Mineralogical Preservation of Solid Samples Collected from Anoxic Subsurface Environments

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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.

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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, FeCO3; mackinawite, FeS; pyrite, FeS2) may undergo rapid oxidation reactions during air exposure and transform to ferric-iron phases (e.g., ferrihydrite, Fe(OH)3; goethite, γ-FeOOH; lepidocrocite, 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...
oxidation. Unpreserved samples containing sulfides can undergo oxidative transformations, changing sample behavior and outcomes of mineralogical, sequential extraction, and batch adsorption tests (Bush and Sullivan, 1997; Carbonaro et al., 2005). A good example of how sample preservation practices can affect the outcome of sediment analyses is discussed in Harrington et al. (1999).

Adequate preservation of samples must encompass the chain of events from sample collection, to sample transport back to the laboratory, to sample storage, and finally to sample preparation and analysis in the laboratory. The strategies most often adopted for preserving the redox status of freshly collected solid materials include sample freezing and/or sample storage in an inert atmosphere. Sample freezing typically involves collection of core or grab samples, placement of samples in containers, followed by freezing in a freezer or flash-freezing using liquid nitrogen. Freezing preserves the redox integrity of samples by decreasing the rate of reaction between reduced solids and atmospheric oxygen or other oxidants. The other principal approach for preserving redox status is to eliminate or minimize sample interactions with oxygen by transferring samples after their collection into an evacuated container or a container purged with an inert gas, such as nitrogen, helium, or argon. Transportation of samples back to the laboratory is an especially vulnerable process for maintaining sample integrity. Once samples are frozen, they must be kept in a frozen state, or samples stored in gas-purged containers must be transported in secondary air-tight containers. After samples have arrived at the laboratory, they may be again transferred to a laboratory freezer or to an anaerobic chamber for drying and homogenization.

Givelet et al. (2004) recently developed a protocol for the collection and handling of peat samples for chemical and mineralogical analyses. Their protocol adopts sample freezing at -18 °C to preserve samples for subsequent mineralogical analyses. Rapin et al. (1986) examined the impact of freezing and other preparation methods on the results of sequential extraction analyses for determining solid-phase partitioning of metals in sediment. Their conclusions were that freeze-drying and oven-drying should be avoided, but that freezing was acceptable for sequential extraction tests. They also noted that partial extraction tests for copper, iron, and zinc were especially sensitive to sample handling protocols. Mudroch and Bourbonniere (1994) proposed that when applying sequential extraction procedures to anoxic sediments all manipulations and extraction steps should be carried out in an anaerobic glove box. Mineralogical studies on the corrosion products in zero-valent iron permeable reactive barriers (PRBs) were conducted by Phillips et al. (2003). After collecting cores from subsurface PRBs, these investigators placed the core materials in PVC chambers purged with argon gas. The cores were stored for up to 2 weeks and argon was recharged into the PVC tubes every 2 to 3 days. Other long-term performance studies of zero-valent iron PRBs have successfully utilized sample freezing to preserve core materials for mineralogical and chemical analyses (U.S. Environmental Protection Agency, 2003).

Several studies have examined the effects of air-drying versus oven-drying on the behavior of soils and sediments in batch adsorption tests. Physical and chemical properties of materials are altered depending on the mode of drying. For example, differences have been observed in sample pH, partition coefficients, and the exchangeable metals fraction depending on whether samples are field-moist, frozen, air-dried, freeze-dried, or oven-dried. Based upon a review of previous work, U.S. Environmental Protection Agency (1992) recommends air-drying of samples over oven-drying in order to minimize changes to the physico-chemical properties of solids used in batch tests for estimating adsorption parameters. The endpoint of air-drying is achieved when the sample moisture content reaches equilibrium with room atmosphere conditions and in practice can be assessed by tracking sample mass to a steady state. Reduced solids collected from anoxic environments should be dried in an anaerobic glove box or glove bag to prevent oxidation (U.S. Environmental Protection Agency, 1992). The analysis of solid materials for inorganic species can be performed on wet, freeze-dried, or air-dried samples. In general, however, sample drying is preferred to eliminate sample homogeneity issues in relating element concentrations from a wet-weight to a dry-weight basis (Muhaya et al., 1998). Water removal may be achieved through various means, including decanting, gravity filtration, vacuum filtration, pressure filtration (e.g., Bottcher et al., 1997), and centrifugation. It is important to note that pore-water solutes can significantly contribute to total element concentrations in dried solids, especially in situations where the solid-phase concentration of the element is low (<10 mg/kg) and the pore-water concentration is high (>1 mg/L).

Methods, Results and Discussion of a Preservation Study

In order to evaluate the effects of sample preservation on the results of selected solid-phase characterization tests, contaminated sediments were collected from a small lake situated adjacent to a Superfund Site located approximately 16 km northwest of downtown Boston, Massachusetts (Industri-Plex Superfund Site). The lake receives discharge of ground water with elevated concentrations of arsenic, ferrous iron, sulfate, and petroleum hydrocarbons. The site has been used to develop an improved understanding of arsenic geochemical cycling at the ground water-surface water interface (U.S. Environmental Protection Agency, 2005). Sediments were retrieved from depths ranging from 0.5 to 4.5 meters using an Eckman dredge. One half of each sample retrieved from the lake bottom was immediately bagged and frozen; the other half was bagged and left unfrozen. During each sampling event approximately 1 L of sediment plus water was collected. The mixture was transferred from the dredge to polyethylene bags and excess air was displaced. Frozen sediment samples were transported back to the laboratory on dry ice. Frozen samples were subsequently thawed and dried at room temperature in an anaerobic glove box (96:4 v/v N₂:H₂ gas mixture). The dried sediments were homogenized with an agate mortar and pestle and kept in the glove box. Unpreserved samples were dried in air and homogenized using an agate mortar and pestle. The color of the unpreserved samples was red, presumably due to the oxidation of ferrous iron and production of ferric oxyhydroxides. Color changes in the unpreserved samples were noted within the first several hours after sample collection. The preserved samples kept in the glove box remained black in color. Solid-phase tests carried out on the preserved and unpreserved sediments included total metals concentrations, metal extractability with 1 M HCl, total sulfur, acid-volatile sulfide, chromium-reducible sulfur, and batch adsorption tests with arsenic and zinc. In addition, X-ray absorption near-edge structure (XANES) spectroscopy was carried out to determine the oxidation state of arsenic in the preserved and unpreserved samples.

Iron and Sulfur Partitioning

Total element concentrations were determined by microwave assisted digestion in nitric acid followed by inductively coupled plasma-optical emission spectroscopy (ICP-OES; modified EPA Method 3051). Figure 1 is a bar graph that shows a comparison of total iron concentrations in the preserved and unpreserved sediment samples. Concentrations of total iron in the sediments range from 1.0 to 11.5 wt%. Total iron concentrations are independent of the mode of preservation; values in the preserved and unpreserved samples deviate within ±10%. Similar correlations are observed for other major and trace elements. As a general rule, therefore,
the total concentration of inorganic components is conservative and independent of the mode of sample preservation. If total concentrations in solid samples are the data objective of a specific site investigation, then it may not be necessary to expend the extra effort and cost to ensure preservation of the sample redox state. Sample preservation may be necessary, however, to maintain solid-phase concentrations of volatile or semi-volatile inorganic components, such as mercury (Muhaya et al., 1998).

Although total concentrations of iron are independent of the mode of sample preservation, the oxidation state of iron in the preserved and unpreserved samples is completely different. Figure 1 shows the amount of ferrous iron in the solid phase compared to total iron concentrations in the preserved versus unpreserved sediments. Ferrous iron content was determined by extracting the sediments in 1 M HCl and measuring the ferrous iron concentration using the 1,10-phenanthroline colorimetric method. In the unpreserved samples, the Fe(II)/FeTotal ratio is <0.03 for all determinations. This ratio in the unpreserved samples may be overestimated because of the possible formation of Fe(III)-phenanthroline complexes (Tamura et al., 1974). This interference is significant when the concentration of Fe(III) is >10 mg/L, a condition that was avoided during the partial extraction tests. In the preserved samples the average Fe(II)/FeTotal ratio is 0.83 (Figure 1). In most samples, concentrations of total iron and ferrous iron are in close agreement. Several other samples, in particular ED-14 and ED-15, were collected from a transitional redox zone so that a mixture of Fe(II) and Fe(III) found in these samples is reasonable. These data demonstrate that: i) the freezing procedure for preserving sample redox integrity is appropriate for iron-bearing phases; and, ii) samples containing ferrous iron, if left unpreserved, will undergo oxidation reactions that result in the conversion of Fe(II) to Fe(III) in the solid phase.

Similar results are observed for sulfur. In Figure 2 data are presented that show the concentration of acid-volatile sulfide in preserved and unpreserved sediment samples compared to total sulfur concentrations. Methods used for determining total sulfur and reduced sulfur partitioning are reported in Wilkin and Bischoff (2006). In the preserved set of samples, concentrations of acid-volatile sulfide range from 0.05 to 5.1 wt% or from about 10 to 79% of the total amount of sulfur contained in the samples. In contrast, the unpreserved samples have acid-volatile sulfide concentrations ranging from 0.01 to 0.18 wt%. Losses of acid-volatile sulfide concentrations range from 95 to 100% in the unpreserved samples. More detailed sulfur partitioning studies indicate that the balance of sulfur in the preserved samples is composed of mixed reduced and oxidized species including chromium-reducible sulfur, sulfate-sulfur, and minor quantities of organic-sulfur (Wilkin and Bischoff, 2006). Similarly to Fe(II), S(-II) is lost from samples that are left unpreserved.

A comparison was made between acid-volatile sulfide concentrations obtained in sediment samples that were thawed and dried in an anaerobic chamber and concentrations in freeze dried samples. Very good agreement was found between the two drying procedures ($R = 0.953; n = 8$). Freeze-drying may be advantageous for sample drying because low temperatures during lyophilization help avoid changes in labile components including the loss of volatile constituents (e.g., mercury, Muhaya et al., 1998), avoid aggregation of particles, and minimize oxidation reactions. A previous study showed, however, that freeze-drying was not effective for samples with low acid-volatile sulfide concentrations (Brumbaugh and Arms, 1996). At acid-volatile sulfide concentrations below 0.2 wt%, Brumbaugh and Arms (1996) noted reductions in concentrations following freeze-drying of up to 95%. They proposed that increases in sample surface area of freeze dried materials render such materials highly susceptible to air-oxidation. Hjorth (2004) also suggests that freeze-drying does not preserve the speciation pattern of major elements, trace metals, and sulfur in anoxic sediments as determined by a 3-step sequential extrac-

![Figure 1.](image1.png)
tion procedure. Although more data are needed, results available in the literature suggest that freeze-drying may not be an ideal approach for samples to be used in redox-sensitive solid-phase measurements; room-temperature drying in an anaerobic environment is preferred.

**Arsenic Oxidation State**

Arsenic may be present in the solid phase in either the As(V) or As(III) oxidation states, or as a mixture of As(V) and As(III). In general, as predicted from thermodynamic reasoning, As(V) is expected to dominate in oxygenated environments and As(III) is expected to dominate in suboxic to anoxic environments. Various mechanisms of arsenic mobilization and immobilization in the environment have been proposed including abiotic and microbially mediated redox processes. Determination of the oxidation state of arsenic in the solid phase is an important component of risk assessments and remediation strategies because both the toxicity and the geochemical mobility of arsenic are strongly dependent on its solid and aqueous phase speciation (e.g., Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002).

Changes in the natural distribution of arsenic species in a sample collected from the field can come about due to several factors including chemical reactions with sample components, interactions with the container material, and microbial activity. All of these factors may in turn be affected by parameters such as temperature, light levels, and pH (Rowland et al., 2005). In this study, XANES spectra were collected to evaluate the oxidation state of arsenic in the preserved and unpreserved sediments. A discussion of data collection and data analysis methods relating to X-ray absorption spectroscopy is presented in a separate report (U.S. Environmental Protection Agency, 2005). As an example, X-ray absorption spectra for preserved and unpreserved samples of ED-03 are shown in Figure 3. The preserved sample shows a single absorption maximum at about 11871 eV. This energy is characteristic of arsenic in the trivalent state dominant in the preserved sample. The unpreserved sample shows two features, a shoulder at 11871 eV and an absorption maximum at about 11874 eV. The second energy feature is characteristic of arsenic in the pentavalent state. Linear combination fitting of the measured spectra indicate that the unpreserved sample contains a mixture consisting of about 54% As(III) and 46% As(V).

Similar to iron and sulfur, the oxidation state of arsenic in the solid phase is highly dependent on the mode of sample preservation. Unless preserved, solid matrices containing arsenic in the trivalent state will likely oxidize to form arsenate. As an example, Bostick et al. (2004) documented arsenic oxidation artifacts encountered during spectroscopic measurements. In this study, sample freezing followed by sample preparation and analysis under an anoxic atmosphere was found to preserve the reduced arsenic oxidation state in solid samples. These findings are consistent with a recent study by Rowland et al. (2005). They noted substantial oxidation of solid-phase arsenic in unpreserved samples and that sandy matrices were particularly susceptible to arsenic oxidation. For sand-dominated samples, Rowland et al. (2005) recommend analysis within two or three weeks of sample collection to minimize oxidation artifacts. The issue of holding time was not specifically examined as an experimental variable in this study. Arsenic XANES data reported here were collected 5 months after sample collection, so over a 5-month period the arsenic oxidation state was maintained in the redox-preserved samples by freezing.

**Figure 2.** Comparison of solid-phase concentrations of total sulfur (wt%) and acid-volatile sulfide (wt%) in a series of sediments with and without preservation.

**Figure 3.** Arsenic K-edge XANES spectra for sample ED-03. The bold blue line is the spectrum collected from the preserved sample and the open circles show the spectrum collected from the unpreserved sample. Sample ED-03 contains a total arsenic concentration of 490 mg/kg; only As(III) is detected in the preserved sample. Inset shows the comparison between total arsenic concentrations in the preserved and unpreserved samples.
**Batch Adsorption Tests**

The capacity of soils, sediments, or aquifer solids to attenuate pollutants is often assessed by using batch-adsorption or static equilibrium tests (U.S. Environmental Protection Agency, 1992). It is reasonable to suspect that the results of such tests will depend on the ways in which sample matrices are preserved and handled after their collection. To examine the effects of preservation on batch-adsorption experiments, tests with zinc and arsenic were carried out using sub-samples of the preserved and unpreserved sediments. Zinc sorption onto the preserved samples was about 5 to 30 times greater than zinc sorption onto the unpreserved samples (Figure 4A). Interestingly, the reverse trend is evident for arsenic, i.e., the unpreserved samples are about 4 times more efficient in removing arsenic from solution compared to the preserved samples (Figure 4B). Figure 4 shows batch sorption data plotted in terms of the aqueous concentrations of zinc or arsenic in mg/L versus the solid-phase concentration of zinc or arsenic in mg/g, respectively. The solid-phase concentration of the inorganic contaminant is calculated based upon the dry sample mass used in the batch adsorption test and the time-dependent loss of zinc or arsenic concentrations from solution. The solid lines are the data fit to the Langmuir isotherm equation; the fitting equation is provided in the caption for Figure 4. The dashed lines in Figure 4 represent the linear distribution coefficient ($K_d$) for zinc and arsenic uptake by the unpreserved and preserved samples, respectively. In these two cases the linear $K_d$ model would appear to be just as appropriate as the non-linear Langmuir model. Results of these tests, however, demonstrate that data collected in batch adsorption experiments are entirely dependent on how samples are preserved. Sample preservation would be just as important for column experiments. If solid-phase testing is used in the context of developing predictive models of contaminant transport and fate or for developing site remediation strategies, it is imperative that the solid-phase tests be carried out only on redox-preserved materials.

Arsenic is preferentially retained on the unpreserved sediment matrix. This behavior is likely due to the fact that both arsenite and arsenate are more favorably adsorbed by ferric oxyhydroxides or hydroxides present in the unpreserved samples as compared to ferrous sulfides that are present in the preserved samples. On the other hand, zinc is preferentially retained on the preserved sediment sample relative to the unpreserved sample. The high acid-volatile sulfide concentrations in the preserved samples provide reactive sulfide for precipitation of insoluble zinc sulfide (ZnS), which is a more effective process for removing zinc from solution than adsorption by ferric oxyhydroxides or hydroxides.

**Summary and Conclusions**

Unless preserved, samples collected from suboxic to anoxic environments should not be submitted for solid-phase tests to assess contaminant partitioning or for determining contaminant uptake capacity. Results of such tests on improperly preserved samples will be unrepresentative at best and misleading in the worst case.

The preservation method tested and recommended here for samples collected from suboxic to anoxic environments involves collection of samples followed by freezing (-18 °C), transporting 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 abundant redox-sensitive constituents in environmental samples.

The method is relatively simple and inexpensive to apply in the field compared to other possible methods of preservation that require liquid nitrogen or compressed gas cylinders containing nitrogen or argon. A selection of solid-phase measurements was carried out on preserved anoxic sediments collected from a contaminated wetland and compared to sample splits in which no preservation was adopted, i.e., the unpreserved samples were allowed to oxidize in air. The examples provided in this Issue Paper show that attention must be paid to sample preservation protocols, especially in site assessments that focus on the details of metal or metalloid partitioning to the solid matrix. Improper preservation practices prior to metal partitioning or batch adsorption tests may result in misleading data that are unrepresentative of site conditions. Changes in the oxidation state of iron and sulfur result in mineralogical changes that significantly impact contaminant behavior during characterization tests. Freezing was found to be
an adequate method for preserving samples containing reduced iron, sulfur, and arsenic. When solid-phase tests such as metal speciation analyses, sequential extraction tests, or batch adsorption experiments are carried out on samples collected from anoxic environments, sample preparation and testing must be conducted in an oxygen-free atmosphere.

Although this study focused on a limited set of redox-sensitive elements from only one environment (i.e., freshwater sediment), it is reasonable to expect that the methods employed would be appropriate in other environmental media and for other redox-sensitive elements of interest (e.g., Mn, Se, U, V). Additional studies are needed to address redox preservation over a more complete range of contaminant types and environmental conditions. Other specific issues that require more study include an analysis of methods for preserving organic carbon fractions such as humic substances and an evaluation of storage times for specific redox-sensitive components.

EPA's Office of Research and Development is preparing a technical resource document for the application of monitored natural attenuation (MNA) to inorganic contaminants in ground water (see, e.g., Reisinger et al., 2005). The technical resource document presents a four-tiered analysis for assessing MNA as a viable remediation option for selected metal, metalloid, and radionuclide contaminants encountered in ground water. Components of the tiered approach include demonstrating contaminant sequestration mechanisms, estimating attenuation rates and the attenuation capacity of aquifer solids, and determining potential reversibility issues. All of these issues require samples that are representative of actual environmental conditions in order to evaluate MNA as a possible remedy for restoring ground water resources. Redox preservation of solids collected from the field will necessarily be a key component of MNA assessments for inorganic contaminants.

Notice
The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Quality Assurance Statement
All research projects making conclusions or recommendations based on environmental data and funded by the U.S. Environmental Protection Agency are required to participate in the Quality Assurance Program. This project was conducted under an approved Quality Assurance Project Plan. The procedures specified in this plan were used without exception. Information on the plan and documentation of the quality assurance activities and results are available from the Principal Investigator.

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References


U.S. Environmental Protection Agency (2002). Workshop on monitoring oxidation-reduction processes for ground-water restoration. USEPA National Risk Management Research Laboratory, EPA/600/R-02/002, Cincinnati, OH.

U.S. Environmental Protection Agency (2003). Capstone report on the application, monitoring, and performance of permeable reactive barriers for ground-water remediation; Volume 1, Performance evaluations at two sites. USEPA National Risk Management Research Laboratory, EPA/600/R-03/045a, Cincinnati, OH.

U.S. Environmental Protection Agency (2005). Field study of the fate of arsenic, lead and zinc at the ground water/surface water interface. USEPA National Risk Management Research Laboratory, EPA/600/R-05/161, Cincinnati, OH.
