionization detection is used to quantify the carbon emitted as the sample is heated from ambient to 870 °C in four heating steps.

9.5 Sample Preservation and Holding Time

9.5.1 Solid Samples

Bulk solid samples were stored at room temperature in sealed containers in a manner consistent with field conditions until processed as a study material. After homogenization, solid samples were stored in 1-L glass jars at a temperature 0-6 °C until they were used for testing. As utilized in this BID, bulk solid materials were used in a comparative manner (i.e., to illustrate differences in experimental treatments) rather than as a characterization material. Therefore, the hold time for solid samples prior to testing was not applicable unless the “as received” samples were part of time-dependent (e.g., aging) study.

9.5.2 Eluate Samples

Eluate samples were preserved according to the determinative methods for chemical analysis for inorganic COPCs, SVOCs, and PFAS. Example preservation protocols were: (i) acidification of eluates for inorganic COPCs with HNO_3 to a final concentration of 1%, (ii) microextraction of aqueous SVOC eluate into MeCl solvent, and (iii) addition of methanol to PFAS samples to maintain constituents in solution. In addition, all eluate samples, aqueous and solvents, were stored at 0-6 °C prior to analysis and, when applicable, shipped under COC with temperature monitoring. Sample analyses were performed within 14 days of generation for SVOCs and 28 days of generation for PFAS and inorganic COPCs.

Table 9-2. QA/QC Metrics, Frequency, Acceptance Criteria, and Corrective Actions for IC, ICP-OES, and ICP-MS Analyses

QA/QC Metric	Frequency	Acceptance Criteria	Completeness	Corrective Action
ICAL Curve	1 per monthly analysis	R^2 ≥0.99	90%	• re-calibrate • make new ICAL standards
ICV Checks	1 per ICAL 1 per analysis	80% ≤ %R ≤ 120%	90%	• make new ICV standard • create new ICAL curve
CCV Standard	1 per 20 samples	80% ≤ %R ≤ 120%	90%	• make new CCV standard • create new ICAL curve
Matrix blanks	Immediately following ICVs and CCVs	conc <MDLs	90%	• make new MB • make new ICAL curve
Matrix spikes	At least 1 per batch or 20 samples, whichever is more frequent	Recovery ±20%	90%	• check for interferences and rerun sample after dilution if appropriate

Table 9-3. QA/QC Metrics, Frequency, Acceptance Criteria, and Corrective Actions for GC-MS Analysis

QA/QC Metric	Frequency	Acceptance Criteria	Completeness	Corrective Action
ICAL Curve	1 per analysis	R^2 ≥0.99	90%	• re-calibrate • make new ICAL standards
ICV Checks	1 per ICAL 1 per analysis	70% ≤ %R ≤ 130%	90%	• re-analyze ICV • make new ICV standard • create new ICAL curve
CCV Standard	1 per 12 hours run time	70% ≤ %R ≤ 130% % drift ≤25%	90%	• re-analysis CCV standard • consider results as estimates
Matrix blanks	Immediately following ICVs, CCVs, and samples expected at high concentration	conc ≤0.5 LLOQ or conc ≤10% of mean sample concentrations	90%	• make new CCV-MB tandem • GC-MS maintenance
Surrogates	All samples	70% ≤ %R ≤ 130%	90% for 2 or 3 surrogates	• re-analyze sample • consider results as estimates
ISTDs	All samples	50% ≤ ISTD ≤ 200%	90%	• check ISTD addition

9.6 Analytical QA/QC Metrics

The section details the rigorous analytical QA/QC metrics used for both organic and inorganic analyses, including the processes for ICALs, verification checks, and sample preparation quality controls. It also outlines the frequency, criteria, and corrective actions for IC, ICP-OES, and ICP-MS (**Table 9-2**), and GC-MS (**Table 9-3**). In addition, matrix blanks, matrix spikes, and duplicates were employed to ensure the integrity of sample analysis, while detection and quantitation limits were established as per EPA recommendations. Acceptance criteria for individual target PFAS are provided in Table 5 of Method 1633 (EPA, 2024).

9.7 Assessments of Data Quality Indicators

The data quality objectives of the study (DQOs) define the critical measurements needed to address the stated objectives and specify tolerable of potential errors associated with the experimental setup. The following measurements have been critical to accomplish the project objectives. Decisions to accept or reject tests were based on engineering judgment used to assess the likely impact of the parameter on the conclusions drawn from the data.

Table 9-4. Data Quality Indicator Goals

Measurement	Sample Types	Testing Method	Accuracy	Precision	Completeness
Moisture Content	solids	ASTM D2216	NA[1]	±10%	100%
Organic COPCs	digests, eluates	Method 8270E Method 8327	±30%[2]	±30%[2]	>90%
Inorganic COPCs	digests, eluate	Method 6020A	±20%	±20%	>90%
pH, Conductivity	eluates	electrode	±2%	±2%	>90%

Notes: [1] accuracy is not applicable for moisture content as no standard MC sample is available.

[2] accuracy and precision for organics analysis will depend on the specific matrix and suite of organic COPCs present in each matrix considered. Values indicated here are initial estimates only.

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