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An Overview of Sequential Extraction Methods to Assess Bioavailability and Mobility of Metals in Sediments

James Fox, Russell Gerads, Ben Wozniak

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What Are Selective Sequential Extractions (SSE)?

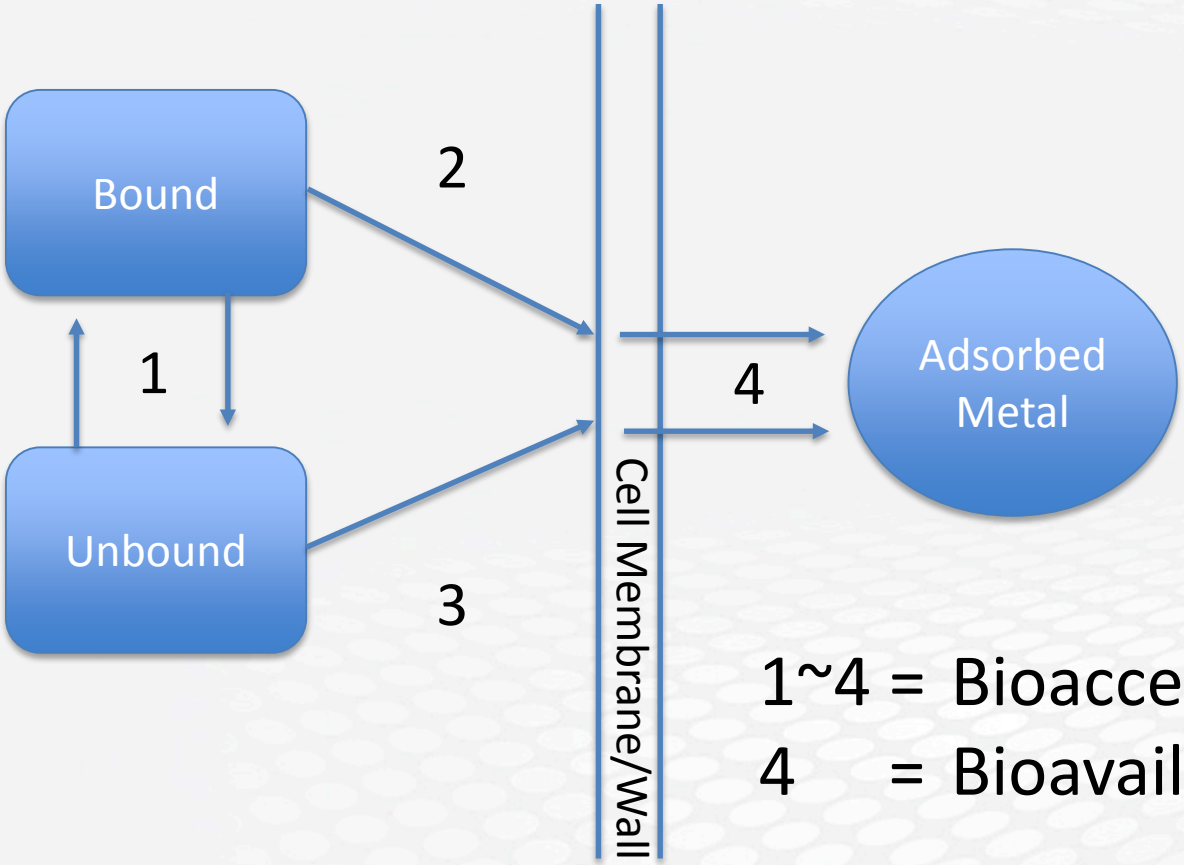
- An attempt to generally characterize the molecular forms of a contaminant of concern and/or determine under what conditions the contaminant is mobile in to the surrounding environment
- SSE not true speciation
  - Total metal concentration by fraction
  - Each fraction represents shared chemical properties

Objective of Project

- Define the data objectives
  - Mobility
  - Risk assessment
  - Fate & transport

- Bioaccessibility vs. bioavailability
  - Different definitions out there
  - Bioaccessibility generally encompasses bioavailability
  - Bioavailability is what is immediately accessible for biological uptake and in an available form

Bioaccessibility vs. Bioavailability



1~4 = Bioaccessible

4 = Bioavailable

Semple, et al., ES&T, 2004, 38, 229A – 231A

What Procedure to Use

- What is the nature of the element?
  - Primarily exist as cationic or anionic molecular forms
- Transition metals
  - BCR, Tessier
- Element Specific (e.g. As, Se)
  - Wenzel
- Mercury
  - Bloom, EPA 3200

Comparison

Cationic Procedures

Method	Steps	Fraction	Assess
Tessier	1: MgCl2 (pH 7)	Exchangeable	Bioavailable
	2: NaOAc/HOAc (pH 5)	Bound to carbonates	
	3: $NH_2OH \cdot HCl$ (pH 2)	Bound to Fe/Mn Oxides	
	4: H_2O_2, HNO_3 (pH 2); NH_4OAc	Bound to organic matter	Bioaccessible
	5: $HF/HClO_4$	Residual	Unavailable
BCR	1: HOAc (pH 2.85)	Exchangeable	Bioavailable
	2: $NH_2OH \cdot HCl$ (pH 2)	Reducible	
	3: H_2O_2; NH_4OAc (pH 2)	Oxidizable	Bioaccessible
	'Modified' Aqua Regia	Residual	Unavailable

Comparison

Cationic Procedures

Method	Steps	Fraction	Assess
Tessier Modified (Singh 1988)	1: $Mg(NO_3)_2$	Exchangeable	Bioavailable
	2: NaOAc (pH 5)	Bound to carbonates	
	3: NaOCl (pH 8.5)	Bound to organic matter	
	4: $NH_2OH{\cdot}HCl$ + HNO3 (pH 2)	Bound to Mn oxides	
	5: $NH_2OH{\cdot}HCl$ + HCl (50° C)	Bound to amorphic Fe oxides	Bioaccessible
	6: (NH_4)-oxalate + $H_2C_2O_4$ + $C_6H_8O_5$ (pH 3)	Bound to crystalline Fe oxides	
	7: $HF/HClO_4$ /HCl	Residual	Unavailable

*Sepahvand, H. & Forghani, A., "Comparison of Two Sequential Extraction Procedures for the Fractionation of Zinc in Agricultural Calcareous Soils." *Chemical Speciation and Bioavailability, (2012), 24(1).*

Comparison

Element Specific Procedure

Method	Steps	Fraction	Assess
Wenzel (Arsenic)	1: NH_4SO_4	Non-specifically sorbed	Bioavailable
	2: $NH_4H_2PO_4$	Specifically sorbed	
	3: $NH_2OH{\cdot}HCl$ (pH 2)	Amorphous and poorly-crystalline hydrous oxides	Bioaccessible
	4: NH_4^+-oxalate, (dark, pH 3.25)	Well-crystallized hydrous oxides of Fe and Al	
	5: HNO_3/H_2O_2	Residual	Unavailable

Comparison

Hg Procedures

Method	Steps	Fraction	Assess
Bloom (Mercury)	1: DI H2O	Water soluble	Bioavailable
	2: HCl/HOAc (pH 2)	Weak acid	
	3: KOH	Organo complexed	Bioaccessible
	4: HNO_3	Strongly complexed	
	5: Aqua regia	Mineral-bound	Unavailable
EPA 3200	1: HNO_3 or HCl/EtOH	Extractable Organic	Bioavailable
	2: SCF - HCl/NaCl eluent	Extractable Inorganic	
	3: HNO_3	Semi-mobile	Bioaccessible
	4: Aqua regia	Non-mobile	Unavailable

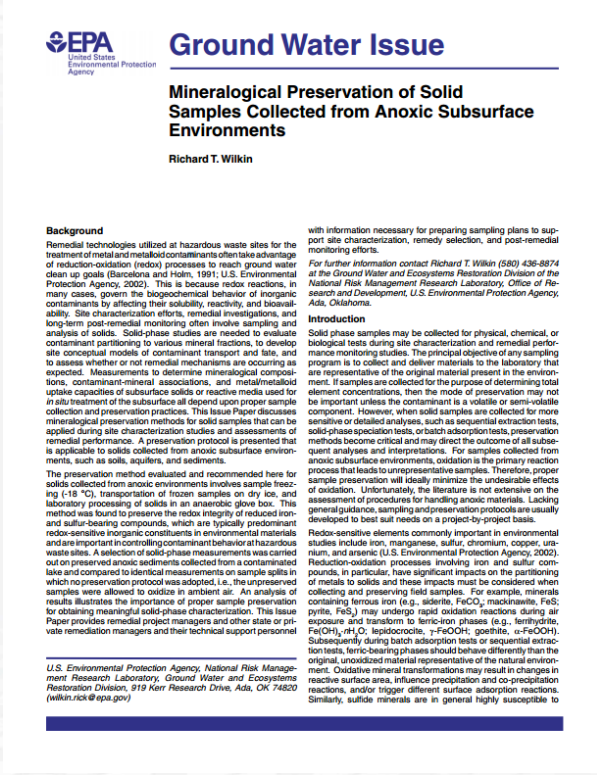
Other Procedures and Considerations

- Many other published and project-specific SSE procedures exist
- Generally based upon Tessier, BCR, or Wenzel
- Scientific application of these procedures to another element requires years of experimentation
- Optimized for specific environments/purposes
  - Pretty much all SSE procedures based on oxygen

Sampling Technique

EPA paper by Richard Wilkin*

- Anoxic sample handling for subsurface soil/sediments required
- Freezing samples with dry ice for shipment to laboratory
- Anaerobic glove box handling during preparation of samples



EPA United States Environmental Protection Agency

Ground Water Issue

Mineralogical Preservation of Solid Samples Collected from Anoxic Subsurface Environments

Richard T. Wilkin

Background

Remedial technologies utilized at hazardous waste sites for the treatment of metal and metalloid contaminants often take advantage of reduction-oxidation (redox) processes to reach ground water clean up goals (Barcelona and Holm, 1991; U.S. Environmental Protection Agency, 2002). This is because redox reactions, in many cases, govern the biogeochemical behavior of inorganic contaminants by affecting their solubility, reactivity, and bioavailability. Site characterization efforts, remedial investigations, and long-term post-remedial monitoring often involve sampling and analysis of solids. Solid-phase studies are needed to evaluate contaminant partitioning to various mineral fractions, to develop site conceptual models of contaminant transport and fate, and to assess whether or not remedial mechanisms are occurring as expected. Measurements to determine mineralogical compositions, contaminant-mineral associations, and metal/metalloid uptake capacities of subsurface solids or reactive media used for *in situ* treatment of the subsurface all depend upon proper sample collection and preservation practices. This Issue Paper discusses mineralogical preservation methods for solid samples that can be applied during site characterization studies and assessments of remedial performance. A preservation protocol is presented that is applicable to solids collected from anoxic subsurface environments, such as soils, aquifers, and sediments.

The preservation method evaluated and recommended here for solids collected from anoxic environments involves sample freezing (-18 °C), transportation of frozen samples on dry ice, and laboratory processing of solids in an anaerobic glove box. This method was found to preserve the redox integrity of reduced iron- and sulfur-bearing compounds, which are typically predominant redox-sensitive inorganic constituents in environmental materials and are important in controlling contaminant behavior at hazardous waste sites. A selection of solid-phase measurements was carried out on preserved anoxic sediments collected from a contaminated lake and compared to identical measurements on sample splits in which no preservation protocol was adopted, i.e., the unpreserved samples were allowed to oxidize in ambient air. An analysis of results illustrates the importance of proper sample preservation for obtaining meaningful solid-phase characterization. This Issue Paper provides remedial project managers and other state or private remediation managers and their technical support personnel with information necessary for preparing sampling plans to support site characterization, remedy selection, and post-remedial monitoring efforts.

For further information contact Richard T. Wilkin (580) 436-8874 at the Ground Water and Ecosystems Restoration Division of the National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Ada, Oklahoma.

Introduction

Solid phase samples may be collected for physical, chemical, or biological tests during site characterization and remedial performance monitoring studies. The principal objective of any sampling program is to collect and deliver materials to the laboratory that are representative of the original material present in the environment. If samples are collected for the purpose of determining total element concentrations, then the mode of preservation may not be important unless the contaminant is a volatile or semi-volatile component. However, when solid samples are collected for more sensitive or detailed analyses, such as sequential extraction tests, solid-phase speciation tests, or batch adsorption tests, preservation methods become critical and may direct the outcome of all subsequent analyses and interpretations. For samples collected from anoxic subsurface environments, oxidation is the primary reaction process that leads to unrepresentative samples. Therefore, proper sample preservation will ideally minimize the undesirable effects of oxidation. Unfortunately, the literature is not extensive on the assessment of procedures for handling anoxic materials. Lacking general guidance, sampling and preservation protocols are usually developed to best suit needs on a project-by-project basis.

Redox-sensitive elements commonly important in environmental studies include iron, manganese, sulfur, chromium, copper, uranium, and arsenic (U.S. Environmental Protection Agency, 2002). Reduction-oxidation processes involving iron and sulfur compounds, in particular, have significant impacts on the partitioning of metals to solids and these impacts must be considered when collecting and preserving field samples. For example, minerals containing ferrous iron (e.g., siderite, $FeCO_3$; mackinawite, FeS; pyrite, FeS_2) may undergo rapid oxidation reactions during air exposure and transform to ferric-iron phases (e.g., ferrihydrite, $Fe(OH)_3 \cdot nH_2O$; lepidocrocite, γ-FeOOH; goethite, α-FeOOH). Subsequently during batch adsorption tests or sequential extraction tests, ferric-bearing phases should behave differently than the original, unoxidized material representative of the natural environment. Oxidative mineral transformations may result in changes in reactive surface area, influence precipitation and co-precipitation reactions, and/or trigger different surface adsorption reactions. Similarly, sulfide minerals are in general highly susceptible to

U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division, 919 Kerr Research Drive, Ada, OK 74820 (wilkin.rick@epa.gov)

*Wilkin, R. “Mineralogical Preservation of Solid Samples Collected from Anoxic Subsurface Environments.” EPA National Service Center for Environmental Publications (2006)

https://nepis.epa.gov/Exe/ZyPDF.cgi/600003I1.PDF?Dockey=600003I1.PDF

Single Extraction Bioaccessibility Procedures

EPA Method 1340

- *In vitro* bioaccessibility assay (IVBA) for Pb

Targeted steps from multi-step procedures

- F4 from Bloom for elemental Hg (discard F1~3)
- F3 Tessier or F2 BCR for “total bioavailability” (not discarding previous fractions)

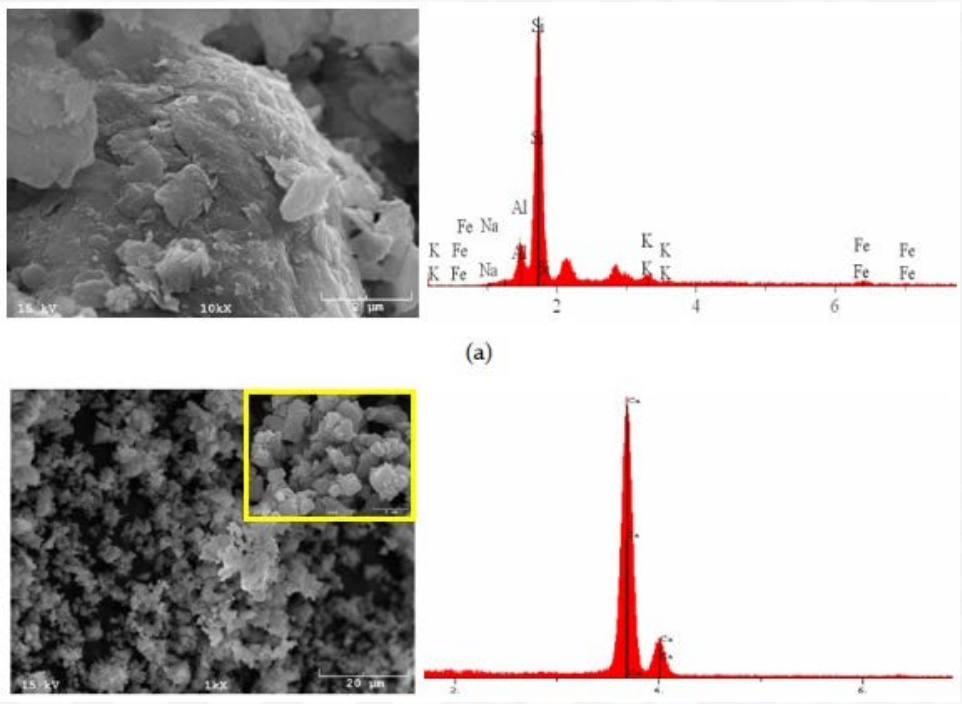
California LUFT method

- Organic lead

Other Techniques

Complementary techniques for insoluble molecular forms

- XANES
- SEM-EDS



Speciation in conjunction with SSE (soluble forms)

- 1st steps only
- Must avoid molecular conversion

*Image from Solanki, P. and Zaman, M., “Mircrostructural and Mineralogical Characterization of Clay Stabilized Using Calcium-Based Stabilizers.” Ch. 38 of *Scanning Electron Microscopy;* book edited by Viacheslav Kazmiruk, ISBN 978-953-51-0092-8, Published: March 9, 2012 under CC BY 3.0 license.

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The Team at Brooks Applied Labs