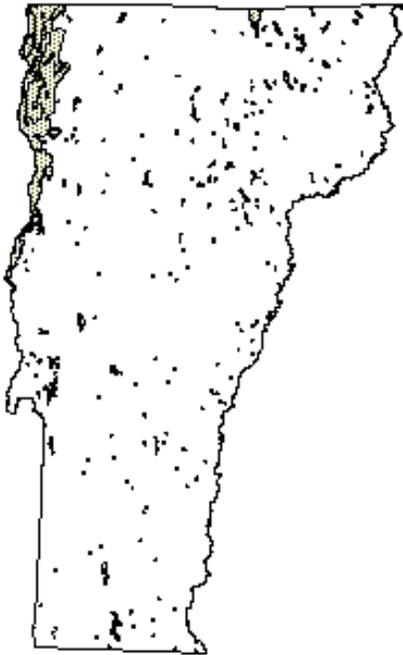


Quality Assurance Project Plan

July 21, 1998

USEPA Region 1 - New England  
Regional Environmental Monitoring and Assessment  
Program

**Assessment of Mercury in Hypolimnetic  
Lake-bed Sediments of Vermont and New  
Hampshire**



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Appendix A **LaRosa Laboratory Quality Assurance Plan**

Appendix B **Standard Operating Procedures from the LaRosa Laboratory Quality Assurance Plan  
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## 1.0 Project Description

### 1.1 General Overview and Experimental Design

The purpose of this research is to characterize concentrations of total and methylmercury in waters and sediments of Vermont and New Hampshire lakes, and to relate these data to commonly measured water column chemical parameters and watershed-level physical attributes. A primary research goal is to identify specific lake types which are likely to have elevated methylmercury in hypolimnetic waters. A subsample of lakes will be sampled for fish tissue mercury contamination to assess whether these 'higher methylation potential' lakes are indeed contributing mercury into the food chain.

The Vermont Department of Environmental Conservation (VTDEC) and New Hampshire Department of Environmental Services (NHDES) will conduct this two-year, stratified, spatially randomized sampling following an EPA-EMAP lake selection design. This study will evaluate a two size-strata, spatially randomized selection of lakes of greater than 20 acres. These strata will be further sub-stratified along their watershed to lake area ratios, since this index has been shown to affect total sediment mercury concentrations (Driscoll, 1996). In addition, we will sample a second group of lakes scheduled for paleolimnological analysis of mercury accretion.

- 1a) A spatially randomized selection of VT and NH lakes of 20 to < 100 acres in size. These lakes will be further stratified into two sub-strata, based upon their lake to watershed area ratio.
- 1b) A spatially randomized selection of VT and NH lakes, 100 or more acres in size. These lakes will also be further stratified into two sub-strata, based upon their lake to watershed area ratio.

-A total of 90 lakes will be sampled. This represents approximately 11 percent of the total number of lakes of 20 acres in size or greater within each State. The number of lakes within each strata, by State, is listed in Table 1.

- 2) Lakes which are sampled in conjunction with the new VT-NH paleolimnological assessment of Vermont lakes.

-A total of 18 such lakes will be sampled.

For groups 1a and 1b, lakes will be visited once, and surficial sediment samples for total and methylmercury will be acquired from a single, representative sampling station. Water samples for total and methylmercury will be procured from the overlying water column using strict mercury-clean collection protocols. Major solutes, and parameters related to methylmercury formation will be procured from the overlying water column using standard limnological collection protocols.

For group two, total mercury in sediments will be analyzed from cores for 18 of the 24 lakes scheduled for sampling in conjunction with the Paleolimnological and Biological Assessment of Northern New England Lakes, which has been funded under section 104(b)3 of the C.W.A. Currently, sediment dating ( $Pb^{210}$  corroborated with  $Cs^{137}$ ) is scheduled for only two of these lakes. This project will date an additional six of these 24 lake cores. Total sediment mercury will be analyzed on at least 6 strata of each undated core, and from 12 strata of each dated core.

Field operations will be conducted by the VTDEC - Water Quality Division, and NHDES - Biology Bureau, and chemical analyses of sediments, fish tissue, and most water samples will be conducted by the VTDEC LaRosa Environmental Laboratory. The University of Maine Sawyer Research Laboratory is one contract laboratory which could conduct analysis of water samples for dissolved organic carbon. Dr. C.T. Driscoll's Syracuse University Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) laboratory will conduct sediment methyl, and aqueous total and methylmercury analyses. A rigorous program of quality assurance and quality control will be applied to both the field and laboratory phases of this project.

Variation in sediment and aqueous total and methylmercury concentrations, water chemistry data, and geo-physical lake and watershed attributes will be analyzed to test three specific project hypotheses elaborated below. Specific data analysis techniques will include applicable regression analyses for determination of relationships between mercury and physico-chemical lake attributes. Multivariate ordination techniques such as clustering, canonical correspondence, and principal components analysis will be investigated to explore the response of sediment mercury concentrations to variation in multiple parameters. The strength of predictive variables can be assessed using multiple step-wise regression. The design of this proposed environmental monitoring effort is such that project hypotheses can be tested, and project objectives will be met. The resulting data will be used to build a ranking system which identifies lake types which manifest high methylmercury concentrations in the water column.

*Table 1. Breakdown of number of lakes by strata and State for the Assessment of Mercury in Hypolimnetic Lake-bed Sediments of Northern New England, with an emphasis on Vermont and New Hampshire.*

	Number of eligible NH lakes	Number of NH lakes to be selected	Number of eligible VT lakes	Number of VT lakes to be selected
20 - < 100 acres Lake - Watershed ratio (%) < 6.0 <sup>1</sup>	308	15	95	13
20 - < 100 acres Lake - Watershed ratio (%) \$6.0 <sup>1</sup>		15	95	13
\$100 acres Lake - Watershed ratio (%) < 6.0 <sup>1</sup>	210	9	45	8
\$100 acres Lake - Watershed ratio (%) \$6.0 <sup>1</sup>		9	45	8
Total Lakes to be sampled, group one.		48		42
Paleolimnology lakes, group two.	12	9	12	9
Total number of lakes under evaluation		57		51

<sup>1</sup> Note: The watershed to lake area ratio breakpoint of six percent is calculated as the median watershed-lake area ratio (%) for Vermont and New Hampshire lakes falling in the two size categories.

As a contribution to this project, EPA-Region 1 and NHDES will collect fish from 20 of the study lakes. These will be analyzed for total mercury. These data will be used to validate relationships observed in the chemical data, and specifically to test the ranking system.

## 1.2 Project Hypotheses and Objectives

### 1.2.1 Project Hypotheses:

1. *Concentration of surficial sediment total and methylmercury in Vermont and New Hampshire lakes is related to physico-chemical lake and watershed characteristics.*

Taken as a whole, Vermont and New Hampshire are divided approximately into two geological 'regions' in which our lakes are located. One of these regions displays typically granitic-derivate bedrock, while the other is characterized by bedrock which is schistic and calcareous. Within this coarse classification, marked variations exist in lake morphology. VTDEC and NHDES's respective lakes and ponds databases contain physical and chemical data on approximately 810 lakes of 20 acres in size or greater. The databases include such physical information as elevation, lake size and morphometry, watershed size, watershed area in wetlands (VT<sup>1</sup>), as well as multiple parameters related to lake water chemistry trophic state. We hypothesize that there is variation in sediment total and methylmercury concentration in Vermont and New Hampshire lakes which can be explained by variation in one or a combination of the lake and watershed physical and trophic parameters. In particular, we propose to use the lake and watershed morphometric variables to evaluate whether there exist significantly detectable variations in sediment-mercury concentrations between lakes with large watershed-lake area ratios as compared with those lakes with small watershed to lake area ratios.

2. *Concentrations of total and methylmercury in VT and NH lake waters are related to sediment mercury concentrations, and to lake and watershed level physical and chemical parameters.*

We hypothesize that water column total and methylmercury varies with: sediment mercury concentrations; with water quality parameters such as major solutes, hypolimnetic sulfide, measures of dissolved organic carbon (DOC), and degree of hypolimnetic anoxia; and with morphological characteristics listed in hypothesis number one (above).

3. *Sediment-mercury concentrations evidenced in the stratigraphy of selected Vermont and New Hampshire lake sediment cores show detectable variation over the past 300 years.*

VTDEC and NHDES have received funding from EPA Region 1 under section 104(b)3 of the C.W.A. to undertake a paleolimnological assessment of northern New England lakes (VT and NH). Sediment-core samples from 18 lakes collected in conjunction with that effort will be analyzed to determine if significant changes in sediment-mercury have occurred between pre-settlement and present times. Six of these lakes will have dated cores which will be used to show patterns of historical mercury accretion in Vermont and New Hampshire lakes, and particular attention will be accorded to the top-most (recent) sediments of the dated cores to determine if recent deposition of

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<sup>1</sup> *The percentage of watershed area occupied by wetlands is not a readily available metric for New Hampshire lakes. Accordingly, we will explore the relationship between DOC and percent wetlands for the test Vermont lakes, in order to use DOC as a surrogate for percent wetlands for the New Hampshire lakes (Driscoll, 1996).*

mercury to sediments is in decline. In order to control for differences in sediment accretion rates, lakes from which dated cores are collected will be carefully selected such that they have similar morphometric and watershed attributes. Selection of 18 of 24 paleolimnology lakes will not be subject to spatial randomization. Where historical data are available, the time-signature of documented watershed disturbances will be correlated with the stratigraphy of mercury in the dated sediment cores. This element of the project represents a significant opportunity for bi-state coordination and leveraging of existing project resources.

### 1.2.2 Project Objectives

1. Measure total and methylmercury concentrations in the water and surficial sediments of approximately 90 Vermont and New Hampshire lakes. Measure fish-tissue mercury levels on 20 of these study lakes.
2. Measure those water chemistry parameters which the scientific literature suggests accentuate methylation in the 90 study lake set.
3. Explore the relationship between sediment total and methylmercury concentrations, physical lake and watershed characteristics, and water chemistry conditions.
4. Explore the relationship between aqueous and total and methylmercury concentrations, physical lake and watershed characteristics, and water chemistry conditions.
5. Evaluate (rank) the potential for migration of total sediment mercury into the water column in methylated form. This will be accomplished by developing a ranking system using the results of Objectives 3 and 4 (above).
6. Calibrate the ranking system using fish tissue mercury data acquired in conjunction with this effort, and validate the ranking system using existing fish tissue data.
7. Investigate the historical deposition patterns of total mercury in dated cores collected from the sediments of six lakes, and relate these patterns to known historical events in the lakes' watersheds where possible. Investigate further the deposition profile of total mercury in undated cores from the sediments of 12 additional lakes. Compare stratigraphy of mercury from Vermont and New Hampshire lakes with that of selected Adirondack, Maine, and Minnesota studies.

### 1.3 Schedule

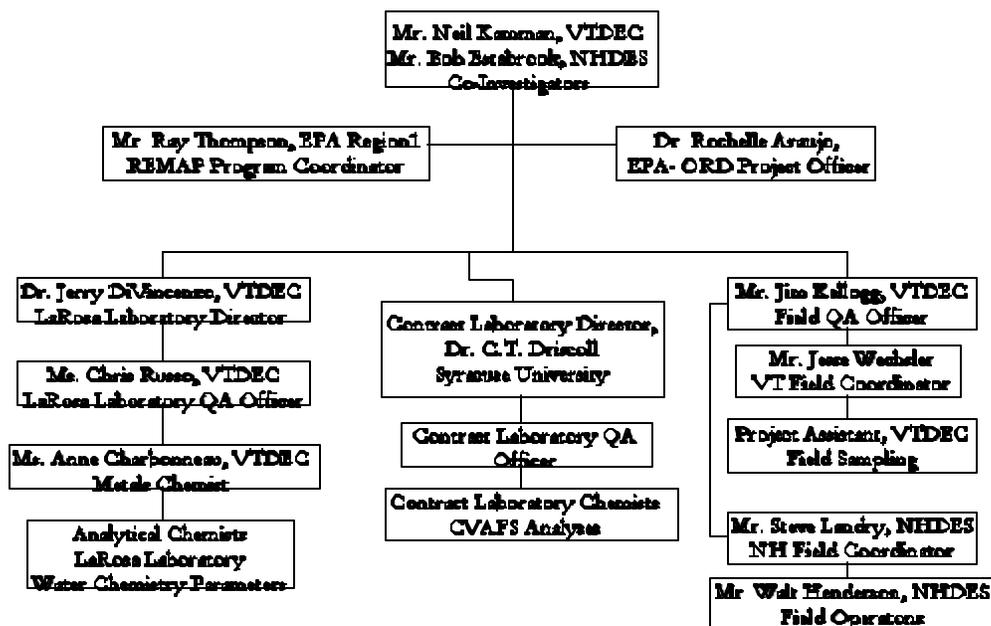
A three-year project plan is envisioned. During year one (1997), the project will be initiated. These tasks include preparation of a Quality Assurance Project Plan (this document), selection of study lakes, logistics planning, and equipment and supplies acquisition. The full field program will be executed during 1998 and 1999. Laboratory analyses and validation, reduction, and analysis of incoming data will be on-going. The project timeline is presented in Table 2.

Table 2. Schedule for the Assessment of Mercury in Hypolimnetic Lake-bed Sediments of Vermont and New Hampshire. (Milestone endpoints are denoted by XX).

	Oct 1997	Jan 97	Apr 1998	Jul 98	Oct 98	Jan 98	Apr 1999	Jul 99	Oct 99	Jan 2000	Apr 00	Jul 00	Oct 00
Project Initiation	X	X	XX										
Field Sampling			X	X	X		X	X	XX				
Laboratory Analysis			X	X	X	X	X	X	X	XX			
Data Analysis				X	X	X	X	X	X	X	X	XX	
Interim Quarterly Reports		X	X	X	X	X	X	X	X	X	X	X	
Annual Report							X				X		
Final Report													XX

## 1.4 Project Organization and Responsibilities

### 1.4.1 Project Organization Chart



## 1.4.2 Personnel Responsibilities

### Vermont Personnel:

#### Neil Kamman, Co-Investigator

Project management and oversight. Responsible for all facets of the program including timely and efficient field operations, data analysis and hypothesis testing, development of contracts, and quarterly and annual report preparation.

#### Jim Kellogg, Field QA Officer

Field operations quality assurance. Responsible for precision, accuracy, and comparability of field sample and data collection procedures for all sampling activities undertaken in conjunction with this project.

#### Kate Peyerl, VT Field Coordinator

Daily field operations and equipment maintenance. Data entry and microcomputer file maintenance. Timely submission of samples to appropriate laboratories.

Project Assistant, field operations.

#### Jerry DiVincenzo, LaRosa Laboratory Supervisor

Oversight of LaRosa laboratory operations and final validation of data to project management

#### Christine Russo, LaRosa Lab QA Officer

Responsible for precision, accuracy, and comparability of data produced from samples delivered to the LaRosa laboratory. Assist project management in the resolution of any problems associated with samples processed.

### New Hampshire Personnel:

#### Bob Estabrook, Co-Investigator

Project management and oversight. Co-responsible for all facets of the program including timely and efficient field operations, data analysis and hypothesis testing, and quarterly and annual report preparation.

#### Steve Landry, NH Field Coordinator

Daily field operations and equipment maintenance. Data entry and microcomputer file maintenance. Timely submission of samples to appropriate laboratories.

Walt Henderson, field operations

## **2.0 Quality Assurance Objectives**

This document relies on the existing, approved VTDEC LaRosa Laboratory Quality Assurance Plan (VTDEC 1992b rev. 1997) for documentation of this studies' Quality Assurance Program. For this reason, the entire LaRosa Plan is included in Appendix A. The reader should note that while the NHDES

laboratory is included in this study, their role is limited to analyses for alkalinity and apparent color. To avoid conflicts between each laboratories quality assurance program, this study will employ the LaRosa laboratories' quality assurance program to provide valid study results. The quality assurance program employed by the CVAFS laboratory will conform to that suggested in Method 1631 (USEPA 1996b).

## ***2.1 Total sediment mercury, total mercury in fish, and all water chemistry parameters:***

### 2.1.1 Precision

Precision of all chemical parameters measured can be assessed by field duplication of the sampling procedures. Field duplication provides an estimate of parameter variability for samples collected in the real-world, field setting. Precision of data results is also assessed by laboratory duplication, or reanalysis. Laboratory duplication of analytical procedures provides a measure of methodological precision. Using field or laboratory duplication, precision is calculated as mean relative percent difference across all sample pair.

Overall precision of chemical measures will be calculated from paired field duplicate samples. Table 4 provides target precision values for parameters measured by this project. Precision of previous sediment mercury field duplicates collected in Vermont (VTDEC, 1992) indicates that the precision of samples collected in the field should be equal to or less than 10 percent.

Laboratory precision is assessed in accordance with section 11.2 of the LaRosa Laboratory Quality Assurance Plan. For water chemistry parameters, sampling precision will also be calculated from paired field duplicate samples, and analytical precision will be evaluated from laboratory reanalysis or laboratory duplicates.

**C For every 10 sediment and water chemistry samples collected, a field duplicate will be collected and analyzed.**

### 2.1.2 Accuracy

Accuracy of aqueous samples is assessed via two procedures. Spiking, the addition of a known quantity of analyte to one of a laboratory duplicate sample pair, permits the calculation of percent recovery. Blanking is the process of analyzing reagent water which has simply been placed into the sampling container (bottle blank), processed through the sampling equipment and stored in the sampling container (equipment blank), or processed through the sampling equipment and stored in the sampling container in the field (field blank).

Accuracy will be determined from samples spiked with a known quantity of analyte or by using referenced check samples (ie. NIST Buffalo River sediment for mercury). Previous lake sediment mercury spikes analyzed in Vermont (VTDEC, 1992) have achieved an accuracy of +/- 10 percent of complete recovery (100%). Section 11.1 of the LaRosa Laboratory Quality Assurance Plan provides detail on procedures to assess accuracy of sample results in the laboratory. Table 4 provides target accuracy values listed in the LaRosa Laboratory QA Plan for parameters measured by this project.

**C For every 10 samples collected, additional aliquot/sediment will be submitted for spike analysis as appropriate to the parameter in question.**

### 2.1.3 Comparability

Methodological: Comparability of data results between study lakes and across studies will be accomplished by employing standardized methods for the collection of water and sediment samples. Clean protocols will be adapted to acquire samples for mercury in sediments (USEPA, 1996a). Section 3.3.3 (below) provides a full discussion and justification of sediment collection protocols. Standard field methods will be employed for the collection of water chemistry samples. These methods are described and referenced in Section 3.3 of this document.

Analytical: Standard and accepted methods for analysis of all water and sediment chemistry parameters will be used. All methods employed are referenced from either Standard Methods (APHA 1995), or commonly used EPA method manuals (ie. USEPA 1979 rev. 1983 and USEPA 1994). A comprehensive and referenced parameter table is provided in Section 4.0 of this document.

To ensure further comparability between this and the many other ongoing mercury sampling initiatives, laboratory split samples will be submitted to an independent laboratory for analysis of total mercury in sediment. Laboratories under consideration for split samples include the Sawyer Research Laboratory at the University of Maine, or an independent contract laboratory specializing in trace metal analysis such as Brooks Rand Ltd., CEBAM Analytical, or Frontier Geosciences Inc.

**C For every 10 sediment samples collected for total mercury analysis, a split sample will be collected for analysis by an independent laboratory.**

## ***2.2 Sediment Methylmercury and Aqueous Total and Methylmercury***

2.2.1 Precision, and,

2.2.2 Accuracy

The field QA program for CVAFS analyses will be similar to that presented above. Specifically, an equipment blank will be submitted every time the SEBS tubing is cleaned. A field blank, field duplicate, and matrix spike sample will be submitted for aqueous total and methylmercury analysis for every 10 samples collected. A field duplicate and matrix spike will be submitted for sediment methylmercury analysis for every 10 samples collected.

In the laboratory, analyses of all sediment and water samples by cold vapor atomic fluorescence spectroscopy will conform to Method 1631 (USEPA 1996b). Quality control procedures required by method 1631 include:

- Initial demonstration of laboratory capability (Method 1631 Section 9.2.1);
- Determination of initial precision and recovery (Method 1631 Section 9.2.2);
- Process matrix spike and matrix spike duplicate for 10% of samples processed (Method 1631 Section 9.3);
- Bubbler and reagent blanks, as required per sample run (Method 1631 Section 9.4.1 and 9.4.2);
- Analysis of Standard Reference Material (ie NIST Buffalo River Sediments), as required per sample run (Method 1631 Section 9.6).

### 2.2.3 Comparability

In order to achieve comparability with other on-going research, strict mercury-clean protocols will be employed in the collection of aqueous total and methylmercury samples. This will permit the analysis of these samples by CVAFS, thus achieving low (ppt), but reliable detection limits. Sediment methylmercury analyses by CVAFS will allow comparability of sediment data with studies conducted in the Adirondacks (Driscoll, 1994), and in Minnesota (Engstrom et al., 1997a).

### 2.3 Completeness and Representativeness

This monitoring effort is complex, and proposes to evaluate a wide variety of relationships involving mercury in lake sediments and other environmental factors. There exist very limited data on mercury in lake sediments in Vermont and New Hampshire, specifically with respect to quality assurance measures of precision and accuracy (a total of only three field duplicate samples are available). Correspondingly, it is difficult to calculate with confidence the power statistics associated with each stated hypothesis. However, we are proposing to evaluate mercury in lake surficial sediments across 90 Vermont and New Hampshire lakes, a large sample representing over 10% of the eligible lake population. This sample size should be sufficient to provide a complete and robust dataset to test all of our working hypotheses. Further, standard and documented methods will be used for all phases of sample analysis, ensuring comparability between this and other studies.

## **3.0 Site Selection and Sampling Procedures:**

### 3.1 Sampling Site Selection

Individual study lakes will be selected by the USEPA National Health and Environmental Effects Research Laboratory in Corvallis, OR. The EMAP, stratified, spatially randomized lake selection process will be employed using a list of lakes provided by VTDEC and NHDES. Lakes will be selected as described in Table 1. Vermont and New Hampshire lakes of 20 acres in size or greater will be considered 'eligible' with the exception of the following:

- 1) Lakes Champlain, Memphremagog, Squam, and Winnepesaukee. The proposed design of this monitoring effort is inadequate to characterize the very large and unique segments of Champlain, Memphremagog, Squam, and Winnepesaukee. Further, Lake Champlain is currently the focus of a comprehensive toxics monitoring effort funded under the Lake Champlain Special Designation Act of 1990 (McIntosh, 1994.). Collection of mercury samples in conjunction with this monitoring effort will not contribute significantly to the current scientific knowledge regarding mercury in Lake Champlain sediments.
- 2) Connecticut River Reservoirs. The configuration and hydrology of Connecticut River Reservoirs is such that they behave in a significantly different manner than other Vermont and New Hampshire lakes and reservoirs. While other reservoirs will be eligible for selection as study lakes, the highly dynamic Connecticut River Reservoirs should be excluded from the pool of potential study lakes.

### 3.2 Site Description and Timing of Collection

Each lake will have a main sampling location, which is centrally-located over the 'deep-hole' of the lake. Many lakes in Vermont and New Hampshire already have such stations established consistent with the EPA Stort database system. When this is the case, the existing stations will be used. Sediment and water column samples will be collected from these stations.

Two critical water quality parameters which mediate methylation, sulfide and dissolved oxygen, are strongly controlled by thermal stratification. The optimal timing for evaluation of waterbodies which display low DO characteristics is a mid-summer index period. This is the time during which stratification is most enhanced, and DO is depressed to its fullest (barring de-stratification which may result from high wind conditions). It is therefore critical that all lakes which have the potential to stratify during the summer months (dimictic) be sampled during that time period. VTDEC and NHDES have sufficient data in their respective databases to know which of the randomly-selected lakes will fall into this category. Every effort will be made to sample the remaining lakes during the mid-summer index period. However, other field commitments may preclude sampling of the smaller lakes which do not stratify during this time period. In this case, these smaller lakes will be sampled during an alternate season, such as late fall. These determinations will be made on a lake-by-lake basis.

### 3.3 Sampling Procedures

The sampling station will be located in the field using non-differential GPS. On lakes on which gasoline powered craft are required for sampling, the engine will be shut off downwind of the station, and staff will row the craft into place. The boat will be secured by anchor, and adequate scope will be let out to avoid contamination of the hypolimnetic zone of interest by the anchor or sediment drift.

For all lakes, collection of parameters requiring clean handling will precede collection of other parameters in like moieties. The order of collection and handling will be as follows:

Arrange sampling equipment ✓ Don sampling attire and gloves ✓ Surface grab for aqueous methylmercury and total mercury sample ✓ Hypolimnetic teflon Kemmerer grab for aqueous methylmercury and total mercury sample ✓ Remove clean attire and gloves ✓ Collect then handle other water chemistry parameters using Kemmerer sampler ✓ Hydrolab® profile and Secchi measurement ✓ Dirty hands collects sediments ✓ 'Clean hands' handles extruded sediment for methylmercury and total mercury analysis.

#### 3.3.1 Acquisition of Water for Mercury and Methylmercury Analysis by CVAFS

A surface grab for aqueous mercury samples will be collected at each study lake. In addition, for those lakes which stratify strongly and have anoxic hypolimnia, a sample will be acquired from one meter above the sediment water interface, using an all-teflon Kemmerer sampler. The sampling depth will be determined by on-board SONAR. Techniques for the collection of aqueous mercury samples will conform to the EPA method 1669 'clean hands-dirty hands' techniques (USEPA, 1996a). In brief, sampling staff will wear clean windsuits and gloves. 'Clean hands' will wear shoulder-length gloves. Gloves will be new from the box at the time they are put on. Aqueous mercury samples will be stored in a separate cooler. Samples will be preserved in situ with 3.6ml concentrated trace-metals grade HNO<sub>3</sub>, using a new pipet tip rinsed twice in mercury-clean 10% HCl, and once in trace metal grade HNO<sub>3</sub>.

#### 3.3.2 Acquisition of Other Water Chemistry Parameters

Water column sampling procedures are referenced in Table 3. Water sample aliquots will be decanted to appropriate laboratory sample containers in the field, and transported on ice to the Vermont Department of Environmental Conservation LaRosa Laboratory for analysis. Aliquots for dissolved parameters will be filtered in the field using Gelman Sciences 0.45u filter membranes. Dissolved organic carbon samples will be transferred to a contract laboratory in a secure cooler.

*Table 3. Referenced field sampling methods (water) for the Assessment of Mercury in Hypolimnetic Lake-bed Sediments of Northern New England, with an emphasis on Vermont and New Hampshire.*

Parameter	Collection Method	Field Method Reference <sup>1</sup>	Field Sample Container	Sample Preservation
Alkalinity	Kemmerer grab or peristaltic pump, as required	2.2.3	250 ml HDPE	4°C,
Dissolved and Apparent Color			50 ml poly-carbonate centrifuge tube.	4°C
Dissolved Organic Carbon			50 ml poly-carbonate centrifuge tube.	4°C, filtered to 0.45 $\mu$ , acidified with H <sub>2</sub> SO <sub>4</sub> to pH #2
Sulfate Chloride			50 ml poly-carbonate centrifuge tube.	4°C
NO <sub>x</sub>			250ml HDPE	4°C, acidified with H <sub>2</sub> SO <sub>4</sub> to pH #2
Sulfide			250 ml glass	4°C, fixed in two stages with Zinc Acetate, then NaOH
Mercury	Surface grab and all-teflon Kemmerer grab (hypolimnion)	1669 <sup>2</sup>	1000ml teflon 500ml teflon	4°C, sealed and double-bagged. Preservation and freezing at laboratory. <sup>3</sup>
Temperature DO, field pH Conductivity	Multi-probe sonde (Hydrolab®), water column profile	Hydrolab®	in situ	N/A
Water Transparency	Secchi disk observation	1.2.1	in situ	N/A

<sup>1</sup>Field Methods Manual, Vermont Department of Environmental Conservation, 1990.

<sup>2</sup>USEPA 1996a.

<sup>3</sup>Samples will be shipped via a courier service which assures acceptable rapid delivery of samples to the laboratory facility.

Water column samples for all parameters will be collected in the epilimnion and hypolimnion of each lake which displays thermal stratification. For epilimnetic samples, a Kemmerer grab from one meter depth, and from one meter above the upper knee of the thermocline will be composited. Hypolimnetic samples will be composited using a Kemmerer grab from one meter below the lower knee of the thermocline, and one meter above the sediment-water interface. For unstratified lakes, a Kemmerer grab from one meter of depth, and one meter above the sediment-water interface will be composited.

### 3.3.3 Acquisition of Sediments for Mercury Analysis by CVAA and CVAFS

There exist a variety of methods by which sediments can be acquired. For this reason, the Co-Investigators thus polled research professionals with experience in the collection of sediments for mercury analysis for their suggestions. The sediment collection methods presented below were designed accounting for these comments and observations. The following researchers provided detailed comments: Dr. J. Becker; Dr. R. Bindler; Dr. C.T. Driscoll; Dr. D. R. Engstrom; Mr. P. Garrison; Dr. M. Ostrofsky; Dr. B. Simmers; Dr. E.B. Swain; and Dr. C.J. Watras.

Sediments will be acquired using a Glew-design, modified KB corer with a 60 cm by 7 cm lexan core tube, or a KB corer with a 60 cm by 5cm lexan tube and a cellulose acetate butyrate liner. The use of core catchers with the KB corer is discouraged due to their potential to contaminate surficial sediments during the coring operation. Prior to initiation of sampling, the core tubes will be acid cleaned. The tubes will be rinsed copiously in lake water prior to use, and will be copiously rinsed in lake water after sediments are removed. Core tubes will be stored in doubled, plastic bags between acquisitions. These bags will be replaced regularly. Core tubes will be re-acidwashed not less than after every tenth sample collected, or when the field coordinator determines that re-cleaning is necessary. Core sectioning tools (scraper, lexan sectioning tray) will be cleaned following the same schedule as core tubes, and will be stored in plastic as well.

Due to high mercury concentrations found in lake sediments, strict mercury-clean techniques will not be required, provided that cores are sectioned in the field, as soon as practical after collection. Project staff will, however, use gloves and an adapted clean hands-dirty hands protocol when collecting and sectioning sediments.

*Coring Procedure:*

- C Two sample bags are labeled. The inner bag with a grease pencil, the outer bag with an adhesive label marked with indelible ink.
- C 'Clean hands' and 'dirty hands' are designated.
- C "Clean hands' gloves.
- C 'Clean hands' rinses and handles the core tube, placing it into the corer head.
- C 'Dirty hands' is responsible for handling the corer head and line, and for collecting the core. The core descent is tracked using SONAR.
- C 'Clean hands' caps the core bottom upon its arrival at the surface.
- C The senior crew member examines the core, deciding to retain or reject it.
- C 'Dirty hands' uses tools to remove the lexan tube from the core head, while 'clean hands' holds the core.
- C 'Clean hands' caps and sets the core to a rack,
- C 'Dirty hands' assembles extrusion equipment.
- C The senior crew member selects a core for extrusion and sectioning.
- C 'Clean hands' places the core onto the extruder.
- C 'Clean hands' affixes sectioning tray onto the core tube.
- C 'Dirty hands' uses tools to tighten associated fasteners.
- C 'Clean hands' prepares sample bags and removes sectioning tools from their bags.
- C While 'dirty hands' controls extrusion from the core bottom, 'clean hands' sections the sediment into the sample bag.

Observations regarding sediment color, texture, degree of hydration, and odor will be noted. Sediment samples will be submitted as bulk (unsieved).

Cores will be rejected and the core re-collected if:

- 1) sediments contact metal portions of the corer head (overflow);
- 2) the sediment-water interface is disturbed;
- 3) the field coordinator judges that a contamination may have occurred, or the core is of poor quality; or
- 4) gaseous ebullition caused by temperature differential causes the core to break apart before sectioning.

#### 3.3.3.1 REMAP study lakes

Two cores will be acquired from the sampling station. The core reflecting the least disturbance will be selected for analysis. The top five centimeters will be extruded onto a copiously-rinsed clean lexan sectioning tray (EPRI, 1996). The extruded sediments will be moved into a new, clean ziplock bag using a plastic scraper. Sediments will be stored in double bags, in a specially designated cooler. At no time will sediment samples be placed into the same cooler as aqueous mercury samples. Samples will be frozen upon return to the laboratory, and stored frozen until analysis for THg by CVAA, MeHg by CVAFS, and other sediment parameters (as described in section 4.0 below).

#### 3.3.3.2 Paleolimnology lakes

Sediment samples collected in conjunction with the paleolimnological assessment of northern New England lakes will be collected using either a KB or Glew-design modified KB corer at the deep lake station. In the field, sediment subsamples (cookies) will be extruded from the top 50 cm of each core.

Two cores will be acquired from the sampling station. The core reflecting the least disturbance will be selected for analysis. The sediments will be extruded onto a copiously-rinsed lexan sectioning tray (EPRI, 1996). For those depths from which mercury samples are to be analyzed, the extruded sediments will be split on the tray, and each half moved into a new, clean whirlpak-type bag using a plastic scraper. Sediments will be stored in double bags, in a specially designated cooler. At no time will sediment samples be placed into the same cooler as aqueous mercury samples.

For the six lakes on which core dating is to be performed, the core will be sectioned at 1 cm intervals, and these will be submitted to the contract laboratory dating laboratory. On the dated cores, a total of 12 subsamples will be submitted to the LaRosa laboratory for THg analysis from the following depths (downcore, in cm): 0; 1; 2; 5; 7; 10; 15; 20; 25; 30; 35; 40. The bottom most depths will be adjusted based upon the actual depth of sediment core acquired.

For the 12 lakes on which dating is not to be performed, a total of 6 subsamples will be submitted to the LaRosa laboratory for THg analysis from the following depths (downcore, in cm): 0; 2; 5; 10; 20; 30; 40. Samples collected for quality assurance purposes will be procured from a duplicate core collected concurrently.

#### 3.3.4 Acquisition of Fish Tissue

Fish will be collected using overnight net 'sets,' or by electroshocking. This element of the project will be conducted by EPA Region 1 staff with assistance from the project field team. Fish will be doubly wrapped in plastic wrap, followed by aluminum foil, and frozen for analysis at the LaRosa laboratory. Fish from New Hampshire will be frozen prior to transport to the LaRosa laboratory. The fish collection design targets 2 composites of 5 yellow perch per test lake, and 2 further composites of 5 higher-level carnivores per test lake, on a total of 20 lakes. In Vermont, existing fish-tissue mercury data suggests that brown bullhead and smaller centrarchids (pumpkinseed, bluegill) do not retain mercury in their tissue. For this reason, it will be undesirable to analyze samples from these species.

A 2 to 4 inch portion (dorsal to ventral) section of fillet will be taken from each individual beginning behind the head using a stainless steel knife, rinsed between each sample. These filet sections will be composited to form a sample for each lake.

### 3.4 Sample Custody

#### 3.4.1 Sample Handling and Transport Protocols, and Labeling and Tracking

Since VTDEC and NHDES maintain their own small and efficient laboratory operations, chain-of-custody procedures typically required of regulatory samples will not be employed in conjunction with field operations. Field personnel will collect and submit samples, in person, to the LaRosa Environmental Laboratory.

In order that sample integrity is retained, and that relevant field data remains linked to sample data, two levels of accession will accompany each sample collected in conjunction with this study. A unique FIELD ID will be attributed to each sample collected in the field. This 7 character FIELD ID will consist of a five character lake identifier concatenated to a two-digit station identifier (ie the field id for Silver Lake in Leicester, VT- Station 1 would be 'SILVL01'). This field id, along with the date and time of sampling, will be clearly labeled on every sample container at the time the sample container is filled. FIELD ID's will be pre-established for each lake prior to the field visit.

Upon arrival at the LaRosa laboratory, samples will be logged into the Laboratory Management System, at which time each sample will be accessioned with an individual LABORATORY ID. This unique sequential identifier represents the actual sample number accepted by the LaRosa laboratory since August, 1992. These FIELD and LABORATORY ID's will accompany all data processed in the Laboratory Management System, and be part of all data output from the system.

Custody for DOC samples, CVAFS samples, and sediment samples for dating will follow the guidance of the Quality Assurance Plan for the respective laboratory.

#### 3.4.2 Field Forms

A standard field form will be filled out and accompany all samples collected in conjunction with this study. Examples of field forms are presented in Appendix D. The field forms will identify the study lake, station location in UTM-18 format from GPS, date and time of sampling, and sampling crew. In order to trace potential contamination problems, serial numbers for sampling equipment will also be included on the field form. This information will be entered into the project database as samples are submitted.

#### 3.4.3 Field Data Entry

In order to avoid potential transcription error and maximize efficiency, data entry will be largely automated. Date, field data and other ancillary information will be entered into the Laboratory Management System at the time of sample log-in, and will thus be available for automated download to the project database. The format of the Lab Management System log-in code for samples submitted in conjunction with this project is as follows:

Standard REMAP samples: FieldId\_Time\_QA\_SampleDepth\_SeccDepth\_Apparatus#

Paleolimnological samples: FieldId\_ "P" \_Time\_CookieDepth\_Apparatus#\_Tube#

For example:

SILVL01\_1200\_A\_16.5\_03.4\_VT-1 consists of a regular sample from Silver Lake (Leicester, VT), collected at noon, using Kemmerer bottle VT-1, at 16.5 meters depth, with a corresponding Secchi transparency of 3.4 meters.

SILVL01\_P\_1353\_08.0\_GL\_01 consists of a sediment sample from Silver Lake (Leicester, VT) from 8 centimeters downcore, collected at 1353 using the Glew corer and core tube 1.

The following QA codes are valid for entry associated with field samples: A- regular sample; B-field blank; D-field duplicate; and S-spike.

Hydrolab data will be ported from the datalogger directly into the project database. In the field, relevant information will be appended to the Hydrolab files such that all data entry is accomplished at the time hydrolab data are collected.

#### **4.0 Analytical Procedures and Calibration:**

Analytical procedures for water and sediment sample analyses are summarized in Table 4. Standard Operating Procedures provide detailed methodological descriptions in Appendix B. Calibration procedures are described in Section 8.0 of the LaRosa Laboratory Quality Assurance Plan (Appendix A).

Analysis of aqueous mercury and sediment methylmercury, and dissolved organic carbon will be conducted by an independent academic or commercial laboratories. The method of choice for the analysis of the mercury at parts-per-trillion levels is cold vapor atomic fluorescence spectrometry. This technique is described by Bloom (1995), and is presented in detail in USEPA Method 1631 (USEPA 1996b). Aqueous methylmercury concentrations in natural systems range from 0.2 ng/l to 1 ng/l, and sediment mercury concentrations vary from 10 to 100 ng/g (Engstrom, 1997b). Practical quantitation limits must achieve this sensitivity. The CVAFS laboratory will provide teflon sample containers which are prepared in a clean-room, and which are double-bagged and ready to accept aliquots. The contract laboratory will also conduct preliminary cleaning of new SEBS tubing to be used for acquisition of aqueous mercury samples.

Dating of sediment cores will be conducted by determination of  $\text{C Pb}^{210}$  emission, if practical corroborated by  $\text{C Cs}^{137}$  emission. These analyses will be contracted to an academic laboratory specializing in such analyses. Dr. P. Appleby's laboratory at University of Liverpool, UK, and Dr. D.R. Engstrom's laboratory at the University of MN conduct this type of work.

*Table 4. Parameter table of referenced analytical procedures for the Assessment of Mercury in Hypolimnetic Lake-bed Sediments of Northern New England, with an emphasis on Vermont and New Hampshire.*

Parameter	Units	PQL/ Hold Time	Target QA Precision(RPD) / Accuracy(% recovery)	S.O.P. Number <sup>a</sup>	Number of Samples	Method Reference	Lab
Dissolved Organic Carbon	mg/l	0.10/ 30d	< 5 mg/l 10/90-110 <sup>8</sup> > 5mg/l 5/90-110	n/a	108	415.1 <sup>1</sup>	Contract-TBD
Dissolved Color	Pt-Co units	0.00	5/NA <sup>8</sup>	n/a	108	Black and Christman , 1963.	LaRosa
Alkalinity	mg/l as CaCO <sub>3</sub>	< 0.0/ 7d	1/NA	5.1.2	216	2320B <sup>2</sup>	LaRosa
Sulfide, iodometric	mg/l	0.20/ 7d	To be determined	5.15	108	4500-S <sup>2</sup> -E <sup>2</sup>	LaRosa
Sulfate, Chloride, by IC	mg/l	0.20/28d 0.02/28d	3/90-110 4/90-120	1.1	216	300.1 <sup>1</sup>	LaRosa
NOx, by AutoAnalyzer	mg/l	.02/28d	2/80-116	1.5	216	353.2	LaRosa
Total Mercury in Solids	Fg/g	0.10/ 28d	6/70-111	2.3.5/ 2.5.7	260	245.5 <sup>3</sup>	LaRosa
Total Mercury in Fish	Fg/g	0.05/ 28d	4/70-114	2.4.1/ 2.5.8	46		
Total and Methylmercury in Waters, Methylmercury in Solids	ng/g, ng/l	0.002 <sup>6</sup> 0.02 <sup>6</sup> / 6 mo. <sup>9</sup>	24/75-125 <sup>7</sup>	n/a	108	1631 <sup>5</sup>	Syracuse University. C.T. Driscoll's clean mercury lab
Percent Solids	percent	0.0 / 6mo. <sup>10</sup>	1/NA	2.3.1	99	2540B <sup>2</sup>	LaRosa
Loss on Ignition	percent	0.0 / 28d	NA	n/a	99	See Appendix B	LaRosa

<sup>a</sup>) VTDEC, (1992b revised 1997)

<sup>1</sup>) EPA 1979 and revisions

<sup>2</sup>) APHA 1995

<sup>3</sup>) USEPA 1994

<sup>4</sup>) USEPA 1987

<sup>5</sup>) USEPA 1996a

<sup>6</sup>) Liang, 1996.

<sup>7</sup>) Minimum acceptance criteria listed for Method 1631 (USEPA 1996b).

<sup>8</sup>) Morrison, 1991.

<sup>9</sup>) Provided that samples are preserved with HCl within 48 hours of collection.

<sup>10</sup>) Provided that subsample is double bagged and maintained frozen.

## **5.0 Data Reduction, Validation, and Reporting**

### 5.1 Data Reduction, Validation, and Reporting

In the laboratory, data reduction, validation, and reporting requirements for this project conform to those detailed in section 10.0 of the VTDEC LaRosa Laboratory Quality Assurance Plan.

Laboratory data are retrieved directly by (reported to) Mr. Kamman using the LaRosa Laboratory Management System. Once downloaded, data are arranged into a matrix in temporary data tables, reviewed by project staff, and archived to the project database.

During the field season all data will be plotted using Tukey plots to determine the presence of high or low values data values. These data are flagged. Further, a rapid screen is conducted to assess data quality as inferred by duplicates and blanks. An excessive number of high/low values, bad duplicates, and/or evidence of blank contamination are cause for immediate corrective action, as described in Section 10.0 below.

After field season, the data will be comprehensively examined as follows:

- C Comparison of field data sheets to entries in the project database. This verifies the project database integrity;
- C Calculation of data quality indicators for field duplicates and equipment and field blanks;
- C Independent calculation of data quality indicators for laboratory matrix spikes and matrix spike duplicates;
- C Evaluation of the above data quality indicators;
- C Plotting of all project data.

Data will be reported as their real value for each test lake. In the case of lakes on which duplicates are collected, the value reported will remain the value of the regular sample, unless the duplicate value is  $<$  or  $>$  twice the regular value, *and* neither the laboratory nor project staff can evidence the reason for the discrepancy (ie. suggest the most appropriate value to use). In this event, the value reported for the study lake will be the average of the regular and duplicate sample.

## 5.2 Usage of Data for Development of a Ranking System

The ranking system we propose to construct will consist of two joined 'modules.' One 'module' will involve those watershed-level metrics which, through this study, are statistically implicated in the variation of sediment-total and methylmercury concentration in lakes. The second 'module' will involve those in-lake physico-chemical parameters which are implicated (statistically) in the variation of the aqueous total and methylmercury. This ranking system will be tested using existing fish-tissue mercury data (where available), as well as tissue data collected in conjunction with this project.

Module construction will follow a procedure known as multi-metric indexing, which is common in the evaluation of biological data for the development of criteria in streams and lakes (Kamman, 1995). Existing literature suggests that the data analysis tools described in Section 1.1 (above) will yield statistically significant relationships between sediment mercury and certain physical lake and watershed characteristics (for module 1) and water column mercury and certain physical lake and watershed characteristics (for module 2). For each module, a score will be accorded along the range of distribution of each significant physical attribute. This score will correspond to a low, medium, or high correlation with the respective response variable (sediment or aqueous total and methylmercury concentration). The scores for each characteristic will then be summed to form an indexed 'grand score' for each lake. For module 1, this indexed grand score will describe a lake's potential to have elevated sediment mercury. For module 2, this index grand score will describe a lake's potential to have water quality conditions which are favorable for methylation.

Once constructed, the two-module ranking system can be applied to any lake for which applicable lake and watershed information is available, subject to the constraints of the dataset from which the ranking system was derived. In this fashion, all of the lakes in Vermont and New Hampshire will be evaluated for their potential to have elevated total mercury in sediments and methylating conditions. These results will be used to direct future fish-tissue monitoring efforts.

In order to verify that the system developed by this effort is robust, newly acquired and existing fish-tissue monitoring data will be used. Elevated methylmercury in lakes is manifested in elevated fish-tissue mercury concentrations below a threshold aqueous DOC concentration (Driscoll et al., 1994). Correspondingly, if the ranking system developed by this project is accurately characterizing test lakes which are at risk of mercury methylation and bioaccumulation, this should be manifested in elevated tissue mercury concentrations for fish from these lakes. Using the three independent tests described below, scores can be statistically compared with mercury concentration data from fish tissue to validate the predictive ranking system. Statistical techniques could include linear and multiple step-wise regression, as well as multivariate analyses such as canonical correspondence analysis.

In the first test, EPA Region 1 will collect fish from 20 (22%) of the study lakes. Target species are discussed in Section 3.3 above. Tissue mercury concentrations will be correlated with lake rankings to determine if the system is adequately characterizing lakes with bioaccumulating mercury.

Second, there exist a total of 41 Vermont and 92 New Hampshire lakes on which fish tissue contaminant data are available through State programs or the USEPA EMAP Northeast Lakes Demonstration Project (1992-1993). This represents 15% and 18% of this project's test lake population for each State respectively. If these percentages are applied to the total number of REMAP test lakes in each State (42 in VT, 48 in NH), then there could potentially be 17 randomly-selected test lakes in total on which independently derived fish-tissue mercury data are available. These fish tissue data will be statistically compared to ranking system scores for lakes in the VT-NH REMAP test set.

A final test will be conducted by applying the ranking system to all of the non-REMAP Vermont and New Hampshire lakes (which meet the minimum data requirements) on which fish-tissue data are available. This would allow an independent test of the ranking system's predictive abilities on a set of lakes outside the REMAP test lake set. This test would use data from up to 110 lakes.

Certain limitations exist regarding the use of existing fish-tissue contamination databases for tests two and three. Specifically, in order to draw meaningful conclusions regarding mercury accretion in fish relative to lake characteristics, it is desirable that both fish species and relative size of individuals be held constant across the test lakes. The EMAP database consists of individual species samples for each lake. The State of Vermont database consists of individuals within species. Species uniformity across lakes is not assured. Therefore, the test scenarios will be performed using pooled fish tissue data.

### 5.3 Description of Project Database

All data generated by the Project will be stored electronically. In the laboratory, data are available in read-only or read-write access to all laboratory personnel associated with the project. Laboratory data are stored and maintained on the Laboratory Management System, on a dedicated server. All laboratory personnel are trained in the use of the Laboratory Management System. System datafiles are backed up to tape nightly. The Laboratory Management System is a custom-designed user interface to multiple data tables using the commercially available Paradox® relational database software.

Validated chemical data are electronically transferred to the VTDEC main computer network, where they are paired with Project field data. Co-Investigator Kamman will be responsible for the design and maintenance of the Project master database. Commercially available Paradox® relational database software will be used to create and manage data tables. This master database will be stored at VTDEC. Mirror database copies will be housed on the NHDES computer network, and at Dr. C.T. Driscoll's CVAFS laboratory.

All datafiles stored on the VTDEC network are stored on a 6 drive, redundant drive array. Data are backed up via drive redundancy upon data entry, and to tape nightly. Tape backups for the Laboratory management system and the VTDEC network are stored in designated locked cabinets, accessible only by information systems staff.

The project database layout will be described and updated in annual project reports submitted to the Project Officer.

After completion of the project, all field and chemical data will be archived to the VTDEC's Storet-compatible Water Quality Database. This database, which houses all Lakes and Ponds related data generated by the Water Quality Division, is managed in whole by Mr. Kamman.

## **6.0 Internal Quality Control Checks**

Internal Quality Control Checks for this project conform to section 11.0 of the VTDEC LaRosa Laboratory Quality Assurance Plan. Building upon section 2.0 above, Table 5 presents a target number of Quality Control sample types to be analyzed. Note that not every Quality Control sample type is appropriate for every parameter. For example, it would be impractical to run an equipment blank for the parameter *Percent Solids in Sediments*.

Field equipment will be serialized, allowing the project QA officer or project staff to trace a potential contamination back to the apparatus used in its' collection. In order to provide a greater level of information for tracking potential QA problems, it is desirable that field blanks be collected at the same sampling station as field duplicate samples.

Table 5. Quality Control Sample Frequency for the Assessment of Mercury in Hypolimnetic Lake-bed Sediments of Vermont and New Hampshire.

Quality Control Sample Type	Frequency (N per N samples)
Equipment Blank (aqueous mercury only)	After cleaning of teflon Kemmerer
Field Blank	1 in 10
Field Duplicate	1 in 10
Matrix Spike / Matrix Spike Duplicate	1 in 10
Analytical Duplicate	1 in 10
Standard reference material -CVAFS -Other	As required by method 1631 (USEPA 1996b) As required by the LaRosa Laboratory QA Plan (VTDEC 1992b rev. 1997)

## 7.0 Performance and System Audits

### Field:

All aspects of field operations including station location, sampling procedures, and sample preparation and handling are the joint responsibility of the project managers and project field quality assurance officer. Field performance audits will occur no less than quarterly during the project period, to be conducted at the discretion of the field quality assurance officer. Further, we request that Dr. Rochelle Araujo (the designated EPA Project Officer) assist the project staff by conducting a project audit annually, or at her discretion. Finally, we anticipate that EPA Region 1 staff will conduct an annual project audit at their discretion.

### Laboratory:

Laboratory performance and systems audits will conform to section 12.0 of the VTDEC LaRosa Laboratory Quality Assurance Plan.

## 8.0 Preventive Maintenance Schedules and Procedures

### Field:

Preventive equipment maintenance will be the responsibility of the project field coordinators, to be conducted at minimum bi-monthly, or as needed. Hydrolab® sondes and data-loggers will be maintained following manufacturers specifications.

### Laboratory:

Preventive Maintenance Schedules and Procedures will conform to section 13.0 of the VTDEC LaRosa Laboratory Quality Assurance Plan.

## 9.0 Calculation of Data Quality Indicators

Mathematical formulae used to calculate data quality indicators are presented in 14.0 of the LaRosa Laboratory Quality Assurance Plan, in Appendix A of this document.

## **10.0 Corrective Action**

Corrective action in response to unacceptable data results for most parameters will follow the general guidelines presented in Section 15.0 of the LaRosa Laboratory Quality Assurance Plan. However, due to the highly technical nature of this study, combined with an intensive field collection phase compressed into a short project period, resolution of problems needs to occur quickly. The high expense of analyzing samples for mercury by CVAFS dictates the need for problems need to be resolved on an on-going basis. In this manner the project will avoid submitting, and thus paying for analysis of, other potentially contaminated samples.

A pro-active approach to corrective action will thus be employed. Specifically, the CVAFS laboratory will be requested to notify Co-Investigators of any Quality Control samples they judge to be out of control limits for precision or accuracy. Critically, the CVAFS laboratory will need to notify Co-Investigators of any field or equipment blanks which fall outside of control limits, at the first opportunity. The CVAFS laboratory QA Officer will make Co-investigators aware of any on-going problems with out-of-control method blanks, analytical duplicates, or matrix spikes.

In response to a report of out-of-control field duplicates for any parameter, the Field QA officer will investigate potential reasons for contamination by tracking the sample from its' collection. Project staff will be queried, and the potential contamination sources or reason for which the sample is out-of-control will be determined. Corrective action can then be taken. If it is judged necessary by the field QA officer, the lake from which the out-of-control samples were collected will be resampled.

In response to a report of out-of-control field blank, the Field QA officer will follow the same protocol. In the case of a problem with a CVAFS blank, the equipment used to collect the sample will be re-cleaned, and an equipment blank submitted before any other project samples are collected. If necessary, reagent water and acids used for cleaning of SEBS tubing at the LaRosa laboratory will be re-tested, and if found contaminated, replaced.

If these measures fail to remediate contamination, sampling will be halted, and the EPA Project Officer, Project Management, and CVAFS laboratory will consult to diagnose the problem and arrive at a working solution.

## **11.0 Quality Control Reports to Management**

Section 16.0 of the LaRosa Laboratory details the process and frequency of quality control reporting to laboratory management. The LaRosa laboratory is located at the Waterbury offices of VTDEC. The Vermont Co-Investigator thus has regular, daily access to the laboratory , and can consult with laboratory staff at any time during working hours. For this reason, additional quality control reporting to this projects' management will not be required of LaRosa staff.

For CVAFS and other contract laboratories (DOC's and sediment dating), results of all Quality Control samples will be requested at the time data are transmitted or send to the Co-investigators.

## 12.0 References:

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**Appendix A**  
**LaRosa Laboratory Quality Assurance Plan**

**Appendix B**  
**Standard Operating Procedures from the LaRosa Quality Assurance Project Plan for**  
**Parameters Germane to this Project**

**Appendix C**  
**Applicable Field Procedures**

**Appendix D**  
**Field Forms**