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Office of Pesticides and Toxic Substances (H-7501C)
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QUALITY ASSURANCE PROJECT PLAN FOR THE NATIONAL PESTICIDE SURVEY OF DRINKING WATER WELLS ANALYTICAL METHOD 5 - METHYL CARBAMATES

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OLS #1993-570

NATIONAL PESTICIDE SURVEY
QUALITY ASSURANCE PROJECT PLAN FOR
ANALYTICAL METHOD 5 - METHYL CARBAMATES

2. TABLE OF CONTENTS

2. TABLE OF CONTENTS (continued)

3. PROJECT DESCRIPTION

The National Pesticide Survey is intended to assess the extent and nature of pesticide presence in well waters used in private and community water supply systems. The statistical design of the survey will suggest from a manageable number of samples and analyses the nature of pesticide presence in such water supplies throughout the nation.

Environmental Science and Engineering, Inc. (ESE) of Gainesville, Florida, has contracted with the U.S. Environmental Protection Agency (EPA) to analyze the collected water samples for carbamates (Method 5) and halogenated fumigants (Method 7). This project plan applies to Method 5, the determination of aldicarb, aldicarb sulfone, aldicarb sulfoxide, baygon, carbaryl, carbofuran, 3-hydroxy-carbofuran, methiocarb, methomyl, and oxamyl in ground waters. Method 5 involves direct injection of an aliquot of the water sample, high-pressure liquid chromatographic separation, derivatization, and fluorescence detection and quantitation. Positive results will be confirmed by second column analysis. Method 5 is an adaptation of EMSL Method 531.1, "Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates in Water by Direct Aqueous Injection HPLC with Post Column Derivatization" (Appendix A).

4. PROJECT ORGANIZATION AND RESPONSIBILITIES

The project staff is specified in ESE's proposal to perform the contract. The project organization chart is given in Exhibit 4-1.

The managing staff are:

Paul C. Geiszler	Project Director
Michael G. Winslow	Project Manager and Technical Contact
Portia O. Pisigan	Quality Assurance Coordinator
Virgina C. O'Brien	Data Management and Sample Control
Bradley A. Weichert	Manager, GC/HPLC Department
W. Scott Keeran	Associate Scientist, Lead Chemist

Certain specific project assignments are handled by others:

Vince Prem-Das	Sample Check-in
D. Michael Ritter	Computer Sample Check-in and Data File Generation
Scott Poole	Sample Custody and Coldroom Support

Samples will generally be received by Vince Prem-Das, ESE, 14220 Newberry Road, Gainesville, FL, 32607; phone (904) 332-3318. It will generally be necessary to ask the ESE switchboard to page Mr. Prem-Das. In his absence, ask for Michael G. Winslow, Project Manager.

The EPA Technical Monitor (primary contact) for Method 5 matters is R. Kent Sorrell, phone (513) 569-7943. The EPA Project Officer is David J. Munch.

EXHIBIT 4-1

PROJECT ORGANIZATION CHART

EPA TECHNICAL MONITOR
K. Sorrell

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ESE PROJECT DIRECTOR
P. Geiszler

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ESE PROJECT MANAGER
M. Winslow

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.

ESE DATA MANAGEMENT	ESE QA COORDINATION
V. O'Brien	P. Pisigan

.
.
.

METHOD 5	ESE TASK MANAGEMENT	METHOD 7
B. Weichert		G. Jackson

.
.
.

HPLC	ESE ANALYSIS	GC
W. Keeran		J. Yeh

5. QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The "estimated detection limit" (EDL) for Method 5 will be determined as follows:

1. Determine the concentration of each analyte which, when injected, yields a 5:1 signal-to-noise ratio, measured as the ratio of the center chromatographic peak height to the edge-to-edge height of the noise envelope.

2. Spike eight HPLC-grade water samples at the concentration determined in 1. and analyze together.

3. Calculate the Estimated Detection Limit (EDL) by multiplying the standard deviation of the concentrations from 2. by the Student t-value 2.998 (7 degrees of freedom, alpha = 0.99, one-sided).

4. The EDL is the greater of the values calculated in 1. and 3.

5. The EDL shall be evaluated by the Technical Monitor.

6. Target EDLs shall be supplied to ESE by the Technical Monitor.

7. Analyze the eight sample aliquots of 2. on the confirmatory column and calculate EDLs as in 1 and 3. The resulting EDLs must roughly equal those of the primary column.

8. GC/MS analyses is not part of Method 5 confirmation.

9. Minimum Reporting Levels (MRL) are 3 times the EDL for each analyte.

10. Report as an occurrence (code -111) any peak matching an analyte retention time at responses between one-half the MRL and the MRL. Such frequent occurrences may lead to confirmations and/or adjustment in the reporting limit. Frequent occurrences of non-analyte peaks will be reported to the Technical Monitor. Criteria for reporting these non-analyte peaks will be supplied by the EPA (Appendix B).

11. The lowest standard solution concentration will approximately equal the MRL for all analytes.

12. Initial demonstration of method performance will be accomplished by the analysis of 20 spiked samples at 10 times the MRL over a four day period (five spiked samples per day). Mean recovery, variance and the standard deviation will be calculated. Relative standard deviation (RSD) will be used to evaluate the precision of the method using the acceptance criteria provided by the EPA.

13. The criteria values will be reviewed by the Technical Monitor.

Samples having any analyte concentration above that analyte's reporting limit will be confirmed on a different HPLC column (see Section 9).

Performance evaluation samples will be analyzed quarterly as part of the overall NPS QA program. The Technical Monitor will work with ESE to resolve any problems discovered as a result of these analyses.

Results from all of the above procedures in this Section will be reported to the Technical Monitor for approval. Data from the Initial Demonstration of Method Performance is appended to this Plan.

During the survey, EPA will conduct a time-storage study and will provide extra field samples (10% of sites) for ESE to assess analyte recoveries from a variety of matrices. Each sample will be spiked with a stock solution in methanol to yield sample concentrations of 2, 10 or 20 times the reporting limit for each analyte (the surrogate will also be added) (Appendix C). This sample will be analyzed and the data reported as a percent recovery. This data is not for laboratory control, and the analysis will be judged to have failed only if the extra sample's surrogate recovery fails the criterion for a regular sample.

6. SAMPLING PROCEDURES

All samples for Method 5 will be received in 250 mL bottles. Samples for Method 5 will include pH 3 buffer and will be shipped iced for overnight delivery. Every set received from a field site will include the following: primary samples and one backup sample for each primary sample. Some sets will include time-storage samples. Some sets (about 10%) will include lab-spike samples (ESE matrix-spikes).

Analysis types and frequency are described on the next page.

The analysis types for Method 5 are:

Primary Analysis:

Method Blank	1 per set	Not chargeable
Calibration Standards	daily	Not chargeable
Field Sample	1 per ESE sample no.	Chargeable
Lab Spike (ESE Matrix Spike)	10%	Chargeable
Day 0 Time-Storage Sample	10%	Chargeable
Day 14 Time-Storage Sample	10%	Chargeable
Performance Evaluation Sample	quarterly	Chargeable
Backup Sample	(a)	(a)

Confirmational Analysis:

Method Blank	1 per set	Not chargeable
Calibration Standards	daily (when conf. is performed)	Not chargeable
Field Sample	(b)	Chargeable

(a) Analyzed when results of initial analysis fails (not chargeable) or at request of Technical Monitor (chargeable).

(b) Analyzed when results of primary analysis are above min. reporting limit.

Each sample's shipping label will be of the form below.

NATIONAL PESTICIDE SURVEY - NPS

PD-0415-4-5-6 DATE 2-11-88

ESE - #5 - T/S_0

SAMPLER NAME _____

The sample bottle number (**PD-0415-4-5-6** in the above example) is constructed as follows:

PD	Pesticide Survey Domestic Well
PC	Pesticide Survey Community Well
PR	Pesticide Survey Resampled Site
PB	Pesticide Survey Performance Evaluation Sample
0415	is the site number
4	is the ESE lab number
5	is the carbamates method number
6	is the bottle number within this site number

The analysis type codes are given below:

FS	**F**ield **S**ample
FD	**F**ield **D**uplicate
BU	**B**ackup **S**ample
LS	**L**ab **S**pike (ESE Matrix Spike; "LS" may be followed by a numeric digit which indicates spike level)
T/S	**T**ime **S**torage (t = 14 days)
T/S_0	**T**ime **S**torage Duplicate (t = 0 days)
T/S_{14}	**T**ime **S**torage Duplicate (t = 14 days)

The sampling contractor will supply a copy of the field sample tracking sheet used for NPS samples.

The spiking solution is prepared fresh daily in chloroacetic buffered water and is prepared from a primary acetonitrile stock. The lab spike is prepared by adding the appropriate volume of the spiking stock (A0 = 200 uL; A1 = 500 uL; A2 = 1000 uL) to 250 uL of 2.5 M chloroacetic buffer and enough HPLC water to yield a final volume of 25.0 mL. Then 10 mL of this solution is filtered through a 0.45 uM Acrodisc filter and spiked with 100 uL of the internal standard. All lab spikes are analyzed on the same day that they are prepared.

In addition, the time storage samples are prepared in exactly the same manner as the above lab spikes. The Day 14 time storage samples are then transferred to a 40 mL amber VOA bottle and stored in the freezer. On the day of analysis, the sample is thawed, filtered, and spiked with the internal standard.

Using the above spiking schemes, the solutions should correspond to: A0 = 2 x MRL; A1 = 5 x MRL; A2 = 10 x MRL.

7. SAMPLE CUSTODY

The sampling contractor (ICF) will supply information about sample shipments and the protocol ESE will follow to notify the sampling contractor about sample receipt and any problems associated with samples received (Appendix D). The project Technical Monitor will also be notified concerning problems with the receipt of samples from the sampling contractor (ie. no ice, incorrect pH, etc).

Holding times for samples to be analyzed by Method 5 are: 14 days maximum holding time for samples, counting day of sampling as Day 0. Upon receipt of samples at the laboratory, a portion of the sample will be removed to facilitate freezing and for pH measurement using disposable pH test strips. Samples will be stored frozen in the dark. Sample disposal will be handled in accordance with Florida regulation.

A series of time storage samples will be collected and analyzed during the NPS study to determine the stability of the compounds in aqueous solution and in the extraction solvent. These samples will be collected at a frequency of 10% over the period of the study.

Four extra aliquots of the samples for the time storage will be collected. Two of the four replicate aliquots will be spiked and analyzed within 4 days of spiking and prior to the 14 day holding time. The remaining two duplicates will be spiked at the same time as the first two duplicates, but will be allowed to sit 14 $\pm$ 4 days before analysis.

Each sample will be spiked with only one mix at the 10X MRL level. Results of the time storage samples will be reported to EPA along with the corresponding regular sample. For data reporting purposes, Day-0 samples (spiked and analyzed within 4 days of spiking) will be referred to as Day-0 Time Storage (DTS). These samples serve a dual role, as lab spikes and DTS. Day-14 time storage samples (spiked and held for 14 $\pm$ 4 days before analysis) will be referred to as Holding Time Samples (HTS). All of the holding time samples will be analyzed in duplicate.

When samples are received at the ESE Receiving Station, 14420 Newberry Road, Gainesville, FL, the receiving employee will deliver the samples to Vince Prem-Das at the sample check-in station, the Hendrickson building. Mr. Prem-Das will then mark the NPS sample tracking form with the required information, and submit the logsheets to Data Management. A Data Management employee will enter the sample information to ESE's database, a process which automatically generates Sample Arrival Notices for the Method 5 Task Manager. The GC/HPLC department schedules the analyses, performs them within the 14-day holding times, and enters the analytical data into the ESE database.

All ESE coldrooms, refrigerators, and freezers holding samples for chemical analysis are monitored daily by ESE personnel, and records are kept daily.

8. CALIBRATION PROCEDURES AND FREQUENCY

The instrumental analysis for Method 5 will be performed on a HPLC instrument including an Shimadzu Gradient HPLC System: 2 LC-6A pumps, SCL-6A system controller, SIL-6A autoinjector, a Kratos post-column reactor, a Shimadzu RF535 fluorescence detector, and a PE/Nelson chromatography data acquisition system. Primary analytical separations will be performed on Waters Nova Pak ODS columns (25 cm length, 4.6 mm ID, 5 micron particle size) or equivalent, and secondary analytical separations will be performed on Supelcosil LC-1 columns (25 cm length, 4.6 mm ID, 5 micron particle size). The mobile phase gradient program will be that described in Method 5 which is appended to this Plan.

ESE analysts will prepare standard solutions in water/chloroacetic acid buffer from dilutions of EPA concentrate solutions at the onset of each analytical set and will keep detailed records of the means used to prepare them on each occasion. Spiking concentrates will be generated by separate dilutions from those used to generate standard solutions. Records of the generation of standards will be kept by the analyst in his permanent notebook. Each set's analytical records will refer to the standard solutions actually used in that day's analysis. New standard dilutions will be checked to insure that the QC criteria, $\pm$ 20% of initial calibration, is met.

ESE plans to calibrate the instrument each day a set is analyzed using a calibration standard concentration chosen, on a rotating basis, from the standard curve. The lowest calibration standard will be at the MRL. The standard relative response must agree within $\pm$ 20% of the previous set's calibration relative response.

For second column confirmation, a single calibration standard will be used for quantitation. The standard will contain analytes at concentrations near that detected during primary analysis. Results of second column confirmation will be within $\pm$ 25% of the primary analysis result. If this criteria is not met the project Technical Monitor will be advised.

9. ANALYTICAL PROCEDURES

Samples will be thawed and brought to room temperature in a warm water bath prior to analysis. The primary analysis begins with the addition of internal standard to an aliquot of water sample. Gradient elution down the reverse-phase HPLC column separates the analytes and other components, and analytes are detected as follows: the analytes are hydrolyzed with 0.05 N sodium hydroxide at 95 °C, the resulting methylamine is reacted with ortho-phthalaldehyde (OPA) and 2-mercaptoethanol, and the resulting highly fluorescent derivative is detected in the flow cell of a fluorescence detector. In confirmatory analysis, the sample aliquot is eluted down a somewhat different column, detection in the same manner verifies or rules out any positive results from the primary analysis.

Primary and confirmatory analyses are performed on an Shimadzu high-pressure liquid chromatograph equipped with a Kratos post-column reaction cell, a Shimadzu fluorescence detector (excitation wavelength = 235nm, emission wavelength = 435nm), and a PE/Nelson chromatography data acquisition system. All data will be transferred to the Chemistry Division database running on 65 AT-class computers served by a 3-drive, 1600-Mbyte Novell network housed in the Chemistry Division.

ESE plans to include no more than 24 field samples in a set (16 hour run), and generally fewer.

ESE plans no significant differences from Method 5, revision dated October 27, 1987 (attached) as provided to ESE in glassware cleaning, reagents, or data reduction. Differences in equipment are listed above in this Section. In the analytical procedure, ESE plans to use Waters Nova Pak ODS columns for the primary analysis and Supelcosil LC-1 columns for the confirmatory analysis.
Any deviations from these procedures or QC requirements after the Plan is approved will only be used if approved by the EPA Technical Monitor in advance. Changes will be documented, signed by the Technical Monitor and appended to the Plan.

10. DATA REDUCTION, VALIDATION REPORTING

Calibration standard concentrations and raw instrument responses for calibration standards and sample aliquots are entered into the ESE Chemistry Division's database. ESE data management will support new in-house sample type codes that the numerous EPA sample types require. The analyst will generate ESE set reports and will verify correct entry and QC data compliance with project criteria. When Data Management receives a signed copy of the set report, they will generate a data file on floppy disk in the NPS format. The project manager will then examine a listing or summary of the file and approve delivery of the floppy disk to EPA.

All data for a set of samples (including QC and confirmatory data) will be reported to the EPA no later than two months from the date of sample collection.

The NPS file format is appended to this Plan (Appendix E, F and G).

Fast Track Reporting (immediate telephone call to the Technical monitor) will be needed for confirmed positive sample concentrations of selected EPA analytes above health advisory levels and situations when results from confirmation columns do not agree with results from primary columns within criteria set by EPA ($\pm$ 25%) (Appendix H.).

Storage of laboratory data will be by ESE standard procedures. Standards and reagent preparation data will reside in the analyst's permanent laboratory notebook. Chromatograms, calibration data, and corrective action records, etc. will reside in an analysis set folder which will be stored permanently in ESE's central filing system. ESE set folders will reside in archival files in ESE's central filing system after all samples have been analyzed.

11. INTERNAL QUALITY CONTROL CHECKS

No lab control spikes are required for Method 5. Analytical quality will be controlled largely by five means:

- Each set will include a chromatogram of a standard, selected on a rotating basis from the calibration standards. The response factors for the standard must be within ± 20 percent (%) of the initial calibration. If the response factors fall outside the ± 20% criteria, the standard will be reanalyzed, if the response factor is still outside the criteria a new initial calibration will be performed.

- Each set's method blank must have analyte responses less than half the minimum reporting limit.

- Internal standard response (peak area) for each sample must be within 20% of the internal standard response from that day's calibration standard.

- The instrument performance sample will meet the criteria described in Method 5, Section 10.8., Table 10.

- If the relative responses of the analytes in each set's standard chromatograms appear to the analyst to have changed significantly (± 20%) from those of the previous set, he will make new standard solutions from the EPA concentrates. The stability of Method 5 analytes suggests that this may be a very unusual occurrence.

- Any analyte detected above the MRL in the primary analysis will be re-analyzed on the confirmation column. Results of the confirmation analysis must agree within ± 25% of the primary analysis. Any deviation from this criteria will be reported to the project Technical Monitor.

No laboratory control standards will be analyzed, and surrogates are not used. The internal standard, 4-bromo-3,5-dimethylphenyl-N-methyl-carbamate (BDMC), supplied by USEPA, will be added to every sample, standard, and method blank before analysis. Internal standard recovery must be evaluated for every sample by determining whether the measured peak area for the internal standard in any sample or method blank deviates by more than 20% from the peak area for the internal standard in that day's calibration standard. In case of such disagreement, reinject the sample. If the second analysis still shows disagreement, add internal standard to a second aliquot of the sample and reanalyze.

However, if more than one sample shows disagreement with the internal standard response of the calibration standard, reanalyze the instrument performance standard, the calibration standard, and the samples which showed the disagreement. If the disagreement still persists, contact the Technical Monitor.

A method blank is analyzed daily. If any analyte is present at half or more of the MRL, the test is considered to have failed, and a new method blank will be generated and analyzed. A second consecutive method blank failure will require in-lab corrective action and reanalysis starting with instrument performance standard and calibration standards.

Each day that NPS Method 5 samples are analyzed, an instrument performance sample will be analyzed and the instrument sensitivity (signal to noise ratio), chromatographic performance (peak symmetry factor and peak gaussian factor), and the column performance (resolution) will be monitored as described in Method 5.

During confirmational analyses, a method blank and standard will be analyzed prior to analysis of samples. All quality control criteria which apply to the primary analysis, with the exception of the instrument performance standard, will also apply to the confirmational analysis. All confirmation data and QC data will be stored with the set in which the field sample number resides.

ESE plans to have in place an NPS option in the ESE set report program. This option will check that all QC is performed, just as is done for all batches currently reported under ESE's standard QC program.

Exhibit 11-1 presents ESE's Internal Quality Control Checklist.

Since (1) ESE will demonstrate its capability to accurately perform Method 5, (2) the instrumental analysis will most often be performed within only hours of first opening the sample bottle, (3) EPA will be sending check samples, (4) the internal standard response on each sample will be controlled, (5) the instrument performance sample will be analyzed in each set, and (6) the above QC checks will be performed on each set, ESE considers the above program sufficient to assure the quality of the data and does not propose additional QC checks.

Quality-Control Corrective Actions - Failure to meet QC criteria specified in this QA plan. Actions consist of two kinds: those resolved within each analytical department by reanalysis, etc.; and those resolved outside the department. All corrective actions will be reported to EPA's Technical Monitor.

EXHIBIT 11-1

INTERNAL QUALITY CONTROL CHECKLIST

U. S ENVIRONMENTAL PROTECTION AGENCY
NATIONAL PESTICIDE SURVEY
METHOD 5

INTERNAL QUALITY CONTROL CHECKS

EPA SET No._____ ESE BATCH No._____

DATE ANALYZED_____ ANALYST_____

		YES	NO
1.	CHROMATOGRAM OF DAILY STANDARD INCLUDED	_____	_____
2.	METHOD BLANK (< 0.5 Minimum Reporting Limit)	_____	_____
3.	INTERNAL STANDARD RESPONSE (Peak Area) (Each Sample ± 20% of Daily Standard)	_____	_____
4.	INSTRUMENT PERFORMANCE SAMPLE		
	A Sensitivity (Signal/Noise > 3.0)	_____	_____
	B Chromatographic Performance	_____	_____
	(1) Peak Symmetry Factor (PSF) (0.9<PSF<1 1)	_____	_____
	(2) Peak Gaussian Factor (PGF) (0.9<PGF<1.1)	_____	_____
	C. Column Performance (Resolution > 1.0)	_____	_____
5.	DAILY STANDARD ANALYTE RESPONSE (Each Analyte ± 20% of Previous Daily Std.)	_____	_____
6	CONFIRMATION (± 25 % of Primary Analysis)	_____	_____

COMMENTS:_____

_____

_____

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_____

QUALITY ASSURANCE COORDINATOR_____ DATE_____

PROJECT MANAGER_____ DATE_____

12. PERFORMANCE AND SYSTEM AUDITS

ESE's Quality Assurance Division, independent of the Chemistry Division and reporting directly to the ESE president, will perform audits of the following types:

- Observation of the analyst analyzing samples during the initial demonstration of capabilities and approximately quarterly thereafter. This audit will include verification that no significant changes have occurred in procedure, instrumentation, analytical environment, or in sample and reagent storage and labelling. The auditor will select items for audit from this QA Plan at his discretion and generally without warning to the analyst. Retrievable errors (those affecting no data yet sent to EPA), will be corrected immediately and a means of assuring its long-term rectification established. Irretrievable errors will prompt written notice to the EPA Technical Monitor.

- Examination of a data set, especially QC and instrument performance parameters. This will be performed in detail during the initial demonstration of capabilities and approximately quarterly thereafter. The latter examinations will be performed on randomly selected data sets. The auditor may question the analyst at his discretion. However, the analyst may postpone for up to 10 working days a prolonged conference with the auditor if (1) the analyst or his department manager considers the current backlog of samples, especially those near holding times, to be too great to allow immediate consideration of the auditor's questions AND (2) if the auditor's questions do not concern data due within a few working days.

In addition to the above in-house audits, EPA will perform audits of the data and systems as the pertain to NPS Method 5. EPA audits will be scheduled approximately every six months during the conduct of Method 5 analyses. ESE will cooperate with the EPA auditor to the extent that the audit does not interfere with the laboratories ability to continue with routine operation.

13. PREVENTIVE MAINTENANCE

The instrumentation ESE specifies for the performance of Method 5 requires little preventive maintenance.

- Check valves will be replaced as needed.
- Pumps are tested for flow rate accuracy when, (1) the analyte retention times change between analytical sets or (3) the pumps are changed or serviced.
- Analytical columns will be protected by use of 3 to 5 cm length pellicular guard columns. Guard columns will be changed when deterioration of the analytical column chromatography (e.g. poor peak shape, loss of resolution, etc.) becomes evident.
- Spare columns, guard-column packing material, instrument cables, and some PC boards are kept to minimize instrument downtime.

14. SPECIFIC PROCEDURES for ASSESSING MEASUREMENT SYSTEM DATA

Relative response of each analyte is calculated as

$$RR_a = A_a / A_{is}$$

where: A_a = peak area of the analyte, and

A_{is} = peak area of the internal standard from the same chromatogram.

During initial demonstration of capabilities, the mean recovery is calculated as the sum of recoveries divided by the number of recoveries included in the sum. The variance is calculated as the sum of the squares of differences between each recovery and the mean recovery, divided by the number of recoveries less one. The standard deviation is the square root of the variance. The relative standard deviation (RSD) is calculated to evaluate precision performance. RSD is calculated as:

RSD = (standard deviation of recoveries/mean recovery) X 100

Each sample's chromatogram's internal standard response (peak area) must be within a range of 0.8 to 1.2 times the mean internal standard response for that day's calibration curve chromatograms.

As mentioned in Section 11, a single standard will be analyzed daily as a check of instrument sensitivity.

Responses of peaks corresponding to the analytes of interest found in the samples (peak area >1/2 MRL) will be subtracted from the responses of analytes found in the spiked samples to correct for concentrations of analytes present in the sample prior to spiking. Found concentrations in the spiked samples will be divided by the "true" value and multiplied by 100 percent to calculate recovery.

An instrument quality control standard will be analyzed with each analytical set and the criteria listed in Method 5, Table 10 will be used to assess instrument performance. Due to coelution of methiocarb and the internal standard on the confirmation, the resolution test can not be performed on this column.

15. CORRECTIVE ACTION

In general, bench-level corrective actions fall into two categories each with differing required action.

- Short-Term Action - Major and minor problems which can be corrected immediately. Examples include failure to date or sign a field form and date entry errors. Generally, the analyst or other employee committing the error can simply correct it, and the record of this corrective action will directly reflect the error and its resolution.

- Long-Term Corrective Action - Minor and major problems which require a series of actions to resolve the problem. Examples include a discovery that part of the analytical or data-handling procedures were not being followed correctly. The actions to be taken are coordinated by the QA Supervisor or his designate, and a QA corrective action and routing form (Figure 15-1) is used to track the action. These corrective actions and their resolutions will be included in monthly reports to EPA.

EXHIBIT 15-1

QUALITY ASSURANCE CORRECTIVE ACTION AND REQUEST FORM

QUALITY ASSURANCE CORRECTIVE ACTION REQUEST AND ROUTING FORM

1. Identification of a Problem: Date:

   Originator:

   Nature of Problem:

2. Determination of Required Action:

   Responsibility Assigned to: Due Date:

   Recommended Action:

3. Implementation of Required Action:

   Responsibility Assigned to: Due Date:

4. Assuring Effectiveness of Action:

   Responsibility Assigned to : Due Date:

   Procedure to assure Effectiveness:

16. QUALITY ASSURANCE REPORTS TO MANAGEMENT

QA activities are reported to management by the QA Coordinator in three ways:

1. Verbal notification of significant QA deficiencies immediately upon discovering the problem,

2. Written interim QA reports, and

3. Written final QA reports.

A final QA report will be prepared for this project. Interim reports will be prepared at the request of ESE management, the Project Manager, or the Contracting Officer.

The contents of interim and final QA reports will be similar except final reports will include summaries of the interim reports.

The following items will be addressed in the reports:

1. An assessment of the precision and accuracy data associated with sample data generated during the report period.

2. Results of all QA audits performed during the report period.

3. Results of the QA data validations performed during the report period.

ESE will send monthly reports to the EPA Technical Monitor. These reports will be in the following format:

- Summary of progress - samples received and samples analyzed, but not validated and status of data processing for analyzed sets of samples and numbers for sets of data sent to the EPA
- Reports on standards - new dilutions and results of checks before using
- Summary list of bench - level corrective actions (as in Section 15 of this Plan).
- Identification of problems about any phase of the project.
- Copies of representative and, if applicable, unusual chromatograms (as requested by Technical Monitor).
- Information requested by the Technical Monitor because of specific methodology or problems encountered.
- Changes in personnel.
- Comments

17. ARCHIVAL OF RAW DATA

In order to assure the continued availability of all documentation necessary to defend NPS Method 5 analytical results, the documentation for each analytical set will be contained in a separate orange file folder and will be comprised of the following:

- HPLC set documentation checklist
- Method 5 internal quality control checklist
- A hard copy of the NPS formatted results
- A hard copy of ESE's formatted results
- All chromatograms and quantitation reports for the following:
  - -- Field samples
  - -- Blanks
  - -- Calibration standards
  - -- Instrument performance standard
  - -- Time-storage samples
  - -- Lab spike samples
- Chromatographic Analysis logsheets
- Instrument logsheet(s)
- Internal Standard Recovery summary
- Copies of NPS sample tracking forms
- Copies of analyst notebook pages
- Standard Curve data sheet
- Instrument Configuration sheet

All set file folders will be stored in banker's boxes. Each box will be labeled with number, a description of its contents (NPS Method 5 set files), a listing of set numbers, the date placed in storage, and the date to be destroyed.

A separate banker's box will contain the following, and be labeled as described above:

- A copy of the QA Project Plan
- Monthly reports to the Technical Monitor
- Original NPS sample tracking forms with original Fed Ex airbills
- Correspondence to and from EPA
- Laboratory data from initial demonstration of capabilities and demonstration of accuracy and precision
- Miscellaneous documentation such as audit reports, internal memos, temperature logs, etc.
- Resumes of NPS participants

All banker's boxes containing the NPS files will be stored for a period of seven years in the Dead File Storage room located in the Maintenance building at ESE's Gainesville location. This room is kept locked at all times and access is limited to its custodian, Virginia O'Brien, Manager of the Information Services Department of ESE's Gainesville laboratory.

A Dead File Storage logsheet listing the same information that is written on bankers boxes will be kept with the storage room custodian and a copy will be sent to the EPA Technical Monitor. In addition, a list of all samples analyzed will be prepared, with cross references to the NPS set number, the ESE batch number, and the ESE internal sample number.

Appendix J provides a copy of ESE's standard operating procedure for batch storage of data. Any changes to the archival procedures described above will be communicated in writing to the Technical Monitor.

APPENDIX A

METHOD 5. MEASUREMENT OF N-METHYLCARBAMOYLOXIMES AND N-METHYLCARBAMATES IN GROUND WATER BY DIRECT AQUEOUS INJECTION HPLC WITH POST COLUMN DERIVATIZATION

Method 5. Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates in Ground Water by Direct Aqueous Injection HPLC with Post Column Derivatization

1. SCOPE AND APPLICATION

1.1 This is a high performance liquid chromatographic (HPLC) method applicable to the determinations of certain N-methylcarbamoyloximes and N-methylcarbamates in ground water. Analytes that can be determined using this method are listed in Table 1.

1.2 This method has been validated in a single laboratory. Estimated detection limits (EDLs) have been determined and are listed in Table 3. Observed detection limits may vary between ground waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of liquid chromatography and in the interpretation of liquid chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 10.2.

1.4 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications must be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

2.1 The water sample is filtered and a 400-µL aliquot is injected into a reverse phase HPLC column. Separation of the analytes is achieved using gradient elution chromatography. After elution from the HPLC column, the analytes are hydrolyzed with 0.05 N sodium hydroxide (NaOH) at 95°C. The methyl amine formed during hydrolysis is reacted with o-phthalaldehyde (OPA) and 2-mercaptoethanol to form a highly fluorescent derivative which is detected by a fluorescence detector.[1]

3. DEFINITIONS

Artificial ground water -- an aqueous matrix designed to mimic characteristics of a real ground water sample. Artificial ground waters should be reproducible for validations performed in other laboratories.

Calibration standard -- a known amount of a pure analyte, dissolved in an organic solvent, that is analyzed under the same procedures and conditions that are used to analyze samples containing that analyte.

Estimated detection limit (EDL) -- the minimum concentration of a substance that can be measured and reported with confidence that the analyte concentration is greater than zero as determined from the analysis of a sample in a given matrix containing the analyte.

Field duplicates -- two samples, collected at the same site, that are treated exactly the same throughout field and laboratory analytical procedures. Analysis of field duplicates provides a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

Instrument quality control (QC) standard -- an aqueous solution containing specified concentrations of specified analytes. The instrument QC standard is analyzed each working day prior to the analysis of sample extracts and calibration standards. The performing laboratory uses this solution to demonstrate acceptable instrument performance in the areas of sensitivity, column performance, and chromatographic performance.

Internal standard -- a pure compound added to a sample in a known amount and used to calibrate concentration measurements of other analytes that are sample components. The internal standard must be a compound that is not a sample component.

Laboratory control standard -- a solution of analytes prepared in the laboratory by dissolving known amounts of pure analytes in a known amount of reagent water. In this method, the laboratory control standard is prepared by adding appropriate volumes of the appropriate standard solution to buffered reagent water.

Laboratory reagent blank -- an aliquot of buffered reagent water, filtered, and analyzed as if it were a sample.

Quality control check sample -- a water-soluble solution containing known concentrations of analytes prepared by a laboratory other than the laboratory performing the analysis. The performing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method. A small measured volume of the solution is added to a known volume of buffered reagent water and analyzed with procedures identical to those used for samples. True values of analytes are known by the analyst.

Stock standard solution -- a concentrated solution containing a certi-fied standard that is a method analyte, or a concentrated solution of an analyte prepared in the laboratory with an assayed reference compound.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in liquid chromatograms. Specific sources of contamination have not been identified. All reagents and apparatus must be routinely demon-strated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 10.6.1.

4.1.1 Glassware must be scrupulously cleaned.[2] Clean all glass-ware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 450°C for 1 hour. Do not heat volumetric ware. Thermally stable materials might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

4.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. A preventive technique is between-sample rinsing of the sample syringe and filter holder with two portions of reagent water. After analysis of a sample containing high concentrations of analytes, one or more laboratory reagent blanks should be analyzed.

4.3 Matrix interference may be caused by contaminants that are present in the sample. The extent of matrix interference will vary considerably from source to source, depending upon the ground water sampled. Positive identifications must be confirmed using the confirmation column specified in Table 2.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current

awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[3-5] for the information of the analyst.

6. APPARATUS AND EQUIPMENT (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLING EQUIPMENT

6.1.1 Grab sample bottle -- 60-mL screw cap vials (Pierce No. 13075 or equivalent) and caps equipped with a PTFE-faced silicone septa (Pierce No. 12722 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the septa to air dry at room temperature, place in a 105°C oven for 1 hour, then remove and allow to cool in an area known to be free of organics. Heat vials at 400°C for 1 hour to remove organics.

6.2 Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.3 FILTRATION APPARATUS

6.3.1 Macrofiltration -- to filter derivatization solutions and mobile phases used in HPLC. Recommend using 47 mm filters (Millipore Type HA, 0.45 μm for water and Millipore Type FH, 0.5 μm for organics or equivalent).

6.3.2 Microfiltration -- to filter samples prior to HPLC analysis. Use 13 mm filter holder (Millipore stainless steel XX300/200 or equivalent), and 13 mm diameter 0.2 μm polyester filters (Nuclepore 180406 or equivalent).

6.4 SYRINGES AND SYRINGE VALVES

6.4.1 Hypodermic syringe -- 10-mL glass, with Luer-Lok tip.

6.4.2 Syringe valve -- 3-way (Hamilton HV3-3 or equivalent).

6.4.3 Syringe needle -- 7 to 10-cm long, 17-gauge, blunt tip.

6.4.4 Micro syringes -- various sizes.

6.5 MISCELLANEOUS

6.5.1 Solution storage bottles -- Amber glass, 10- to 15-mL capacity with TFE-fluorocarbon-lined screw cap.

6.5.2 Helium, for degassing dissolved oxygen.

6.6 HIGH PERFORMANCE LIQUID CHROMATOGRAPH (HPLC)

6.6.1 HPLC system capable of injecting 200 to 400-µL aliquots, and performing binary linear gradients at a constant flow rate.

6.6.2 Primary column -- 250 mm x 4.6 mm I.D. stainless steel packed with 5 µm Altex Ultrasphere ODS. Validation data presented in this method were obtained using this column. Alternate columns may be used in accordance with the provisions described in Section 10.2.

6.6.3 Confirmation column -- 250 mm x 4.6 mm I.D. stainless steel packed with 5 µm Supelco LC-1.

6.6.3 Detector -- Post column derivatization detector composed of a post column reactor and a fluorescence detector. This detector has proven effective in the analysis of spiked reagent and artificial ground waters. The post column derivatization detector (PCD) was used to generate the validation data presented in this method. A block diagram of the PCD is shown in Figure 2.

6.6.3.1 Post column reactor -- Capable of mixing reagents into the mobile phase. Reactor should be equipped with pumps to deliver 0.1 to 1.0 mL/min of each reagent; mixing tees; two 1.0-mL delay coils, one thermostated at 95°C; and constructed using PTFE tubing (Kratos URS 051 and URA 100 or equivalent).

6.6.3.2 Fluorescence detector -- Capable of excitation at 230 nm and detection of emission energies greater than 418 nm. A Schoffel Model 970 fluorescence detector was used to generate the validation data presented in this method.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 Reagent water -- reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., 1801 Lone Eagle St., Columbus, Ohio 43228.

7.2 Methanol -- Distilled-in-glass quality or equivalent.

7.3 HPLC MOBILE PHASE

7.3.1 Water -- HPLC grade (available from Burdick and Jackson).

7.3.2 Methanol -- HPLC grade. Filter and degas with helium before use.

7.4 POST COLUMN DERIVATIZATION SOLUTIONS

7.4.1 Sodium hydroxide, 0.05 N -- Dissolve 2.0 g of sodium hydroxide (NaOH) in reagent water. Dilute to 1.0 L with reagent water. Filter and degas with helium just before use.

7.4.2 2-Mercaptoethanol (1+1) -- Mix 10.0 mL of 2-mercapto- ethanol and 10.0 mL of acetonitrile. Cap. Store in hood (CAUTION - stench).

7.4.3 Sodium borate (0.05 N) -- Dissolve 19.1 g of sodium borate ($Na_2B_4O_7.10H_2O$) in reagent water. Dilute to 1.0 L with reagent water. The sodium borate will completely dissolve at room temperature if prepared a day before use.

7.4.4 OPA reaction solution -- Dissolve 100 ± 10 mg of o-phthalaldehyde (mp 55-58°C) in 10 mL of methanol. Add to 1.0 L of 0.05 N sodium borate. Mix, filter, and degas with helium. Add 100 µL of 2-mercaptoethanol (1+1) and mix. Make up fresh solution daily.

7.5 Monochloroacetic acid buffer (pH3) -- Prepare by mixing 156 mL of 1.0 M monochloroacetic acid and 100 mL 1.0 M potassium acetate.

7.6 4-Bromo-3,5-dimethylphenyl N-methylcarbamate (BDMC) -- >98% purity, for use as internal standard (available from Aldrich Chemical Co.).

7.7 ARTIFICIAL GROUND WATERS -- Two artificial ground waters were used to generate the validation data in this method. The first artificial ground water was used to mimic a hard ground water, and the second artificial ground water was used to mimic a ground water with moderately high organic content.

7.7.1 Hard artificial ground water -- The hard artificial ground water used to generate the validation data in this method was Absopure Natural Artesian Spring Water obtained from the Absopure Water Company in Plymouth, Michigan.

7.7.2 Organic-contaminated artificial ground water -- The organic-contaminated artificial ground water used to generate the validation data in this method was reagent water spiked with fulvic acid at the 1 mg/L concentration level. A very well-characterized fulvic acid, available from the International Humic Substances Society (associated with the United States Geological Survey in Denver, Colorado), was used.

7.8 STOCK STANDARD SOLUTIONS (1.00 µg/µL) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.8.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in HPLC quality methanol and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.8.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap vials. Store at room temperature and protect from light.

7.8.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory control standards indicates a problem.

7.9 INTERNAL STANDARD SPIKING SOLUTION -- Prepare an internal standard spiking solution by accurately weighing 0.0010 g of pure BDMC. Dissolve the BDMC in pesticide-quality methanol and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard spiking solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of µL of the internal standard spiking solution to 50 mL of sample results in a final internal standard concentration of 10 µg/L.

7.10 INSTRUMENT QC STANDARD -- Prepare instrument QC standard concentrate by adding 20 µL of the 3-hydroxycarbofuran stock standard solution, 1.0 mL of the aldicarb sulfoxide stock standard solution, 200 µL of the methiocarb stock standard

solution, and 1 mL of the internal standard spiking solution to a 10-mL volumetric flask. Dilute to volume with methanol. Thoroughly mix concentrate. Prepare instrument QC standard by placing 100 µL of the concentrate solution into a 100-mL volumetric flask. Dilute to volume with buffered reagent water. Thoroughly mix instrument QC standard and transfer to a sealed bottle. Store at room temperature.

8. SAMPLE COLLECTION, PRESERVATION AND HANDLING

8.1 Grab samples must be collected in glass containers. Conventional sampling practices[8] should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION/PH ADJUSTMENT -- Oxamyl, 3-hydroxycarbofuran, and carbaryl can all degrade quickly in water held at room temperature.[6,7] This short term degradation is of concern during the time samples are being shipped and the time processed samples are held at room temperature in autosampler trays. Samples targeted for the analysis of these three analytes must be preserved at pH 3. The pH adjustment also minimizes analyte biodegradation. Preservation study results given in Table 10 indicate that method analytes are stable in water samples for at least 28 days when stored using the following conditions:

8.2.1 The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

8.2.2 Add 0.6 mL of monochloroacetic acid buffer to the 60-mL sample bottle. Add buffer to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site.

8.2.3 After sample is collected in bottle containing buffer, seal the sample bottle and shake vigorously for 1 min.

9. CALIBRATION

9.1 Establish HPLC operating conditions equivalent to those indicated in Table 2. Calibrate the HPLC system using the internal standard technique (Section 9.2).

9.2 INTERNAL STANDARD CALIBRATION PROCEDURE. The analyst must select one or more internal standards similar in analytical behavior to the analytes of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. BDMC has been identified as a suitable internal standard.

9.2.1 Prepare calibration standards at a minimum of three (suggested five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with buffered reagent water. To prepare buffered reagent water, add 10 mL of 1.0 M monochloroacetic acid buffer to 1 L of reagent water. One of the standards should be representative of an analyte concentration near, but above, the MDL. The other concentrations should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector.

9.2.2 Inject 400 µL of each calibration standard and tabulate the relative response for each analyte (RR_a) to the internal standard using the equation:

$$RR_a = A_a/A_{is}$$

where: A_a = the peak area of the analyte, and
A_{is} = the peak area of the internal standard.

Generate a calibration curve of analyte RR_a versus analyte concentration in the sample in µg/L.

9.2.3 The working calibration curve must be verified on each working shift by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that analyte.

10. QUALITY CONTROL

10.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of the following: an initial demonstration of laboratory capability; the analysis of QC, laboratory control, and spiked samples as a continuing check on recovery performance; the analysis of field duplicates as a continuing check on precision; the analysis of reagent blanks as a continuing check on contamination; and frequent analysis of the instrument QC standard to assure acceptable instrument performance.

10.2 INITIAL DEMONSTRATION OF CAPABILITY -- To establish the ability to perform this method, the analyst must perform the following operations.

10.2.1 Select a representative spike concentration for each analyte to be measured. Using stock standards that differ from calibration standards, prepare a laboratory control check sample concentrate in methanol 1000 times more concentrated than the selected spike concentrations.

10.2.2 Using a syringe, add 50 µL of the check sample concentrate to each of a minimum of four 50-mL aliquots of reagent water. Add 0.5 mL of 1.0 M monochloroacetic acid buffer to each spiked sample. A representative ground water may be used in place of the reagent water, but one or more unspiked aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 11.

10.2.3 Calculate the average percent recovery (R), and the standard deviation of the percent recovery (s), for the results. Ground water background corrections must be made before R and s calculations are performed.

10.2.4 Tables 3-9 provide single operator recovery and precision data obtained for the method analytes from reagent and artificial ground waters. Similar results should be expected from reagent water for all compounds listed in the method. Compare the results obtained in section 10.2.3 to the values listed in Tables 3-9. If the results are not comparable, review potential problem areas and repeat the test.

10.3 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 10.2.

10.4 ASSESSING ANALYTE RECOVERY

10.4.1 Each quarter, it is essential that the laboratory analyze (if available) QC check standards for each contaminant. If the criteria established by USEPA and provided with the QA standards are not met, corrective action needs to be taken and documented.

10.4.2 After every 10 samples, and preferably in the middle of each day, analyze a laboratory control standard. Calibration standards may not be used for accuracy assessments, and the laboratory control standard may

not be used for calibration of the analytical system.

10.4.2.1 Laboratory control standard concentrate -- Internally prepared laboratory control standards are used to provide the routine assessment of recovery. They should be prepared from a separate set of stock standards, i.e., different from calibration standards.

10.4.2.2 Laboratory control standard -- Add an appropriate aliquot of the control standard concentrate to 50 mL of buffered reagent water in a 50 mL volumetric flask.

10.4.2.3 Analyze the 50 mL laboratory control standard as described in Section 11. For each analyte in the laboratory control standard, calculate the percent recovery (P_i) using the equation:

$$P_i = \frac{100S_i}{T_i}$$

where: S_i = the analytical result from the laboratory control standard in µg/L, and

T_i = the known spiked concentration of the laboratory control standard in µg/L.

10.4.3 It is essential that the laboratory analyze an unknown performance evaluation sample (when available) once per year for all regulated contaminants measured. Results need to be within acceptable limits established by USEPA for each analyte.

10.4.4 The laboratory is required to collect in duplicate a portion of the samples to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10 percent of all samples, or one spiked sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 11.

10.5 ASSESSING ANALYTE PRECISION

10.5.1 Precision assessments for this method are based upon the analysis of field duplicates. Analyze field duplicates for at least 10 percent of all samples. To the extent practical, the duplicated sample should contain reportable levels of method analytes.

10.5.2 For each analyte in each duplicate pair, calculate the relative range (RR_1) using the equation:

$$RR_1 = \frac{100R_1}{X_1}$$

where: R_1 = the absolute difference between the duplicate measurements X_1 and X_2 in µg/L, and

X_1 = the average concentration found ($[X_1 + X_2]/2$) in µg/L.

10.5.3 Individual relative range measurements are pooled to determine the average relative range or to develop an expression of relative range as a function of concentration.

10.6 ASSESSING CONTAMINATION

10.6.1 Laboratory reagent blanks -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. This is accomplished by the analysis of a laboratory reagent blank. A laboratory reagent blank is a 50 mL aliquot of reagent water analyzed as if it were a sample. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank must be processed to assess laboratory contamination. If the reagent blank exhibits a peak within the retention time window of any analyte which is greater than or equal to one-half the MDL for that analyte, determine source of contamination before proceeding.

10.7 ASSESSING INSTRUMENT PERFORMANCE -- The laboratory is required to demonstrate the ability to generate acceptable HPLC performance for each analyte. Analyte peak shapes comparable to those shown in Figure 1 should be demonstrated. Instrument performance should be monitored on a daily basis by analysis of the instrument QC standard.

10.7.1 Instrument QC standard -- The instrument QC standard contains compounds designed to indicate appropriate instrument sensitivity, column performance, and chromatographic performance. Instrument QC standard components and performance criteria are listed in Table 11. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the HPLC-UV system. An HPLC-UV chromatogram generated from the analysis of the instrument QC standard is shown in Figure 3.

10.8 ANALYTE CONFIRMATION -- When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as chromatography with a dissimilar column, or ratio of absorbance at two or more wavelengths must be used. A suggested confirmation column is described in Table 2.

10.9 ADDITIONAL QC -- It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples.

11. PROCEDURE

11.1 PH ADJUSTMENT AND FILTRATION

11.1.1 Adjust the pH of the sample or standard to pH 3 $\pm$ 0.2 by adding 0.5 mL of 1.0 M monochloroacetic acid buffer to each 50 mL of sample. This step is not necessary if sample pH was adjusted during sample collection as a preservation precaution. Fill a 50-mL volumetric flask to the mark with the sample. Add 5 µL of the internal standard spiking solution and mix by inverting the flask several times.

11.1.2 Affix the three-way valve to a 10-mL syringe. Place a clean filter in the filter holder and affix the filter holder and the 7- to 10-cm syringe needle to the syringe valve. Rinse the needle and syringe with reagent water. Prewet the filter by passing 5 mL of reagent water through the filter. Empty the syringe and check for leaks. Draw 10 mL of sample into the syringe and expel through the filter. Draw another 10 mL of sample into the syringe, expel through the filter, and collect the last 5 ml for analysis. Rinse the syringe with reagent water. Discard the filter.

11.2 LIQUID CHROMATOGRAPHY

11.2.1 Table 2 summarizes the recommended operating conditions for the liquid chromatograph. Included in Table 2 are retention times observed using this method. An example of the separations achieved using these conditions is shown in Figure 1. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.2 are met.

11.2.2 Calibrate the system daily as described in Section 9. The standards and extracts must be in pH3 buffered water.

11.2.3 Inject 400 µL of the sample extract. Record the volume injected and the resulting peak size in area units.

11.2.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.2.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

12. CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the relative response for the analyte (RR_a) to the internal standard using the equation the calibration curve described in Section 9.3.2.

12.2 For samples processed as part of a set where the laboratory control standard recovery falls outside of the control limits in Section 10.4, data for the affected analytes must be labeled as suspect.

13. PRECISION AND ACCURACY

13.1 In a single laboratory, analyte recoveries from reagent water were determined at five concentration levels. Results were used to determine analyte EDLs and demonstrate method range. EDL determination results are given in Table 3. Method range results are given in Tables 4-7.

13.2 In a single laboratory, analyte recoveries from two artificial ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices. Analyte recoveries from the two artificial matrices are given in Tables 8 and 9.

13.3 In a single laboratory, analyte recoveries from a ground water preserved by adjusting to pH 3 with monochloroacetic acid buffer were determined 0, 14, and 28 days after sample preparation. Samples were stored at 4°C or -10°C and were protected from light. Results were used to predict expected analyte stability in ground water samples. Analyte recoveries from the preserved, spiked ground water samples are given in Table 10.

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TABLE 1. METHOD ANALYTES

Analyte	Chemical Abstracts Service Registry Number	Ident. Code(a)
Aldicarb	116-06-3	6
Aldicarb sulfone	1646-88-4	2
Aldicarb sulfoxide	1646-87-3	1
Baygon	114-26-1	8
Carbaryl	63-25-2	9
Carbofuran	1563-66-2	7
3-Hydroxycarbofuran	16655-82-6	5
Methiocarb	2032-65-7	10
Methomyl	16752-77-5	4
Oxamyl	23135-22-0	3

(a) Code used for identification of peaks in figures; IS = internal standard.

TABLE 2. PRIMARY AND CONFIRMATION CHROMATOGRAPHIC CONDITIONS

Analyte	Retention Time for Given Conditions	
	Primary (a)(c)	Confirmation (b)(d)
Aldicarb	0.761	21.4
Aldicarb sulfone	0.429	12.2
Aldicarb sulfoxide	0.421	17.5
Baygon	0.834	23.4
Carbaryl	0.867	25.4
Carbofuran	0.824	24.4
3-Hydroxycarbofuran	0.657	19.0
Methiocarb	0.984	28.6
Methomyl	0.518	14.8
Oxamyl	0.489	14.6

(a) Retention time relative to BDMC internal standard which elutes at 35.5 min.
(b) Absolute retention time in minutes.
(c) Primary conditions:

Column:	250 mm x 4.6 mm I.D. Altex Ultrasphere ODS (5 μm)
Mobile phase:	Linear gradient from 15:85 methanol:water to methanol in 32 min
Flow rate:	1.0 mL/min
Injection volume:	400 μL
Detector:	Fluorescence; excitation 230 nm; emission 418 nm

(d) Confirmation conditions:

Column:	250 mm x 4.6 mm I.D. Supelco LC-1 (5 μm)
Mobile phase:	Linear gradient from 15:85 methanol:water to methanol in 32 min
Flow rate:	1.0 mL/min
Injection volume:	400 μL
Detector	Fluorescence; excitation 230 nm; emission 418 nm

TABLE 3. RECOVERIES OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 1) AND EDLs (a)

Analyte	Spiking Level, µg/L	Amt in Blank, µg/L	n(b)	R(c)	S(d)	RSD(e)	EDL(f)
Aldicarb	1.0	ND (g)	8	107	0.0728	7	1.0
Aldicarb sulfone	2.0	ND	8	83	0.337	20	2.0
Aldicarb sulfoxide	2.0	ND	8	47	0.196	21	2.0
Baygon	1.0	ND	7	101	0.323	32	1.0
Carbaryl	2.0	ND	8	97	0.443	23	2.0
Carbofuran	1.5	ND	7	90	0.166	12	1.5
3-Hydroxycarbofuran	2.0	ND	8	108	0.626	29	2.0
Methiocarb	4.0	ND	8	82	0.638	19	4.0
Methomyl	0.50	ND	7	102	0.0931	18	0.50
Oxamyl	2.0	ND	8	82	0.287	17	2.0

(a) Amounts corrected for levels detected in blank.
(b) n = number of recovery data points.
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) EDL = estimated detection limit in sample in µg/L; calculated by multiplying standard deviation (S) times the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom, or a level of compound in sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.
(g) ND = interference not detected in blank.

TABLE 4. RECOVERIES OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 2) (a)

Analyte	Spiking Level, µg/L	Amt in Blank, µg/L	n(b)	R(c)	S(d)	RSD(e)
Aldicarb	2.0	ND (f)	8	113	0.125	6
Aldicarb sulfone	4.0	ND	8	100	0.251	6
Aldicarb sulfoxide	4.0	ND	8	73	0.283	10
Baygon	2.0	ND	8	97	0.181	9
Carbaryl	4.0	ND	8	94	0.292	8
Carbofuran	3.0	ND	8	93	0.151	5
3-Hydroxycarbofuran	4.0	ND	8	93	0.392	11
Methiocarb	8.0	ND	7	80	0.246	4
Methomyl	1.0	ND	8	76	0.0893	12
Oxamyl	4.0	ND	8	88	0.246	7

(a) Amounts corrected for amount found in blank.
(b) n = number of recovery data points
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) ND = interference not detected in blank.

TABLE 5. RECOVERIES OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 3) (a)

Analyte	Spiking Level, µg/L	Amt in Blank, µg/L	n(b)	R(c)	S(d)	RSD(e)
Aldicarb	5.0	ND (f)	8	115	0.172	3
Aldicarb sulfone	10	ND	8	101	0.407	4
Aldicarb sulfoxide	10	ND	8	97	0.441	5
Baygon	5.0	ND	8	106	0.152	3
Carbaryl	10	ND	8	97	0.607	6
Carbofuran	7.5	ND	8	102	0.346	5
3-Hydroxycarbofuran	10	ND	8	102	0.386	4
Methiocarb	20	ND	7	94	0.453	2
Methomyl	2.5	ND	8	105	0.0951	4
Oxamyl	10	ND	8	100	0.423	4

(a) Amounts corrected for amount found in blank.
(b) n = number of recovery data points
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) ND = interference not detected in blank.

TABLE 6. RECOVERIES OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 4) (a)

Analyte	Spiking Level, µg/L	Amt in Blank, µg/L	n(b)	R(c)	S(d)	RSD(e)
Aldicarb	10	ND (f)	8	105	0.300	3
Aldicarb sulfone	20	ND	8	91	0.657	4
Aldicarb sulfoxide	20	ND	8	92	0.441	2
Baygon	10	ND	8	94	0.309	3
Carbaryl	15	ND	8	112	0.298	2
Carbofuran	15	ND	8	96	0.247	2
3-Hydroxycarbofuran	20	ND	8	92	0.910	5
Methiocarb	40	ND	8	83	0.722	2
Methomyl	5.0	ND	8	96	0.0912	2
Oxamyl	20	ND	8	90	0.501	3

(a) Amounts corrected for amount found in blank.
(b) n = number of recovery data points
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) ND = interference not detected in blank.

TABLE 7. RECOVERIES OF ANALYTES FROM REAGENT WATER (SPIKING LEVEL 5) (a)

Analyte	Spiking Level, µg/L	Amt in Blank, µg/L	n(b)	R(c)	S(d)	RSD(e)
Aldicarb	25	ND (f)	8	98	1.31	5
Aldicarb sulfone	50	ND	8	92	2.06	4
Aldicarb sulfoxide	50	ND	8	96	2.76	6
Baygon	25	ND	8	91	1.03	4
Carbaryl	50	ND	8	83	1.76	4
Carbofuran	38	ND	8	91	1.82	5
3-Hydroxycarbofuran	50	ND	8	90	2.00	4
Methiocarb	100	ND	8	82	5.85	7
Methomyl	13	ND	8	98	0.529	4
Oxamyl	50	ND	8	89	1.80	4

(a) Amounts corrected for amount found in blank.
(b) n = number of recovery data points
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) ND = interference not detected in blank.

TABLE 8. RECOVERIES OF ANALYTES FROM HARD ARTIFICIAL GROUND WATER (SPIKING LEVEL 3) (a)

Analyte	Spiking Level, µg/L	Amt in Blank, µg/L	n(b)	R(c)	S(d)	RSD(e)
Aldicarb	5.0	ND (f)	8	106	0.177	3
Aldicarb sulfone	10	ND	8	98	0.441	4
Aldicarb sulfoxide	10	ND	8	105	0.393	4
Baygon	5.0	ND	8	96	0.224	5
Carbaryl	10	ND	8	94	0.454	5
Carbofuran	7.5	ND	8	102	0.245	3
3-Hydroxycarbofuran	10	ND	8	98	0.494	5
Methiocarb	20	ND	8	102	0.856	4
Methomyl	2.5	ND	8	98	0.0863	4
Oxamyl	10	ND	8	97	0.269	3

(a) Amounts corrected for amount found in blank.
(b) n = number of recovery data points
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) ND = interference not detected in blank.

TABLE 9. RECOVERIES OF ANALYTES FROM ORGANIC-CONTAMINATED ARTIFICIAL GROUND WATER (SPIKING LEVEL 3) (a)

Analyte	Spiking Level, µg/L	Amt in Blank, µg/L	n(b)	R(c)	S(d)	RSD(e)
Aldicarb	5	ND (f)	8	102	0.406	8
Aldicarb sulfone	10	ND	8	95	0.981	10
Aldicarb sulfoxide	10	ND	8	94	1.05	11
Baygon	5	ND	7	97	0.300	6
Carbaryl	10	ND	8	104	1.08	10
Carbofuran	7.5	ND	7	100	0.524	7
3-Hydroxycarbofuran	10	ND	8	101	0.969	10
Methiocarb	20	ND	7	112	0.660	3
Methomyl	2.5	ND	8	105	0.244	9
Oxamyl	10	ND	8	102	1.03	10

(a) Amounts corrected for amount found in blank.
(b) n = number of recovery data points
(c) R = average percent recovery.
(d) S = standard deviation.
(e) RSD = percent relative standard deviation.
(f) ND = interference not detected in blank.

TABLE 10. RESULTS FROM METHOD 5 PRESERVATION STUDIES (c)

Analyte	Spiking Level, g/L	Day 0		Day 14 (-10°C)		Day 14 (4°C)		Day 28 (-10°C)		Day 28 (4°C)	
		R(a)	RSD(b)	R	RSD	R	RSD	R	RSD	R	RSD
Aldicarb	5.0	100	9	100	4	110	2	100	6	83	1
Aldicarb sulfone	10	99	9	93	3	99	3	97	0	86	8
Aldicarb sulfoxide	10	100	9	91	6	100	2	98	2	91	5
Baygon	5.0	98	10	91	2	100	4	88	2	93	9
Carbaryl	10	100	6	92	4	95	3	99	18	89	5
Carbofuran	7.5	100	9	95	3	110	7	95	2	93	3
3-Hydroxycarbofuran	10	95	9	89	6	100	3	100	8	95	11
Methiocarb	20	110	4	100	1	98	1	99	0	94	6
Methomyl	2.5	110	12	90	6	96	5	93	2	96	5
Oxamyl	10	98	6	85	4	95	5	100	11	94	9

(a) R = average percent recovery.
(b) RSD = percent relative standard deviation.
(c) Storage temperature given in parentheses.

TABLE 11. QUALITY CONTROL STANDARD

Test	Analyte	Conc, g/L	Requirements
Sensitivity	3-Hydroxycarbofuran	2	Detection of analyte; S/N > 3
Chromatographic performance	Aldicarb sulfoxide	100	0.95 <PSF<1.05 (a) 0.95 <PGF<1.05 (b)
Column performance	Methiocarb	20	Resolution >1.0 (c)
	4-Bromo-3,5-dimethylphenyl N-methylcarbamate (IS)	10	

(a) PSF = peak symmetry factor. Calculated using the equation:

$$PSF = \frac{w(1/2)}{0.5 \times W(1/2)}$$

where w(1/2) is the width of the front of the peak at half height and W(1/2) is the peak width at half height.

(b) PGF = peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height.

(c) Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

APPENDIX B

NPS ANALYTE REPORTING BELOW MRL AND IDENTIFYING UNKNOWN PEAKS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL CHEMISTRY LABORATORY, NASA/NSTL
BUILDING 1105, NSTL, MISSISSIPPI 39529

June 1, 1988

MEMORANDUM

SUBJECT: NPS Analyte Reporting Below MRL and Identifying Unknown Peaks

FROM: Bob Maxey, Analytical Coordinator
Environmental Chemistry Laboratory

Bob Maxey

TO: Dave Munch, Analytical Coordinator
TSD-Cincinnati

Aubry E. Dupuy, Jr., Technical Monitor
Environmental Chemistry Laboratory

Attached are the procedures that NPS analytical contractors and referee laboratories must adhere to in complying with the OPP request to report the presence of analytes below the Minimal Reporting Limits and to attempt identification of unknown peaks. Please see that your contractors and Technical Monitors get this information and that applicable parts are incorporated into their respective QAPPs.

If you have any questions, give me a call.

Determining and Reporting the Presence of NPS Analytes Below The Minimal Reporting Levels and Identifying Unknown Peaks

Background Information

The Office of Pesticide Programs (OPP) has requested that the NPS analytical contractors and referee laboratories make an effort to report the presence of NPS analytes below the Minimal Reporting Levels (MRL). We have also been requested to attempt to identify unknown peaks or responses. To assure that spurious or ambiguous data is not reported and that a uniform system or analytical routine is used at all laboratories to accomplish these requests, criteria have been developed for handling both situations.

Procedure for Determining and Reporting the Presence of NPS Analytes Below the MRL

1. For methods 1-7, only peaks with responses of between one-half the establis ed MRL and the MRL [A/] on the primary column will be investigated. A respon on the "secondary" GC column, indicating the presence of the analyte, is al required for additional work.

2.a The first occurrence of a peak meeting the requirements of (1) is noted and reported to the Technical Monitor, but no action is taken [B/]. Upon a secon occurrence of the same suspect analyte, additional work is required as follows. After five successive failures to "confirm" on the secondary column the response on the primary column, discussions with OPP personnel will tak place before continuing low-level analytical work on the analyte(s).

b With methods 1,2,3, 6 and 7, for responses meeting the requirements of (1) and (2), the laboratory will attempt LR GC/MS [C/] confirmation if the GC/MS analyst feels it is within the capability of his instrument. If the confir mation is not within the capability of the laboratory, such extracts are sent weekly, under iced conditions by next-day air, to the appropriate referee laboratory having HR GC/MS [C/] capabilities. Copies of chromatograms and all pertinent sample information must be sent along with the extracts including extracts of the related Method Blank. (NPS will absorb the cost of these shipments.) It is preferred that extracts be in sealed glass ampules, but other vials and teflon-faced closures are acceptable if they provide a tight seal and do not contribute interferences to the extracts. Volume level must be marked on the outside of the vial or ampule.

A/ = NPS method 1 MRL = 4 x EDL
NPS method 2 MRL = 5 x EDL
NPS method 3 MRL = 5 x EDL
NPS method 4 MRL = 5 x EDL
NPS method 5 MRL = 3 x EDL
NPS method 6 MRL = 3 x EDL
NPS method 7 MRL = 3 x EDL

B/ = Method 6 has an MRL > the Health Advisory Level. All suspect ETU responses of 1/2 MRL - MRL require additional work for this method.

C/ = LR = GC/MS = Low Resolution mass spectrometry.
HR GC/MS = High Resolution mass spectrometry.

c. For Methods 4 and 5, HPLC Methods, there is no provision for GC/MS confirmation. Suspect analytes between 1/2 MRL - MRL will be subject to (1) and (2a) above.

Provisions of (2b) also apply except references to GC/MS requirements.

3. Whether the identification of the analyte is attempted at the contractor laboratory or at the referee laboratory, only analytes positively confirmed by GC/MS will be reported beyond the Technical Monitor for the Method and the Analytical Coordinators. No unconfirmed data will be reported outside the NPS analytical system. Unsuccessful attempts at confirmation will also be reported to the Technical Monitor.

4. Following either the successful GC/MS confirmation of two such responses for the same analyte or two successive failures to confirm the analyte by GC/MS without any prior successful GC/MS confirmation on any samples, discussions with OPP personnel will take place before continuing low level analytical work on that analyte.

Procedure for Determining the Identity of Non-NPS Analytes

It is expected that, over the course of the NPS Program, numerous extraneous responses will be evident on chromatograms from the various methods. The contractor or referee laboratories will be required to attempt identification of peaks or responses on the primary column exhibiting the minimal criter below.

1. For Methods 1, 2, 3, 6, and 7, if, upon initial analyses, the response of an extraneous peak on the primary column is equal to or greater tha the response of the nearest NPS analyte on that column at 10 x MRL (Minimal Reporting Level), an attempt must be made to identify that un known peak or response by GC/MS. Full scan spectra and subsequent library search are expected and must be followed by comparison of the spectra of the unknown compound with those of an authentic standard of the suspected compound.

2. The work in (1) must be attempted by the contractor and/or referee lab oratories on the first occurrence of such a peak and the results of th attempt reported to the Technical Monitor for the Method. If the analytical contractor feels his system or instrument is not capable of the confirmatory work, he must send both that extract and that of the related Method Blank to the appropriate referee lab under iced conditions by next-day air.

   It is preferred that extracts be in sealed glass ampules, but other vials and teflon-faced closures are acceptable if they provide a tight seal and do not contribute interferences to the extracts. Volume leve must be marked on the outside of the vial or ampule. (NPS will absorb costs of these shipments.)

Specific sample and analytical information must accompany each such extract.

- o Sample i.d. number, weight of sample matrix contained in the ampule, copies of chromatograms from the primary GC column, identification of the retention window for the unknown response(s) as defined by the last NPS analyte to elute before the unknown peak or response and the first NPS analyte to elute following the unknown response.

3. Whether the identification of the unknown compound is attempted at the Contractor Laboratory or at the referee laboratory, only the compounds positively confirmed by GC/MS will be reported beyond the Technical Monitor for the Method and the Analytical Coordinators. No unconfirmed data will be reported outside the NPS analytical system. Unsuccessful attempts at identification will also be reported to the Technical Monitor.

4. Following either the successful confirmation of two such extraneous peaks proving to be the same compound or two failures to identify a response with the same retention time without a prior successful GC/MS confirmation on a sample, discussions with OPP personnel will take place before continua with identification work on that particular compound.

THE QUALITY ASSURANCE PROJECT PLANS FOR BOTH THE ANALYTICAL CONTRACTORS AND REFEREE LABORATORIES FOR METHODS 1, 2, 3, 6, AND 7 MUST REFLECT THEIR COMMITMENTS TO THESE TWO REQUIREMENTS.

THE QUALITY ASSURANCE PROJECT PLANS FOR BOTH THE ANALYTICAL CONTRACTORS AND REFEREE LABORATORIES FOR METHODS 4 AND 5 MUST REFLECT THEIR COMMITMENTS TO THE REQUIREMENT FOR DETERMINING AND REPORTING NPS ANALYTES BELOW THE MRL.

APPENDIX C

CHANGES IN NPS LABORATORY PROCEDURES

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI OHIO 45268

MEMORANDUM

DATE: July 14, 1988

SUBJECT: Changes in NPS Laboratory Procedures

FROM: David J. Munch, TSD Project Manager
National Pesticide Survey

TO: NPS Technical Monitors (See below)

The following minor changes in laboratory operations are being made.

1. Spiking Levels (Methods 1-7)

Currently, selected NPS samples are being spiked at either Level 1 (5 times MRL), Level 2 (10 times MRL), or Level 3 (20 times MRL). In many cases, spiking at Level 3 has created analyte concentrations in samples which exceed the linear range of the instrumentation. Any Level 3 spiked samples currently on hand should be analyzed; however, no further requests will be made to spike samples at Level 3.

In order to maintain three spiking levels, a Level 0 (2 times MRL) is being added. Laboratory Control Standards and Time Storage Samples are to continue to be spiked at Level 2 (10 times MRL).

2. Spiking Levels (Method 9)

Currently, sample spiking levels used for Method 9 are, Level 1 (2 times MRL), Level 2 (10 times MRL), and Level 3 (10,000 ug/L). The spiking levels are to remain the same; however, Level 0 will now be 1 times MRL, Level 1 10 times MRL, and Level 3 10,000 ug/L.

3. Data Reporting Format

In order for the data reporting format to match the requirements for reporting suspected NPS analytes observed on the primary column, at a concentration between 1/2 MRL and MRL (see memorandum entitled "Determining and Reporting the Presence of NPS Analytes below the Minimum Reporting Levels and Identifying Unknown Peaks," by Bob Maxey 6/1/88), further clarification is required. In those cases where the presence of an NPS analyte at a concentration between 1/2 MRL and the MRL is successfully confirmed, the primary and confirmational column data for that analyte should be reported as "-111". In those cases where confirmational analyses are either not required, or the confirmational analyses did not confirm the presence of the analyte, the primary column data for that analyte should be reported as "-222".

Please transmit this information to both your contract and referee laboratories, as soon as possible. If you have any questions concerning these items, please let me know.

Addressees:

A. Dupuy
L. Kamphake (TSD)
C. Madding (TSD)
R. Maxey (OPP)
K. Sorrell (TSD)
R. Thomas (TSD)

cc:

H. Brass (TSD)
C. Freebis (CSD)
A. Kroner (TSD)

APPENDIX D

NPSIS SAMPLE RECEIPT SOFTWARE FOR LABORATORIES

MEMORANDUM 4/5/88

TO: DATA MANAGER, EPA/TSD LAB

FROM: CHIP LESTER, ICF INC. (703) 934-3431 Beth

RE: NPSIS SAMPLE RECEIPT SOFTWARE FOR LABORATORIES

ICF's National Pesticide Survey Information System (NPSIS) is ready to collect information from you regarding the receipt of well water samples and their condition. Please find enclosed the following items: 1) A users memo containing all operating instructions, and 2) A copy of Carbon Copy software which is necessary to establish communications with NPSIS over phone lines. As mentioned previously, the software allows you to report the receipt of a one or more sample kits. It also prompts you for details regarding the condition of the samples. Additional features include; a bulletin board which allows you to interactively send messages to ICF staff via your computer keyboard, file transfer, and access to the ICF computerized mail system for sending memos. It is also possible for you to speak over the phone to an ICF staff member during your session.

It is important that you test the communications link between the NPSIS computer and yours. We have experienced trouble when using Carbon Copy software with a computer which has a Manzana 3.5 inch disk drive, and also with computers which have a non-Hercules or non-EGA compatible graphics card.

For testing purposes, your sample kit identification numbers and FedEx airbill numbers (respectively) are: PD-0000-711 and 1111111111, and PD-9999-711 and 2222222222. Use these sample kit identification numbers when trying out the NPSIS Sample Receipts Program.

We feel that it would be helpful to both parties if you could call us when you are ready to test the NPSIS system, and we will assist you over the phone during your session. If you would like to do this, please call Beth Estrada at (703) 934-3431. NPSIS will be available for access 24-hours a day, seven days a week. We appreciate hearing any comments you have regarding NPSIS.

THE NPSIS SAMPLE RECEIPT PROGRAM

NPSIS is designed to keep track of the day to day operations of the National Pesticide Survey. You play an important role in NPS and your timely notification of receiving a kit of samples is essential to the success of NPS. We have designed the Sample Receipt Program with your busy schedule in mind. NPSIS will obtain the minimum amount of information necessary while still maintaining a secure system. You will be entering data into the NPSIS personal computer via your own computer, modem, and Carbon Copy software.

1.1 Hardware and Software Requirements.

The NPSIS Sample Receipt Program has a minimum hardware and software requirement. Here is a list of items you will need:

Hardware:

- One (1) IBM PC, XT, AT, or Personal System model with at least 640K memory.
- One (1) 2400 or 1200 baud Hayes or Hayes compatible modem with cables. (See Carbon Copy guide for cabling requirements and a description of usable modems)
- One (1) data transmission phone line.

Software:

- NPSIS Sample Receipt Program access provided for you by ICF.
- One (1) copy Carbon Copy software which is provided to you by ICF for the duration of NPS.

1.2 Initial Installation Steps.

Before you can access and use NPSIS, you must first load the Carbon Copy software onto your PC. The directions are provided in the Carbon Copy manual. One item you will want to include is an entry into the "Call Table". This entry will include a name, telephone number, and password for the NPSIS computer. To enter these items into the Call Table, press "2" from the Carbon Copy Parameters' Screen. The information you must enter consists of the following:

- **Name:** NPS
- **Telephone Number:** 703-961-0629
- **Password:** NPS

1.3 Parameters for Communications.

NPSIS will maintain a set configuration throughout operation. Any changes due to updates in equipment or the system which will affect your ability to communicate through Carbon Copy will be forwarded to you. The parameters which will be maintained at this time are:

- 2400 baud modem speed.
- Answer ring count equal to one.
- Re-boot on exit after 5 minutes. (If there is a power failure or some other type of interruption, you can log back on to NPSIS and resume your session.)
- Five minute inactivity time constraint.
- Two password attempts.

2 REPORTING A SAMPLE RECEIPT TO NPSIS.

2.1 Establishing a Communications Link.

Once you have installed Carbon Copy and have all of the necessary hardware, you are ready to "log on" to the NPSIS computer at ICF. To do this:

Type: C:> **CCHELP NPS** in your directory containing Carbon Copy.

This command will automatically dial the NPSIS computer, send your password for verification, and establish a data link between the two computers. You will be able to discern what is taking place by messages to your screen.

2.2 Entering A Sample Receipt Into NPSIS.

Once you have established a data link, (e.g., are "logged on"), you will see on the screen exactly what is on the screen of the NPSIS computer. This screen you are viewing is the main menu for the Sample Receipt Program. Remember that you are controlling the NPSIS computer via a 2400 baud phone line and your typing will appear on the screen at a much slower rate than you are accustomed to. A few tips on how to use the system are outlined in the next section.

2.2.1 Useful Tips on How to Use NPSIS.

Before you start, a few things to remember are:

- Pressing the "Esc" key will cancel all changes for the screen you are currently in and return you to the previous screen. Pressing "Esc" at the Searching Screen returns you to the main menu.

- Pressing "PgDn" or "PgUp" will save the items you have entered in the current screen and place you in the next or previous screen, respectively. This feature is handy to use when you only have a fe items to enter in a screen which prompts for several items.

- Pressing "Enter", "arrow up", or "arrow down" will move the cursor from field to field in each screen. Remember that using the sideways arrows will not work.

- Pressing the "Alt" and "Right Shift" keys together will place the Carbon Copy Control Screen over the NPSIS Sample Receipt Program. You can then use the communications features in Carbon Copy. Pressing "F10" again when you are through will replace the NPSIS Sample Receipt Program screen you were currently in back on your screen, and

- Because you will are most likely to be entering information regarding a number of kits at one time, after you save or cancel your entries for one kit, you will be placed at the initial Sample Searching Screen for a new kit. If you are finished with your data entry, simply press "Esc" to exit the Sample Searching screen and be placed in the main menu.

2.3 A Basic Outline of the Sample Receipt Program.

The NPSIS Sample Receipt Program has three basic features:

- Initial reporting of a NPS sample kit of sample bottles.

- Ability to edit or re-edit an existing report of a kit receipt, and

- Access to ICFs computerized mail system which provides the ability to send memoranda to ICF staff.

The information obtained in an entry for a kit of bottles is:

- The kit identification number, the FedEx airbill number, and the last name of the person making the entry.

- Any damage to the kit as a whole such as melted ice or any breakage of the cooler.

- Verification of which bottles belong in a kit or cooler, notification of any missing bottles or any additional bottles, and

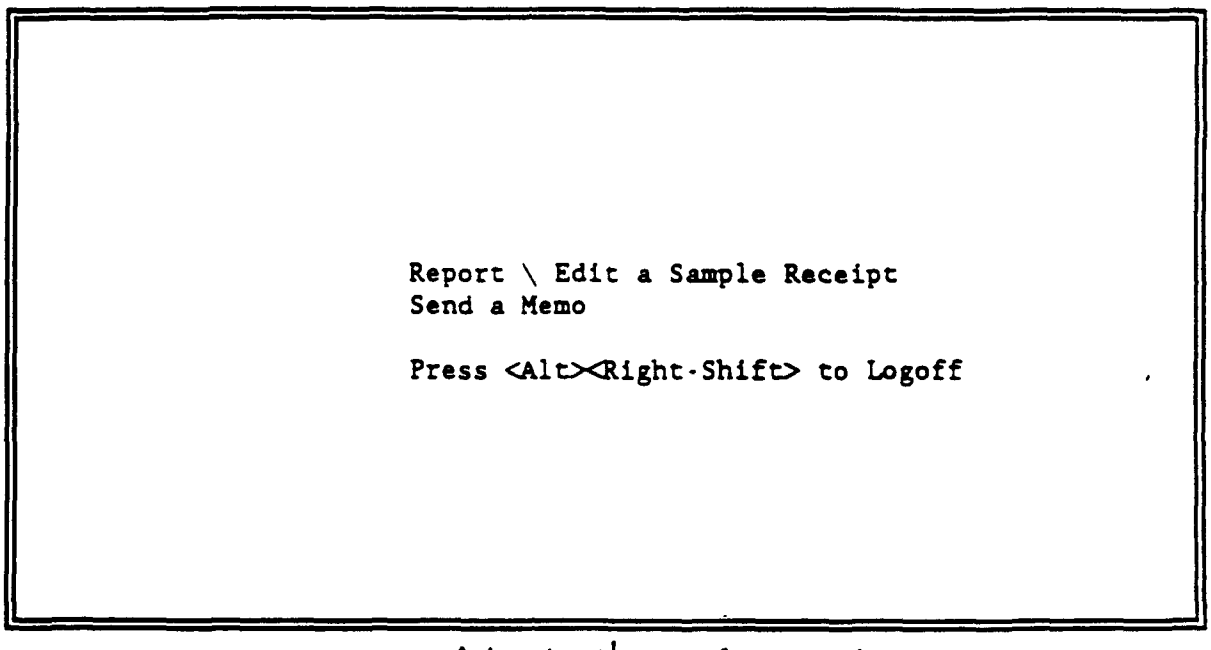
- Any damage to each sample bottle which renders it unusabl for analysis and testing.

2.4 NPSIS Sample Receipt Program Screens.

When you have completed the logon procedure, you will see the following main menu on your computer screen:

NATIONAL PESTICIDE SURVEY INFORMATION SYSTEM

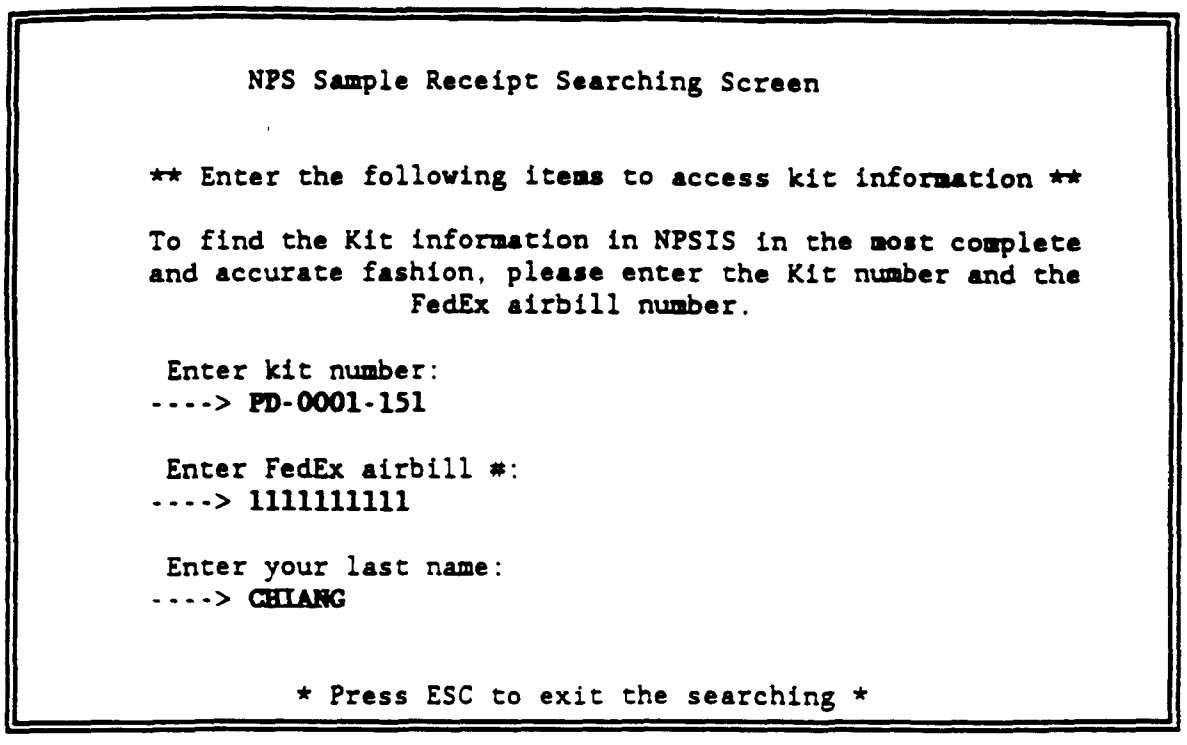
SELECTION MENU FOR REPORTING SAMPLE RECEIPTS 04/05/88



use ↑ ↓ and ↵ to select option.

The screens provided in this memo will show all of the screens available and thus represent the maximum number of screens you will encounter with NPSIS. It is most likely that you will not have the need to enter informatio reporting damaged kits or samples. Therefore, not all of the screens depicte below will appear in your normal session.

If you choose the first item on the menu, "Report \ Edit a Sample Receipt", you will then be prompted for the kit identification number and the FedEx airbill number associated with the specified kit. The screen will appear like this:



If the kit number you have entered is incorrect, or if the kit number and FedEx airbill number combination is incorrect, NPSIS will prompt you to try to enter these number again, as illustrated on the next page. It is possible that the FedEx airbill number on the kit is not the same as the FedEx airbill number which was entered into the NPSIS system. This could happen if the field team loses or damages the airbill.

ERROR!! The kit you entered cannot be found. . .

Kit number: PD-0001-151
AND
FedEx airbill number: 1111111111

Please check these numbers and try again!

****
NPSIS is designed to track Kits and FedEx airbill numbers.
The Kit and FedEx airbill number combination you have entered
does not match what is currently in the system. Please enter
the correct combination. If you still have problems, try
leaving the FedEx airbill # BLANK. Only enter the Kit number.
****

Press any key to continue...

Then, you will encounter this screen insuring that you have entered the FedEx airbill number:

Kit No.: PD-0001-151

Did you enter the correct Kit number and FedEx airbill number?

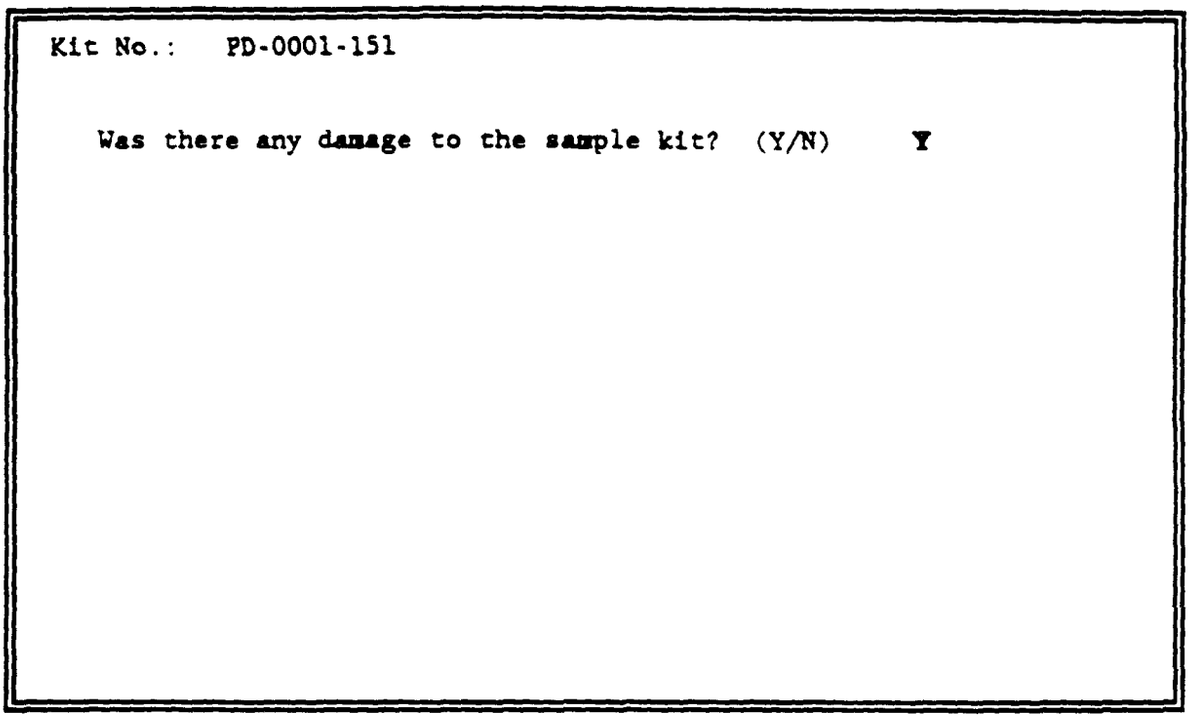
NPSIS is designed to store and track all FedEx airbill numbers. This Kit may have a different FedEx airbill number than the system, please enter the new FedEx airbill number:

---->

Note: if the correct airbill number was entered before, hit ENTER.

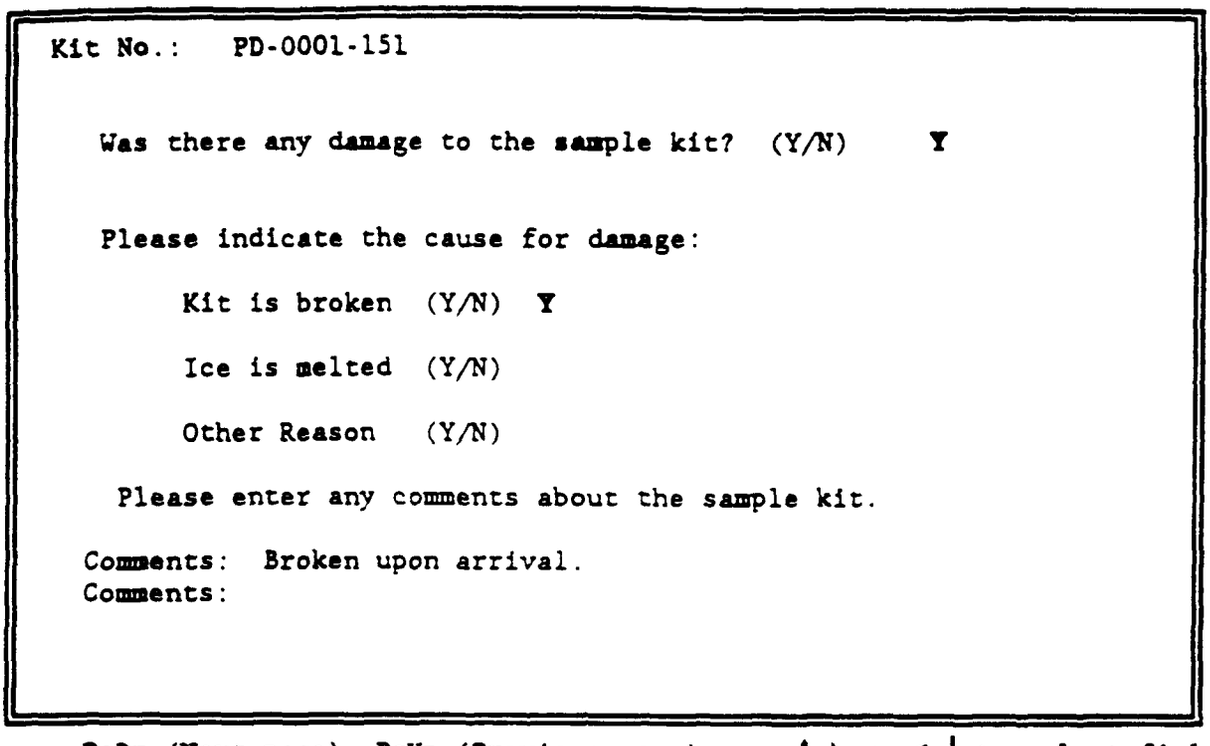
PgDn (Next page), PgUp (Previous page), Esc (Exit)

Once you have correctly identified the sample kit, NPSIS will ask you there is any damage to the kit as a whole:



PgDn (Next page), PgUp (Previous page), Esc (Exit)

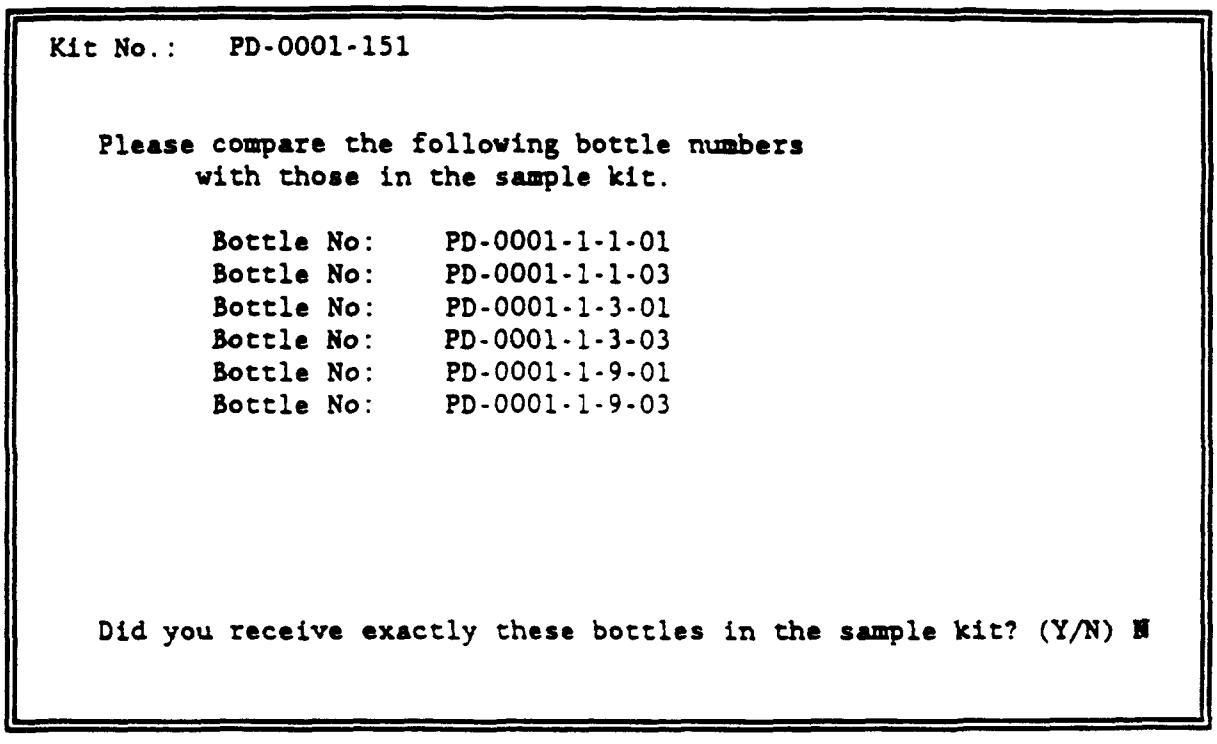
If you press "Y", NPSIS will then prompt you for the apparent cause of damage:



PgDn (Next page), PgUp (Previous page), use ↑ ↓ or ↵ to select field.

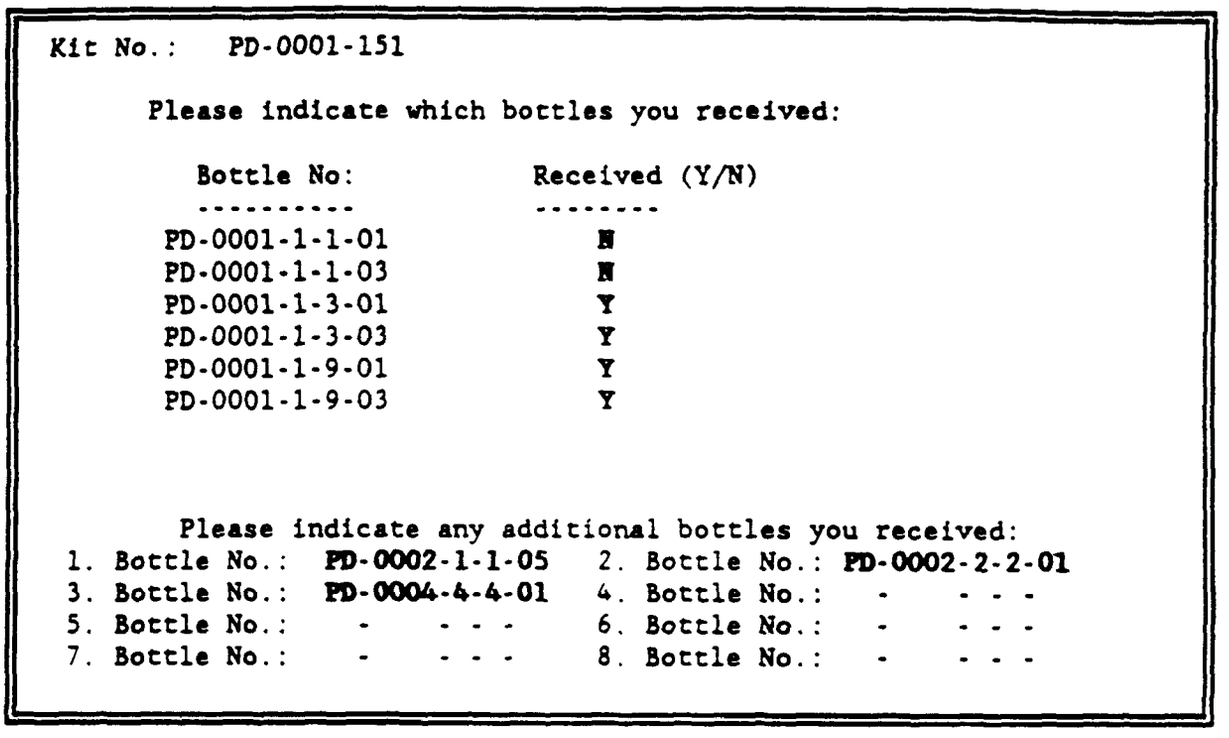
There may already be comments regarding the kit in the comment field shown in the above screen. In this case, please enter your comments after any which already appear. This insures that no information is destroyed.

Next, NPSIS will ask you to survey the contents of the kit and check tha which bottles are contained within the kit. You should then look at the bottle labels and determine if any are missing. Don't forget to check and determine if any bottles have been included in the kit which do not appear on the list provided by NPSIS on this screen:



PgDn (Next page), PgUp (Previous page), Esc (Exit)

If you have pressed "N", indicating that you did not receive exactly what NPSIS assumes you have received, you will be prompted to enter the appropriate information. This information includes pressing a "Y" or a "N" beside each bottle, and entering the bottle number found on the labels of any additional bottles you have received:



Kit No.: PD-0001-151

Please indicate which bottles you received:

Bottle No:	Received (Y/N)
PD-0001-1-1-01	N
PD-0001-1-1-03	N
PD-0001-1-3-01	Y
PD-0001-1-3-03	Y
PD-0001-1-9-01	Y
PD-0001-1-9-03	Y

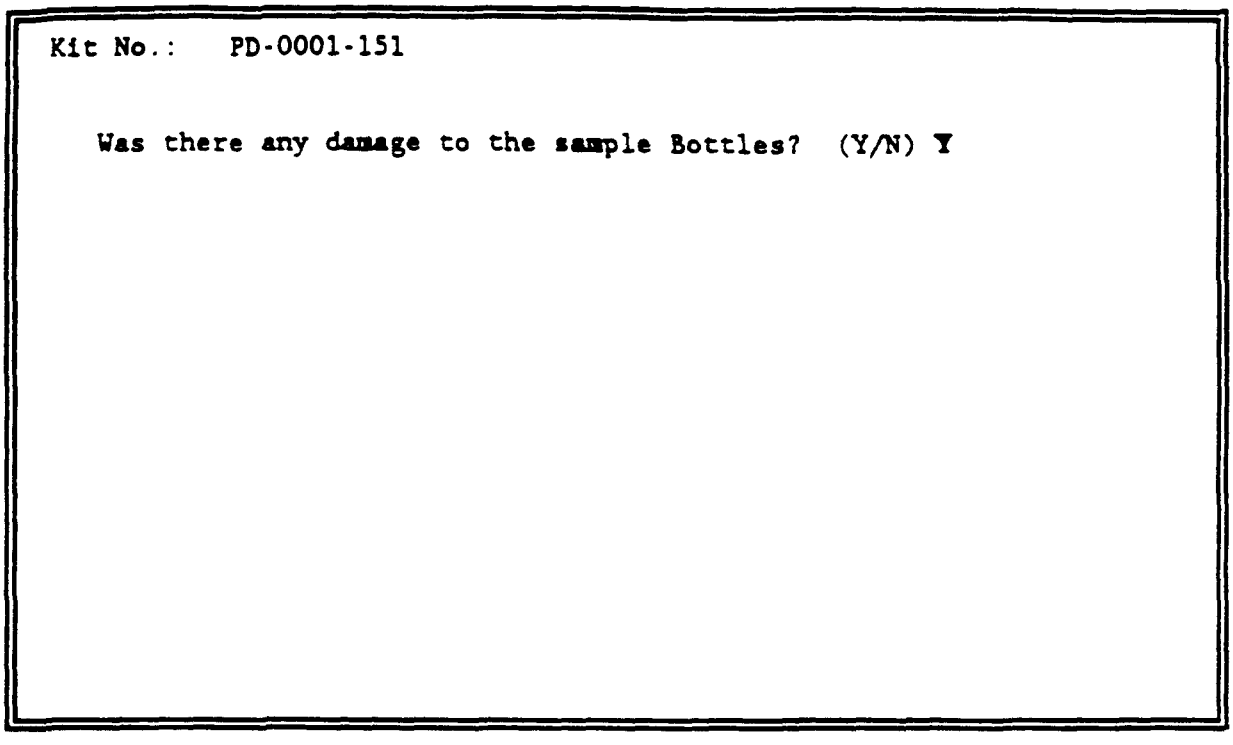
Please indicate any additional bottles you received:

1. Bottle No.:	PD-0002-1-1-05	2. Bottle No.:	PD-0002-2-2-01
3. Bottle No.:	PD-0004-4-4-01	4. Bottle No.:	- - - -
5. Bottle No.:	- - - -	6. Bottle No.:	- - - -
7. Bottle No.:	- - - -	8. Bottle No.:	- - - -

PgDn (Next page), PgUp (Previous page), use ↑ ↓ or ←┘ to select field.

Notice that the user has indicated that he did not receive the first two bottles on the list. Also note that the user has indicated additional bottles which have come in the sample kit, but which were not on the list.

Next, NPSIS prompts you to indicate if any of the individual bottles have been damaged and rendered unusable for analysis:



PgDn (Next page), PgUp (Previous page), Esc (Exit)

In order to complete the appropriate information on damaged samples, you must first press a "Y" or a "N" in the field labeled "Damaged Y/N". If you have entered a "Y" in this field, you must then identify what the cause of the damage is, to the best of your abilities. As noted on the computer screen below, the "Other" category should be used if the sample is unusable but is not broken. Please try to comment whenever possible.

Kit No.: PD-0001-151

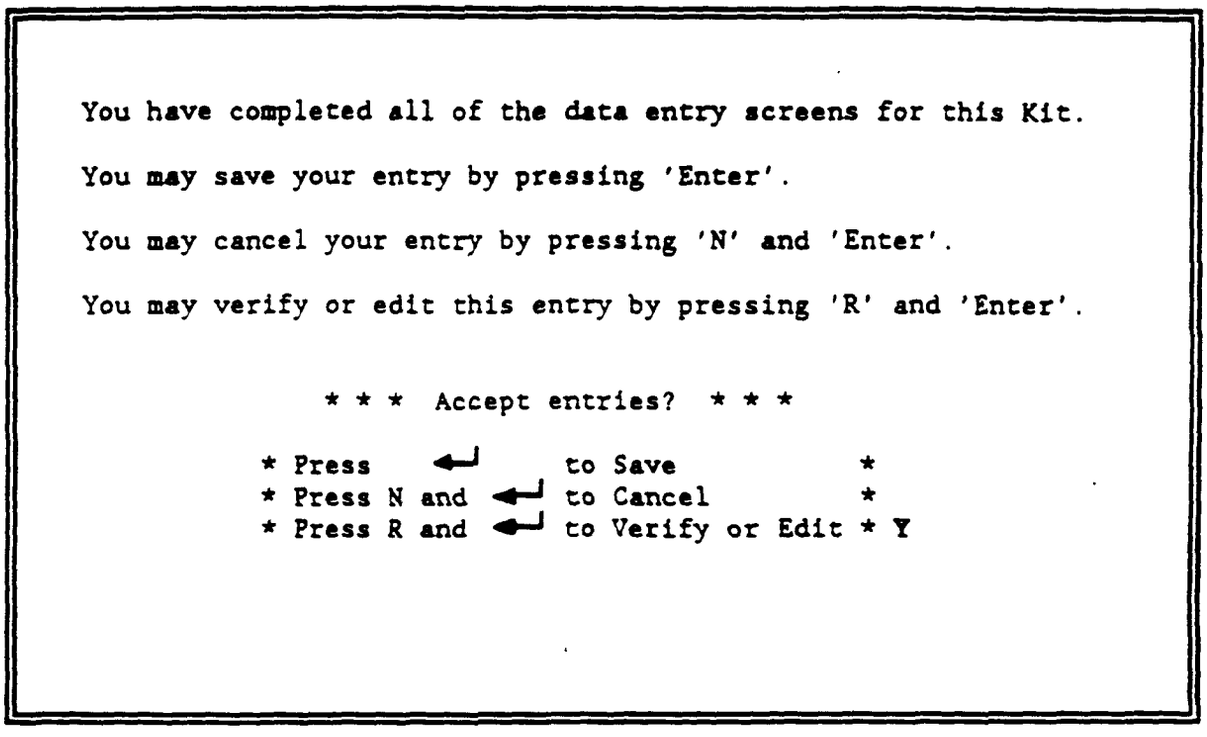
Please indicate which bottles are damaged by entering Y or N, and for those which are damaged, indicate the cause of damage.

Bottle No:	Damaged (Y/N)	--- CAUSE --- Broken (Y/N)	Other (Y/N)	Comment
PD-0001-1-3-01	N			
PD-0001-1-3-03	N			
PD-0001-1-9-01	N			
PD-0001-1-9-03	N			
PD-0002-1-1-05	N			
PD-0002-2-2-01	Y	Y		
PD-0004-4-4-01	N			

The 'Other' cause category is for reporting contamination of a sample, e.g. contamination noted on the Sample Tracking Form, air bubbles, or other reasons a sample is unusable.

PgDn (Next page), PgUp (Previous page), use ↑ ↓ or ↵ to select field.

Now you have completed all of the necessary information needed to verify that the proper samples have reached their final destination in usable condition. You may save your kit entry by pressing "Enter". If you wish to cancel your kit entry and try again, press "N" and "Enter". If you wish to view or edit the current kit entry, press "R" and "Enter" and NPSIS will plac you back at the beginning of your entry.



By pressing "Enter" , you have saved all of the information necessary for a particular sample kit. NPSIS assumes that you will enter more than one kit entry per session. Therefore, you will be placed at the initial "Searching Screen". If you are finished, press "Esc" and you will be returned to the main menu. You can then log off of NPSIS by pressing "Alt" and "Right shift" at the same time. You may also send a memo through the ICF computerized mail system. To do this, cursor down to the second menu choice and press "Enter".

The next two pages of this memo describe how to use the ICF electronic mail system. Note that the password for you is NPS. The mail system software program will prompt you for this password before it will allow access to the system. Also, when you are selecting the recipients of your memo, please press the space bar beside the initials "NPS". This will send your memo to all ICF staff involved in the NPS project. If you wish to send memos to a particular ICF staff member, please call Beth Estrada for the identification number of the desired ICF employee.

ELECTRONIC MAIL

Function
Augment office communications with electronic transfer of notes and files.

Summary
Electronic Mail (E-Mail) allows you to send, receive, read, and subsequently save or discard notes and attached files.

When you power up your workstation you will automatically enter E-Mail if you have received any mail. Enter your password to check your mail, or press <ESC> twice to avoid E-Mail and continue to the Assist main menu.

Instructions
Operation of E-Mail is similar to Lotus 1-2-3. Press the F1 key to receive help at any time during operation. If any more help is needed contact workstation support to receive a manual.

For more information on any feature of electronic mail, use Network Courier's on-line help or refer to the User's Manual.

Passwords

Your password will be "password" until you change it yourself. Once you have given your password and entered E-Mail, you can change your password by selecting Options, then Password.

Reading Mail

1. Select "Read" from your menu. Highlight read, then press <ENTER>.
2. Select the note to read:
   a. Highlight the note (using the arrow keys); and press <ENTER>.
   B. To save the note, select "Storage", then "Save". Enter the name of the file to which the note should be saved.
3. Press <ESC> to select another note.

Writing Mail

1. Select "Compose", then "edit".
2. Press <ENTER> when the highlight moves to "TO".
3. Select the recipients(s):
   a. Move the highlight to the first recipient's initials.
   b. Press the space bar. A small mark will appear.
   c. Repeat steps a and b for all recipients. Press the space bar twice to "de-select" recipients. The small mark will disappear.
   d. Press <ESC> to cancel the entire list.
4. Select the initials of those who will receive copies:
   a. Press the down arrow to mov to "CC".
   b. Select recipients as instructed above (step 3, a-d)

Writing Mail, continued

5. Enter a subject and priority. (optional)
6. Select attachments (optional):
   a. Press <ENTER> and type the path for the document(s).
   b. Press <ENTER> and select the document(s) to be attached.
   c. Repeat steps a and b for documents in another directory.
7. Enter the text of your message.
8. Press <ESC> when finished.
9. Select "Transmit" to post the note and attachments.

Quitting the Mail Program

1. Press <ESC> from the menu.
2. Select "YES".

APPENDIX E

FORMAT FOR NPS DATA

FORMAT FOR NATIONAL PESTICIDE SURVEY (NPS) DATA

LINE	COLUMNS	DESCRIPTION
1	1-6	I_Temp
	9-14	S_Temp
	17-24	Date_Sam
	27-34	Date_Shp
	37-44	Date_Rec
	47-54	Time_Sam
	57-64	Time_Ice
	[FOR METHODS 5 AND 9 ONLY]	
	68-69	pH
2	1-6	enter INITIAL TEMPERATURE OF WATER
	9-14	enter STABILIZED TEMPERATURE OF WATER
	17-24	enter DATE SAMPLED
	27-34	enter DATE SHIPPED
	37-44	enter DATE RECEIVED
	47-54	enter TIME SAMPLED
	57-64	enter TIME ICED
	[FOR METHODS 5 AND 9 ONLY]	
	67-70	enter pH
3	BLANK	
4	1-17	Receipt Condition
5	1-80	enter CONDITION OF SAMPLE UPON RECEIPT AT LABORATORY
6	BLANK	
7	1-6	Samp #
	16-18	Lab
	21-25	Set #
	28-35	Date_Spk
	38-45	Date_Ext
	48-55	Date_Ana
	58-63	Column
8	1-13	enter SAMPLE IDENTIFICATION NUMBER
	16-18	enter LAB ABBREVIATION
	21-25	enter SET NUMBER
	28-35	enter DATE SPIKED
	38-45	enter DATE EXTRACTED
	48-55	enter DATE ANALYZED
	58-63	enter ANALYSIS COLUMN
9	BLANK	

FORMAT FOR NATIONAL PESTICIDE SURVEY (NPS) DATA (cont.)

LINE	COLUMNS	DESCRIPTION
10	1-4	Type
	8-13	Spiker
	16-22	Extract
	25-31	Analyst
	34-40	Sam_Vol
	43-49	Ext_Vol
	52-60	Int. Std.
	65-70	% Surr
11	1-5	enter SAMPLE TYPE
	8-13	enter SPIKER'S INITIALS
	16-22	enter EXTRACTOR'S INITIALS
	25-31	enter ANALYST'S INITIALS
	34-40	enter VOLUME OF SAMPLE
	43-49	enter VOLUME OF EXTRACT
	52-62	enter INTERNAL STANDARD
	65-70	enter PERCENT RECOVERY OF SURROGATE
12	BLANK	
13	1-8	Comments
14	1-80	enter ANY PERTINENT COMMENTS ON SAMPLE AND ANALYSIS
15	BLANK	
16	1-7	Analyte
	29-33	Conc.
	39-45	Analyte
	67-71	Conc.
17-?	1-25	enter ANALYTE'S NAME
	28-34	enter CONCENTRATION OR PERCENT RECOVERY
	39-63	enter ANALYTE'S NAME
	66-72	enter CONCENTRATION OR PERCENT RECOVERY

FORMAT FOR NATIONAL PESTICIDE SURVEY (NPS) INSTRUMENT CONTROL DATA

LINE	COLUMNS	DESCRIPTION
1	1-3	Lab
	6-11	Method
	14-21	Date_Ana
	24-30	Analyst
	35-37	S/N
	42-44	PSF
	49-51	PGF
	55-58	Res.
2	BLANK	
3-?	1-3	enter LAB ABBREVIATION
	6-11	enter METHOD NUMBER
	14-21	enter DATE ANALYZED
	24-30	enter ANALYST'S INITIALS
	33-37	enter SIGNAL TO NOISE RATIO
	40-44	enter PEAK SYMMETRY FACTOR
	47-51	enter PEAK GEOMETRY FACTOR
	54-58	enter RESOLUTION

NOTES ON NPS DATA FORMATS

1. The format for any date is mm/dd/yy

   A missing date should be entered 01/01/60

2. The format for any time is hh:mm in military time

   A missing time should be entered 00:00

3. Any other data that is missing should be entered with a period (.)

4. The number of decimal places should be as follows:

Concentration	3
Percent Recovery	1
Internal Standard	0
Instrument Controls	2
pH	1
Temperatures	0
Volumes	0

5. The codes for Column are as follows:

Primary	PRIM
Confirmatory	CONF
Third	GCMS

6. The codes for Lab are as follows:

TSD	TSD
OPP	OPP
WERL	WER
Radian	RAD
Battelle	BCD
James M. Montgomery	JMM
Alliance	ALL
Environmental Sciences and Engineering	ESE

7. The codes for Type are as follows:

Field Sample	SAMP
Shipping Blank	SBLK
Method Blank	MBLK
Lab Control Standard	LCS@
Lab Spike Sample	LSS@#
Time Storage for Extract	HTE@
Time Storage for Sample	HTS@
Day@Time Storage	DTS@

where @ is the mix letter (A,B,C or D)
and # is the spiking level (1,2 or 3)

if only one mix use "A"

8. There should be at least one blank line between samples in the NPS data file.

9. The codes for Concentrations and Percent Recoveries are as follows:

Not Analyzed	.
Not Detected (< Estimated Detection Limit)	-999
Saturated	-777
Other	-333
Below Reporting Limit, but above EDL	-111
Above Reporting Limit, but not Quantified	888

10. If a reported value is greater than (>) some number in the NPS instrument control data, then use a minus sign (-) instead of >

APPENDIX F

DATA REPORTING FORMAT CHANGES

MEMORANDUM

DATE: April 18, 1988

SUBJECT: Data Reporting Format Changes

FROM: David J. Munch, Chemist
Drinking Water Quality Assessment Branch

TO: NPS Technical Monitors (See below)

The purpose of this memorandum is to consolidate the changes to the NPS data reporting format, which have occurred since it was originally constructed. You have previously been supplied with most of these changes, but please check to be sure that they have all been relayed to your contract and referee laboratories.

1. Line 2, columns 1-6 are to be used to record the pH measured in the field. This data will be found on the field sample tracking sheet.

2. Line 2, columns 67-70 are to be used to record the pH measured upon sample receipt at the laboratory. This only applies to methods 5 and 9.

3. Line 8, columns 1-13, Sample Identification Number, have been expanded to columns 1-14.

4. The data entered on line 10, columns 52-60, concerning the internal standard, it should be entered not as the peak area but as the "percent recovery" as compared to the mean observed for the calibration curve.

In order to simplify the "Sample Type" code (line 11, columns 1-5), the following codes should be used to designate the various types of spiked samples.

LCS@ = Laboratory Control Sample
LSS@f = Laboratory Spiked Sample
DTS@ = Day 0 Time Storage Sample
HTE@ = Extract Time Storage Sample
HTS@ = Sample Time Storage Sample

In addition, two clarifications have been made to the codes for analyte concentration entries.

-999 = Not Detected (< 1/2 Minimum Reporting Limit)
-111 = Below Minimum Reporting Limit but greater than or equal to 1/2 the Minimum Reporting Limit.

Format for National Pesticide Survey (NPS) Data

LINE	COLUMNS	DESCRIPTION
1	1-6	[redacted] Fld_pH
	9-14	S_Temp
	17-24	Date_Sam
	27-34	Date_Shp
	37-44	Date_Rec
	47-54	Time_Sam
	57-64	Time_Ice
	68-69	pH Note: Method 9 only
2	1-6	enter ~~INITIAL TEMPERATURE OF WATER~~ Field_pH
	9-14	enter STABILIZED TEMPERATURE OF WATER
	17-24	enter DATE SAMPLED
	27-34	enter DATE SHIPPED
	37-44	enter DATE RECEIVED
	47-54	enter TIME SAMPLED
	57-64	enter TIME ICED
	68-69	enter pH Note: Method 9 only
3	BLANK	
4	1-17	Receipt Condition
5	1-80	enter CONDITION OF SAMPLE UPON RECIEPT AT LABORATORY
6	BLANK	
7	1-6	Samp #
	16-18	Lab
	21-25	Set #
	28-35	Date_Spk
	38-45	Date_Ext
	48-55	Date_Ana
	58-63	Column
8	1-13	enter SAMPLE IDENTIFICATION NUMBER
	16-18	enter LAB ABBREVIATION (JMM)
	21-25	enter SET NUMBER
	28-35	enter DATE SPIKED
	38-45	enter DATE EXTRACTED
	48-55	enter DATE ANALYZED
	58-63	enter ANALYSIS COLUMN
9	BLANK	

APPENDIX G

DATA REPORTING CODES

DATE: September 9, 1988

SUBJECT: Data Reporting Codes

FROM: Christopher Frebis, CSC Statistician

TO: Distribution

The purpose of this memorandum is to discuss the reporting codes used in the National Pesticide Survey. There has been some confusion over these codes as to when and where to use them and their exact meaning.

Table 1 identifies the unique sample types (SAMP - field sample, MBLK - method blank, SBLK - shipping blank, LCS - lab control standard, and LSS, DTS, HTE, and HTS - spiked field samples — these last three are each a type of time storage sample). Under each unique sample type are the only possible codes that can appear for that sample type. (Note: -555 has been added for the situation where the contract lab sends the extract to the referee lab for GCMS analysis, and the code -222 has been deleted.) There is also a type of decision tree for field samples since they are a little more complicated with three analyses for confirmation and qualitative only analytes.

I hope this memorandum helps to put everyone on similar terms as well as clearing the muddy water. If there are any questions of different scenarios you wish to discuss, please call me at (513) 569-7498.

Distribution: Herb Brass, Technical Support Division
Aubry Dupuy, Environmental Chemistry Laboratory
Carol Madding, Technical Support Division
Bob Maxey, Environmental Chemistry Laboratory
Dave Munch, Technical Support Division
Kent Sorrell, Technical Support Division
Bob Thomas, Technical Support Division

TABLE 1: USES OF DATA CODES IN NPS

SAMPLE TYPE				
SAMP	MBLK	SBLK	LCS	LSS,DTS HTE,HTS
. (a)	. (a)	. (a)	. (b)	. (b)
-111 (c)	-111 (c)	-111 (c)	****	****
-333 (d)	-333 (d)	-333 (d)	****	-333 (d)
-444 (e)	****	-444 (e)	****	-444 (e)
-555 (f)	-555 (f)	-555 (f)	****	****
-666 (g)	****	-666 (g)	****	****
-777 (h)	-777 (h)	-777 (h)	-777 (h)	-777 (h)
888 (i)	888 (i)	888 (i)	****	****
-999 (j)	-999 (j)	-999 (j)	****	****
conc (k)	conc (k)	conc (k)	% rec (l)	% rec (l)

(a) Analyte dropped from survey (Demeton-S and Carboxin sulfoxide) or not analyzed on the second column or in GCMS analysis.

(b) Analyte not in mix.

(c) Analyte's concentration between MRL/2 and MRL. (If no confirmation is run, a comment as to why should be made.)

(d) A lab mishap, e.g. sample lost during extraction or sample dropped etc., This is a unique situation. (A comment should give further explanation.)

(e) This analyte fails QC in this set (e.g. LCS out of control or positive method blank or time to extraction or analysis is too long) and therefore cannot be reported, however the analyte does not require a qualitative challenge. This code also applies to any spike sample in a set where the LCS is out of control.

(f) GCMS only: Sent to referee lab for GCMS analysis.

(g) This analyte fails QC in this set and therefore cannot be reported, however the analyte requires a qualitative challenge.

(h) Analyte was saturated. Should be diluted and re-done, if observed in a field sample. (Another sample with the exact same header information should appear, analytes not saturated in the original sample should be reported as ., and saturated analytes should be reported as their concentration.)

(i) Positive, can occur in two fashions: 1) any analyte in GCMS analysis; or 2) a qualitative only analyte on either of the first two columns.

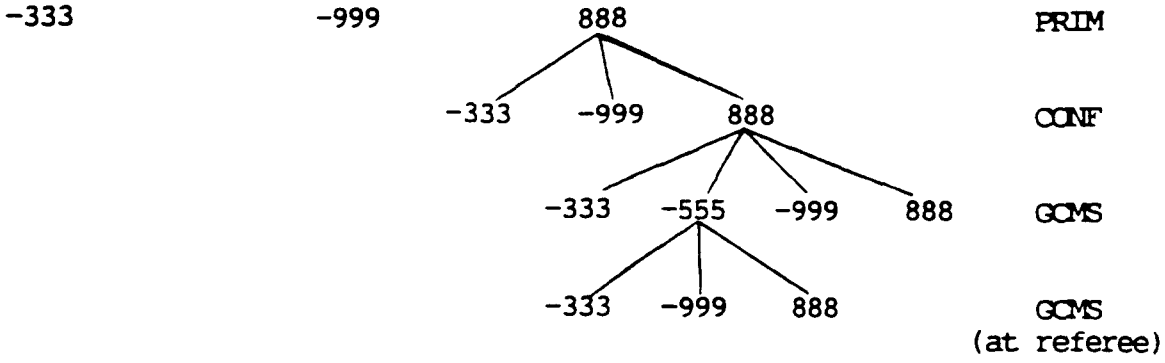
(j) Analyte's concentration below MRL/2.

(k) Concentration above MRL for quantitative analytes, reported to three significant figures.

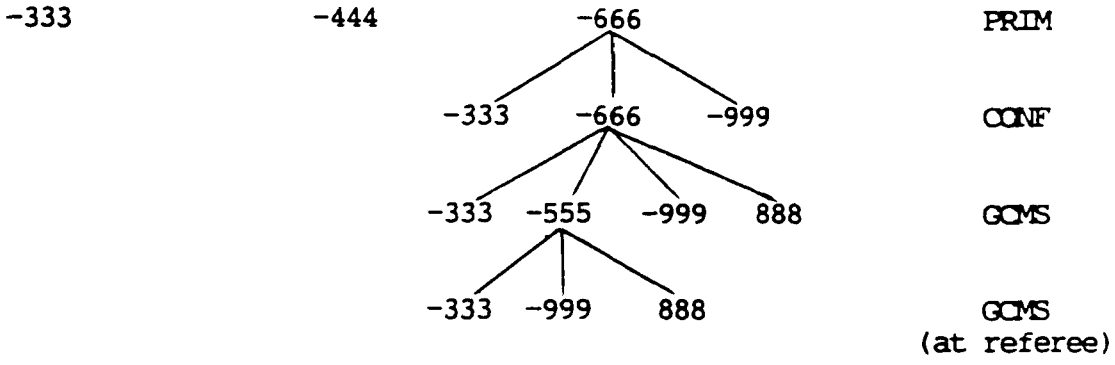
(l) Percent recovery, reported to one decimal place (even if recovery is 0.0%).

**** Code not applicable.

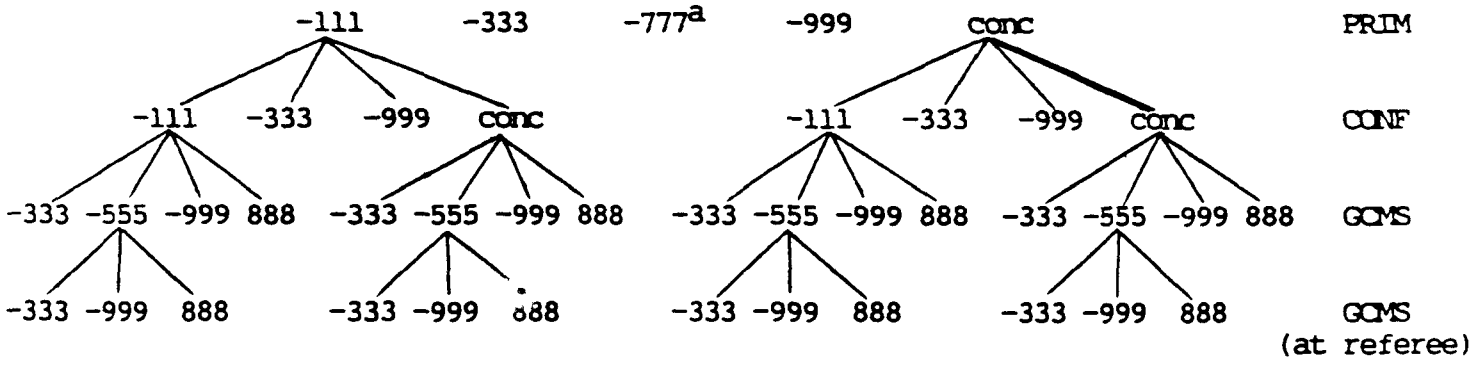
Sample (Qualitative only analyte)



Sample (Quantitative analyte with QC failure)



Sample (Quantitative analyte with no QC failure)



a = Dilute and reanalyze

APPENDIX H

NPS RAPID REPORTING SYSTEM

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

MEMORANDUM

DATE: April 12, 1988

SUBJECT: NPS Rapid Reporting System

FROM: David J. Munch, Chemist DJM
Drinking Water Quality Assessment Branch

TO: NPS Technical Monitors

Jerry Kotas has requested that any confirmed results of health significance be reported as quickly as possible. Therefore, if an analyte listed in the attached tables is observed in the primary analyses, at or above the rapid reporting limit, the following actions should be instituted. For any listed analyte where the rapid reporting level is less than or equal to 1/2 the minimum reporting level (MRL), any occurrence at or above 1/2 the MRL should also be processed as below. (Note: The procedures for determining the occurrence of NPS analytes that may occur below the MRL, and are not listed on the attached tables, have not yet been finalized.)

1. The appropriate confirmational analyses (GC/MS for methods 1-3, 6-7, second column for Method 5) should be performed as soon as practical.

2. The laboratory should telephone their Technical Monitor, the same day the confirmation is completed.

3. The laboratory should immediately document the observed result in a letter to their Technical Monitor.

4. As quickly as possible on the day the above telephone call is received from the laboratory, the Technical Monitor should inform their Laboratory Analytical Coordinator of the finding. The Technical Monitor should forward on to the Laboratory Analytical Coordinator the above documentation, with any comments he/she may have concerning the validity of the result.

5. The Laboratory Analytical Coordinator should inform Jerry Kotas and the second Analytical Coordinator of the finding by telephone the same day if possible, and in writing after the documentation is received from the Technical Monitor.

6. The Analytical Coordinators are to request, through the appropriate Technical Monitors, that all analyses for this sample site be conducted, and reported in writing, as soon as practical.

If you have any questions concerning these procedures, please let Bob Maxey or me know. Also, please pass on this information to your contract and referee laboratories. They will need to have this information in hand prior to their conducting the dry run.

Attachment

Addressees:

A. Dupuy
L. Kamphake
C. Madding
R. Maxey
R. Sorrell
R. Thomas

cc:

J. Kotas
H. Brass
A. Kroner
J. Orme

METHOD #1

ANALYTE	RAPID REPORTING LEVEL
Alachlor	44 ug/L
Ametryn	300 ug/L
Atrazine	35 ug/L
Bromacil	2,500 ug/L
Butylate	700 ug/L
Carboxin	1,000 ug/L
Diphenamid	300 ug/L
Fenamiphos	5.0 ug/L
Hexazinone	1,050 ug/L
Metolachlor	300 ug/L
Metribuzin	250 ug/L
Propazine	500 ug/L
Simazine	50 ug/L
Tebuthiuron	125 ug/L
Terbacil	250 ug/L

METHOD #2

ANALYTE	RAPID REPORTING LEVEL
alpha-Chlordane	0.5 ug/L
gamma-Chlordane	0.5 ug/L
Chlorothalonil	150 ug/L
Dacthal (DCPA)	5,000 ug/L
Dieldrin	0.5 ug/L
Propachlor	130 ug/L
Trifluralin	25 ug/L

METHOD #3

ANALYTE	RAPID REPORTING LEVEL
Acifluorfen	130 ug/L
Bentazon	87.5 ug/L
2,4-D	100 ug/L
Dalapon	800 ug/L
Dicamba	13 ug/L
Dinoseb	3.5 ug/L
Pentachlorophenol	300 ug/L
Picloram	700 ug/L
2,4,5-T	105 ug/L
2,4,5-TP	70 ug/L

METHOD #4

ANALYTE	RAPID REPORTING LEVEL
Cyanazine	13 ug/L
Diuron	70 ug/L
Fluometuron	438 ug/L
Propham	595 ug/L

METHOD #5

ANALYTE	RAPID REPORTING LEVEL
Aldicarb	10 ug/L
Baygon	40 ug/L
Carbaryl	1,000 ug/L
Carbofuran	50 ug/L
Methomyl	250 ug/L
Oxamyl	175 ug/L

METHOD #6

ANALYTE	RAPID REPORTING LEVEL
ethylene thiourea	1.05 ug/L

METHOD #7

ANALYTE	RAPID REPORTING LEVEL
dibromochloropropane	2.5 ug/L
1,2-dichloropropane	56 ug/L
cis/trans 1,3-dichloropropene	11 ug/L
ethylene dibromide	0.04 ug/L

METHOD #9

ANALYTE	RAPID REPORTING LEVEL
Nitrate/Nitrite	10,000 ug/L

DIXON'S TEST

Dixon's test is used to confirm the suspicion of outliers of a set of data (for example, control chart data points). It is based on ranking the data points and testing the extreme values for credibility. Dixon's test is based on the ratios of differences between observations and does not involve the calculation of standard deviations.

The procedure for Dixon's test is as follows (from Taylor, 1987):

1) The data is ranked in order of increasing numerical value. For example:

$$X_1 < X_2 < X_3 < \ldots < X_{n-1} < X_n$$

2) Decide whether the smallest, X_1, or the largest, X_n, is suspected to be an outlier.

3) Select the risk you are willing to take for false rejection. For use in this QAPP we will be using a 5% risk of false rejection.

4) Compute one of the ratios in Table 1. For use in this QAPP we will be using ratio r_{22}, since we will be using between 20 and 17 points for the control charts.

5) Compare the ratio calculated in Step 4 with the appropriate values in Table 2. If the calculated ratio is greater than the tabulated value, rejection may be made with the tbulated risk. Fort his QAPP we will be using the 5% risk values (bolded).

Example (from Taylor)

Given the following set of ranked data:

10.45, 10.47, 10.47, 10.48, 10.49, 10.50, 10.50, 10.53, 10.58

The value 10.58 is suspected of being an outlier.

1) Calculate r_{11}

$$r_{11} = \frac{10.58 - 10.53}{10.58 - 10.47} = \frac{0.05}{0.11} = 0.454$$

2) A 5% risk of false rejection (Table 2), $r_{11} = 0.477$

3) Therefore there is no reason to reject the value 10.58.

4) Note that at a 10% risk of false rejection $r_{11} = 0.409$, and the value 10.58 would be rejected.

TABLE 1

CALCULATION OF RATIOS

Ratio	For use if n is between	if X_n is suspect	if X_1 is suspect
r_{10}	3 - 7	$\frac{(X_n - X_{n-1})}{(X_n - X_1)}$	$\frac{(X_2 - X_1)}{(X_n - X_1)}$
r_{11}	8 - 10	$\frac{(X_n - X_{n-1})}{(X_n - X_2)}$	$\frac{(X_2 - X_1)}{(X_{n-1} - X_1)}$
r_{21}	11 - 13	$\frac{(X_n - X_{n-2})}{(X_n - X_2)}$	$\frac{(X_3 - X_1)}{(X_{n-1} - X_1)}$
r_{22}	14 - 25	$\frac{(X_n - X_{n-2})}{(X_n - X_3)}$	$\frac{(X_3 - X_1)}{(X_{n-2} - X_1)}$

Note that for use in this QAPjP ratio r_{22} will be used.

TABLE 2

VALUES FOR USE WITH THE DIXON TEST FOR OUTLIERS

		Risk of False Rejection			
Ratio	n	0.5%	1%	5%	10%
	3	0.994	0.988	0.941	0.806
	4	0.926	0.889	0.765	0.679
r_{10}	5	0.821	0.780	0.642	0.557
	6	0.740	0.698	0.560	0.482
	7	0.080	0.637	0.507	0.434
	8	0.725	0.683	0.554	0.479
r_{11}	9	0.677	0.635	0.512	0.441
	10	0.639	0.597	0.477	0.409
	11	0.713	0.679	0.576	0.517
r_{21}	12	0.675	0.642	0.546	0.490
	13	0.649	0.615	0.521	0.467
	14	0.674	0.641	0.546	0.492
	15	0.647	0.616	0.525	0.472
	16	0.624	0.595	0.507	0.454
	17	0.605	0.577	0.490	0.438
	18	0.589	0.561	0.475	0.424
	19	0.575	0.547	0.462	0.412
r_{22}	20	0.562	0.535	0.450	0.401
	21		0.524	0.440	0.391
	22		0.514	0.430	0.382
	23		0.505	0.421	0.374
	24		0.497	0.413	0.367
	25		0.489	0.406	0.360

Note that for this QAPjP the 5% risk level will be used for ratio r_{22}.

Reference:

John K. Taylor, Quality Assurance of Chemical Measurements, Lewis Publishers, Chelsea, MI, 1987.

APPENDIX J

STANDARD OPERATING PROCEDURE:
BATCH FILING SYSTEM

APPENDIX J

STANDARD OPERATING PROCEDURE: BATCH FILING SYSTEM

PURPOSE

To centralize the storage of ESE analytical data batches and all associated documentation for each batch.

PROCEDURE

All data batches created by the various departments will be placed in departmentally assigned colored batch files. All associated documentation for each batch will be included in each folder as well as a documentation checklist. The checklist will be marked by the analyst noting everything included in the batch file and will be signed and dated by the analyst and a review person.

The batch file must also have the "Computer QC Checks" and the "Internal QA/QC Batch Checklist" section located at the end of each batch marked, signed and dated by the analyst. The batch then must be reviewed, signed and dated by the Department Manager. If the batch fails any of these checks, the corresponding Lab Coordinator(s) for all samples in the batch must also sign and date the batch and may add comments.

The batch file is then signed-in to Information Services to document chain-of-custody of the raw data.

Each batch will then be finalized and filed numerically by department in locked file cabinets located in the Information Services department. Each department manager will have a key to his/her file cabinet and Information Services will retain a key to all cabinets.

Since only the most recent batches can be filed in the file cabinets, all "older" batches are filed by department in a separate, locked storage room with access available only to Information Services.

All data batches including those in the storage room are available for checkout at any time. All batches are signed out to the individual with a hard copy as well as an electronic file kept of all checkouts.