DQO Process for Soil and Sediment Studies
Coeur d'Alene River Soils and Sediments Bioavailability Studies

U.S. EPA Region 10 (February 2001)

1.0 INTRODUCTION

In February 2001 a "Consensus Plan" for soil and sediment studies in the Coeur d'Alene River Basin was finalized by a number of Coeur d'Alene Basin stakeholders (USEPA Region 10, 2001). As part of this Consensus Plan, a DQO (Data Quality Objectives) process was established to ensure that data collected as part of these studies are of sufficient quality and quantity to support selection of effective soil amendments. The DQO process outlined here follows the EPA's Data Quality Objectives (DQO) framework (EPA 1994) and is a systematic planning approach based on the Scientific Method for establishing criteria for data quality and for developing data collection designs.

The Consensus Plan outlined the experiments to be conducted and the methodology. The objectives of the study are to identify amendment(s) that will make lead less bioavailable to waterfowl and to identify amendments that will reduce metal leachability. It was recognized as part of the DQO process that additional experimental detail would need to be provided. Further, it was recognized that the type, quantity, and quality of data need to be assessed in order to verify that the planning objectives, quality assurance project plan components, and sample collection procedures are satisfied and that the data are suitable for their intended purposes (EPA 1998).

This document augments the Consensus Plan by providing additional experimental detail in Sections 2.0 and 3.0. The DQO and DQA (Data Quality Assessment) processes are discussed generically in Sections 4.0 and 5.0. In Section 6.0, the seven steps of the DQO process are applied to the two studies (IDEQ and FWS).

Whether one uses the term soils or sediments is often related to scientific discipline. Regardless of the term used, soils and sediments are closely related spatially and functionally in riverine and riparian ecosystems. Accordingly, soils and sediments are used interchangeably in this document.

2.0 IDAHO DEPARTMENT OF ENVIRONMENTAL QUALITY FIELD STUDY

This study focuses on the metal (e.g., arsenic, cadmium, lead, and zinc) content of Coeur d'Alene River soils and sediments and the metal leachability after treatment with candidate amendments. The study is to be conducted with funding supplied by the Coeur d'Alene Basin Commission. It is being conducted in partnership with the U.S. Fish and Wildlife Service which is conducting waterfowl feeding studies using amended and unamended soils and sediments to determine the effectiveness of amendments in reducing lead bioavailability.

Philosophy: Remain compatible with previous studies by McGeehan and Williams (1999, 2000), and with proposed new agricultural practice improvement studies by F. Frutchey and M. Schlepp (Frutchey 1994 plus ongoing work). Assist FWS in determining the effects of field conditions on soil amendments in contrast to controlled laboratory settings.

First Objective: To investigate soil amendments that reduce the bioavailability of lead in soils by the formation of low-solubility lead compounds, such as lead phosphate minerals.

Second Objective: To investigate the ability of soil amendments to reduce the solubility and leachability of lead, zinc, cadmium, and arsenic into groundwater and surface water.

Summary: The field-based studies will occur in late winter at two field locations, Bull Run Lake and Black Rock Slough. These same sites will used in a U.S. Fish and Wildlife Service (FWS) waterfowl feeding study (Bull Run Lake and Black Rock Slough; sites at Harrison Slough and Round Lake will be used as controls for the FWS study). Soils in the study areas are a mixture of formed-in-place soil, fluvially deposited sediments, and organic matter. Two amendments will be applied along the northwest side of Bull Run Lake (wetland, anaerobic setting) and along the northeast side of Black Rock Slough. Access to both is available by dirt roads. The study sites are owned by the State of Idaho and managed by Idaho Department of Fish and Game personnel.

A 100-ft x 30-ft test area will be laid out roughly parallel to the water's edge at each site. Exposed vegetation (i.e., not roots) will be removed. After the clearing operations, four 25 ft x 30 ft subplots (2 for amendments, 1 with lime only, and 1 control) will be laid out and permanently staked at each site (Bull Run Lake and Black Rock Slough). These permanent subplots may be shifted somewhat from the initial layout in order to address unforeseen conditions or circumstances. It is anticipated that clearing will be done with a low-ground-pressure dozer and that tilling will be done, depending on soil conditions, on site using a tractor and rototiller or, alternatively, a track-hoe with a long arm or any other equipment that can accomplish tilling from outside the test site.

After clearing, but prior to applying the soil amendments, samples will be collected at four locations in each subplot to a depth of 8 inches. The sample will be collected evenly over the entire 8-inch interval. These samples will not be composited in order to represent the heterogeneity that exists in each plot. However, samples from each sampling location will be homogenized by thoroughly mixing the sample in a plastic wheelbarrow (or other acceptable container) with a shovel or other suitable tool. At least for the plots to be treated with phosphoric acid, samples will be collected with a shovel because of the relatively large sample sizes required for the FWS feeding study (150 pounds for two of the eight feeding groups, Table 1) and the metal analyses. Samples from those plots treated with fishbone apatite, treated with lime, and untreated may be sampled with a smaller tool. The shovel or other sampling tool and mixing container will be scrubbed and rinsed with distilled water before each sample is taken. Samples will be placed in plastic, ziplock bags that have been labeled with a unique sample number, the date of sampling, and the sampler's initials.

Four 1-liter sample splits of the soil samples from the two plots to be treated with phosphoric acid and four 1-liter samples from each of the other three subplots (both at Bull Run Lake and Black Rock Slough) will be sent for chemical analyses. Samples and a completed chain-of-custody/transmittal form will be shipped to the Idaho Department of Environmental Quality's (IDEQ) contracted laboratory via FedEx soon after finishing the sampling event. Chemical analyses will include total P, As, Cd, Pb, and Zn, TCLP extractable metals (As, Cd, Pb, and Zn), SPLP extractable metals (As, Cd, Pb, and Zn), and soil pH (see Table 1).

Four 0.66 cubic foot sample splits of the soil samples from the two plots to be treated with phosphoric acid will be sent to the FWS Patuxent laboratory for use in the feeding studies. It is presumed that FWS will composite them and analyze the composite for total P, As, Cd, Pb, and Zn, and soil pH (see Table 1).

Samples will be taken of water that infiltrates soil sample location holes. Water samples will be collected in pre-rinsed plastic bottles, labeled in the same manner as the soil samples, and shipped to the lab with a completed chain-of-custody/transmittal form by FedEx within 24 hours of sample collection. Samples will be analyzed for pH, temperature, alkalinity, conductivity, dissolved oxygen and dissolved P, As, Cd, Pb, and Zn (see Table 1). Dissolved inorganic constituents will be defined as those constituents passing a 0.45 um filter. One of the four water samples from each subplot at each site will additionally be analyzed for major anions and cations (Ca, Mg, Na, K, Cl^-, and SO_4^{2-}). An analysis of major cations and anions can aid in an understanding of interactions that may take place between the major cations and anions and metals of interest. For example, Ca^{2+} competes with Pb^{2+} for adsorption sites. Similarly, SO_4^{2-} can compete with PO_4^{3-} and AsO_4^{3-} for adsorption sites.

After the first sampling event, the amendments will be applied, tilled to a depth of 12 in. and allowed time to react. It is anticipated that tilling will be done, depending on soil conditions, on site using a tractor and rototiller or, alternatively, a track-hoe with a long arm or any other equipment that can accomplish tilling from outside the test site. Tilling will be done roughly perpendicular to the water's edge and be restricted to four 20 x 30 ft swaths so as to provide a 5-foot buffer zone between subplots. Amendments to be tested are liquid phosphate (phosphoric acid) and solid phosphate (apatite in the form of fishbone).

For the liquid phosphate applications, a fertilizer designated as 0-52-0 will be used. One-percent phosphate as P by weight will be applied to each subplot (20-ft X 30-ft). Therefore, 2,400 pounds of fertilizer as 0-52-0 will be applied to one 20-ft X 30-ft subplot at the two field locations being tested (Bull Run Lake and Black Rock Slough). After a period of one week, 28 pounds of potassium chloride salt (KCl) and approximately 40 pounds $CaCO_3$ equivalent will be tilled into each subplot that received the phosphoric acid treatment. The quantity of calcium carbonate required would be determined experimentally by mixing calcium carbonate with a soil sample and measuring the pH. Enough calcium carbonate (calcite) or, equivalent, would be applied to raise the soil pH to 7.0 or higher. Furthermore, calcium carbonate or equivalent will be applied to one unamended subplot (20-ft X 30-ft plot) at each of the two field locations to raise the soil pH to 7.0 or higher. This subplot will aid in separating the effects of the calcium carbonate from effects of the phosphate amendments. Reagents will be applied by hand using a spreading device and tilled once to achieve mixing.

Fishbone will be used for the solid phosphate applications. As with the liquid applications, the goal is to achieve a phosphate concentration, as P, of one percent by weight. The major inorganic constituent of teeth and bones is hydroxyapatite, $Ca_5(PO_4)_3OH$. Assuming that the composition of the fishbone is $Ca_5(PO_4)_3OH$, 2,900 pounds of apatite would be applied to one 20-foot by 30-foot subplot at each of the two field locations (Bull Run Lake and Black Rock Slough). After a period of one week, approximately 40 pounds of $CaCO_3$ equivalent would also be tilled into the same subplot. The quantity of calcium carbonate required would be determined experimentally by mixing calcium carbonate with a soil sample and measuring the pH. After reagent application by hand using a spreading device, the amended subplots will be tilled once to achieve mixing.

For each subplot, a piezometer or other equipment will be installed to allow monitoring of pore water quality. At 6 months, 12 months, 24 months, and 36 months after amendment application, porewater samples will be collected at an average depth of 8 inches from each piezometer and sent to the laboratory for chemical analyses. The samples will be analyzed for pH and dissolved P, As, Cd, Pb, Zn, alkalinity and some field parameters (see Table 1).

One week after amendment application and also 6 months after amendment application, additional sampling events will occur. For the plots (both at Bull Run and Black Rock) treated with phosphoric acid, 4 samples taken over the 8-inch depth interval will be taken from each plot. A 1-liter sample split will be taken and sent to IDEQ's lab for chemical analysis. Chemical analyses will include total P, As, Cd, Pb, and Zn, TCLP extractable metals (As, Cd, Pb, and Zn), SPLP extractable metals (As, Cd, Pb, and Zn), and soil pH (see Table 1). During the 6 month sampling event, but not the one week event, the remainder of the 4 sample splits, each at least 0.33 cubic foot in volume, will be sent to the FWS Patuxent lab for use in the feeding studies. Four samples will also be taken from each of the other 3 plots (fishbone apatite, lime, and untreated) at both sites during both events and then sent to the IDEQ lab for chemical analysis (Table 1). As before, the shovel or other sampling tool and mixing container will be scrubbed and rinsed with distilled water before each sample is taken. Samples will be placed in plastic, ziplock bags that have been labeled with a unique sample number, the date of sampling, and the sampler's initials.

At 12 months, 24 months, and 36 months after amendment application soil samples will be obtained in each subplot over the 8-inch depth interval. The soil samples (4 per subplot) will be composited by mixing the samples in a plastic wheelbarrow or other appropriate receptacle and analyzed as indicated by Table 1. As before, the shovel and mixing container will be scrubbed and rinsed with distilled water before each sample is taken. Samples will be placed in plastic, ziplock bags that have been labeled with a unique sample number, the date of sampling, and the sampler's initials.

Only the soils amended with the liquid phosphoric acid will be used in the FWS feeding study in 2001. It is hoped that additional studies can be done in 2002 to test bioavailability reductions with the fishbone apatite amendment.

Measurements: The analytical protocols for the various tests will those specified in the Idaho Department of Environmental Quality analytical contract which complies with the EPA Contract Laboratory Program. Protocols include those indicated below and in Table 2. Table 2 also contains recommended control frequencies for quality control samples.

Soil metal contents: As, Cd, Pb, Zn, Ca, K, Mn, and Na (Method IN-CLP, IN-CLP-LOW, SW-846 6010B)

Toxicity Characteristics Leaching Procedure (TCLP) (EPA Method SW-846 1311)

Synthetic Precipitation Leaching Procedure (SPLP) (EPA Method SW-846 1312)

Soil pH (Standard Method 150.1, EPA Method SW-846 9045C)

Dissolved metals contents in water: As, Cd, Pb, Zn, Ca, K, Mn, and Na (Method DIN-CLP-LOW, Standard Method D200.7, EPA Method SW-846 D6010B, EPA Method SW-846 D7000 series for specific metals)

Water pH (Standard Method 150.1, EPA SW-846 9040B)

3.0 U.S. Fish and Wildlife Service (FWS) Field/Laboratory Study

This study focuses on the bioavailability of lead in Coeur d'Alene River sediments treated with phosphoric acid amendments. The study is to be conducted in collaboration with USGS, IDEQ, and EPA, and is described by Audet (2000).

Philosophy: Remain compatible with previous FWS studies by Heinz et al. (1999), and Hoffman et al. (2000); control as many variables as possible.

Objectives: To determine the bioavailability of lead to mallards in Coeur d'Alene Basin River sediments treated with phosphoric acid amendment and to measure the change in mallard lead uptake associated with soil treatment.

Amendment: Liquid apatite (phosphoric acid) at a rate of approximately 1% phosphate, as P, by dry weight of soil. Soil pH should be raised to 7.0 or higher with lime and/or limestone if it is initially below 6.0. Chloride salt will also be added to promote the formation of chloropyromorphite. This amendment combination should be effective under all moisture regimes; lead will be permanently bound, although zinc and cadmium probably will be adsorbed and therefore may be re-released if conditions change. Note that until mineralization occurs, phosphoric acid will have a tendency to release phosphate, which may create a nutrient pollution problem. Reaction time should be approximately six months.

Summary: One group of fully grown male mallards (each group will consist of 10 ducks) will serve as controls and be fed a diet containing 12% clean sediment from Round Lake. A second group will be fed a diet containing 12% lead-contaminated sediment collected from Harrison Slough in the Coeur d'Alene River. Four additional groups will be fed a diet containing 12% lead-contaminated sediment treated with phosphoric acid. There will also be two additional non-amendment groups for a total of eight groups. The sediment used will be composited and homogenized, mixed with the amendments and allowed time to react; the resulting mix will then be added to commercial waterfowl diet and pelletized. The study will be conducted during cool weather, in the fall of 2001, following a 30-day period of quarantine.

Based on the consensus of stakeholders, the following treatment groups will be included in the FWS's study (Table 3).

Group 1	Round Lake, controlled lab setting, no amendment (low lead control)
Group 2	Harrison Slough, controlled lab setting, no amendment
Group 3	Harrison Slough, controlled lab setting, amendment (phosphoric acid w/ lime or limestone and w/chloride salt) applied in lab and aged
Group 4	Black Rock Slough, controlled lab setting, no amendment
Group 5	Black Rock Slough, field test plot, collect sample after amendment (phosphoric acid w/ lime or limestone and w/ chloride salt) applied and aged in the field plot
Group 6	Bull Run Lake, controlled lab setting, no amendment
Group 7	Bull Run Lake, controlled lab setting, amendment (phosphoric acid w/ lime or limestone and w/ chloride salt) applied and aged in lab
Group 8	Bull Run Lake, field test plot, collect sample after amendment (phosphoric acid w/ lime or limestone and w/ chloride salt) applied and aged in the field plot

Measurements: Protocols are those described in Heinz et al. (1999).

- Bird body weight and concentrations of lead measured in blood, liver, and kidney at 8 weeks

- Hematocrit, hemoglobin, protoporphyrin, and delta-aminolevulinic acid dehydratase (ALAD)

It is expected that the USFWS and the Patuxent Wildlife Research Center will develop and publish manuscripts presenting the study results.

3.0 DATA QUALITY OBJECTIVES (DQO) PROCESS

To ensure that data collected as part of these studies is of sufficient quality and quantity to support selection of effective soil amendments, the study designs follow the EPA's Data Quality Objectives (DQO) framework (EPA 1994). The DQO process is a systematic planning approach based on the Scientific Method for establishing criteria for data quality and for developing data collection designs.

DQOs are qualitative and quantitative statements derived from the outputs of the first six steps of the DQO Process that:

1. Clarify the study objective

2. Define the most appropriate type of data to collect

3. Determine the most appropriate conditions from which to collect the data

4. Specify tolerable limits on decision errors, which will be used as the basis for establishing the quantity and quality of data needed to support the decision

The DQOs are then used to develop a scientific and resource-effective data collection design. The DQO Process consists of the following seven steps:

1. State the Problem. Concisely describe the problem to be studied. (e.g., "Contaminated sediments have negatively impacted waterfowl in the Lower Coeur d'Alene River. Different treatment technologies have been proposed but need to be evaluated for effectiveness.")

2. Identify the Decision. Identify what questions the study will attempt to resolve, and what actions may result. (e.g., "Are the different soil amendments being proposed effective at reducing lead concentrations in waterfowl? Are the different soil amendments being proposed effective in reducing the leachability of arsenic, cadmium, lead, and zinc in sediments?")

3. Identify Inputs to the Decision. Identify the information that needs to be obtained and the measurements that need to be taken to resolve the decision statement, e.g.:

    - List of proposed soil amendments (with rationale for selection)
    - Mallard duck blood lead levels
    - Pre-treatment and post-treatment sediment concentrations

4. Define the Boundaries of the Study. Specify the time periods and spatial area to which decisions will apply.

5. Develop a Decision Rule. (e.g., "If average lead concentrations in blood samples collected from mallard ducks is less than ? ug/dL (action level), then soil amendment A will be selected as a preferred treatment technology. If average lead concentrations in treated soil after 36 months leaches less than ? mg/L, then soil amendment A will be selected as a preferred treatment technology.")

6. Specify Limits on Decision Errors. (e.g., for a 30 ft x 25 ft test plot, N number of samples should be collected using a random sample collection method to estimate average metals concentrations with a 95% confidence). The DQO guidance should be consulted on procedures for determining N from a known action level and desired decision error rate.

7. Optimize the Design for Obtaining Data. Review all of the above before finalizing plans.

4.0 DATA QUALITY ASSESSMENT (DQA)

The purpose of data quality assessments is to assess the type, quantity, and quality of data in order to verify that the planning objectives, quality assurance project plan components, and sample collection procedures were satisfied and that the data are suitable for their intended purposes (EPA 1998).

Data Quality Assessment is a five step procedure for determining statistically whether or not a data set is suitable for its intended purpose. DQA is a scientific and statistical evaluation of data to determine if it is of the type, quantity, and quality needed. The DQA process may be performed either during a project to check the progress of data collection or at the end of a project to check if objectives were met. DQA refers to specific data quality objectives established during the preparation of the sampling plan, as discussed above.

1. Review the Data Quality Objectives
2. Conduct a Preliminary Data Review
3. Select the Statistical Test
4. Verify the Assumptions of the Test
5. Draw Conclusions From the Data

The DQA process will be based on the data quality objectives selected through the DQO process and will be detailed when the initial data set (initial soil quality data) becomes available. At this time, the data will be reviewed and the sampling strategy will be readjusted if necessary.

5.0 APPLIED DQO PROCESS

5.1 IDEQ Field Study

A fundamental question that needs to be answered during the DQO process is how to separate real effects from the inherent variability of the system. Specifically, we want to know the probability of committing a Type I error. In a Type I error, for example, there would be no effect from the amendment additions but the results would be significant (e.g., indications of reductions in bioavailability) by chance because of system variability. Inherent variabilities in the system can arise from: (1) the heterogeneity of soils and soil formation in general; (2) the processes through which the sediments became commingled with mine waste, then deposited in the wetlands of the Lower Coeur d'Alene River; (3) the sampling methods used; (4) the application method(s) to be used for the proposed treatments; (5) external events (e.g., floods, trespassing from recreational vehicles) occurring between sampling rounds. We need to be able to quantify and manage the risk that changes observed in constituent concentrations or other parameters measured may be due purely to those sources rather than to the applied treatments.

1. <u>State the Problem</u>. "Contaminated sediments have negatively impacted waterfowl in the Lower Coeur d'Alene River. Different treatment technologies have been proposed but need to be evaluated for effectiveness in reducing the bioavailability and leaching potential of metals. The contaminated sediments are heterogeneous with variable lead (and other metals') concentrations, and the effects of random variation must be separated from the treatment effects."

2. <u>Identify the Decision</u>. "Are the different soil amendments being proposed effective in reducing the bioavailability of lead in sediments or are the changes measured due to background variation? If the treatment is responsible for a reduction in bioavailability, it will be studied further for full-scale application." The first objective is addressed in the feeding study discussed below. Another objective and decision point is addressed by the following question; "Are the different soil amendments being proposed effective in reducing the leachability of arsenic, cadmium, lead, and zinc in sediments or are the changes measured due to background variation? If the treatment is responsible for a reduction in metal leachability, it will be studied further for full-scale application."

3. <u>Identify Inputs to the Decision</u>. Pre- and post-treatment constituent concentrations and variance in the soils of the study area with respect to:

   - total P, As, Cd, Pb, and Zn
   - TCLP extractable metals (As, Cd, Pb, and Zn)
   - SPLP extractable metals (As, Cd, Pb, and Zn), and
   - soil pH.

   Reece (1974) collected soil samples from locations in Cataldo Flats and the Main Stem Delta. Based on the averages and standard deviations for metal concentrations in these areas, the mean lead concentration and standard deviation are approximately 4,000 mg/kg and 370 mg/kg, respectively. Data from the TDM database (URS 2000) indicate that the mean lead concentration and standard deviation at Black Rock Slough are approximately 5,200 mg/kg and 1,800 mg/kg, respectively. These data also indicate that the mean lead concentration and standard deviation at Bull Run Lake are approximately 5,200 mg/kg and 910 mg/kg, respectively.

4. <u>Define the Boundaries of the Study</u>. Physical: Four 20 ft x 30 ft subplots at Bull Run Lake and four at Black Rock Slough. Each field plot location is comprised of one subplot without amendment, one subplot with pH adjustment only, one subplot with pH adjustment plus phosphoric acid, and one subplot with pH adjustment plus powdered

fishbone (apatite). Temporal: From initial tilling (planned for March 2001) through completion of the study, with sampling events at time 0 (pretreatment) and at 6 months after treatment.

5. Develop a Decision Rule. "If the leachable metal concentrations (by TCLP and SPLP) from treated subplots are less than for the control subplots, then the soil amendment will be considered a potential treatment technology and studied for full-scale application."

6. Specify Limits on Decision Errors. The objective of sampling is to collect a sufficient number of samples so that there is a 90% confidence that the sample mean is within +/– 400 mg/kg of the population mean. As indicated, data from Reece (1974) indicate that the mean lead concentration in the Cataldo Flats area is approximately 4,000 mg/kg with a standard deviation of approximately 370 mg/kg. Assume that the data of Reece (1974) reflect the mean and standard deviation of the sediment lead concentrations in the areas to be sampled. Also assume that random sampling will occur and that parametric estimation methods are applicable. Parametric estimation methods apply because soil and aqueous metal concentrations are lognormally distributed (URS 2000). Collection of four samples from each of the subplots will result in a 90% confidence that the sampling mean is within +/– 400 mg/kg of the true mean. Therefore, four samples will be collected from each of the subplots at each sampling interval.

   The unpaired student t-test will be used to determine if metal concentrations in leachates from the TCLP and SPLP leaching tests are significantly different than leachates from the control (unamended) samples. The significance level will be set at $\alpha < 0.05$ where α (alpha) is the Greek letter used as the symbol for the probability of a Type I error. That is, there must be less than a 5 percent chance of committing a Type I error. Accordingly, we would obtain significant results by chance less than 5% of the time. Therefore, if leaching data from amended sediments are significantly different (lower) than similar data from unamended sediments at $\alpha < 0.05$, it will be assumed that the amendments were responsible for the reductions in bioavailability.

7. Optimize the Design for Obtaining Data. Design optimization has occurred based on discussions with stakeholders and will continue to occur subsequent to additional conversations with and evaluations by stakeholders.

5.2 USFWS Field/Laboratory Study

The central question of the study is whether or not the phosphoric acid amendment is able to reduce lead bioavailability to waterfowl, and thereby decrease the risk of waterfowl mortality.

1. State the Problem. "Contaminated sediments have negatively impacted waterfowl in the Lower Coeur d'Alene River. Different treatment technologies for sediments have been proposed but need to be evaluated for effectiveness in reducing bioavailability."

2. Identify the Decision. "Is the phosphoric acid soil amendment being proposed able to reduce lead concentrations in waterfowl tissues? If the treatment is able to cause sufficient reductions in bioavailability of lead to waterfowl, it will be studied further for full-scale application."

3. Identify Inputs to the Decision.

   - Bird body weight and concentrations of lead in blood, liver, and kidney lead at 8 weeks.

   - Effects of lead on blood parameters. [Hematocrit, hemoglobin, protoporphyrin, and delta-aminolevulinic acid dehydratase (ALAD)].

4. Define the Boundaries of the Study. Eight groups of 10 ducks at USGS Patuxent laboratory, studied for eight weeks, approximately from late September through late November.

5. Develop a Decision Rule. "If the concentrations of lead in blood, liver, and kidney from mallard ducks fed sediment treated with amendment are sufficiently less than those fed sediment without amendment, then the amendment could be considered a viable treatment technology and studied for full-scale application in areas where the treatment is anticipated to result in no injury to waterfowl."

6. Specify Limits on Decision Errors. Analysis of variance will be used to check for differences among groups. When an analysis of variance is significant at $\alpha < 0.05$, Tukey's multiple-comparison test will be used, also at $\alpha < 0.05$, to separate means. When required, a log transformation will be used on data to achieve homogeneity of variances. In statistical tests, a level of one-half the detection limit will be assigned to samples in which lead in tissues is below the detection limit.

7. Optimize the Design for Obtaining Data. Design optimization has occurred based on discussions with stakeholders and will continue to occur subsequent to additional conversations with and evaluations by stakeholders.

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Table 1
Analyses for Pre- and Post-Amendment Applications for IDEQ and FWS**
(Analyses with ** are by FWS – all others by IDEQ)

Location	Round Lake**	Harrison Slough**	Bull Run Lake	Black Rock Slough
Subplots	No subplots	No subplots	4 (phosphoric acid, apatite, lime only, and control)	4 (phosphoric acid, apatite, lime only, and control)
Field Parameters: soil pH, Bd, moisture content, lime/limestone requirement	** One sample – soil pH only	** One sample – soil pH only	Four samples	Four samples
IDEQ Soil Analyses*	Not applicable	Not applicable	Pre-Amendment - 4 x 4 = 16 Post-Amendment 4 X 4 X 2 = 32 (4 samples from each of 4 subplots at two time periods (1 week and 6 months); 12, 24 and 36 months may use composites	Pre-Amendment - 4 x 4 = 16 Post-Amendment 4 x 4 X 2 = 32 (4 samples from each of 4 subplots at two time periods; (1 week and 6 months); 12, 24 and 36 months may use composites
FWS Soil Analyses **	** 4 from 150 lb. composite sent to Patuxent	** 4 from each of two 150 lb. Composite sent to Patuxent (total of 8)	** 4 x 3 = 12; 4 from each of 3 separate 150 lb. composites sent to Patuxent (1 composite pre-amendment, 1 after amendment application by FWS and 1 six months after application in field.)	** 4 x 2 = 8; 4 from each of 2 separate 150 lb. Composites sent to Patuxent (1 composite pre-amendment and 1 six months after application in field.)
Water Analyses +	Not applicable	Not applicable	Pre-Amendment 4 x 4 = 16 Post-Amendment (6, 12, 24, and 36 months) 4 x 4 = 16	Pre-Amendment 4 x 4 = 16 Post-Amendment (2, 12, 24, and 36 months) 4 x 4 = 16
Water Analyses ++	Not applicable	Not applicable	Pre-Amendment – 4 x 1 = 4	Pre-Amendment - 4 x 1 = 4
Quantity sent to Patuxent	150 lbs. or approx. 1.25 ft^3	300 lbs. Or approx. 2.5 ft^3 (150 lbs. For each of 2 groups)	450 lbs. or approx. 3.75 ft^3 (150 lbs. for each of 3 groups)	300 lbs. or approx. 2.5 ft^3 (150 lbs. for each of 2 groups)

Note: Soil weights are wet weights
*Soil analyses for total P, As, Cd, Pb, and Zn and SPLP and TCLP extractable metals (As, Cd, Pb, and Zn), & soil pH
**Soil analyses for total P, As, Cd, Pb, and Zn by FWS; analyses conducted by FWS are ICP metal scans, minimally P, As, Pb, Cd, and Zn will be reported; field parameters as indicated.
+ Water analyses for dissolved P, As, Cd, Pb, and Zn, conductivity, temperature, dissolved oxygen, alkalinity, and aqueous pH

++ Water analyses for dissolved P, As, Cd, Pb, Zn, Ca, Mg, Na, Cl, and SO_4^{2-}, conductivity, temperature, dissolved oxygen, alkalinity and aqueous pH

Table 2
Analyses and Methods

Analyte and Method	Matrix	Lab QC Frequency		Field QC Frequency		
		MS	*Dup*	*Dup*	*RB*	*PE*
Metals	Soil	5%	5%	10%	1/event metals only	1/event metals only
Metals, TCLP,SW-846 1311	Soil	5%	5%	10%	1/event metals only	1/event metals only
Metals, SPLP,SW-846 1312	Soil	5%	5%	10%	1/event metals only	1/event metals only
Metals, SW-846 D7000 series	Water	5%	5%	10%	1/event metals only	0
pH, Method 150.1, SW-846 9045C)	Soil	5%	5%	10%	0	0
pH, Method 150.1, SW-846 9040B	Water	5%	5%	10%	0	0
Chloride, 325.3	Water	5%	5%	10%	1/event	0
Phosphates 365.1, 375.1, through 375.1	Water	5%	5%	10%	1/event	0
SO_4^{2-}, Method 300.0	Water	5%	5%	10%	1/event	0
Redox potential	Water	0	0	10%	0	0
Temperature	Water	0	0	10%	0	0
Dissolved oxygen	Water	0	0	10%	0	0
Alkalinity	Water	5%	5%	10%	0	0
Conductivity	Water	0	0	10%	0	0
Body Weight	Bird	Per protocols established in: Heinz et al. 1999; Hoffman et al., 2000				
Hematocrit	Blood	Per protocols established in: Heinz et al. 1999; Hoffman et al., 2000				
Hemoglobin	Blood	Per protocols established in: Heinz et al. 1999; Hoffman et al., 2000				
Protoporphyrin	Blood	Per protocols established in: Heinz et al. 1999; Hoffman et al., 2000				
ALAD	Blood	Per protocols established in: Heinz et al. 1999; Hoffman et al., 2000				

Temperature, pH, dissolved oxygen, and conductivity by field instrument B Horiba U-22 or equivalent
D B duplicate, MS B matrix spike, PE B performance evaluation samples, QC B quality control, RB B rinsate blank, HDPE B high-density polyethylene

Table 3
Breakdown of Waterfowl Study Groups

Group Number	Location	Aged in Lab	Aged in Field	Comments
Group # 1	Round Lake			Low (Pb) control
Group # 2	Harrison Slough			No amendment
Group # 3	Harrison Slough	X		
Group # 4	Black Rock Slough			No amendment
Group # 5	Black Rock Slough		X	
Group # 6	Bull Run Lake			No amendment
Group # 7	Bull Run Lake	X		
Group # 8	Bull Run Lake		X	