The Next Frontier Towards Waste Characterization – Upcoming Activities of SW-846 Methods

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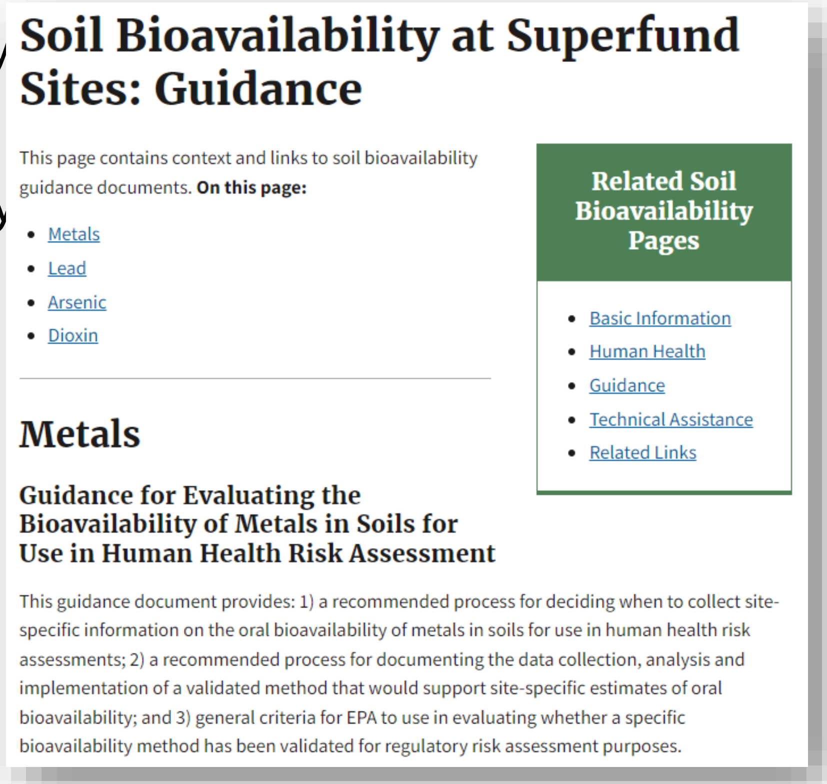
Overview

Topics

1	Method 1340 – In Vitro Bioaccessibility Assay for Lead and Arsenic in Soil
2	Method 6200 – X-Ray Fluorescence Spectrometry for Elemental Concentrations
3	Method 3060 – Alkaline Digestion for Cr(VI)
4	ASTM / EPA Collaborative Methods
5	Guidelines on Validation of Non-Regulatory Methods
6	Guidelines on Sample Collection and Processing of Waste
7	Additional Methods

Method 1340 – In Vitro Bioaccessibility Assay for Lead and Arsenic in Soil

- Standard Operating Procedure for an In Vitro Bioaccessibility Assay for Pb and As in Soil
- Validation Assessment of the In Vitro Arsenic Bioaccessibility Assay for Predicting Relative Bioavailability of Arsenic in Soils and Soil-like Materials at Superfund Sites (OLEM 9355.4-29 April 20, 2017)
- Guidance for Sample Collection for In Vitro Bioaccessibility Assay for Arsenic and Lead in Soil and Applications of Relative Bioavailability Data in Human Health Risk Assessment
- Fact Sheet: Relative Bioavailability and In Vitro Bioaccessibility of Lead in Soil
- Fact Sheet: Relative Bioavailability and In Vitro Bioaccessibility of Arsenic in Soil



Soil Bioavailability at Superfund Sites: Guidance

This page contains context and links to soil bioavailability guidance documents. **On this page:**

- Metals
- Lead
- Arsenic
- Dioxin

Related Soil Bioavailability Pages

- Basic Information
- Human Health
- Guidance
- Technical Assistance
- Related Links

Metals

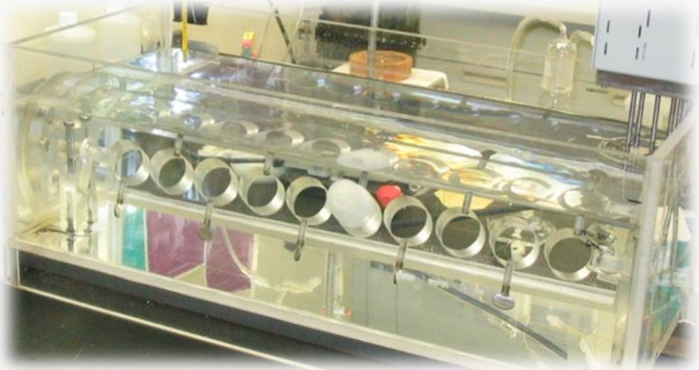
Guidance for Evaluating the Bioavailability of Metals in Soils for Use in Human Health Risk Assessment

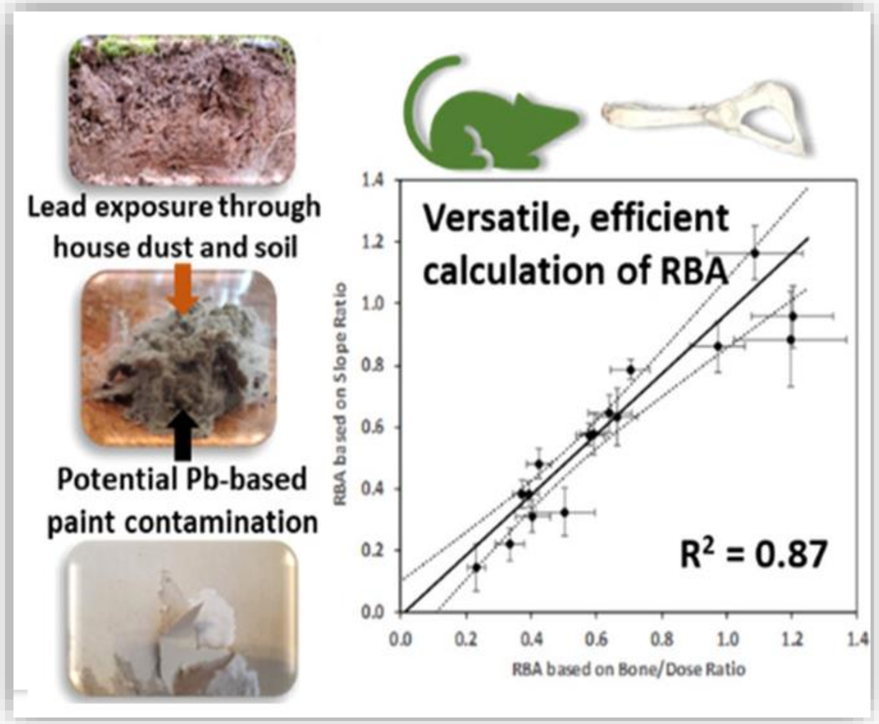
This guidance document provides: 1) a recommended process for deciding when to collect site-specific information on the oral bioavailability of metals in soils for use in human health risk assessments; 2) a recommended process for documenting the data collection, analysis and implementation of a validated method that would support site-specific estimates of oral bioavailability; and 3) general criteria for EPA to use in evaluating whether a specific bioavailability method has been validated for regulatory risk assessment purposes.

https://www.epa.gov/superfund/soil-bioavailability-superfund-sites-guidance

Why a Method for Pb and As Bioaccessibility?

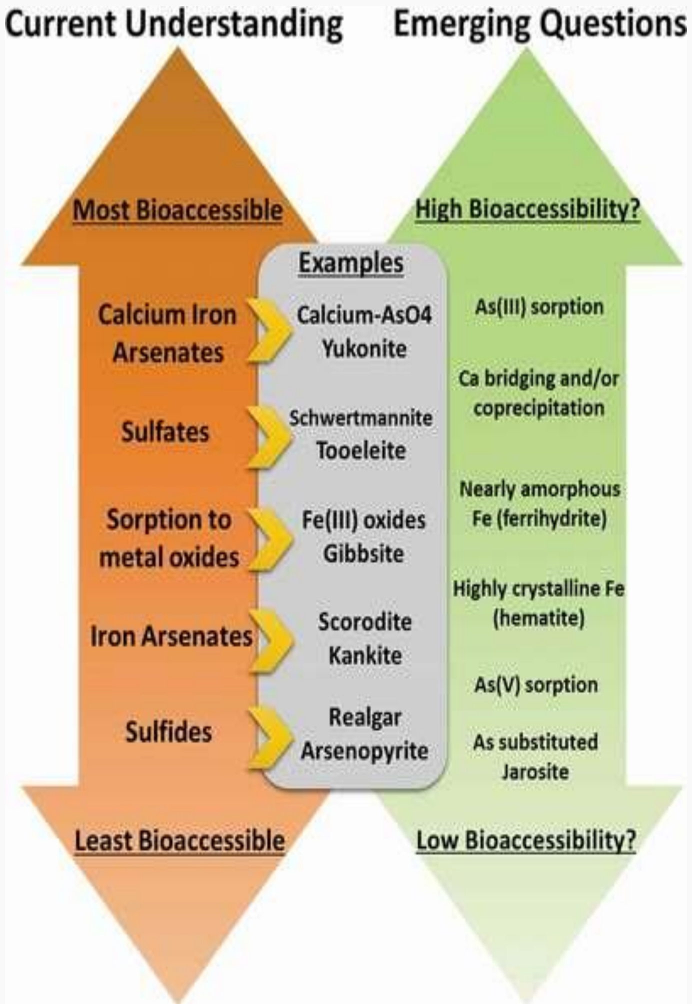
- Determining bioavailability for soil contaminants is important for understanding site-specific risk
- Previous *in vivo* method – cost prohibitive
- Method 1340 (*in vitro)* – reliable, rapid, reproducible, considerably less expensive
  - reduces the clean-up costs at contaminated hazardous waste sites





Why a Method … (contd.)

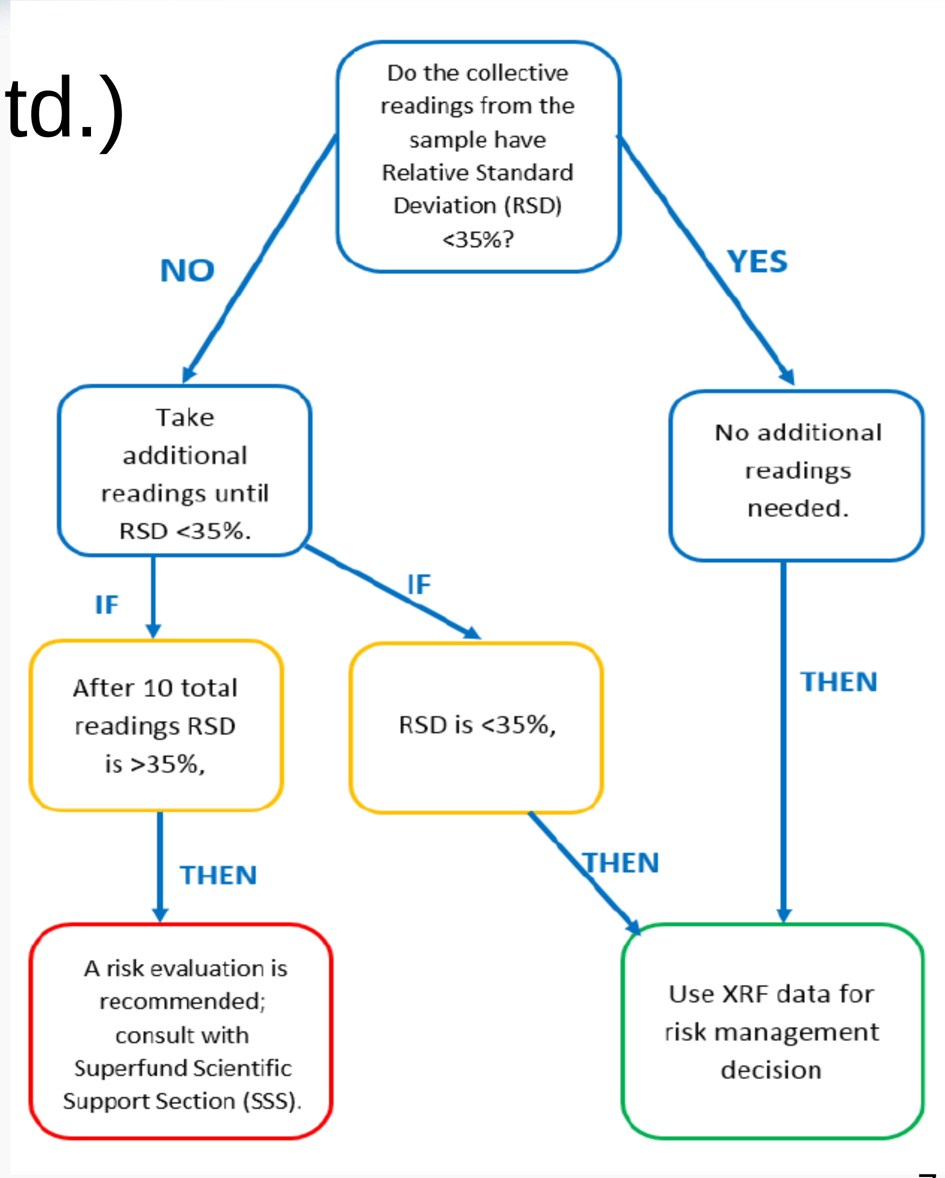
- Commonly found together at sites and accurately measuring their RBA has a significant impact on the risk assessment and on the selection of cleanup levels.
- Does not require the use or sacrifice of animals. and the reduced cost per sample allows risk assessors to obtain a more representative number of samples per exposure unit.
- Incorporation of As into the already existing method for Pb means that laboratories already have experience performing the assay.



Updating **Method 6200** – X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment

Updating **Method 6200** (contd.)

- XRF can guide real-time, in-field choices, set decision unit (DU) boundaries, and evaluate sample processing.
- Technological progress enabled broadening of elements, rapid, low cost, and nondestructive analysis - detection limits for most of trace elements are usually below regulatory levels.
- Does not produce analytical waste, low energy consuming, safe and easy to operate.



Method 3060 – Alkaline Digestion for Cr(VI)

Method Parameters

- High pH (~13) and high carbonate
- Liquid : solid ratio = 20 mL/g
- Borosilicate glass or quartz extraction vessels
- Stir samples at 90-95ºC for at least 1 hour
- Adjust pH to 7.5 with nitric acid

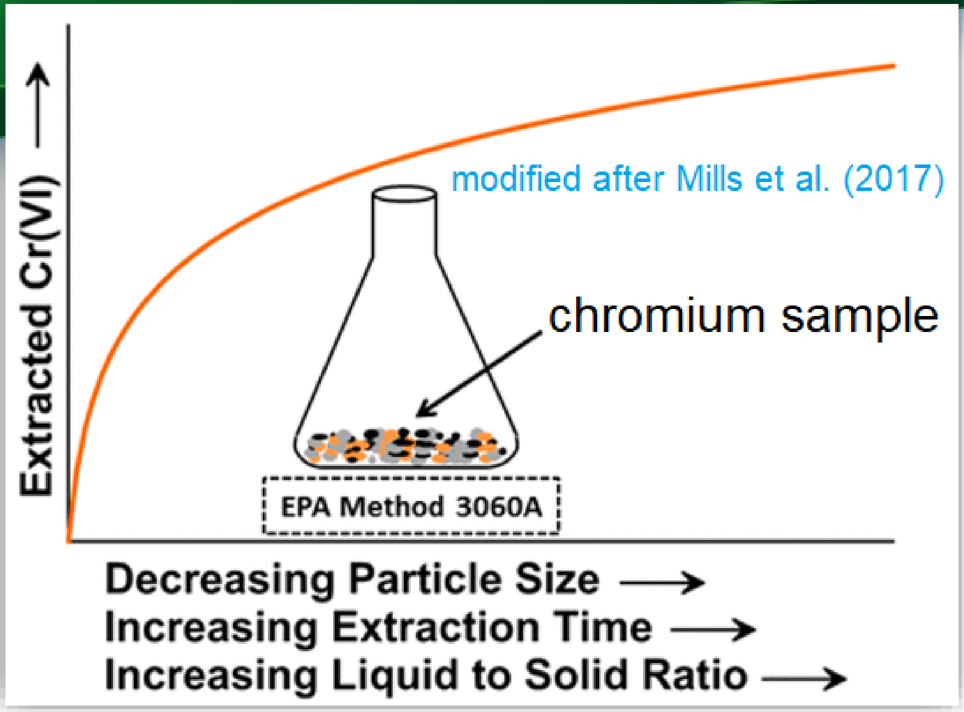
Analysis

- 7196A Visible Spectrophotometry
- 7199 Ion Chromatography
- 6800 Speciated Isotope Dilution Mass Spectrometry

Challenges of Existing Method 3060

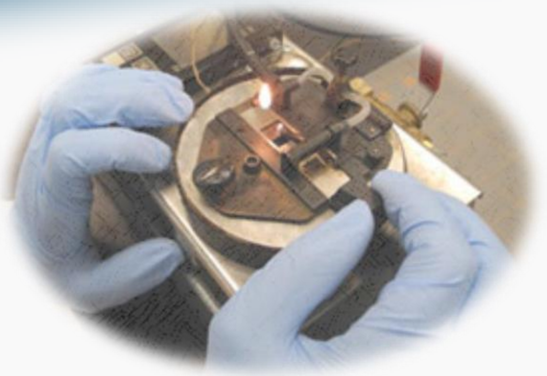
- Incomplete Cr(VI) Extraction
  - USGS studies show extraction of Cr(VI) is not quantitative compared to X-ray absorption near edge structure (XANES) spectroscopy results.
- Difficult to Operate
  - Does not address heterogeneity or particle size.
  - Addition of $MgCl_2$ causes immediate precipitation of hydroxides and carbonates.
  - Interferences due to phosphate.
  - Large amounts of chromite/magnetite coat stir bars which interferes with their function and may affect extraction efficiency.

Potential Updates - Method 3060



- Particle Size
  - Smaller size
- Extraction Vessel
  - High pH/high carbonate extraction fluid dissolved borosilicate glass
  - PTFE extraction vessels
- Liquid to Solid Ratio
  - ~1000 (50x that of 3060A prescribed ratio)
- Extraction Time
  - Dissolution of mineral phases and exchange processes may be kinetically limited (48 hours)

ASTM / EPA Collaboration



- Interlaboratory studies for D8174-18, D8175-18
  - Modernizing Ignitable Liquids Determinations rule finalized in 2020, incorporated D8174 and D8175: RCRA ignitability characteristic regulation
  - Based on ASTM D3278-78 (Small scale closed cup), D93-79/D93-80 (Pensky-Martens)
  - Maintain method-defined elements - cup dimensions, materials of construction, sample size, heating rate
  - Standards need interlaboratory studies to generate precision statements
  - SW-846 methods team working with National Enforcement Investigations Center laboratory, D34 committee

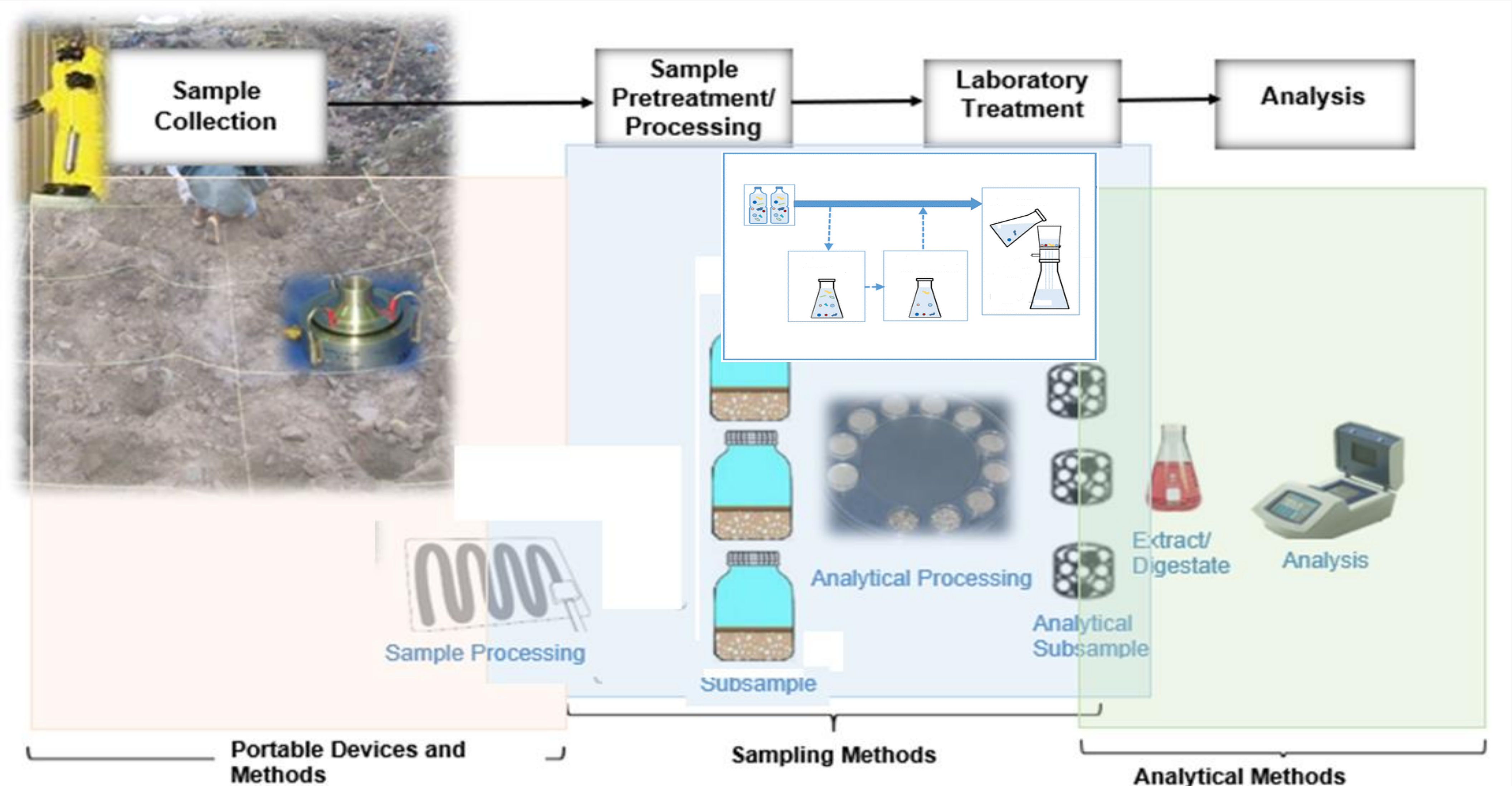
Updates to **SW-846 Method Validation Guidance**

New!!!

"***Guidelines on Validation of Non-Regulatory Chemical and Radiochemical Methods***", EPA/600/B-**22**/001 https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=354570&Lab=IO

- Based on memos written in 1992: https://www.epa.gov/hw-sw846/guidance-methods-development-and-methods-validation-resource-conservation-and-recovery-act
- Benefits of revision:
  - ✓ Better define EPA's expectations of data to support publication of methods
  - ✓ Standardize evaluation of method performance
  - ✓ Streamline project planning
- References:
  Guidelines for evaluation of multi-laboratory validation data (e.g., AOAC, ASTM, EPA)

Sample Collection and Processing of Waste



Soil is a natu
organic matte
surface, occu
of the followi
from the initi
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ability to sup
Factors affec
pathogens are
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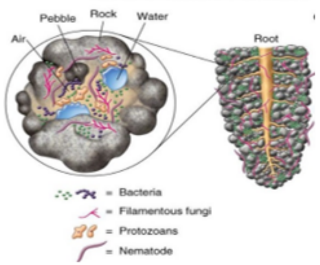
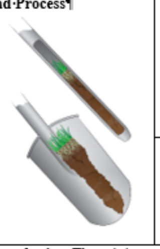


Soil Sampling Strategies: Size, Number and Type of Samples

Soil Sample Collection - Planning/Preparation and Process
• Identification and selection of sam
• Sample containers of the proper siz
• Quality control samples (e.g., field duplicates, performance evaluatio
• Bound field logbook, writing instru and permanent markers), camera a batteries.
• Appropriate paperwork (e.g., Chai and Calibration forms)
• Sample labels



Sampling Process Most pathogenic test end points measured are often th volume of soil per test) can be differ should be stored immediately and re should be tested as soon as possible influence the biological activity.

Sample size: The minimum volume (or mass) of soil required de site conditions, and the tests to be conducted. A few examples o characteristics are indicated below.
Bulk Density: Soil with high bulk density (e.g., sandy soil or c require a greater mass of sample compared to low bulk density forest soil).
Moisture Content: Moisture content at the time of collection requirements in a test method are recommended based on dry very moist, more soil should be collected than if the soil at a si
Impurities: If the site soil contains significant amount of large or plant roots, then more soil should be collected.
Nature, Extent, and Distribution of Pathogens: Pathogen m the surface soil with greatest concentrations in the top few cen are taken at depth (e.g., 0 to 30 cm) to meet the soil volume re homogenization the pathogen concentrations in the test sample longer represent the site. A better approach would be to collec that represent the depth of contamination (e.g., 0 to 5 cm).
Number: The number of soil samples to collect depends on the s desired level of certainty, and site specific considerations such as heterogeneity of the soil, test requirements, and the size and hom and location of samples can be determined using two dimensiona transect, two-stage, and grid sampling) or three-dimensional sam
Type of Soil Samples - Point, Composite and Bulk: Point Sam individual blocks of soil removed from one location by a samplir samples comprising of two or more point samples. When point s locations are pooled together, the pooled sample is a composite s (e.g., >1L) point samples that consists of more than one individu by a sampling device and often collected to satisfy the large volu

Surface soil: Bulk soil samples are easily obtained that samples are taken to exactly the same depth on contamination a sterile spatula can be used to scrape contamination can also occur between samples, whi washing the auger with water, then rinsing it with 7 Soil adhering to the plant roots is considered to be r soil. Surface soil sample usually undergoes sieving to facilitate sieving. Care should be taken so that th microbial populations.
Subsurface soil: Subsurface soil samples have lowe Mechanical approaches (such as drill rigs) may be n saturated or unsaturated. Air rotary drilling can be u effectively sterilized, posing difficulty for subseque control dust and cooling purposes, coring can be pe process was pre-filtered through a 0.3-µm high-effic scraped away with a sterile spatula, and then subcor in a sterile plastic bag or sleeves and should be anal and outside biological contaminant may significantl interferences from non-target substances in the sam

Sample Storage: Preservation Method and Maxi

- Analyses should be performed as soon as possible field, sample characteristics can and will change r prior to analysis.
- Storage at 4°C should not exceed 3 months.
- Samples should be stored in darkness (to avoid gr
- Samples should not be stacked, nor should be too that samples do not dry out and that anaerobic co
- Samples must not dry out or become waterlogged

Containers for Soil Samples Collected

Container Material of Construction and Type	Sa
HDPE bucket	
SS bucket with push-fit lids	
Polyethylene bag	
Teflon bag	
Glass wide-mouthed jars with polyethylene/polypropylene caps or HDPE lids	
Plastic wide-mouthed jars with plastic caps and HDPE lids (plastic jar materials include polypropylene, polystyrene, HDPE, and polystyrene)	

Representative Soil Sampling Devices

Designation	Type of Sample	Soil Type	Soil Sample Area/Volume	Penetration Depth	A
Shovel, Scoop, Spoon, Trowel, Spade	Unconsolidated	All soil types including non-cohesive sandy or loose soils	0.5 to 4 L	Surface, shallow subsurface	• Collection soil can be easily • Collects bl • Easy to dec
Cutting/Sampling Frame	Unconsolidated	Organic horizon(s), mineral A horizon(s)	100 to 900 cm²	Surface	• Efficient w representat
Ring Sampler	Consolidated or Unconsolidated	Cohesive soils	0.5 to 20 com diameter	Surface	• Easy to use • Precise cor
Bulb Planter	Consolidated or Unconsolidated	Cohesive soils	1.5 L	Surface (0 to 15 cm)	• Large core
Cutting Cylinder (Soil Punch)	Consolidated or Unconsolidated	Organic, A horizon	59 to 556 cm³	Surface	• Soil cores a efficiently
Soil Corer (manual)	Consolidated or Unconsolidated	Cohesive soils	2.5 to 10 cm (dia.) 30 to 60 cm (height)	0 to 60 cm	• Easy to use • Precise cor • Easy to cle • Can use lin
Slide-hammer Core Sampler	Consolidated or Unconsolidated	Cohesive soils	2.5 to 10 cm (dia.) 30 to 60 cm (height)	0 to 60 cm	• Easy to use • Precise cor • Easy to cle • Can use lin
Auger (manual)	Unconsolidated	Cohesive soils	2.5 to 15 cm long	0 to 60 cm	• Easy to use • Can handle soils
Split Spoon or Tube Sampler	Consolidated or Unconsolidated	Cohesive soils and hard soils	Variable (up to 10 cm (dia.) and up to 2 kg sample		• Easy to use • Precise cor • Large core • Can use lin
Shelby Tube Sampler	Consolidated or Unconsolidated	Cohesive soils and hard soils	Variable (up to 10 cm (dia.)	0 to 40 cm or 0 cm to bedrock	• Easy to use • Precise cor • Large core • Can use lin
Piston Sampler	Consolidated or Unconsolidated	Non-cohesive soils, wet soils, wet clay, dry and wet peat	Variable	Surface Shallow subsurface	• Holds mois materials i
Direct Push Corer Tubes (GeoProbe™)	Consolidated	Cohesive soils	Tubes: 5 or 7 cm (dia.) and 1.2 m long Size of probes and liners vary	Surface Subsurface	• Saturated s collected • Consolidat classify soi
Rotary (hollow stem) Auger with lined or unlined core barrels	Consolidated	Cohesive soils and soft bedrock	Variable	Surface to bedrock	• Saturated s collected
Rotary (solid stem) Auger	Unconsolidated	Cohesive soils, frozen soils, and soft bedrock	15 cm and larger	Surface to bedrock	• Easy to use • Faster than • Provides c information

Field Analytical Methods	Field-portable instrumentation provides useful information for critica screening or semi-quantitative data during the initial screening phase

PPE and Emergency Equipment

- N95 (or better) Respirators (enough for all team members plus extras)
- Eye-protection, goggles (face shields if required)
- Disposable/Nitrile gloves
- Reusable and disinfect-able leather or heavy gloves
- Protective suits, gowns, coveralls, or full length dedicated field garments
- Basic first aid ki
- Emergency expo
- Working commu
- Emergency resp

15. Passive Samplers

Selecting pathogen samplers and sampling methods depends on the site-specific questions that need to be addressed. Since samples for active pathogen sampling methods, described in previous sections, are collected from single points in time, the data are representative "snapshots" of the pathogens. Thus, multiple sampling might be used to describe how pathogen conditions vary over time. Passive pathogenic sampling devices are incubated within the sampled environment for weeks (typically 15 - 90 days) and depend on the formation and collection of biofilms that grow on surfaces or within a solid matrix. The passive samplers provide a more time-integrated sample of pathogens from the sampled environment. In active monitoring a pathogenic air sampler physically draws a known volume of air through or over a particle collection device which can be a liquid or a solid culture media or a nitrocellulose membrane and the quantity of pathogens present is measured (for example in CFU/m³ of air). Passive monitoring uses settle plates, which are standard Petri dishes containing culture media, that are exposed to the air for a given time in order to collect biological particles, which settle out and are then incubated. Results are expressed in CFU/plate/time or in CFU/m2/hour. Passive sampling provides a valid risk assessment as it measures the harmful part of the airborne population that falls onto a critical surface (French et al. 1980; Matysik et al. 2009; Napoli et al. 2012; Mills et al. 2014). Table A-9 provides advantages and challenges of commonly used passive samplers.

Table A-7. Advantages and Challenges of Passive Samplers

Advantages	Challenges
• Sampling devices are relatively easy to deploy and recover. • Sample collection over an extended period of time might be desirable at certain conditions compared to single, grab-sample collection of pathogen. • Passive sampling devices can concentrate contaminants.	• Sampling devices require several days of placement in the sampled environment and require two mobilizations to the site to install and then retrieve the sampling devices. • The solid matrix of most passive microbial sampling devices is a surrogate; thus, differences may exist between pathogens colonizing the sampling device and native material.

Even though the implementation might vary between different types of passive samplers, nearly all share certain common characteristics, the most important of which is the presence of a barrier between the sampled medium and the collecting medium. The barrier defines the rate at which analytes are collected at a given concentration, which is crucial for quantitative analysis. An effective sampler should eliminate or minimize the effects of external factors (such as the velocity of the sampled medium at the face of the sampler, humidity, and temperature) on the sampling rate. In practice, the barrier usually falls into one of two categories: (1) diffusion or (2) permeation. Schematic diagrams of the two types of samplers are given in Figure A-3. The sampling process is similar for both categories of samplers.

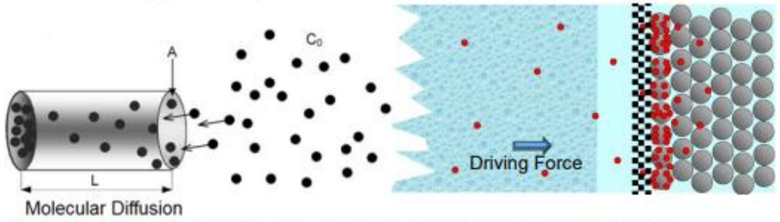


Figure A-3. Schematic diagram of passive samplers: (a) Diffusion, (b) Permeation.

Additional Methods

Method 3110 – Extraction of Seafood for Arsenic Species
Method 6870 – Arsenic Speciation Analysis in Seafood Using IC/ICP-MS
Method 6850 – Perchlorate in Water, Soils, and Solid Wastes Using High Performance Liquid Chromatography/Electrospray Ionization/Mass Spectrometry (HPLC/ESI/MS)
Method 6860A – Perchlorate in Water, Soils, and Solid Wastes Using Ion Chromatography/Electrospray Ionization/Mass Spectrometry (IC/ESI/MS)

… and several others.

Reminder about SW-846 Methods

- Use of the latest version of SW-846 methods
- Choose an appropriate and reliable method
- The user must be able to demonstrate that the method generates data that is appropriate for its intended use
- In situations where it may not be appropriate to use the latest method in SW-846, earlier versions may be used.
- “Measurement objectives”, Not on measurement technologies
- Performance Based approach because it enables the method flexibility necessary for the analysis of complex RCRA wastes.
- Seeks approval of their project plan before applying any method on a specific project.

Questions?

https://www.epa.gov/hw-sw846