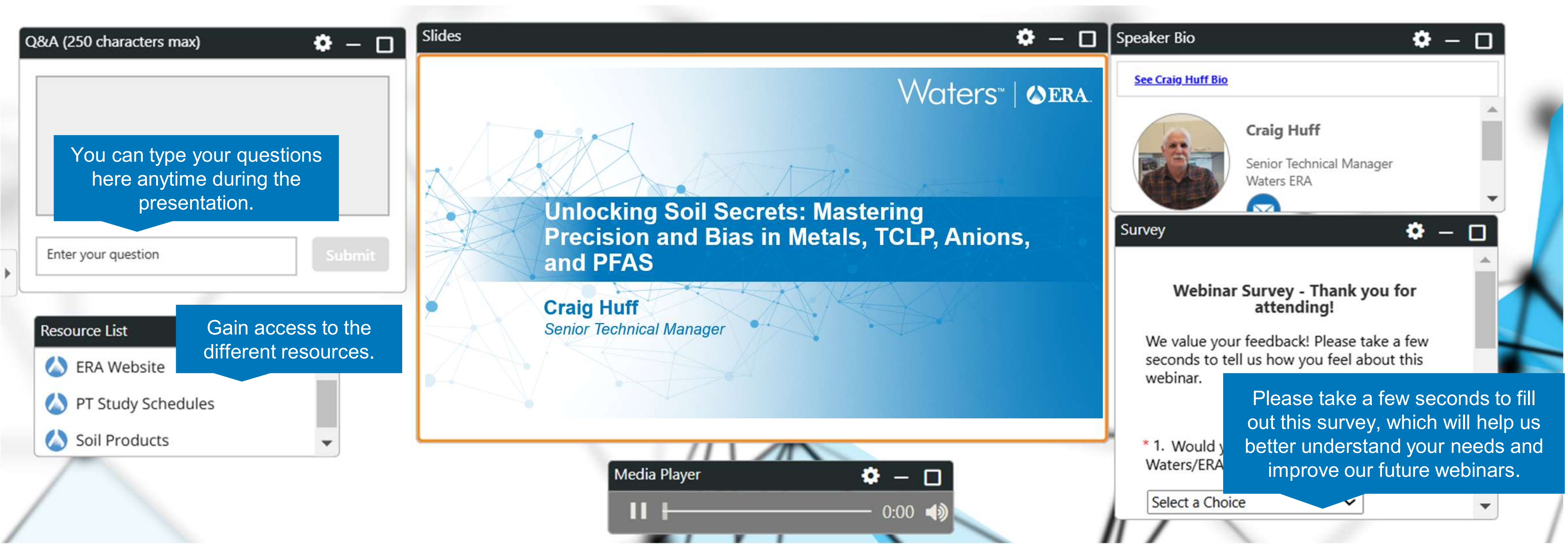
Unlocking Soil Secrets: Mastering Precision and Bias in Metals, TCLP, Anions, and PFAS

Craig Huff
Senior Technical Manager

Webinar survey – your feedback is appreciated!



©2025 Waters Corporation

Unlocking Soil Secrets

- Key Learning Topics
  - Manufacturing processes and tips for optimizing digestion process
  - Soil method performance data
  - Anion testing
  - PFAS analysis methods
- Speaker – Craig Huff
  - Senior Technical Manager

©2025 Waters Corporation

Outline

- Metals in Soil - Precision & Bias
  - Assigned values and homogeneity
  - Digestion hints
- TCLP Metals in Soil - Precision & Bias
  - Assigned values and homogeneity
  - Observations
- Anions in Soil - Precision & Bias
  - Assigned values and homogeneity
  - Extraction information & observations
- PFAS in Soil - PT Studies - Method Performance Observations

©2025 Waters Corporation

Metals in Soil

What do the Data Represent?

- Data represent the last 10 years of PT studies
- Approximately 40 PT studies
- Represent thousands of data points per analyte
- Multiple types of soil utilized
- Represent multiple analytical methods
  - Data can be segregated by analytical methods, however it is consolidated in this presentation
- Represent multiple digestion methods
  - Unfortunately, the data could not be segregated by digestion method

©2025 Waters Corporation

Metals in Soil

Precision & Bias Summary

Analyte	Mean (% Recovery) Historical	Standard Deviation (%) Historical	Failure Rate (%) Historical
Aluminum	86.4	24.1	3.2
Antimony	43.4	57.7	1.6
Arsenic	86.2	9.2	2.2
Barium	94.4	8.8	2.7
Beryllium	92.2	8.6	2.2
Boron	81.0	13.5	3.2
Cadmium	89.4	8.8	2.0
Calcium	95.2	8.9	3.1
Chromium	90.2	9.3	2.1
Cobalt	90.5	8.6	2.2
Copper	90.6	8.5	2.3
Iron	89.6	20.9	1.6
Lead	91.1	9.3	2.3
Lithium	89.1	19.0	25.0
Magnesium	93.2	11.7	2.1

Analyte	Mean (% Recovery) Historical	Standard Deviation (%) Historical	Failure Rate (%) Historical
Manganese	97.7	8.9	3.0
Mercury	98.2	13.7	5.0
Molybdenum	83.4	10.6	2.4
Nickel	88.0	9.1	2.1
Potassium	93.8	13.5	3.0
Selenium	90.0	10.6	2.7
Silver	91.0	10.4	6.0
Sodium	94.3	12.6	5.6
Strontium	94.9	9.5	2.9
Thallium	88.5	9.9	2.6
Tin	89.4	11.0	4.1
Titanium	87.0	34.5	1.8
Uranium	99.2	12.0	7.6
Vanadium	86.6	11.2	1.9
Zinc	93.8	9.7	2.1

Side note: Al & Fe have high native concentrations in the soil matrix

©2025 Waters Corporation

Metals in Soil

Assigned Values, Assurance of Homogeneity and Digestion Hints

- PT study assigned values = Study mean per TNI FoPT table
- CRM assigned values = ERA "made-to" values based on weights and measures + measured background concentrations
- Homogeneity testing is conducted by analyzing multiple samples, randomly selected from across the batch.
  - Samples are tested both across the batch and within each bottle before release
- Digestion Method = Method 3050B with ICP-AES and/or ICP/MS analyses
  - Mercury is analyzed per Method 7471(CVAA)
- Digestion Hints:
  - If using block digestors, make sure proper temperature is achieved, consistent and maintained in <u>each</u> well
  - Addition of HCl (per Method 3050), will enhance ICP-AES recoveries for many analytes!
  - Freshly prepared reagents are a must for mercury analyses!

©2025 Waters Corporation

TCLP Metals in Soil

What do the Data Represent?

- Data represent the 5 years of PT studies
- 19 PT studies
- Multiple types of soil utilized
- Assigned values = ERA recoveries using Method 1311 extraction with ICP-AES and CVAA (Hg) analyses
- Failure rates based on acceptance limits equal to ± 3 standard deviations applied around the study mean for each analyte
- Only TCLP extraction fluid #1 was used

©2025 Waters Corporation

TCLP Metals in Soil

Precision Summary

Analyte	Average Standard Deviation (%)	Total (n)	Average Failure Rate (%)
Antimony	11.5	789	5.8
Arsenic	11.2	1045	4.6
Barium	10.0	1043	5.6
Beryllium	11.3	756	4.9
Cadmium	9.4	1067	3.3
Chromium	11.0	1065	4.0
Lead	16.1	1102	5.5
Mercury	24.7	787	5.2
Nickel	9.9	851	3.7
Selenium	11.5	1037	3.4
Silver	21.3	998	5.9
Zinc	10.9	843	4.4

± 3 S.D. Acceptance Limits Also Note Hg & Ag %RSDs

©2025 Waters Corporation

TCLP Metals in Soil

Notes and Observations on ERA Internal and PT Data

- Percent recoveries using Method 1311 extraction yield only a fraction of actual amounts of each metal spiked onto soil
- Similar soil matrices (i.e., similar % sand/silt/clay content) yield consistent results based on ERA internally derived data and PT data
- Precision data should not be extrapolated to other real-world solid wastes or extractions using TCLP extraction fluid #2
- Extracting for shorter or longer periods than prescribed in Method 1311, will yield different recoveries (no surprise there…)
- Mercury and silver variability due inconsistent extraction efficiencies

©2025 Waters Corporation

Anions in Soil

What do the Data Represent?

- Data represent the last 10 years of PT studies
- Approximately 40 PT studies
- Represent thousands of data points per analyte
- Multiple types of soil utilized
- Represent multiple analytical methods…but most common method is Ion Chromatography (Methods 9056x & 300.0)
  - Data can be segregated by analytical methods, however it is consolidated in this presentation
- Represents deionized water extraction only

©2025 Waters Corporation

Anions in Soil

Precision and Bias Summary

Analyte	Mean (%) Recovery	Standard Deviation (%)	Failure Rate (%)
	Historical	Historical	Historical
Bromide	91.5	9.0	6.8
Chloride	97.0	10.3	6.6
Fluoride	33.6	26.5	3.3
Nitrate as N	76.8	8.8	5.1
Nitrate + Nitrite as N	76.8	8.8	3.2
ortho-Phosphate as P	32.3	34.9	3.6
Sulfate	85.2	14.0	7.1

Note precision and accuracy for F^- and PO4-P

©2025 Waters Corporation

Anions in Soil

Assigned Values, Assurance of Homogeneity and Extraction Information / Observations

- PT study assigned values = Study mean per TNI FoPT table
- CRM assigned values = ERA "made-to" values based on weights and measures + measured background concentrations
- Nitrite is unstable in this matrix and does not contribute to Nitrate + Nitrite as N assigned value
- Homogeneity testing is conducted by analyzing multiple samples, randomly selected from across the batch
  - Samples are tested both across the batch and within each bottle before release
- Fluoride and Phosphate extraction efficiencies and overall precision can be improved by using weak HCl extraction solution…however, this solution cannot be used with this sample design due to method interference concerns and TNI FoPT table regression equations for precision

©2025 Waters Corporation

PFAS in Soil

What do the Data Represent?

- Data represent the last 5 years of PT studies
- 20 PT studies
- Multiple types of soil utilized
- Failure Rates based on acceptance limits of 50-150%
- Most commonly reported methods:
  - DoD/DoE QSM table x
  - 1633 DRAFTx
  - 537(Mod)
  - ASTM D7968
  - EPA 8327
  - “Internal”

©2025 Waters Corporation

PFAS in Soil

Precision & Bias Summary

Analyte	Mean (%) Study	Std Dev (%) Study	(n)	Failure Rate (%) Study
11chloroeicosafluoro3oxaundecane1sulfonic acid (11ClPF3OUdS)	91.7	18.3	308	3.0
9chlorohexadecafluoro3oxanonane1sulfonic acid (9ClPF3ONS)	96.2	13.5	304	1.0
4,8dioxa3Hperfluorononanoic acid (DONA)	89.4	16.4	313	1.0
Nethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)**	87.5	17.5	93	0.9
1H, 1H, 2H, 2HPerfluorodecanesulfonic acid (8:2 FTS)	85.3	18.6	352	5.4
1H, 1H, 2H, 2HPerfluorohexanesulfonic acid (4:2 FTS)	88.4	14.4	331	1.2
1H, 1H, 2H, 2HPerfluorooctanesulfonic acid (6:2 FTS)	88.2	15.7	350	3.0
Hexafluoropropylene oxide dimer acid (HFPODA)	87.5	14.7	337	0.0
Nmethyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)**	85.7	15.2	91	2.0
Perfluorobutanesulfonic acid (PFBS)	91.5	12.4	384	1.8
Perfluorobutanoic acid (PFBA)	91.1	14.4	377	1.6
Perfluorodecane sulfonic acid (PFDS)	90.0	14.8	370	1.2
Perfluorodecanoic acid (PFDA)	90.2	13.7	377	2.5
Perfluorododecanoic acid (PFDoA)	91.5	13.7	376	1.9
Perfluoroheptane sulfonic acid (PFHpS)	91.6	12.6	347	2.3
Perfluoroheptanoic acid (PFHpA)	91.2	12.2	379	1.4
Perfluorohexanesulfonic acid (PFHxS)	89.5	11.0	380	2.1
Perfluorohexanoic acid (PFHxA)	90.8	13.3	380	0.3
Perfluorononane sulfonic acid (PFNS)	92.3	12.1	323	1.6
Perfluorononanoic acid (PFNA)	87.9	13.2	381	1.8
Perfluorooctane sulfonamide (PFOSAm)	92.5	16.2	351	0.5
Perfluorooctanesulfonic acid (PFOS)	93.1	14.1	389	2.4
Perfluorooctanoic acid (PFOA)	91.1	13.8	392	2.4
Perfluoropentanoic acid (PFPeA)	89.4	13.5	375	1.4
Perfluoropentane sulfonic acid (PFPeS)	89.2	13.6	331	1.2
Perfluorotetradecanoic acid (PFTDA)**	92.2	11.7	77	8.0
Perfluorotridecanoic acid (PFTrDA)**	92.6	13.0	120	3.8
Perfluoroundecanoic acid (PFUnDA)	92.8	13.9	376	0.7

** Branched and Linear isomers. Also note low F.R's.

©2025 Waters Corporation

PFAS in Soil

Notes and Observations

- PT study assigned values = ERA “made-to” values based on weights and measures
- 4 Analytes composed of both branched and linear isomers
- Mean recoveries and standard deviations are actually pretty good overall
- PT Acceptance limits of ± 50% may be too wide?
- False positive reporting very insignificant! (data not illustrated in previous table)
- PFAS is a constantly evolving group of analytes. ERA’s most recent studies contain an expanded analyte list of analytes and we anticipate this to change going forward

©2025 Waters Corporation

Thank you!

craig_huff@waters.com

©2025 Waters Corporation

Live Q&A Session: Unlocking Soil Secrets: Mastering Precision and Bias in Metals, TCLP, Anions, and PFAS

Please submit your questions into the Q&A Chatbox

https://www.eraqc.com