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Subject: EPA No. X-82907801-0
Techniques for Identifying and Correcting Illicit and Inappropriate Discharges
Task #2 Technical Memorandum

This memo summarizes research to date on methodologies to detect inappropriate connections in municipal separate storm sewer systems (MS4s) regulated under NPDES Phase I rules. A primary reference for this Memo is the attached and much more detailed "Methods for Detection of Inappropriate Discharges to Storm Drainage Systems" (Pitt, 2001), which builds on Pitt and Lalor's previous "Investigation of Inappropriate Pollutant Entries into Storm Drainage Systems: A User's Guide." The more detailed information provided in Pitt (2001) is condensed here, and supplemented with information from the inappropriate connection program survey conducted under Task 1 of this grant. This memo is organized as follows:

INTRODUCTION

A simple flow chart for investigating inappropriate connections (Figure 1) was developed by Pitt (2001). In this methodology, mapping and other "in-office" resources are used to prioritize outfalls for field screening. These field screening techniques are then used to identify probable locations of inappropriate discharges. The highest priority (pathogenic/toxic) outfalls are then investigated first, followed by nuisance or aquatic/life threatening discharges. These three terms are defined as follows:

1) **Pathogenic/Toxic**: Discharges in this category are the most severe, potentially causing disease upon water contact or consumption and significant impacts on receiving water organisms. Example sources include most commercial and industrial land uses, sanitary wastewater, and other residential sources including inappropriate household toxicant disposal, automobile engine de-greasing, vehicle accident clean-up, and irrigation runoff from landscaped areas excessively treated with chemicals (fertilizers and pesticides).

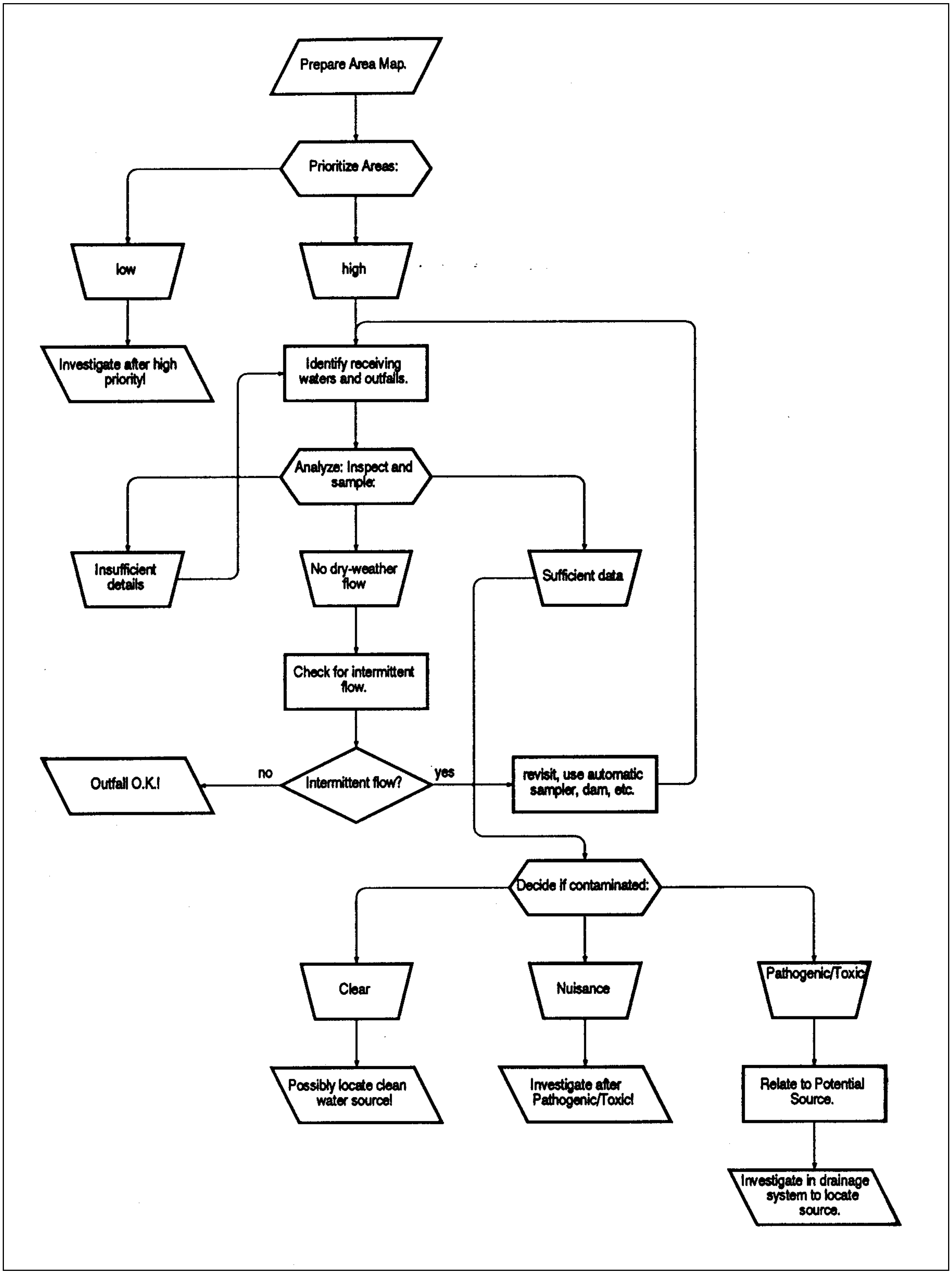


FIGURE 1. FLOW CHART FOR INVESTIGATIVE PROCEDURES. (PITT, 2001)

2) **Nuisance/ Aquatic Life Threatening**: This category primarily results in downstream problems such as algal growth and odorous waters. Examples include: automobile washing, construction site dewatering, and laundry wastewater.

3) **Clean Source:** This category includes tap water sources as well as natural waters.

In order to step through this process, a successful program needs to be able to systematically prioritize outfalls or stream reaches based on in-office information, accurately and efficiently identify probable "problem outfalls" from initial field screening, and conduct more detailed studies to locate specific discharges. Particularly when inappropriate connection programs are extended to small Phase II communities (relative to Phase I), programs should focus on cost-effective methodologies that can lead to the most significant water quality improvements.

SECTION 1. INFORMATION GATHERING / IDENTIFYING PRIORITY WATERSHEDS

Identifying inappropriate connections can be time consuming, and it is unrealistic to assume that communities will develop a program to remove or even identify all inappropriate connections in a short time frame. Thus, one of the most important components of an inappropriate discharge program is to identify priority watersheds or outfalls to focus initial efforts. While many established programs include continuous screening of all outfalls, program screening efforts should first focus on outfalls and watersheds with the greatest potential for contamination.

Mapping

A key component of inappropriate connection screening is the prioritization of problem outfalls and streams. This process combines mapping data and other available information to prioritize which outfalls and stream segments should be surveyed first. Maps should include the following items:

- Land Use.
- Outfall Locations (refined with field visits).
- Drainage areas to outfalls (refined with field visits).
- Storm drain system (if available).
- Locations of septic systems.
- Locations of older residential developments (have a high potential for sanitary sewer breaks).
- Standard Industrial Classification (SIC) Codes of industrial sites (if available).
- Key potential infiltration or connection areas (e.g., landfills).

Other key features can also be used to prioritize watersheds or outfalls for screening. Some of these include:

- Stream monitoring data
- Citizen complaints at outfalls
- Past Infiltration and Inflow studies

Initial mapping data has two purposes: these data can be used to prioritize field visits (as described here) and simple maps play a key role in the actual field screening.

Techniques to Prioritize Field Screening

All inappropriate connection and elimination programs are ultimately judged by their ability to improve water quality, and in particular to remove pathogenic and toxic connections. Communities have used several different techniques to prioritize areas for initial field screening, largely depending on the nature of problems within the jurisdiction, and the level and intensity of development. Three techniques are described below:

Technique 1: Receiving Water Quality

Many communities prioritize outfall screening based on receiving water quality. Two examples are Baltimore, Maryland and Houston, Texas. In both cases, in-stream monitoring data is used as an initial screening factor to focus inappropriate connection detection and elimination efforts. In Baltimore, in-stream citizen monitoring for ammonia is used to identify problem areas. In Houston (Glanton et al., 1992) the first set of problem areas was identified based on comprehensive monitoring that revealed waters where water quality use standards were exceeded.

Technique 2: Land Use

In municipalities with distinctly different catchment types, or with a variety of industries, land use can be a useful indicator to screen areas with potential inappropriate connections. Some key mapping features that can help identify potential problem areas include industrial SIC codes and areas with older infrastructure. These prioritization techniques can range from the relatively simple to very detailed. As GIS systems become more and more accessible, they are playing a greater role in aiding communities in this task.

Wayne County, Michigan, uses GIS mapping to a great extent to prioritize inappropriate connection identification (Tuomari, 1996). Industrial land uses dominate the county, which includes Detroit. The community has at its disposal a detailed GIS layer of SIC codes for various industries. Each SIC code is assigned a priority level from 1 to 4 based on an industry’s likelihood to store contaminants, or have inappropriate connections. The 467 square mile Rouge River Basin was divided into 335 drainage areas, and each drainage area is prioritized based on its weighted score. County staff members inspect areas with the highest scores (and present the greatest risk) before other catchments. The GIS system is also used to highlight specific SIC codes within a drainage area to conduct on-site investigations.

A similar, but much less detailed technique, is used in the less industrial City of Knoxville, Tennessee. Here, the City is divided into a grid, and outfalls are prioritized based solely on the presence of industrial land uses. This system is then used to direct the city’s regularly scheduled outfall monitoring program. Outfalls with industrial land uses in their drainage areas are screened annually, while residential and commercial outfalls are screened every two years.

Technique 3: Responses to Citizen Hotlines

A less formal but also very important measure of water quality are citizen complaints. The Center’s survey (CWP, 2002) indicated that citizen hotlines were the tool most often used to identify illicit discharges, surpassing outfall screening. Citizen hotlines can also help to identify sources that are difficult to detect using from outfall screening alone, such as spill events that may cause serious contamination but are sporadic.

SECTION 2. INITIAL FIELD SCREENING

Once priority outfalls or stream reaches have been identified, these areas are then targeted for field screening. This screening typically includes a combination of physical and chemical parameters sampled at mapped outfalls to determine the presence of inappropriate discharges, verify existing mapping and to find outfalls that may not have appeared on the original maps. This section outlines some of the key techniques used in outfall screening, and includes:

2.1 A Framework for Field Screening
2.2 Strategies in the Field
2.3 Measuring Flow
2.4 Intermittent Flows
2.5 Physical Parameters
2.6 Chemical Parameters
2.7 Distinguishing Specific Flow Sources

2.1 A Framework for Field Screening

The results of field screening can be used for different purposes, depending on the drainage area and its land use complexity. At a minimum, field screening can be used to distinguish “contaminated” sources, such as sanitary wastewater, industrial process water, and washwater, from “uncontaminated” sources such as spring water or shallow groundwater. Additional screening factors can be used to distinguish between a suite of different flow sources.

Research to date suggests that the original field screening flow chart proposed by Pitt and Lalor (1993) is still a good method for characterizing the probable flow components of inappropriate discharges (Figure 2). Practice has shown that the presence of detergents alone can be used to distinguish between contaminated versus uncontaminated flows, at least in commercial and residential watersheds.

Some other parameters also help to distinguish contaminated sources from uncontaminated sources. For example, the City of Baltimore, Maryland uses ammonia alone as an indicator of contamination while acknowledging that it is not always the most sensitive method. In addition, Pitt’s (2001) research indicates that color or conductivity can distinguish contaminated flows from uncontaminated flows, but only if flows at the outfall come from a single source (e.g., completely composed of sanitary wastewater with no groundwater present).

Many communities find it useful to distinguish discharges from the most serious sanitary wastewater discharges from the less severe washwater discharges. Furthermore, a community may wish to separate tap water sources from natural spring water or groundwater. By adding ammonia, potassium and fluoride as screening parameters, one can further distinguish between wastewater and washwater sources, and between tap water and natural water sources (Figure 2).

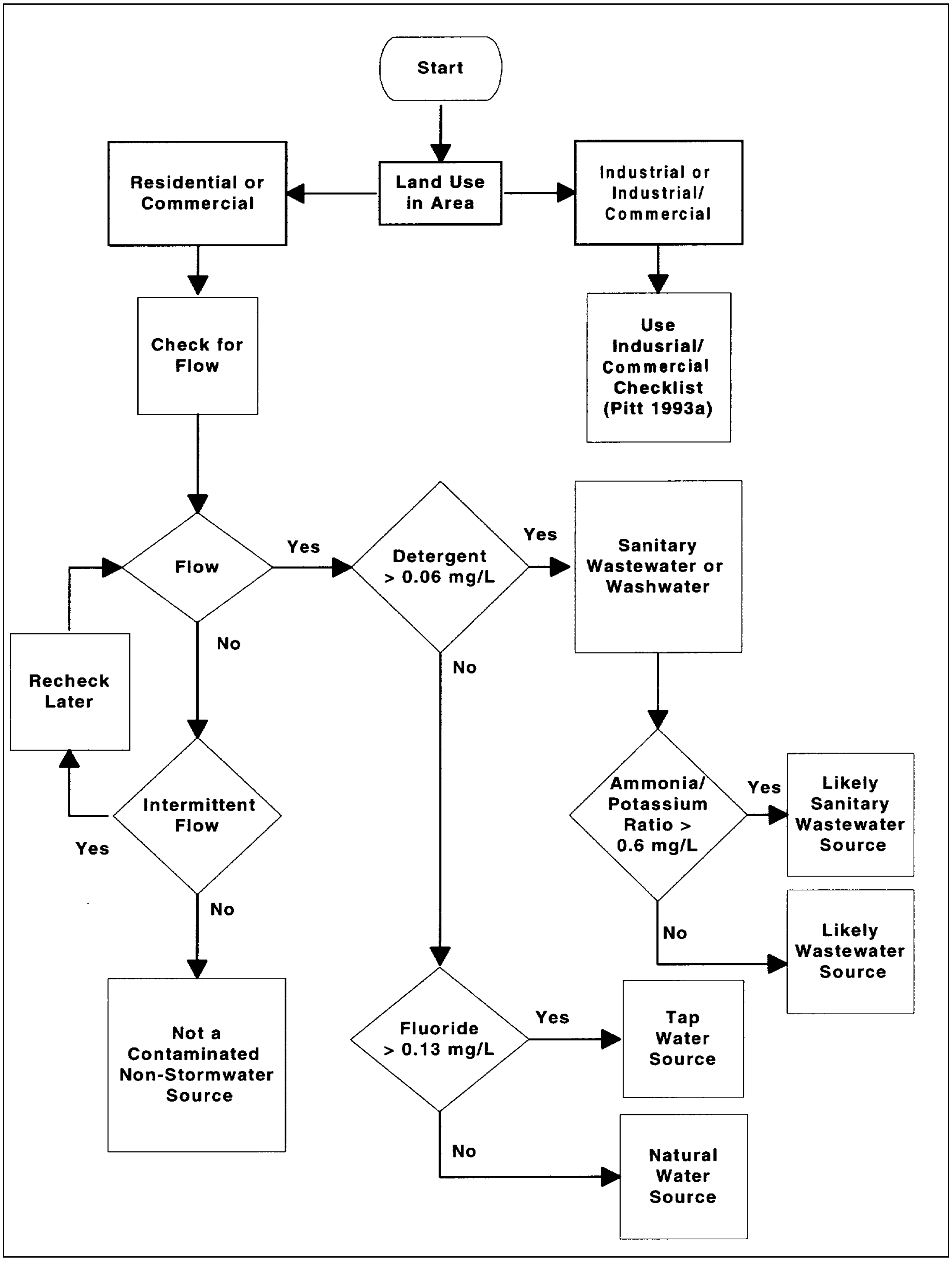


FIGURE 2: SIMPLE FLOW CHART METHOD TO IDENTIFY SIGNIFICANT CONTAMINATING SOURCES (PITT AND LALOR, 1993)

Pitt (2001) focused on distinguishing between more distinct flow components. In this research, a complete suite of parameters, including both physical and chemical, can be used to distinguish between these groups. As indicated in Table 1, some parameters have relatively high or low concentrations depending on the flow source, and these differences can potentially be used to characterize outfall flows. A numeric method for characterizing flow sources is described in Section 2.7.

TABLE 1: FIELD SURVEY PARAMETERS AND ASSOCIATED NON-STORMWATER FLOW SOURCES (PITT, 2001)

Parameter	Natural Water	Potable Water	Sanitary Sewage	Septage Water	Indus. Water	Wash Water	Rinse Water	Irrig. Water
Fluorides	-	+	+	+	+/-	+	+	+
Hardness change	-	+/-	+	+	+/-	+	+	-
Surfactants	-	-	+	-	-	+	+	-
Florescence	-	-	+	+	-	+	+	-
Potassium	-	-	+	+	-	-	-	-
Ammonia	-	-	+	+	-	-	-	-
Odor	-	-	+	+	+	+/-	-	-
Color	-	-	-	-	+	-	-	-
Clarity	-	-	+	+	+	+	+/-	-
Floatables	-	-	+	-	+	+/-	+/-	-
Deposits and stains	-	-	+	-	+	+/-	+/-	-
Vegetation change	-	-	+	+	+	+/-	-	+
Structural damage	-	-	-	-	+	-	-	-
Conductivity	-	-	+	+	+	+/-	+	+
Temperature change	-	-	+/-	-	+	+/-	+/-	-
pH	-	-	-	-	+	-	-	-

Note:
- implies relatively low concentration
+ implies relatively high concentration
+/- implies variable conditions

2.2 Strategies for Field Screening

The purpose of field screening is to monitor outfalls for flow and contaminants, and to verify mapping and locate outfalls. Field screening should include all outfalls, and every effort should be made to locate them. Although most programs focus on major, or large diameter, outfalls as required by EPA Phase I, Pitt's (2001) research suggests that small may be at least as important. In a Birmingham, AL demonstration project, the median outfall diameter was only 36" (Figure 3), implying that sampling only those outfalls larger than 36" in diameter would capture only one half of the outfalls. Furthermore, these relatively small outfalls can capture surprisingly large drainage areas. While smaller outfalls typically have smaller drainage areas, they can capture areas up to 400 acres (Figure 3).

The research in Birmingham also indicated that these small outfalls can be the worst in terms of probability of illicit connection, and water quality. About five percent of the outfalls sampled exhibited dry-weather flows, which were extremely toxic, or were raw, undiluted, sanitary wastewater. Each of these contaminated outfalls were 20 in., or less, in diameter. Furthermore, some of the worst dry-weather flow discharge problems were associated with very small (4 in. diameter) pipes draining automobile service areas adjacent to the creek.

Outfall screening should typically be conducted during the late morning hours to detect sanitary flows, and should also be conducted during dry weather. Most communities in the Center's survey conduct monitoring after 72 hours of dry weather (<0.1" of rain) per EPA guidance, although Pitt (2001) recommends flexibility and indicates that as little as twelve hours may be sufficient, depending on the system characteristics.

It is generally more efficient, effective, and safe to preserve samples and send them to a laboratory rather than analyze samples in the field, with the exception of temperature and conductivity, and of course observational parameters such as odor. Field screening can be completed with a three-person crew, and relatively simple field equipment (See Table 2). Two people walk the stream, sampling and marking outfalls with spray paint, recording GPS coordinates, and filling out simple field sheets for all outfalls. Where dry weather flows exist, flow is collected for future analysis. Otherwise, physical observations are noted. The third person drives to an upstream location, and prepares samples collected from the previous reach. These samples are then analyzed in a laboratory after the days' work is complete.

2.3 Measuring Flow

Is there dry weather flow, and how much? This simple question is key to identifying inappropriate discharges in any urban or suburban watershed. Two techniques are commonly used to measure flow from storm drain outfalls (Glanton et al., 1992). In the first, a vessel of known volume is held below the outfall, and the time it takes to fill the vessel is recorded. In outfalls with greater than 20 gpm, or where the outfall does not have significant drop to fit a vessel below the outfall, a second option is used. In this option, a three-foot long PVC pipe with fluorescent tape at one-foot intervals is anchored to the bottom of the storm drain pipe, and a marker is floated along the pipe. The depth of flow, pipe geometry, and measured velocity, are combined to estimate flow.

2.4 Intermittent Flows

One challenge to successfully identifying inappropriate discharges is that many of these discharges occur in intermittent, or sporadic, flows. Some sources that can contribute to these intermittent discharges include:

- Wash-up operations at the end of a work shift, or job activity.
- Wash-down following irregular accidents and spills.
- Disposal of process batches or rinse water baths.
- Over-irrigation of lawns.
- Vehicle maintenance, e.g., automobile washing, radiator flushing, and engine de-greasing.

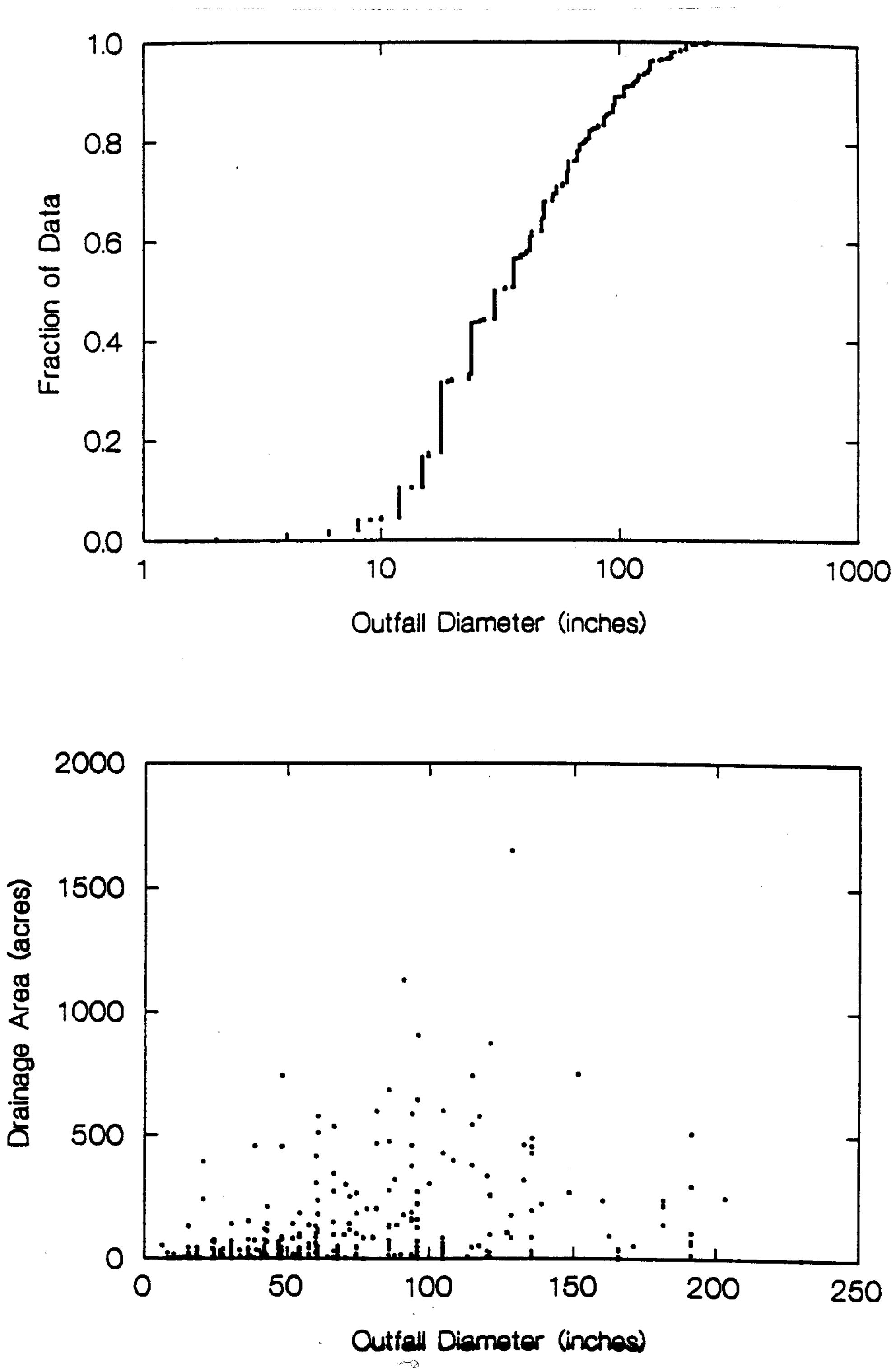


FIGURE 3: OUTFALL DIAMETER DISTRIBUTION IN BIRMINGHAM, AL (PITT, 2001)

TABLE 2: FIELD EQUIPMENT CHECKLIST (ADAPTED FROM PITT, 2001)

- ☐ Vehicle
- ☐ Temperature and specific conductivity meter
- ☐ Field notebook containing maps and non-stormwater flow evaluation field sheets
- ☐ Waterproof marker/pen
- ☐ Camera and film
- ☐ Spray paint
- ☐ Tape measures (both 3m and 30m)
- ☐ Flashlight
- ☐ Watch (with second hand)
- ☐ Glass sample containers with waterproof labels (500 ml)
- ☐ Plastic sample containers with waterproof labels (1 to 2 liter)
- ☐ Ice boxes with ice (left in vehicle)
- ☐ Backpack
- ☐ Grab water sampler (dipper on long pole)
- ☐ Hand operated vacuum pump sampler for shallow flows
- ☐ Waders and walking stick
- ☐ First aid kit and pocket knife
- ☐ Self protection pepper spray
- ☐ Two-way radios for communication between field crew and vehicle driver
- ☐ Hand held global positioning satellite (GPS) system receiver (best resolution available within budget, at least 6’ accuracy)

Pitt's (2001) research indicates that a significant fraction of flows can occur intermittently, particularly those from industrial land uses. Intermittent flows account for approximately one third of outfalls with dry weather flow. From a total of 17 stormwater outfalls that experienced dry weather flow in a Birmingham test watershed, 6 flowed intermittently. Intermittent flows were more prevalent in industrial areas: of eighteen direct outfalls to the creek from nearby industries and commercial areas, 10 were dry, 6 had intermittent flow, and two flowed continuously.

Although no set of physical observations is perfect, a combination can be used to indicate the presence of intermittent flows. Common indicators include:

- Abnormal increase or decrease in vegetation at the outfall
- Cracking or spalling of the concrete
- Sedimentation or debris build-up
- Staining
- Oily sheen
- Odors

Other indicators, such as the presence of known likely industrial dischargers, known poor water quality in dry weather, or past citizen complaints, may also warrant follow-up visits to a particular outfall.

Analyzing pooled water immediately below the outfall or collected between visits in small, constructed dams within the storm drain can also identify intermittent discharges. Similarly, coarse solids and/or floatables can be captured through the erection of coarse screens and/or booms at the mouth of the outfall or in the receiving stream. It may be necessary to visit suspect outfalls frequently. However, it is virtually impossible to be able to capture a short-term intermittent flow (such as from the illegal dumping of wastes into the storm drainage system) from outfall visits.

Another technique to identify persistent but intermittent water quality problems is the use of toxicity monitors at storm outfalls. One technique, known as the "stream sentinel," was pioneered by the City of Fort Worth (Rattan and Camp, 1995). Here, perforated bottles filled with minnows are placed at storm drain outfalls. The minnows are checked once or twice a week and tracked for mortality. When outlets have a relatively high mortality rate, this can be an indicator of a consistent problem within the drainage to the outfall.

2.5 Physical Parameters

A wide range of simple physical parameters can be used in the field to characterize inappropriate discharges. Physical parameters can be observed in the field without equipment, and can identify highly contaminated outfalls. Some commonly used physical parameters are profiled in Table 3. As indicated in the table, these physical parameters are generally well suited to identify industrial dischargers. These parameters cannot be relied on alone to predict inappropriate discharges, because they generally result in a relatively high false negative result. A false negative result would show that no inappropriate discharges exist when they are in fact present. Due this potential to miss inappropriate discharges, physical monitoring needs to be supplemented with chemical testing.

Pitt's (2001) research reveals a relatively high false negative rate for physical indicators. While turbidity and obvious odors appeared to be the best indicators of contamination, turbidity resulted in a 24% false negative result, and odors resulted in a 33% false negative. Similarly, data from the State of Maryland found virtually no relationship between physical parameters, and odor and turbidity in particular, and the presence of detergents (a highly successful indicator of contamination) in the discharge. Maryland's data suggests false negatives of 76% and 85% for turbidity and odor, respectively. Similar results were reported in Houston's early field testing (Glanton *et al*., 1992), with 22 of 26 outfalls testing positive for detergents, but only 10 with high turbidity and 16 with obvious odors.

Other physical observations have been used to identify probable inappropriate discharges at outfalls. Some of these parameters can be customized regionally. For example, opportunistic red-eared turtles, which congregate near areas high in nutrients, were used as indicators of intermittent water quality problems in Houston, Texas. Also in Houston, Sphaerotilus bacteria, commonly known as "sewage fungus" was an indicator of a sewage discharge, and disappeared within 48 hours of removing the discharge.

2.6 Chemical Parameters

The technique outlined in Figure 2 suggests that, at least in watersheds dominated by residential and commercial land uses, screening can be accomplished with relatively few parameters. In fact, Pitt's research suggests that this technique identified every wastewater contaminant, and consistently distinguished between sanitary and washwater discharges. Further, detergent alone could identify all wastewater sources, but could not easily distinguish between the most severe problems (e.g., sanitary wastewater discharges) versus the second tier washwater discharges.

Consequently, research has focused on the five parameters identified in Figure 2 (ammonia, detergents as measured by surfactants, detergents measured as fluorescence, potassium, and fluoride) along with three very simply measured parameters: conductivity, hardness, and toxicity. The values of each of these parameters are summarized in Table 4. Four other parameters were selected for research because the EPA has historically recommended them, although these parameters have demonstrated little value in detecting inappropriate discharges. These include: pH, chlorine, copper, and phenols. While pH may help to identify some industrial contaminants, the other three show less promise. In general, they are often not detected at field screening, even when detergents indicate contamination. For example, data collected by inappropriate discharge monitoring in Maryland reveals that these parameters are detected less than half as often as detergents (See Figure 4).

In addition to the selection of parameters for discharge detection, research to date has focused on the best techniques to identify each contaminant, and is briefly depicted in Table 5. A more detailed description of this research is provided in Appendix A of this document. The brand names indicated in Table 5 are not necessarily an endorsement of these products, but are presented to demonstrate the types of methods investigated.

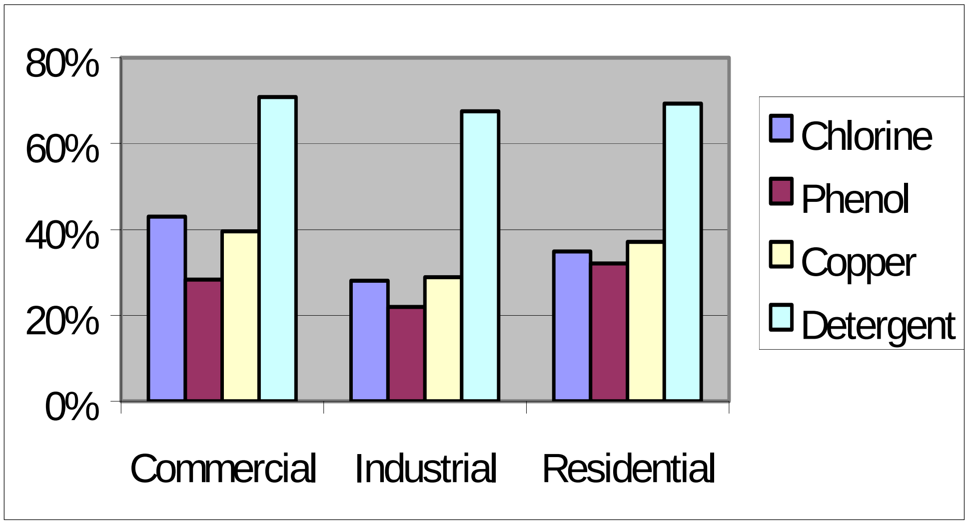
TABLE 3: PHYSICAL OBSERVATION PARAMETERS AND LIKELY ASSOCIATED FLOW SOURCES (PITT, 2001)

PARAMETER	INTERPRETATION
Odor	*sewage:* smell associated with stale sanitary wastewater, especially in pools near outfall. *sulfur ("rotten eggs"):* industries that discharge sulfide compounds or organics (meat packers, canneries, dairies, etc.). *oil and gas:* petroleum refineries or many facilities associated with vehicle maintenance or petroleum product storage. *rancid-sour:* food preparation facilities (restaurants, hotels, etc.).
Color	*cloudy:* sanitary wastewater, concrete or stone operations, fertilizer facilities, automotive dealers. *opaque:* food processors, lumber mills, metal operations, pigment plants.
Turbidity	*cloudy:* sanitary wastewater, concrete or stone operations, fertilizer facilities, automotive dealers. *opaque:* food processors, lumber mills, metal operations, pigment plants.
Floatable Matter	*oil sheen:* petroleum refineries or storage facilities and vehicle service facilities. *sewage:* sanitary wastewater.
Deposits and Stains	*sediment*: construction site erosion. *oily:* petroleum refineries or storage facilities and vehicle service facilities.
Vegetation	*excessive growth:* food product facilities. *inhibited growth:* high stormwater flows, beverage facilities, printing plants, metal product facilities, drug manufacturing, petroleum facilities, vehicle service facilities and automobile dealers.
Damage to Outfall Structures	*concrete cracking, concrete spalling, industrial flows, metal corrosion:* industrial flows

TABLE 4: CHEMICAL PARAMETERS FOR FUTURE RESEARCH (PITT, 2001)

Parameters	Potential Use
Detergents (Surfactants)	Measure of MBAS (methylene blue active substances) to detect sanitary wastewater or washwater
Fluorescence	Also an indicator of detergents. Better technique to identify septic system discharges.
Potassium	Used with ammonia to distinguish washwater from sanitary wastewater.
Ammonia	Used with potassium to distinguish washwater from sanitary wastewater.
Fluoride	Useful to identify tap waters and distinguish from natural waters.
Conductivity	Cheap to measure. May distinguish between clean sources and wastewater.
Hardness	Depending on natural concentrations, may be useful to distinguish between natural sources, tap water, and wastewater.
Toxicity	Useful to identify highly toxic outfalls.

FIGURE 4: FREQUENCY OF DETECTION AT MARYLAND OUTFALLS (MDE, 1997)



Of the techniques investigated, most are relatively low cost and easy to implement. The two exceptions to this rule are fluorescence, which is relatively expensive, and detergents, which is a time consuming process that uses a toxic reagent (benzene). Future research will focus on alternative methods to measure detergents and fluorescence, which are key to finding wastewater connections. In addition, the probes investigated in these studies consistently had problems with membrane fowling. New probes are presently being evaluated to determine if this problem persists in newer models.

Most testing methodologies fall into a few broad types as follows:

ISE: Otherwise known as ion selective electrodes, these are probes that detect concentrations based on the presence of ions.

Spectrophotometer: In these techniques, concentrations are determined by placing a vial that contains the sample and a reagent into a spectrophotometer, which determines the concentration based on the amount of light at a particular wavelength which passes through the sample.

Flame Atomic Absorption: Operates on the same principle (light absorption) as the spectrophotometer. However, light is passed through an air column which includes an aerosol of the liquid sample mixed with flammable gasses and burned, rather than a vial of the liquid mixed with a reagent. The concentration is determined based on the energy loss of a characteristic wavelength as it passes through the air column.

Titration: Process of chemical analysis in which the quantity of some constituent of a sample is determined by adding an exactly known quantity of another substance with which it reacts in a definite, known proportion.

Test Strips: These are strips of paper having contact patches of reagents that turn the contact patches particular colors when they come in contact with specific concentrations of certain constituent chemicals. The researcher then compares the resulting test strip colors to a reference sheet illustrating the contact patch colors associated with known pH or concentrations of the targeted chemicals.

Colorimetric: In these tests, the sample is mixed with a reagent, and the resulting color is compared with a color wheel or example sheet to determine the concentration.

Other: There exist other tests and procedures for identifying chemical constituents of samples, and they are generally named after the proprietary developers of the procedures. Microtox™, for example, has developed a screening procedure for identifying relative toxicity.

TABLE 5. METHODS EVALUATED FOR PARAMETER MEASUREMENT (PITT, 2001)

Parameter	Methods Investigated (Selected method in **Bold**)	Justification
Conductivity & Temperature	**YSI Conductivity Meter (Model 33**)	--
Fluoride	HACH Ion Specific Electrode (ISE) **HACH DR/2000 Spectrophotometer (AccuVac: SPADNS Method)**	ISE method required frequent replacement of the membrane of the probe.
Hardness	HACH DR/2000 Spectrophotometer (Calmagite Method) **HACH Field Titration Kit (EDTA Titration)** Quant Test Strips	Spectrophotometer and test strips did not allow analysis within the broad range needed for IDDE work.
Detergents (Surfactants)	**HACH Detergent Test Kit (MBAS Colorimetric)** Orion Surfactants Kit (ISE and Titration)	The colorimetric method was more sensitive.
Fluorescence	**Turner Filter Fluorometer (Model 111)**	--
Potassium	**HACH DR/2000 Spectrophotometer** HACH ISE Flame Atomic Absorption	The ISE method needed frequent membrane replacement, and the flame atomic absorption method was costly.
Ammonia	**HACH DR/20000 Spectrophotometer** HACH ISE Test Strips Hanna and Chemetrics Field Test Kits	Other methods had problems with interferences, long analysis times, poor performance, and inconsistency.
Toxicity	**Microtox™ (Microbics, Inc.)**	--
Color[1]	**HACH Color Kit**	--
pH[2,3]	**Fisher Accument Model 610A** Test Strips	Test strips were relatively inaccurate.
Total Chlorine[3]	**HACH DR/2000 Spectrophotometer** HACH Titration Quant Test Strips	The Spectrophotometer was the only method with sufficient resolution.
Total Copper[3]	**HACH DR/2000 Spectrophotometer** Quant Test Strips Chemet Field Test Kit	Test strips did not have sufficient resolution.
Total Phenols[3]	**HACH Colorimetric Method**	--

1: This measurement of color is a different measurement than the narrative description of color discussed as a “physical parameter”
2: Best suited to identify industrial sources
3: Parameter evaluated because it is recommended in EPA guidance materials.

2.7 Distinguishing Specific Flow Sources

A significant focus of Pitt's (2001) research has been development of techniques that can be used to distinguish not only between broad categories of flows, but also between specific sources. In this methodology, statistical characteristics, including the mean, standard deviation, and type of distribution, are developed for a suite of parameters for each source type. Using these data requires the use of probabilistic linear algebra solutions to estimate the probable percent flow from each source. To simplify these calculations, a FORTRAN program was developed to solve these equations. This program is currently being refined and converted into a more usable format as a part of continuing research.

Various background flow sources within a watershed need to be characterized to distinguish between specific flows. To establish background conditions, an investigator must take samples from each of the various local flow sources such as tap water, groundwater, sewage, septic effluent, and washwater, and develop a statistical characterization of this source. In some cases, it may be useful to separate data within one of these source categories depending on location within a community or between watersheds. Causes of variation may include differences in water source for tap water (e.g., individual wells versus water from a municipal supply) and changes in ground water quality depending on localized geologic features. Some sources, such as septic effluent, may not be a concern in some watersheds, and should therefore be eliminated from the background characterization analysis.

As a first step toward testing this technique in Birmingham, researchers began by developing distributions within that City (Table 6). Although matrix algebra computation is complicated when considering probability, a simple premise is that useful variables are those that can easily distinguish one source from another and have a relatively "tight" distribution, as indicated by a low coefficient of variation.

Initial testing of this methodology yielded mixed results. Initial "cluster analysis" indicated that when all of the sample data were assembled, flow from different sources naturally fell into different groups (e.g., spring water, laundry waste water, septage), indicating that this methodology could be used to distinguish between broad sources of flow.

When subject to further testing, however, the method did not perform as well. First, samples flows from each source were characterized. In these tests, the model was used to characterize the components of a sample which was, for example, 100% septage (See Table 7). The method always predicted the actual source as a major component (more than 10%) of the flow. However, for many sources, it also predicted that various other sources were significant. For example, shallow ground water was predicted to be a significant component of every "contaminated" source flow.

Table 6. Summary of Chemical Characteristics of Source Samples Collected in Birmingham, Alabama (Pitt, 2001)

Source	Conductivity (μS/cm)	Fluoride (mg/L)	Hardness (mg/L as $CaCO_3$)	Detergent (mg/L)	Fluorescence % scale	Potassium (mg/L)	Ammonia (mg/L)	Color (units)	Chlorine (mg/L)
Spring Water									
mean	301	0.03	240	0.00	6.80	0.73	0.01	0.0	0.00
COV	0.04	1.00	0.03	--	0.43	0.10	2.00	--	--
distribution	normal	normal	normal	uniform	normal	normal	L-norm	uniform	uniform
Shallow Ground Water									
mean	51.4	0.06	27.3	0.00	29.9	1.19	0.24	8.0	0.02
COV	0.84	0.50	0.39	--	1.55	0.44	1.26	1.42	1.62
distribution	normal	L-norm	normal	uniform	L-norm	normal	normal	L-norm	normal
Tap Water									
mean	112	0.97	49.3	0.00	4.63	1.55	0.03	0.0	0.88
COV	0.01	0.01	0.03	--	0.08	0.04	0.23	--	0.68
distribution	normal	normal	normal	uniform	normal	normal	normal	uniform	bi-modal
Landscaping Irrigation									
mean	105	0.90	40.2	0.00	214.4	6.08	0.37	10.0	0.03
COV	0.07	0.11	0.04	--	0.16	0.26	0.25	0.36	1.02
distribution	normal	normal	normal	uniform	normal	normal	normal	normal	normal
Sewage									
mean	420	0.76	143	1.50	251.0	5.97	9.92	37.9	.01
COV	0.13	0.23	0.11	0.82	0.20	0.23	0.34	0.55	2.00
distribution	normal	normal	normal	normal	normal	normal	L-norm	normal	L-norm
Septic Tank Discharge									
mean	502	0.93	56.8	3.27	382	18.82	87.21	70.6	0.07
COV	0.42	0.39	0.36	1.33	0.22	0.42	0.40	0.39	1.30
distribution	normal	normal	L-norm	L-norm	normal	normal	normal	normal	normal
Carwash									
mean	485	12.30	157	49.0	1190	42.69	0.24	221.5	0.07
COV	0.06	0.19	0.05	0.10	0.11	0.37	0.28	0.35	1.14
distribution	normal	normal	normal	normal	normal	normal	normal	normal	bi-modal
Laundry									
mean	563	32.82	36.2	26.9	1024	3.48	0.82	46.7	0.40
COV	0.21	0.38	0.08	0.25	0.12	0.11	0.14	0.27	0.26
distribution	normal	normal	normal	normal	normal	normal	normal	normal	normal

TABLE 7. TESTING OF THE MASS BALANCE MODEL ON "UNIFORM" SAMPLES (PITT, 2001)

Source	**Predicted % Contribution (Median and Range)**	**Other Sources Predicted as Significant***
Spring Water	99 (90-100)	None
Tap Water	99 (78-100)	None
Irrigation	88 (52-97)	Shallow Ground Water, Tap Water
Shallow Ground Water	49 (25-76)	Spring, Irrigation, Sewage
Sewage	44 (16-79)	Spring, Shallow Ground Water, Tap Water, Irrigation
Septic Discharge	21 (15-47)	Spring, Shallow Ground Water, Tap Water, Irrigation, Sewage
Carwash	27 (16-49)	Spring, Shallow Ground Water, Irrigation, Sewage
Laundry	25 (17-71)	Shallow Ground Water, Tap Water, Irrigation, Sewage
* Note: Significant means a median contribution of 10% or greater, or any sample with 20% or greater contribution.		

The ultimate test of this methodology is its ability to predict the fraction of each source in flow at an outfall. Model results were compared with the confirmed sources for various outfall samples (Table 8). The model generally predicted that the source flows are at least a portion of the flow, but often mischaracterized the major sources (Table 8). One problem researchers encountered was that some source flows were not exactly the same chemically as those initially tested. For example, the laundry detergent at outfall 31 was of a different type than that characterized at the beginning of the study.

Research to date concluded that this method can possibly be improved by weighting variables, specifying more parameters, or linking variables with high correlation coefficients. One potential problem with using this program in municipalities, however, is that specific sources cannot be accurately characterized unless adequate data are available to initially characterize them.

TABLE 8. TESTING OF THE MODEL ON ACTUAL OUTFALL SAMPLES (PITT, 2001)

Outfall Number	Predicted Flow Source	Confirmed Flow Source
14	88% Spring (7% Sewage) (5% Tap)	100% Spring
20	60% Tap 32% Spring (8% Irrigation)	67% Tap 33% Spring
21	55% Sewage 35% Ground (8% Car Wash) (2% Laundry)	100% Washwater (Automotive)
26	74% Spring Water 18% Tap Water (8%Sewage)	100% Spring Water
28	46% Ground Water 21% Irrigation Water 18% Sewage 10% Spring Water (5%Tap Water)	100% Wash Water (Restaurant)
31	55% Sewage 25% Spring Water 18% Laundry (1% Carwash Water)	100% Laundry (Motel)
40z	27% Sewage 23% Tap Water 19% Ground Water 12% Spring Water 11% Septic Tank Discharge (8% Irrigation Water)	Shallow Ground Water and Septic Tank Discharge
42	63% Spring Water 28% Tap Water (9% Sewage)	100% Spring Water
48	79% Sewage 15% Spring Water (5% Carwash Water) (1% Septage)	50% Sewage 50% Spring Water
60a	56% Tap Water 37% Irrigation Water (7% Sewage)	100% Irrigation Water

SECTION 3. SPECIAL CONSIDERATIONS FOR INDUSTRIAL WATERSHEDS

Industrial land watersheds differ significantly from those dominated by residential and commercial uses. From an inappropriate discharge standpoint, it is often much more complicated to identify industrial sources with outfall screening techniques. This challenge results because industrial areas can have a wide variety of constituents depending on industries present. Additionally, inappropriate industrial discharges are often sporadic, making them even more elusive and challenging to detect. Consequently, there is no simple flowchart to identify inappropriate discharges from industrial land uses. One potential outfall screening technique is the use of toxicity testing to prioritize industrial outfalls. Identifying a particular industrial source, however, often relies on monitoring for specific metals or other tracers, or a combination of physical parameters.

The characteristics outlined in Table 9 can sometimes be used to narrow the range of possibilities of potential industrial dischargers, based on a combination of indicators observed at an outfall. This technique becomes complicated, however, when a wide range of industrial uses are often present within a given drainage area.

At the same time, the risk of discharge from industrial land uses is significantly higher than for residential users. This is particularly true for certain industries. For example one study found that 10% of all automobile industries had inappropriate discharges (Johnson, 1998).

Consequently, programs that have focused on industrial discharges often go “straight to the source”, and prioritize investigations solely based on the land use type. One example is the Rouge River program in Wayne County, Michigan. The program was initially established to address inappropriate discharges from industries, and did not address residential land uses. Outfall monitoring was not a major component of their program. Rather, site visits and dye testing, combined with mapping prioritization described in Section 1, have been key to identifying and removing these industrial discharges (Tuomari, 1996).

TABLE 9. CHEMICAL AND PHYSICAL PROPERTIES OF INDUSTRIAL NON-STORMWATER DISCHARGES (PITT, 2001)

Industrial Categories Major Classifications SIC Group Numbers	Odor	Color	Turbidity	Floatables	Debris and Stains	Structural Damage	Vegetation	pH	Total dissolved solids
Primary Industries 20 Food and Kindred Products									
201 Meat Products	Spoiled Meats, Rotten Eggs and Flesh	Brown to Reddish-Brown	High	Animal Fats, Byproducts, Pieces of Processed Meats	Brown to Black	High	Flourish	Normal	High
202 Dairy Products	Spoiled Milk, Rancid Butter	Grey to White	High	Animal Fats, Spoiled Milk Products	Grey to Light Brown	High	Flourish	Acidic	High
203 Canned and Preserved Fruits and Vegetables	Decaying Products Compost Pile	Various	High	Vegetable Waxes, Seeds, Skins, Cores, Leaves	Brown	Low	Normal	Wide Range	High
204 Grain Mill Products	Slightly Sweet & Musty, Grainy	Brown to Reddish Brown	High	Grain Hulls and Skins, Straw & Plant Fragments	Light Brown	Low	Normal	Normal	High
205 Bakery Products	Sweet and or Spoiled	Brown to Black	High	Cooking Oils, Lard, Flour, Sugar	Grey to Light Brown	Low	Normal	Normal	High
206 Sugar and Confectionary Products	NA	NA	Low	Low Potential	White Crystals	Low	Normal	Normal	High
207 Fats and Oils	Spoiled Meats, Lard or Grease	Brown to Black	High	Animal Fats, Lard	Grey to Light Brown	Low	Normal	Normal	High
208 Beverages	Flat Soda, Beer or Wine, Alcohol, Yeast	Various	Mod.	Grains 6 Hops, Broken Glass, Discarded Canning Items	Light Brown	High	Inhibited	Wide Range	High
21 Tobacco Manufactures	Dried Tobacco, Cigars, Cigarettes	Brown to Black	Low	Tobacco Stems& Leaves, Papers and Fillers	Brown	Low	Normal	Normal	Low
22 Textile Mill Products	Wet Burlap, Bleach, Soap, Detergents	Various	High	Fibers, Oils, Grease	Grey to Black	Low	Inhibited	Basic	High
23 Apparel and Other Finished Products	NA	Various	Low	Some Fabric Particles	NA	Low	Normal	Normal	Low

TABLE 9. CHEMICAL AND PHYSICAL PROPERTIES OF INDUSTRIAL NON-STORMWATER DISCHARGES (CONTINUED)

Industrial Categories Major Classifications SIC Group Numbers	Odor	Color	Turbidity	Floatables	Debris and Stains	Structural Damage	Vegetation	pH	Total dissolved solids
Material Manufacture									
24 Lumber & Wood Products	NA	NA	Low	Some Sawdust	Light Brown	Low	Normal	Normal	Low
25 Furniture & Fixtures	Various	Various	Low	Some Sawdust, Solvents	Light Brown	Low	Normal	Normal	Low
26 Paper & Allied Products	Bleach, Various Chemicals	Various	Mod.	Sawdust, Pulp Paper, Waxes, Oils	Light Brown	Low	Normal	Wide Range	Low
27 Printing, Publishing, and Allied Industries	Ink, Solvents	Brown to Black	Mod.	Paper Dust, Solvents	Grey to Light Brown	Low	Inhibited	Normal	High
31 Leather & Leather Products	Leather, Bleach, Rotten Eggs or Flesh	Various	High	Animal Flesh & Hair, Oils, Grease	Grey to Black, Salt Crystals	High	Highly Inhibited	Wide Range	High
33 Primary Metal Industries	Various	Brown to Black	Mod.	Ore, Coke, Limestone, Millscale, Oils	Grey to Black	High	Inhibited	Acidic	High
34 Fabricated Metal Products	Detergents, Rotten Eggs	Brown to Black	High	Dirt, Grease, Oils, Sand, Clay Dust	Grey to Black	Low	Inhibited	Wide Range	High
32 Stone, Clay, Glass, and Concrete Products	Wet Clay, Mud, Detergents	Brown to Reddish-Brown	Mod.	Glass Particles Dust from Clay or Stone	Grey to Light Brown	Low	Normal	Basic	Low
Chemical Manufacture									
28 Chemicals & Allied Products									
2812 Alkalies and Chlorine	Strong Halogen or Chlorine, Pungent, Burning	Alkalies - NA Chlorine - Yellow to Green	Low	NA	Alkalies – White Carbonate Scale Chlorine - NA	High	Highly Inhibited	Basic	High
2816 Inorganic Pigments	NA	Various	High	Low Potential	Various	Low	Highly Inhibited	Wide Range	High
282 Plastic Materials and Synthetics	Pungent, Fishy	Various	High	Plastic Fragments, Pieces of Synthetic Products	Various	Low	Inhibited	Wide Range	High

TABLE 9. CHEMICAL AND PHYSICAL PROPERTIES OF INDUSTRIAL NON-STORMWATER DISCHARGES (CONTINUED)

Industrial Categories Major Classifications SIC Group Numbers	Odor	Color	Turbidity	Floatables	Debris and Stains	Structural Damage	Vegetation	pH	Total dissolved solids
Chemical Manufacture (continued)									
283 Drugs	NA	Various	High	Gelatin Byproducts for Capsulating Drugs	Various	Low	Highly Inhibited	Normal	High
284 Soap, Detergents & Cleaning Preparations	Sweet or Flowery	Various	High	Oils, Grease	Grey to Black	Low	Inhibited	Basic	High
285 Paints, Varnishes, Lacquers, Enamels and Allied Products (SB - Solvent Base)	Latex - Ammonia SB - Dependent Upon Solvent (Paint Thinner, Mineral Spirits)	Various	High	Latex - NA SB - All Solvents	Grey to Black	Low	Inhibited	Latex- Basic SB - Normal	High
286 Indust. Organic Chemicals									
2861 Gum and Wood Chemicals	Pine Spirits	Brown to Black	High	Rosins and Pine Tars	Grey to Black	Low	Inhibited	Acidic	High
2865 Cyclic Crudes, & Cyclic Intermediates Dyes, & Organic Pigments	Sweet Organic Smell	NA	Low	Translucent Sheen	NA	Low	Highly Inhibited	Normal	Low
287 Agricultural Chemicals									
2873 Nitrogenous Fertilizers	NA	NA	Low	NA	White Crystalline Powder	High	Inhibited	Acidic	High
2874 Phosphatic Fertilizers	Pungent Sweet	Milky White High		NA	White Amorphous Powder	High	Inhibited	Acidic	High
2875 Fertilizers, Mixing Only	Various	Brown to Black	High	Pelletized Fertilizers	Brown Amorphous Powder	Low	Normal	Normal	High
29 Petroleux Refining and Related Industries									
291 Petroleum Refining	Rotten Eggs, Kerosene, Gasoline	Brown to Black	High	Any Crude or Processed Fuel	Black Salt Crystals	Low	Inhibited	Wide Range	High
30 Rubber & Miscellaneous Plastic Products	Rotten Eggs, Chlorine, Peroxide	Brown to Black	Mod.	Shredded Rubber Pieces of Fabric or Metal	Grey to Black	Low	Inhibited	Wide Range	High

TABLE 9. CHEMICAL AND PHYSICAL PROPERTIES OF INDUSTRIAL NON-STORMWATER DISCHARGES (CONTINUED)

Industrial Categories Major Classifications SIC Group Numbers	Odor	Color	Turbidity	Floatables	Debris and Stains	Structural Damage	Vegetation	pH	Total dissolved solids
Transportation & Construction									
15 Building Construction	Various	Brown to Black	High	Oils, Grease, Fuels	Grey to Black	Low	Normal	Normal	High
16 Heavy Construction	Various	Brown to Black	High	Oils, Grease, Fuels, Diluted Asphalt or Cement	Grey to Black	Low	Normal	Normal	High
Retail									
52 Building Materials, Hardware, Garden Supply, and Mobil Home Dealers	NA	Brown to Black	Low	Some Seeds, Plant Parts, Dirt, Sawdust, or Oil	Light Brown	Low	Normal	Normal	Low
53 Gen. Merchandise Stores	NA	NA	NA	NA	NA	Low	Normal	Normal	Low
54 Food Stores	Spoiled Produce, Rancid, Sour	Various	Low	Fragments of Food, Decaying Produce	Light Brown	Low	Flourish	Normal	Low
55 Automotive Dealers & Gasoline Service Stations	Oil or Gasoline	Brown to Black	Mod.	Oil or Gasoline	Brown	Low	Inhibited	Normal	Low
56 Apparel & Accessory Stores	NA	NA	Low	NA	NA	Low	Normal	Normal	Low
57 Home Furniture, Furnishings, & Equip. Stores	NA	NA	Low	NA	NA	Low	Normal	Normal	Low
58 Eating & Drinking Places	Spoiled Foods Oil & Grease	Brown to Black	Low	Spoiled or Leftover Foods	Brown	Low	Normal	Normal	Low
Coal Steam Electric Power	NA	Brown to Black	High	Coal Dust	Black Amorphous Powder	Low	Normal	Slightly Acidic	Low
Nuclear Steam Electric Power	NA	Light Brown Low		Oils, Lubricants	Light Brown	Low	Normal	Normal	Low

SECTION 4. HOMING IN ON THE PROBLEM

Once an outfall has been identified as potentially having an inappropriate discharge, a more detailed investigation is needed to pinpoint the source of the discharge. Six techniques have been identified to date, and include:

- Divide the sewer trunk
- Segregate with a tracer
- Move down the system
- TV surveys
- Aerial/Infrared photography
- Smoke and dye testing

Divide the Sewer Trunk

In this technique, based on the process of elimination, the sewer trunk is divided into equal segments by length, such as in tenths. The manhole nearest the downstream end of each segment is then monitored for flow and contamination. A field crew tests each manhole in a downstream direction until contamination is found. It is assumed that all segments upstream of the contaminated one do not contribute to inappropriate discharges. Investigations are then conducted at branches off the trunk sewer. The branches can be divided into roughly three segments, and the same process of elimination is continued in each branch until the source is confirmed.

Segregate with a tracer

In this technique, the main sewer trunk is sampled first at an upstream location, the midpoint along its length, and outfall. The mass flow rate of a parameter (often ammonia) is tested at each location. When the mass flows are equal between two points, it is assumed that the discharge does not enter the system between them. When a change is detected between two points, their midpoint is monitored to further isolate where the change occurs, and so on. Once potential branches have been isolated, similar investigations continue up suspect branches until potential sources are identified and smoke or dye tests can be conducted.

Move down the system

An innovative technique was used in the Stony Brook Conduit in Boston, Massachusetts (Jewell, 2001). In this watershed, a large number of inappropriate discharges were anticipated. Investigators started in the headwater branches of the sewer system, and move downstream to the first “juncture manhole” or manhole receiving flow from two or more storm drainpipes. This manhole is then investigated for flow or evidence of contamination.

If dry weather flow is observed, it is tested for ammonia and surfactants. If this test is positive, upstream segments are investigated. If it is negative, the investigation continues downstream to the next juncture manhole. If dry weather flow is not present, the manhole is inspected for obvious signs of contamination. If no signs of contamination exist at the juncture manhole or in upstream branches, then sand bags are placed at the juncture to capture any intermittent flows.

When contamination is observed at a juncture manhole, sandbags are placed at each branch leading to the juncture to determine which branch, if not both, is contaminated. The contaminated branch is then investigated more thoroughly. Manholes are inspected progressively in an upstream direction until no contamination is observed. Potential sources between the juncture manhole and the “clean” manhole are then dye tested.

Once the dye testing reveals an inappropriate connection, downstream investigations are discontinued until the problem is corrected. Sandbagging below this point is used to confirm that the corrective action did in fact remove the problem connection(s) above the juncture manhole. At this point, investigations continue downstream.

Aerial and Aerial Infrared Photography

Aerial photographs can also be used to identify continuous discharges to surface drainages, such as sump discharges, and to identify storage areas that may be contributing significant amounts of pollutants during rains. Key parameters to identify septic systems from aerial photograh review include wet spots on lawns or excessive vegetation. Reviewing aerial infrared photographs can be useful in identifying areas having failing septic systems. For example, the Tennessee Valley Authority (TVA), among other agencies, has extensively used aerial photography (stereo color infrared) to identify pollution sources, especially from failing septic tanks (Perchalski and Higgins, 1988) by observing color coded areas according to heat presence associated with discharges to the land surface or to surface waters.

TV Testing

Following techniques used to isolate specific sewer branches or in areas suspected of contamination, TV testing can be used to visually inspect lengths of storm drain for evidence of connections. In TV testing, a crew sends a robotic camera and light source through a pipe while viewing images returned to a closed circuit monitor. By viewing the monitor operators can visually inspect the system to identify locations of connections or changes in flow or color of discharge. This technique is particularly valuable in small diameter pipes (8” diameter or larger) or confinements otherwise inaccessible to people.

Smoke and Dye Testing

Smoke or dye testing is conducted once a relatively small area of high potential for inappropriate discharges is isolated. Dye testing involves placing dye in plumbing fixtures (e.g., toilets, sinks, floor drains) of suspected dischargers and tracing the dye through both the sanitary sewer and storm drain. Tracing the dye can help to determine whether the fixture is attached to the sanitary sewer or the storm drain. Smoke testing involves pumping smoke upstream through a cordoned off section of the storm drain system. Inappropriate connections are confirmed when smoke rises through the connection (e.g., comes up through a floor drain). Dye testing is practiced more frequently than smoke testing, although both methods demonstrate success in locating inappropriate connections.

Jewell (2001) identified some key considerations for dye testing as follows: A household may have a single appliance connected to the storm drain, implying that investigators should confirm that every appliance connects to a single drain, or conduct more than one dye test at the household, and, dye appearing in both the sanitary and storm drains as a result of dye testing may be the result of a broken sanitary sewer leaking into the storm drain.

SECTION 5. EXPERIMENTAL TECHNOLOGIES

Several indicators in addition to those profiled above have been used to detect inappropriate discharges into the storm drain system. Examples of some of these options are presented in Table 10 below. With the exception of tracers specifically targeting detergents, most of these options are experimental, and best used in specific applications.

TABLE 10. COMPARISON OF MEASUREMENT PARAMETERS USED FOR IDENTIFYING INAPPROPRIATE DISCHARGES INTO STORM DRAINAGE (PITT, 2001)

Parameter Group	Comments	Recommendation
Fecal coliform bacteria a/o fecal coliform:fecal strep ratio	Indicator of presence of sanitary sewage.	Not very useful as many other sources of fecal coliforms are present, and ratio not accurate for old or mixed wastes.
Coprostanol and other fecal sterol compounds	Indicator of presence of sanitary sewage.	Possibly useful. Expensive analysis. Not specific to human wastes or recent contamination. Most useful when analyzing particulate fractions of wastewaters or sediments.
Specific detergent compounds (fabric whiteners/perfumes)	Indicator of presence of sanitary sewage.	Possibly useful. Expensive analyses with HPLC. A good and sensitive confirmatory method.
Boron	Indicator of presence of sanitary sewage and wash waters.	Not very useful. Easy and inexpensive analysis, but recent laundry formulations in US have minimal boron components.
Pharmaceuticals (colfibric acid, aspirin, steroids, etc.)	Indicator of presence of sanitary sewage.	Possibly useful. Expensive analyses. A good and sensitive confirmatory method.
Caffeine	Indicator of presence of sanitary sewage.	Not very useful. Expensive analyses. Numerous false negatives.
DNA profiling of microorganisms	Identifies sources of microorganisms	Likely useful, but currently requires extensive background information on likely sources. Could be useful if method can be simplified.
UV absorbance at 228 nm	Identifies 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 investigation of sensitivity in field trials req'd.
Stable isotopes of oxygen	Identifies 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.
E. coli and enterococci bacteria	Indicator of sanitary sewage than coliform tests.	Recommended in conjunction with chemical tests. Relatively inexpensive and easy analyses.

SECTION 6. PRIMARY CONCLUSIONS AND FUTURE INVESTIGATIONS

Pitt's (2001) research to date, combined with initial data collected in the Phase I survey conducted under this grant, has resulted in a few major conclusions that can help "point the way" for this project, both in terms of initial recommendations and areas of focus for project research. Key conclusions include:

- Scanning only major (36" or greater diameter) outfalls may miss the most serious contamination. Field screening should include all outfalls.
- Detergents are a key parameter for identifying sanitary sources, but most methodologies are time consuming, expensive, or dangerous. Innovative and simple ways to detect detergents are a key area of future research.
- GIS are a useful tool to prioritize outfall screening and manage data. Community visits conducted under this grant will explore the variety of ways that communities use GIS in inappropriate discharge detection programs.
- The original techniques developed by Pitt and Lalor (1993) are still excellent tools for identifying inappropriate discharges in commercial and residential watersheds, and will most likely be used as a framework for recommended field screening techniques in products from this grant.
- Detection of inappropriate discharges in predominantly industrial land use watersheds require a different set of parameters than in residential and commercial land use watersheds, and rely heavily on physical observations.
- Communities use different techniques to prioritize outfalls for screening. This will be an area of focus for community visits. Typically, the customized techniques used by communities involve a combination of physical location, visual screening and chemical tracer analyses.
- New technologies are constantly emerging for inappropriate discharge detection applications. Research will focus on testing some of these techniques in the field and continuing to gather information on simple field techniques currently in use by communities.

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APPENDIX A. TESTING PROCEDURES FROM PITT (2001)

Evaluation of Analytical Methods

Analytical methods for the parameters used in this research were selected from a group of methods which had been initially identified with expense, portability and ease of use in mind. Interferences, detection limits, and accuracy (precision and bias) influenced the final selection. The following procedures were used in this selection process.

Initially, dry-weather flows were sampled at 12 locations from a grass swale drainage system serving a residential area containing septic tanks. Samples were obtained during an excessively dry summer period. Each of these 12 samples was analyzed using the entire group of representative methods which had been identified for each of the tracer parameters of interest. Analytical methods tested using these 12 samples are listed in Table A-1.

In addition, four representative samples from this area were further examined using standard addition methods (known amounts of standards were added to each sample, and results were then compared to unaltered samples), to identify matrix interference problems. Analysis methods were also tested against a series of standard solutions to identify detection limits and repeatability. A discussion of analytical methods considered and selected follows.

Results of Comparison Tests of Analytical Procedures

Conductivity--

Conductivity is quickly and easily measured in the field using a dual dedicated (temperature/conductivity) meter. A YSI conductivity meter, model 33, was used. Both specific conductivity and temperature must be calibrated against standard specific conductivity solutions and a standard thermometer. Specific conductivity should also be corrected to standard values obtained at 25°C (APHA, *et al.* 1989):

$$K= (K_mC)/[1+0.0191(t-25)]$$

where K = specific conductivity at 25°C
K_m = measured specific conductivity at temperature t^oC
and C = cell constant

The cell constant is a correction factor determined by measuring a 0.01M KCl solution at 25°C, after three rinses, compared to 1413 μS/cm, the expected value. This equation results in about a 2% change in specific conductivity for every degree in temperature difference from 25°C. The SI specific conductivity unit of measurement is the μS/cm which is numerically equivalent to the U.S. Customary unit, μmhos/cm.

Fluoride--

An ion selective electrode (ISE) with millivolt meter and a spectrophotometric method (utilizing the SPADNS method without distillation) were tested. Fluorides are easily detected using a field spectrophotometer (HACH DR/2000) and evacuated reagent and sample vessels (AccuVac). The AccuVac procedure works well for samples with concentrations of less than 2.5 mg/L fluoride. Higher concentrations of fluoride require sample dilution because of non-linear responses. Standard addition tests showed error levels at or below

5%. Multiple measurements of fluoride standards resulted in a standard deviation of 0.02 mg/L (coefficient of variation 0.02). Resolution (the level of detail, or significant figures achievable) for this method was 0.01 mg/L.

Ion selective electrode (ISE) membranes fouled quickly in wastewater and had to be changed often (after 5 to 10 samples). Again, error levels were at, or below, 5%. However, use of the spectrophotometer was chosen due to the inconvenience and cost of frequent membrane replacement with the ISE method.

TABLE A-1: ANALYTICAL PROCEDURES INVESTIGATED

Parameter	Analysis Method
Conductivity & Temperature	YSI Conductivity Meter (Model 33)
Fluoride	HACH Ion Specific Electrode (ISE) HACH DR/2000 Spectrophotometer (AccuVac: SPADNS Method)
Hardness	HACH DR/2000 Spectrophotometer (Calmagite Method) HACH Field Titration Kit (EDTA Titration) Quant Test Strips
Detergents	HACH Detergent Test Kit (MBAS Colorimetric) Orion Surfactants Kit (ISE)
Fluorescence	Turner Filter Fluorometer (Model 111)
Potassium	HACH DR/2000 Spectrophotometer (Tetraphenylborate Method) HACH ISE Flame Atomic Absorption
Ammonia	HACH DR/20000 Spectrophotometer (Nessler Method - direct) HACH ISE Quant Test Strips Hanna Field Test Kit Chemet Field Test Kit
Color	HACH Color Kit
Toxicity	Microtox™ (Microbics, Inc.)
pH	Fisher Accument Model 610A Test Strips
Total Chlorine	HACH DR/2000 Spectrophotometer (AccuVac: DPD Method) HACH Titration Quant Test Strips
Total Copper	HACH DR/2000 Spectrophotometer (AccuVac: Bicinchonianate Method) Quant Test Strips Chemet Field Test Kit
Total Phenols	HACH Colorimetric Method

Hardness--
A digital titration kit, test strips, and a spectrophotometric method were tested. The HACH digital titration kit has a suitable range, was easy to use, and standard addition techniques revealed errors of less than 2.5%. A standard deviation of 0.02 mg/L (coefficient of variation 0.0002) as $CaCO_3$ was obtained, and the resolution of this method was 1 mg/L. The range for the spectrophotometric technique proved to be much too low for the samples being studied. Test strips identified hardness within a relatively wide range only, and were therefore not specific enough for this application. However, the hardness test paper can be used to estimate the titration end point. The HACH digital titration kit was selected for use.

Detergents--
A comparative colorimetric method and titration in combination with an ion selective electrode (ISE) were tested. Although sample dilution was sometimes necessary, the HACH comparative color detergent test kit proved much easier to use and was more sensitive than the ion selective surfactant electrode, which required prior knowledge of the expected sample range in order to select an appropriate concentration of titrant. The comparative colorimetric procedure must be carried out under a laboratory fume hood. Tests on standards revealed a standard deviation of 0.02 mg/L (coefficient of variation 0.03) MBAS using the comparative colorimetric method. The resolution of this method was 0.01 mg/L.

Fluorescence--
A Turner Filter Fluorometer (Model 111) was used to measure relative fluorescence. The repeatability was determined to be ± 2% of full scale (3.5 ppb as Rhodamine WT). General purpose filters (#546 primary filter and #590 secondary filter) and lamp (G4T4/1) were used to be most sensitive to detergent fluorescence, and dilutions of Intracid Rhodamine WT liquid (Compton and Knowles, Reading, PA) were tested as a reference. For the smallest aperture (slit 1x, the least sensitive position), the following equation relating % scale and ppb Rhodamine WT dye (standard 20% stock solution) was found:

$$\text{ppb Rhodamine WT} = 0.975 + 1.271\ (\text{percent scale reading})$$

Potassium--
Ion selective electrode, spectrophotometric, and flame atomic absorption methods were tested. During standard addition tests, the HACH tetraphenylborate spectrophotometric method yielded errors at or below 8% and was quite easy to use. A standard deviation of 0.13 mg/L K (coefficient of variation 0.03) was obtained. The resolution for this method was 0.01 mg/L. Flame atomic absorption resulted in smaller errors, but is a more costly technique. A specific-ion probe was also evaluated, but was not chosen because of rapid membrane fouling, long analysis times and inconsistent results. Error levels with standard additions were as high as 50% using the ion probe method.

Ammonia--
Ion specific electrode, spectrophotometric, and test strip methods were evaluated. Ammonia can be easily measured in the laboratory using a direct Nesslerization procedure and a spectrophotometer (HACH DR/2000). The standard deviation for this method was found to be 0.038 mg/L ammonia, and the resolution was 0.01 mg/L.

Errors and standard deviation were unacceptably high using a simpler salicylate spectrophotometric technique. The use of various indicator test papers for ammonia determination gave poor results and had insufficient resolution. As before, specific ion probe membranes fouled quickly in wastewater and gave inconsistent results. Typical problems encountered for other ammonia field test kit procedures, except for the direct Nesslerization procedure, were color interferences, long analysis times, inconsistent results, and poor performance when standard solutions were analyzed.

pH--

An accurately calibrated pH meter was used to measure pH on fresh samples in the laboratory. Measurements using pH test paper were found to be within one unit of the laboratory meter, but this difference was too large. The resolution and standard deviation of the Fisher Accumet Model 610A pH meter used was 0.01 pH unit.

Small "pen" pH meters most suitable for field use can easily be off by a 0.5 pH unit and are relatively hard to calibrate. They accordingly must be used with care.

Total Chlorine--

Titration (utilizing a digital titrator), a spectrophotometric method and test strip methods were evaluated. The DPD spectrophotometric method (HACH DR/2000 and AccuVac) proved to be the method of choice. The resolution was 0.01 mg/L using this method, and the standard deviation was found to be 0.02 mg/L (coefficient of variation was 0.05). Digital titration with phenylarsine oxide only provided 1 mg/L resolution, which is insufficient for this application. Test strips also had insufficient resolution.

Total Copper--

Test strip and spectrophotometric methods were tested. The bicinchoninate spectrophotometric method (HACH DR/2000 with AccuVac) provided a resolution of 0.01 mg/L copper, with a standard deviation of 0.009 mg/L (coefficient of variation 0.009). The resolution and detection limits provided by test strips were not sufficient.

Total Phenols--

A new direct colorimetric technique developed by HACH specifically for stormwater testing was used to measure total phenols. This technique is based on the 4-aminoantipyrine method and has a range of 0 to 5 mg/L phenol with a resolution of 0.1 mg/L. Repeatability was found to be within 0.2 mg/L.

Color--

Color was quantified using a simple colorimetric comparator with a resolution of 1 unit (HACH). The apparent color is measured in APHA Platinum Cobalt Units.

Toxicity--

The Microtox™ (Microbics, Inc.) screening test was evaluated for use as an indicator of relative baseflow toxicity. Microtox is relatively easy and inexpensive, as bioassays go, and it was hoped that this test might be an efficient indicator of general outfall contamination, identifying outfalls requiring further investigation, and eliminating the need for other tests.

The Microtox procedure utilizes a luminescent marine bacteria, *Photobacterium phosphoreum*. The living microorganisms emit light as a product of their metabolic processes. Any change in those processes, caused by exposure to a toxic test sample, causes a decrease in light output. Reduction of the light is proportional to the toxicity of the sample. Toxicity values reported in this research reflect the percent reduction in light emitted by the test organisms in a sample matrix, as compared to a control organism mixture, after 25 minutes of exposure (I25).

The Microtox Analyzer is a temperature-controlled photometer that brings test organisms and samples to standard temperatures, and measures the light output of the microorganisms under controlled test conditions. Test results demonstrate an average coefficient of variation of 0.16. Good repeatability (precision) and good sensitivity allows small changes in toxicity to be noted.

Toxicity screening tests have been found to be very useful as indicators of contamination of storm drains. The Microtox™ (from Microbics) toxicity screening test can be used for relative toxicity values. The 100 percent screening test was most commonly used. If the light output decrease after 25 minutes (the I_{25} value) was greater than 50 percent, then the standard Microtox test was used to determine the sample dilution required for a 50 percent light decrease (the EC50 value). If a sample results in a large toxic response, then specific toxicant analyses (organics and metals) could be performed to better identify the toxicant source. In general, the Microtox™ screening test was found to be an efficient method for toxicity analysis, particularly for identifying samples requiring further analyses. (A number of simple test kits were used for specific heavy metal analyses, but with very poor results. High-detection limits and interferences make these methods impractical, unless an outfall is grossly contaminated with a concentrated source, such as raw plating bath wastewater.)

Results of Dilution Studies

After suitable analytical methods were identified, mixtures of some potential contaminating flow sources and local spring waters were prepared and analyzed in order to determine functional limitations of procedures when trying to identify small levels of contamination. Mixtures of sanitary sewage, septage, and plating bath waters with spring water were prepared in the following percentages: 0, 0.1, 1, 5, 10, 25, 50, 75, 90, 99, 99.9, and 100. These wastewaters were chosen because they were readily available and were thought to represent extremes, in terms of pathogenicity and toxicity, of wastewaters likely to be encountered in dry-weather flow. One liter of each mixture was prepared.

Results from the sewage dilution study are presented in Table A-2. The sewage sample used for this test was collected from influent to Jefferson County's Cahaba Wastewater Treatment Plant in Birmingham, Alabama. No chlorine, copper or phenols were detected in the sewage sample or spring water. Prior to measuring fluorescence, samples were filtered through a washed 0.45 μm glass fiber filter. This was necessary in order to achieve a stable reading on the fluorometer. With the exception of color, errors for all parameters, ((measured - expected)/expected) x 100), were less than, or equal to, 10% for dilutions containing 5% or more sewage. Errors observed in color measurements were high. The spring water had no color, and small additions of sewage (with a color of 30 units) resulted in color changes too small to be discerned by the human eye. The resolution of the manual color wheel used was 1 unit. Working with such relatively colorless samples, even half unit discrepancies between observed and expected values resulted in large errors. Expected values were calculated based on anticipated linearity. Toxicity and pH measurements will not be linear, and the dilution tests results confirmed the absence of linearity.

Table A-3 presents results from the septage dilution study. Septage, rather than septic tank discharge, was chosen for this portion of the study because it was much more easily accessible. The septage used was obtained from a residential septage tank cleaning truck. The septage was pre-filtered through a quarter-inch stainless steel sieve, followed by an eighth-inch sieve. Final filtration was through 1.5 feet of coarse sand supported by 3 inches of river rock on a quarter-inch sieve in order to simulate septic tank effluent after partially traveling through a leaching field. Before fluoride, fluorescence, detergent or hardness measurements were taken, samples were filtered through a washed 0.45 μm glass fiber filter in order to minimize color interference. With the exception of color and fluorescence, errors for all parameters were less than 8% for samples containing at least 5% septage. At 5% septage, the fluorescence value measured differed from the expected value by 12%. Color values exhibited errors of less than 8%, with the exception of samples containing 0.1% and 99% septage. Septage is much more highly colored than sewage, with a value of about 1000 color units at full strength. Therefore, even small additions of septage to spring water resulted in color additions which were discernible. Once again, toxicity and pH data confirmed their lack of linearity.

Results from the dilution study using metal plating bath wastes are presented in Table A-4. Plating bath wastewater was obtained from a local metal plating company, and samples were filtered through a washed 0.45 μm glass fiber filter before fluoride, fluorescence, detergent and hardness measurements were taken. With the exception of fluorescence, errors observed in all samples containing at least 5% plating wastes were below 8%. An error of 9% was noted between expected and observed fluorescence values for the 10% plating waste mixture. Toxicity and pH values were again observed to be non-linear on dilution.

These results indicate that, with the exception of color and fluorescence, measurements made using the analytical methods selected should be accurate to within 10%, even if inappropriate flows comprise as little as 5% of the total outfall flow. In addition, with the exception of toxicity and pH, the dilutions affected the measurements in a linear manner over the complete concentration ranges.

TABLE A-2. RESULTS FROM SEWAGE DILUTION STUDY

	% Sewage in Spring Water											
Parameter	0.0	0.1	1.0	5.0	10.0	25.0	50.0	75.0	90.0	99.0	99.9	100.0
Conductivity (μS/cm)												
expected	350	350.12	350.20	356	362	380	410	440	458	468.8	469.88	470
observed	350	.50	350	351	355	371	400	435	451	470	470	470
% error	0	0.03	0.06	1.40	1.93	2.11	2.44	1.14	1.53	0.26	2.03	0
Fluoride (mg/L)												
expected	0.06	0.06	0.07	0.10	0.14	0.27	0.48	0.69	0.82	0.89	0.90	0.90
observed	0.06	0.07	0.09	0.11	0.14	0.28	0.47	0.65	0.78	0.85	0.89	0.90
% error	0	-16.67	-28.57	-10.00	0	-3.70	2.08	5.80	4.88	4.67	10.2	0
Hardness (mg/L as $CaCO_3$)	227	226.89	225.94	221.7	216.4	200.5	174	147.5	131.6	122.06	121.11	121
expected	227	232	229	218	217	199	176	148	128	122	121	121
observed	0	-2.25	-1.35	1.66	-0.28	0.75	-1.15	-0.34	2.74	0.05	0.09	0
% error												
Detergent (mg/L)												
expected	0	0.01	0.07	0.33	0.66	1.65	3.3	4.95	5.94	6.54	6.59	6.6
observed	0	0	0.05	0.31	0.62	1.60	3.28	4.68	5.46	6	6.6	6.6
% error	0	100	28.57	6.06	6.06	3.03	6.06	5.45	8.08	8.26	-0.1	0
Fluorescence (% scale)												
expected	7	7.46	11.55	29.75	52.5	120.75	234.5	348.25	416.5	457.45	461.5	462
observed	7	7	10	28	50	114	224	335	390	448	462	462
% error	0	6.17	13.42	5.88	4.76	5.59	4.48	3.80	6.36	2.06	-.11	0

TABLE A-2. (CONTINUED)

	% Sewage in Spring Water											
Parameter	0.0	0.1	1.0	5.0	10.0	25.0	50.0	75.0	90.0	99.0	99.9	100.0
Potassium (mg/L)												
expected	0.72	0.72	0.76	0.93	1.14	1.77	2.82	3.87	4.5	4.88	4.92	4.92
observed	0.72	0.73	0.78	0.95	1.18	1.79	2.85	3.96	4.62	5.02	4.96	4.92
% error	0	-1.39	-2.63	-2.15	-3.5	-1.13	-1.06	-2.33	-2.67	-2.66	-0.81	0
Ammonia (mg/L)												
expected	0.02	0.33	0.15	0.68	1.35	3.34	6.66	9.98	11.97	13.17	13.29	13.3
observed	0.02	0.04	0.13	0.687	1.42	3.52	7.11	10.19	11.67	13.06	13.16	13.3
% error	0	-20.19	14.92	0.58	-5.34	-5.39	-6.76	-2.10	2.5	0.81	0.95	0
Color (units)												
expected	0	0.03	0.3	1.5	3	7.5	15	22.5	27	29.7	29.97	30
observed	0	0	0	3	4	7	13	20	27	30	30	30
% error	0	100	100	-100	-25	6.67	13.33	11.11	0	-1.01	-1.01	0
pH (units)												
expected	7.02	7.02	7.02	7.03	7.04	7.07	7.12	7.17	7.20	7.22	7.22	7.22
observed	7.02	7.08	7.11	7.13	7.15	7.15	7.15	7.15	7.15	7.21	7.20	7.22
% error	0	0.9	1.3	1.4	1.6	1.1	0.4	-0.3	-0.7	-0.2	-0.3	0
Toxicity (% reduction)												
expected	0	0.08	0.82	4.09	8.17	20.43	40.85	61.28	73.53	80.90		81.7
observed	0	0	0	0	2.38	23.80	61.40	77.5	78.50	80.70	NA	81.7
% error	0	-100	-100	-100	-70.87	16.50	50.31	26.49	6.76	-0.25		0

NA: Data not available

TABLE A-3. RESULTS FROM SEPTAGE DILUTION STUDY

	% Septage in Spring Water											
Parameter	0.0	0.1	1.0	5.0	10.0	25.0	50.0	75.0	90.0	99.0	99.9	100.0
Conductivity (µS/cm)												
expected	340	340.58	345.85	369.25	398.5	486.25	632.5	778.75	866.5	919.15	924.42	925
observed	340	342	345	351	390	480	610	740	820	905	924	925
% error	0	-4.2	0.25	4.95	2.13	1.29	3.56	4.98	5.37	1.54	0.05	0
Fluoride (mg/L)												
expected	0.26	0.26	0.26	0.28	0.31	0.38	0.51	0.63	0.70	1.75	0.75	0.75
observed	0.26	0.27	0.27	0.29	0.30	0.36	0.49	0.60	0.69	0.73	0.73	0.75
% error	0	-3.85	-3.85	-3.57	3.23	5.26	3.92	4.76	1.43	2.66	2.66	0
Detergent (mg/L)												
expected	0	0.02	0.24	1.2	2.4	6	12	18	21.6	23.76	23.98	24
observed	0	0	0.25	1.2	2.5	5.80	12.6	18	21	24	24	24
% error	0	100	-4.17	0	-4.17	3.33	-5	0	2.78	-1.01	-0.08	0
Fluorescence (% scale)												
expected	7	8.64	2324	88.20	169.40	413	819	1225	1468.6	1614.76	1629.38	1631
observed	7	7.2	20	77.8	158.6	441.1	768.2	1194	1362.8	1492.6	1529.4	1631
% error	0	16.67	13.94	11.79	6.38	-6.8	6.2	6.61	7.2	7.56	6.14	0

TABLE A-3. (CONTINUED)

	% Septage in Spring Water											
Parameter	0.0	0.1	1.0	5.0	10.0	25.0	50.0	75.0	90.0	99.0	99.9	100.0
Potassium												
(mg/L)												
expected	1.2	1.22	1.39	2.17	2.95	6.03	10.85	15.68	18.57	20.31	20.48	20.5
observed	1.2	1.22	1.36	20.7	2.95	5.55	10.9	16	18.8	20	20.5	20.5
% error	0	0	2.16	4.61	0	7.96	-0.56	2.04	-1.24	1.53	0.10	0
Ammonia												
(mg/L)												
expected	0.08	0.14	0.64	2.90	5.72	14.19	28.30	42.40	50.87	55.95	56.45	56.51
observed	0.08	0.09	0.56	2.71	6	13.45	26.91	39.86	51.68	52.77	54.91	56.51
% error	0	34.03	13.08	6.60	-4.84	5.20	4.89	5.98	-1.60	5.68	2.73	0
Color												
(units)											1039.0	
expected	0	1.04	10.4	52	104	260	520	780	936	1029.6	1040	1040
observed	0	0	10	50	100	270	485	810	885	945	-0.10	1040
% error	0	100	3.85	3.85	3.85	-3.85	6.73	-3.85	5.45	8.22		0
pH												
(units)												
expected	7.30	7.30	7.30	7.31	7.32	7.36	7.42	7.48	7.52	7.54		7.54
observed	7.30	7.33	7.36	7.37	7.36	7.36	7.36	7.37	7.45	7.50	NA	7.54
% error	0	0.4	0.8	0.8	0.5	0	-0.8	-2.0	-0.9	-0.5		0
Toxicity												
(% reduction)												
expected	0	0.08	0.81	4.04	8.08	20.19	40.39	60.58	72.69	79.96	80.69	80.77
observed	0	0	0	0	12.33	36.43	50.03	68.57	72.70	74.13	79.73	80.77
% error	0	-100	-100	-100	52.60	80.43	23.87	13.19	0.01	-7.29	-1.20	0

NA: Data not available

TABLE A-4. RESULTS FROM METAL PLATING BATH DILUTION STUDY

	% Metal Plating Bath Waste in Spring Water											
Parameter	0.0	0.1	1.0	5.0	10.0	25.0	50.0	75.0	90.0	99.0	99.9	100.0
Conductivity (μS/cm)												
expected	320	324.68	364.8	544	768	1440	2560	3680	4352	4755.2	4795.52	4800
observed	320	328	368	525	775	1500	2700	3850	4320	4750	4800	4800
% error	0	-1.08	-0.88	3.69	-0.91	-4.17	-5.47	-4.62	0.74	0.11	-0.09	0
Fluoride (mg/L)												
expected	0.10	0.10	0.12	0.19	0.28	0.54	0.98	1.42	1.68	1.84	1.86	1.86
observed	0.10	0.10	0.13	0.20	0.28	0.55	1.00	1.38	1.66	1.86	1.88	1.86
% error	0	0	-8.33	-5.26	0	-1.85	-2.04	2.81	1.19	-1.09	-1.08	1.86
Hardness (mg/L as $CaCO_3$)												
expected	222	228.56	227.53	249.65	277.3	360.25	498.5	636.75	719.7	769.47	774.95	775
observed	222	228	237	242	263	345	485	625	700	760	769	775
% error	0	-2.44	-4.16	3.06	5.16	4.23	2.71	1.84	2.74	1.23	0.70	0
Detergent (mg/L)												
expected	0	0.01	0.1	0.5	1	2.5	5	7.5	9	9.9	9.99	10
observed	0	0	0.09	0.48	1.06	2.4	4.65	7.6	9.2	9.68	9.79	10
% error	0	100	10.00	4.00	-6.00	4.00	7.00	-1.38	-2.22	2.22	2.00	0
Fluorescence (% scale)												
expected	6	6.10	7.04	11.2	16.4	32	58	84	99.6	108.96	109.90	110
observed	6	6	8	11	15	30	54	79	93	104	108	110
% error	0	1.64	-13.64	1.79	8.53	6.25	6.90	5.9	6.62	4.55	1.73	0

TABLE A-4. (CONTINUED)

	% Metal Plating Bath Waste in Spring Water											
Parameter	0.0	0.1	1.0	5.0	10.0	25.0	50.0	75.0	90.0	99.0	99.9	100.0
Potassium (mg/L)												
expected	1.21	1.66	5.70	23.65	46.09	113.41	225.61	337.80	405.12	445.51	449	450
observed	1.21	1.99	6.32	25	48	117	230	350	420	442	444	450
% error	0	-19.88	-10.88	-5.71	-4.14	-3.17	-1.95	-3.61	-3.67	0.79	1.11	0
Ammonia (mg/L)												
expected	0	0	0.03	0.15	0.31	0.76	1.53	2.29	2.75	3.01	3.05	3.05
observed	0	0	0.02	0.16	0.29	0.74	1.62	2.29	2.75	3.01	3.05	3.05
% error	0	0	33.33	-6.67	6.45	2.63	-5.56	0	0	0	0	0
Color (units)												
expected	0	0.21	2.12	10.6	21.2	53	106	159	190.8	209.88	211.79	212
observed	0	0	3	10	20	55	110	162	194	216	212	212
% error	0	100	-41.5	5.67	5.67	-3.78	-3.78	-1.89	-1.68	-2.92	-0.01	0
pH (units)												
expected	7.90	7.90	7.91	7.93	7.96	8.05	8.20	8.35	8.44	8.49	8.50	8.50
observed	7.90	7.89	7.88	7.87	7.87	7.94	8.18	8.41	8.48	8.50	8.51	8.50
% error	0	-0.13	-0.38	-0.76	-1.13	-1.37	-0.24	0.72	0.47	0.12	0.12	0
Toxicity (% reduction)												
expected	0	0.1	1	5	10	25	50	75	90	99	99	100
observed	0	10.81	40.40	44.60	96.50	100	100	100	100	100	NA	100
% error	0	10710	3940	792	865	300	100	33.33	11.11	1.01		0

Recommended Analytical Methodology

An important part of the development of these investigation procedures and the demonstration project was the laboratory and field testing of the alternative analytical methods, described previously. Dry-weather outfall samples were subjected to different tests which compared several analytical methods for each of the major tracer parameters of interest. Tests were conducted to enable comparison of the results of alternative tests with standard procedures and to identify which methods had suitable detection limits, based on real samples. In addition, representative samples were further examined using standard addition methods (known amounts of standards added to the sample and results compared to unaltered samples) in order to identify matrix interferences. Matrix interferences are generally caused by contaminants in the samples interfering with the analysis of interest. Many of the analysis methods were also tested against a series of standard solutions to identify analytical precision (repeatability), linearity, and detection limits.

Table A-5 lists the analytical methods selected and the lower limit of detection determined for each of these methods. The lower limit of detection is defined in *Standard Methods* as the standard deviation multiplied by 3.29 (APHA 1989).

Most of the recommended analyses are conducted using small “field-type” instruments. However, despite their portability, the use of these instruments in the field can introduce many errors. Temperature and specific conductivity are the only analyses that are recommended for field analyses. For the other analyses, samples are collected at the site, iced, and taken back to the laboratory for analyses. The recommended analysis procedures can be easily conducted in a temporary laboratory; all that is needed is a work space and adequate ventilation. Access to power and water would be helpful, but all of the equipment can be operated with batteries. At each outfall, a 2 L sample of dry-weather discharge needs to be collected and stored in a polyethylene container. Another (500 mL) sample can also be collected in a glass container having a Teflon-lined lid for toxicity screening and selected toxicant analyses. All samples must be analyzed (or extracted) within accepted time limits. Table A-6 is an example of the laboratory analyses reporting sheet for the above analyses.

TABLE A-5. ANALYTICAL PROCEDURES SELECTED

Parameter	Analysis Method	Lower Limit of Detection
Conductivity & Temperature	YSI Conductivity Meter (Model 33)	17 μS/cm
Fluoride	HACH DR/2000 Spectrophotometer (AccuVac: SPADNS Method)	0.07 mg/L
Hardness	HACH Field Titration Kit (EDTA Titration)	0.07 mg/L
Detergents	HACH Detergent Test Kit (MBAS Colorimetric)	0.06 mg/L
Fluorescence	Turner Filter Fluorometer (Model 111)	3% of scale (4 ppb Rhodamine equiv.)
Potassium	HACH DR/2000 Spectrophotometer (Tetraphenylborate Method)	0.4 mg/L
Ammonia	HACH DR/2000 Spectrophotometer (Nessler Method - direct)	0.12 mg/L
Color	HACH Color Kit	3 color units
Toxicity	Microtox™ (Microbics, Inc.)	I_{25} = 0.15 (15% light attenuation after 25 minutes exposure)
pH	Fisher Accumet Model 610A	0.03 units
Total Chlorine	HACH DR/2000 Spectrophotometer (AccuVac: DPD Method)	0.07 mg/L
Total Copper	HACH DR/2000 Spectrophotometer (AccuVac: Bicinchonianate Method)	0.03 mg/L
Total Phenols	HACH Colorimetric Method	0.66 mg/L

NA: Not Applicable

TABLE A-6. SAMPLE ANALYSES LAB SHEET

Sample number: ______________________________

Date: ______________________________

Location: ______________________________

Outfall #: ____________

Specific conductivity YSI™ SCT meter (field) ____________________

Temperature YSI™ SCT meter (field) ____________________

pH pH meter (lab) ____________________

Ammonia Direct Nesslerization (lab) ____________________

Color HACH™ color kit (lab) ____________________

Fluoride HACH DR/2000™ spect. with AccuVacs™ (lab) ____________________

Hardness HACH™ field titration kit (lab) ____________________

Surfactants HACH™ detergent field kit (lab) ____________________

Fluorescence Turner™ fluorometer (lab) ____________________

Potassium HACH DR/2000™ spect. (lab) ____________________

Turbidity HACH™ Nephelometer (lab) ____________________

Chlorine HACH DR/2000™ spect. with AccuVacs™ (lab) ____________________

Toxicity Microtox™ 100% sample screen (lab) ____________________