



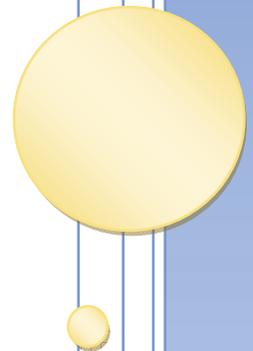
STORM WATER SPILL AND ILLICIT DISCHARGE RESPONSE PLAN

(SWSRP)



City of Lodi

June 2014





Storm Water Spill and Illicit Discharge Response Plan

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SPILL PLAN REVISIONS

Revision No.	Date	Revised By	Reason for Revision	Sections Revised
0	6/12/14	KMG	Initial Preparation	All New



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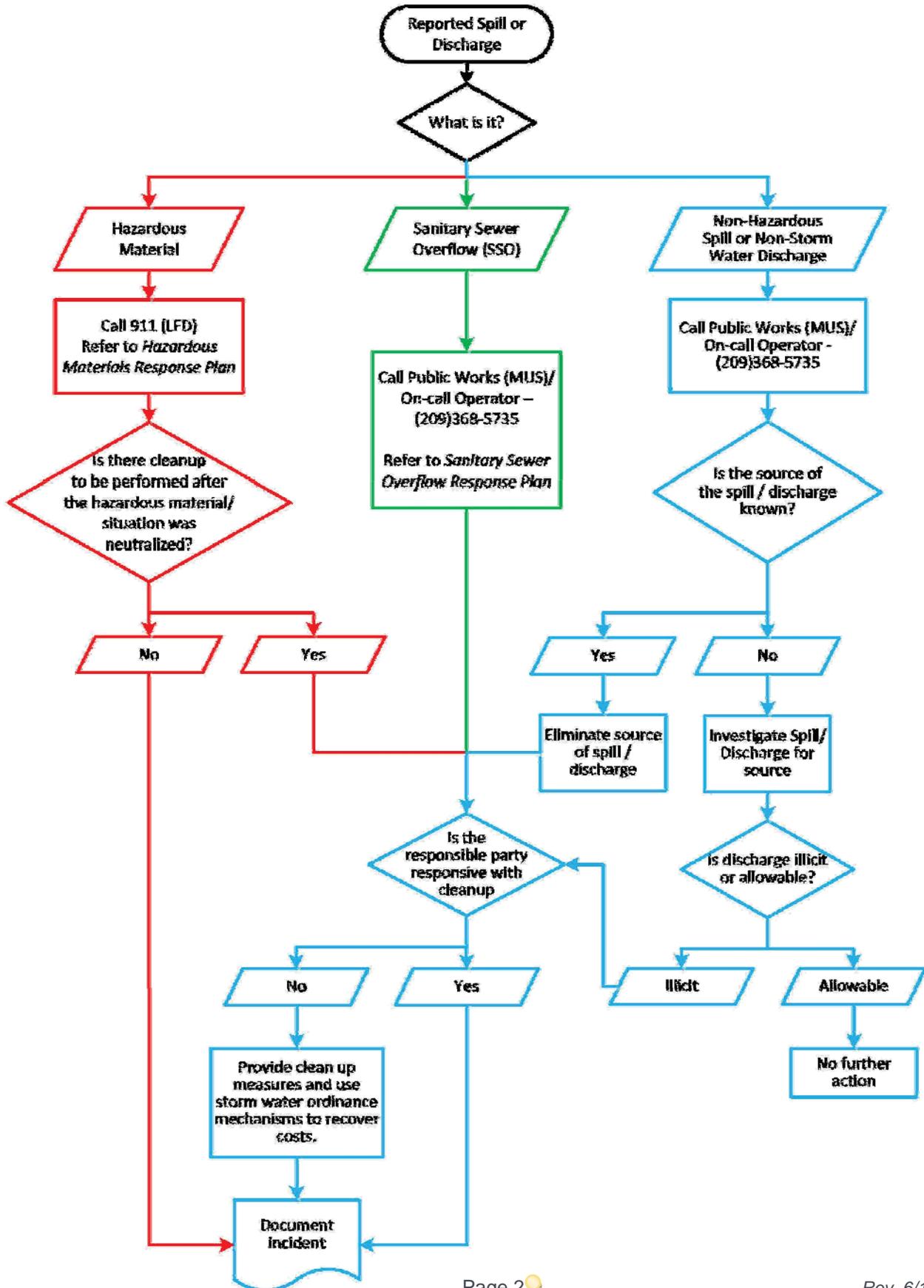
1.0 Agency Roles & Responsibilities

The purpose of this Storm Water Spill and Illicit Discharge Response Plan is to provide a framework for spill and illicit discharge response procedures in the City of Lodi and to comply with the Phase II Small MS4 NPDES General Permit Order No. 2013-0001-DWQ. This spill plan is designed to provide general response procedures to the City of Lodi employees. However, each situation is unique and field conditions may necessitate a variation from these procedures. The plan does not specifically address follow up measures for hazardous materials spills or sanitary sewer overflows (SSOs). The City’s Fire Department will respond to hazardous materials spills within the City under the direction of their Hazardous Materials Response Plan. The City’s Public Works Department, Municipal Utility Services (MUS), will respond to SSOs under the direction of their Sanitary Sewer Overflow Response Plan.

Department	Contact / Phone	Responsibilities
Fire Department	Emergency – 911 Non Emergency – (209) 333-6735	<ul style="list-style-type: none"> ▪ Hazardous Materials ▪ Unknown/Unidentifiable Materials ▪ Emergency Response
Police Department	Emergency – 911 Non Emergency – (209) 333-6727	<ul style="list-style-type: none"> ▪ Emergency Response (Access Control)
Utilities - Wastewater Operations & Maintenance	MUS / On-call Operator – (209) 368-5735	<ul style="list-style-type: none"> ▪ Sanitary Sewer Overflows (SSOs) ▪ 24-Hour Reporting Line ▪ Illicit Discharge Identification ▪ Non-Hazardous Material Response
Code Enforcement	(209) 333-6823	<ul style="list-style-type: none"> ▪ Enforcement / Mitigation



Storm Water Spill and Illicit Discharge Response Plan





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2.0 Procedures for Responding to Complaints

Every spill situation is different and typically requires a varied approach to the response.

Upon discovering or being notified of a spill or illicit discharge, it is crucial to obtain as much information about the incident as possible. This information will assist in establishing the severity of the incident and how to proceed with the cleanup efforts. The stages involved in spill and illicit discharge response and cleanup are:

- I. Discovery and Notification
- II. Coordination and Containment
- III. Cleanup, Evidence Collection, and Documentation
- IV. Evaluation and Reporting

2.1 Responding to Spill Reports

The City has several notification mechanisms for identifying spills and illicit discharges. These mechanisms include phone reporting (911 and 24-hour reporting line), online compliant forms (Code Enforcement), and field identification by Operations and Maintenance and emergency responders (i.e. Fire Department).

3 Typical Methods of Incident Reporting:

There are generally three types of spill or illicit discharge discovery situations.

- **Public Reporting:** Incidents that have been reported to the municipality by members of the general public
- **Employee Discovery:** Incidents where a municipal employee comes across a spill or illicit discharge during regular work activities.
- **Illicit Substances Detected due to Field Screening:** Incidents of spills and illicit discharges during regular work activities.

Use the Spills/Illicit Discharge Initial Contact Form in **Appendix A** to compile as much information as possible.

The responding department(s) will perform a response based upon their established procedures. The following information should attempt to be recorded when taking the call:

- a) Full name of caller (first/last name) *May be anonymous*
- b) Caller's contact information (phone number, address, company name, etc.) *May be anonymous*
- c) Date and time call received
- d) Location of spill / discharge
- e) Description of the spill / discharge
- f) Date and time spill / discharge was first observed by the caller
- g) Observations of the caller
- h) Other relevant information that will enable the MUS to quickly locate, assess, and stop the spill / discharge (e.g. estimated spill volume, suspected cause of spill, are any hazardous chemicals involved)



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After the initial call, there may be other callers reporting the spill. Their name & number should also be recorded and their call returned once the problem has been resolved.

Regardless of who reports the incident, the first priority is to determine if there is any fire, explosion or safety hazard to life, health or the environment or a need to evacuate. If any of these situations are present the incident will be referred to the Fire Department.

Hazardous Materials Response:

See the Fire Department's Hazardous Materials Response Plan.

Sanitary Sewer Overflow:

See the Utilities Department's Overflow Emergency Response Plan.

After Collecting the Reporting Person(s) Information...

Notify the O & M staff via the phone and / or radio as soon as possible in the following order (move to the next position on the list if no answer to first caller):

- a. Utility Superintendent
- b. Streets & Drainage Supervisor
- c. Wastewater Supervisor
- d. Staff Person doing Work Orders
- e. On-call radio

Send an email with the following information to the **Emergency Spill Response Group** (distribution list found in outlook)

- a. Information taken from call (First Step)
- b. Name of employee whom spill was reported to (Second Step)

2.2 Reporting Scenarios

Various reporting scenarios will possibly trigger different required responses. The following are examples of reporting scenarios and recommended City response actions.

Public Reporting:

- a. A phone call is received from the general public that someone was observed putting grass clippings into the storm sewer.

Recommended Action: Complete the Spills/Illicit Discharge – initial Contact Form and route to the Utility Superintendent

- b. A phone call is received from the general public that a sheen and gasoline odor was observed along the river.

Recommended Action: Complete the Spills/Illicit Discharge – Initial Contact Form and contact 911 immediately. Notify the Utility Superintendent by giving them a copy of the Spills/Illicit Discharge – Initial Contact Form

Employee Discovery:

- a. During routine maintenance an employee reported spill of a small quantity of oil.

Recommended Action: The employee should follow the municipality's standard policy and procedure in containment, clean up and disposal of material (e.g. using oil dry and sweep up). **Note: For large hazardous spills or releases that the City of Lodi is the**



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Responsible Party first call 911, then call Cal OES State Warning Center (800) 852 – 7550 to report the incident. Review the Cal OES Spill / Release Notification Guidance in Appendix B.

- b. While out on an inspection an employee notices a large quantity of an unidentified substance along the river.

Recommended Action: The employee should call 911 immediately or, radio their supervisor and/or the Utility Superintendent to call 911 immediately. The Spills/Illicit Discharge – Initial Contact Form should be completed and routed to the Utility Superintendent.

Illicit Substance Detected due to Field Screening:

- a. While doing a field inspection for illicit discharges an employee comes across a small quantity of an unknown material/substance at the outfall.

Recommended Action: The employee should contact the Utility Superintendent. The Spills/Illicit Discharge – Initial Contact Form should be completed.

- b. While doing a field inspection for illicit discharges an employee comes across a large quantity of a material with unusual color and odor.

Recommended Action: The employee should contact 911 immediately and then contact the Utility Superintendent relaying as much information as possible. The Spills/Illicit Discharge – Initial Contact Form should be completed.

3.0 Spill / Illicit Discharge Investigations

Once a spill or discharge is found, additional efforts usually are necessary to determine the source and responsible party. There are many methods that can be used to find the source of a spill or illicit discharge, including:

- Tracing the spill or illicit discharge upstream – beginning at the outfall
- Tracing the discharge upstream through the MS4 using available maps
- Televising the storm and/or sanitary sewers
- Uncovering manholes upstream to identify where flow may be coming from
- Checking for amount of flow in discharge
 - Sanitary blockages (usually higher flows)
 - Cross-connects (usually much lower flows)
- Dye testing storm sewers and connections
- Smoke testing sanitary sewers
- Visual and smell indicators
- Obtaining access to perform test and obtain samples



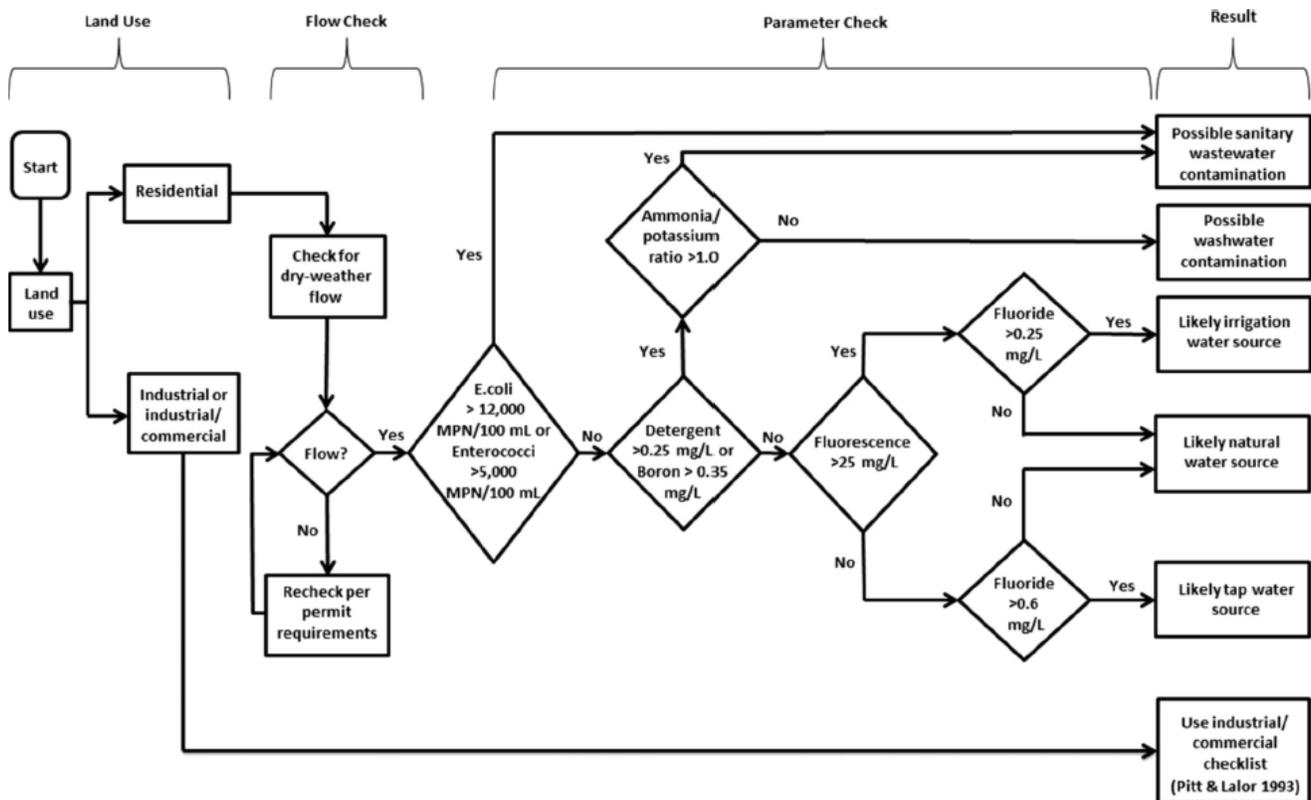
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3.1 Indicator Monitoring

The City's Phase II Small MS4 NPDES General Permit requires indicator monitoring of outfalls that are discovered to have an active flows or ponding more than 72 hours after the last rain event. Indicator monitoring is only required to be performed when the source or pollutant associated with the flow is unknown. Indicator monitoring assists in the detection of the likely source(s) based upon analytical characteristics. In the illustration below (Figure 1-1), each of the detected parameters is a clue to the potential source(s) of the discharge. By using the indicator parameter results, a more directed source investigation can be performed. The indicator parameter monitoring will consist of the following parameters:

- Ammonia
- Color
- Detergents-Surfactants
- Fluoride
- Hardness
- pH
- Potassium
- Turbidity

Figure 1-1



Kim Irvine, Mary C. Rossi, Stephen Vermette, Jessica Bakert & Kerry Kleinfelder (2011): Illicit discharge detection and elimination: Low cost options for source identification and trackdown in stormwater systems, Urban Water Journal, 8:6, 379-395



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Indicator monitoring may be performed in the field by using field instruments or utilizing a certified laboratory for parameter analysis. Guidance for indicator monitoring is included in **Appendix C**. An example chain of custody document to be included with laboratory submitted sample is included in **Appendix D**.

If any of the indicator analysis is in excess of the Action Level Concentrations, the City will perform follow up investigations as described in Section 3.0.

Indicator Parameter	Action Level Concentration
Ammonia	>= 50 mg/L
Color	>= 500 units
Conductivity	>= 2,000 µS/cm
Hardness	<= 10 mg/L as CaCO3 or >= 2,000 mg/L as CaCO3
pH	<= 5 or >=9
Potassium	>= 20 mg/L
Turbidity	>= 1,000 NTU

Common Illicit Discharge Origination Sources:

- An internal plumbing connection (e.g., the discharge from a washing machine is directed to the building’s storm lateral; the floor in a garage is connected to the building’s storm lateral)
- A service lateral cross-connection (e.g., the sanitary lateral from a building is connected to the MS4)
- An infrastructure failure within the sanitary sewer or MS4 (e.g., a collapsed sanitary line is discharging into the MS4)
- An indirect transitory discharge resulting from leaks, spills, or overflows.

3.2 Evidence Collection

It is important to capture evidence of the spill or illicit discharge upon arrival on scene, during the cleanup, and after the work has been completed. Samples and photographs should be obtained prior to the evidence being changed or destroyed by weather or cleanup crews. If there are multiple agencies working on a single incident, sharing information is imperative so that duplication of efforts is minimized.

Evidence will be used to hold the responsible party accountable, for successful enforcement of civil/criminal statutes, and to recover cleanup costs. Uniform procedures should be followed when documenting an incident through sampling, photographs, and collecting other information. This includes maintaining a “chain of custody” on all samples and other evidence.

Document the following evidence information:

- Date and time of photos
- Name of the responsible party
- Exact location and site description
- The photographer’s name



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- Keep an on-going written log
Statements should be taken while eyewitnesses are still available. Written documentation should include notes or a log of your observations, conversations, statements from witnesses, decisions, actions, sampling activity, and photographs. Include names, addresses, dates, and times in your notes. Also, obtain copies of any shipping papers, material safety data sheets (MSDS), and statements from responsible parties regarding product, vehicle numbers, etc. Make certain you have the correct spelling of each chemical name (common and scientific).

- Take pictures
Take pictures before the spill site has changed, during the cleanup, and after the work has been completed. Color photographs are preferred. The more pictures you take, the better the documentation.

Pictures should show the source or possible sources, path of discharge, the extent of the discharges, damage to the environment, and any other objects or scenes which will make the case clearer for other Municipal Staff, San Joaquin County Environmental Health Department staff, State Regulators, prosecutors, and the courts.

3.3 Collect Samples

Sampling is critical to identification of the spilled material and may aid in determining the responsible party or parties. Sampling is to be completed by a City of Lodi Environmental Compliance Inspector (ECI) with the following guidelines.

1. Supporting sample documentation includes maintaining and chain of custody, pictures of sampling locations, sampling parameters, sample results, etc.

2. Those collecting samples should understand and have available the following before beginning sample collection:
 - Appropriate PPE (Personal Protection Equipment) for the situation
 - Sample collection jars
 - Sample preservation
 - Sample analytical parameters
 - Chain of Custody
 - Sample packaging for shipping

3. Document the following information on each sample and in your reports:
 - Date and time collected
 - Name of the responsible party
 - Exact location and site description
 - Name of person collecting the sample



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3.4 Create Sketches or Maps

Sketches and maps should show the extent of the environmental impacts, discharge point, location of vehicles, permanent reference points, sampling locations etc. This information is valuable in explaining and understanding the spill incident.

Add the following information on each map or sketch:

- Date and time of the sketch
- Name of the responsible party
- Location and site description
- The name of person completing sketch
- Location of permanent reference points such as street intersection, building corner, fire hydrant, trees, etc.
- Scale measurement used

3.5 Other Data

Check container shapes, markings, colors, placards, identification number and labels that may indicate the presence of hazardous material. Talk with the drivers; check shipping paper information (most reliable), vehicle ID numbers and/or initials to identify hazardous material cargo.

4.0 Cleanup Efforts

In the event of a spill or illicit discharge, it is the responder's role to protect public health, the environment, and property from spills / illicit discharge and to restore the area to normal as soon as possible.

4.1 Coordinate Efforts

Coordinate efforts of the City's responders and resources involved in managing the incident. Cleanup includes transportation and disposal of the spill or illicit discharge substance. Efforts should be coordinated with other agencies with a notable interest in the cleanup. Contact a hazardous waste cleanup / hauler contractor if the spill / illicit discharge are hazardous in nature.

Clean Up Crew Response...

Upon receipt of a report of a potential spill or illicit discharge, all response crew members shall proceed to the Corporate Yard where they will gather all necessary equipment and resources before proceeding to the site of the spill/discharge. Delays or conflicts in assignments and issues regarding equipment and resources should be reported to their supervisor.

4.2 Locate the Source

The City of Lodi will use any combination of the following strategies to locate the source and responsible party of a spill or illicit discharge:

- Visual and smell indicators
- Field test kit



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- Uncover manholes upstream to identify where flow may be coming from and use additional samples to test as needed to isolate potential source areas
- Utilize available MS4 mapping to assist in tracking upstream of the incident
- Dye-test storm and sanitary sewers
- Smoke test sanitary storm sewers
- Televisе sanitary and/or storm sewers
- Obtain access to private property to obtain samples and perform tests

4.3 Attempt to Locate the Responsible Party

The Responsible Party shall provide adequate cleanup for a spills or illicit discharges.

If the Responsible Party cannot be identified, the City of Lodi will work with San Joaquin County Environmental Health Department (SJEHD) or The Office of Emergency Services (OES) to ensure that the necessary steps are taken to clean up the spill or illicit discharge.

4.4 Perform Cleanup

Parties responding to the incident will work downstream to determine the extent of cleanup required. Cleanup shall be conducted to remove pollutant potential as a result of the spill or illicit discharge to the maximum extent possible. The City shall use the following indicators, where appropriate to assess removal of pollutant potential:

- Analytical data
- Return to natural color, odor, and/or appearance
- Removal of sheens
- Removal of engrained pollutants with potential to release overtime
- Removal of stained or saturated soil
- Removal of all cleanup materials (i.e. absorbents)

4.5 Work Toward Cost Recovery

If the Responsible Party is identified, every effort should be made to receive cost recovery for fund expended by the City of Lodi. The City of Lodi will follow the enforcement procedures as outlined in *1.10.320 Abatement of a public nuisance by the city*.

5.0 Documentation and Reporting

5.1 Spill Documentation

Each reported spill, regardless of volume, should be documented in a unique file. The file should contain pertinent information that may be necessary to respond to future regulatory audits or actions. Documentation from the process of identifying, containing and cleaning up spills and illicit discharges should be collected. Documented actions should be provided to the City of Lodi Watershed Program Coordinator and Compliance Engineer to be tracked in the annual report. These actions should be included in annual reports including such as: the number of outfalls screened; any complaints received and corrected; the number of discharges and quantities of



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flow eliminated; the number of dye or smoke test conducted, etc. This illustrates that progress is being made to eliminate illicit connections.

In addition, the following items should be documented:

1. Call / complaint data
 - a. Date and time received
 - b. Caller name (if available)
 - c. Caller address (if available)
 - d. Caller telephone (if available)
 - e. Location of spill / discharge
 - f. Description of problem
2. Provide accurate flow measurements and duration of the spill.
3. Provide a map of the problem location (inlets / outfalls involved) and where the spill discharged (storm drain, field, stream, Sewer System Facilities Map).
4. Take photos of events if possible
5. Actions taken during response (including people, equipment, and activities)
6. Mitigation and clean up measures taken
7. Record of corrective actions (enforcement, referrals, etc.)

5.2 Additional Documentation

Fire Department Response Logs:

The City will annually attempt to collect response logs from the fire department for all applicable hazardous spill / discharge response calls. The logs will be incorporated into annual reporting.

SSO Documentation:

All data collected in accordance with the City's Sanitary Sewer Overflow Response Plan will be annually collected and incorporated into the annual reporting.



Storm Water Spill and Illicit Discharge Response Plan

APPENDIX A – Initial Contact Form



Stormwater Spills/Illicit Discharge – Initial Contact Form

(Please print)

COMPLETE BOTH SIDES

Page 1 of 2

Date: _____

Photos Taken: Before Cleanup _____(min 2) Video

Time: _____ am/pm

After Cleanup _____(min2) Video

Location (Nearest Address): _____ Cross Street: _____

Name of Caller (if provided): _____ Phone #: _____

Description of discharge: _____

Type: _____ Color: _____ Odor: _____

Odor: _____ Noticeable Conditions: _____

Solid Liquid Floatables Comments: _____

Spill Amount _____Gallon(s) Recovered Amount _____Gallon(s)

Was this verified by Inspector? Yes No Notes: _____

Spill Source: Who is doing it? _____ Witnessed by: _____

Vehicle Info: Make/Model: _____ License No.: _____

Other descriptors: _____

Was this verified by Inspector? Yes No Notes: _____

Spill to: Street/Curb & Gutter Other Paved Surface Storm Drain Inlet Unpaved Surface/Ground

Surface Water Alley Drainage Channel

Weather: Clear Overcast/Cloudy Rain (light/heavy) Fog Hot Cold

Response Activities: Cleaned-up/Mitigated effects Contained All/Portion Determine Cause

Collected Sample(s) Other (specify) _____

Clean-up Methods Used: High Pressure Water Vacuum up Spill Fluid Other (specify) _____

Corrective Action: Repair Failure Treatment & Disposal Notify Responsible Party _____

Monitor Other (specify) _____

Did Stormwater Spill/Illicit Discharge Reach Surface Water?

Surface Waters Reached: Mokelumne River Lodi Lake WID Canal None

Spill Volume to Surface Water: _____ Gallons

Signs Posted: Yes No Notified Public: Yes No Barricaded: Yes No

May affect Fish/Wildlife: Yes No Flyers Distributed: Yes No

WATER QUALITY MONITORING:

Samples Taken: Yes No Sampling time: _____am/pm Sampling Date: _____



Stormwater Spills/Illicit Discharge – Initial Contact Form

(Please print)

COMPLETE BOTH SIDES

Page 2 of 2

CONTACTS MADE:

Police (Only if there is a fire, explosion, life, health, environmental threat or a need to evacuate): **911** Hours: 24/7

Office of Emergency Services: **(800) 852-7550** Hours: 24/7

Contact Name: _____ Time: _____ Control #: _____

Responsible Party:

Name: _____ Time: _____ Cost Recovery Implemented

ADDITIONAL COMMENTS/SPILL VOLUME CALCULATION:

Sketch of site:

Report Completed by: _____ Date: _____

Name & Title (Print): _____

Investigated by: _____ Date: _____

Name & Title (Print): _____

Utility Superintendent: _____ Date: _____

Compliance Engineer: _____ Date: _____

EQUIPMENT USED:

- Sand Bags Plastic Sheeting Hydrant # _____
- Shovels Brooms Drain Mats (sticky)
- Air Tank Compressor Generator
- Snake CCTV Van Mini Camera
- Plugs (Sizes) _____ Plugs (Sizes) _____
- Vac-con # _____ Vac-con # _____
- Truck # _____ Truck # _____
- Other (Specify) _____

NAMES OF ALL CREWS AT SCENE:



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APPENDIX B – Cal OES Spill / Release Notification Guidance



Cal OES

**GOVERNOR'S OFFICE
OF EMERGENCY SERVICES**

**California
Hazardous Materials
Spill / Release
Notification Guidance**

To Report all significant releases or threatened releases of hazardous materials:

First Call:

9-1-1

(or local emergency response agency)

Then Call:

***Cal OES State Warning Center
(800) 852 - 7550 or (916) 845 - 8911***

February 2014



Edmund G. Brown Jr., Governor

Mark S. Ghilarducci, Director

Revised by: Trevor Anderson, Bill Potter & Jon Kolman

Layout by: Jon Kolman



February 2014

This guidance summarizes pertinent emergency notification requirements. For precise legal requirements, review specific laws and regulations. This guidance applies to all significant releases of hazardous materials. Refer to the Safe Drinking Water Act of 1986, better known as Proposition 65, and §9030 of the California Labor Code for additional reporting requirements.

The State of California makes no warranty, expressed or implied, and assumes no liability for omissions or errors contained in this publication.

SPILL OR RELEASE NOTIFICATION

Q: What are the emergency notification requirements in case of a spill or release of hazardous materials?

A: All significant releases or threatened releases of a hazardous material, including oil and radioactive materials, require emergency notification to government agencies. The law specifies:

- Who must notify
- What information is needed
- Which government agencies must be notified
- When must government agencies be notified
- Release quantity or basis for the report

WHO MUST NOTIFY

Q: Who is obligated to notify?

A: Requirements for immediate notification of all significant spills or threatened releases cover:

- Owners
- Operators
- Licensees
- Persons in Charge
- Employers

Notification is required regarding significant releases from:

- Facilities
- Vehicles
- Vessels
- Pipelines
- Railroads

State law: Handlers, any employees, authorized representatives, agent or designees of handlers shall, upon discovery, immediately report any release or threatened release of hazardous materials (Health and Safety Code §25510).

Federal law: Notification to the National Response Center is required for all releases that equal or exceed federal reporting quantities:

- (EPCRA) Owners and Operators to report, and
- (CERCLA) Person in Charge to report

WHEN TO NOTIFY

Q: When must emergency notification be made?

A: All significant spills or threatened releases of hazardous materials, including oil and radioactive materials, **must be immediately** reported. Notification shall be made by telephone.

Also, written Follow-Up Reports (Section 304) are required within **7 days** if the release equals or exceeds the Federal Reportable Quantities. (see web site for more information)

WHAT INFORMATION

Q: What information is required?

A: State notification requirements for a spill or threatened release include (as a minimum):

- Identity of caller
- Exact location, date and time of spill, release or threatened release
- Location of threatened or involved waterway or stormdrains
- Substance, quantity involved, and isotope if necessary
- Chemical name (if known, it should be reported if the chemical is extremely hazardous)
- Description of what happened

Federal notification required additional information for spills (CERCLA chemicals) that exceed federal reporting requirements, which includes:

- Medium or media impacted by the release
- Time and duration of the release
- Proper precautions to take
- Known or anticipated health risks
- Name and phone number for more information

WHICH AGENCIES

Q: Who must be notified?

A: Notification must be given to the following agencies:

- **The Local Emergency Response Agency**
9-1-1 or the local Fire Department
- **The Local Unified Program Agency (UPA), if different from local fire.**

Note: The UPA may designate a call to the 9-1-1 emergency number as meeting the requirement for notifying the UPA.

Phone: _____
enter local number

And

- **The California Governor's Office of Emergency Services, California State Warning Center:**
Phone (800) 852-7550 or (916) 845-8911

And, if appropriate:

- **The California Highway Patrol:**
Phone: 9-1-1

(The California Highway Patrol must be notified for spills occurring on highways in the State of California. (CVC 23112.5))

In Addition, as necessary, one or more of the following:

National Response Center

If the spill equals or exceeds CERCLA Federal Reportable Quantities, Phone: (800) 424-8802

United States Coast Guard

Waterway Spill / Release

Sectors:

San Francisco: (415) 399-3547

Los Angeles/Long Beach: (310) 521-3805

San Diego: (619) 278-7033

California Occupational Safety and Health Administration (Cal/OSHA)

For serious injuries or harmful exposures to workers, contact the local Cal/OSHA District Office

California Department of Health Services, Radiological Health Branch

All radiological incidents, contact the California State Warning Center

Department of Toxic Substances Control (DTSC)

Hazardous waste tank system releases, and secondary containment releases, contact the appropriate DTSC Regional Office

Department of Conservation

Division of Oil, Gas, and Geothermal Resources (DOGGR) Release of Oil and Gas at a Drilling and Production Facility, contact the appropriate DOGGR Office

Public Utilities

Natural Gas Pipeline Releases, contact the Public Utilities Commission (PUC)

Department of Fish and Wildlife, Office of Spill Prevention and Response (DFW)

Waterway Spill/Release, contact the appropriate DFW Office or the California State Warning Center

Regional Water Quality Control Board (RWQCB)

Waterway Spill/Release, contact the appropriate RWQCB Office

Notification must also be made to the California Governor's Office of Emergency Services, California State Warning Center for the following:

- Discharges or threatened discharges of oil in marine waters
- Any spill or other release of one barrel (42 gallons) or more of petroleum products at a tank facility
- Discharges of any hazardous substances or sewage, into or on any waters of the state
- Discharges that may threaten or impact water quality
- Any found or lost radioactive materials
- Discharges of oil or petroleum products, into or on any waters of the state
- Hazardous Liquid Pipeline releases and every rupture, explosion or fire involving a pipeline

WRITTEN REPORTS

Q: When are written reports required?

A: Different laws have different time requirements and criteria for submitting written reports. After a spill or release of hazardous materials, including oil and radioactive materials, immediate verbal emergency notification should be followed up as soon as possible with a Written Follow-Up Report, if required, to the following agencies:

- 1) California Governor's Office of Emergency Services
Section 304 Follow Up Report.
- 2) The responsible regulating agency such as:
 - California Department of Health Services, Radiological Health Branch, Radiological Incident Reporting.
 - Department of Toxic Substances Control, Facility Incident or Tank System Release Report.
 - Cal/OSHA, serious injury or harmful exposure to workers.
- 3) U.S. DOT and DOE, transportation-related incidents.

PENALTIES

Federal and state laws provide for administrative penalties of up to \$25,000 per day for each violation of emergency notification requirements. Criminal penalties may also apply.

STATUTES

Q: What statutory provisions require emergency notification?

A: Many statutes require emergency notification of a hazardous chemical release, including:

- Health and Safety Code §25270.8, 25510
- Vehicle Code §23112.5
- Public Utilities Code §7673 (General Orders #22-B, 161)
- Government Code §51018, 8670.25.5 (a)
- Water Code §13271, 13272
- California Labor Code §6409.1 (b)
- Title 42, U.S. Code §9603, 11004

Q: What are the statutory provisions for written Follow-Up Reports (Section 304)?

A: Written reports are required by several statutes, including:

- Health and Safety Code §25503 (c) (9)
- California Labor Code §6409.1 (a)
- Water Code §13260, 13267
- Title 42, U.S. Code §11004
- Government Code §51018

REGULATIONS

In addition to statutes, several agencies have notification or reporting regulations:

- Title 8, CCR, §342
- Title 13, CCR, §1166
- Title 14, CCR, §1722 (h)
- Title 17, CCR, §30295
- Title 19, CCR, §2703, 2705
- Title 22, CCR, §66265.56 (j), 66265.196 (e)
- Title 23, CCR, §2230, 2250, 2251, 2260
- Title 40, CFR, §263 esp. Section §263.30
- Title 49, CFR, §171.16

WEBSITES

State Regulations

<http://www.oal.ca.gov>

State Statutes

<http://leginfo.legislature.ca.gov>

Federal Regulations

<http://www.gpo.gov/fdsys/>

Federal Reportable Quantities

<http://www.epa.gov/superfund/policy/release/rq/index.htm>

See California Labor Code §9030 and the Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65) for other reporting requirements.

DEFINITIONS

Q: What is a “Hazardous Material”?

A: “Any material that, because of its quantity, concentration, or physical or chemical characteristics, poses a significant present or threatened hazard to human health and safety or to the environment, if released into the workplace or the environment...” (Health and Safety Code, §25501 (m))

Q: What is a release?

A: “Any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment, unless permitted or authorized by a regulatory agency”.

(Health and Safety Code, §25501 (q) and CERCLA §101 (22))

Q: What is a threatened release?

A: A threatened release is a condition creating a substantial probability of harm that requires immediate action to prevent, reduce, or mitigate damages to persons, property, or the environment. (Health and Safety Code §25501 (u))

DEFINITIONS...cont

Q: What hazardous material release requires notification?

A: All significant spills, releases, or threatened releases of hazardous materials **must be immediately** reported.

In addition, all releases that result in injuries, or workers harmfully exposed, **must be immediately** reported to Cal/OSHA (CA Labor Code §6409.1 (b)). Notification covers significant releases or threatened releases relating to all of the following:

“Hazardous Substances”

As listed in 40 CFR §302.4; Clean Water Act §307, §311; CERCLA §102; RCRA §3001; Clean Air Act §112; Toxic Substance Control Act §7, and as defined by California Health and Safety Code §25501 (n).

“Extremely Hazardous Substances”

As required by Chapter 6.95 Health and Safety Code, EPCRA §302

“Radioactive Materials”

As required by Title 17 §30100

Illegal releases of hazardous waste

Employee exposures resulting in injuries

As required by California Labor Code §6409.1 (b)

“Sewage”

As required by Title 23 CCR §2250 (a) (Reportable quantity is 1,000 gallons or more for municipal and private utility waste water treatment plants).



SEWAGE RELEASES

State Law requires that an unauthorized discharge of sewage into or onto state waters must be reported to the Cal OES Warning Center. The Reportable Quantity for sewage spills is 1000 gallons or more, as established in regulation (Title 23, CCR, §2250 (a)).

Please note that the Regional Water Quality Control Boards and Local Health Departments may have additional reporting requirements - Please contact these offices to determine what requirements may pertain to you.

PETROLEUM (OIL) DISCHARGES

If a release of oil in any way causes harm or threatens to cause harm to public health and safety, the environment, or property, immediate notification must be made to the Cal OES Warning Center.



State Law requires that **ANY** discharge or threatened discharge of oil into **STATE WATERS** must be reported to Cal OES. (California Government Code (GC) §8670.25.5; California Water Code (WC) §13272, California State Oil Spill Contingency Plan).



If the release of oil is on **LAND** and is not discharged or threatening to discharge into State Waters; and (a) does not cause harm or threaten to cause harm to the public health and safety, the environment, or property; **AND** (b) is **under** 42 gallons, then no notification to the Cal OES Warning Center is required.



INCIDENT/RELEASE ASSESSMENT FORM

*Handlers of hazardous materials are required to report releases. The following is a tool to be used for assessing if a release is potentially reportable as required by Chapter 6.95 of the California Health and Safety Code. This assessment tool does not replace good judgement, Chapter 6.95, or other state or federal release reporting requirements. **If in doubt, report the release. If an emergency, call 9-1-1.***

Questions for Incident Assessment

- | | Yes | No |
|---|--------------------------|--------------------------|
| 1. Was anyone killed or injured, or did they require medical care or admitted to a hospital for observation? | <input type="checkbox"/> | <input type="checkbox"/> |
| 2. Did anyone, other than employees in the immediate area of the release, evacuate? | <input type="checkbox"/> | <input type="checkbox"/> |
| 3. Did the release cause off-site damage to public or private property? | <input type="checkbox"/> | <input type="checkbox"/> |
| 4. Is the release greater than or equal to a reportable quantity (RQ)? | <input type="checkbox"/> | <input type="checkbox"/> |
| 5. Was there an uncontrolled or unpermitted release to the air? | <input type="checkbox"/> | <input type="checkbox"/> |
| 6. Did an uncontrolled or unpermitted release escape secondary containment, or extend into any sewers, storm water conveyance systems, utility vaults and conduits, wetlands, waterways, public roads, or off-site? | <input type="checkbox"/> | <input type="checkbox"/> |
| 7. Will control, containment, decontamination, and/or clean up require the assistance of federal, state, county, or municipal response elements? | <input type="checkbox"/> | <input type="checkbox"/> |
| 8. Did the release or threatened release involve an unknown material or contain an unknown hazardous constituent? | <input type="checkbox"/> | <input type="checkbox"/> |
| 9. Is the incident a threatened release? (a condition creating a substantial probability of harm that requires immediate action to prevent, reduce, or mitigate damages to persons, property, or the environment.) | <input type="checkbox"/> | <input type="checkbox"/> |
| 10. Is there an increased potential for secondary effects including fire, explosion, line rupture, equipment failure, or other outcomes that may endanger or cause exposure to employees, the general public, or the environment? | <input type="checkbox"/> | <input type="checkbox"/> |

If the answer is **YES** to any of the above questions - report the release to the California Governor's Office of Emergency Services Warning Center at (800) 852-7550 or (916) 845-8911, and to your local UPA. Note: Other state and federal agencies may require notification depending on the circumstances.

If in doubt, report the release!

EMERGENCY NOTIFICATION SUMMARY

Telephone Calls are Required For All Significant Releases of Hazardous Materials.

**At a MINIMUM, the Spiller should call:
9-1-1 or the Local Emergency Response Agency
(e.g. Fire Department)**

AND/OR

Local Unified Program Agency

AND

**The California Governor's Office of Emergency Services, California
State Warning Center
(800) 852-7550 or (916) 845-8911**

In addition to 9-1-1 and Cal OES, the following apply under varying circumstances:

Spill Type/Location/Injuries	Who to Call
Releases that equal or exceed Federal Reportable Quantities (CERCLA)	Call the National Response Center (NRC)
All releases on-highway	Call California Highway Patrol (CHP)
All hazardous waste tank releases	Call Department of Toxic Substances Control Regional Office (DTSC)
All serious worker injuries or harmful exposures	Call Cal/OSHA District Office
All oil spills at drilling and production fixed facilities	Call Department of Conservation, Division of Oil, Gas, and Geothermal Resources (DOGGR)
All spills with a potential to impact water quality	Call Cal OES
All potential or actual railroad releases (California definition of hazardous materials)	Call the Local Emergency Response Agency and the Public Utilities Commission (PUC)
All Hazardous Liquid Pipelines	Call local fire department (Hazardous Liquid Pipeline Safety is State Fire Marshal jurisdiction)
All Natural Gas Pipelines	Call Public Utilities Commission (PUC)
All incidents involving Radioactive Material	Call California Department of Public Health (CDPH), Radiological Preparedness Branch

IMPORTANT PHONE NUMBERS

Space has been provided below to allow you to enter important phone numbers for easy reference.

Agency Name	Phone Number
California State Warning Center (Cal OES)	(800) 852-7550 or (916) 845-8911
National Response Center	(800) 424-8802
United States Coast Guard San Francisco Sector: Los Angeles/Long Beach Sector: San Diego Sector:	(415) 399-3547 (310) 521-3805 (619) 278-7033
Unified Program Agency (UPA) (Local #)	
California Occupational Safety and Health Administration (Cal/OSHA) (Local #)	
Department of Toxic Substances and Control (DTSC) (Local #)	
California Department of Health Services, Radiological Health Branch (Local #)	
Department of Conservation	
California Public Utilities Com- mission (PUC)	(800) 649-7570
Department of Fish and Wildlife, Office of Spill Prevention and Re- sponse (OSPR) (Local #)	
Regional Water Quality Control Board (RWQCB) (Local #)	

ACRONYMS

Cal EPA - California Environmental Protection Agency

Cal OES - California Governor's Office of Emergency Services

Cal/OSHA - California Occupational Safety and Health Administration

CCR - California Code of Regulations

CDPH - California Department of Public Health

CERCLA - Comprehensive Environmental Response, Compensation, and Liability Act (aka Superfund)

CFR - Code of Federal Regulations

CHP - California Highway Patrol

DFW - Department of Fish and Wildlife (formerly Department of Fish and Game)

DOGGR - California Division of Oil, Gas, and Geothermal Resources

DTSC - Department of Toxic Substances Control

U.S. EPA - U.S. Environmental Protection Agency

EPCRA - Emergency Planning and Community Right-to-Know Act (SARA Title III)

GC - California Government Code

HSC - Health and Safety Code

LEPC - Local Emergency Planning Committee

NRC - National Response Center

OEHHA - Office of Environmental Health Hazard Assessment

OSFM - Office of the State Fire Marshal

OSPR - Office of Spill Prevention and Response

PUC - Public Utilities Commission

RCRA - Resource Conservation and Recovery Act

SERC - State Emergency Response Commission

UPA - Unified Program Agency

USCG - United States Coast Guard

U.S. DOT - U.S. Department of Transportation

WC - California Water Code

CONTRIBUTORS

This guidance was developed with input from the following agencies:

California Governor's Office of Emergency Services (Cal OES)

Office of the State Fire Marshal (OSFM)

California Highway Patrol (CHP)

California Environmental Protection Agency (Cal EPA)

- Department of Toxic Substances Control (DTSC)
- State Water Resources Control Board (SWRCB)
- Air Resources Board (ARB)
- Department of Pesticide Regulation (DPR)
- Department of Resources, Recycling, and Recovery (Cal Recycle)
- Office of Environmental Health Hazard Assessment (OEHHA)

Department of Fish and Wildlife (DFW)

- Office of Spill Prevention and Response (OSPR)

Department of Food and Agriculture (DFA)

Department of Public Health (CDPH)

Department of Industrial Relations

- California Occupational Safety and Health Administration (Cal/OSHA)

Department of Transportation (CalTrans)

U.S. Environmental Protection Agency, (U.S. EPA) Region IX

Department of Conservation, Division of Oil, Gas, and Geothermal Resources (DOGGR)

Department of Water Resources (DWR)

San Diego County Department of Environmental Health

State Lands Commission (SLC)

ADDITIONAL NOTES

ADDITIONAL NOTES

For questions concerning the
federal Emergency Planning and
Community Right-to-Know Act
Call EPCRA Title III Hotline:
(800) 424 - 9346



California Governor's Office of Emergency Services
Fire and Rescue Division
Hazardous Materials Section
3650 Schriever Ave
Mather, California 95655



Storm Water Spill and Illicit Discharge Response Plan

APPENDIX C – Indicator Parameter Overview

APPENDIX F1: INDICATOR PARAMETER OVERVIEW

Ammonia

Ammonia is a good indicator of sewage, since its concentration is much higher there than in groundwater or tap water. High ammonia concentrations may also indicate liquid wastes from some industrial sites. Ammonia is relatively simple and safe to analyze. Some challenges include the tendency for ammonia to volatilize (i.e., turn into a gas and become non-conservative) and its potential generation from non-human sources, such as pets or wildlife.

Boron

Boron is an element present in the compound borax, which is often found in detergent and soap formulations. Consequently, boron is a good potential indicator for both laundry wash water and sewage. Preliminary research from Alabama supports this contention, particularly when it is combined with other detergent indicators, such as surfactants (Pitt, IDDE Project Support Material). Boron may not be a useful indicator everywhere in the country since it may be found at elevated levels in groundwater in some regions and is a common ingredient in water softeners products. Program managers should collect data on boron concentrations in local tap water and groundwater sources to confirm whether it will be an effective indicator of illicit discharges.

Chlorine

Chlorine is used throughout the country to disinfect tap water, except where private wells provide the water supply. Chlorine concentrations in tap water tend to be significantly higher than most other discharge types. Unfortunately, chlorine is extremely volatile, and even moderate levels of organic materials can cause chlorine

levels to drop below detection levels. Because chlorine is non-conservative, it is not a reliable indicator, although if very high chlorine levels are measured, it is a strong indication of a water line break, swimming pool discharge, or industrial discharge from a chlorine bleaching process.

Color

Color is a numeric computation of the color observed in a water quality sample, as measured in cobalt-platinum units (APHA, 1998). Both industrial liquid wastes and sewage tend to have elevated color values. Unfortunately, some “clean” flow types can also have high color values. Field testing by Pitt (IDDE Project Support Material) found high color values associated for all contaminated flows, but also many uncontaminated flows, which yielded numerous false positives. Overall, color may be a good first screen for problem outfalls, but needs to be supplemented by other indicator parameters.

Conductivity

Conductivity, or specific conductance, is a measure of how easily electricity can flow through a water sample. Conductivity is often strongly correlated with the total amount of dissolved material in water, known as Total Dissolved Solids. The utility of conductivity as an indicator depends on whether concentrations are elevated in “natural” or clean waters. In particular, conductivity is a poor indicator of illicit discharge in estuarine waters or in northern regions where deicing salts are used (both have high conductivity readings).

Field testing in Alabama suggests that conductivity has limited value to detect sewage or wash water (Pitt, IDDE Project Support Material). Conductivity has some

value in detecting industrial discharges that can exhibit extremely high conductivity readings. Conductivity is extremely easy to measure with field probes, so it has the potential to be a useful supplemental indicator in subwatersheds that are dominated by industrial land uses.

Detergents

Most illicit discharges have elevated concentration of detergents. Sewage and washwater discharges contain detergents used to clean clothes or dishes, whereas liquid wastes contain detergents from industrial or commercial cleansers. The nearly universal presence of detergents in illicit discharges, combined with their absence in natural waters or tap water, makes them an excellent indicator. Research has revealed three indicator parameters that measure the level of detergent or its components-- surfactants, fluorescence, and surface tension (Pitt, IDDE Project Support Material). Surfactants have been the most widely applied and transferable of the three indicators. Fluorescence and surface tension show promise, but only limited field testing has been performed on these more experimental parameters. Methods and laboratory protocols for each of the three detergent indicator parameters are reviewed in Appendix F2.

***E. coli*, Enterococci and Total Coliform**

Each of these bacteria is found at very high concentrations in sewage compared to other flow types, and is a good indicator of sewage or septage discharges, unless pet or wildlife sources exist in the subwatershed. Overall, bacteria are good supplemental indicators and can be used to find “problem” streams or outfalls that exceed public health standards. Relatively simple analytical methods are now available to test for bacteria indicators, although they still suffer

from two monitoring constraints. The first is the relatively long analysis time (18-24 hours) to get results, and the second is that the waste produced by the tests may be classified as a biohazard and require special disposal techniques.

Fluorescence

Laundry detergents are highly fluorescent because optical brighteners are added to the formula to produce “brighter whites.” Optical brighteners are the reason that white clothes appear to have a bluish color when placed under a fluorescent light. Fluorescence is a very sensitive indicator of the presence of detergents in discharges, using a fluorometer to measure fluorescence at specific wavelengths of light. Since no chemicals are needed for testing, fluorometers have minimal safety and waste disposal concerns.

Some technical concerns do limit the utility of fluorescence as an indicator of illicit discharges. The concerns include the presence of fluorescence in non-illicit flow types such as irrigation water, the considerable variation of fluorescence between different detergent brands, and the lack of a readily standard or benchmark concentration for optical brighteners. For example, Pitt (IDDE Project Support Material) measured fluorescence in mg/L of TideTM brand detergent, and found the degree of fluorescence varied regionally, temporally, and between specific detergent formulations.

Given these current limitations, fluorescence is best combined with other detergent indicators such as surfactants. Appendix F3 should be consulted for more detailed information on analytical methods and experimental field testing using fluorescence as an indicator parameter.

Fluoride

Fluoride is added to drinking water supplies in most communities to improve dental health, and normally found at a concentration of two parts per million in tapwater. Consequently, fluoride is an excellent conservative indicator of tap water discharges or leaks from water supply pipes that end up in the storm drain. Fluoride is obviously not a good indicator in communities that do not fluoridate drinking water, or where individual wells provide drinking water. One key constraint is that the reagent used in the recommended analytical method for fluoride is considered a hazardous waste, and must be disposed of properly.

Hardness

Hardness measures the positive ions dissolved in water and primarily include magnesium and calcium in natural waters, but are sometimes influenced by other metals. Field testing by Pitt (IDDE Project Support Material) suggests that hardness has limited value as an indicator parameter, except when values are extremely high or low (which may signal the presence of some liquid wastes). Hardness may be applicable in communities where hardness levels are elevated in groundwater due to karst or limestone terrain. In these regions, hardness can help distinguish natural groundwater flows present in outfalls from tap water and other flow types.

pH

Most discharge flow types are neutral, having a pH value around 7, although groundwater concentrations can be somewhat variable. pH is a reasonably good indicator for liquid wastes from industries, which can have very high or low pH

(ranging from 3 to 12). The pH of residential wash water tends to be rather basic (pH of 8 or 9). The pH of a discharge is very simple to monitor in the field with low cost test strips or probes. Although pH data is often not conclusive by itself, it can identify problem outfalls that merit follow-up investigations using more effective indicators.

Potassium

Potassium is found at relatively high concentrations in sewage, and extremely high concentrations in many industrial process waters. Consequently, potassium can act as a good first screen for industrial wastes, and can also be used in combination with ammonia to distinguish wash waters from sanitary wastes. (See Chapter 12). Simple field probes can detect potassium at relatively high concentrations (5 mg/L), whereas more complex colorimetric tests are needed to detect potassium concentrations lower than 5 mg/L.

Surface Tension

Surfactants remove dirt particles by reducing the surface tension of the bubbles formed in laundry water when it is agitated. Reduced surface tension makes dirt particles less likely to settle on a solid surface (e.g., clothes or dishes) and become suspended instead on the water's surface. The visible manifestation of reduced surface tension is the formation of foam or bubbles on the water surface. Pitt (IDDE Project Support Material) tested a very simple procedure to measure surface tension that quantifies the formation of foam and bubbles in sample bottles. Initial laboratory tests suggest that surface tension is a good indicator of surfactants, but only when they are present at relatively high concentrations. Section F3 provides a more detailed description of the surface tension measurement procedure.

Surfactants

Surfactants are the active ingredient in most commercial detergents, and are typically measured as Methyl Blue Active Substances (or MBAS). They are a synthetic replacement for soap, which builds up deposits on clothing over time. Since surfactants are not found in nature, but are always present in detergents, they are excellent indicators of sewage and wash waters. The presence of surfactants in cleansers, emulsifiers and lubricants also makes them an excellent indicator of industrial or commercial liquid wastes. In fact, research by Pitt (IDDE Project Support Material) found that detergents were an excellent indicator of “contaminated” discharges in Alabama (i.e., discharges that were not tap water or groundwater). Several analytical methods are available to monitor surfactants. Unfortunately, the reagents used involve toluene, chloroform, or benzene, each of which is considered hazardous waste with a potential human health risk. The most common analysis method uses chloroform as a reagent, and is recommended because it is relatively safer when compared to other reagents.

Turbidity

Turbidity is a quantitative measure of cloudiness in water, and is normally measured with a simple field probe. While turbidity itself cannot always distinguish between contaminated flow types, it is a potentially useful screening indicator to determine if the discharge is contaminated (i.e., not composed of tap water or groundwater).

Research Indicators

In recent years, researchers have explored a series of other indicators to identify illicit discharges, including fecal steroids (such as coprostanol), caffeine, specific fragrances associated with detergents and stable isotopes of oxygen. Each of these research indicators is profiled in Pitt (IDDE Project Support Material) and summarized below in Table F1. Most research indicators require sophisticated equipment and specific expertise that limit their utility as a general indicator, given the high sampling cost and long turn-around times needed. To date, field tests of research indicators have yielded mixed results, and they are currently thought to be more appropriate for special research projects than for routine outfall testing. While they are not discussed further in this manual, future research and testing may improve their utility as indicators of illicit discharges.

Table F1: Summary of Research Indicators Used for Identifying Inappropriate Discharges into Storm Drainage		
Parameter Group	Comments	Recommendation
Coprostanol and other fecal sterol compounds	Used to indicate presence of sanitary sewage	Possibly useful. Expensive analysis with GC/MSD. Not specific to human wastes or recent contamination. Most useful when analyzing particulate fractions of wastewaters or sediments.
Specific detergent compounds (LAS, fabric whiteners, and perfumes)	Used to indicate presence of sanitary sewage	Possibly useful. Expensive analyses with HPLC. A good and sensitive confirmatory method.
Pharmaceuticals (colfibric acid, aspirin, ibuprofen, steroids, illegal drugs, etc.)	Used to indicate presence of sanitary sewage	Possibly useful. Expensive analyses with HPLC. A good and sensitive confirmatory method.
Caffeine	Used to indicate presence of sanitary sewage	Not very useful. Expensive analyses with GC/MSD. Numerous false negatives, as typical analytical methods not suitably sensitive.
DNA profiling of microorganisms	Used to identify sources of microorganisms	Likely useful, but currently requires extensive background information on likely sources in drainage. Could be very useful if method can be simplified, but with less specific results.
UV absorbance at 228 nm	Used to identify presence of sanitary sewage	Possibly useful, if UV spectrophotometer available. Simple and direct analyses. Sensitive to varying levels of sanitary sewage, but may not be useful with dilute solutions. Further testing needed to investigate sensitivity in field trials.
Stable isotopes of oxygen	Used to identify major sources of water	May be useful in area having distant domestic water sources and distant groundwater recharge areas. Expensive and time consuming procedure. Can not distinguish between wastewaters if all have common source.
GC/MSD - Gas Chromatography/Mass Selective Detector HPLC - High Performance Liquid Chromatography		

Appendix F2: “Off-the Shelf” Analytical Methodologies

F2.1 AMMONIA (0 TO 0.50 MG/L NH₃-N)

Equipment/Supplies Needed

- Hach bench top or portable spectrophotometer or colorimeter (see ordering information below)
- ammonia nitrogen reagent set for 25-mL samples
- ammonia nitrogen standard solution

Procedure

Refer to Hach method 8155 for Nitrogen, Ammonia Salicylate Method (0 to 0.50 mg/L NH₃-N) for a 25mL sample. In this method, ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of sodium nitroprusside catalyst to form a blue-colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green-colored solution.

Duration of Test for Each Sample

Because of the duration of this test, samples should be run in batches of about six. From start to finish, each batch of six samples takes about 25 minutes, including the time taken to clean the sample cells and reset the instrument between each batch.

Hazardous Reagents

According to good laboratory practice, the contents of each sample cell, after the analysis, should be poured into another properly-labeled container for proper disposal.

Ease of Analysis

This procedure is time-consuming and should be performed indoors.

Ordering Information

Vendor: Hach Company
 PO Box 389
 Loveland, CO 80539-0389
 Tel: 800-227-4224
 Fax: 970-669-2932
 Website: www.hach.com

[Note: The direct-Nessler method may be preferred due to its faster reaction times, but Nessler reagent is toxic and corrosive. Nessler reagent, according to its MSDS, causes severe burns, is an acute and a cumulative poison, and is a teratogen. It also contains from 5 to 10% mercuric iodide. It is now recommended that the more sensitive salicylate method because of the lower concentrations experienced in this research, and because of its lower toxicity and easier disposal requirements. The salicylate method was therefore used for this project, although prior research found it to be somewhat less satisfactory than the Nessler method.]

Equipment/Supplies Needed for Ammonia Analysis		
Item (Catalog Number)	Quantity	Price
<i>One of the colorimeters, or spectrophotometers, listed previously will be needed. Alternatively, a dedicated colorimeter can be used, but that will only be useable for a single analyte.</i>		
Ammonia-Nitrogen Reagent Set (25mL test) salicylate method (2243700)	1 set of 100 tests	\$180.56
Ammonia cyanurate reagent powder pillows (2395566)	1 pk of 50 pillows	\$ 20.20
Ammonia salicylate reagent powder pillows (2395366)	1 pk of 50 pillows	\$ 25.55

F2.2 BORON (Low range 0 to 1.50 mg/L as B)

Equipment/Supplies Needed

- A Hach bench top or portable spectrophotometer or colorimeter (see ordering information below)
- Boron test kit
- 1-inch plastic sample cells (at least 2).

Procedure

Refer to Hach Azomethine-H Method 10061, which is adapted from ISO method 9390. In this procedure, Azomethine-H, a Schiff base, is formed by the condensation of an aminonaphthol with an aldehyde by the catalytic action of boron. The boron concentration in the sample is proportional to the developed color. Follow the Hach instructions that come with the reagent set for the specific procedure.

Duration of Test for Each Sample

Each batch of six samples takes approximately 20 minutes.

Hazardous Reagents

Standard laboratory practice requires that all unwanted chemicals be properly disposed.

Ease of Analysis

The procedure is a little time consuming, but several samples can be analyzed together.

Ordering information

Vendor: Hach Company
 PO Box 389
 Loveland, CO 80539-0389
 Tel: 800-227-4224
 Fax: 970-669-2932
 Website: www.hach.com

Equipment/Supplies Needed for Boron Analysis		
Item (Catalog Number)	Quantity	Price*
Boron Test Kit (0-1.5 mg/L) BoroTrace (Azomethine-H) Method (2666900)	1 set of 100 tests	\$50.00
BoroTrace 2 reagent (2666669)	1 pk of 100 pillows	\$30.00
BoroTrace 3 reagent (2666799)	1 pk of 100 pillows	\$20.65
EDTA Solution 1M (2241925)	50 mL	
DR/890 portable colorimeter Programmed with 90 tests. Includes 2 sample cells, COD & TnT tube adapter, instrument, procedure manual and batteries. Portable instrument that can be used for many different analytes, but fewer than the following instruments. (48470000) ¹	1	\$929.00
DR/2500 spectrophotometer includes 6 one-inch round sample cells, instrument and procedure manual, and DR/Check Absorbance Standards. Compact laboratory instrument having many capabilities. (5900000) ¹	1	\$2200.00
DR/2400 portable spectrophotometer includes one-inch sample cells, instrument and procedures manuals. Portable instrument having many capabilities. (5940000) ¹	1	\$1,995.00
DR/4000 V Spectrophotometer. Visible spectrum only (320 to 1100nm). Includes 1-inch matched sample cells/ AccuVacc and 16-mm vial adapters; a Single Cell Module; 1-inch and 1-cm cell adapters; dust cover; replacement lamp kit; an illustrated manual set; and a power cord. UV-Vis laboratory instrument having vast capabilities. (48100-00) ¹	1	\$5500.00
¹ Only one spectrophotometer is needed		
*The per-sample expendable cost is therefore about \$2.00.		

F2.3 COLOR (0 – 100 APHA Platinum Cobalt Units)

Equipment/Supplies needed

One Hach color test kit Model CO-1 which measures color using a color disc for comparison.

Procedure

The following procedure is described in the test kit.

Low Range

1. Place the lengthwise viewing adapter in the comparator.
2. fill one sample tube to the line underlining “Cat. 1730-00” with the sample. This will be approximately 15mL. If not using 1730-00 tubes, fill to the line found at approximately 3 inches up from the bottom of the tube.
3. Place the tube containing the water sample into the comparator in the right-hand position.
4. Fill the other sample tube with colorless water to the line underlining “Cat. 1730-00.” Insert this tube in the left-side comparator opening.
5. Hold the comparator with the tube tops pointing to a window or light source at approximately a 45 degree angle (with the light coming in through the top of the tubes). View through the openings in the front of the comparator. When viewing, use care to not spill samples from unstoppered tubes.

6. Rotate the disc until a color match is obtained. The reading obtained through the scale window is the apparent color in APHA Platinum Cobalt Units.

High Range

1. If the lengthwise viewing adapter is in place, remove it.
2. Fill one of the tubes to the 5mL mark with the water sample.
3. Insert the tube in the right top opening of the comparator.
4. Fill the other tube to the 5mL mark with clear water and insert this tube into the left opening of the comparator.
5. Hold the comparator up to a light source as explained above. The reading obtained through the scale window is multiplied by 5 to obtain the apparent color.

Duration of Test for Each Sample

One minute

Hazardous Reagents

None.

Ease of Analysis

This procedure easy and fast and can be performed outside of the laboratory.

Ordering Information

Vendor: Hach Company
 PO Box 389
 Loveland, CO 80539-0389
 Tel: 800-227-4224
 Fax: 970-669-2932
 Website: www.hach.com

Equipment/Supplies Needed for Color Analysis		
Item (Catalog Number)	Quantity	Price
Color Test Kit (0-100 mg/L) (223400)	one kit	\$51.50

F2.4 CONDUCTIVITY

Equipment/Supplies Needed

- Cardy pocket-sized conductivity meter model B-173 made by Horiba
- Conductivity standard that comes with the meter.

Calibration

Before any measurements can be performed the instrument must first be calibrated. The meter should hold its calibration for an extended period, but it is best to check the calibration before each sample batch.

1. Press the POWER button.
2. Place a drop of the 1.41 $\mu\text{S}/\text{cm}$ standard solution onto the sensor cell.
3. Press the CAL/MODE button to display the CAL mark and 1.41. Calibration is complete when the CAL mark disappears.
4. Wash the sensor with tap water, and dry with a tissue.

Measurement

1. Check first to see which mode the instrument is in by looking for the arrow pointing at the mS/cm or $\mu\text{S}/\text{cm}$.
2. Add a drop of the sample onto the sensor cell using a pipette (or the sensor may be immersed into the sample).
3. When the smiley face ☺ appears, take a reading. Be sure to note the units.

Duration of Test for Each Sample

1 minute

Hazardous Reagents

None

Ease of Analysis

Simple and fast. Can be used in the field.

Ordering Information

Vendor: Cole-Parmer Instrument Company
625 East bunker Court
Vernon Hills, IL 60061-1844
Phone: 1-800-323-4340
FAX: 847-247-2929
Website: www.coleparmer.com

Equipment/Supplies Needed for Conductivity Analysis	
Item (Catalog Number)	Price
Cardy pocket-sized conductivity meter and accessories (EW-05751-10)	\$269.00
Replacement cardy conductivity sensor cartridge (EW-05751-52)	\$ 82.00
Replacement cardy conductivity solution kit (EW-05751-70)	\$ 43.00

F2.5 DETERGENTS (0-3 ppm)

Equipment/Supplies needed

- Detergents (anionic surfactants) kit from *CHEMetrics*.

Procedure

The following procedure comes with the Detergents kit. The Detergents CHEMets[®] test employs the methylene blue extraction method. Anionic detergents react with methylene blue to form a blue complex that is extracted into an immiscible organic solvent. The intensity of the blue color is directly related to the concentration of “methylene blue active substances (MBAS)” in the sample. Anionic detergents are one of the most prominent methylene blue active substances. Test results are expressed in mg/L linear alkylbenzene sulfonate.

1. Rinse the reaction tube with sample, and then fill it to the 5 mL mark with sample.
2. While holding the double-tipped ampoule in a vertical position, snap the upper tip using the tip-breaking tool.
3. Invert the ampoule and position the open end over the reaction tube. Snap the upper tip and allow the contents to drain into the reaction tube.
4. Cap the reaction tube and shake it vigorously for 30 seconds. Allow the tube to stand undisturbed for approximately 1 minute.
5. Make sure that the flexible tubing is firmly attached to the CHEMet ampoule tip.
6. Insert the CHEMet assembly (tubing first) into the reaction tube making sure that the end of the flexible tubing is at the bottom of the tube. Break the tip of the CHEMet ampoule by gently pressing it against

the side of the reaction tube. The ampoule should draw in fluid only from the organic phase (bottom layer).

7. When filling is complete, remove the CHEMet assembly from the reaction tube.
8. Invert the ampoule several times, allowing the bubble to travel from end to end each time.
9. Using a tissue, remove the tubing from the ampoule tip. Wipe all liquid from the exterior of the ampoule, then place a small white cap firmly onto the tip of the ampoule.
10. Place the CHEMet ampoule, flat end downward into the center tube of the comparator. Direct the top of the comparator up toward a source of bright light while viewing from the bottom. Rotate the comparator until the color standard below the CHEMet ampoule shows the closest match. If the color of the CHEMet ampoule is between two color standards, a concentration estimate can be made.

Duration of Test for Each Sample

Approximately 7 minutes per sample.

Hazardous Reagents

The main components of the double-tipped ampoule are considered hazardous, and possibly carcinogenic (contains chloroform). The used ampoule should be placed back in the test kit box for later disposal at a hazardous waste facility. Use proper safety protection when performing this test: laboratory coat, gloves, and safety glasses. It is also strongly recommended that the test be performed under a laboratory fume hood. Wash hands thoroughly after handling the kit.

Ease of Analysis

This procedure may be performed outside of a standard laboratory, if well ventilated.

Produces hazardous chemicals.

Ordering Information

Vendor: CHEMetrics, Inc
4295 Catlett Rd
Calverton, VA 20138
Phone 1-800-356-3072
FAX 1-540-788-4856
Website: www.chemetrics.com

Equipment/Supplies Needed for Detergents Analysis		
Item (Catalog Number)	Quantity	Price*
Detergent kit (anionic surfactants) (K-9400)	20 tests	\$63.15
Detergent kit refill (R-9400)	20 tests	\$50.45
<i>*The per-sample expendable cost is therefore \$2.52.</i>		

F2.6 *E. COLI*

Equipment/Supplies Needed

- Colilert reagent, sterile sample bottles for 100 mL samples
- Quanti-Tray 2000
- Colilert comparator predispensed in a Quanti-Tray/2000 incubator
- UV light from IDEXX.

Enumeration Procedure

1. Add contents of one Colilert snap pack to a 100 mL room temperature water sample in a sterile vessel. The standard Colilert reagent is recommended when evaluating Enterococci simultaneously so the samples are both ready to read in 24 hours. If only *E. coli* are to be evaluated, then the faster Colilert-18 reagent can be used if reading the results in 18 hours instead of 24 hours is important.
2. Cap vessel and shake until dissolved.
3. Pour sample/reagent mixture into a Quanti-Tray/2000 and seal in an IDEXX Quanti-Tray Sealer.
4. Place the sealed tray in a 35±0.5° C incubator for 24 hours.
5. Read results according to the Results Interpretation table below. Count the number of positive wells and refer to the MPN table provided with the Quanti-Trays to obtain a Most Probable Number.

Results Interpretation

Appearance	Result
Less yellow than the comparator	Negative for total coliforms and <i>E. coli</i>
Yellow equal to or greater than the comparator	Positive for total coliforms
Yellow and fluorescence equal to or greater than the comparator	Positive for <i>E. coli</i>

Duration of Test for Each Sample

Once the Quanti-Tray sealer is warm (10 min), it takes approximately 5 minutes per sample to label, seal and incubate the Quanti-Tray. After 24 hours, it takes 1-2 minutes to read the sample results under the UV lamp.

Hazardous Reagents

Used Quanti-Trays must be disposed of in a biohazard bag and handled by appropriate biohazard disposal facility, using similar practices as for alternative bacteria analysis methods.

Ease of Analysis

Not a difficult procedure to learn. Knowledge of proper handling of bacterial specimens is necessary. Cannot be performed in the field.

Ordering information

Vendor: IDEXX
 1 IDEXX Drive
 Westbrook, ME 04092
 Phone: 1-800-321-0207
 Fax: 207-856-0630
 E-mail: water@idexx.com
 Website: www.idexx.com/water

Appendix F: Analytical Procedures for Outfall Monitoring

Equipment/Supplies Needed for <i>E. coli</i> Analysis		
Item (Catalog Number)¹	Quantity	Price*
Colilert reagent for 100mL sample (WP200)	200-pack	\$1,020.00
120mL vessel with 100mL line, sodium thiosulfate & label (WV120ST-200)	200-pack	\$90.00
97-well sterile Quanti-Tray/2000 trays (WQT-2K)	100-pack	\$110.00
Quality control kit (E. coli, Klebsiela, Pseudomonas A). (WKT 1001)	n/a	\$120.00
Colilert comparator predispensed in a Quanti-Tray/2000 (WQT2KC)	1	\$6.00
Quanti-Tray Sealer (115V) with 51-well rubber insert (WQTS2X-115)	1	\$3,500.00
6 watt UV lamp 110 volt (WL160)	1	\$89.00
Incubator 120V, 30-65°C, 14"x14"x14" (WI300)	2	\$389.00
¹ See the Enterococci table above for equipment that can be shared when conducting both analyses. *The per-sample expendable cost (reagent, bottle, and tray) is about \$6.65.		

F2.7 ENTEROCOCCI

Equipment/Supplies Needed

- Enterolert reagent
- Sterile sample bottles for 100 mL samples
- Quanti-Tray 2000
- Incubator
- UV light from IDEXX

Enumeration Test Procedure

1. Carefully separate a Snap Pack from its strip, taking care not to accidentally open the next pack.
2. Tap the reagent snap pack to ensure that all of the Enterolert powder is in the bottom part of the pack.
3. Open the pack by snapping back the top at the score line. Caution: Do not touch the opening of the pack.
4. Add the reagent to a 100 mL water sample in a sterile bottle.
5. Aseptically cap and seal the vessel.
6. Shake to completely dissolve reagent.
7. Pour the sample/reagent mixture into a Quanti-Tray avoiding contact with the foil pull tab. Seal the tray according to Quanti-Tray instructions.
8. Incubate for 24 hours at $41^{\circ}\pm 5^{\circ}$ C.
9. Read the results at 24 hours by placing a 6 watt, 365 nm wavelength UV light within five inches of the Quanti-Tray in a dark environment. Be sure the light is facing away from your eyes and toward the Quanti-Tray. Count the number of fluorescent Quanti-Tray wells. The fluorescence intensity of positive wells may vary.
10. Refer to the MPN table provided with the Quanti-Tray to determine the Most Probable Number of Enterococci in your sample.

Procedural Notes

If the sample is inadvertently incubated over 28 hours without observation, the following guidelines apply:

- Lack of fluorescence after 28 hours is a valid negative test
- Fluorescence after 28 hours is an invalid result
- Use sterile water, not buffered water for making dilutions. Enterolert is already buffered. Always add Enterolert to the proper volume of diluted sample after making dilutions.
- For comparison, a water blank can be used when interpreting results.

Duration of Test for Each Sample

Once the Quanti-Tray sealer is warm (10 min), it takes approximately 5 minutes per sample to mix, label, seal and place the Quanti-Tray in the incubator. After 24 hours, it takes 1-2 minutes to read the sample results under the UV lamp.

Hazardous Reagents

Used Quanti-Trays must be disposed of in a biohazard bag and handled by appropriate biohazard disposal facility, just like any other bacteria analysis materials.

Ease of Analysis

Not difficult procedure to learn. Knowledge of proper handling of bacterial specimens is necessary. Cannot be performed in the field.

Ordering Information

Vendor: IDEXX

1 IDEXX Drive
Westbrook, ME 04092
Phone: 1-800-321-0207
Fax: 207-856-0630
E-mail: water@idexx.com
Website: www.idexx.com/water

Appendix F: Analytical Procedures for Outfall Monitoring

Equipment/Supplies Needed for Enterococci Analysis		
Item (Catalog Number)	Quantity	Price*
<i>Enteroletert reagent for 100 mL samples (WENT200)</i>	200-pack	\$ 1,020.00
120 mL pre-sterilized vessel with 100 mL line, sodium thiosulfate & label (WV120ST-200) ¹	200-pack	\$ 90.00
97-well sterile Quanti-Tray/2000 trays (WQT-2K) ¹	100-pack	\$ 110.00
Quality control kit (E. coli, Klebsiela, Pseudomonas A). (WKT 1001)	n/a	\$ 120.00
Quanti-Tray Sealer (115V) with 51-well rubber insert (WQTS2X-115) ¹	1	\$ 3,500.00
6 watt UV lamp 110 volt (WL160) ²	1	\$ 89.00
Incubator 120V, 30-65°C, 14"x14"x14" (WI300) ³	2	\$ 389.00
¹ Same expendable materials as for the E. coli method, additional should be ordered for each method ² Same as for the E. coli method and can be shared ³ Although the same, a second incubator is needed for the E. coli method because of the different temperature settings and the normal need to evaluate Enterococci and E. coli simultaneously * The per-sample expendable cost (reagent, bottle, and tray) is about \$6.65.		

F2.8 FLUORIDE (0 TO 2.00 MG/L F⁻)

Equipment/Supplies Needed

- Hach bench top or portable spectrophotometer or colorimeter (see ordering information below)
- AccuVac Vial Adaptor (for older spectrophotometers)
- SPADNS Fluoride Reagent AccuVac Ampuls.

Procedure

Refer to Hach SPADNS Method 8029 which is adapted from Standard Methods for the Examination of Water and Wastewater. This procedure involves the reaction of fluoride with a red zirconium-dye solution. The fluoride combines with part of the zirconium to form a colorless complex, thus bleaching the red color in an amount proportional to the fluoride concentration.

Duration of Test for Each Sample

Each samples takes an average of 3 minutes to test.

Hazardous Reagents

The SPANDS reagent is a hazardous solution. The used AccuVacs should be placed back in the Styrofoam shipping container for storage and then disposed properly through a hazardous waste disposal company.

Ease of Analysis

The procedure is relatively easy and fast and can be performed in the field using a portable spectrophotometer or colorimeter. However, as for all tests, it is recommended that the analyses be conducted in a laboratory, or at least in a work room having good lighting and water.

Ordering information

Vendor: Hach Company
PO Box 389
Loveland, CO 80539-0389
Tel: 800-227-4224
Fax: 970-669-2932
Website: www.hach.com

Equipment/Supplies Needed for Fluoride Analysis	
Item (Catalog Number)	Price
Fluoride Reagent (SPADNS) AccuVac Ampuls [1 set of 25 AccuVacs (2 needed per test)] (2506025)	\$ 17.00
Adapter, AccuVac vial (needed for older spectrophotometers DR/2000 and DR/3000) (43784-00)	\$ 5.40
DR/890 portable colorimeter programmed with 90 tests. Includes 2 sample cells, COD & TnT tube adapter, instrument, procedure manual and batteries. Portable instrument that can be used for many different analytes, but fewer than the following instruments. (48470000) ¹	\$ 929.00
DR/2500 spectrophotometer includes 6 one-inch round sample cells, instrument and procedure manual, and DR/Check Absorbance Standards. Compact laboratory instrument having many capabilities. (5900000) ¹	\$ 2,200.00
DR/2400 portable spectrophotometer includes one-inch sample cells, instrument and procedures manuals. Portable instrument having many capabilities. (5940000) ¹	\$ 1,995.00
DR/4000 V Spectrophotometer. Visible spectrum only (320 to 1100nm). Includes 1-inch matched sample cells/ AccuVacc and 16-mm vial adapters; a Single Cell Module; 1-inch and 1-cm cell adapters; dust cover; replacement lamp kit; an illustrated manual set; and a power cord. UV-Vis laboratory instrument having vast capabilities. (48100-00) ¹	\$ 5,500.00
¹ only one spectrophotometer is needed	
*The per-sample expendable cost is about \$1.36.	

F2.9 pH

Equipment/Supplies Needed

- Cardy pocket-sized pH meter model B-213 made by Horiba
- pH standards that come with the meter.

Calibration

The meter should hold its calibration for an extended period, but it is best to check the calibration before each sample batch.

1. Press the ON/OFF button.
2. Place approximately 1 mL of the yellow pH 7.0 standard solution onto the sensor cell (be careful not to touch the sensor with the dropper or pipette, the cell is covered with a very thin and fragile glass cover slip).
3. Press the CAL button to display the black CAL mark in the upper right corner and 7.0.
4. Calibration is complete when the CAL mark disappears. Wash the sensor with tap or distilled water and dry with a tissue.
5. Press CAL again so that 4.01 and CAL are displayed to calibrate using the pink pH 4.01 buffer. Follow the same procedure as above.

Measurement

1. Place a drop of the sample water onto the sensor cell (usually around 1 mL). Alternatively, you may dip the meter into the water to be tested.
2. When the smiley face ☺ appears, read the number.
3. Press the ON/OFF button to turn the power OFF.
4. Wash the sensor with tap water or distilled water. Wipe off any residual water on the sensor with a tissue.
5. Be sure the protective cap is covering the sensor and put the pH meter back in its protective case.

Duration of Test for Each Sample

Calibration takes around 3 minutes, and testing of each sample is only about 30 seconds.

Hazardous Reagents

None

Ease of Analysis

Simple and fast. Can be used in the field.

Ordering Information

Vendor: Cole-Parmer Instrument Co.
625 East Bunker Court
Vernon Hills, IL 60061-1844
Phone: 1-800-323-4340
FAX: 847-247-2929
Website: www.coleparmer.com

Equipment/Supplies Needed for pH Analysis	
Item (Catalog Number)	Price
Cardy twin pH meter and accessories (EW-05759-00)	\$238.00
Replacement pH sensor cartridge (EW-05759-0)	\$105.00
Replacement pH solution kit (EW-05751-70)	\$ 29.00

F2.10 POTASSIUM

Equipment/Supplies Needed

- Cardy potassium compact meter by Horiba model C-131
- Accessories that come with the meter.

Two-Point Calibration (Monthly)

1. Turn the power ON
2. Open the sensor cover and wipe the sensor pad clean with a piece of tissue and deionized water, then wipe it dry with a piece of tissue. Repeat this several times.
3. Place a piece of sampling sheet onto the sensor pad, and drip 2 to 5 drops of the standard STD solution onto it (or drip the solution directly onto the sensor pad).
4. After the readout has stabilized, adjust the STD dial so that the display reads 20X100. After cleaning the sensor according to step (2), follow the same procedure using the standards SLOPE solution and after the readout has stabilized, adjust slope volume so that the display reads 15X10.
5. After cleaning several times with deionized water, measure the standard STD solution again.
6. Recalibrate if the reading is not $(20 \pm 2) \times 100$.
7. Wipe the sensor pad with deionized water, then wipe it dry.

One-Point Calibration (Daily)

1. Turn the power ON.
2. Open the sensor cover, and wipe the sensor pad clean with deionized water, then wipe it dry.
3. Repeat this procedure several times.
4. Place a piece of sampling sheet onto the sensor pad, and drip 2 to 5 drops of the standard STD solution on it

(or drip the solution directly onto the sensor pad).

5. After the readout has stabilized, adjust the STD dial so that the display reads 20X100.
6. Wipe the sensor pad with deionized water, and then wipe it dry.
7. If the sample is below 500 ppm (mg/L), use the SLOPE solution and adjust the STD dial to read 15X10.

Measurement

1. Place the sample directly onto the sensor pad or measurement can be aided by placing the sample onto a piece of sampling sheet.
2. Read the concentration directly from the display.
3. Clean the sensor with deionized water and wipe it clean after each sample is analyzed.
4. When finished with all samples, turn the power OFF.
5. Clean the surface of the sensor pad with deionized water and wipe dry for storage.

Duration of Test for Each Sample

Calibration takes around 5 minutes and testing of each sample is only 30 seconds.

Hazardous Reagents

None

Ease of Analysis

Simple and fast. Can be used in the field.

Ordering information

Vendor: Cole-Parmer Instrument Company
625 East Bunker Court
Vernon Hills, IL 60061-1844
Phone: 1-800-323-4340
FAX: 847-247-2929
Website: www.coleparmer.com

Equipment/Supplies Needed for pH Analysis	
Item (Catalog Number)	Price
Cardy potassium compact meter and accessories (EW-05755-00)	\$239.00
Replacement cardy potassium sensor cartridge (EW-05755-500)	\$ 64.00
Replacement cardy potassium solution kit (EW-05755-60)	\$ 33.00

Note: This procedure is rapid and inexpensive, however, it only has a detection limit of about 1 mg/L, and reads in increments of 1 mg/L. This level of precision is not typically a problem for moderately contaminated samples (when the results are most useful); however, it presents challenges when used for cleaner water. Specifically, since the Flow Chart Method relies on the ammonia to potassium ratio to distinguish between washwaters and sanitary

wastewaters, a “non detect” (i.e., <1) potassium concentration results in an indeterminate ratio value. Where clean water is being analyzed and more sensitive potassium values are needed, the only real option is to use other laboratory methods (either ICP or atomic absorption). Other simple field procedures (such as the method supplied by HACH) rely on a photometric measurement of a floc and are not very repeatable for these types of samples.

F2.11 TOTAL HARDNESS (10 – 4000 mg/L as CaCO₃)

Equipment/Supplies Needed

- Hach digital titrator
- Total hardness titration cartridge
- ManVer 2 hardness indicator
- Hardness 1 buffer solution.

Procedure

Refer to Hach Method 8213 for Hardness, Total (10-4000 mg/L as CaCO₃) digital titrator method using EDTA. This procedure involves buffering the sample first to pH 10.1, adding of the ManVer 2 Hardness Indicator, which forms a red complex with a portion of the calcium and magnesium in the sample, and then titrating with EDTA. The EDTA titrant reacts first with the free calcium and magnesium ions, then with those bound to the indicator, causing it to change to a blue color at the end point.

Duration of Test for Each Sample

Approximately 5 minutes.

Hazardous Reagents

The mixture of sample, buffer solution, hardness indicator, and EDTA must be stored properly in a labeled container until disposal by a hazardous waste disposal facility.

Ease of Analysis

This procedure is not recommended to be performed in the field. Produces hazardous chemicals.

Ordering information

Vendor: Hach Company
 PO Box 389
 Loveland, CO 80539-0389
 Tel: 800-227-4224
 Fax: 970-669-2932
 Website: www.hach.com

Equipment/Supplies Needed for Total Hardness Analysis		
Item (Catalog Number)	Quantity	Price*
Digital Titrator with plastic case, manual and 5 straight delivery tubes (1690001)	1 titrator	\$105.00
Total hardness titration cartridge (EDTA 0.0800M) (1436401)	1	\$10.70
Total hardness titration cartridge (EDTA 0.800M) (1439901)	1	\$10.70
Delivery tube, (straight with J hook) for titration (1720500)	Pack of 5	\$4.85
ManVer 2 Hardness Indicator Powder Pillow (85199)	1 pack of 100 pillows	\$9.85
Hardness 1 buffer solution (42432)	One 100 mL bottle	\$8.40
<i>*The per sample expendable cost is about \$0.25, depending on the hardness level.</i>		

F2.12 TURBIDITY

Equipment/Supplies Needed

- Benchtop or portable turbidimeter. The range of readings in NTU will depend upon the instrument.

Procedure

(This is a general procedure for turbidity. Follow your turbidimeter's instructions):

1. First, the instrument must be calibrated using the standards supplied with the instrument. If calibration is satisfactory, continue with sample measurement.
2. Samples are normally stored under refrigeration. Before analyzing for turbidity, the samples must first be brought back to room temperature. This is done to prevent the formation of frost on the outside of the glass sample cells used in the turbidity measurement.
3. Pour the sample into a sample cell (until almost full or to the fill line), cap the cell, then turn it upside down 2 to 3 times for mixing. Do not shake vigorously.

4. Keep the sample cell vertical for 4-5 seconds and wipe the outside to remove fingerprints.
5. Place the cell into the turbidity meter and take a reading.

Duration of test for each sample

Approximately one minute. This does not include the time spent bringing the sample to room temperature.

Hazardous Reagent

None

Ease of Analysis

Relatively simple and may be performed outside of the laboratory using a portable turbidimeter.

Ordering Information

Vendor: Hach Company
 PO Box 389
 Loveland, CO 80539-0389
 Tel: 800-227-4224
 Fax: 970-669-2932
 Website: www.hach.com

Equipment/Supplies Needed for Turbidity Analysis		
Item (Catalog Number)	Quantity	Price
2100P Portable Turbidimeter range 1-1000 NTU Includes nine sample cells, primary standards, silicone oil & oiling cloth, manual, quick reference card and case. (4650000)	1	\$837.00

Appendix F3. METHODOLOGIES AND LAB TESTING OF TECHNIQUES TO
MEASURE DETERGENTS

F3.1 CHEMETRICS DETERGENT TEST KIT

Detergents were measured using the *CHEMetrics* detergent test kit, which detects Methylene Blue Active Substances (MBAS), an important ingredient of detergent products. The minimum detection limit (MDL) of the kit is 0.25mg/L. This is a very simple test, but the accuracy of the tests depends on the analyst's skill with the color comparator. One of the problems with this method is the upper limit of 3 mg/L. Higher values can only be measured with dilution of the sample prior to analysis. This extra step requires extra time when measuring laundry, carwash and sewage samples, when the detergent values are in hundreds of mg/L.

This kit also contains chloroform, an expected carcinogen. Great care must therefore be taken when conducting this analysis and when handling the kit materials. The alternative detergent field test kit from HACH uses much larger quantities of benzene, also a known carcinogen, and is not as well contained as the chloroform in this preferred kit. An important aspect of this research was investigating alternative analytes that could be used instead of detergents.

The main components of the *CHEMetrics* detergent test kit (Figure F3.1) are:

1. Test tube
2. Comparator device
3. Snapper
4. Double tipped ampoule containing chloroform and other reagents (blue stained)
5. CHEMets ampoule (empty vacuum ampoule)



Figure F3.1: *CHEMetrics* detergent test kit components

Test Procedure Summary

This test should preferably be conducted in a laboratory fume hood due to the possibility of exposure to chloroform.

1. Pour 5 mL of the sample into the test tube.
2. Snap one tip of the double tipped ampoule, keeping the other tip inside the tube, but above the sample level. Invert the snapped tip into the tube and snap the other tip of the ampoule. Let the blue chemical (containing chloroform) completely empty into the test tube.
3. Cap the tube tightly and shake the solution for 30 seconds. Keep the solution undisturbed for 1 minute in a test tube rack.
4. Remove the cap from the tube and insert the vacuum CHEMetrics ampoule into the test tube. Care must be taken so that the small plastic tube at the tip of the ampoule touches the bottom of the tube.
5. Snap the CHEMetrics ampoule tip by the side of the test tube and let the solution flow through the tube into the CHEMetrics ampoule.
6. Take off the plastic tube and wipe off the tip of the ampoule. Put the provided white cap on the tip of the ampoule and place it in the color comparator.
7. Compare the color of the solution inside the ampoule with the color

comparator. The colors range from light blue (0.25 mg/L) to dark blue (3 mg/L). If the color is darker than the given colors in the comparator, the sample needs to be diluted and retested. No color indicates <0.25 mg/L value for detergents. The test tube needs to be disposed of carefully because it contains a hazardous chemical (chloroform).

Harmful Chemicals in CHEMetrics Detergent Test Kit

The main components of the double tipped ampoule are methylene blue, sulfuric acid, sodium phosphate, water and chloroform. Chloroform may affect the liver, kidney and central nervous system, and is a known carcinogen. On exposure, it causes irritation to eyes, skin and mucous membranes. It may also cause burning of the throat, mouth esophagus and stomach. It may also cause nausea, vomiting and diarrhea. Wash your hands thoroughly after handling the kit and conduct the analysis in a well-ventilated area, preferably in a laboratory fume hood. Avoid contact with the eyes. Safety glasses and gloves are required while doing this test. If there is a spill, take up with an absorbent material. Keep the reagents in the ampoule for final disposal, in accordance with regulations.

F3.2 FLUORESCENCE MONITORING USING THE GFL-1 FLUOROMETER

Introduction

Fluorescence is the property of the whiteners in detergents that cause treated fabrics to fluoresce in the presence of ultraviolet rays, giving laundered materials an impression of extra cleanliness. These are also referred to as bluing, brighteners or optical brighteners and have been an important ingredient of most laundry detergents for many years. The effectiveness of the brighteners varies by the concentration of the detergents in the wash water. The detection of optical brighteners has been used as an indicator for the presence of laundry wastewater, and municipal sewage, in urban waters.

One method of quantifying fluorescence in the laboratory is by using a fluorometer calibrated for detergents. In our tests, we used the GFL-1 Portable Field fluorometer (Figure F3.2).

The components of the GFL-1 Fluorometer are the power switch, sample chamber, battery compartment, source module, detector filter cartridge, display, keypad, and the interface port. A 1.2 Ah rechargeable lead-acid battery powers the unit when in the field. The fluorometer contains high efficiency interference filters optimized for fluorescence detection. It contains a silicon photodiode detector and a LED source. The interface port is also used as the battery charger port. A 192 X 192 dot LCD screen is used for text and graphical data presentation.

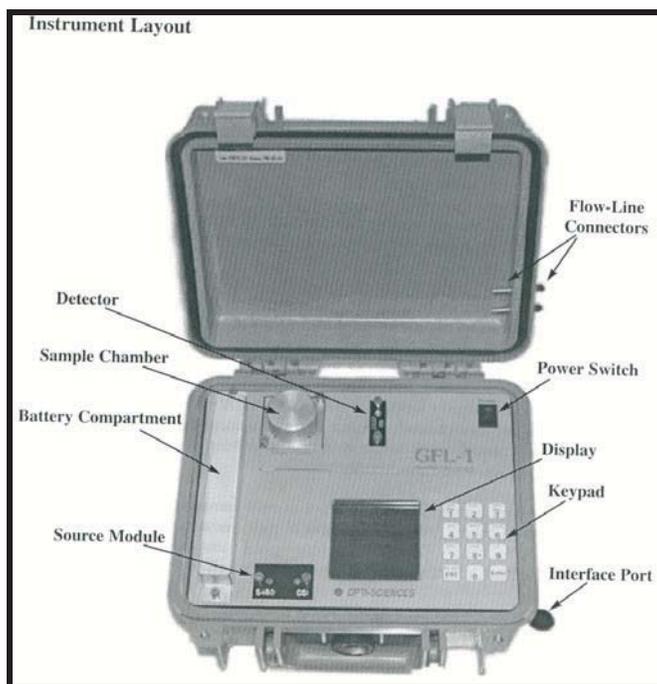


Figure F3.2: GFL-1 Portable Field Fluorometer

Calibration

Before the instrument is used, it should be calibrated with a detergent solution. No general standard detergent solution is available, so a commercially available detergent is used to prepare standard solutions. For this research, a common commercial detergent, Procter & Gamble's *Tide™* was used. The purpose of calibrating the fluorometer is to set the instrument fluorescent signal levels to correspond to different concentrations of this commercial detergent. Single point and multipoint calibrations are available with this fluorometer. The manufacturers report that the solution used in calibration is unimportant in that the procedure is the same regardless of the solution used. A five-point calibration method is used for instrument calibration. To test a sample, the instrument must be in "test mode." The test mode cannot be used until a calibration table has been built, or an existing one is made active. If there is no active calibration table, the test mode screen will automatically default to the "calibration menu" screen.

To install a new calibration table, select CREATE CAL TABLE by pressing 1 on the keypad. Soon the cal table builder screen appears on the display. Since a five point calibration is being done, six different concentrations of Tide detergent were made: 0.5mg/L, 5mg/L, 10mg/L, 50mg/L, 100mg/L, 500mg/L. A concentration of 25 mg/L of Tide corresponds to a typical working solution for a batch of laundry. The sample bottles for the GFL-1 fluorometer come with the instrument. These are the only sample bottles that can be used for the measurement of fluorescence. There are five steps in making a calibration table:

Step 1

The screen will prompt to insert the most concentrated reference in order to set the detector gain. In this case, the highest concentration is 500mg/L. Press ENTER.

Step 2

Insert the blank and press ENTER.

Step 3

The next step is to enter the calibration units (e.g., mg/L). Pressing the ENTER key takes the user to the next step.

Step 4

This step prompts the user to insert a reference sample of any concentration. After inserting the reference sample, press ENTER. The screen will then prompt the user to enter the concentration value for the inserted reference sample. After setting the known reference, the screen will ask whether or not to do another point. Press YES and repeat the above sequence until you have inserted all the prepared reference samples. The reference samples should be inserted in a random fashion and not in the order of increasing or decreasing values of concentration.

Step 5

The last step prompts the user to name the calibration table. It should be noted that calibration tables are not saved until a name is given to the table. Then press ENTER.

Now the fluorometer is ready to start running samples.

Sample Test Mode

Figure F3.3 is the first screen display shown after switching on the fluorometer. Press 1 for the test mode, since the calibration table has already been saved.

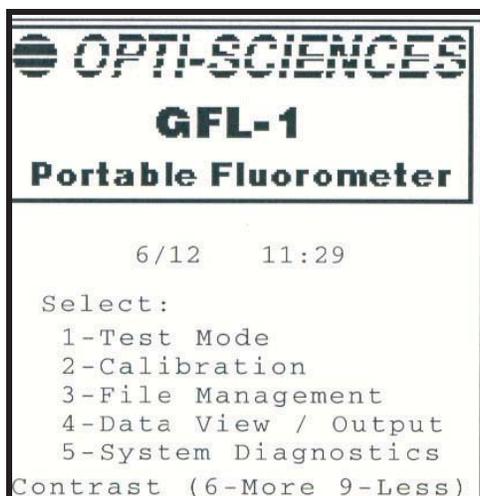


Figure F3.3: Main Menu

The screen will then display the following (Figure F3.4):

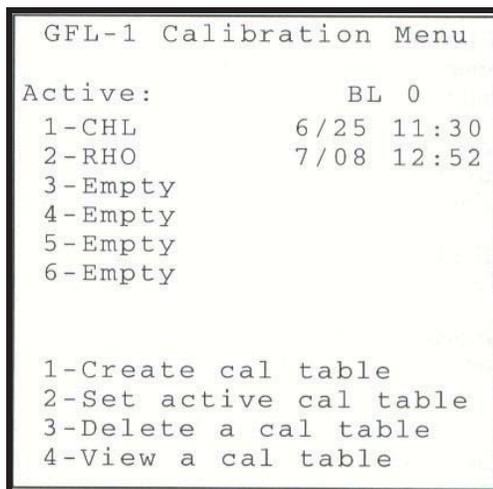


Figure F3.4: Calibration Menu

Press 2 for using the saved calibration table as the active calibration table in the memory. The next screen would prompt you to enter the desired table number saved. If you have saved only one calibration table, press 1.

Place a blank sample in the sample chamber and press ENTER (Figure F3.5). You will then see the screen displayed in Figure F3.6.



Figure F3.5: Placing Sample into Sample Chamber

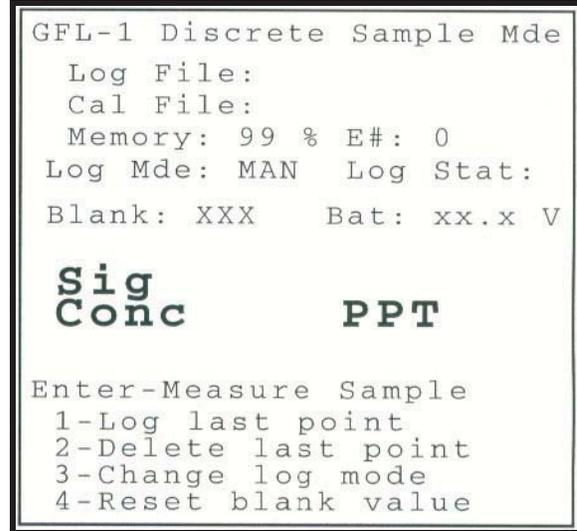


Figure F3.7: Discrete Sample Mode

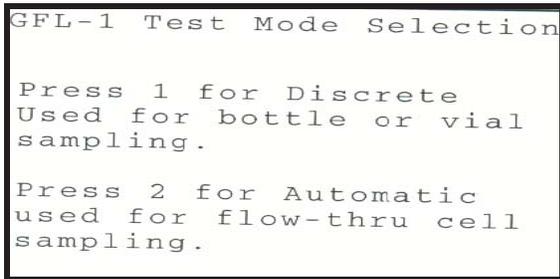


Figure F3.6: Test Mode Selection

Press 1 for doing discrete bottle sampling. A new screen will appear (Figure F3.7).

With calibration complete, the instrument is ready to analyze the samples. To run a test, simply load a sample into the chamber and press ENTER. The unit will measure the sample and present the data a few seconds later. A busy message indicates that the test is in progress. Press ESC to return to the main menu.

Initial Tests using the Fluorometer

Initial tests were conducted after the first calibration to get an indication of the repeatability and drift of the results obtained from the new instrument. Five different concentrations of Tide detergent samples were made and tested for fluorescence after varying periods of time. The results of these tests are shown in Figure F3.8.

It is obvious that the fluorescence signal from Tide degrades with time and that the analyses should be evaluated within two hours. Other samples of commercial and household detergents were also evaluated and degradation of fluorescence with time was also identified. The largest changes occurred between about one and two hours after sample preparation. There was very little change after this initial two hour period. In the real world, the time between mixing of a laundry detergent with the washwater at the laundry, its discharge, and its analysis in the laboratory is at least two hours. Therefore, the fluorescence values used are those obtained after the signals have reached a relatively constant value. The results of the tests on certain commercial and household detergents are shown in Figure F3.9.

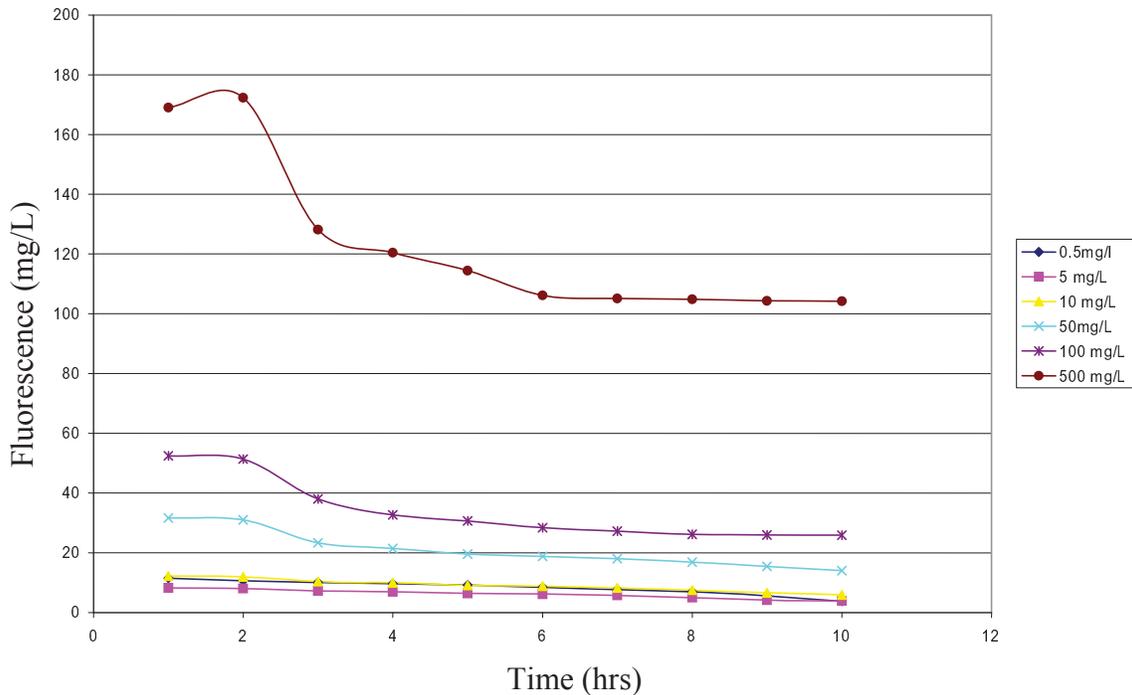


Figure F3.8: Changes in Tide Detergent Fluorescence over Time

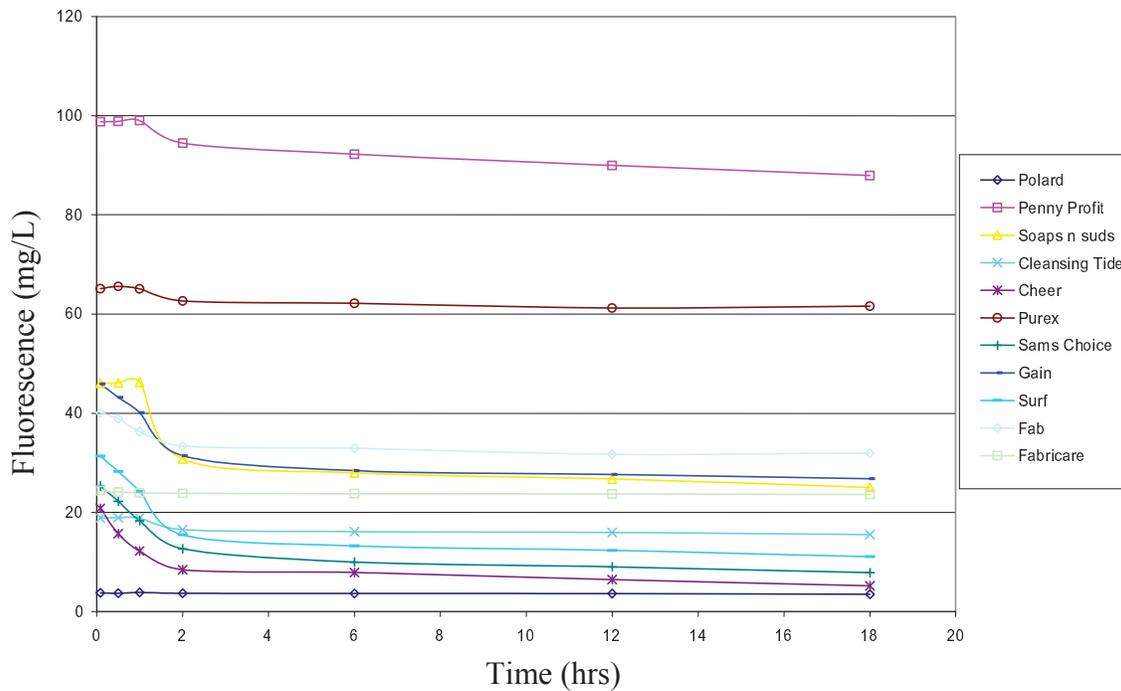


Figure F3.9: Changing Fluorescence with Time

The commercial laundry detergent samples in this graph were *Polard*, *Penny Profit*, *Soaps n Suds*, and *Cleansing Tide*. The others are household detergents (*Cheer*, *Purex*, *Sam's Choice*, *Gain*, *Surf*, *Fab*, and *Fabricare*). *Soaps n Suds* had a steep drop in fluorescence after one hour of preparation of the sample. After two hours, the fluorescence values stayed relatively constant without further changes. There was only one sample (*Polard*, a commercial detergent) that did not show any change in its fluorescence value. This detergent also had the lowest fluorescence signal of any of the samples. Although equal concentrations of all of these detergents were evaluated (50 mg/L), the fluorescence values ranged from 5 mg/L to 100 mg/L, as Tide. Obviously, the ingredients of the different detergents varied greatly.

F3.3 SURFACE TENSION TEST FOR THE DETECTION OF DETERGENTS

Introduction

This discussion presents a proposed sensitive method to detect detergents without hazardous chemicals and with standard laboratory equipment. The method uses the property of the detergent to decrease the surface tension of the bubbles formed when the sample is agitated. Different detergents at different pHs were used during these tests. Results indicate that the method can be used to detect detergent concentrations above 1 mg/L, and can be used as a presence/absence test for concentrations above 0.3 mg/L. The method also was verified with samples collected from a known inappropriate detergent discharge.

One of the effects of detergents in water is the reduction in surface tension. When a sample of water with detergent is agitated, air is mixed with water, creating bubbles. Because the surface tension is reduced, the tension that controls the pressure of the air is low and the surface film is not destroyed. This property can be used to estimate the detergent concentration based on the amount of foam produced after the sample is agitated.

The amount of foam formed after a sample of water with detergent is agitated can be affected by various parameters. Temperature can affect the surface tension of the water. An increase in the temperature will reduce the surface tension. Foam production can also be affected by the chemical composition of the water. As an example, low pH will decrease the foam production.

The following discussion presents an inexpensive, safe, and reasonably sensitive method to estimate the detergent concentrations in a water sample using common laboratory equipment and without hazardous reagents.

Methods

General laboratory equipment was used to generate foam from samples of distilled water and detergent at different concentrations. The idea of the experiment was to drop the sample inside a burette from a constant elevation and to measure the height of the foam created 10 seconds and 1 minute after the last drop fell.

Apparatus:

- A rectangular base support and rod assembly
- A 50 mL burette
- A clamp to hold the burette

- A 25 mL blowout pipette
- Two 10 mL pipettes
- A stop watch
- A 200 mL volumetric flask
- A portable pH meter

A rectangular base support was used to hold the burette vertically. Using a 25 mL pipette, a 25 mL sample was released into the 50 mL burette. The sample was released by free fall from near the top of the burette, taking care that the sample does not touch the wall of the burette to maximize the amount of bubbles that can be produced. An initial reading of the foam height was taken 10 seconds after the pipette was drained. A final reading was obtained 50 seconds later.

Reagents:

- Detergent (Tide)
- Distilled water
- 500 mL NaOH 1N
- 500 mL H₂SO₄ 0.02N

Four samples at the same concentration were created at the same time. Four stands and four burettes were used for each concentration. After the reading, the burettes were washed for more than 2 minutes until they were clean.

To obtain more foam during the experiment, the pH was increased up to 12. The sample was diluted with distilled water and 10 mL of 1N NaOH added. The sample was prepared in a 200 mL volumetric flask. NaOH was selected because it is present in most of the detergents. After the reading was taken, the sample (200 mL) was neutralized with 100 mL 0.05N H₂SO₄ before disposal.

Results

Table F3.11 shows the foam reading above the water surface 10 seconds and 1 minute after the last drop.

The results indicate that this method can be used as a presence/absence test for detergent concentrations between 0.2 and 1 mg/L (as Tide) and to estimate concentrations above 1 mg/L. The method is simple and does not require specialized equipment.

An advantage of this method is that the equipment is easily available and inexpensive. The disadvantages are the variability in readings due to changes in temperature and characteristics of the detergents.

Figure F3.10 shows the results from concentrations between 10 and 50 mg/L. For readings above 10 mg/L, if the level of detergent increases the height of the foam also increases in a parabolic shape. It was also observed that the repeatability of the results decrease at high levels.

For levels of detergent lower than 10 mg/L, there is not an important change in the reading. The minimum reading that can be

obtained from the burette is 0.05 mL. For samples in this range the reading is close to the precision of the instrument. Figure F3.11 shows the results from concentrations between 0 and 5 mg/L.

Readings below 1.0 mg/L create a circle of bubbles around the wall of the pipette. This circle was not present when distilled water was used. This procedure can be used as a presence/absence test. The circle was observed for concentration of detergent higher than 0.2 mg/L.

Conclusions

The new method is an inexpensive, safe and moderately accurate method to estimate the presence of detergents in concentrations above 0.2 mg/L. For detergent concentrations above 10 mg/L, the method can be used to quantify the concentrations. These higher concentrations have been observed in sewage, industrial discharges, laundries and car wash areas.

Table F3.11: Foam Readings Over Time		
Concentration (mg/L, as Tide)	Foam Height after 10 sec. (mL)	Foam Height after 1 min. (mL)
0	0	0
0.1	0	0
0.2	T	T
0.3	T	T
0.4	T	T
0.5	T	T
0.7	T	T
1	0.05, 0.05, 0.05, 0.05	0.05, 0.05, 0.05, 0.05
2	0.1, 0.1, 0.1, 0.1	0.1, 0.1, 0.1, 0.1
3	0.1, 0.1, 0.15, 0.15	0.1, 0.1, 0.15, 0.15
5	0.15, 0.15, 0.15, 0.15	0.15, 0.15, 0.15, 0.15
10	0.2, 0.2, 0.2, 0.2	0.35, 0.4, 0.4, 0.4
20	0.8, 0.6, 0.6, 0.6	1.5, 1.3, 1.4, 1.3
50	2.6, 2.6, 3.0, 2.8	3.8, 3.5, 3.7, 3.6

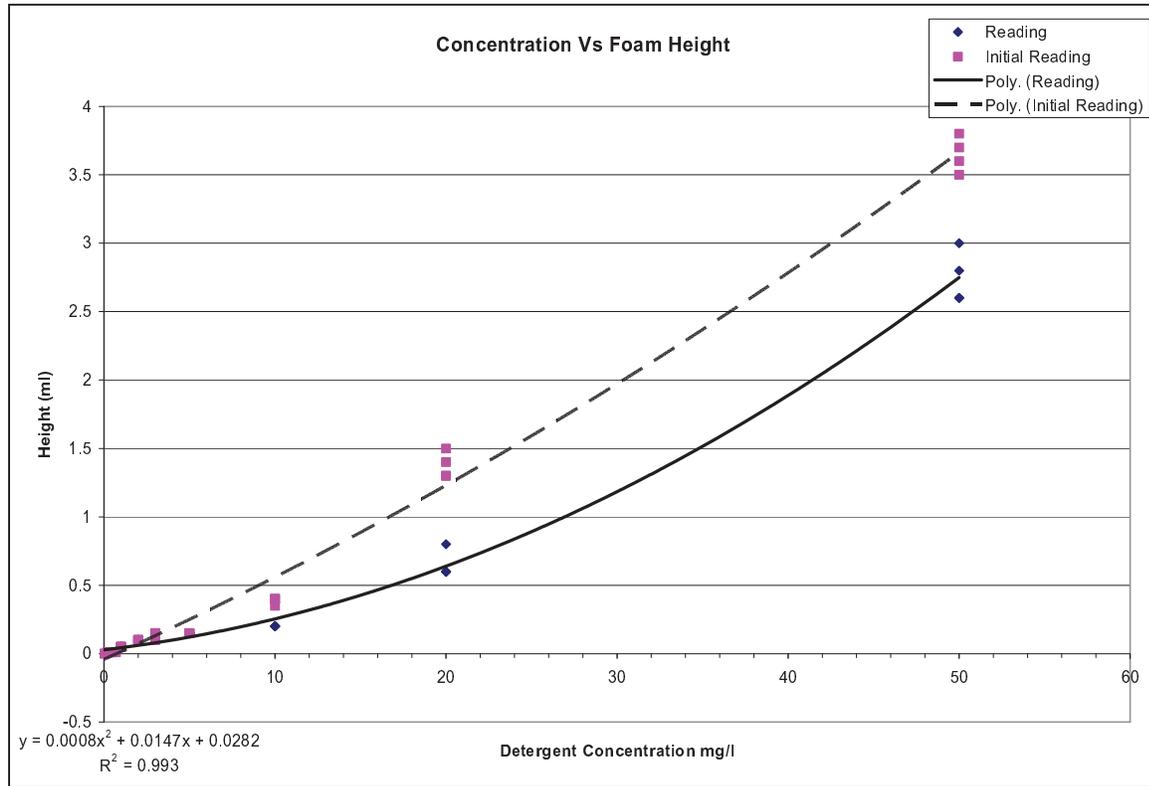


Figure F3.10: Correlation Between Concentration and Foam Height at Higher Concentrations

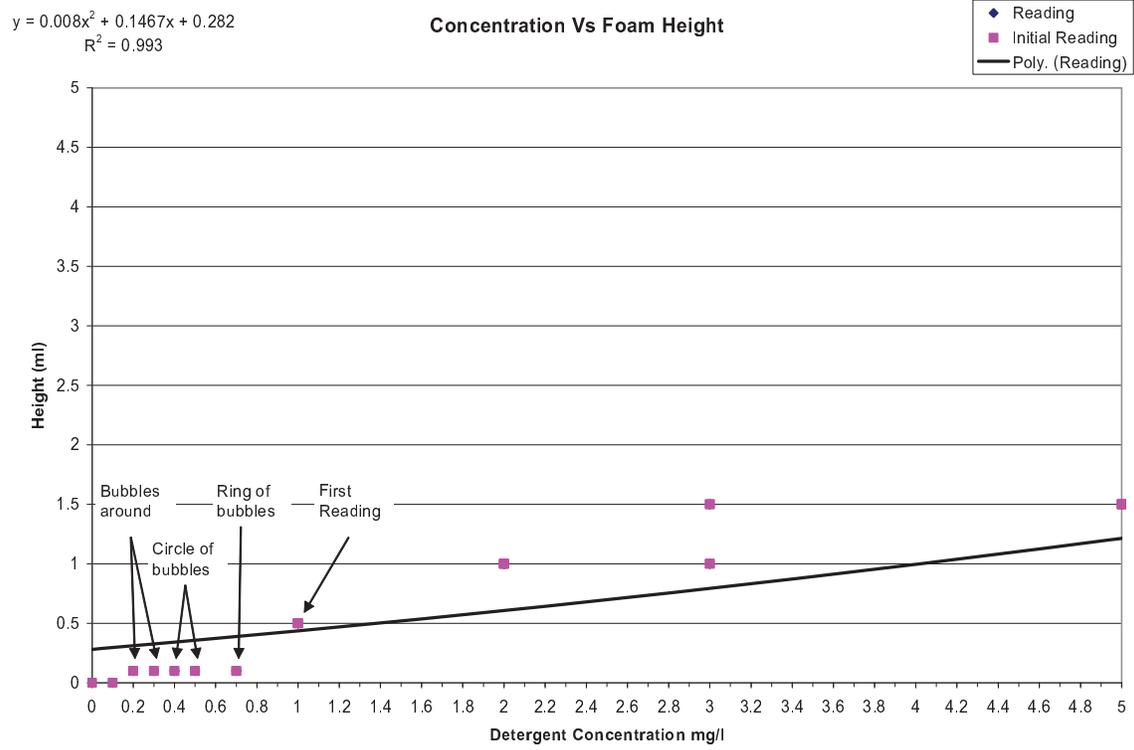


Figure F3.11: Correlation Between Concentration and Foam Height at Lower Concentrations

APPENDIX D – Indicator Monitoring Chain of Custody (COC)

