

**QUALITY ASSURANCE PROJECT PLAN  
FOR THE STATE OF RHODE ISLAND  
DEPARTMENT OF ENVIRONMENTAL MANAGEMENT  
DIVISION OF AGRICULTURE  
PESTICIDE ENFORCEMENT COMPLIANCE MONITORING PROGRAM  
AND  
WATER PROTECTION MONITORING PROGRAM**

RHODE ISLAND DEPARTMENT OF HEALTH  
DIVISION OF LABORATORIES  
50 ORMS STREET  
PROVIDENCE, R.I. 02908

And

RHODE ISLAND DEPARTMENT OF ENVIRONMENTAL MANAGEMENT  
DIVISION OF AGRICULTURE  
PESTICIDE SECTION  
235 PROMENADE STREET  
PROVIDENCE, R.I. 02908

Plan Coverage: This Quality Assurance Project Plan covers all comprehensive pesticide laboratory and field activities.

**QUALITY ASSURANCE PROJECT PLAN  
FOR THE  
STATE OF RHODE ISLAND DIVISION OF AGRICULTURE  
LABORATORY PESTICIDE PROGRAM**

Approval for Implementation by the State of Rhode Island

**DEPARTMENT OF HEALTH**

LABORATORY DIRECTOR

Name: Ewa King, Ph.D

Title: Laboratory Director

Signature: \_\_\_\_\_ Date: April 22, 2008

LABORATORY QUALITY ASSURANCE OFFICER

Name: Henry Leibovitz

Title: Chief Registered Environmental Laboratory Scientist

Signature: \_\_\_\_\_ Date: April 23, 2008

**DEPARTMENT OF ENVIRONMENTAL MANAGEMENT**

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Name: W. Michael Sullivan, Ph.D

Title: Director

Signature: \_\_\_\_\_ Date: April 15, 2008

DEM QUALITY MANAGEMENT OFFICER

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Title: Ombudsman

Signature: \_\_\_\_\_ Date: April 15, 2008

BUREAU OF NATURAL RESOURCES

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Title: Associate Director

Signature: \_\_\_\_\_ Date: April 16, 2008

DIVISION OF AGRICULTURE

Name: Kenneth Ayars

Title: Division Chief

Signature: \_\_\_\_\_ Date: April 04, 2008

DEM QUALITY ASSURANCE OFFICER

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Title: Deputy Chief, Division of Agriculture

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Approval by the U.S. EPA Region I

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Name: Raymond Putnam

Title: Pesticide Program Grants Coordinator

Signature: \_\_\_\_\_ Date: June 04, 2008

Regional Quality Assurance Officer

Name: Nora Conlon

Title: QA Chemist

Signature: \_\_\_\_\_ Date: June 03, 2008

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- B. Memorandum of Agreement between DEM and the DOH Laboratories
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## INTRODUCTION

The US Environmental Protection Agency (EPA) defines the Quality Assurance Project Plan (QAPP) as a document describing in comprehensive detail the necessary quality assurance (QA), quality control (QC), and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria. A generic QAPP addresses the general, common activities of the program that are to be conducted at multiple locations or over a long period of time. This document will serve as the generic QAPP for the RI DEM Division of Agriculture Pesticide Program Activities, including the Pesticide Enforcement Program and the Water Protection Program.

Under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) as amended, cooperative enforcement agreements have been developed between the U.S. Environmental Protection Agency (EPA) and the Rhode Island Department of Environmental Management (DEM), Division of Agriculture. The Division of Agriculture is the state lead agency in Rhode Island for pesticide regulatory programs and is authorized under the R.I.G.L. 23-25 to conduct enforcement programs in the state. The purpose of the cooperative enforcement agreements is to delegate to and support state pesticide programs and related inspectional work such as Pesticide Use Inspections, Producer Establishment Inspections, Marketplace Inspections, Experimental Use Inspections and informal referrals from EPA under FIFRA Sections 26 and 27. Monitoring programs include surface and ground water protection, endangered species protection, and worker protection. In addition, state policy on groundwater monitoring for pesticides is described in DEM “Rhode Island’s Management Plan for the Protection of Groundwater from Pesticides and Nitrogenous Fertilizer” (Edition August 23, 1996)

The R.I.G.L 23-25-16 authorizes the DEM’s Division of Agriculture to establish and maintain surface and ground water monitoring and enforcement programs for pesticides and other agricultural chemicals. DEM does not maintain its own laboratory, the Rhode Island Department of Health, Division of Laboratories serves as the state central laboratory for both departments. Thus, to support the activities of the various pesticide programs, pesticide residue and water samples are submitted to this laboratory for chemical analysis. Official formulation and/or pesticide residue samples are occasionally taken for chemical analysis in connection with the enforcement-related activities cited above. However, there are occasions when this laboratory does not have the capability to process the sample collected. The Division of Agriculture may enter cooperative agreements with other federal and state agencies or local governments for various pesticide projects. The Division of Agriculture has authority to contract for analytical services for pesticide programs and projects with other federal and state governmental units, local governments, Indian tribes, researchers and/or others. Currently, to meet the analytical needs of its present programs, the Division of Agriculture has Memorandum of Agreements with the RI Department of Health Laboratories and with Mississippi State Chemical Laboratory for analytical services for both legal and non-legal samples.

Designated field personnel are responsible for collecting and documenting representative samples and for maintaining chain of custody of the samples until they are officially transferred to the appropriate laboratory. The laboratory is responsible for analyzing the samples using appropriate analytical techniques and methods according to the quality assurance protocols

outlined herein, and for transmitting analytical results, including quality control data, to the appropriate agency or person.

To support this project plan, Standard Operating Procedures (SOPs) will be developed as necessary to describe detailed laboratory and field procedures. SOPs will be developed as necessary to cover routine activities that affect the overall quality and defensibility of analytical data. The Division of Agriculture is currently developing SOP's for it's enforcement and water quality activities and will be forwarded to EPA as soon as DEM staff and QA Manager approve them.

## **PROJECT BACKGROUND**

**Pesticide Enforcement Program** - The Division of Agriculture Pesticide Enforcement Program 's objective is to determine through various inspectional activities if pesticides are being manufactured, sold and used according to applicable federal and State Statues and Regulations, as well as ensuring that the use of pesticides do not pose any adverse effects to public health and the environment. The inspectional activities include Marketplace Inspections, Use Observation Inspection to both agricultural and non-agricultural establishments, Producer Establishment Inspection, as well as responding to complaints regarding the use and distribution of pesticides.

**Water Protection Program-** The Division of Agriculture Water Protection Program goal is to assess the potential for pesticide contamination problems and to collect water samples where threats are the highest or sites that are most vulnerable to potential pesticide contamination.

In order to support both of these programs divisional staff is responsible for collecting and documenting representative samples and maintaining chain-of-custody until samples are officially transferred and/or shipped to the laboratory.

In order to support each of the project plans, additional details will be spelled out in the Divisions SOP once they are developed and approved. SOPs will be developed for all routine and ongoing activities that affect the overall quality and defensibility of analytical data.

## **PROJECT ORGANIZATION AND RESPONSIBIBITIES**

The State of Rhode Island Pesticide Laboratory is managed by the Rhode Island Department of Health, Division of Laboratories. The Laboratory Supervisor is responsible to the Department of Health for laboratory activities. The laboratory is responsible to the Department of Environmental Management's Division of Agriculture for pesticide testing by contract. The organizational hierarchy of that laboratory programs are in Figure I. An organizational chart for the Environmental Sciences Division of the Laboratories is shown in Figure II. A Chart of how Department of Environmental Management's Division of Agriculture programs is organized is shown in Figure III. An organizational chart for the Division of Agriculture's Pesticide Section is shown in Figure IV.

**DEPARTMENT OF HEALTH  
Pesticide Laboratory**

Names, titles, and responsibilities of personnel responsible for laboratory and field quality assurance (QA) are listed below.

**Laboratory Director**

Name: Ewa King, Ph.D. Phone: 401-222-1999

Title: Associate Director of Health

QA Responsibilities: The Laboratory Director is responsible for overall laboratory policy, for management of personnel, budgets and operations, and for ensuring compliance with cooperative agreements or contracts.

Name: Henry Leibovitz, Ph.D. Phone: \_\_\_\_\_

Title: Chief Registered Environmental Laboratory Scientist

QA Responsibilities: The Chief is responsible for the management of the Environmental Sciences Section in the Division of Laboratories

**QUALITY ASSURANCE OFFICER**

Name: Christopher Ellis, Ph.D. Phone: 401-222-5578

Title: Quality Assurance Specialist

QA Responsibilities: Responsibilities include ensuring compliance with the section's quality assurance program.

**Supervising Environmental Laboratory Scientist/Pesticide Program Administrator**

Name: Mitchell Foresti Phone: 401-222-5583

Title: Supervising Registered Environmental Laboratory Scientist

QA Responsibilities: The Supervising Laboratory Scientist is responsible for the overall operation of the laboratory. Duties may include coordination of programs and personnel, implementation and review of quality assurance, program work assignments, and prioritizing samples for analysis, review and evaluation of analytical data, check sample programs, record keeping and data reporting systems, training of personnel, analytical methods, calibration and maintenance of instruments, and the safety program. It is also the duty of the Supervising Laboratory Scientist to initiate corrective action when a review of the quality assurance program indicates a need. Corrective actions are a cooperative effort of the Supervising Laboratory Scientist, the Associate Director of Environmental Science Section of the Rhode Island Health Laboratories (Chemistry), Quality Assurance Officer/Certification Officer and EPA personnel.



## SAMPLE CUSTODIAN

In addition to the Supervising Laboratory Scientist there are four Sample Custodians in the State of Rhode Island Pesticide Laboratory, Residue Section who are charged with reception of samples. Depending upon staff scheduling any one of these individuals may perform QA and custody functions. They are as follows:

Name: Anna Sullivan Phone: 401-222-5583  
Title: Senior Registered Environmental Scientist

Name: Jennifer Herbert Phone: 401-222-5590  
Title: Senior Registered Environmental Scientist

Name: Leslie Nolan Phone: 401-222-5583  
Title: Senior Registered Environmental Scientist

Name: Karen Soper Phone: 401-222-5583  
Title: Senior Registered Environmental Scientist

QA Responsibilities: Sample Custodians are responsible for accepting samples submitted to the laboratory, logging in samples, maintaining sample custody within the laboratory, and assuring proper storage of samples.

## DEPARTMENT OF ENVIRONMENTAL MANAGEMENT DIVISION OF AGRICULTURE

Names, titles, and responsibilities of personnel responsible for field quality assurance (QA) within the Department of Environmental Management are listed below.

### **Bureau of Natural Resources**

Name: Lawrence Mouradjian Phone: 401-222-6605  
Title: Associate Director

QA Responsibilities: The Associate Director is responsible for overall policy for natural resource management, for management of personnel, budgets and operations, and for ensuring compliance with cooperative agreements or contracts.

### **Division of Agriculture**

Name: Kenneth Ayars Phone: 401-222-2781  
Title: Division Chief

QA Responsibilities: The Division Chief is responsible for overall Division policy, for management of Division personnel, budgets and operations, and for ensuring compliance with Division cooperative agreements or contracts.

### **Pesticide Program Supervisor**

Name: Eugene B. Pepper Phone: 401-222-2781

Title: Senior Environmental Scientist

QA Responsibilities: Responsibilities include the administration of the pesticide program assignments, administration of budget, supervision of personnel, coordination of pesticide programs, and ensuring compliance with the pesticide's quality assurance program. In addition, the Senior Environmental Scientist is responsible for the overall enforcement operations of the Pesticide of Agriculture's Pesticide Section. Duties may include coordination of programs and personnel, development and implementation of programs, and review of the field quality assurance program for sampling and for sample documentation. The Senior Environmental Scientist may also be responsible for developing and supervising inspection, investigate and incident response procedures and standard operating procedures for sample collection.

### **Field and Technical Services Quality Assurance Officer**

There are three areas of field and technical services quality assurance for pesticide monitoring programs: Ground Water, Worker Protection, and Other.

#### **1.) Ground Water Monitoring**

Name: Eugene Pepper Phone: 401-222-2781

Title: Senior Environmental Scientist

QA Responsibilities: The Senior Environmental Scientist is responsible for the surface and ground water monitoring programs. Responsibilities include overall water resource program operations. Duties may include coordination of programs and personnel, development and implementation of programs, and review of the field quality assurance program for sampling and for sample documentation as well as data analysis and report development. Responsibilities also include developing and supervising investigative and incident response procedures and standard operating procedures for sample collection.

#### **2.) Worker Protection Monitoring**

Name: Eugene Pepper Phone: 401-222-2781

Title: Senior Environmental Scientist

QA Responsibilities: The Senior Environmental Scientist is responsible for the worker protection-monitoring program. Responsibilities include overall worker protection program operations. Duties may include coordination of programs and personnel, development and implementation of programs, and review of the field quality assurance program for sampling and for sample documentation. Responsibilities also include developing and supervising inspection, investigative and incident response procedures and standard operating procedures for sample collection.

### 3.) Special Projects Monitoring

Name: Eugene B. Pepper Phone: 401-222-2781

Title: Senior Environmental Scientist

QA Responsibilities: The Senior Environmental Scientist is responsible for other special projects monitoring programs. Special projects monitoring programs may include such things as endangered species, targeted enforcement, air, schools and other indoor monitoring, etc. These types of monitoring programs are outside of those specified in 1 and 2 above. Duties may include coordination of programs and personnel, development and implementation of programs, and review of the field quality assurance program for sampling and for sample documentation. Responsibilities also include developing and supervising investigative and incident response procedures and standard operating procedures for sample collection, along with data analysis and report generation.

#### Sample Collectors

Division of Agriculture, Pesticide Section staff including the above named individuals named , are charged with the responsibility of collecting and delivering pesticide samples under this program to the Pesticide Laboratories. Staff who collect these samples are as follows:

Name: Robin Mooney Phone: 401-222-2781

Title: Plant Pathologist

Name: \_\_\_\_\_ Phone: 401-222-2781

Title: Senior Plant Pathologist

Name: Steven Scandariato Phone: 401-222-2781

Title: Plant Pathologist

Name: Eugene B. Pepper Phone: 401-222-2781

Title: Senior Environmental Scientist

Name: \_\_\_\_\_ Phone: 401-222-2781

Title: Sample Collector

QA Responsibilities: The Sample Collector is a part time or seasonal position responsible for collecting, transporting, and submitting samples to the laboratory, logging in samples, maintaining sample custody to the laboratory, and assuring proper collection, custody, and storage of samples.

## QAPP DISTRIBUTION LIST

Eugene Pepper, RI DEM/Division of Agriculture  
Field Inspectors, RI DEM/Division of Agriculture  
Thomas Getz, RI DEM/Director's Office

Henry Leibovitz  
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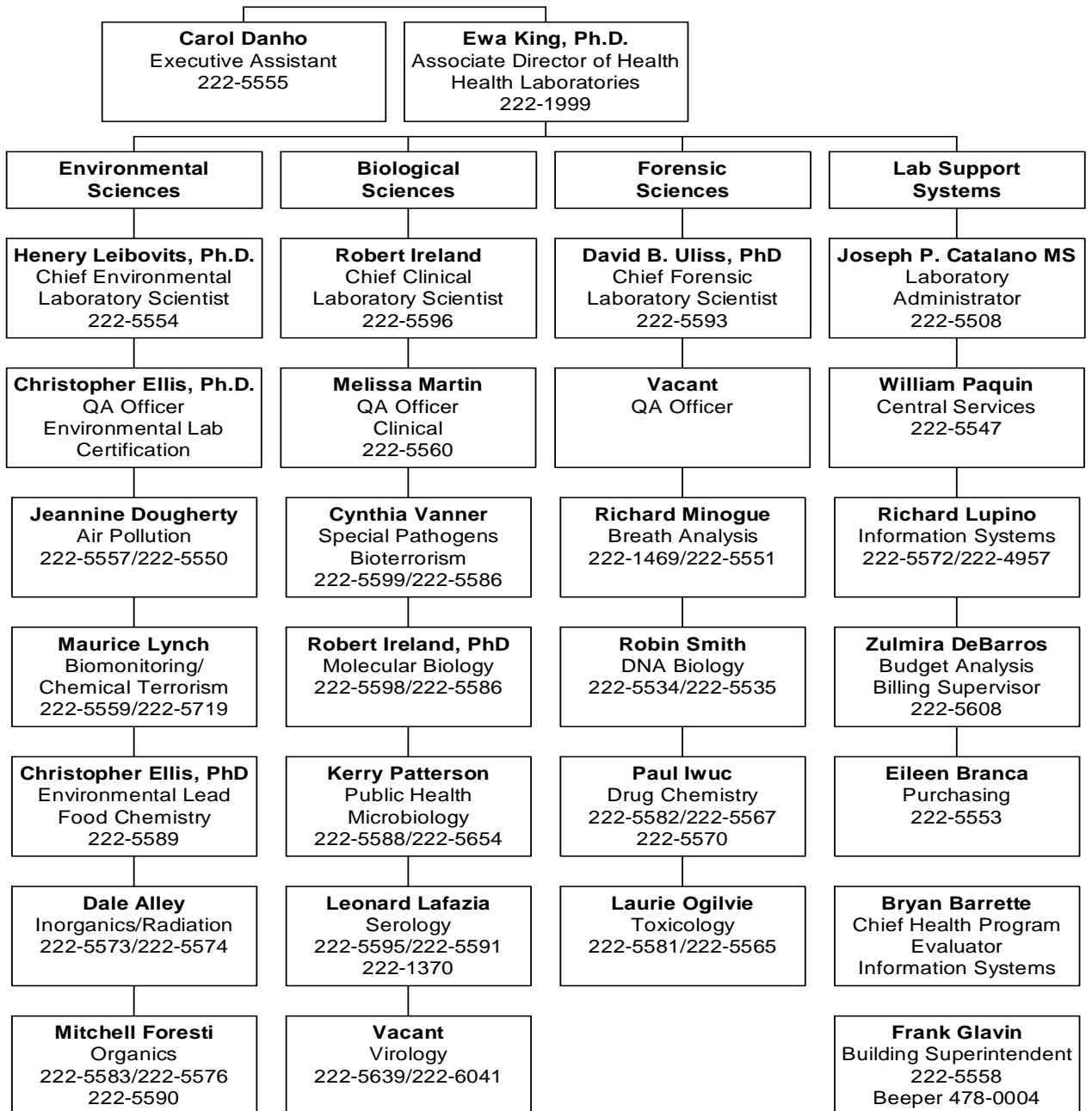
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Boston, Ma. 02114-2023

Figure 1

Rhode Island Health Laboratory  
Organizational Chart



*Figure II*  
*Environmental Sciences- Organizational Chart*

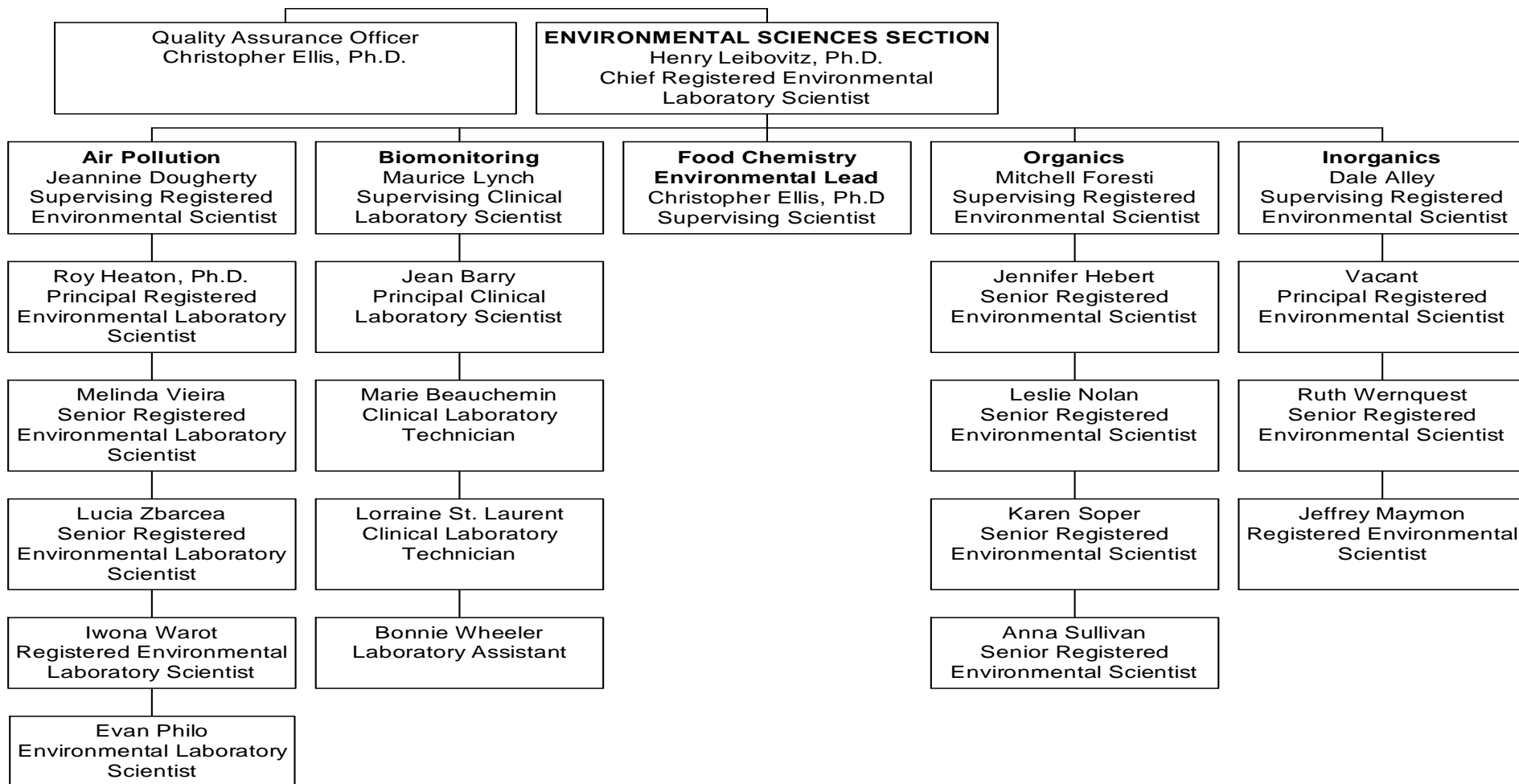


Figure III  
Department of Environmental Management  
Division of Agriculture

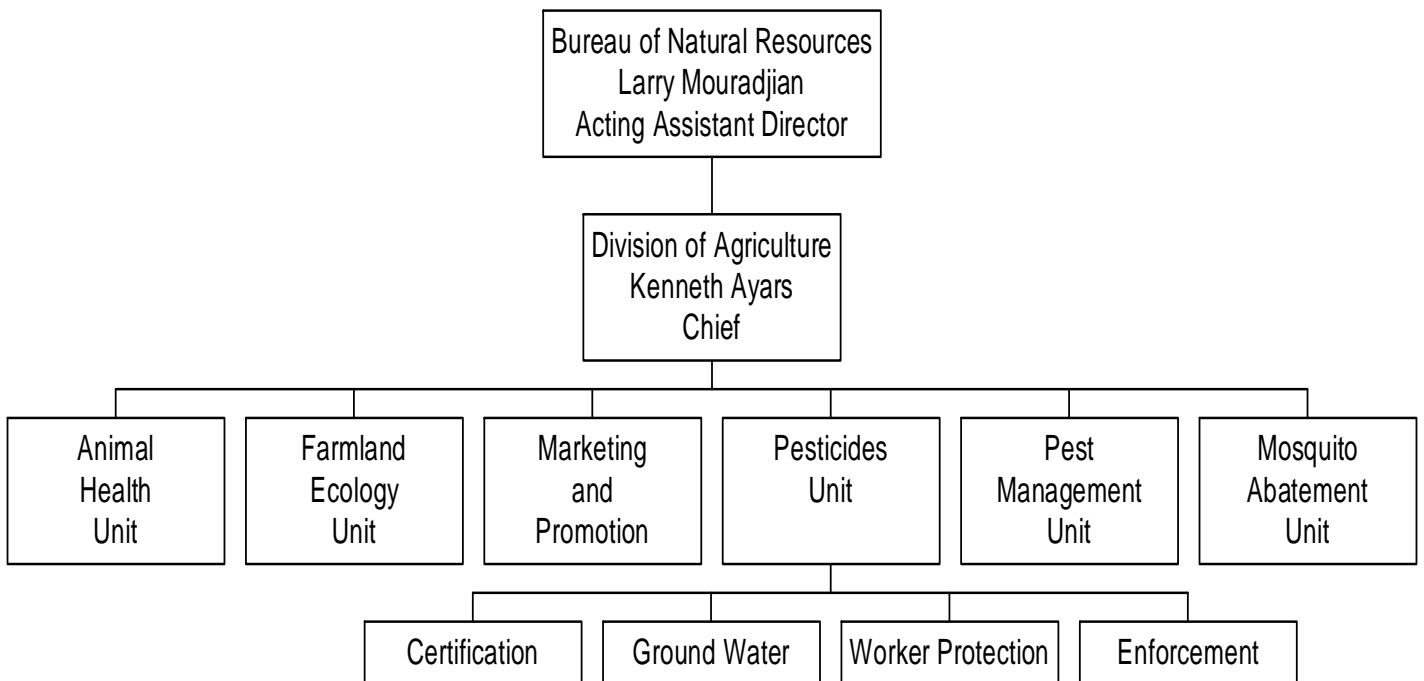
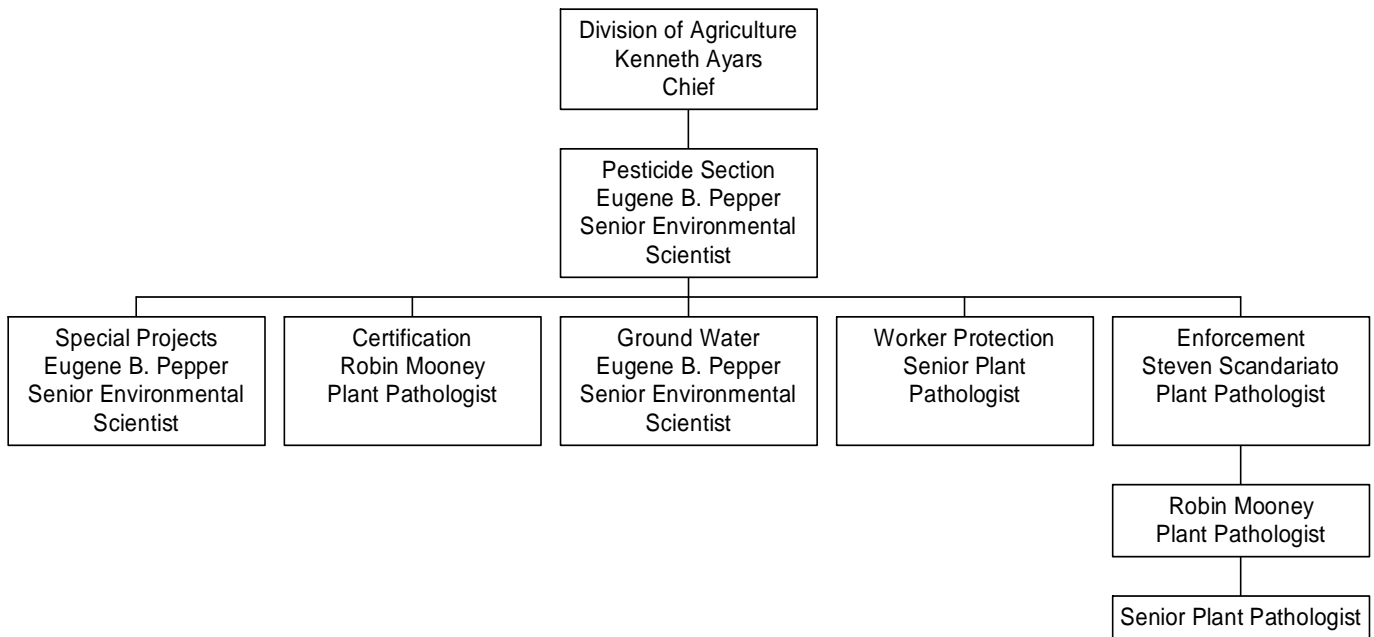


Figure IV  
Department of Environmental Management  
Division of Agriculture  
Pesticide Section





## **QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY**

Precision, accuracy, completeness, sample representativeness and data comparability are necessary attributes to ensure that analytical data are reliable, scientifically sound, and defensible. Each analytical result or set of results generated for the various enforcement programs should be fully defensible in any legal action, whether administrative, civil or criminal.

The extent and form of data collection and confirmation depends on whether the sample(s) is residue (environmental) or formulation (product). Analysis of residue samples frequently involves the detection and measurement of unknown pesticides at unpredictable levels in different matrices. Analysis of formulation samples typically requires specific assay procedures to verify compliance with a known label declaration for the active ingredients in the product. Formulated products in probable violation will be identified after the first analysis. Thus, quality control measures for formulation analyses will concentrate on those products identified as potentially violative.

The precision and accuracy of each pesticide residue method is dependent on the sample matrix and analyze concentration. Therefore, for residue analysis, the matrix and concentration determine the values of precision and accuracy (bias), which are acceptable.

Pesticide related inspections or investigations frequently generate a few unique or localized samples that do not lend themselves to the quality control practices recommended for long-range environmental monitoring programs. In these cases, the laboratory must provide adequate quality control and adhere to established standard operating procedures (SOPs) to ensure reliable data. The data must be of sufficient quality that the analysis will stand on its own merit.

Monitoring programs are commonly lengthy programs, which generate large numbers of samples. Types of samples monitored may be ground water, soil, or plant materials. For these programs, the laboratory must demonstrate the ability to generate acceptable analytical results.

The protocols for demonstrating analytical capability are specified in approved analytical methods.

## **QUALITY OBJECTIVES AND CRITERIA FOR MEASURING DATA**

The objective of data collection in terms of precision, accuracy, completeness, representativeness and comparability, as applicable, is to produce data that is reliable, scientifically sound, defensible and reflective of state-of the art methodology. Ultimately each analytical result or set of results generated in support of the pesticide enforcement program should be able to be defended in any legal action, whether administrative, civil or criminal in nature.

The degree and form of data collection and confirmation will vary according to whether the sample in question is residue (i.e. environmental) related to misuse investigations or formulation (product or tank mix) in nature. Residue samples will generally involve the detection and measurement of known or unknown pesticides at unspecified and unpredictable levels. Formulation samples require specific assay procedures to verify compliance with a predetermined or known label declaration for the pesticide product in question; those products in probable violation will be indicated after the first analysis. Thus, quality control measures for formulation analysis will concentrate on those identified potentially violative samples.

In general, a pesticide investigation will consist of a small number of localized and/or unique samples that do not lend themselves toward establishment of ongoing quality control data as is necessary for long range monitoring programs. It will be the objective and policy of the laboratory to provide adequate quality control and adherence to established practices such that each sample or group of samples will stand on its own merit with respect to the establishment of a reliable data quality.

Data completeness is expressed as the percent of the total data, which are valid. It is expected to be 100% for reported data from all work areas.

Comparability of data is ensured by adherence to the method protocols and by reporting data in the units and format specified.

Representativeness of samples is ensured by adherence to standard field sampling protocols and to standard laboratory subsampling/aliquotting protocols.

It is difficult to define the precision and accuracy of pesticide sample analysis in a general document. Each analysis is greatly dependent on the sample matrix, which determines what precision, and accuracy is acceptable. For example, an analysis of water to detect Heptachlor may attain a level of 95% accuracy. However, if it is an analysis of an oil water mixture, the level of accuracy may be only 50%. This matrix dependence requires professional judgments by the chemists. It is not possible to list all the pesticides the state laboratories analyze in all the matrices in this document. Representativeness is assured by following the sampling procedures in the FIFRA Inspection Manual (EPA305B02-001), using certified laboratory methods, etc.

## **SPECIAL TRAINING REQUIREMENTS/CERTIFICATION**

Any employee of the Rhode Island Department of Health Laboratory should have knowledge of appropriate laboratory procedures, as well as explicit knowledge and experience dealing with pesticide sampling and the analytical methods employed for such analyses. To the extent resources allow, lab personnel attend training conferences periodically to hone their skills and keep abreast of the latest advances. It is up to the discretion of the laboratory supervisor to ensure that the employees of lab are properly training in the use of laboratory equipment and sample custody.

DEM/Division of Agricultural Pesticide Enforcement field inspectors are trained on the proper equipment and techniques for pesticide residue and concentrate sampling. In addition, there is extensive training on preventing cross contamination, sample handling and determining sample locations.

Initial training involves reviewing inspection manuals and mentoring with experienced inspectors. Ongoing refresher training takes place during annual regional training and the Pesticide Inspectors Residential Training (PIRT) Workshops periodically offered by EPA.

Division staff involved in water protection sampling should be familiar and understand all of the related QA/QC documents once they are developed. In addition, staff will be encouraged to attend EPA sponsored pesticides regulatory education program (PREP) related to water quality/protection topics. The water program staff person will also attend where possible the EPA sponsored Regional Roundtable Meetings held approximately twice a year with other New England states as well as on occasion Region II state representatives. It will be the responsibility of the water protection staff person to maintain records of any conferences or training sessions related to water quality.

## **DOCUMENTATION AND RECORDS**

Included in the final sample report for both the enforcement and water protection monitoring activities are the following:

- Methods employed in analysis and associated detection limits
- Results of samples, included but not limited to sample blanks, fortified samples and the samples themselves
- Person responsible for the analysis
- Original sample number and information from the sample container (location, sample ID, date of sample collection)

Additional documentation available upon request includes the following information:

- Chromatograms of target analytes
- Extractions/storage log, including
  - Chain of Custody Information
  - Date(s) and time(s) of any and all sample extractions
  - Location of storage before and after extraction

The DEM/Division of Agriculture Pesticide Inspectors also maintains case files for every compliance incident. Case files maintained by these inspectors include, but are not limited to “Notice of Inspections” or “Notice of Pesticide Use/Misuse Inspections,” “Chain of Custody Forms,” “Collection Reports,” “Use Inspection reports,” Narrative reports, “Site Diagrams and when necessary written statements from the affected parties. Hard copies of the files are maintained for at least two years in file cabinets located in the office or storage areas. The water protection program also maintains files on sampling results of its monitoring activities. The Division maintains hard copies as well as electronic copies of these files for at least two years.

## **DATA GENERATION AND ACQUISITION**

### **PESTICIDE ENFORCEMENT PROGRAM**

Pesticide enforcement personnel are responsible for selecting appropriate sample locations and numbers of samples. They rely on their on-going training and may refer to the Inspector’s Manual or other recognized sampling procedures for additional information specific to gathering residue, wipe, ground water, surface water, product and animal samples when necessary. Similarly they are responsible for determining, upon consultation with the Senior Environmental Scientist, which analytes should be assayed by the laboratory. All samples delivered to the lab will be analyzed according to the request specified on the Chain of Custody Form. Laboratory personnel should assist field staff in developing appropriate sampling, sample preservation, packaging, and sample submission procedures, and proper documentation procedures. Enforcement samples are primarily sent to either the Mississippi State Laboratory or the Rhode Island Department of Health Laboratory, however, other state or certified labs may be used depending upon the nature of the chemical involved in the case. Laboratory selection is based upon laboratory certification, lab capabilities and turn around time.

### **WATER PROTECTION PROGRAM**

Divisional staff will meet with appropriate state, federal and other agencies and entities (e.g. NRDC, grower groups, extension, water supply boards) to identify priority projects to be implemented in conjunction with resource limitations, regulatory requirements and state and federal goals. Information on pesticide use is obtained from the Division’s Pesticide Use reporting requirements for restricted use pesticides and compared with pesticide leaching and runoff characteristics to identify high-risk pesticides. In the decision-making process staff also consider and utilize GIS mapping data, soil profiles, hydrogeology criteria in assessing sampling

sites. The water protection staff person is responsible for communicating with the lab prior to sampling to make sure the lab has the ability to perform the analysis.

Sampling procedures will follow prescribed procedures set forth in:

- National Enforcement Investigation Center (NEIC) Pesticides Sampling Guide, March 1981. Available from Us EPA, National Enforcement Investigations Center, PO Box 25227, Denver, Co. 80225
- EPA Pesticide Inspection Manual (latest edition), Contract No. EPA 68-01-7379-2
- Ground water sampling procedures for use by DEM Sampling Custodians are defined in ground water monitoring sampling procedure component of this section.
- Other recognized state, federal or association procedures, as applicable.

It is management policy to consider the quality assurance program an integral and essential part of the overall laboratory operation. If adequate personnel, instruments or supplies or appropriate analytical methods are not available to maintain quality control, the request for sample analyses may be declined. Therefore, it is desirable for field personnel to make arrangements with the laboratory before submitting samples.

Samples are properly documented, preserved, packaged, maintained under custody and transferred to the laboratory in a defensible manner. The Supervising Environmental Laboratory Scientist should notify the appropriate field project leader when problems are encountered with the quality of incoming pesticide samples or when laboratory problems arise that could affect the reliability and/or defensibility of analytical results.

## **Ground Water Sampling Procedures**

### **I. Monitoring Well Sampling**

The sampling procedures described here shall be used when sampling wells, which have been installed specifically for the purposes of monitoring ground water. In addition state policy on groundwater monitoring for pesticides is described in Rhode Island's Draft Management Plan for the Protection of Groundwater from Pesticides and Nitrogenous Fertilizers (last draft 1996).

#### **A. Sampling Equipment**

Sampling equipment used by sample custodians collecting samples shall at a minimum include, but may not be limited to:

Dedicated Disposable Bailers  
Latex Disposable Gloves  
Field Log

Well Sounder  
Needle Nose Pliers  
Rain Gear  
Sampling Pail  
Cooler and Ice  
Sampling Bottles  
Dedicated Nylon Cord  
Keys (to monitoring well locks)  
Site Map  
Pry Hook  
Adjustable Wrench  
Portable Submersible Pumps  
Portable Peristaltic Pumps  
12-Volt Batteries

B. Preparation For Sampling

Prior to sampling, all sampling personnel will be trained in proper sampling methods, techniques, and procedures. Any supplies that cannot be properly decontaminated or cleaned will be dedicated to that well and discarded later.

Upon arrival at a previously established and DEM designated monitoring well, sampling personnel will check the well for damage, record the well designation, clean any debris from around the well, and then remove the locking well cap and wipe off the top of the well with clean cloth. Then the depth of the well will be measured using a well sounder, and the volume of water will be calculated.

Upon arrival at a monitoring well, which has not been previously designated by DEM, sampling personnel will obtain the following information:

- (a.) Well Identification Number (to be assigned by the Division of Agriculture)
- (b.) Name, address, and phone number of owner
- (c.) Name, address, and phone number of contact or responsible person.
- (d.) Well location (latitude/longitude, street address, GIS location, etc.)
- (e.) Well type, depth (in feet), top and bottom perforation depths (in feet), depth of standing water at the time of sampling (in feet), and year the well was installed.
- (f.) Date of sample (month/day/year).

- (g.) Record sampling agency and sampling person.
- (h.) Record sampling location.

Sampling personnel will then check the well for damage proper drainage, clean any debris from around the well – if well is privately owned, owner must remove debris, and then wipe off the top of the well with clean clothe. Measure the water depth of the well using a well sounder, and calculate the volume of water.

A volume of water equal to three to five times the volume of standing water in the monitoring well will be removed (evacuated) from the well casing prior to collecting ground water samples. The volume of standing water in each well will be calculated using the following equation:  $V=(\pi) (r^2) (h)$  where,

V= volume in cubic feet (ft<sup>3</sup>)

r= well radius (ft)

h= column of water in well (total depth of well being from casing top in feet)-(depth to water in feet)

A minimum of three to five times the calculated volume of water in the well will be removed so that the sample subsequently collected will be representative of the zone screened. If the well cannot maintain a continuous yield until three to five columns are evacuated, it will be bailed dry and then sampled as soon as there is sufficient water for sampling. Water evacuated during sampling will be discharged to land surface.

#### C. Sampling Procedure for Monitoring Wells

Within one hour or less of well evacuation, a ground water sample will be collected with a disposable bailer or suitable pump.

##### Sampling with a Bailer

All bailers are pre-wrapped and will be fastened with a nylon cord. The bailer will be slowly lowered into the well in order to minimize any water disturbance. Water

will enter the bailer through an end plug in the bottom of the bailer and will be prevented from draining out by an inert ball check-valve. Sampling personnel will wear a new pair of gloves for each well sampled and when handling a clean bailer. Sample containers will be inspected to ensure that they are the correct type and number, and have the correct preservative, if required. Sample labels will be properly filled out and affixed to the containers.

Samples will be carefully poured into the containers, avoiding agitation or turbulence, which might result in the loss of pesticide due to volatilization. Care will be exercised to avoid breakage and to eliminate the entry or contact of any

substance with the interior surface of the bottles, vials or caps, other than the water sample being collected. Caps will not be removed until the actual sampling time and then just long enough to fill the container. The containers for pesticide analyses will be topped off to eliminate any headspace or air bubbles and will be tightly closed with Teflon-lined septa held in place by open-top screw caps.

The dedicated bailer will be left in the well suspended above the top of the water so as not to permanently contaminate the bailer for future sampling. The well cap will then be closed and the well will be locked. Samples will be packed on ice in a cooler and the RI DOH's sampling form will be filled out in triplicate. Samples will be delivered or shipped to the laboratory within 24 hours after sample collection and the receiver's signature will be obtained on the sampling form. Methods for completing sampling forms are outlined on RI DOH Quality Control Document re. No. 4.2-4.1.2.4 and 4.1.2.6-4.2.1.

### Sampling with a Pump

The pump will be slowly lowered into the well in order to minimize any water disturbance. Sampling personnel will wear a new pair of gloves for each well sampled and when handling a clean pump. Sample containers will be inspected to ensure that they are the correct type and number, and have the correct preservative, if required. Sample labels will be properly filled out and affixed to the containers.

Samples will be carefully poured into the containers, avoiding agitation or turbulence, which might result in loss of pesticide due to volatilization. Care will be exercised to avoid breakage and to eliminate the entry or contact of any substance with the interior surface of the bottles, vials or caps, other than the water sample being collected. Caps will not be removed until the actual sampling time and then just long enough to fill the container. The containers for pesticide analyses will be topped off to eliminate any headspace or air bubbles and will be tightly closed with Teflon-lined septa held in place by open-top screw caps.

When the sample has been collected the pump will be decontaminated using a rinse of distilled water or water of known quality which does not contain residual pesticides. The pump will be stored for transport so as not to become contaminated with pesticide residue during transport. The well cap will then be closed and the well locked. Samples will be packed on ice in a cooler and the RI DOH's sampling form will be filled out in triplicate. Samples will be delivered or shipped to the laboratory within 24 hours after the sample collection and the receiver's signature will be obtained on the sampling form. Methods for completing sampling forms are outlined on RI DOH Quality Control Document re.no.4.2-4.1.2.4 and 4.1.2.6-4.2.1.



### Peristaltic Pump

The suitable plastic tube of drinking water quality will be slowly lowered into the well in order to minimize any water disturbance. This tube will be connected to the pump. Sampling personnel will wear a new pair of gloves for each well sampled and when handling a clean pump. The well will be pumped for three to five well volumes as previously outlined. If it is not possible to pump the well for three volumes the pump will flush for five minutes before the sample is collected. Sample containers will be inspected to ensure that they are the correct type and number, and have the correct preservative, if required. Sample labels will be properly filled out and affixed to the containers.

Samples will be carefully poured into the containers, avoiding agitation or turbulence, which might result in the loss of pesticide due to volatilization. Care will be exercised to avoid breakage and to eliminate the entry or contact of any substance with the interior surface of the bottles, vials, or caps, other than the water sample being collected. Caps will not be removed until the actual sampling time and then just long enough to fill the container. The containers for pesticide analyses will be topped off to eliminate any headspace or air bubbles and will be tightly closed with Teflon-lined septa held in place by open –top screw caps.

The tubing may be left suspended in the well as a dedicated sample tube for future sampling. If the tube is removed it will be placed in a clean plastic bag, it shall be designated for that well. The bag will be labeled with the well identification information. This tube will be used for all future sampling of this well only. The well cap will then be closed and the well will be locked. Samples will be packed on ice in a cooler and the RI DOH's sampling form will be filled out in triplicate. Samples will be delivered or shipped to the laboratory within 24 hours after sample collection and the receiver's signature will be obtained on the sampling form. Methods for completing sampling forms are outlined on the RI DOH Quality Control Document re.no. 4.2-4.1.2.4 and 4.1.2.6-4.2.1.

## **OTHER PESTICIDE SAMPLING PROCEDURES**

### **I. Formulation and Use Dilution Sampling Procedures:**

Sampling procedures for formulation and use dilutions shall conform to the procedures outlined in the National Enforcement Investigation Center (NEIC) Pesticides Sampling Guide and the EPA FIFRA Inspection Manual (EPA305B02-001).

### **II. Residue Sampling Procedures:**

Sampling procedures for residues shall conform to the procedures outlined in the National Enforcement Investigation Center (NEIC) Pesticides Sampling Guide and the

EPA FIFRA Inspection Manual (EPA305B02-001). Except that those prescribed for ground water as outlined in this document shall be applied by all field sampling staff.

With respect to Pesticide Compliance Activities, pesticide samples will only be taken as needed to establish compliance or violation of existing state or federal laws. Professional judgment will be exercised in the field to obtain adequate numbers and types of samples to establish or confirm pesticide misapplication, product quality or poor disposal practices. Professional judgment and guidelines, as listed above, will also be employed to assure obtaining representative samples that are free from sampler-induced cross-contamination. Likewise, all samples will be properly documented, packaged (preserved, if necessary), maintained under custody and delivered to the laboratory in a fully defensible manner. In cases where pesticide samples must be shipped via a transport carrier to for example the Mississippi State Chemical Laboratory, then samples will be packaged and shipped according to the shipper's requirements as well as follow shipping requirements and regulations established by the U.S. Department of Transportation. It will be the inspector's responsibility to seek assistance as required from the senior laboratory staff when new situations, new pesticides or unique circumstances are encountered in the field. Likewise, it is incumbent upon the Supervising Laboratory to notify the appropriate inspectional staff and the Pesticides Enforcement Person when problems are encountered that may impact the quality of incoming pesticide samples which could affect the reliability and defensibility of analytical results.

It is incumbent upon the inspectional and laboratory staff to see that holding times and preservation requirements are met for residue samples. In extreme heat or cold weather, samples will be stored in an insulated cooler during the collection and transportation of that sample. Pesticide residue samples may have a short holding time depending on the pesticide or substrate. Holding time is defined as beginning when the sample is collected and ended when the sample is extracted at the lab. As a rule of thumb, water samples should be extracted within seven days of collection. The field staff will deliver residue water samples to the lab within 24 hours. Once, collected samples are either refrigerated or frozen as soon as possible once staff has returned to the office if samples cannot be delivered to the laboratory immediately.

For formulation and dilution samples, holding times and preservation requirements are usually less restrictive. These samples should be delivered to the lab within 5 days of collection. Most formulation and dilution samples are sent to Mississippi State Chemical Lab for analysis.

## SAMPLE PRESERVATION AND HOLDING TIMES

Sample Matrix	Minimum Quantity	Container	Preservation	Holding Time
Foliage-Residue	½ pound	Sealed Plastic Bag	Insulated cooler, then freeze as soon as possible	Indefinite after freezing
Soil-Residue	500 ml	Amber Glass w/Teflon cap, pre-cleaned & certified for Pesticides	Insulated cooler and refrigerated as soon as possible	Deliver to lab as soon as possible.
Wipe or Swap Sample	1 wipe or swab place in vial then placed in 250 ml jar.	Amber Glass w/Teflon lid, pre-cleaned & certified for Pesticides	Insulated cooler, then refrigerator as soon as possible	Deliver to lab as soon as possible
Surface Water	500 ml	Amber glass w/Teflon lid, pre-cleaned & certified for pesticides	Ice, remove from light and refrigerate	Delivered to lab within 24 hours
Ground water	20 ml per assay or method	Disposable scintillation vial	Ice, remove from light and refrigerate	Delivered to lab within 24 hours

## SAMPLE CUSTODY

Sample custody consists of two components: documentation and actual physical custody of a sample; and three distinct phases: custody in the field, custody in the laboratory, and custody of the evidence file. The following principles apply to handling of samples from the point of collection through placement of a sample in permanent abeyance (when all contemplated or actual legal actions are completed). A sample is considered in someone's custody if:

- It is in one's actual physical possession or view
- It is retained in a secured area with restricted access
- It is placed in another container and secured with an official seal(s) or evidence tape so the sample cannot be reached without breaking the seal(s) or rupturing the outer container

Field personnel initiate sample custody as the sample(s) is collected. Field custody procedures conform to the National Enforcement Investigation Center (NEIC) Pesticides Sampling Guide or equivalent standard operating procedure. An example of a form used to record the transfer of custody of a sample from the field to the laboratory is shown in Figure 3.

All custody procedures in the laboratory follow those specified in the laboratory's standard operating procedure. The laboratory's standard operating procedure conforms to the requirements in the Pesticide Cooperative Agreement Guidance and the EPA/NEIC Pesticides Products Procedures Manual.

Upon receipt of the sample(s), the sample custodian inspects the shipping container(s), the sample(s), the official seal(s), and documentation related to the sample(s) and other records. If accepted for analysis, the sample(s) are entered by the sample custodian into the sample logbook or computer system and assigned a unique laboratory number. A sample jacket (or project file) is prepared for each sample or group of samples. All pertinent information regarding the sample(s) is placed in this folder. A custody form is completed by the sample custodian for each sample or group of samples and placed in the sample jacket. An example of the Chain of Custody Transfer Record is shown in Figure 5. The sample custodian then identifies the initial storage location and the sample(s) are transferred to the designated freezer or refrigerator. The sample(s) is kept in the designated, secured storage area until requested by an analyst.

A supervisor assigns the sample(s) to an analyst. After assignment, the sample custodian retrieves the sample(s) and transfers it to the analyst who completes the appropriate lines on the custody form. If the sample(s) is assigned to a different analyst, the appropriate lines in the second column of the custody form are completed by the new analyst. Similarly, the third column or even additional sheets can be used to document additional sample transfers within the laboratory. The original seal(s) should be kept with the sample(s) and maintained in a legible condition. An example of an official seal is shown in Figure 5. Upon completion of the analyses, the analyst reseals the sample(s), completes the appropriate lines on the custody form and returns the sample(s) to the sample custodian for storage.

Field custody problems identified by laboratory personnel are to be immediately relayed by the laboratory manager to the appropriate program representative for corrective action, which may include re-sampling.

Since pesticides in environmental samples are relatively unstable and may degrade, once a sample is extracted, that extract shall be considered the official sample. Disposal of the actual physical sample may occur after the acceptable holding time has elapsed. Any extract remaining after analysis will be retained until the case is held in permanent abeyance. Formulation samples will be physically retained until the case becomes permanently abeyed, at which time disposal may occur.

## **INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES**

Pesticide Enforcement Program – All supplies are obtained from Fisher Scientific whenever possible, or another equally reputable source in the case that the order cannot be fulfilled by Fisher Scientific. The manufacturing facilities at Fisher Scientific are ISO 9002 certified. Sample bottles purchased are I-Chem certified.

Water Protection Program- Whenever possible, all pesticide standards used for qualitative and/or quantitative analysis will be of analytical quality and will be obtained from the EPA Environmental Science Center, 701 Mapes Road, Fort Meade, MD. Sample bottles are obtained and prepared by the RI DOH Pesticide Lab.

## **INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY**

Each instrument used routinely in the laboratory should be adequately maintained, calibrated and monitored. Specifications for instrument maintenance, calibration and monitoring are described in manufacturer's manuals, in analytical methods, and/or appropriate standard operating procedures. If an instrument malfunctions, or if improper sensitivity, resolution and/or reproductively is detected, corrective action is necessary before analyses are attempted.

Analytical standards used to prepare calibration or standard solutions are obtained from the National Institute for Standards and Technology (NIST), EPA, USDA, FDA or other reliable sources. Stock standard solution(s) are prepared as specified in the method. All information on their preparation is recorded in the designated logbook(s).

Unless otherwise specified in the analytical method, calibration standards used in environmental analytes are prepared at a minimum of three concentration levels for each analyte or group of analytes. One of the calibration standards should represent an analyte concentration near, but above, the method detection limit. The other concentrations should correspond to the concentration range expected in the sample. Information related to the calibration standards is recorded in designated logbooks. Both calibration standards and stock standard solution(s) should be traceable to their sources.

A calibration curve of analyte response versus analyte concentration is prepared for each analyte before a method can be used or each time there is a change in instrument conditions. The calibration curve is then verified on each working shift by the measurement of one or more calibration standards. A response which varies from the predicted response by more than  $\pm 20\%$ , unless otherwise specified in the analytical method, indicates a problem. Therefore, the calibration must be repeated using a freshly prepared standard and a new calibration curve prepared. Each EPA method for pesticides in ground water specifies calibration procedures and frequency, which must be followed.

## **NON –DIRECT MEASUREMENTS**

Non-direct measurements are not used, except in the case where a particular method of analysis is unfamiliar to the laboratory personnel. In this case the EPA's pesticide analytical methods are referred to and accepted for use.

## **DATA MANAGEMENT**

Pesticide Enforcement Program- Most data originating from the labs is managed both electronically and on hard copy. Once the Division of Agriculture receives the data it is incorporated in the hard copy case file and retained for a minimum of two years. Some data elements are also managed electronically. All complaints and compliance cases are tracked electronically as are routine pesticide inspections.

Documentation from the labs includes:

- Completed History of Official Samples
- Report of Analysis which lists chemicals analyzed; Person responsible for the analysis

Water Protection Program- Documentation from the lab for each sampling activity includes the following:

- Methods employed in analysis
- Person responsible for the analysis
- Original sample number and information from the sample container(location, sample ID, date/time of sample collection)
- Chain of Custody Form
- A Quarterly Sample Summary Report

All data is managed electronically and on hard copy.

The Division of Agriculture has a relationship with the Rhode Island Department of Health,(DOH) Drinking Water Program. DOH provides on a bi-annual basis the state's drinking water/source water monitoring data for synthetic organic chemicals (SOC's) . This helps to identify any potential problems of pesticide contamination. All data is submitted electronically utilizing Microsoft product such as Access and Excel. If mathematical functions are necessary, the mathematical functions within Excel spreadsheets are used.

## **ANALYTICAL PROCEDURES**

Whenever possible, official (collaborated) or standard (professionally accepted) methods are used for both residue and formulation analyses. Methodology is particularly important when verifying compliance with regulatory, tolerance or action levels. In-house procedures can often provide a higher sample throughput; however, all such routinely used procedures must be validated by establishing precision/accuracy data and/or comparison with more established procedures. For in-house residue procedures, the method must be further validated by performing duplicate matrix controls, four matrix spikes for each sample matrix and a solvent blank. In addition, a solvent blank, matrix control and matrix spike for each analyze in each matrix must be analyzed with each group of not more than ten residue samples.

Currently, DOH's Division of Laboratories is unable to conduct formulation and dilution testing. However, if during the course of this plan the Division of Laboratories develops such

capability it will follow EPA/NEIC guidelines for formulation samples requiring repeat analysis of a potentially violative sample. When an official method is not available for confirmation analysis of a compound, a new in-house procedure may be used after validation. The procedure can be validated by replicating analysis a minimum of three times, and analyzing one blank and matrix spikes.

With respect to the Pesticide Enforcement Program, analytical procedures or methodology to the degree possible, potential violations (i.e., verification of misuse and product non-compliance) are confirmed using methodology from the following recognized sources whenever possible:

Residues:

1. Pesticide Analytical Manual, Food And Drug Administration Vols. 1-4, U.S. Department of Health, Education, and Welfare. Published 08/01/1977 and updated periodically.
2. Official Methods of Analysis of the Association of Official Analytical Chemists (latest edition). Published by the Association of Official Analytical Chemists, Suite 400, 2200 Wilson Boulevard, Arlington, VA 22201.
3. U.S. EPA National Pesticide Survey Methods 1-6. Private communication with EPA Technical Support Division, Office of Drinking Water, Cincinnati, OH 45268
4. Methods for the Determination of Organic Compounds in Drinking Water (latest edition). EPA 600/4-88/039, Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, OH 45268.
5. Manual of Analytical Methods for the Analysis of Pesticide Residues in Human and Environmental Samples (latest edition). J.F. Thompson, Editor, U.S. Environmental Protection Agency, Health Effects Research Laboratory, Environmental Toxicology Division Research Triangle Park, North Carolina.
6. Analytical Methods For Pesticides, Plant Growth Regulators, and Food Additives, Vol. I-XVII, Gunter Zweig, Ed., Vol. VI-XVII edited by J. Sherma, Academic Press Inc., 111 Fifth Avenue, New York, NY 10003.
7. Test Methods for Evaluating Solid Waste, SW-846, Vol. 1-2, EPA, Office of Solid Waste and Emergency Response, Washington, DC 20460.

Formulations:

1. Official Methods of Analysis (latest edition) of the Association of Official Analytical Chemists. Published by the Association of Official Analytical Chemists, Suite 400, 2200 Wilson Boulevard, Arlington, VA 22201.
2. Manual of Chemical Methods for Pesticides and Devices (and supplements). EPA, Office of Pesticides Programs, Technical Services Division, Washington, DC.
3. CIPAC Handbooks, Volume I, IA, IB, IC, and ID Analysis of Technical and Formulated Pesticides. Collaborative International Pesticides Analytical Council Limited, 1970 (I), 1980 (IA), 1983 (IB), 1985 (IC) and 1988 (ID). Published by W.H. Heffer and Sons, Ltd., King's Hedges Road, Cambridge, CB4 2PQ, England.
4. Analytical Methods for Pesticides, Plant growth regulators & Food Additives. Volumes 1-XVII, Gunter Zweig, Ed. Volumes VI-XI edited by J.Shema, Academic Press Inc., 111 Fifth Avenue, New York, NY 10003.
5. Pesticide Product Procedures Manual, Agriculture Canada, Ottawa, Ontario, K1A 0C6, 07/30/89

Journals:

1. Journal of the Association of Official Analytical Chemists. Published by the Association of Official Analytical Chemists, Suite 400, 2200 Wilson Boulevard, Arlington, VA, 22201.
2. Journal of Agricultural and Food Chemistry (ACS).
3. Journal of Chromatographic Science (Preston Tech. Services).
4. Pesticide and Toxic Chemical News (General Information on Pesticide Issues, 1101 Pennsylvania Ave., S.E., Washington, DC 20003.
5. Laboratory Information Bulletin (available from FDA, 5600 Fishers Lane, Rockville, MD 20857).
6. Analytical Chemistry (ACS).
7. Analytical Toxicology (Preston Tech. Services).
8. Journal of Analytical Toxicology (Preston Tech. Services).



## **ASSESSMENT AND OVERSIGHT**

### **Assessments and Response Actions**

Laboratory internal assessments will be conducted periodically and corrections and improvements will be made where applicable. The laboratory is fully committed to analyzing all available and appropriate performance samples and lending itself to any necessary on-site system audits by qualified representatives of EPA. The laboratory is also committed to using the results of such performance and systems audits to improve the reliability, defensibility, capability and efficiency of the laboratory operations to the degree possible.

Qualified representatives of EPA will perform systems audits, generally from the Regional Office. The audit will be conducted upon joint consent of the Regional Office and the Division of Agriculture and a report of all findings and recommendations will be made promptly to the Division of Agriculture.

The laboratory will participate in pesticide performance audits as available. Some of these performance audits are currently provided and available from the American Association of Pesticide Control officials (AAPCO) through the affiliated Laboratory Directors Working Group, Check Sample Program. As other pesticide check sample programs in pertinent matrices become available, the laboratory may choose to participate. The laboratory will also participate in AOAC collaborative studies for pesticide analysis as time allows

### **Reports to Management**

Pesticide Enforcement Program – Whenever quality assessments reveal significant concerns, or updated procedures come to light, laboratory personnel or the Division of Agriculture will report the new information to the other party. Laboratory personnel will include recommended solutions with their report on the new information.

Water Protection Program – Upon completion of each sampling activity or monitoring project, personnel will prepare a report summarizes the results and findings of the sampling period. On occasion findings may also be presented to the regulated community. Through attendance at workshops or grower meetings.

Some of the topics or issues that may generate the need to submit a report are:

- Changes in Quality Assurance Project Plan
- Summary of quality assurance/quality control programs, training and accomplishments
- Results of technical systems and performance evaluation audits

- Significant quality assurance/quality control problems, recommended solutions and results of corrective actions
- Summary of data quality assessment for precision, accuracy, representativeness, completeness, comparability and method detection limit
- Discussion of whether the quality assurance objectives were met and the resulting impact on technical and enforcement areas
- Limitations on use of the measurement data and discussion of the effects of such limitations on the defensibility of the data.

## **DATA REDUCTION, VALIDATION AND REPORTING**

This section describes the basic procedures for data reduction, validation and reporting for the comprehensive pesticide laboratory programs.

Data reduction is performed on a sample-by-sample basis, or on a case-by-case basis, as necessary for enforcement activities. For chromatographic procedures, the initial qualitative identification of target compounds is based on the retention times of the peaks compared to the retention times for reference standards in the calibration mixture. To confirm the presence of each compound, retention time is compared to that of a standard on a second chromatographic column and/or different detector. Non-target compounds are qualitatively identified by retention times or by relative retention time compared to an appropriate internal standard.

Analytes are quantitated by comparing values of peaks of analytes to values of peaks of calibration standards. Peak values may be peak height, peak area or other measure of peak size. An integrator, data station or other electronic device can be used to capture signals and record the information which is used for both qualitative and quantitative identification.

Validation of data is described in detail in the laboratory standard operating procedures. In most cases, data validation consists of a review of the analytical method, chromatograms, calculations and quality control results. Initial review is done by the analyst, and final review by the Supervising Laboratory Scientist or a designated Senior Scientist. When a review indicates a need, the analysis is repeated by a different analyst using either the same method or an alternate method. Questionable data may result from the condition of the sample, inadequacy of the method, lack of validation, time constraints or other factors. Any questionable data will be clearly identified and qualified. The Quality Assurance Officer conducts periodic in-depth audits to assure compliance with the validation requirements.

Analytical data is reported according to the format(s) provided in the standard operating procedures. In addition to the analytical results, the reference for the method and quality control results are reported. Quality control results may include spike recovery, results of duplicate analyses and analysis of reagent blanks, but are not limited to these. When the compound(s) of interest is not detected in the sample(s), it is reported as such with the method detection limit. Any pertinent observations about the samples or the analytical process are also reported. All reports are reviewed by the Supervising Laboratory Scientist, who has responsibility for the final

report. The respective program manager is responsible for conveying results to the appropriate parties.

### **INTERNAL QUALITY CONTROL CHECKS**

The internal quality control (QC) checks are a systematic in-house approach to ensure the production of high quality data. The objectives of these control checks are:

- To provide reliable and defensible analytical results
- To provide a measure of the precision and accuracy of the analytical methods
- To monitor the accuracy and precision of the analyst
- To identify problematic methods which can be flagged for further research
- To detect training needs within the laboratory
- To provide a permanent record of instrument performance which is used for validating data and projecting instrument repair or replacement needs
- To monitor the effectiveness of the quality assurance program and laboratory performance and provide a basis for modifications of the quality assurance program.

The quality control procedures for analytical methods used for misuse cases may include:

- Demonstration of analytical capability
- Analysis of a quality control check sample, when available
- Daily calibration check
- Recoveries of surrogate standard or matrix spikes
- Analysis of reagent blank
- Duplicate analysis
- Analysis of laboratory control standards
- Blind performance evaluation samples
- Analysis of instrument quality control standards
- Confirmation of analyze

Monitoring programs include ground water projects, and monitoring during misuse investigations of raw agricultural products or other foodstuffs. For these programs, a summary of internal quality control procedures, including acceptance criteria and corrective action, follows. The procedures listed are followed unless specified otherwise in the method. Any method specific quality control checks are performed in addition to those listed.

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Calibration Check	Daily prior to analysis	Measured RF within $\pm 30\%$ of predicted response for each analyte or as per method or SOP	<ol style="list-style-type: none"> <li>1. Repeat with a fresh standard</li> <li>2. Prepare a new calibration curve</li> </ol>
Surrogate Recovery	Each sample	Recovery of surrogate within $\pm 30\%$ of mean recovery or as per method or SOP	<ol style="list-style-type: none"> <li>1. Check calculations for errors</li> <li>2. Check internal and surrogate standard solutions for abnormalities</li> <li>3. Check instrument performance</li> <li>4. Reanalyze the extract</li> <li>5. Extract and analyze backup sample</li> </ol>
Laboratory Control Sample	10% or 1 per sample set	Recoveries within the criteria established during the initial demonstration of capabilities or as per method or SOP	<ol style="list-style-type: none"> <li>1. Review calculations and techniques</li> <li>2. Repeat test</li> <li>3. Check instrument performance</li> <li>4. Reextract laboratory control sample and all samples in sample set</li> </ol>
Matrix Spikes	10% or 1 per sample set	As established for each matrix or as per method or SOP	<ol style="list-style-type: none"> <li>1. Repeat analysis</li> </ol>
Matrix Control	1 per sample set	As defined by the supplier	<ol style="list-style-type: none"> <li>1. Repeat analysis</li> </ol>
Duplicate Analysis	10% or 1 per sample set	Relative range measurements within those established by inter laboratory method performance study	<ol style="list-style-type: none"> <li>1. Repeat analysis</li> <li>2. Obtain 3<sup>rd</sup> value</li> <li>3. Flag data and continue analysis</li> </ol>
Laboratory Reagent Blanks	10% or 1 per sample set	Analyze concentration values of less than one-half of method reporting limit or	<ol style="list-style-type: none"> <li>1. Check for instrument contamination</li> </ol>

		as per method or SOP	<ol style="list-style-type: none"> <li>2. Check for reagent contamination</li> <li>3. Repeat analysis after determining source of contamination</li> </ol>
Instrument QC Standard	Daily	Criteria listed with each method or as per method or SOP	<ol style="list-style-type: none"> <li>1. Perform instrument maintenance</li> <li>2. Repeat standard</li> </ol>
Internal Standard Area Counts	Each sample	Within $\pm 30\%$ of average area counts or as per method or SOP	<ol style="list-style-type: none"> <li>1. Re inject the sample</li> <li>2. Check calibration curve</li> <li>3. Prepare a new calibration curve</li> <li>4. Re extract and reanalyze the sample</li> </ol>
New Calibration Standards	Each time prepared	$\pm 20\%$ of existing calibration standards or as per method or SOP	<ol style="list-style-type: none"> <li>1. Repeat analysis</li> <li>2. Prepare new standards</li> </ol>
Check Second Column/Detector Confirmation	Each analyze positive on primary column or detector	Quantitation within $\pm 30\%$ of that on primary column or as per method or SOP	<ol style="list-style-type: none"> <li>1. Repeat analysis</li> <li>2. Call supervisor</li> </ol>

Pesticide formulation samples that have been analyzed by standard methodology (e.g., gas or high-performance liquid chromatography) and found to be consistent with the label claims are not normally of enforcement interest. Therefore, quality control efforts for pesticide formulation analysis are focused on those official samples found to be potentially violative, since these may have to be defended in a legal action. Specific quality control procedures are documented in a standard operating procedure, and may include one or more of the following:

- Check analysis by a second qualified analyst
- Replicate analysis – at least triplicate to calculate a standard deviation
- Use of alternate official method, if available
- Use of two or more methods employing different principles of separation and/or detection
- Use of at least two analytical reference standards for calibration purposes.

## **PERFORMANCE AND SYSTEMS AUDITS**

The Department of Health, Division of Laboratories and the Department of Environmental Management, Division of Agriculture are committed to participate in the evaluation of the laboratory and field quality assurance programs and to lend themselves to any coordinated on-site systems audits by qualified representatives of EPA. The department is also committed to using the results of such performance and systems audits to improve the reliability, defensibility, capability and efficiency of the laboratory and field operations.

Systems audits, laboratory and field, are performed by qualified representatives of EPA Region I and/or the National Enforcement Investigation Center (NEIC) of EPA. The audit is conducted upon joint consent of EPA Region I, DOH and DEM. The report of all findings and recommendations are made promptly to the state. The systems audit includes areas in the laboratory and field programs immediately impacting overall quality assurance and call also include specific program grant requirements.

The laboratory participates in pesticide performance sample audits when available for a given program. The laboratory reserves the right to exclude samples that are not applicable to their cooperative pesticide program. The following performance check samples are provided by various sources:

- EPA/NEIC pesticide formulation and residue check samples
- AAPCO pesticide formulation check samples
- EPA performance check sample for pesticide residues in water

Unsatisfactory results are evaluated and, when possible, the analysis promptly repeated.

The Quality Assurance Officer shall perform [yearly] in-house systems audits to identify strengths, weaknesses, potential problems and solutions to problems. The audits provide an evaluation of the adequacy of the overall measurement systems to provide data of sufficient quantity and quality to meet the comprehensive laboratory pesticide program's objectives. The in-house systems audits are the basis for quality assurance reports to management (see Section 16).

The in-house systems audit consist of observing the various aspects of the pesticide project sampling and analytical activities. Check lists which delineate the critical aspects of each procedure are used during the audit and serve to document all observations. At a minimum, the following topics will be evaluated during the internal audit:

1. GENERAL PROCEDURES
  - A. Procedures for Sampling and Sample Documentation
  - B. Documentation of Procedures
  - C. Sample Receipt and Storage
  - D. Sample Preparation
  - E. Sample Tracking

## 2. INSTRUMENTAL METHODS

- A. General Instrumentation Procedures
- B. Calibration Procedures
- C. Internal Quality Control
- D. Data Handling Procedures

### **PREVENTATIVE MAINTENANCE**

The primary objective of a comprehensive maintenance program is to ensure the timely and effective completion of a measurement effort. Detailed preventative maintenance is described in the laboratory or field standard operating procedures (SOPs). It is designed to minimize the down time of crucial sampling and/or analytical equipment due to component failure. The focus of the program is in three primary areas:

- Establishment of maintenance responsibility
- Establishment of maintenance schedules for major and/or critical instrumentation and apparatus
- Establishment of an adequate inventory of critical spare parts and equipment.

The Quality Assurance Officer is responsible for maintenance of laboratory and instruments. Field equipment maintenance is the responsibility of the Field and Technical Services Quality Assurance Officer. With assistance from the Supervising Laboratory Scientist or a designated Senior Scientist, he or she establishes maintenance procedures and schedules for each piece of major equipment. Responsibility for individual items is delegated to technical personnel. The manufacturer's recommendations and/or the protocols for instrument maintenance and calibration are followed. Each piece of major equipment is designated a repair and maintenance logbook where all maintenance activities are dated and documented by laboratory or field personnel.

In the interest of maintaining instruments in top operating condition, it is management's policy to secure annual service contracts with instrument manufacturers whenever financially possible. The service contracts are especially desirable for laboratory instruments. Under the service contracts, certified service engineers perform preventative maintenance, calibration and repair for instruments. Laboratory personnel perform routine maintenance and repair between manufacturer's services to ensure correct performance of an instrument.

Certified service engineers service analytical balances at least once a year. In addition to performing repair and maintenance, the engineer calibrates and certifies each analytical balance. Laboratory personnel check the calibration of the balance with a class S weight at least four times a year.

Digital Ph meters are checked before each use with standards and calibrated according to the manufacturer's directions. Freezers and refrigerators are monitored to assure that proper temperatures are maintained and that failure has not occurred.

An adequate inventory of spare parts is maintained to minimize equipment down time. This inventory emphasizes those parts which:

- Are subject to frequent failure
- Have limited useful lifetime
- Cannot be obtained in a timely manner should failure occur.

### **SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS**

An objective of the laboratory is to demonstrate that performance on all pesticide analysis is in statistical control. Routine procedures used to assess reliability and quality of data are specified in the laboratory standard operating procedures (SOPs) and the National Enforcement Investigation Center (NEIC) Pesticides Sampling Guide. Formulation and residue sampling and analysis are addressed separately in the manual.

For formulation analysis, precision is established through replicate analysis on all potentially violative samples and all heterogeneous samples. Replicate sub samples are analyzed using separately prepared standards. Accuracy is established through confirmation analysis by a second analyst, use of officially/standard methodology and verification of calculations. If necessary, two or more methods and/or standards are used to confirm accuracy.

For residue analysis, replicates are used to establish precision, spike sample recoveries are used to establish accuracy and blanks are analyzed to assure non-interference from solvents, reagents and laboratory environment.

Precision refers to the reproducibility of replicate results about a mean, which is not necessarily the true value. Replicate analysis is the primary means of evaluating measurement data variability or precision. Two commonly used measures of variability which adjust for the magnitude of analyze concentration are coefficient of variation and relative percent difference.

The coefficient of variation is used most often when the size of the standard deviation changes with the magnitude of the mean. Coefficient of variation (CV), also called relative standard deviation (RSD), is defined:

$$CV = RSD = (s/y) \times 100\%$$

Where: y = mean of replicate analyses  
s = sample standard deviation, defined as:



$$S = \sqrt{\sum}$$

Where:  $y$  = measured value of the  $i$ th replicate  
 $\bar{Y}$  = mean of replicate analyses  
 $n$  = number of replicates

Sample standard deviation ( $s$ ) and coefficient of variation ( $CV$ ) are used when there are at least three replicate measurements.

The second measure of variability, which adjusts for the magnitude of the analyte, is relative percent difference (RPD) or relative range (RR). This measure is used when duplicate measurements are made and is defined:

$$RR = RPD = [(C - C) \times 100\% / (C + C)/2]$$

Where:  $C$  = larger of the two observed values  
 $C$  = smaller of the two observed values

Plotting control charts for repetitive analysis monitors precision. A warning limit of  $\pm 2s$  is established with a control limit of  $\pm 3s$  (see Section 5).

Accuracy is the nearness of a result to the true value and is often described as error, bias or percent recovery. Accuracy estimates are frequently based on the recovery of surrogate spikes and/or the recovery of known analytes. The percent recovery is calculated as:

$$\%R = 100\% \times (S - U/C)$$

where:  $\%R$  = percent recovery (of matrix or surrogate spikes)  
 $S$  = measured concentration in spiked aliquot  
 $U$  = measured concentration in unspiked aliquot  
 $C$  = actual concentration of spike added

When repetitive analysis provides sufficient data, accuracy control charts are plotted for each analyte and method and for each control sample matrix. The matrix of the control sample should match the matrix of the sample being analyzed as closely as possible. The warning and control limits are established at  $\pm 2s$  and  $\pm 3s$ .

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount expected to be obtained under correct, normal conditions. For all measurements, completeness is defined:

$$\%C = 100\% \times (V/n)$$

where: %C = percent completeness  
V = number of measurements judged valid  
n = number of measurements necessary to achieve a specified statistical level of confidence in decision making

To determine “n” a judgment must be made regarding the amount of data required to provide adequate evidence that a system is in control. Completeness is calculated for monitoring programs where similar analyses are performed on a regular basis. Loss of data due to such occurrence as breakage of containers, spilling of the sample, contamination, instrument failure or exceeding holding time before analysis must account for no more than 10% of all requested analysis. If excessive loss of data occurs, the reasons must be identified and evaluated and, if necessary, action must be taken to solve the problem(s).

### **CORRECTIVE ACTION**

Corrective action is taken whenever data is determined as unacceptable. Data may be determined unacceptable through comparison with pre-established quality control criteria, as a result of scientific evaluation by the Laboratory Manager, senior analyst(s) or Quality Assurance Officer, or through an apparent conflict of results with a second analyst or laboratory.

Corrective action is taken in the order listed below. The first are most likely to identify the source(s) of error:

- Review of sample collection procedures
- Review of analytical raw data and calculations
- Review of laboratory procedures – Was the analytical method followed?
- Review of analytical method – Is it applicable?
- Review of instrument operation, calibration and maintenance
- Review of the calibration standard(s) used
- Review of quality control measurement (spike, duplicate, etc.).

As a result of the above review, further corrective action may be identified and pursued as necessary:

- Repeat the sampling and corresponding documentation
- Issuing an amended analytical report
- Repeat analysis (confirmation methods)
- Repair, recalibration or replacement of instrumentation
- Additional training of staff.

Persistent problems require a thorough review of all field and analytical data (including quality control measurements and procedures), increased check sample and reference

material analyses and additional field and/or analytical system evaluations by outside agencies or individuals.