QUALITY ASSURANCE PROJECT PLAN

ORGANOCHLORINE AND METAL CONTAMINANT LEVELS IN HUDSON RIVER, NEW YORK REPTILES AND AMPHIBIANS

HUDSON RIVER NATURAL RESOURCE DAMAGE ASSESSMENT

HUDSON RIVER NATURAL RESOURCE TRUSTEES

STATE OF NEW YORK

U.S. DEPARTMENT OF COMMERCE

U.S. DEPARTMENT OF THE INTERIOR

FINAL
PUBLIC RELEASE VERSION*

REVISION NO. 1

AUGUST 11, 1998

Available from:
U.S. Department of Commerce
National Oceanic and Atmospheric Administration
Hudson River NRDA, Lead Administrative Trustee
Damage Assessment Center, N/ORR31
1305 East-West Highway, Rm 10219
Silver Spring, MD 20910-3281

**Names of certain individuals and affiliations have been removed for purposes of litigation*

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Prepared for

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Environmental Conservation
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Revision No: 1
August 11, 1998

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HUDSON RIVER, NEW YORK

APPROVALS:

_____ 9 / 8 / 98
Project Manager Date

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION
BUREAU OF HABITAT


8 / 14 / 98
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1.0 PROJECT DESCRIPTION

This project will involve the collection and contaminant analysis of snapping turtles (*Chelydra serpentina*) and green frogs (*Rana clamitans*). Sampling of both frogs and turtles will be done in three geographically distinct areas of the Hudson River in order to obtain information about the distribution of contaminant concentrations. The sampling will be performed during 1998.

1.1 INTRODUCTION

In 1987, New York State passed Section 11-0306 of the Environmental Conservation Law, known as the Hudson River Estuary Management Act. This law has resulted in the development of the Hudson River Estuary Management Plan (HREMP) which characterizes the priority problems affecting the Hudson River and identifies specific objectives to improve the estuarine ecosystem. This project has been undertaken under the auspices of this plan. The project supports the following planning objectives:

HREMP Objective

LR-EP-8 Manage the physical and chemical properties of the estuary's water column and sediments (substrate) to ensure optimal production of the estuary's living resources.

LR-EP-9 Reduce chemical contaminant levels to concentrations that will not impair the successful survival, reproduction and growth of sensitive species nor impair secondary consumers of fish shellfish and wildlife.

HEP Objective

Goal H-2 Restore and maintain an ecosystem which supports an optimum diversity of living resources on a sustained basis.

1.2 INVESTIGATION OBJECTIVES

The objective of the Organochlorine and Metal Contaminant Levels in Hudson River Reptiles and Amphibians study is to provide the New York State and federal Natural Resource Trustees with body burden information to be used for analysis of contaminant caused injury to selected reptiles and amphibians within the Hudson River ecosystem (see Figure 1.1). The specific species that will be sampled are the green frog, *Rana clamitans*, and snapping turtle, *Chelydra serpentina*. The contaminants of concern are PCBs, other organochlorines, and metals, including cadmium, mercury and lead. Sampling of both frogs and turtles will be done in three geographically distinct areas of the Hudson River in order to obtain information about the distribution of contaminant related injuries.

1.3 DATA QUALITY OBJECTIVES (DQO)

The data quality objectives (DQOs) for the project include the collection, shipment, and analysis of sufficient samples to fulfill the Study Objectives identified in Section 1.2. Since the data may be used to substantiate Natural Resource Damage claims, chemical analysis of the tissue samples will use methods which meet EPA DQO Level IV or V. Level IV analyses require EPA Contract Laboratory Program (CLP) routine analytical services with rigorous quality assurance/quality control protocols and documentation. DQO Level V analyses are laboratory methods with rigorous quality assurance/quality control protocols and documentation that are not CLP routine analytical services. The DQOs for the specimen measurements, composite sample preparation, and gut contents will use methods which are equivalent to EPA DQO Level I. Level I analyses are field analyses using portable instruments, in this case portable scales and measuring rules.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

2.1 PROJECT ORGANIZATION

The project management organization provides clear lines of authority and a control structure to support this study. The structure provides:

1. clearly identified lines of communication
2. management of key technical resources
3 provisions to ensure the health and safety of site workers and the public
4. project quality assurance and quality control

The organizational structure for the project team is shown in Figure 2.1.

2.2 SUBCONTRACTORS

A herpetologist has been retained to perform specimen collection and documentation of pertinent environmental conditions relative to the target species. A biomedical waste contractor for disposal of biological waste and a chemical waste contractor for disposal of spent decontamination chemicals have also been retained. Overall management and coordination and review of subcontractors' activities will be provided.

The analytical laboratory is a subcontractor to the New York State Department of Environmental Conservation (NYSDEC). The NYSDEC laboratory at Hale Creek Field Station will perform the metals analyses.

3.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

3.1 FIELD INVESTIGATIONS

Fifteen (15) adult snapping turtles and thirty (30) adult green frogs will be collected, five (5) turtles and ten (10) frogs at each of three locations.

Suitable habitats have been established as collection sites through consultation with the Project Manager in:

1. the upper Hudson, from Hudson Falls to the Troy Dam - Coveville
2. the mid-Hudson, from the Troy Dam to Catskill - Stockport Creek
3. the lower Hudson, from Catskill to the Tappan Zee Bridge - Vanderburgh Cove

See figures 4.1, 4.2, and 4.3.

Capture techniques will be determined by the contractor.

Each specimen will be tagged and assigned a unique identification number as soon as it is collected. The specimens will be maintained alive until samples are prepared.

New York State Amphibian & Reptile Atlas records and instructions for their use will be supplied by the Project Manager, and must be completed for each location at which collection efforts are made.

3.2 SAMPLE COLLECTION

The media being sampled and an estimate of the numbers of samples being collected are summarized in Table 7-1. In addition to the project samples, requirements and procedures for the collection of field QA/QC samples for the Site will be adhered to as discussed below. The frequency and type of QA/QC samples being collected is summarized in Table 3-1.

3.2.1 Duplicate Samples

Tissue samples will be collected from two species, green frog and snapping turtle, from three separate geographical locations. Ten frogs and five turtles will be collected from each geographical sample location. The sampling events at the three locations will take place on different days. The NYSDEC has indicated a duplicate sample requirement of 20 %. Duplicates will be prepared from the homogenized tissue samples. Two duplicates of frog muscle will be required per site, and one duplicate each for turtle muscle, turtle adipose tissue, turtle liver, and turtle kidney will be required per site.

The analysis results of the duplicate samples will be used as a check of the precision of the field sampling event. A duplicate sample will be prepared from the homogenized tissue sample. The entire tissue sample will be ground by the NYSDEC laboratory. Duplicates will be prepared from this homogenized tissue. They will be analyzed for the same parameters as the original sample.

3.2.2 Matrix Spikes

Matrix spike samples will be collected for the organic chemical analyses. One additional duplicate sample will be prepared from the homogenized tissue by the laboratory for matrix spikes and matrix spike duplicates (MS/MSD).

3.2.3 Preparation of Blanks

Tissue blanks will be prepared by the analytical laboratory performing the chemical analysis at the same time that the samples are prepared for analysis. The results from the tissue blank will be reported with the other analytical results.

Table 3-1
QA/QC Sample Summary
Organochlorine and Metal Contaminant Levels in
Hudson River Reptiles and Amphibians, Hudson River, New York

Media	Samples	Duplicates		Matrix Spike
		Metals	Organics	
Muscle *R. clamitans*	30	6	6	3
Muscle *C. serpentina*	15	3	3	3
Adipose *C. serpentina*	15	3	3	3
Liver *C. serpentina*	15	3	3	3
Kidney *C. serpentina*	15	3	3	3
Total	90	18	18	15

Note: 20% QA/QC samples

3.2.4 *Trip Blanks*

Trip blanks are not required for these types of analysis.

3.2.5 *Field Blanks*

Field blanks are not used for this type of analysis. Decontaminated, disposable scalpels will be used to obtain tissue samples.

3.2.6 *Storage Blanks*

Storage blanks are not required for these types of analysis.

3.3 SAMPLING TECHNIQUES

Sampling techniques and procedures are discussed in Section 4.0.

3.4 SAMPLE REPRESENTATIVENESS AND COMPLETENESS

3.4.1 Representativeness

Representativeness expresses the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition. Representativeness is a qualitative parameter concerned with the proper design of the sampling program. The representativeness criterion is best satisfied by making certain that sampling locations are selected properly, sampling techniques are adequately described and adhered to, and a sufficient number of samples are collected. The sampling program has been designed by the NYSDEC to meet its research goals based on its knowledge of the study areas, the resources being studied, and previous research of a similar nature.

3.4.2 Completeness

With respect to data collection, completeness is a measure of the amount of valid data obtained compared to the amount that was specified or expected to be obtained under normal conditions. The measure is usually expressed as a percentage. If the data are complete, that is, if the valid data are equal in quantity to the amount specified to be collected, then it is referred to as 100 percent complete. Occasionally, completeness is something less than 100 percent due to difficulties in collection and analysis of environmental samples. In such cases, the extent of completeness must be viewed on a relative basis because the required amount of valid data anticipated or specified prior to the sampling episodes may not accurately define the amount of data necessary to render a correct decision. Given these circumstances, a completeness of 90 percent is generally acceptable and will be the standard applied for this project since the goal is to accept all sizes of snapping turtle greater than 3 lbs. In weight collected in the traps, smaller individuals may not provide sufficient volume of tissue for all of the chemical analyses. The completeness goal may need to be reassessed following the results of the field collection effort. Completeness with respect to specific measurement systems is discussed in more detail in Section 12.0.

3.4.3 Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. Sample data should be comparable with other measurement data for similar samples and sample conditions. This goal is achieved through using standard techniques to collect and analyze representative samples and reporting analytical results in appropriate units. Comparability is limited to the parameters of precision, accuracy, representativeness, and completeness because it is only when these parameters are known that data sets can be compared with confidence.

3.5 LABORATORY QUALITY ASSURANCE AND QUALITY CONTROL

Integrity and usefulness of the analytical results constitute the primary objectives of the analytical quality assurance and quality control processes. The primary objective of the analytical laboratory with respect to QA/QC is to achieve the acceptance criteria for a given analytical method when a sample is analyzed. The quality of the data is indicated by the parameters of representativeness, precision, accuracy, completeness, and comparability.

3.5.1 Representativeness of Analytical Measurements

Representativeness of analytical measurements will be based on a comparison of analytical results for duplicate samples.

3.5.2 Completeness of Analytical Measurements

The goal for completeness of analytical results is 100 percent. However, the objectives of this project can be addressed with a 90 percent completeness for the laboratory analyses. As noted above, there is a risk that if a number of small turtle specimens are collected, the 90 % completeness goal for the analysis of turtle tissue may not be realized.

3.5.3 Accuracy and Precision of Analytical Measurements

Accuracy and precision of analytical results will be evaluated based on criteria specified in the analytical methods used. Such criteria will include, but not be limited to, blank results, matrix spike recoveries, surrogate percent recovery values, correlation coefficients, and detection limits. The NYSDEC will determine if these parameters have been met.

3.5.4 Comparability of Analytical Measurements

The analytical results are expected to be comparable between the three specimen collections locations because the same methods will be used. The results are also expected to be compared to historical data, where available, collected at this Site.

4.0 FIELD INVESTIGATION AND SAMPLING PROCEDURES

4.1 FIELD COLLECTION

Fifteen (15) adult snapping turtles and thirty (30) adult green frogs will be collected, five (5) turtles and ten (10) frogs at each of three locations in the Hudson River (See Figure 4.1). The capture techniques will be as permitted in the New York State Biological Collectors Permit. Specimen collection will be performed by a herpetologist and the Research Supervisor. The turtles will be collected by trap and the green frogs will be collected by hand or with hand nets. The herpetologist will make written field observations during sample collection and will assign the specimen numbers. The specimens will be delivered alive and in good condition for tissue sample preparation.

Suitable habitats have been established, through consultation with the NYSDEC Project Manager, as collection sites in:

1. the upper Hudson, from Hudson Falls to the Troy Dam - Coveville
2. the mid-Hudson, from the Troy Dam to Catskill - Stockport Creek
3. the lower Hudson, from Catskill to the Tappan Zee Bridge - Vanderburgh Cove

See Figures 4.2, 4.3, and 4.4. Data that characterizes the sample location will be entered in the field as described in Section 4.3.5. In addition, photocopies of topographic maps (7½ minute quads) indicating the precise location of collections will be provided to the Project Manager.

Turtles will be trapped in 30-inch hoop traps with 1-inch mesh. Traps will be staked and baited with sardines in soy oil. Traps will be set out overnight. Baits will be changed after 24 hours, if sufficient specimens have not been collected. The number of traps set will depend on the sample area but 8 traps are estimated per collection site. Turtles larger than 3 lbs are

estimated to provide sufficient tissue for analysis. Frogs will be caught by hand or with hand nets, either from shore or from the water.

Each specimen will be tagged and assigned a unique identification number as soon as it is collected. Pre-printed, numbered labels will be used on the tags. The specimens will be weighed and measured in the field. Measurements will be reported to the nearest gram or one-quarter ounce for weight and nearest two millimeters or one quarter inch for length. Length measurements for the frogs will be taken from snout to vent. Carapace length will be recorded for turtles. The specimen number and specimen data will be recorded on field data sheets as described in Section 4.3.5. The specimens will be maintained alive until delivery to the laboratory for sample preparation. Animals will be rinsed with clean water in the field to dislodge sediment or other foreign material from their skin. The samples will be transported from the field to the laboratory under Chain-of-Custody as described in Section 5.0.

All capture equipment (nets, traps, pails, other containers, *et cetera*) will be thoroughly washed with soap and water and then rinsed with clean water before the operation is moved between collection sites.

4.2 SAMPLING PROTOCOL

The smooth functioning of the sample collection and analysis process is based on a clear understanding of the relationship between the field sampling team and the field and laboratory analysis teams and the tasks and responsibilities of each. Adherence to the protocol presented here is essential to minimize problems in maintaining data quality and integrity.

The field and sample preparation personnel will carry out the following protocols prior to initiating any field work or laboratory work involving the collection of samples:

1. Schedule the specimen collection with the tissue preparation laboratory and the tissue analyses with the analytical laboratory or laboratories designated by the NYSDEC.

2. Notify the NYSDEC Project Manager

3. Determine the type, size, and quantity of sample containers required, and the maximum holding times for each sample.

4. Identify all of the tasks, determine the equipment required for each, and make sure that it is available.

5. Read and understand all Standard Operating Procedure (SOPs) and Sampling descriptions for the necessary tasks.

6. Ensure that all measuring equipment is in proper repair, properly calibrated, supplied with fully charged batteries and replacement batteries, and that each has received the appropriate quality control checks.

7. Establish next available specimen and sample ID numbers for sampling event.

8. Obtain sample containers, trip blanks from the laboratory.

9. Obtain Chain-of-Custody Forms, chain-of-custody tapes, document envelopes, shipping forms and sealing tape.

10. If samples are to be shipped by overnight carrier, confirm the location of the carrier's service office and their hours of operation.

11. Determine that all sampling equipment and accessories have been appropriately decontaminated.

4.3 SAMPLING PROCEDURES

Specimens will be delivered alive to the tissue preparation laboratory by the herpetologist. Specimens will be maintained alive in the laboratory until they are processed for tissue preparation. The specimens will be logged into a bound laboratory sample log book by date, time, and specimen number. The collection of tissue samples will be performed as soon as possible after arrival of the specimens to the laboratory. Specimens will be processed within 24 hours of arrival to the laboratory. Specimens will be held in coolers, maintained moist, and chilled to slow metabolism.

The following data will be recorded on a *Specimen Collection Record* for each turtle or frog from which samples are prepared:

1. Tag number
2. Date and time collected
3. Species
4. Sex
5. Length and weight (carapace length for turtles; snout-vent length for frogs)
6. Method of collection
7. Location of collection (water body and distance and direction from nearest prominent and identifiable landmark)
8. Habitat (describe: substrate, dominant vegetation, water depth)
9. Gut contents (food items should be identified to lowest practical taxon and they should be counted)
10. Observed pathological lesions (if any)
11. Comments
12. Name of collector or collectors.

Data from field books and field collection sheets will be entered into the Specimen Collection Record. The data recorded on laboratory bench sheets will be added to this record after sample preparation. See section 4.3.5 for description of the sample documentation.

4.3.1 Tissue Sample Preparation

Specimens will be humanely dispatched by cooling them to slow reflexes and then pithing prior to examination. The specimen will then be rinsed and placed on a stainless steel tray. A necropsy will be performed on all specimens following guidelines agreed to by the NYSDEC. Results of the external and internal visual examination will be entered on a laboratory bench sheet. Laboratory bench sheets will be pre-numbered and retained in a looseleaf notebook. The specimen will be rinsed with distilled water prior to making any incisions. A new pair of clean, powder free, latex gloves will be worn for each specimen. Similarly, all dissection equipment (scalpels, pins, forceps, pans, *et cetera*) will be washed with soap and water, rinsed with distilled water, and then rinsed with hexane or acetone after each specimen. Tissue samples for chemical analysis will be excised using a new disposable scalpel that has been cleaned with hexane or acetone prior to use. Tissue will be placed in the hexane or acetone rinsed disposable weigh pans. A new weigh pan will be used for each type of tissue from each organism and the weigh pans will be discarded after use. Weights will be recorded to the nearest 0.5 gm.

Gut contents will be removed placed in a clean glass container, and preserved in formalin or denatured ethanol for later sorting, and identification to the lowest practical taxon. Each tissue sample will be immediately placed on ice and then frozen to -20°C as soon thereafter as is practical.

For the turtles:

- All adipose tissue will be dissected from each carcass, assembled into a composite sample and weighed. The weight will be recorded on the laboratory bench sheet. Each sample will be placed in a laboratory cleaned glass jar and labeled as described in Section 4.4.

- Kidneys and the liver will be dissected and weighed. Care will be taken to avoid the inclusion of the gall bladder in liver tissue.

- Muscle tissue will be taken from both hind limbs. If this does not provide enough material, additional muscle tissue will be taken from the forelimbs.

The sample weight will be recorded on the laboratory bench sheet. Each sample will be placed in a laboratory cleaned glass jar and labeled as described in Section 4.4 and frozen.

For the frogs, only muscle tissue samples are required. The muscle tissue will be dissected from the hind limbs and weighed. The weight will be recorded on the laboratory bench sheet. If sufficient material is not obtained from the hind limbs, additional muscle tissue will be collected from the forelimbs. Each sample will be placed in a laboratory cleaned glass jar and labeled as described in Section 4.4 and frozen.

4.3.2 Scheduling

All sampling must be scheduled in advance. The NYSDEC Project Manager will be provided with a schedule of the sampling events.

The Project Manager will contact the laboratory not less than ten days prior to the collection of samples. The Project Manager will advise the laboratory of the following information:

1. analyses to be performed
2. media to be sampled
3. sample containers and preservatives needed
4. trip, field, and storage blank requirements
5. shipping and receiving requirements

The Project Manager will advise the laboratory in advance if weekend or holiday pickup or delivery is required. The contract laboratory will send the sample containers according to the shipping requirements, and not less three days prior to the sampling event.

To the extent appropriate, sample labels and numbers, documentation, chain-of-custody and traffic reports will be filled out before sampling begins.

4.3.3 Sample Containers

As indicated at Section 3.2 of this QAPP, samples, where appropriate, will be collected in laboratory cleaned sample glassware where Data Quality Objectives (DQO) Level 4, or 5 analyses are required. Sample bottle requirements specific to organic and inorganic analyses are shown in Table 4-1.

Table 4-1
Sampling and Analysis Requirements
Organochlorine and Metal Contaminant Levels in
Hudson River Reptiles and Amphibians
Hudson River, New York

Analysis	Required Volume[1]	Container Type	Preservation	Maximum Holding Times
PCBs, Organochlorines, and pesticides	20 g[2]	wide mouth amber glass jars	Freezing, -20˚C	N/A if frozen
Metals - Hg, Cd, Pb	3 g	wide mouth glass jars	Freezing, -20˚C	N/A if frozen
Gut contents	All per specimen	wide mouth glass jars	Formalin or 70% ethanol	None

1 For turtle adipose tissue, and organs entire mass per specimen will be collected, to be divided equally for metals and PCB-Pesticide Analyses after grinding.
2 Analysis will be performed on samples less than 20 g but detection limits will be higher.

4.3.4 Preservation and Storage

Proper preservation and storage of sample containers is required to maintain sample quality. Samples shall be preserved as indicated in Table 4-1. Tissue samples shall be stored and shipped frozen to -20˚ Celsius from the time of preparation to the point of analysis. Gut contents will be preserved with formalin or ethanol and stored at room temperature. The appropriate Chain-of-Custody documentation will be maintained at all times.

There are two types of preservation requirements indicated in Table 4-1: temperature and chemical. To confirm temperature maintenance during field storage, a thermometer will be placed in the laboratory freezer to confirm the temperature. This temperature will be read and recorded in the appropriate laboratory log book each day that samples are being stored and that personnel are present or a minimum of three times per week.

No special monitoring is required for the chemical preservation of the gut contents.

4.3.5 Shipping

Specimens will be transferred directly from subcontractor personnel to personnel at the tissue preparation laboratory. Specimens will be transported in ventilated containers and cooled to maintain them alive and in good condition.

Samples shall be packaged to prevent damage to the sample containers, sample labels, and cooler seals. Samples will be shipped in insulated containers. "Blue ice" or dry ice coolant will be used to maintain the samples frozen during shipment. Coolers will be labeled to indicate that contents need to be maintained frozen. Samples shall be shipped by courier or overnight express carrier and delivered to the laboratory within 24 hours of dispatch from the Site. The laboratory shall be notified by phone in advance of shipment to assure that the laboratory staff will be present to receive frozen samples.

4.4 DOCUMENTATION

4.4.1 Field Documentation

Dedicated field books will be used for field collections. The field books will be used to record sampling location, date, and time, collection data needed to document the collection methods as required for the New York State Collectors permit, the environmental data required for the Specimen Collection Record (See Appendix A), tag numbers for specimens, and notes concerning the sampling event. *New York State Amphibian & Reptile Atlas* records

and instructions for their use will be supplied by the Project Manager; they must be completed for each location at which collection efforts are made. Each specimen will be tagged and assigned a unique identification number as soon as it is collected. The label information is described in Section 4.4.2 and sample labels are shown in Appendix A.

The specimens will be maintained alive until samples are prepared. Length and weight will be recorded as soon as possible after collection and before freezing. Other data should be recorded in the field upon collection. The Project Manager will provide forms for this purpose. In addition, photocopies of topographic maps (7½ minute quads) indicating the precise location of collections must be provided to the Project Manager.

4.4.2 *Specimen and Sample Processing Documentation*

All specimens received and samples shipped or archived in the tissue preparation laboratory during this project will be logged into the laboratory log book maintained in a bound notebook. This log will record the unique sample or specimen identification number, log-in date, log-out date, type of sample and disposition.

A pre-numbered sample label will be affixed to each specimen or sample. The label will include the following information:

1. Project: Hudson River Reptiles and Amphibians
2. Sampling location identification: Predetermined sampling location or new location, as appropriate (specimen tags only).
3. Serial No.: 000001 et. seq.
4. Sample Media: specimen or tissue type
5. Date:
6. Time:
7. Parameters to be analyzed:
8. Preservative:
9. Initials of sampler:

The following data will be recorded on a *Specimen Collection Record* for each turtle or frog from which samples are prepared:

1. Tag number

2. Date and time collected
3. Species
4. Sex
5. Length and weight (carapace length for turtles; snout-vent length for frogs)
6. Method of collection
7. Location of collection (water body and distance and direction from nearest prominent and identifiable landmark)
8. Habitat (describe: substrate, dominant vegetation, water depth)
9. Gut contents (food items should be identified to lowest practical taxon and they should be counted)
10. Observed pathological lesions (if any)
11. Comments
12. Name of collector or collectors.

See Appendix A. The information in the specimen collection record will be linked to the electronic data file for the tissue analysis.

Laboratory bench sheets will be used to record data generated in the tissue preparation laboratory. The bench sheet pages will be pre-numbered and maintained in a looseleaf notebook. For this project bench sheets will be used to record the following information for each specimen:

- Necropsy Record
- Tissue samples taken and sample weights
- Gut Contents Identification

Data from these bench sheets will be entered into the electronic data base for this project. Data entries will be proof read by a person who did not perform the data entry.

Calibration books for scales and a daily freezer log will be maintained for this project. Copies of the freezer log pages will be provided to the NYSDEC and copies of the relevant calibration book pages will be provided, if requested.

Specimens and samples will be handled under Chain-of-Custody procedures as described in Section 5.0. Copies of the Chain-of-Custody documents will be provided to the NYSDEC Project Manager.

5.0 SAMPLE CUSTODY

Proper documentation of samples is essential to quality assurance. Each sample submitted for analysis must be accompanied by proper information and forms to ensure timely, correct and complete analysis for parameters requested. Such documentation is necessary to support subsequent legal use. Two necessary forms are 1) the Chain-of-Custody Form and 2) the Lab Sample Identification Label.

5.1 SAMPLE IDENTIFICATION

Each specimen will be identified, labeled and recorded at the time it is collected in the field as described in Section 4.1 and each tissue sample container will be labeled when it is filled in the tissue preparation laboratory. A pre-numbered sample label will be affixed to each specimen or sample. The label will include the following information:

1. Project: Hudson River Reptiles and Amphibians
2. Sampling location identification: Predetermined sampling location or new location, as appropriate (specimen tags only).
3. Serial No.: 000001 et. seq.
4. Sample Media: specimen or tissue type
5. Date:
6. Time:
7. Parameters to be analyzed:
8. Preservative:
9. Initials of sampler:

All of the information necessary to identify the sample and the sampling event will be recorded in the appropriate field notebook, field sheet, bench sheet, or laboratory log book. That information will include not only the information on the sampling label, but will also identify which samples are blanks and which are duplicates.

Once collected, preserved and labeled, the handling of the sample is governed by the chain-of-custody standard operating procedure (SOP-007) which is included in Appendix B. To comply with NYSDEC requirements, signatories to the Chain-of-Custody form must also print their signatures.

5.2 CHAIN-OF-CUSTODY PROCEDURES

The purpose of chain-of-custody procedures is to document the possession of the sample from the time of collection to the time of analysis. The objective is to maintain the integrity of the sample.

The person collecting the samples is the individual who has custody of the samples until such time as they are transferred or dispatched. The NYSDEC QA Officer determines whether the proper custody procedures have been observed and whether additional samples shall be taken if custody procedures have been broken.

The Chain-of-Custody Form shall accompany the specimens the field collection location to the tissue preparation laboratory. A second Chain-of-Custody form shall accompany sample containers from the time of sample container preparation until they are logged in at the analytical laboratory. The transfer of possession from one individual to the next is documented by signatures relinquishing and receiving possession with hour and date of the time of signing. The Chain-of-Custody Form shall include:

1. project identification
2. sampling site location
3. Serial No.
4. sample media
5. date of sample collection
6. time of sample collection
7. sample collector
8. sample description (type and quantity)

9. analyses to be performed
10. chain-of-custody seal numbers

For specimen transport, the back copy of the Chain-of-Custody Form will be detached retained by the subcontractor and filed with the sampling field notebook. The original and remaining copies will be placed in a clear plastic envelope following relinquishment endorsement and taped to the shipping container. A copy of the white original will be returned to the Subcontractor. For the tissue samples, the back copy of the Chain-of-Custody Form will be detached and retained and filed with the sample logbook. The original and remaining copies will be placed in a clear plastic envelope following relinquishment endorsement by the transporter and taped to the shipping cooler. A copy of the Chain-of-Custody form to be used on this project is provided in the SOP-007-1. Shipping containers and coolers will be sealed with a Chain of Custody tapes applied so that they must be broken to remove the contents of the shipping container.

5.3 SHIPPING CONTAINERS

Samples shall be frozen prior to shipping to maintain the temperature at -20 ˚C. The shipping container will be cooled with "blue ice" or similar dry cooling methods. The individual sample containers shall be wrapped in bubble pack or other shock absorbing media. It is desirable to place an absorbent and cushioning media in the bottom of the shipping cooler to absorb liquids in the event of breakage.

Coolers shall be securely sealed with suitable packing tape wrapped all the way around the shipping cooler to secure the lid during transit. It is desirable to tape over the latching handle to minimize the chance of accidental release.

The shipping containers and their contents will conform to current local, state, and federal shipping regulations.

5.4 CUSTODY SEALS

Custody seals are used to ensure that a sample shipping container has not been opened, and that custody has been maintained in transit. Following the securing of the shipping cooler lid with packing tape, custody seals will be placed across the lid opening of the shipping cooler. A minimum of two (2) custody seals will be used in case one seal is damaged during shipping even though the container lid remains closed.

The sample collector will record each custody seal number on the Chain-of-Custody Form prior to its attachment to the shipping cooler. The laboratory will compare the number of the custody seal(s) on the sample container against the Chain-of-Custody forms and report the seals' condition as intact or broken upon receipt. The laboratory will notify the Project Managers in writing, within 24 hours if a custody seal or container is received broken.

5.5 SAMPLE PACKAGING AND SHIPPING

The packaging, labeling, and shipping of hazardous wastes and substances when shipped by common carrier is regulated by the U.S. Department of Transportation (DOT) under 49 CFR. Samples from hazardous waste sites are classified as "Low", "Medium", or "High" level according to pollutant concentration. Low level samples, generally dilute in nature, are usually collected from areas surrounding a spill or disposal area. Medium level samples are generally collected on-site in areas of moderate dilution by normal environmental processes. The high level samples are generally collected from fresh spills, containers, lagoons, and waste piles, and contain greater than 15 percent of any individual chemical contaminant. Because of their potential toxicity or hazard, medium and high level samples require special handling procedures and must be shipped in compliance with DOT requirements.

The samples from this project will be considered as environmental, low level samples unless data which suggest otherwise are available.

5.5.1 Packaging

The User's Guide to the Contract Laboratory Program (U.S. EPA 1988) outlines CLP protocols for packaging and shipping or transportation of samples. They include:

1. Cool samples of low concentration to at or below 4 degrees C.
2. Pack medium and high concentration sample containers in metal cans.
3. Separate and surround cooler contents with vermiculite or equivalent packaging.
4. Fill out the Chain-of-Custody Form completely for each cooler of samples shipped.
5. Place the Chain-of-Custody form in a plastic bag with a watertight seal.
6. Include a return address label for the cooler.
7. Tape the sealed bag to the underside of the cooler lid.
8. Seal the cooler by placing custody seals across the joint between the lid and body.

5.5.2 Labeling and Marking the Cooler

The shipping labels shall be clear and correct. Conflicting labels from prior use shall be removed or covered with opaque tape.

The carrier's shipping label shall be on the top of the cooler. The name, address (delivery location), and telephone number of both the shipper and the receiving laboratory shall be included on the label. The shipper's return address shall be affixed to the top of the cooler with a durable label or with indelible felt marker. The sides of the cooler should be clearly marked with a label stating "This End Up" with arrows pointing to the top of the cooler.

5.6 RECEIVING SAMPLES AT THE ANALYTICAL LABORATORY

Upon receipt of the sample cooler at the analytical laboratory, the sample custodian shall inspect the cooler and the custody seals, noting any damage to the cooler and whether the custody seals are broken or intact. The custodian will then inspect each sample container for damage and note its condition and the condition of its custody seal. The number of each custody seal shall be verified against the number on the Chain-of-Custody Form and any discrepancies noted. Each sample container shall be inspected to verify that it has a sample tag or label and that the information is consistent with that on the Chain-of-Custody Form. Inconsistencies

between the information on the Chain-of-Custody Form and the container and seal information as received shall be reported by the laboratory to the Project Managers immediately.

If the chain-of-custody error was caused by the sampler, the sampler must correct the problem with a signed and dated correction memorandum to the Project Manager. Once validated, the correction memorandum will be sent to the NYSDEC QA/QC Manager, requesting that the modifications be made. The correction memorandum becomes a permanent part of the sample documentation and a copy of the correction memorandum, showing the date received by the laboratory, shall be submitted with the data package. Chain-of-Custody inconsistencies must be resolved before the results from the analysis are released for validation.

The laboratory will prepare Internal Chain-of-Custody (ICOC) Forms to accompany the samples through the analytical process. Copies of the ICOC will accompany the original sample, unused portions of samples, digestates, or extracts derived from the samples, raw instrumental data, and completed data packages as integral parts of the raw data. The details of the analytical laboratory QA/QC protocols will be presented in the laboratory Quality Assurance Project Plan.

6.0 CALIBRATION PROCEDURES

6.1 GENERAL

Calibration of field and laboratory equipment is necessary to ensure the accuracy and precision of the collected data. All instruments used in the sampling and analysis will have a complete maintenance and repair history through the duration of the project activities. This history will include, but will not be limited to, the following:

1. The equipment's identification by model and serial number.

2. The equipment's calibration and maintenance schedule, including the last date of routine maintenance and/or factory calibration, the name of the individual conducting the work, any deviations or abnormalities detected, and the tasks that were undertaken to correct any deficiencies.

3. A record of equipment failures and manufacturer's conducted repairs, calibrations, and maintenance and brief description of the cause of the failure that required manufacturer's service will be included, if available.

Any instrument that does not perform according to its specifications as stated by the manufacturer will be clearly labeled as such and returned for repair.

6.2 FIELD INSTRUMENTATION

The field instruments necessary for use in this investigation will be available from one or more study participants. The instruments will be maintained and calibrated in accordance with standard maintenance and calibration procedures. Manufacturers' recommendations for maintenance and calibration of instrumentation are followed where applicable. Calibration of field instruments will be performed by qualified personnel or by qualified manufacturers' representatives. Instrument calibration and maintenance procedures are kept on file. Relevant product literature including calibration and maintenance procedures is frequently an integral part of the Standard Operating Procedures, which accompany the equipment.

Any deviation from the recommended procedures will be documented in the field book of the individual performing the calibration or maintenance, or the laboratory log maintained for the project and in the pertinent calibration book.

7.0 ANALYTICAL PROCEDURES

A summary of the analytical methods and sample requirements proposed for this project are presented in Table 7-1. The methods and holding times are summarized in Table 4-2. Method detection limits for tissue analysis proposed for this project are summarized in Table 7-2. The tissues prepared from the specimens collected for the field program (See Section 4.0) will be analyzed for PCBs, other organochlorines, metals, cadmium, mercury, and lead, percent moisture, and percent lipid. A laboratory prepared tissue blank will be used..

The analytical methods for the analysis of PCB, organochlorine pesticides, percent lipid and percent moisture content will be according to the U. S. Fish and Wildlife Service protocols based on U.S. Environmental Protection Agency methodology. The method is presented in Appendix C-1. A silicic acid column clean-up is used in the presence of PCBs to eliminate PCB interferences. Toxaphene interference will be handled by dilution unless it is encountered at concentrations greater than 50 times the concentration of other organochlorine analytes. In that case the toxaphene component will be quantified from a toxaphene standard. The clean-up procedures are described in Appendix C-1. The metals analyses for mercury, cadmium, and lead are presented in Appendix C-2. The PCB and organochlorine pesticide analysis will be performed by the contracted organics laboratory and the metals analyses will be performed by the NYSDEC laboratory at Hale Creek Field Station.

The analytical method for the metals mercury, cadmium, and lead is presented in Appendix C-2.

Table 7-1
Summary of Samples Collected for Laboratory Analysis
(including QA/QC samples[1])
Organochlorine and Metal Contaminant Levels in Hudson River Reptiles and Amphibians
Hudson River, New York

Media	Species	PCBs, organo-chlorines, pesticides	% Moisture	% Lipid	Mercury	Cadmium	Lead
Muscle	*R. clamitans*	36	36	36	36		
Muscle	*C. serpentina*	18	18	18	18	18	18
Adipose	*C. serpentina*	18	18	18	18	18	18
Liver	*C. serpentina*	18	18	18	18	18	18
Kidney	*C. serpentina*	18	18	18	18	18	18
TOTAL		108	108	108	108	72	72

[1] For QA/QC samples 20% duplicates, see QAPP Section 3.2

Table 7-2
Method Detection and Quantitation Limits
Organochlorine and Metal Contaminant Levels in
Hudson River Reptiles and Amphibians
Hudson River, New York

PCBS AND PESTICIDES		
Compound	Quantitation Limit (µg/Kg)[1]	MDL (µg/Kg)[2]
PCB 1242	30	20
PCB 1248	30	20
PCB 1254	30	20
PCB 1260	30	20
HCB	10	2
alpha BHC	10	5
beta BHC	10	5
gamma BHC	10	5
delta BHC	10	5
alpha Chlordane	10	5
gamma Chlordane	10	5
Oxychlordane	10	5
cis-Nonachlor	10	5
trans-Nonachlor	10	5
Heptachlor epoxide	10	5
p,p'-DDT	10	2
p,p'-DDE	10	2
p,p'-DDD	10	2
o,p'-DDT	10	2
o,p'-DDE	10	2
o,p'-DDD	10	2
Endrin	10	5
Dieldrin	10	5
Toxaphene	50	50

Table 7-2
Method Detection and Quantitation Limits
Organochlorine and Metal Contaminant Levels in
Hudson River Reptiles and Amphibians
Hudson River, New York

Mirex	10	2
METALS		
Compound	Quantitation Limit (mg/Kg)	MDL (mg/Kg)
Cadmium	10	2
Mercury	10	8
Lead	15	15
OTHER PARAMETERS		
Percent Moisture	0.5	0.5
Percent Lipids	0.05	0.05

[1] The quantitation limits for PCBs, pesticides and other parameters are the "Lower limits of detection" of the proposed contractor. All values at or above the "Lower limits of detection" are to be reported by the contractor; values below the "Lower limit of detection" are to be reported as not detected.

[2] The values used are (except Toxaphene) those of the Department's laboratory at the Hale Creek Field Station, Gloversville, New York.

8.0 DATA REDUCTION, VALIDATING, EVALUATION AND REPORTING

8.1 GENERAL

All data collected for this project will be appropriately identified and validated. Where test data have been reduced, the method of reduction will be described in the text of such reports. Validation of all laboratory analytical data will be performed by the NYSDEC Data Validator.

8.2 DATA VALIDATION - LABORATORY

The Laboratory Quality Assurance Officer will perform all in-house analytical data reduction and QA/QC procedures. The Laboratory Quality Assurance Officer will be responsible for reporting any and all deficiencies to the Laboratory Project Manager, who in turn reports to the NYSDEC Data Validator, and the NYSDEC Project Manager, and NYSDEC QA/QC Manager. A deficiency report will include a discussion of why the data are suspect, the reasoning behind the possible unreliability, and possible courses of action that can be taken to remedy the situation. Any course of action to rectify suspect data shall be agreed upon by the NYSDEC Data Validator, the NYSDEC Project Manager and the Laboratory Project Manager. Any data that fail to meet the validation requirements, and cannot be adequately rectified, shall be rejected and excluded from consideration during data analysis. This information will accompany any data packages.

8.3 DATA VALIDATOR

The NYSDEC will provide the independent data validation for the analytical laboratory data.

8.4 DATA VALIDATION - FIELD MEASUREMENTS

All data from field measurements and measurements taken during tissue sample preparation will be validated by a scientist who has not been involved in the data collection. This validation will include a review of the methods and/or SOPs used for the collection of the data, and the field and laboratory notes/results that are collected. Any data

that cannot be validated will be documented and excluded from further consideration. All data entry to computer files will be checked by another person who will initial and date a hard copy of the data reviewed.

8.5 DATA EVALUATION

The contaminant data will be summarized statistically by sex and species using small sample statistical methods such as Mann-Whitney U or similar method agreed to with the NYSDEC. The sex distribution in such a small sample as 5 turtles and 10 frogs per site may not allow a statistical evaluation by sex. Qualitative discussion of the data by sex will be included.

8.6 REPORTING REQUIREMENTS

The final data report shall meet the requirements of the NYSDEC. The chemical laboratory data package will include:

1. A summary of all results showing amounts detected and detection limits.
2. A tabulation of all surrogate recoveries; matrix spikes and duplicates; trip, field, and equipment blanks; and all calibration raw data and results.
3. Chain-of-Custody Forms for each sample shipment.
4. All calculation work sheets used to reduce the raw data, including all chromatogram and instrument printouts.

Copies of the field and laboratory data generated during specimen collections and sample preparation will be provided to the NYSDEC. Copies of calculation sheets generated during data analysis will also be provided. These data reports will be available for review during data analysis.

9.0 INTERNAL QUALITY CONTROL CHECKS AND FREQUENCY

9.1 DATA HANDLING

All analytical chemistry data shall be submitted by the analytical laboratory to the NYSDEC Project Manager and NYSDEC Data Validator. Data packages shall be assembled in accordance with CLP protocols for all samples analyzed under CLP protocols. For those samples analyzed under non-CLP protocols, adequate QA procedures will be followed to allow the comparison between the non-CLP and the CLP results.

9.2 DATA VALIDATION

All chemical data included in the project database and in interim and final reports shall be validated by the NYSDEC Data Validator. This validation shall include an independent audit of all laboratory data and all QA/QC samples and procedures. This audit shall assess the validity of the data and determine its acceptability.

9.3 DATA REDUCTION

All of the chemical data and field data that are generated during the project will be entered into an electronic database. This electronic database will be provided to the NYSDEC Bureau of Habitat with the project final report. The validated chemical data will be provided by the NYSDEC for data reduction.

10.0 PERFORMANCE AND SYSTEM AUDITS

Performance and system audits for the analytical laboratory will be performed as specified by the NYSDEC. Performance and system audits for the data generated during field collection and sample preparation will consist of the review of all sampling information, raw data, data entry, and calculations by a scientist who did not participate in generation of the data.

11.0 PREVENTIVE MAINTENANCE

The purpose of preventive maintenance is to have instruments and equipment always in condition to properly and correctly carry out the function for which the unit is designed, and to do so with minimum adjustment, calibration, or down time at the time of use.

An inventory control system for instruments that may be used in the laboratory or for sampling purposes will be maintained. The inventory record will be maintained at the offices of the Project Manager. Each unit of field monitoring instruments shall have current documentation which includes:

1. type and title of unit
2. manufacturer, model number, and serial number
3. identification number
4. date of purchase
5. service Company (name, address, telephone and FAX numbers)
6. type of service policy
7. routine maintenance, servicing and calibration (timing, frequency)
8. date of and cause for last service (other than routine)
9. date of last calibration
10. adjustment required to recalibrate equipment, and any deviation to complete calibration following adjustment.

Field measurement instruments shall be maintained in accordance with SOPs and manufacturers' instructions (which may be appended to the SOP). Instruments shall be checked prior to use by the operator. The use of the instrument shall be recorded in the log book and that record shall include a report of problems encountered with the instrument, a description of the symptoms, and corrective actions taken. Problems with the instrument will be corrected before use is resumed.

Instruments shall be cleaned, repaired, and recharged (if appropriate) following use so that they are ready for the next application.

12.0 PRECISION, ACCURACY AND COMPLETENESS OF ANALYTICAL DATA

12.1 GENERAL

This section describes the QA/QC procedures that will be established to ensure that the analytical data generated for the project are accurate, precise and complete. The collection and analysis of representative samples will insure the best chance of obtaining accurate results that reflect the conditions of the specimens. The laboratory will either analyze the complete sample or a smaller portion of the sample that is representative of all that material in the container. Data that meet these criteria will be considered representative..

12.2 DEFINITIONS

The following definitions will be used to structure the QA/QC procedures.

1. Accuracy: The amount of agreement between the true value of a parameter and the measured value. Accuracy is a measurement of the bias in a parameter.

2. Precision: The measurement of the agreement between samples from the same population. Precision can be expressed as the standard deviation between independent samples or as the relative percent difference (RPD) between duplicate samples.

3. Completeness: The measure of the amount of validated data obtained compared to that which was expected to be obtained.

12.3 EQUATIONS

The following equations are required to estimate the accuracy, precision, and completeness in a QA/QC program for organic, inorganic and semi-volatile analysis of various matrices.

12.3.1 Percent Recovery

$$(\text{Spike Sample}) = \frac{RSS - RUS}{SA} \times 100$$

Where: RSS = Results of Spike Sample
RUS = Results of the Unspiked Sample
SA = Amount of Spike Added

This analysis of the chemical data will be performed as specified by the NYSDEC Data Validator

12.3.2 Relative Percent Difference

$$(RPD) = \frac{D_1 - D_2}{0.5(D_1 + D_2)} \times 100$$

Where: D_1 = First Sample Results
D_2 = Duplicate Sample Results

12.3.3 Percent Completeness

$$= \frac{\text{Number of Valid Results}}{\text{Number of Possible Results}} \times 100$$

12.4 MINIMUM REQUIREMENTS

The minimum requirements needed to demonstrate the analytical laboratory's capability to meet the QC requirements for analysis of the target compound list will be those set forth in the method protocols accepted by the NYSDEC.

12.4.1 Blank Samples

Blank samples will be used to evaluate sources of contamination inherent in laboratory or sampling procedures that are not attributable environmental contamination. Method blanks prepared from clean tissue will be used by the analytical laboratories.

12.4.2 Spiked Samples

Matrix spikes and matrix spike duplicates will be used to evaluate the accuracy and precision of the laboratory's analysis. Spiking samples and blanks prior to analysis will be used to evaluate analytical accuracy of the laboratory. Performance will be measured by the percent recovery of the spike material using Equation 12.3.1. Corrective action shall be taken if the one surrogate compound is outside the required recovery limits in either the method blank or sample. Notification of deviations will be made immediately to both the laboratory Quality Assurance Manager, the NYSDEC Project Manager, and the NYSDEC Data Validator. Method details will be addressed in the laboratory QA plans prepared by the analytical laboratory.

12.4.3 Duplicate Samples

Duplicate tissue samples will be prepared and submitted to the analytical laboratory. The number of duplicate samples will represent 20 percent of the total sample number. Enough material will be collected so that a laboratory duplicate sample may be prepared from the tissue samples submitted, after the sample is properly homogenized. Duplicate samples will be collected in the same manner, using the same equipment and by the same personnel. Duplicate samples will be analyzed using identical methods for the same parameters. These samples will be used to evaluate the analytical precision of the field sampling event.

13.0 CORRECTIVE ACTION

Any non-conformance or deficiencies detected in any activities shall be reported to the appropriate Project Manager responsible for the activity. The Project Manager will be responsible for non-conformance or deficiencies reported during field collection and sample preparation, and the NYSDEC Project Manager will be responsible for non-conformance or deficiencies reported during chemical analysis. A description of the non-conforming situation, and of the corrective actions taken, will be recorded by the project personnel in the deviation memorandum filed with the Project Manager and the NYSDEC QA/QC Manager.

14.0 QUALITY ASSURANCE REPORTS

A letter report will be submitted to the NYSDEC Project Manager that includes discussion of the data accuracy, precision, and completeness; the results of all performance audits and tests performed; and all problems discovered and the corrective actions that were taken. A summary of this report shall be included in the final report.

FIGURES

Hudson River Watershed

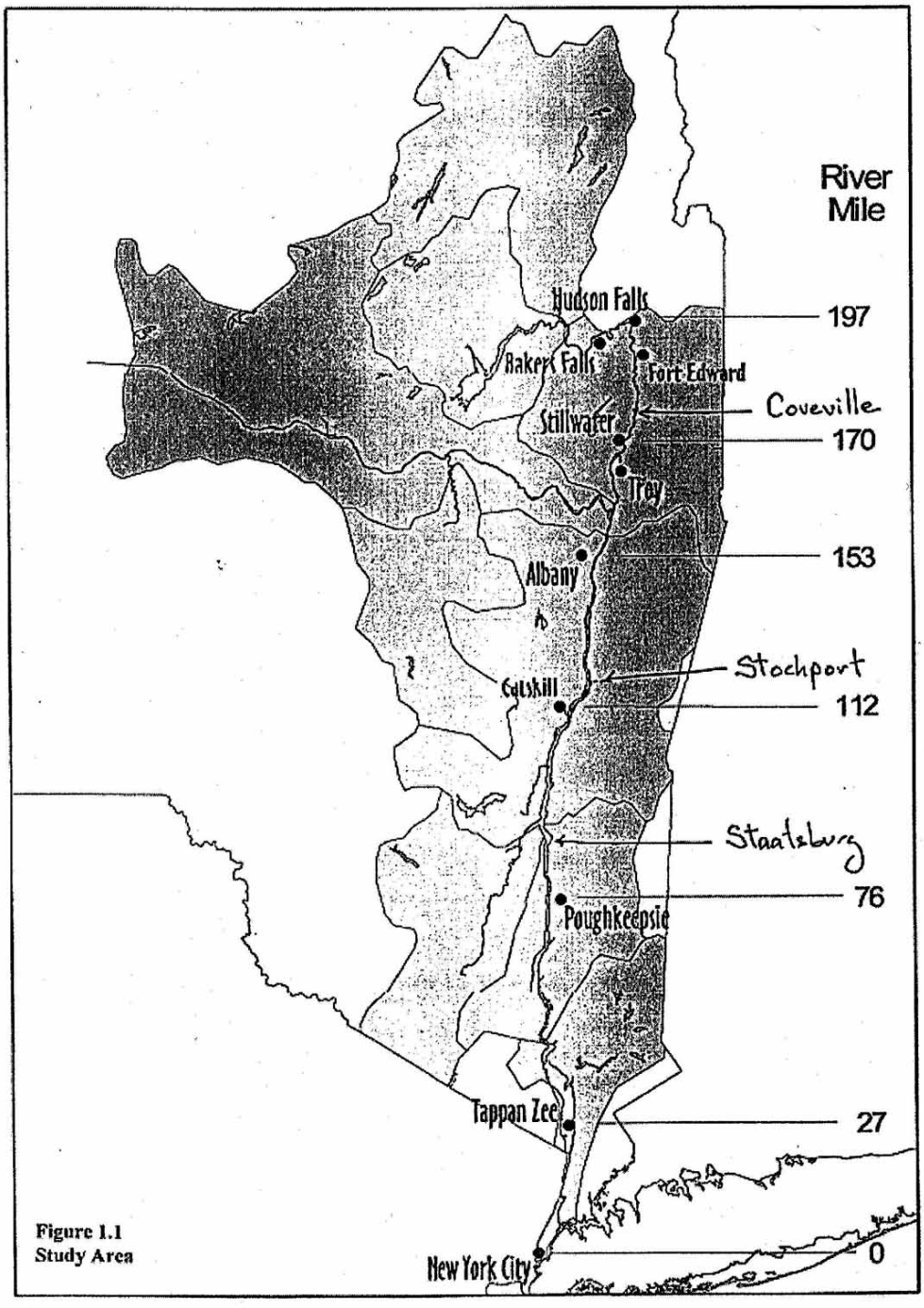

Figure 1.1
Study Area

10 0 10 20 30 40 50 Miles

Judy Marth Stevens, NYSDEC Bureau of Habitat, May '98.

ORGANOCHLORINE & METAL CONTAMINANT LEVELS
IN HUDSON RIVER REPTILES AND AMPHIBIANS

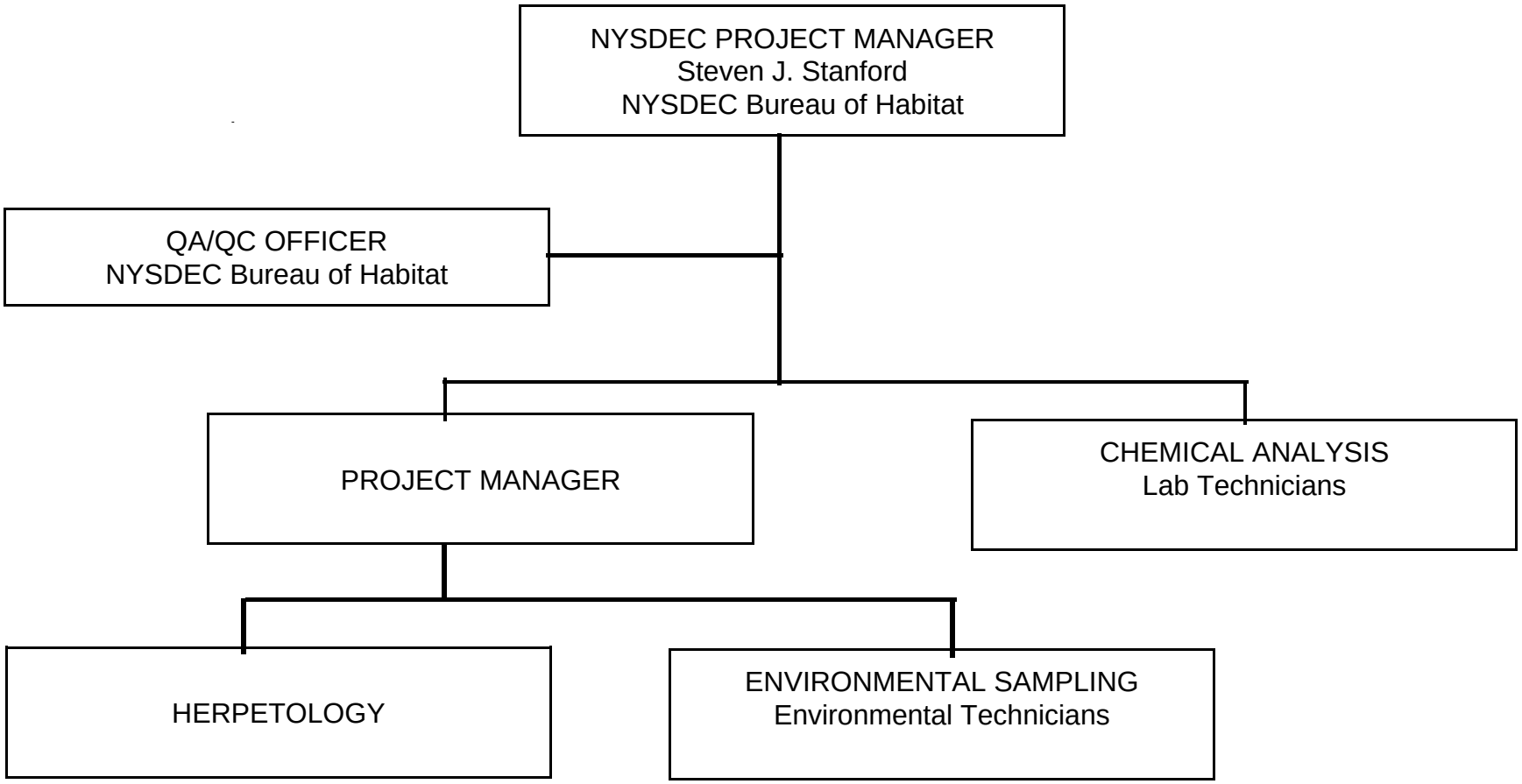

FIGURE 2-1: PROJECT ORGANIZATION CHART
N.Y. DEPT. OF ENVIRONMENTAL CONSERVATION
HUDSON RIVER, NEW YORK

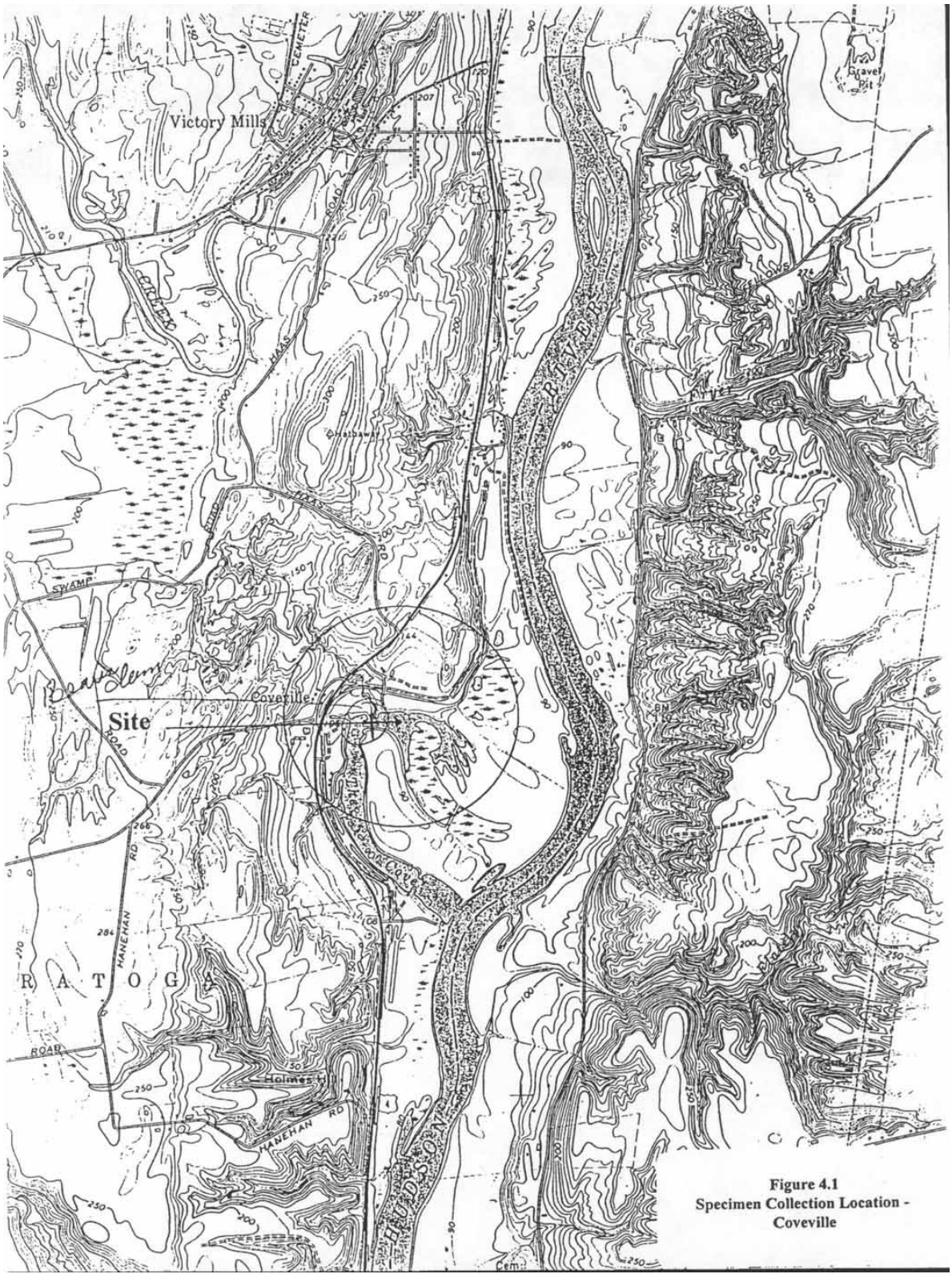

Figure 4.1
Specimen Collection Location - Coveville

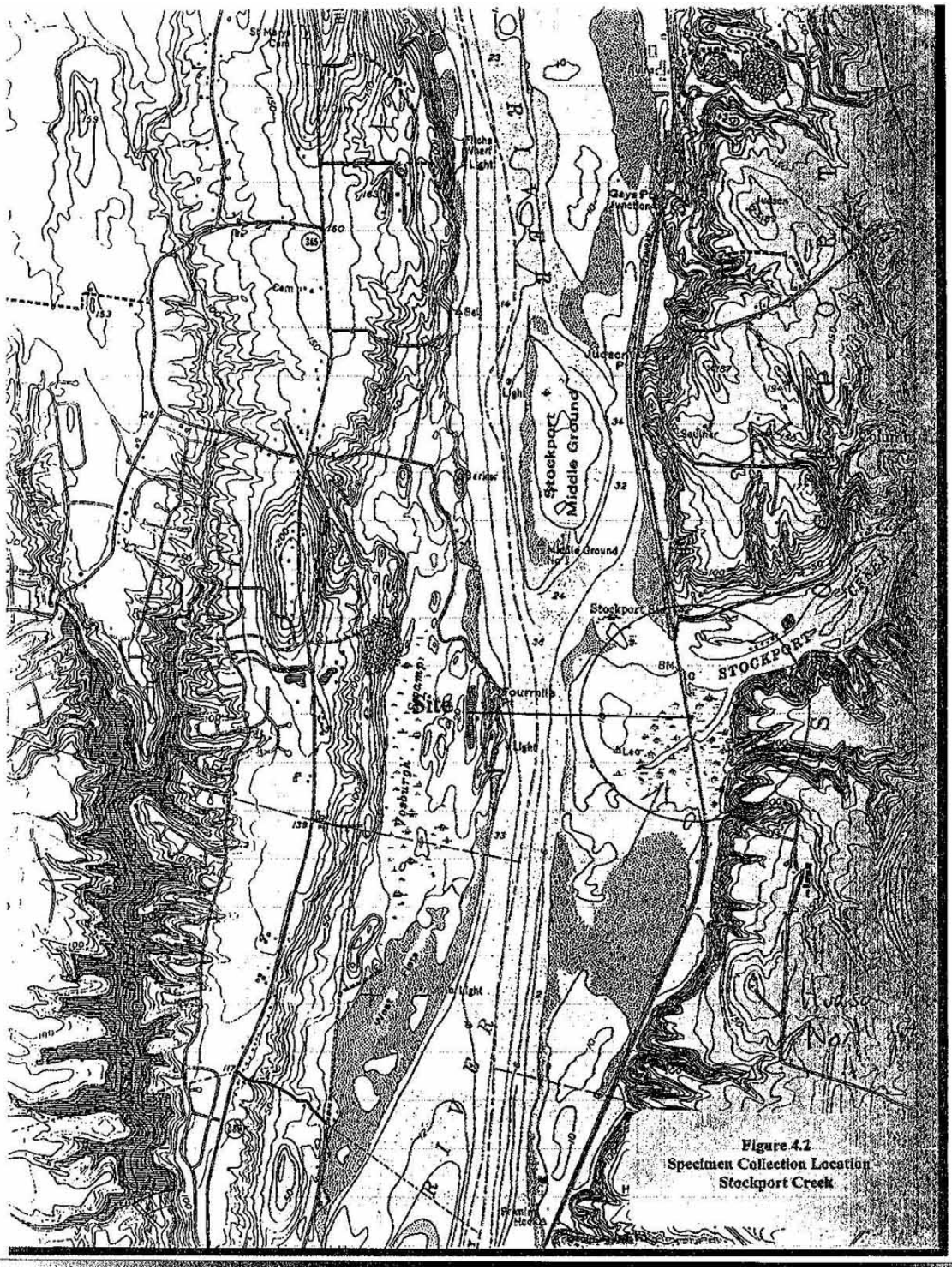

Figure 4.2
Specimen Collection Location - Stockport Creek

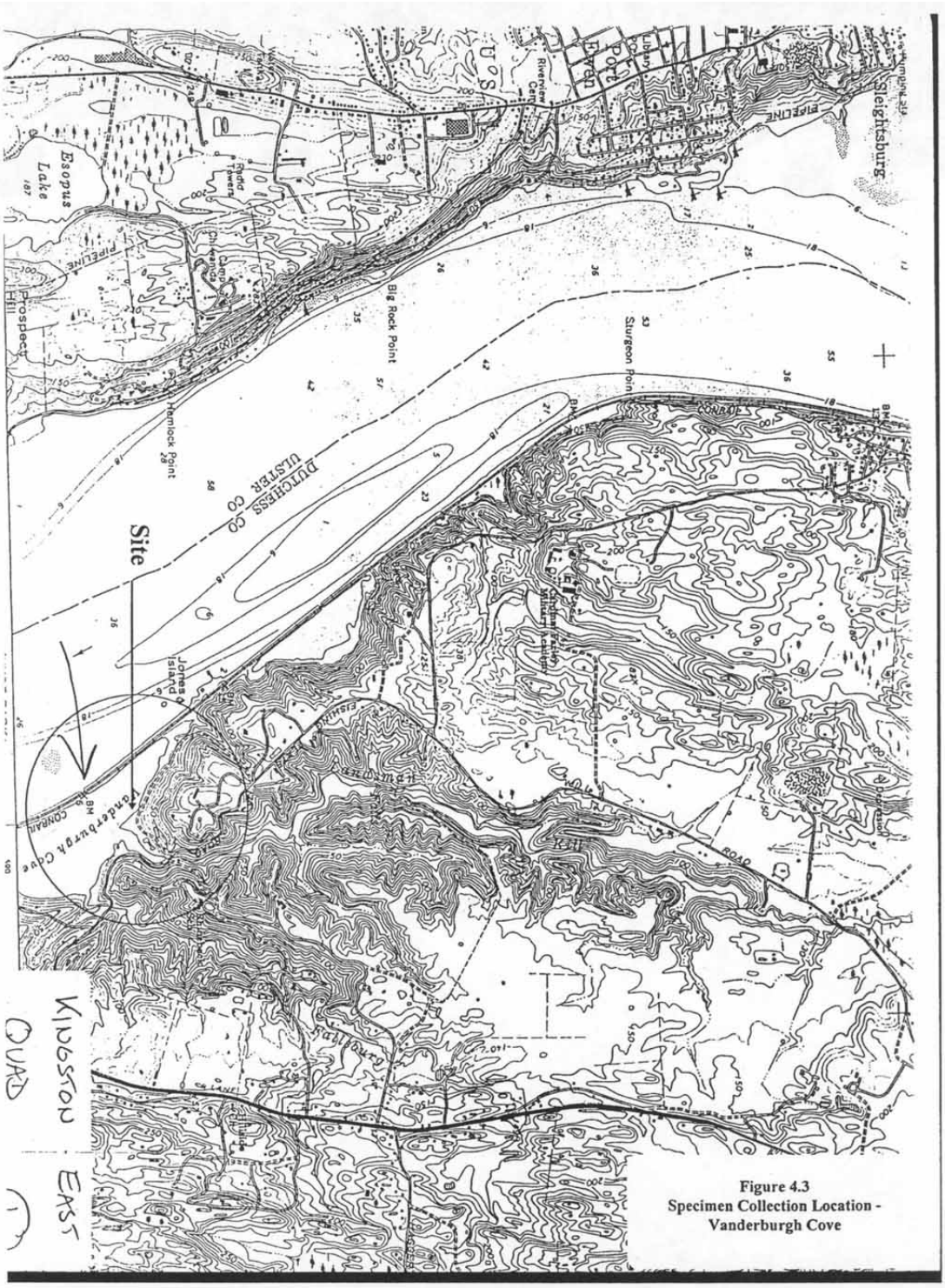

Figure 4.3
Specimen Collection Location - Vanderburgh Cove

Appendix A

Sample Forms

LABORATORY LOG BOOK FORMAT

Specimen/ Sample#	Log-in-Date	Log-out Date	Type	SUB SAMPLES				
				Muscle	Liver	Kidney	Adipose	Gut Contents

Laboratory Name
Laboratory Address
NYSDEC Bureau of Habitat
Hudson River Reptiles and Amphibians
Sample ID: HR-98-001
Analysis: Media: HERP
Preservative:
Date: Time: By:

Laboratory Name
Laboratory Address
NYSDEC Bureau of Habitat
Hudson River Reptiles and Amphibians
Sample ID: HR-98-002
Analysis: Media: HERP
Preservative:
Date: Time: By:

Laboratory Name
Laboratory Address
NYSDEC Bureau of Habitat
Hudson River Reptiles and Amphibians
Sample ID: HR-98-003
Analysis: Media: HERP
Preservative:
Date: Time: By:

Laboratory Name
Laboratory Address
NYSDEC Bureau of Habitat
Hudson River Reptiles and Amphibians
Sample ID: HR-98-004
Analysis: Media: HERP
Preservative:
Date: Time: By:

Laboratory Name
Laboratory Address
NYSDEC Bureau of Habitat
Hudson River Reptiles and Amphibians
Sample ID: HR-98-005
Analysis: Media: HERP
Preservative:
Date: Time: By:

Laboratory Name
Laboratory Address
NYSDEC Bureau of Habitat
Hudson River Reptiles and Amphibians
Sample ID: HR-98-006
Analysis: Media: HERP
Preservative:
Date: Time: By:

Laboratory Name
Laboratory Address
NYSDEC Bureau of Habitat
Hudson River Reptiles and Amphibians
Sample ID: HR-98-007
Analysis: Media: HERP
Preservative:
Date: Time: By:

Laboratory Name
Laboratory Address
NYSDEC Bureau of Habitat
Hudson River Reptiles and Amphibians
Sample ID: HR-98-008
Analysis: Media: HERP
Preservative:
Date: Time: By:

Laboratory Name
Laboratory Address
NYSDEC Bureau of Habitat
Hudson River Reptiles and Amphibians
Sample ID: HR-98-009
Analysis: Media: HERP
Preservative:
Date: Time: By:

Laboratory Name
Laboratory Address
NYSDEC Bureau of Habitat
Hudson River Reptiles and Amphibians
Sample ID: HR-98-010
Analysis: Media: HERP
Preservative:
Date: Time: By:

Appendix B

Standard Operating Procedures

Standard Operating Procedure
For
Chain-of-Custody Records

INTRODUCTION

The chain-of-custody record allows for the tracking of possession and handling of individual samples from the time of field collection through laboratory analysis. All samples released from field operations shall be accompanied by a Chain-of-Custody Form (Attachment 007-1). This is done to insure the legal integrity of the sample materials collected. Every effort shall be made to keep as few people as possible in the chain of sample possession.

PROCEDURE

1. A completed Chain-of-Custody Form shall accompany each set of samples released from the study site. The Chain-of-Custody Form for all samples shall include the following information:

    a. Signature of Sampler
    b. Client/Project name
    c. Project Location
    d. Field Logbook Number (e.g. page no. in field book)
    e. Sample Number, Identification
    f. Date and time of sample collection
    g. Type of Sample (Air, water, soil, etc.)
    h. Analysis requested
    i. Preservative Added (Remarks section)
    j. Source of the Sample (Remarks section)
    k. Chain-of-Custody Tape Number
    l. Inclusive Dates of Possession
    m. Signatures of persons involved in chain of possession
    n. Name of person the analytical results are to the attention of (in lower right corner of the form).

2. The Chain-of-Custody Form is designed in quadruplicate. Each of the individual four sheets is a different color. Along the bottom of each sheet are the instructions describing who gets which copy. These instructions are as follows:

White Copy:	Original sheet to accompany sample to the lab and return to the Project Manager
Yellow Copy:	Laboratory Copy
Pink Copy:	Transporter Copy (optional)
Orange Copy:	Sampler Copy

Therefore, after the Chain-of-Custody Form has been completely filled out, the sampler signs the initial "Relinquished by" along with date and time and obtains the signature of the next person (i.e., transporter) in the chain-of-custody (in the initial "Received by" box along with date and time. The sampler then tears off the back (orange) copy for his records. Then the transporter delivers the samples to the analytical lab, he signs the second "Relinquished by" box along with date and time. and a laboratory representative signs the second "Received by" box along with the date and time. At this point, the transporter has the option of retaining the pink copy for his records.

Instructions shall be given to the laboratory regarding their responsibilities in returning the top sheet (white copy) to the Project Manager with the lab results. This sheet contains all sample information and original signatures. The lab should retain the yellow copy for their records.

If the sampler his- or herself delivers the samples to the laboratory, then the sampler should make certain the receiving party at the lab signs in the proper space, i.e., "Received for Laboratory".

3. The Chain-of-Custody form shall be completed in legible hand writing with indelible ink, with all appropriate information completed. Once completed, the form is either:

   a. placed in a plastic-wrap and included with the samples in the cooler, or

   b. fixed in an envelope taped securely in top of the cooler or plastic packing slip container (if available). This method allows for signatures to be included with each transfer of custody. This method is mandatory in the event a non-commercial courier is utilized to transport samples.

4. The sample container shall be sealed with chain-of-custody tape, containing the designation, date, and sampler's signature. The custody tape is especially important when shipping the container via overnight courier such as Federal Express and United Parcel Service.

Revision
Author: _____ Date: 3/13/96
Scientist, Engineer or Technician

Reviewed: _____ Date: 3/13/96
Director, Quality Assurance Unit

Approved: _____ Date: 3/13/96
Vice President

ATTACHMENT SOP-007-1

Chain-of-Custody Form (following page)

CHAIN OF CUSTODY RECORD

Nº 00

Client/Project Name	Project Location	ANALYSES
Project No.	Field Logbook No.	
Sampler: (*Signature*)	Chain of Custody Tape No.	

Sample No./ Identification	Date	Time	Lab Sample Number	Type of Sample							REMARKS

Relinquished by: (*Signature*)	Date	Time	Received by: (*Signature*)	Date	Time
Relinquished by: (*Signature*)	Date	Time	Received by: (*Signature*)	Date	Time
Relinquished by: (*Signature*)	Date	Time	Received for Laboratory: (*Signature*)	Date	Time
Sample Disposal Method:	Disposed of by: (*Signature*)			Date	Time
SAMPLE COLLECTOR	ANALYTICAL LABORATORY				

1974-3-84

WHITE - To accompany sample to the lab and returned to the Poject Manager. YELLOW - Lab copy PINK - Transporter copy ORANGE - Sampler copy

Standard Operating Procedure For
Deviation from Protocols or Standard Operating Procedures
and for Notation, Correction and Documentation of
an Unforeseen Circumstance

INTRODUCTION:

The objective of this procedure is to ensure the study quality and integrity in the event of:

(a) deviations from approved protocols or standard operating procedures and
(b) unforeseen circumstances which may affect the quality of the study.

The procedure set forth herein is appropriate and desirable in all studies. However, it is a requirement of regulatory law for studies conducted under 40 CFR Part 160, the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), Good Laboratory Practice Standards and 40 CFR Part 792, Toxic Substance Control Act (TSCA), Good Laboratory Practice Standards.

Specifically, FIFRA requires at 40 CFR § 160.81 (Standard Operating Procedures) that

"(a) A testing facility shall have standard operating procedures in writing setting forth study methods that management is satisfied are adequate to insure the quality and integrity of the data generated in the course of a study. All deviations in a study from standard operating procedures shall be authorized by the Study Director and shall be documented in the raw data. Significant changes in established standard operating procedures shall be properly authorized in writing by management."

At 40 CFR 160.33 (Study Director)... "The Study Director shall assure that:

(a) the protocol, including any change, is approved as provided by §160.120 and is followed. [Emphasis added]

...
(c) unforseen [sic] circumstances that may affect the quality and integrity of the study are noted when they occur, and corrective action is taken and documented. [Emphasis added]

...
"(e) all applicable good laboratory practice regulations are followed".

Further, at 40 CFR § 160.35 (Quality assurance unit)
...

"(b) The quality assurance unit shall:

...

(5) Determine that no deviations from approved protocols or standard operating procedures were made without proper authorization and documentation." [Emphasis added.]

PROCEDURE:

A. Record of Deviation from Protocol or Standard Operating Procedure

1. Record the facts of the deviation legibly in ink using Form QAU-005 or a field book, bench log, or other recognized and reliable record keeping device at the time of the deviation. Initial and date each page of entry at that time.

   The facts of the deviation should include but not necessarily be limited to:

   Date of occurrence:
   Time:
   File No.:
   Study designation:
   Test Substance:
   CAS No.:
   Study sponsor:
   Study phase or segment (Ref: Protocol):
   Weather:
   Temperature:
   Personnel on site:
   Visitors:
   Contractors:
   Equipment:
   Standard Operating Procedure (title and number):
   Protocol (title, date, section):
   Type of deviation (inadvertent or planned):
   Nature of deviation:
   Observations:
   Problems:

2. List anticipated consequences of deviation.

3. Determine correction action alternatives and rank with most desirable first.

4. Contact Study Director/Project Manager as soon as conveniently possible for authorization to proceed with corrective action.

5. Document the corrective action, e.g. change in procedure, materials, equipment, personnel, time.

6. Retain all notes and records of the deviation for archiving as raw data.

7. Prepare full documentation of the facts of deviation, authorization and corrective action on Form QAU-005.

8. Sign and date Form QAU-005.

9. Obtain authorj:zation signature of Study Director/Project Manager on Form QAU-005.

10. Obtain signature of Quality Assurance Unit Director indicating review of completed Form QAU-005.

B. Record of Unforeseen Circumstances which may Affect the Quality of the Study

1. Record the facts of the unforeseen circumstances legibly in ink using form QAU-005 or a field book, bench log, or other recognized and reliable record keeping device at the time of occurrence. Initial and date each page of entry at that time. The facts of the unforeseen circumstances should include but not necessarily be limited to those items listed under A. 1. above. A wide variety of unforeseen circumstances may impinge on the quality of a study. For example, a lightning strike induces a charge on a cable and distorts information in the data logger or destroys a sensing unit at the weather station; a hurricane flood submerges monitoring wells; a bee sting or threat of snake bite causes personnel to drop a box of water samples; or an accident delays delivery of refrigerated samples.

2. List the consequences of the unforeseen circumstance.

3. Determine if corrective action is possible.

4. List corrective action alternatives with most desirable first.

5. Notify Study Director/Project Manager as soon as conveniently possible of unforeseen circumstances.

6. Obtain authorization from Study Director/Project Manager to proceed with corrective action.

7. Document the corrective action, e.g. change in procedure, materials, equipment, personnel, time.

8. Retain all original notes and records of the unforeseen circumstances for archiving as raw data.

9. Prepare full documentation of the facts of the unforeseen circumstances, notification, authorization, and corrective action on Form QAU-005.

10. Sign and date form QAU-005

11. Obtain authorization signatures of Study Director/Project Manager of Form QAU-005

12. Obtain signature of Quality Assurance Unit Director indicating review of completed Form QAU-005.

Revision
Author: _____ Date: 7/12/94
Scientist, Engineer or Technician

Reviewed: _____ Date: 7/12/94
Director, Quality Assurance Unit

Approved: _____ Date: 7/12/94
Vice President

Quality Assurance Unit
Record of
(Check One)

❑ A. *Deviation from Protocol or Standard Operating Procedure*
or
❑ B. *Notation, Correction and Documentation of Unforeseen Circumstances*

Ref: 40 CFR § 160.81, § 160.33 and § 160.35 and SOP-018

Dates of Occurrence:

Study Designation:

Study Location:

Test substance: CAS No.:

Study Sponsor:

Study phase (or segment):

Site of problem:

Scientist, engineer or technician: Initials: _____Date: _____

Findings:

Weather: F; Sky: Clear, Partly Cloudy, Fair, Rain, Snow; Wind-

List: Personnel, Visitors, Contractors:

Equipment (e.g. Permeameter, Data Logger, Drill rig, Dozer):

Protocol title, date and section number:

Standard Operating Procedure title:

SOP No.:

Type of deviation (inadvertent or planned):

Nature of deviation or unforeseen circumstance:

Observations:

Problems:

Continuation Sheet

Initials: _____ Date:_____

(Instruction: Number paragraphs consistent with the numbers of items listed under Procedure A or B in SOP 118. Begin with No. 2. Sheet 1 of this report addresses Item No. 1.)

Continuation Sheet Initials: _____ Date:_____

Report Prepared by: _____ Date _____
Scientist, Engineer or Technician

Authorized by: _____ Date _____
Study Director/Project Manager

Reviewed by: _____ Date _____
Vice President

Appendix C

Laboratory Methods

Appendix C-1

PCB and Organochlorine Pesticides Methods

APPENDIX D

Analytical methods for analysis of PCB, organochlorine pesticides, lipid and moisture content used by the contract laboratory; the methods are those of the US Fish and Wildlife Service based on US Environmental Protection Agency methodology.

Methodology currently in Use

Code	Method Title
001	Analysis for Organochlorine Pesticides and PCBs in Animal and Plant Tissue.
002	Analysis for Organochlorine Pesticides and PCBs in Soil and Sediment.
005	Analysis for Organochlorine Pesticides and PCBs. Aliphatic and polynuclear Aromatic Hydrocarbons in Water.
006	Analysis for Chlorinated Hydrocarbon Pesticides and Related Compounds - Micro Method.
011	Analysis for Organochlorine Pesticides and PCBs in Blood .Serum, Plasma or Whole Blood.
015	Elution Profiles for Florisil, Silica Gel and Silicic Acid Column Separations.

Method 1. Analysis For Orqanochlorine Pesticides and PCBs in Animal and Plant Tissue.

Ten gram tissue samples are thoroughly mixed with anhydrous sodium sulfate and soxhlet extracted with hexane for seven hours. The extract is concentrated by rotary evaporation; transferred to a tared test tube, and further concentrated to dryness for lipid determination. The weighed lipid sample is dissolved in petroleum ether and extracted four times with acetonitrile saturated with petroleum ether. Residues are partitioned into petroleum ether which is washed, concentrated; and transferred to a glass chromatographic column containing 20 grams of Florisil. The column is eluted with 200. ml 6% diethyl ether/94% petroleum ether (Fraction I) followed by 200 ml 15% diethyl ether/85% petroleum ether (Fraction II). Fraction II is concentrated to appropriate volume for quantification of residues by packed or capillary column electron capture gas chromatography. Fraction I is concentrated and transferred to a Silicic acid chromatographic column for additional cleanup required for separation of PCBs from other organochlorines. Three fractions are eluted from the silicic acid column. Each is concentrated to appropriate volume for quantification of residues by packed or megabore column, electron capture gas chromatography. PCBS are found in Fraction II.

Method 6. Analysis For Chlorinated Hydrocarbon Pesticides And Related Compounds - Micro Method

This method is necessary when sample size is limited (below 4 g. approximately) and in case of organ tissue as substrate and is a modified version of the method described In Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples, EPA-600/B-80-038; June 1980, Section 5, A (2). It is suitable for adipose, kidney, liver, muscle, brain, and other tissues:

1. Weigh 0.5 g or less of well-mixed tissue into a size 22 Duall tissue grinder.
2. Extract tissue by grinding three times with acetonitrile: the first time being with 4 ml followed by two 2.5 ml portions.
3. Remove the pestle after each grinding and centrifuge, decanting the extract into a 50 mm glass stoppered graduated mixing cylinder.
4. Combine all extracts and record the total volume of the three extracts.
5. Add a volume of PRQ water equivalent to 3.3 times the extract volume. Then add 2 ml saturated NaCl solution.
6. Extract the aqueous acetonitrile mixture with 5 ml. hexane by vigorous shaking for 1 minute.
7. Allow layers to separate and remove the hexane layer with a Pasteur pipet into a 15 ml screw-capped culture tube.
8. Re-extract twice with 2 ml hexane each time, combining the extracts into the culture tube.
9. Concentrate the combined hexane extracts under nitrogen to approximately 0.5 ml volume.

10. Clean-up on a florisil mini-column as described in Method 2, steps 8, 9, 10, and 11.

Note For brain tissue additional treatment is necessary before column clean-up:

11. Proceed through Steps 1-9 above, add 0.3 ml acetic anhydride and 0.3 ml pyridine, cap tightly and incubate for 30 minutes in a water bath at 60-65^{o}C.

12. Add 8 ml PRQ water and 1 ml saturated NaCl and extract three times with 2 ml hexane, combining the extracts into a clean tube.

13. Concentrate the combined extracts under nitrogen to about 0.3 ml and proceed with florisil mini-column clean-up. (Step 10)

Note The following changes in sample handling, particularly column clean-up, should be observed for Kepone analysis:

14. Maintain the integrity of the analyte in sample extracts by insuring that the samples are not allowed to reach dryness during concentration steps. Kepone easily adheres to glass, but the use of polar solvents, such as methanol and acetonitrile within the analysis will provide better recoveries of this analyte.

15. Modifications to florisil mini-column clean-up are as follows;

    * Following addition of sample to the column, apply a 1 ml rinse of 1% methanol in hexane to the sample tube. This rinse should be added after the first phase of the first fraction (12 mls hexane) and will insure removal of trace quantities of kepone adhered to glass. Decrease the total volume of the second phase of the first fraction (12 mls 1% methanol/hexane) to 11 mls.

    * Modify the total volume of the second fraction from 24 mls to 36 mls 1% methanol/hexane. This fraction contains Kepone.

* Concentrate column fractions on N-EVAP and transfer with 1% methanol/hexane to calibrated test tubes. Adjust sample volume to calibrated level and proceed to determination by gas chromatograph.

Elution Profiles for Florisil, Silica Gel and Silicic Acid Column Separations

A. Florisil Column:

1. Fraction I (6% ethyl ether containing 2% ethanol, 94% petroleum ether). HCB, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, oxychlordane, heptachlor epoxide, gamma-chlordane, trans-nonachlor, toxaphene, PCBs, o,p'-DDE, alpha-chlordane, p,p'-DDE, p,p'-DDT, cis-nonachlor, o,p'-DDT, p,p'-DDD, p,p'-DDT, mirex, dicofol, endosulfan I (Split with FII), octachlorostyrene, chlorpyrilfos, ,and .methyl chlorpyrifos.
2. Fraction II (15% ethyl ether containing 2% ethanol, 85% petroleum ether) dieldrin, endrin, dacthal, endosulfan I (split with FI), endosulfan II (split with FIII), endosulfan sulfate (split with FIII), diazinon, EPN, ethyl parathion, and methyl parathion.
3. Fraction III (50% ethyl ether containing 2% ethanol, 50% petroleum ether) endosulfan II (split with FII), endosulfan sulfate (split with FII), malathion.

B. Florisil Mini-Column:

1. Fraction I (12 ml hexane followed by 12 ml 1% methanol in hexane)

   HCB, gamma-BHC (2.5%),. alpha-BHC (splits with FII),

   trans-nonachlor, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD (splits with FII), o,p'-DDT, p,p'-DDT, mirex, cis-nonachlor, cis-chlordane, trans-chlordane,PCBs, Photomirex and derivatives.

2. Fraction II (24 ml 1% methanol in hexane)

   gamma BHC (75%), beta-BHC, alpha-BHC (splits with FI), delta-BHC, oxychlordane, heptachlor epoxide, toxaphene, dicofol, dacthal, endosulfan I, endosulfan II, endosulfan sulfate, octachlorostyrene, Kepone (with additional 12mls 1% methnol in hexane), alachlor, atrazine, chlorpyrifos, diazinon, EPN, ethyl parathion, malathion, methyl chlorpyrifos, methyl parathion, metolachlor, metribuzin, propazine, simazine.

C. Silica Gel:

1. SG Fraction I (120 ml petroleum ether)

   n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane, n-heptadecane, n-octadecane, n-nonadecane, n-eicosane, n-heneicosane, n-docosane, n-tricosane. n-tetracosane, n-pentacoscne, n-hexacosan, n-heptacosane, n-octacosane, n-nonacosane, n-tricontane, n-hentriacontane, n-dotriacontane,. n-tritriaconfane, n-teratriacontane, pristane,and phytane.

2. SG Fraction II (100 ml 40% methylene chloride in petroleum ether followed by 50 ml methylene chloride).

naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, 2-6-dimethylnaphthalene, acenaphthalene, acenaphthene, 2,3,5-trimethylnapthalene, fluorene, dibenzothiophene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benzo[a]anthracene, chrystene, benzo[b]pyrene, perylene, indeno[1,3,3-cd]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene.

D. Silicic Acid:

1. SA Fraction I (20 ml petroleum ether)

   HCB, mirex, octachlorstyrene

2. SA Fraction II (100 ml petroleum ether)

   PCBs, photomirex derivatives

3. SA Fraction III (20 ml mixed solvent: 1% acetonitrile, 80% methylene chloride, 19% hexane)

   alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, oxychlordane, heptachlor epoxide, gamma-chlordane, trans-chlordane, toxaphene, o,p'-DDE, alpha-chlordane, p,p'-DDE, o,p'-DDT, cis-nonachlor, o,p'-DDT, p,p'-DDD, p,p'-DDT, dicofol.

Procedure for the Quantification of a Multi-Residue Sample in the Presence of Interferences.

If preliminary examination of a sample by EC/GC indicates the presence of PCBs, further fractionation of the analytes in the sample extract is performed using a silicic acid column. The result is three fractions, one of which contains PCBs separate, from other analytes. This step effectively eliminates PCB interferences in quantitation of other analytes present in the extract.

All samples for multi-residue organochlorine analyses are determined by a single injection split onto two different megabore capillary columns enabling closely eluting pairs from one column to be, completely resolved on the other column. In such cases, the value from the. column giving complete resolution is reported; otherwise when a value is obtainable from each column, the mean value is normally reported.

If toxaphene is encountered at concentrations greater than 50 times that of the other OC analytes, an interfering toxaphene component can be quantified from a toxaphene standard and an appropriate correction factor applied; thereby giving a net value for calculating the resultant value for the analyte. Again, two column analysis often results in a completely resolved analyte from which quantification can be made. Historically, toxaphene, when encountered, is less than 50 times the concentration of the other OC analytes, and because its response factor is so much less than that of the other analytes, interference from toxaphene can be diluted out so that its interference with the other analytes is negligible.

Appendix C-2

Metals, Hg, Cd, Pb Methods

STANDARD OPERATING PROCEDURE
HG.1998.FISH.1
MERCURY IN FISH TISSUES

ABSTRACT: Samples are digested and analyzed for total mercury by cold vapor atomic absorption spectrometry (CVAAS), using a Leeman Labs AP/PS200II Mercury Analysis System. A tissue sample is digested in concentrated nitric acid and sulfuric acid, then oxidized with potassium permanganate and potassium persulfate. Sodium chloride-hydroxlamine sulfate is added to reduce excess potassium permanganate. The sample is reduced with stannous chloride and mercury vapor is carried by argon gas to an optical cell with a mercury lamp (254nm). Concentration is determined directly from a calibration curve.
BASIS: The method is based on EPA Method 245.6 - Determination of Mercury in Tissues by Cold Vapor Atomic Absorption Spectrometry, Revision 2.3 (April 1991).

Introduction. This is a standard operating procedure in the Analytical Services Unit of Hale Creek Field Station, NYSDEC, Gloversville, NY for the analysis of total mercury in fish. **WARNING: MERCURY IS EXTREMELY TOXIC AND SHOULD BE HANDLED WITH EXTRA CARE. ACIDS, OXIDIZERS AND REDUCING AGENTS, USED IN THIS PROCEDURE, ARE EXTREMELY CORROSIVE. INHALATION AND CONTACT WITH EYES AND SKIN SHOULD BE AVOIDED.**

Digestion. Digest samples using a Leeman Labs AP200II (Ref: LEEMAN 1997).

PROTECTIVE CLOTHING REQUIRED: (1) Lab coat and apron, (2) vinyl, latex or neoprene gloves, and (3) protective eyewear for all work involving handling of chemicals.

MATERIALS NEEDED: (1) 50 ml glass, polyethylene or polypropylene tubes - 28.7mm x 103mm (Leeman or Nalge). (2) tracemetal nitric acid (Leeman or Fisher). (3) tracemetal sulfuric acid (Leeman or Fisher). (4). certified ACS nitric acid (Fisher). (5) potassium permanganate 5% (Leeman or LabChem). (6) potassium persulfate 5% (Leeman or LabChem). (7) Sodium chloride-hydroxylamine sulfate 12% (Leeman or GFS Chemicals). (8) deionized water (dH20). (9) reference material, if available, or matrix spikes at 0.5 to 5x the expected concentration in the samples. (10) Mercury Reference Standard Solution (Leeman or Fisher - 1000 ppm). (11) Saran Wrap - 11.5 in. width. (12) Leeman Labs AP/PS200II Mercury Analysis System.

PROCEDURE: (1) Prep the AP200II: Turn on the argon supply and the hood over the AP200II; Perform scheduled maintenance, as required; Vent rinse bottles; Fill reagent bottles, if necessary and enter volumes in Reagent Selection; Replace rinse with reagent bottles; Pressurize and run the Change Reagents Macro; Empty and rinse the waste tube; Change dH20 in the rinse tank; Empty water bath drain pan; Fill water bath supply carboy.

(2) Weigh samples or reference material into tared 50 ml tubes; enter weights and sample rack data. Use approximately 0.5 g (0.4-0.6 g) of fish tissue or 0.08 g (0.06 -1.0 g) of dried reference material. Rinse spatula with 20% HNO3 (reagent grade),-tap water and dH20 and dry with acetone prior to using for reference material. Rinse spatula with 20% HNO3 (reagent grade), tap water and dH20 prior to using for each sample. Include one procedure blank, one reference sample or matrix spike, and one duplicate sample per 20-sample batch. Add 500ul dH20 to the procedure blank and 420ul dH20 to the dried reference material to make these volumes equivalent to the samples.

(3) Prepare calibration standards in 50 ml tubes.

For Std. Conc.	Use 500ul of	
0 ppb	dH20	
4 ppb	8 ppb	(F)
25 ppb	50 ppb	(E)
100 ppb	200 ppb	(D)
300 ppb	600 ppb	(C)
600 ppb	1200 ppb	(B)

Preparation Method*		Final Conc.
A.	1ml (1000ppm) to 100ml	10 ppm
B.	12ml (A) to 100ml	1200 ppb
C.	6ml (A) to 100ml	600 ppb
D.	2ml (A) to 100ml	200 ppb
A1.	5ml (A) to 50ml	1000 ppb
E.	5ml (A1) to 100ml	50 ppb
F.	4m1 (D) to 100ml	8 ppb

* using 1.8% tracemetal HNO3 as diluent

Using the above calibration standards, the equivalent mercury concentration in samples (when 0.5 g of sample is used) and the approximate percent of samples that will be below that concentration (when 0.5 g of sample is used) are as follows:

Std. Conc.	Sample Conc.	% Below Conc.*
4 ppb	8 ppb	4%
25 ppb	50 ppb	12%
100 ppb	200 ppb	51%
300 ppb	600 ppb	92%
600 ppb	1200 ppb	99%

* based on 2113 samples analyzed prior to 1997

Other standard concentrations can be used, depending on the expected concentration range of the samples.

(4) Prepare 2 calibration check standards per 20 sample- batch at standard concentration = 100 ppb.

(5) Add 5 ml dH20 to each standard. Place a vapor barrier and frame on each sample and standard rack.

PRIOR TO STEP 6 THE VERTICAL SASH HOOD IN THE METALS LAB SHOULD BE TURNED ON AND SHOULD REMAIN ON FOR THE DURATION OF THE DIGESTION AND ANALYSIS.

(6) **CAREFULLY**, add 3 ml tracemetal H2SO4 to each sample, standard and QC sample. [If the automated dispenser on the AP200II adds H2SO4 (see step 7), omit step 6]

(7) Place racks in water bath and start digestion (F9). The program will add reagents according to the entries in Reagent Additions. 3 ml H2SO4 and 0.8 ml HNO3 are added to each cup. The water bath fills and heats for 40 minutes to 80C. The heater turns off and the bath is drained. The bath is refilled with water to cool the samples. 10 ml 5% potassium permanganate and 6 ml 5% potassium persulfate are added to each cup. The water bath fills and heats for 90 minutes at 30C. The water bath drains and refills, then pauses.

(8) Add 5 ml dH20 to each sample and QC sample. Empty the waste tube (0-7).

(9) Restart the program. 8 ml NaCl-hydroxylamine sulfate 12% is added to each cup. After 15 minutes, there is a final mixing step.

(10) At the end of the digestion, cover the racks with Saran Wrap and allow to stand overnight.

(11) Shut down the AP200II: Vent the reagent bottles; Replace the reagent bottles with rinse bottles; Pressurize and run the Change Reagents Macro; Empty and rinse the waste tube (0-7).

Analysis. Determine total mercury by atomic absorption spectroscopy, using a Leeman Labs PS200II (Ref: LEEMAN 1997).

PROTECTIVE CLOTHING REQUIRED: For preparation of standards, handling digested samples and cleaning glassware: wear lab coat, gloves and protective eyewear.

MATERIALS NEEDED: (1) tracemetal HNO3 (Leeman or Fisher). (2) certified ACS pitric acid (Fisher). (3) Stannous Chloride 10% (Leeman, Fisher or GFS Chemicals). (4) Leeman Labs AP/PS200II Mercury Analysis System.

PROCEDURE: (1) Prep the PS200II: Turn on the argon supply; Perform scheduled maintenance, as required; Fill rinse tank with 5% tracemetal nitric acid in dH20; Place reductant tube in reductant and sample tube in rinse tank; Secure PS pump tubing; Start argon, pump, HG lamp.

(2) Mix samples and standards.

(3) Set up the run: Autosampler setup; Open new folder; Reset for new calibration. Program at least two replicate readings for each sample, standard or blank.

(4) Analyze standards (F6) - calibration is performed by direct determination of concentration from a calibration curve. [The standard enters the system an is mixed with stannous chloride to form mercury vapor. Argon carries the vapor to an optical cell. A mercury lamp delivers a source of emission at 254nm. Absorbance is measured by a detector.] Check and accept calibration.

(5) Analyze samples (F8) and check standards (F7); print report (F4).

(6) Place reductant tube in rinse tank for 10 minutes. Remove reductant tube and sample tube from rinse tank. Empty rinse tank.

(7) Turn off lamp, pump, argon gas. Loosen pump tubing.

(8) Clean glass tubes: soak and brush with solution of PEX and warm water; rinse 2x with tap water, 2x with 20% HNO3 (certified ACS), 2x with tap water and 3x with dH20; dry in drying oven at 120C overnight.

Quality Control. The following QC should be a part of every analysis:

(1) Reference Material (e.g. DORM-2 dogfish muscle, NRC, Canada) should be analyzed once per 20 samples or once per batch, whichever is more frequent. Percent recovery should be 85%-115% (Ref: USEPA 1995).

(2) Check Standards should be analyzed once per 10 samples. Percent recovery should be 80% -120% (Ref: USEPA 1995).

(3) Procedure Blanks should be analyzed once per 20 samples or once per batch, whichever is more frequent. Mercury concentration should be less than the MOL (Ref: USEPA 1995).

(4) Laboratory Duplicates should be analyzed once per 20 samples or once per batch, whichever is more frequent. [RPD] should be less than or equal to 20% (Ref: USEPA 1995).

(5) Analytical Replicates (replicate analyses of the same subsample digest) should be routine. Each subsample should be analyzed at least in duplicate (Ref: USEPA 1995). The RSD should be. less than or equal to 15% (this a laboratory-determined limit).

(6) Calculated recovery from calibration standards should be 95%-105%, if using a 3-point calibration (Ref: USEPA 1995). If more than 3 points are used, a correlation coefficient r >= .9995 is also acceptable (this is a laboratory-determined limit).

Results.

CALCULATIONS: PPM = calculated ppb concentration
X dilution factor X 0.001
/ weight of subsample in g

METHOD DETECTION LIMIT (MDL) = $t_{(0.9.9)}$ **X** S, where t is the appropriate (i.e n-1 degrees of freedom) one-sided 99% Student's t-statistic and S is the standard deviation from a minimum of seven replicate analyses of a fish sample with an Hg concentration 3 to 5x the MDL.

Conclusions. I am confident that the method described above is technically justified to address issues relating to total mercury contamination in fish in New York State.

3/11/98

References.

Leeman Labs, 1997. AP/PS200II Mercury Analysis Systems Manual #150-00103. Leeman Labs Inc., Hudson, NH.

USEPA, 1995. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume 1: Fish Sampling and Analysis. 2nd Edition. U.S. Environmental Protection Agency, Washington, DC.

STANDARD OPERATING PROCEDURE
CD-AT-3

CADMIUM IN ANIMAL TISSUE - 3

ABSTRACT: Samples are digested in concentrated nitric acid in a CEM Model MDS 81-D microwave oven. The digestions are performed in closed CEM 120 ml PFA teflon vessels. Cadmium is analyzed on a Perkin-Elmer Model 5100 Atomic Absorption Spectrophotometer (Zeeman), equipped with an HGA-600 Graphite Furnace, AS-60 Autosampler, and AA WinLab software. An electrodeless discharge lamp, graphite tubes fitted with L'vov platforms and an ammonium phosphate/magnesium nitrate matrix modifier are used. Wavelength, slit width, lamp current and furnace temperature are set according to the manufacturer's recommendations. Concentration is determined directly from a calibration curve.

Introduction. This is a standard operating procedure in the Analytical Services Unit of Hale Creek Field Station, NYSDEC, Gloversville, NY for the analysis of total cadmium in animal tissues. **WARNING: CADMIUM IS TOXIC AND SHOULD BE HANDLED WITH EXTRA CARE. NITRIC ACID, USED IN THIS PROCEDURE, IS CORROSIVE AND CONTACT WITH EYES AND SKIN SHOULD BE AVOIDED.**

Digestion. Digest samples in concentrated nitric acid in a CEM Model MDS 81-D microwave oven (CEM Corp., 1985).

PROTECTIVE CLOTHING REQUIRED: (1) Lab coat and apron. (2) vinyl, latex or neoprene gloves for all procedures. (3) protective eyewear for all work involving handling of concentrated acid.

MATERIALS NEEDED: (1) CEM 120 ml PFA teflon vessels. (2) high purity concentrated HN03 (Ultrex .II, J.T. Baker). (3) Fisher tracemetal nitric acid. (4) Fisher certified ACS nitric acid. (5) deionized water (dH20). (6) reference material (e.g. DORM-1 or DORM-2 (NRC dogfish muscle), SRM 1566a (NIST oyster tissue), SRM 1577b (NIST bovine liver) or TORT-2 (NRC lobster hepatopancrea)). (7) 25 ml volumetric flasks. (8) Whatman 20 cc syringes. (9) 50 ml VWR polypropylene centrifuge tubes. (10) CEM Model MDS-81D Microwave Oven.

PROCEDURE: (1) Weigh sample or reference material into tared CEM vessel and record weight and vessel number - use approximately 1.0 g of wet sample or 0.2 g of dried reference material. Rinse spatula with 20% HNO3 (reagent grade), tap water and dH20 and dry with acetone, if necessary, prior to using for reference material. Rinse spatula with 20% HNO3 (reagent grade), tap water and dH20 prior to using for each sample. Include one procedure blank, one reference sample and one duplicate sample per 10-vessel batch.

(2) In the hood, add 9 ml Fisher tracemetal nitric acid to each vessel. If fewer than ten vessels are used for digestion, add 9.0 ml dH20 to each of the remaining vessels (to make a total of ten) or use sufficient additional "ballast" in Procedure Step 3 to avoid overheating.

(3) Still in the hood, place the relief valve on top of the vessel with the flat side down and cap the vessel hand-tight. Torque the vessel cap in the capping station. Connect teflon tubing between each vessel and the center container of the carousel and tighten finger-tight. Put 60 ml dH20 in each of two beakers and place them in the carousel opposite each other as "ballast" to avoid overheating.

(4) Place the carousel in the oven and digest the samples at the following power: 15 min at 30%, 10 min at 0%, 7 min at 60%,40 min at 0%.

WARNING: During operation of the microwave oven, the turntable must be on, the fan in the oven must be ON THE HIGHEST SETTING, the hood in the laboratory must be ON, and the window in the pesticide prep lab must be open a crack. During operation of the oven, THE OVEN MUST NOT BE LEFT UNATTENDED. IF POPPING OR RELEASE SOUNDS ARE HEARD FROM THE VESSELS, THE OVEN ENERGY MUST BE STOPPED IMMEDIATELY. The fan, however, shou1d remain on to expel any released gases to the hood. In addition, care must be taken to PROTECT PERSONS PASSING BY THE OVEN FROM POSSIBLE INJURY (e.g. don't 1et persons stand in front of the oven while it is in operation).

(5) When the cycle is completed, release the pressure on the vessel in the hood, loosen the cap using the capping station and uncap the vessel. Transfer the digestate to a labeled 25 ml volumetric flask, using a Whatman 20 cc syringe. Rinse the inside of the vessel 3x with dH20 and transfer the rinsate to the flask. Dilute to volume with dH20. Transfer the digestate from the volumetric flask to a 50 ml VWR polypropylene centrifuge tube.

(6) Clean all glassware and digestion vessels thoroughly. A procedure to clean digestion vessels is as follows:

Scrub each vessel out with soapy water (PEX). Add 50 ml 50% HNO3 (certified ACS grade), place the relief valve (flat side down) on each vessel, cap and torque. Connect a teflon tube between each vessel and the center container. Heat at 100% power for 10 minutes (See **WARNING** above; in addition, if fewer than 10 vessels are used, sufficient "ballast" must be present to avoid, overheating). Cool at 0% for 10 minutes. In the hood, release the pressure. Uncap and empty each vessel to waste. Rinse 2X with cold tap water and 3X with dH20. Dry in the hood.

Analysis. Determine elemental cadmium by atomic absorption spectroscopy (Perkin-Elmer, 1986 and Perkin-Elmer, 1996)

PROTECTIVE CLOTHING -REQUIRED: For work involving preparation of standards, chemical solutions or sample dilutions and for cleaning glassware: wear lab coat, gloves and protective eyewear.

MATERIALS NEEDED: (1) 0.2% solution of Ultrex II HNO3 in dH20 for diluent and blanks. (2) Fisher Chemical Cadmium Reference Solution SC1l8-l00 for 0.5, l.0 and 2.0 ppb standards in 0.2% HNO3. (3) 10% ammonium phosphate, monobasic: NH4H2P04 (Perkin-Elmer PIN N930-3445). (4) magnesium nitrate: Mg(NO3) 2*6H20 (Johnson Matthey puratronic 10799). (5) Perkin Elmer Model 5100 Atomic Absorption Spectrophotometer.

PROCEDURE: Determine cadmium by atomic absorption spectroscopy using a Perkin-Elmer Model 5100 Atomic Absorption Spectrophotometer, equipped with an HGA-600 Graphite Furnace, Zeeman Furnace Module, an electrodeless discharge lamp (Perkin- Elmer P/N 305-0615), AS-60 Autosampler, and AA WinLab software. Use graphite tubes with L'vov platforms (CPI or Perkin-Elmer) in the furnace. The conditions of operation are described in the method file 'Cd228' (attached). Wavelength, slit width and lamp current are set according to the manufacturer's (Perkin-Elmer) recommended conditions. A one percent solution of Ultrex II HNO3 is used as flushing liquid between sample analyses.

The solutions in the autosampler cups contain 1000 ul sample, standard or diluent and 125 ul matrix modifier. Five ul of the matrix modifier contains 200 ug NH4H2PO4 and 10 ug Mg (NO3)2. The matrix modifier is prepared by combining 60 ml of magnesium nitrate solution (0.576 g Mg(NO3)2*6H2O in 100 ml dH2O) with 40 ml of 10% NH4H2PO4.

Calibration is performed by direct determination of concentration from a calibration curve. A calibration curve is plotted using 0.5, 1.0 and 2.0 ppb standards.

Quality Control. The following QC should be a part of every analysis:

(1) Reference Material (e.g. SRM 1577b, NIST bovine liver) should be analyzed once per 20 samples or once per batch, whichever is more frequent. Percent recovery should be 85%-115% (Ref: USEPA 1995).

(2) Check Standards should be analyzed once per 10 samples. Percent recovery should be 80%-120% (Ref: USEPA 1995) .

(3) Procedure Blanks should be analyzed once per 20 samples or once per batch, whichever is more frequent. Cadmium concentration should be less than the MDL (Ref: USEPA 1995).

(4) Laboratory Duplicates should be analyzed once per 20 samples or once per batch, whichever is more frequent. IRPDI should be less than or equal to 20% (Ref: USEPA 1995).

(5) Analytical Replicates (replicate analyses of the same subsample digest) should be routine. Each subsample should be analyzed at least in duplicate (Ref: USEPA 1995). The RSD should be less than or equal to 15% (this a laboratory-determined limit).

(6) Correlation coefficient (r) for the calibration curve should be , at a minimum, >= 0.995. Preferably, r should be >= 0.998 (this is a laboratory-determined limit).

(7) Method Detection Limit (MDL) should be determined. MDL = $t_{(0.99)}$ **X** S, where t is the appropriate (i.e n-1 degrees of freedom) one-sided 99% Student's t-statistic and S is the standard deviation from a minimum of seven replicate analyses of a fish sample with a Cd concentration 3 to 5x the MDL.

An analysis is rejected if the QC is not within acceptable limits or if any of the following conditions exist:

1) the matrix has a significant effect on the analyte present in the sample. This is visually checked by looking at atomic peak profiles of the readings. If there is an obvious difference between the sample and the standards, the sample can be diluted and retested or the method of additions can be tried (Method CD-AT-1); or

2) the calculated characteristic mass at the beginning or end of a run is too high or low (the characteristic mass for these conditions is approximately 0.6-0.7 pg/0.0044 A-s); or

3) a determined value grossly deviates. on the basis of an outlier test from other values determined for the same sample digest.

Results.

CALCULATIONS: PPM = (mg/l concentration of analyte in injected solution) X (dilution factor) X (final volume of digestate in ml) / (weight of digested sample in g).

Conclusions. I am confident that the method used for digestion and analysis of cadmium described above is technically justified to address the issues of chemical contaminants in animal tissues in New York State.

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References.

CEM Corporation. 1985. Microwave Digestion System Model MDS81-D. CEM Corporation, Indian Trail, NC.

Perkin-Elmer. 1986. Reference Manual - Model 5100 Atomic Absorption Spectrophotometer. Vols. 1 and 2. Perkin-Elmer Corp., Norwalk, CT.

Perkin-Elmer. 1996. AA WinLab Software Guide. Perkin-Elmer Corp., Norwalk, CT.

Attachments:

- Method File Cd228 (2 pages)

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July 1, 1998

Identification
Method Name: Cd228
Technique: Furnace
Method Desc: Cdtest

Element: Cd
Instrument Model: 5100

Remarks

Instrument
Wavelength (nm): 228.8
Slit Width: 0.7

Read Time (sec): 5.0
Read Delay (sec): 0.0
BOC Time (sec): 2

Signal Type: Zeeman AA
Signal Measurement: Peak Area

Modified Spectrometer Settings: No

Calibration

Equations, Units, and Replicates: Element Calibration Equation	Calibration Units	Sample Units	Max Decimal Places	Max Significant Figures
Cd Non-linear	µg/L	µg/L	3	4

Replicates: Variable
Variable Replicate Parameters
Samples
Measure 1 replicates from the same cup unless concentration less than or equal to 2 use 3, concentration greater than – use 1.
Recovery Measurements: Same as sample
Calibration Solutions: Measure 3 replicates for all standards and blanks.
QC Samples: Use the number of replicates specified for the samples.

Sample
Sample Volume (µL): 20 Diluent Volume (µL): 0 Diluent Location: 36

Matrix Modifiers:	Modifier 1	Modifier 2
Volume (µL):	0	0
Location:	15	0
Add to blank and standards:	Yes	No
Add to reagent blank and samples:	Yes	No

	ID	Conc. (µL/L)	A./S Loc	Stock (µL)	Diluent (µL)
Calib. Blank	Calib Blank		36	20	0
Calib. Std. 1		0.50	37	20	0
Calif. Std. 2		1.00	38	20	0
Calif. Std. 3		2.00	39	20	0

Furnace Conditions

Step #	Temp (°C)	Ramp Time	Hold Time	Internal Flow	Gas Type	Read Step
1	120	10	50	300	Normal	
2	850	1	30	300	Normal	
3	20	1	15	300	Normal	
4	1650	0	5	0	Normal	X
5	2600	1	5	300	Normal	

Extraction System: No Injection Temp. (°C): 20

Furnace Clean-out? No

Sequence

Step	Action and Parameters
A	Piplet sample/std
B	Run furnace steps 1 to end

Pipet Speed (%): 100

Checks

Check correlation coefficient?	No
Recalibrate instrument periodically?	No
Analyze standards at end of run?	No
Check Precision?	No
Reanalyze samples beyond calibration range?	No
Perform matrix check calculations?	No
Perform recovery measurements?	No

Quality Control
Concentration Units: Calibration (µg/L)

Periodic Timing of Analyses
Count: Samples Interrupt sample to analyze QC: No
Frequency: Same for all QC's, 1

Maximum Retries After QC Failure
Maximum allowed reanalyses: 1 Action when maximum exceeded: Continue

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Options
Results Display/Printed Log - Modified Settings: No

Peaks to Save: Last Replicate for Each Sample

STANDARD OPERATING PROCEDURE
PB-AT-2

LEAD IN ANIMAL TISSUE - 2

ABSTRACT: Samples are digested in concentrated nitric acid in a CEM Model MDS 81-D microwave oven. The digestions are performed in closed CEM 120 ml PFA teflon vessels. Lead is analyzed on a Perkin-Elmer Model 5100 Atomic Absorption Spectrophotometer (Zeeman), equipped with an HGA-600 Graphite Furnace, AS-60 Autosampler, and AA WinLab software. An electrode less discharge lamp, graphite tubes fitted with L'vov platforms and an ammonium phosphate/magnesium nitrate matrix modifier are used. Wavelength, slit width, lamp current and furnace temperature are set according to the manufacturer's recommendations. Concentration is determined directly from a calibratiqn curve.

Introduction. This is a standard operating procedure in the Analytical Services Unit of Hale Creek Field Station, NYSDEC, Gloversville, NY for the analysis of total lead in animal tissues. **WARNING: LEAD IS TOXIC AND SHOULD BE HANDLED WITH EXTRA CARE. NITRIC ACID, USED IN THIS PROCEDURE, IS CORROSIVE AND CONTACT WITH EYES AND SKIN SHOULD BE AVOIDED.**

Digestion. Digest samples in concentrated nitric acid in a CEM Model MDS 81-D microwave oven (CKM Corp., 1985).

PROTECTIVE CLOTHING REQUIRED: (1) Lab coat and apron. (2) vinyl, latex or neoprene gloves for all procedures. (3) protective eyewear for all work involving handling of concentrated acid.

MATERIALS NEEDED: (1) CEM 120 ml PFA teflon vessels. (2) high purity concentrated HNO3 (Ultrex II, J.T.. Baker). (3) Fisher tracemetal nitric acid. (4) Fisher certified ACS nitric acid. (5) deionized water (dH20). (6) reference material (e.g. NRC or NIST). (7) 25 ml volumetric flasks. (8) Whatman 20 cc syringes. (9) 50 m1 VWR polypropylene centrifuge tubes. (10) CEM Model MDS-81D Microwave Oven.

PROCEDURE: (1) Weigh sample or reference material into tared CEM vessel and record weight and vessel number -use approximately 1.0 g of wet sample or 0.2 g of dried reference material. Rinse spatula with 20% HNO3 (reagent grade), tap water and dH2O and dry with acetone, if necessary, prior to using for reference material. Rinse spatula with 20% HNO3 (reagent grade), tap water and dH2O prior to using for each sample. Include one procedure blank, one reference sample and one duplicate sample per 10-vessel batch.

(2) In the hood add 9 ml Fisher tracemetal nitric acid to each vessel. If fewer than ten vessels are used for digestion, add 9.0 ml dH2O to each of the remaining vessels (to make a total of ten) or use sufficient additional "ballast" in Procedure Step 3 to avoid overheating.

(3) Still in the hood, place the relief valve on top of the vessel with the flat side down and cap the vessel hand-tight. Torque the vessel cap in the capping station. Connect teflon tubing between each vessel and the center container of the carousel and tighten finger-tight. Put 60 ml dH2O in each of two beakers and place them in the carousel opposite each other as "ballast" to avoid overheating.

(4) Place the carousel in the oven and digest the samples at the following power: 15 min at 30%, 10 min at 0%, 7 min at 60%, 40 min at 0%.

WARNING: During operation of the microwave oven, the turntable must be ON, the fan in the oven must be ON THE HIGHEST SETTING, the hood in the laboratory must be ON, and the window in the pesticide prep lab must be open a crack. During operation of the oven, THE OVEN MUST NOT BE LEFT UNATTENDED. IF POPPING OR RELEASE SOUNDS ARE HEARD FROM THE VESSELS, THE OVEN ENERGY MUST BE STOPPED IMMEDIATELY. The fan, however, shou1d remain on to expel any released gases to the hood. In addition, care must be taken to PROTECT PERSONS PASSING BY THE OVEN FROM POSSIBLE INJURY (e.g. don't let persons stand in front of the oven while it is in operation).

(5) When the cycle is completed, release the pressure on the vessel in the hood, loosen the cap using the capping station and uncap the vessel. Transfer the digestate to a labeled 25 ml volumetric flask, using a Whatman 20 cc syringe. Rinse the inside of the vessel 3x with dH2O and transfer the rinsate to the flask. Dilute to volume with dH2O. Transfer the digestate from the volumetric flask to a 50 ml VWR polypropylene centrifuge tube.

(6) Clean all glassware and digestion vessels thoroughly. A procedure to clean digestion vessels is as follows:

Scrub each vessel out with soapy water (PEX). Add 50 ml 50% HNO3 (certified ACS grade), place the relief valve (flat side down) on each vessel, cap and torque. Connect a teflon tube between each vessel and the center container. Heat at 100% power for 10 minutes (See **WARNING** above; in addition, if fewer than 10 vessels are used, sufficient "ballast" must be present to avoid overheating). Cool at 0% for 10 minutes. In the hood, release the pressure. Uncap and empty each vessel to waste. Rinse 2X with cold tap water and 3X with dH20. Dry in the hood.

Analysis. Determine elemental lead by atomic absorption spectroscopy (Perkin-Elmer, 1986 and Perkin-Elmer, 1996).

PROTECTIVE CLOTHING REQUIRED: For work involving preparation of standards, chemical solutions or sample dilutions and for cleaning glassware: wear lab coat, gloves and protective eyewear.

MATERIALS NEEDED: (1) 0.2% solution of Ultrex II HNO3 in dH2O for diluent and blanks. (2) Fisher Chemical Lead Reference Solution SL21 -100 for 25, 50 and 100 ppb standards in 5.0% HNO3. (3) 10% ammonium phosphate, monobasic: NH4H2PO4 (Perkin-Elmer PIN N930-3445). (4) magnesium nitrate: Mg(NO3)2*6H20 (Johnson Matthey puratronic 10799). (5) Perkin-Elmer Model 5100 Atomic Absorption Spectrophotometer.

PROCEDURE: Determine lead by atomic absorption spectroscopy using a Perkin-Elmer Model 5100 Atomic Absorption Spectrophotometer, equipped with an HGA-600 Graphite Furnace, Zeeman Furnace Module, an electrodeless discharge lamp, AS-60 Autosampler, and AA WinLab software. Use graphite tubes with L'vov platforms (CPI or Perkin-Elmer) in the furnace. Wavelength, slit width and lamp current are set according to the. manufacturer's (Perkin-Elmer) recommended conditions. A one percent solution of Ultrex II HNO3 is used as flushing liquid between sample analyses.

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Calibration is performed by direct determination of concentration from a calibration curve. A calibration curve is plotted using 25, 50 and 100 ppb standards.

Quality Control. The following QC~should be a part of every analysis:

(1) Reference Material (e.g. SRM 1577b, NIST bovine liver) should be analyzed once per 20 samples or once per batch, whichever is more frequent. Percent recovery should be 85%-115% (Ref: USEPA 1995).

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(7) Method Detection Limit (MDL) should be determined.
MDL = $t_{(0.99)}$ **X** S, where t is the appropriate (i.e n-l degrees of freedom) one-sided 99% Student's t-statistic and S is the standard deviation from a minimum of seven replicate analyses of a fish sample with a Ph concentration 3 to 5x the MDL.

An analysis is rejected if the QC is not within acceptable limits or if any of the following conditions exist:

1) the matrix has a significant effect on the analyte present in the sample. This is usually checked by looking at atomic peak profiles of the readings. If there is an obvious difference between the sample and the standards, the sample can be diluted and retested or the method of additions can be tried;
or

2) the calculated characteristic mass at the beginning or end of a run is too high or low; or

3) a determined value grossly deviates, on the basis of an outlier test, from other values determined for the same sample digest.

Results.

CALCULATIONS: PPM = (mg/l concentration of analyte in injected solution) X (dilution factor) X (final volume of digestate in ml) / (weight of digested sample in g).

Conclusions. I am confident that the method used for digestion and analysis of lead described above is technically justified to address the issues of chemical contaminants in animal tissues in New York State.

References.

CEM Corporation. 1985. Microwave Digestion System Model MDS81-D. CEM Corporation, Indian Trail, NC.

Perkin-Elmer. 1986. Reference Manual - Model 5100 Atomic Absorption Spectrophotometer, Vols. 1 and 2. Perkin-Elmer Corp., Norwalk, CT.

Perkin-Elmer. 1996. AA WinLab Software Guide. Perkin-Elmer Corp., Norwalk, CT.

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August 17, 1998


U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849


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NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
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DEPARTMENT OF ENVIRONMENTAL CONSERVATION
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