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Assessment Strategy for Evaluating the Environmental and Health Effects of Sanitary Sewer Overflows from Separate Sewer Systems

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Notice

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Foreword

Today’s rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts and search for solutions.

The National Risk Management Research Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensive engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and user community.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

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Some of the material included in this report is also being simultaneously published in the book: *Manual for Evaluating Stormwater Runoff Effects in Receiving Waters,* by Allen Burton and Robert Pitt, CRC/Lewis Publishers, New York, to be published in 1998. This book was partially supported by an earlier EPA sponsored research project.

Section 1 - Introduction

Assessment Strategy for Evaluating the Environmental and Health Effects of Sanitary Sewer Overflows from Separate Sanitary Sewer Systems

Appendix B contains a general discussion on the statistical basis for sampling. It contains guidance on determining the sampling effort needed, based on specific program objectives. It is foolhardy to assume that sophisticated statistical analysis can salvage data collected with little forethought given to the actual project needs. The basic questions that need to be addressed when designing an investigation to evaluate the environmental and health effects of separate sanitary sewer overflows are as follows:

- what needs to be analyzed and what analytical techniques should be used?
- where and how to sample?
- how many samples are needed?
- how to analyze the data?

Appendix B addresses the last two elements on this list, while Sections 2 through 6 of this report discuss the first two elements.

Obviously, before any monitoring activity is carried out, clearly defined objectives are needed, such as comparing water quality upstream and downstream of a SSO, or calibrating and verifying a receiving water model to predict fates of SSO discharges needed to support an ecological and human risk assessment. As such, many options need to be considered. The main sections of this report, therefore, discuss these options.

There are many excellent references that describe standard protocols for collecting and analyzing water and stream sediment samples. The most recent edition of *Standard Methods for the Examination of Water and Wastewater* needs to be readily available to anyone conducting a water quality investigation. In addition, ASTM (1995) has published a compilation of standards for environmental sampling that should also be consulted.

Note: This report contains numerous listings of vendors, catalogue numbers, and prices for specific sampling equipment. These are given as examples of availability and for preliminary sampling budget purposes. The reader needs to verify availability and current prices (given here as mid-1996, mostly), plus possible alternative sources, and select the most appropriate equipment for the specific purpose and location of their studies.

Section 2 - Risk Assessment of Community SSO Exposure

Risk Assessment

Risk assessment is a broad term, which encompasses both risk characterization and risk management. The distinction between these two terms is an important one. The National Research Council's 1983 report on risk assessment in the federal government distinguished between risk assessment and risk management.

> "Broader uses of the term [risk assessment] than ours also embrace analysis of perceived risks, comparisons of risks associated with different regulatory strategies, and occasionally analysis of the economic and social implications of regulatory decisions functions that we assign to risk management." (U.S. EPA, 1995)

The U.S. EPA has made the additional distinction of separating risk assessment from risk characterization. Risk characterization is the last step in risk assessment, is the starting point for risk managers, and the foundation for regulatory decision making. The risk characterization identifies and highlights the noteworthy risk conclusions and related uncertainties. (U.S. EPA, 1995)

The term risk assessment will be used here to describe the process of the application of scientific principles to study a particular environmental or health risk, and assess, or quantify, the magnitude of risk posed. This process is characterized by obtaining information regarding hazard identification, dose-response, and exposure assessments. The following discussion will describes each of these three steps using waterborne pathogens in SSO discharges as and example.

Hazard Identification

The first step, hazard identification, can be examined by gathering information regarding waterborne disease outbreaks. The agent that causes disease could be chemical, physical, or biological. However, in this case we will focus on biological causes, or infectious agents, i.e., pathogenic microorganisms. Table 2.1 shows the agents that have caused waterborne disease outbreaks in the United States, from 1971 to 1990. Notice that the vast majority of known agents are microorganisms.

Table 2.1. Causative Agents of Waterborne Disease Outbreaks, 1971 to 1990

	Outbreaks		Illness	
	Number of Cases	Percentage of Total	Number of Cases	Percentage of Total
Gastroenteritis - unknown cause	293	49.66%	67,367	47.60%
Giardiasis	110	18.64%	26,531	18.75%
Chemical poisoning	55	9.32%	3,877	2.74%
Shigellosis	40	6.78%	8,806	6.22%
Viral gastroenteritis	27	4.58%	12,699	8.97%
Hepatitis A	25	4.24%	762	0.54%
Salmonellosis	12	2.03%	1,370	0.97%
Camplylobacterosis	12	2.03%	5,233	3.70%
Typhoid fever	5	0.85%	282	0.20%
Yersiniosis	2	0.34%	103	0.07%
Cryptosporidiosis	2	0.34%	13,117	9.27%
Chronic gastroenteritis	1	0.17%	72	0.05%
Toxigenic E. coli	2	0.34%	1,243	0.88%
Cholera	1	0.17%	17	0.01%
Dermatitis	1	0.17%	31	0.02%
Amebiasis	1	0.17%	4	0.00%
Cyanobacteria-like bodies	1	0.17%	21	0.01%
Total	590	100%	141,535	100%

	Outbreaks		Illness	
	Number of Cases	Percentage of Total	Number of Cases	Percentage of Total

(Source: Committee on Ground Water Recharge, 1994)

Table 2.2 shows additional data compiled from waterborne disease outbreaks. This table shows the agent associated with the disease.

Table 2.2. Waterborne Disease Outbreaks due to Microorganisms[a]

Disease	Agent	Outbreaks[b] (%)	Cases[c] (%)
Bacteria			
Typhoid fever	*Salmonella typhi*	10	0.1
Shigellosis	*Shigella* spp.	9	2.6
Salmonellosis	*Salmonella paratyphi* and other *Salmonella* species	3	3.5
Gastroenteritis	*Escherichia coli*	0.3	0.7
	Campylobacter spp.	0.3	0.7
Viruses			
Infectious hepatitis	Hepatitis A virus	11	0.5
Diarrhea	Norwalk virus	1.5	0.6
Protozoa			
Giardiasis	*Giardia lamblia*	7	3.8
Cryptosporidiosis[d]	*Cryptosporidium parvum*	0.2	71
Unknown etiology			
Gastroenteritis		57	16.7

[a] Compiled from data provided by the Centers for Disease Control, Atlanta, GA.
[b] Of more than 650 outbreaks in recent decades.
[c] Of 520,000 cases over the same period.
[d] A single outbreak of cryptosporidiosis in 1993 caused illness in 370,000 individuals from Milwaukee, WI. This is the largest single recorded outbreak of a waterborne disease in history.
(Source: Brock, 1997)

The Centers for Disease Control (CDC) keep detailed records regarding notifiable, or reportable, diseases. There are legal requirements for reporting of cases for these diseases. This list of notifiable diseases includes cryptosporidiosis. As of mid-April 1998, there have been 520 cases of cryptosporidiosis (not notifiable in all fifty states) (CDC, 1998). The fact that this disease is notifiable means that it is recognized as being extremely hazardous.

Dose Response

The concept of dose response is critical to risk assessment. Briefly, dose response describes a relationship between a given level of contaminant and the biological response induced. This relationship is usually incremental, i.e., increase in the dose causes an increase in the response. In this particular case, the dose is the number of pathogenic microorganisms that the human subject is exposed to (through ingestion, swimming, wading, etc.) and the response is a level of infection. Generally, there is a minimum infective dose threshold that must be reached in order to infect a given individual. Once an individual has been infected there are increasing degrees of infection severity. A *subclinical* infection describes the case where the pathogen produces a detectable immune response or organisms may be found that are growing in the human host, however the subject exhibits no clinical signs or symptoms, e.g., diarrhea, vomiting, etc. A *clinical* infection refers to the condition whereby there are clinical signs and symptoms present. In layman's terms, one would refer to a person with a clinical infection as being 'ill'. The most severe response to infection would be death, i.e., a *fatality*. Therefore, one usually refers to the MID_{50}, that is the minimum infective dose that will cause subclinical infection in 50% of people exposed to that number of pathogens. The minimal infective dose (MID) varies widely with the type of pathogen, see Table 2.3 (Bitton, 1994). Of those infected, a percentage will show clinical signs; this is referred to as the ratio of clinical illness to infection. In

addition, a percentage of those infections will result in fatalities; this is referred to as the case fatality rate. Table 2.4 shows example values for these various levels of response to infection.

Table 2.3. Minimal Infective Doses for Some Pathogens and Parasites

Organism	Minimal infective dose
Salmonella spp.	10^4 to 10^7
Shigella spp.	10^1 to 10^2
Escherichia coli	10^6 to 10^8
Vibrio cholerae	10^3
Giardia lamblia	10^1 to 10^2 cysts
Cryptosporidium	10^1 cysts
Entamoeba coli	10^1 cysts
Ascaris	1 – 10 eggs
Hepatitis A virus	1 – 10 PFU

(Source: Bitton, 1994)

Table 2.4. Values Used to Calculate Risks of Infection, Illness and Mortality from Selected Enteric Microorganisms

	Probability of Infection from Exposure to One Organism (per million)	Ratio of Clinical Illness to Infection (%)	Mortality Rate (%)	Secondary Spread (%)
Campylobacter	7,000			
Salmonella typhi	380			
Shigella	1,000			
Vibrio cholerae	7			
Coxsackieviruses		5-96	0.12-0.94	76
Echoviruses	17,000	50	0.27-0.29	40
Hepatitis A virus		75	0.6	78
Norwalk virus			0.0001	30
Poliovirus 1	14,900	0.1-1	0.9	90
Poliovirus 3	31,000			
Rotavirus	310,000	28-60	0.01-0.12	
Giardia lamblia	19,800			

(Source: Committee on Ground Water Recharge, 1994)

Notice that higher probabilities, rates, or percentages correspond to pathogens with higher virulence. For example, if one million people are exposed to one rotavirus, then 310,000 will be infected. In contrast, if one million people are exposed to one *Vibrio cholerae* bacterium, then only seven will be infected. In general, viral pathogens are much more virulent than bacterial ones.

Research studies to determine dose response relationships for various pathogenic microorganisms are beyond the scope of this project. Fortunately, several studies of this type have been conducted in the past and the results have been published. Therefore, this project will rely heavily upon published rates of infection values for the pathogens being studied.

Table 2.5 shows another example of data that can be obtained from published studies. This data shows, for instance, that once infected by *salmonella* bacteria, approximately forty-one percent will exhibit clinical infection. In addition, *cryptosporidium* infection results in a seventy-one percent clinical infection frequency.

Table 2.5. Ratio of Clinical to Subclinical Infections and Case Fatality Rates for Enteric Microorganisms

Microorganism	Frequency of clinical illness (%)	Case:fatality Rate (%)
Viruses		
Hepatitis (adults)	75	0.6
Rotavirus	25 - 60	0.01
Astrovirus (adults)	12.5	
Coxsackie A16	50	0.12
Coxsackie B	5 – 96	0.59 – 0.94
Bacteria		
Salmonella	41	0.1
Shigella	46	0.2
Protozoan parasites		
Giardia	50 – 67	
Cryptosporidium	71	

(Source: Gerba et al., 1996)

Another study (DuPont et. al., 1995) published results pertaining to infection rates from the oral introduction of *cryptosporidium* oocysts into healthy volunteers. Various doses of oocysts, from thirty to one million, were given to volunteers in gelatin capsules, and then these subjects were followed up to record the incidence of infection. Table 2.6 gives these results. A linear regression analysis of the data yielded a correlation coefficient of 0.983, and an infectious dose fifty of 132 oocysts. This is an excellent example of the dose response relationship as increasing doses of oocysts caused increasing rates of infection.

Table 2.6. Rate of Infection, Enteric Symptoms, and Clinical Cryptosporidiosis, According to the Intended Dose of Oocysts

Intended dose of oocysts	No. of subjects	Infection	Enteric symptoms	Crypto-sporidiosis
		Number (percent)		
30	5	1 (20)	0	0
100	8	3 (37.5)	3 (37.5)	3 (37.5)
300	3	2 (66.7)	0	0
500	6	5 (83.3)	3 (50)	2 (33.3)
> 1000	7	7 (100)	5 (71.4)	2 (28.6)
Total	29	18	11	7

(Source: DuPont, 1995)

Exposure Assessment

Several factors contribute to whether or not contact with a particular pathogen may cause disease. Among these factors are virulence, mode of transmission, portal of entry, and host susceptibility. Virulence is defined as a particular organism's ability to cause disease in humans, and is related to the dose of infectious agent necessary for host infection and causing disease (Bitton, 1994). The mode of transmission is the particular method in which the organism is transported from the reservoir to the host, i.e., person-to-person, waterborne, or foodborne. The following figure illustrates possible SSO exposure pathways.

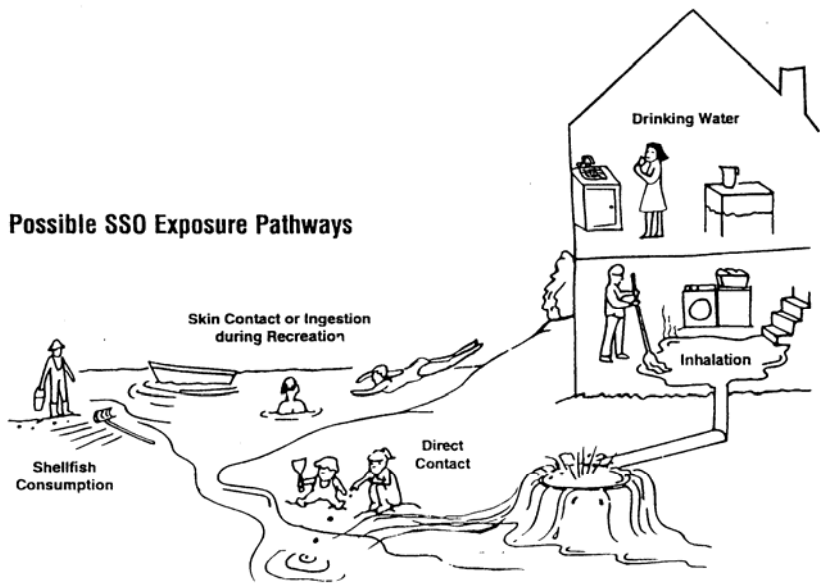


Figure 2.I. Possible SSO Exposure Pathways

This research concentrates on the waterborne transmission route, but exposure assessment will be evaluated based upon portal of entry. The portal of entry is dictated by the mechanism of contact; examples or entry portals are access through the gastrointestinal tract, respiratory tract, or skin. Host susceptibility is dependent upon resistance to infectious agents which consists of the roles of the immune system and nonspecific factors (Bitton, 1994). Immunity can be both natural (genetic), and acquired from previous contact with the pathogen.
There are many documented examples of waterborne transmission of pathogenic microorganisms. Recently, in the U.S., there has been widespread concern about *cryptosporidium* contamination of water supplies. This would be an example of waterborne transmission via drinking water supply. Table 2.7 summarizes the available information regarding *cryptosporidium* outbreaks in the U.S. Outbreaks caused by this organism are a significant health threat (over four hundred thousand people were infected during the 1993 Milwaukee outbreak). Moreover, notice that the suspected source of contamination is likely to be sewage. In fact, wastewater was implicated as the source in roughly half of the outbreaks (Solo-Gabriele and Neumeister, 1996). The remaining ones were likely caused by agricultural runoff.

Table 2.7. Affected Populations and Characteristics of the Raw Water Supply.

County, State (City)	Date	Estimated # of People Affected (Confirmed Cases)[a]	Raw Water Source	Suspected Sources of Contamination
Bexar County, TX (Braun Station)	May-Jul 1984	2,000 (47)	Well	Raw Sewage[b]
Bernalillo County, NM (Albuquerque)	Jul-Oct 1986	(78)	Surface Water	Surface runoff from livestock grazing areas
Carroll County, GA (Carrollton)	Jan-Feb 1987	13,000	River	Raw sewage and runoff from cattle grazing areas
Berks County, PA	Aug 1991	551	Well	Septic tank effluent, nearby creek
Jackson County, OR (Talent and Medford)	Jan-Jun 1992	15,000	Spring/river	Surface water, treated wastewater[b], or runoff from agricultural areas

County, State (City)	Date	Estimated # of People Affected (Confirmed Cases)[a]	Raw Water Source	Suspected Sources of Contamination
Milwaukee County, WI (Milwaukee)	Jan-Apr 1993	403,000	Lake	Cattle wastes, slaughterhouse wastes, and sewage carried by tributary rivers
Yakima County, WA	Apr 1993	7 (3)	Well	Infiltration of runoff from cattle, sheep, of elk grazing areas
Cook County, MN (Grand Marais)	Aug 1993	27 (5)	Lake	Backflow of sewage or septic tank effluent into distribution, raw water inlet lines, or both
Clark County, NV (Las Vegas)	Jan-Apr 1994	(78)[c]	Lake	Treated wastewater, sewage from boats
Walla Walla County, WA	Aug-Oct 1994	86 (15)	Well	Treated wastewater[b]
Alachua County, FL	Jul 1995	(72)	N/A	Backflow of contaminated water

[a] Estimates are based on epidemiologic studies; confirmed cases correspond to patients whose stool samples tested positive for *Cryptosporidium*.
[b] Strong evidence to support effect of wastewater.
[c] 103 laboratory-confirmed cases were associated with the outbreak; 78 of these were documented during the epidemiologic study period.
(Source: Solo-Gabriele and Neumeister, 1996)

Another important mode of transmission is via water-contact recreation. This type of transmission is usually associated with swimming beach exposures. Recall Table 2.1 gives a summary of many studies that have been conducted showing an association between illness and swimming near stormwater, SSO, or CSO (combined sewer overflow) outfalls. In general, most of these studies found an increased risk of illness resulting from swimming in waters that contained fecal contamination indicators or pathogenic microorganisms. The SMBRP (Santa Monica Bay Restoration Project) Study is unique in that it found a distance-dependant association between contamination sources and health effects. In this study, there was a higher rate of enteric illness in swimmers who swam within five hundred feet of a stormwater outfall than those who swam more than five hundred feet away. The pathogens contained in stormwater are likely from sewage contamination. Pitt and Lalor conducted a study of inappropriate pollutant entries into storm drainage systems in which many illegal sanitary sewer connections to storm drain systems were found (Pitt and Lalor, 1993).

Another possible exposure route is through the consumption of contaminated fish or shellfish. One example of this type of outbreak occurred in Louisiana in 1993 (Kohn, 1995). This outbreak was caused by contamination of oysters that were then consumed raw. The agent implicated in this outbreak was Norwalk virus, which causes gastroenteritis. Seventy (83%) of eighty-four who ate raw oysters became ill. The epidemiologic investigation found that this outbreak was probably caused by overboard sewage disposal by harvesters near the oyster bed.

An additional consideration that one must account for when assessing the adverse health effects of contact with pathogenic microorganisms is that certain individuals within the population are at higher risk for serious infections. Individuals who are at higher risk are the very young, the elderly, pregnant individuals, and the immunocompromised (organ transplants, cancer patients, AIDS patients) (Gerba et. al., 1996). This collective group represents almost 20% of the current U.S. population (Table 2.8). In addition, the elderly and immunocompromised are an increasing segment within the population.

Table 2.8. Sensitive Populations in the United States

Population	Individuals	Year
Pregnancies	5,657,900	1989
Neonates	4,002,000	1989
Elderly (over 65)	29,400,000	1989
Residences in nursing homes or related care facilities	1,553,000	1986
Cancer patients (non-hospitalized)	2,411,000	1986
Transplant organ patients (1981 – 1989)	110,270	1981-1989
AIDS patients	142,000	1981-1990

(Source: Gerba et al., 1996)

Section 3 – Human Health Effects of Sanitary Sewer Overflows

Human Health Effects of Sanitary Sewer Overflows

There are several mechanisms where exposure to contaminated urban receiving waters can cause potential human health problems. These include exposure at swimming areas affected by SSO discharges, drinking water supplies contaminated by SSO discharges, and the consumption of fish and shellfish that have been contaminated by SSO pollutants. Understanding the risks associated with these exposure mechanisms is difficult and not very clear. Receiving waters where human uses are evident are usually very large and the receiving waters are affected by many sanitary sewage and industrial point discharges, along with upstream agricultural nonpoint discharges, in addition to the local stormwater discharges. In receiving waters only having stormwater discharges, it is well known that inappropriate sanitary and other wastewaters are also discharging through the storm drainage system. These "interferences" make it especially difficult to identify specific cause and effect relationships associated with SSO discharges alone. Therefore, much of the human risk assessment associated with SSO exposure must use theoretical evaluations relying on likely SSO characteristics and laboratory studies in lieu of actual population studies. However, some site investigations, especially related to swimming beach problems associated with nearby sewage discharges, have been conducted.

Population Exposure to SSO Components

Epidemiological Studies and Human Exposures to Waterborne Pathogens

Epidemiology can be defined as the study of the occurrence and causes of disease in human populations and the application of this knowledge to the prevention and control of health problems. The general population often views epidemiology and associated risk assessments with skepticism when risks associated with seemingly everyday activities are quantified, especially when associated with periodic "food scares" that are typically exaggerated or misinterpreted in the press. Technical experts also may feel uncomfortable with the results of epidemiological studies because of the typically very low numbers of affected people in a study population. However, much of the information that is used in developing environmental regulations protecting human health originates with epidemiological studies and a more through understanding of the science of epidemiology would dispel much of the confusion associated with these studies.

Epidemiology has routinely been used to assess risks associated with contaminants in drinking waters. Epidemiology has also recently been used to investigate human health risks associated with swimming in waters contaminated by sewage and stormwater discharges. However, Craun, *et al.* (1996) state that the results of environmental epidemiology studies (the assessment of human health effects associated with environmental contaminants, where indicators of disease are mostly studied instead of the disease itself) have provoked controversy. Their excellent review article on epidemiology applied to water and public health discusses many of these problems and offers suggestions to enable better interpretation of existing studies and better design of future studies. The following paragraphs are summarized from their article.

The definition of terms is important. For example, epidemiologists use several measures to describe disease frequency. The following discussion is from Craen, *et al*. (1996) who presented an excellent review of epidemiological principles to water borne disease exposure. Incidence is the rate at which new cases of disease occur, whereas prevalence measures both new and existing cases in the total population. Therefore, prevalence is "the proportion of people who have a specific condition at any specific time" and is typically measured as a

percentage of the total population. Incidence considers the duration of exposure, and the incidence rate may be expressed as the number of cases observed per person-years of exposure, for example. The attack rate is a measure of the cumulative incidence during an outbreak of the disease, and is usually expressed in terms of numbers of cases of disease per population unit (such as per 10,000 people in the population). Secondary outbreaks can also occur for communicable disease and the secondary attack rate refers to the cases of disease attributed to exposure to people having the disease during the primary attack. The secondary rate is usually expressed in terms of susceptible contacts. Geographic-specific (such as part of town receiving water from a specific source) and vehicle-specific (such as waterborne specific disease) attack rates help to determine the source of the disease. Attack rates can also be examined in terms of water consumption by separating the attack rate into different categories associated with different amounts of water consumed, for example. Mortality rate and case fatality rate are also measures of disease frequency. The mortality rate indicates the number of deaths from a certain disease, and or time period, per the total population. The case fatality rate is the proportion of diagnosed individuals having the disease who die of the disease. The crude rates should be standardized to account for differences in demographic characteristics of the population, especially age.

Association is a measure of the dependence between exposure to a contaminant and the onset of disease, but does not necessarily indicate a cause and effect relationship between the variables. Both experimental (clinical or population) and observational (descriptive or analytical) epidemiologic studies are used to determine associations. In clinical experimental studies, active intervention may be used to expose the subjects to specific doses of an infective agent to determine the infective dose of a pathogen, for example. In population experimental studies, the population may be randomly grouped according to different levels of drinking water treatment, and the households would then be extensively examined to determine any differences in disease outbreaks. In descriptive observational studies, information is available about the occurrence of disease and about exposure to specific compounds, exposure periods, and different demographic information. Analytical observational studies test specific hypotheses to evaluate associations between exposure and disease and to confirm the mode of transmission. Ecological studies (or correlation or aggregate studies) examine associations between routinely gathered health and demographic statistics and available environmental measures (such as drinking water constituent concentrations). These studies are typically controversial because the statistical demographic information pertains to groups (lumped information which makes it difficult to identify confounding factors or to normalize) and not to individuals within the groups. Difficulties also relate to incomplete information concerning potential causative agents. Therefore, analytical observational studies (where individuals are studied and more detailed information concerning the potential causative agents can be obtained) should be used to follow up hypotheses developed in ecological studies.

The experimental design of epidemiological studies is very critical. The study must be of sufficient size and have adequate statistical power to detect the hypothesized association. Randomness is also very critical in epidemiological studies to control systematic errors. In most cases, epidemiological studies compare disease rates between a test and a control population. Positive associations (where there is a statistically significant difference between the rates of the two groups) can be caused by random errors. This likelihood can be estimated by calculating the confidence interval of the statistical significance of the association. However, statistical significance (even at a very high level) does not imply a cause and effect relationship between the hypothesized factor and disease. Statistical power can be used to identify the minimum risk that a study is capable of detecting. An environmental epidemiological study should not be conducted “unless the exposure assessment is expected to be reasonably appropriate and accurate.” Adequate and complete data to make the exposure assessment must be assured before the study is conducted.

Interpreting associations is based on examining the rate differences (RD), which is the absolute differences in the two rates (incidence rate of disease for the test, or exposed, group minus the incidence rate of disease for the control, or unexposed, group), or the rate ratio (RR), which is the ratio of the rates from the two groups. The odds ratio (OR) is the ratio of the odds of disease of the test group to the odds of disease of the control group, and is interpreted similarly to the rate ratio. If the RR or OR is close to 1.0, there is no association or increased risk between the two groups. If the ratio is 1.8, there is an 80 percent increased risk of disease for the exposed individuals, compared to the unexposed group. The confidence interval of the ratio is used to identify significance of the association. A 95 percent confidence interval of 1.6 to 2.0 signifies a statistically significant estimate because the range does not include 1.0. The relatively narrow range also implies a precise estimate of the association. In contrast, a 95 percent

confidence interval of 0.8 to 14.5 does not signify a significant difference because the range includes the value of 1.0. In addition, the wide range also implies an imprecise estimate of the association. Craun, *et al.* (1996) presents Table 3.1 (from Monson 1980) indicating different rate ratios and strengths of associations. Weak associations (ratios of <1.5) are difficult to interpret. Very large range ratios are unlikely to be completely explained by unidentified or uncontrolled confounding characteristics. However, the magnitude of the rate ratio has no bearing on the likelihood that the association is attributed to bias, but causal association cannot be ruled out simply because of a weak association. In many environmental epidemiological studies, the rate ratio is frequently smaller than 1.5, causing speculation that the association may actually be caused by bias. "High quality exposure and study design are important for interpreting risks of this magnitude."

Table 3.1. Rate Ratios and Strengths of Associations for Epidemiological Studies (Monson 1980)

Rate Ratio, or Odd Ratio	Strength of Association
1.0	None
>1.0 to <1.5	Weak
1.5 to 3.0	Moderate
3.1 to 10.0	Strong
>10.0	Infinite

With the low rate ratios frequently encountered in environmental epidemiological studies, cautious interpretations are necessary. Craun, *et al.* (1996) present the following criteria that are used to assess associations and causality:

- Exposure must occur before the onset of disease (temporal association)
- A sufficient number of participants are needed to prevent random error, and the study is well conducted (study precision and validity)
- The range ratio (or odds ratio) should be large enough to minimize spurious associations (strength of association)
- Repeated observations are needed under different conditions to support causality (consistency)
- The absence of specificity does not rule out causality, but a commonly accepted effect associated with a specific exposure certainly reinforces causality (specificity)
- An association supported by scientific evidence supports causality (biological plausibility)
- Higher risks should be associated with higher exposures (dose-response relationship)
- The removal of a potential causative agent should reduce the risk of disease (reversibility)

Therefore, an effective and convincing interpretation can be supported if many of these above factors are successfully addressed by an environmental epidemiological study.

Exposure to SSO Contaminants During Water Contact Recreation Activities

The following discussion presents an overview of the development of water quality criteria for water contact recreation, plus the results of several epidemiological studies that have specifically examined human health problems associated with swimming in sewage contaminated water. In most cases, the levels of indicator organisms and pathogens causing increased illness were well within the range found in urban streams.

Development of Bathing Beach Bacteriological Criteria and Associated Epidemiological Studies

Human health standards for body contact recreation (and for fish and water consumption) are based on indicator organism monitoring. Monitoring for the actual pathogens, with few exceptions, requires an extended laboratory effort, is very costly and not very accurate. Therefore, the use of indicator organisms has become established. Dufour (1984a) presents an excellent overview of the history of indicator bacterial standards and water contact recreation, summarized here. Total coliforms were initially used as indicators for monitoring outdoor bathing waters, based on a classification scheme presented by W.J. Scott in 1934. Total coliform bacteria refers to a number of

bacteria including *Escherichia*, *Klebsiella*, *Citrobacter*, and *Enterobacter* (DHS 1997). They are able to grow at 35°C and ferment lactose. They are all gram negative asporogenous rods and have been associated with feces of warm blooded animals. They are also present in soil. Scott had proposed four classes of water, with total coliform upper limits of 50, 500, 1,000, and >1,000 MPN/100 mL for each class. He had developed this classification based on an extensive survey of the Connecticut shoreline where he found that about 93% of the samples contained less than 1,000 total coliforms per 100 mL. A sanitary survey classification also showed that only about 7% of the shoreline was designated as poor. He therefore concluded that total coliform counts of <1,000 MPN/100 mL probably indicated acceptable waters for swimming. This standard was based on the principle of attainment, where very little control or intervention would be required to meet this standard. In 1943, the state of California independently adopted an arbitrary total coliform standard of 10 MPN/1 mL (which is the same as 1,000 MPN/100 mL) for swimming areas. This California standard was not based on any evidence, but it was assumed to relate well with the drinking water standard at the time.

Dufour points out that a third method used to develop a standard for bathing water quality used an analytical approach adopted by H.W. Streeter in 1951. He used a ratio between *Salmonella* and total coliforms, the number of bathers exposed, the approximate volume of water ingested by bathers daily, and the average total coliform density. Streeter concluded that water containing <1,000 MPN total coliforms/100 mL would pose no great *Salmonella typhosa* health hazard. Dufour points out that it is interesting that all three approaches in developing a swimming water criterion resulted in the same numeric limit.

One of the earliest bathing beach studies to measure actual human health risks associated with swimming in contaminated water was directed by Stevenson (1953), of the U.S. Public Health Service's Environmental Health Center, in Cincinnati, Ohio, and was conducted in the late 1940s. They studied swimming at Lake Michigan at Chicago (91 and 190 MPN/100 mL median total coliform densities), the Ohio River at Dayton, KY (2,700 MPN/100 mL), at Long Island Sound at New Rochelle and at Mamaroneck, NY (610 and 253 MPN/100 mL). They also studied a swimming pool in Dayton, KY. Two bathing areas were studied in each area, one with historically poorer water quality than the other. Individual home visits were made to participating families in each area to explain the research program and to review the calendar record form. Follow up visits were made to each participating household to insure completion of the forms. Total coliform densities were monitored at each bathing area during the study. More than 20,000 persons participate in the study in the three areas. Almost a million person-days of useable records were obtained. The percentage of the total person-days when swimming occurred ranged from about 5 to 10 percent. The number of illnesses of all types recorded per 1,000 person-days varied from 5.3 to 8.8. They found an appreciably higher illness incidence rate for the swimming group, compared to the nonswimming group, regardless of the bathing water quality (based on total coliform densities). A significant increase in gastrointestinal illness was observed among the swimmers who used one of the Chicago beaches on three days when the average coliform count was 2,300 MPN/100 mL. The second instance of positive correlation was observed in the Ohio River study where swimmers exposed to the median total coliform density of 2,700 MPN/100 mL had a significant increase in gastrointestinal illness, although the illness rate was relatively low. They suggested that the strictest bacterial quality requirements that existed then (as indicated above, based on Scott's 1934 work) might be relaxed without significant detrimental effect on the health of bathers.

It is interesting to note that in 1959, the Committee on Bathing Beach Contamination of the Public Health Laboratory Service of the UK concluded that "bathing in sewage-polluted seawater carries only a negligible risk to health, even on beaches that are aesthetically very unsatisfactory" (Cheung, *et al.* 1990 and Alexander, *et al.* 1992).

Dufour (1984a) pointed out that total coliforms were an integral element in establishing fecal coliform limits as an indicator for protecting swimming uses. Fecal coliform bacteria are a subgroup of the total coliform group. They grow at 44.5°C and also ferment lactose. They are restricted to the feces of warm blooded animals and can be used to separate bacteria of soil and animal origin (DHS 1997). They do survive for variable periods of time in fecal contaminated soil and water, however. As a result of the Stevenson (1953) study, reported above, a geometric mean fecal coliform level of 200 MPN per 100 mL was recommended by the National Technical Advisory Committee (NTAC) of the Federal Water Pollution Control Administration in 1968 and was adopted by the U.S. Environmental Protection Agency in 1976 as a criterion for direct water contact recreation (Cabelli, *et al.* 1979). This criterion was adopted by almost all states by 1984. It was felt that fecal coliforms was more specific to sewage contamination and

had less seasonal variation that total coliforms. Since fecal coliform exposures at swimming beaches had never been linked to disease, the NTAC reviewed the USPHS studies, as published by Stevenson (1953). The 2,300 MPN/100 mL total coliform count association with gastrointestinal disease was used in conjunction with a measured ratio of fecal coliform to total coliform counts (18%) obtained at the Ohio River site studied earlier. It was therefore assumed that a health effect could be detected when the fecal coliform count was 400 MPN/100 mL (18% of 2,300 = 414). Dufour (1984a) pointed out that a detectable health effect was undesirable and that the NTAC therefore recommended a limit of 200 MPN/100 mL for fecal coliforms. Dufour (1984a) points out that, although likely coincidental, the 1968 proposed limit for fecal coliforms (200 MPN/100 mL) was very close to being theoretically equivalent to the total coliform limit of 1,000 MPN/100 mL that was being replaced (200/0.18 = 1100).

Dufour (1984a) lists the ideal characteristics of bacterial indicators of fecal contamination, as presented by various authors. The authors were in agreement concerning many of the criteria (correlation to pathogens, unable to grow in aquatic environments, more resistant to disinfection than pathogens, and easy to isolate and enumerate), but two important aspects were seldom mentioned, namely that the indicator should have a direct relationship to fecal contamination, and that the indicator density should correlate with health hazards. Many of the follow-up studies conducted since the mid 1970s examined these additional criteria.

E. coli, a member of the fecal coliform group, has been used as a better indicator of fresh fecal contamination. Table 3.2 indicates the species and subspecies of the Streptococcus and Enterococcus groups of bacteria that are used as indicators of fecal contamination (DHS 1997).

Table 3.2. Streptococcus Species used as Indicators of Fecal Contamination

Indicator organism	Enterococcus group	Streptococcus group
Group D antigen		
Streptococcus faecalis	X	X
S. facealis subsp. *liquifaciens*	X	X
S. faecalis subsp. *zymogenes*	X	X
S. faecium	X	X
S. bovis		X
S. equinus		X
Group Q antigen		
S. avium		X

Source: DHS (1997)

Fecal streptococci bacteria are indicators of fecal contamination. The enterococcus group is a subgroup that is considered a better indication of human fecal contamination. S. bovis and S. equinus are considered related to feces from non-human warm blooded animals (such as from meat processing facilities, dairy wastes, and feedlot and other agricultural runoff), indicating that enterococcus may be a better indication of human feces contamination. However, *S. facealis* subsp. *liquifaciens* is also associated with vegetation, insects, and some soils (DHS 1997).

The Cabelli, *et al.* (1979) study was undertaken to address many remaining questions pertaining to bathing in contaminated waters. Their study examined conditions in New York (at a Coney Island beach, designated as barely acceptable, and at a Rockaway beach, designated as relatively unpolluted). About 8,000 people participated in the study, approximately evenly divided between swimmers and nonswimmers at the two beaches. Total and fecal coliforms, *Escherichia*, *Klebsiella*, *Citrobacter-Enterobacter*, Enterococci, *Pseudomonas aeruginosa*, and *Clostridium perfringens* were evaluated in water samples obtained from the beaches during the epidemiological study. The most striking findings were the increases in the rates of vomiting, diarrhea, and stomachache among swimmers relative to nonswimmers at the barely acceptable beach, but not at the relatively unpolluted beach. Ear, eye, nose, and skin symptoms, as well as fever, were higher among swimmers compared to nonswimmers at both beaches. They concluded that measurable health effects do occur at swimming beaches that meet the existing health standards. Children, Hispanic Americans, and low-middle socioeconomic groups were identified as the most susceptible portions of the population.

Cabelli, *et al*. (1982) presented data from the complete EPA sponsored swimming beach study, conducted in New York, New Orleans, and Boston. The study was conducted to address issues from prior studies conducted in the 1950s (including Stevenson's 1953 study noted above) that were apparently contradictory. They observed a direct, linear relationship between highly credible gastrointestinal illness and enterococci. The frequency of gastrointestinal symptoms also had a high degree of association with distance from known sources of municipal wastewater. Table 3.3 shows correlation coefficients for total gastrointestinal (GI) and highly credible gastrointestinal (HCGI) symptoms and mean indicator densities found at the New York beaches from 1970 to 1976. The best correlation coefficients were found for enterococci. In contrast, the correlation coefficients for fecal coliforms (the basis for most federal and state guidelines) were poor. Very low levels of enterococcus and *Escherichia coli* in the water (about 10 MPN/100 mL) were associated with appreciable attack rates (about 10/10,000 persons).

Table 3.3. Correlation Coefficients between Gastrointestinal Symptoms and Bacterial Densities at New York City Beaches (Cabelli, *et al.* 1982)

Indicator	HCGI correlation coefficient	GI correlation coefficient	Number of observations
Enterococci	0.96	0.81	9
Escherichia coli	0.58	0.51	9
Klebsiella	0.61	0.47	11
Enterobacter-Citrobacter	0.64	0.54	13
Total coliforms	0.65	0.46	11
Clostridium perfringens	0.01	-0.36	8
Pseudomonas aeruginosa	0.59	0.35	11
Fecal coliforms	0.51	0.36	12
Aeromonas hydriphila	0.60	0.27	11
Vibrio parahemoylticus	0.42	0.05	7

Figure 3.1 shows regressions of swimming associated gastrointestinal symptom rates (swimmer rates minus nonswimmer rates) against the mean enterococcus and *E. coli* densities of the water samples. The results clearly show that the risk of gastrointestinal symptoms associated with swimming in marine waters contaminated with municipal wastewater is related to the quality of the water, as indicated by the enterococcus density of the water. They also felt there was a strong case for causality between enterococci and gastrointestinal symptoms, based on the good association, the consistency at the different locations over different years, the reasonable nature of the relationship between enteric disease and fecal contamination, and the coherent association based on observations of waterborne disease transmission during prior outbreaks.

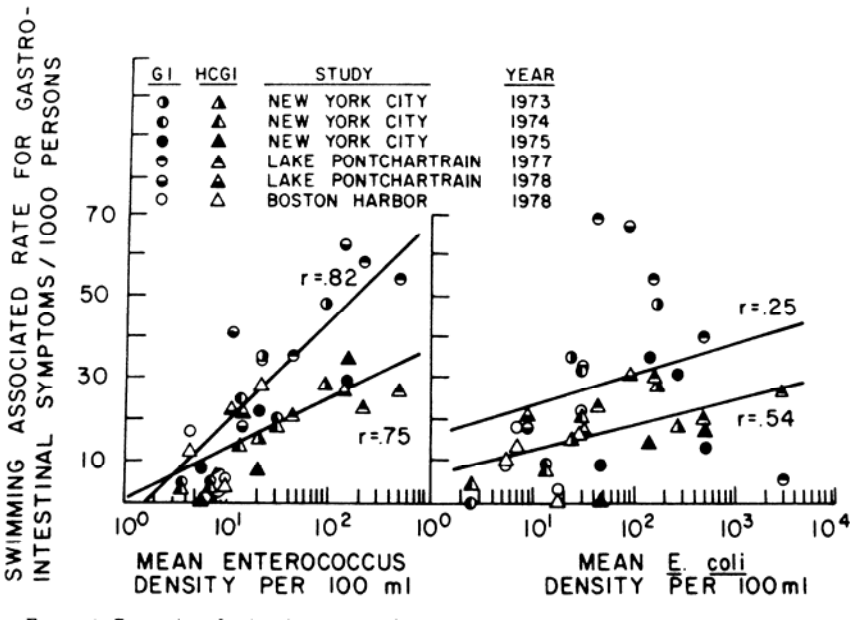


Figure 3.1. Regression of swimming-associated (swimmer minus nonswimmer) rates for gastrointestinal (GI) symptoms on the mean enterococcus and *E. coli* densities in the water. Corelation coefficients ® are as given. HCGI, highly credible gastrointestinal (Cabelli, *et al.* 1982)

They concluded that swimming in even marginally polluted marine bathing water is a significant route of transmission for observed gastrointestinal illness. They felt that the gastrointestinal illness was likely associated with the Norwalk-like virus that had been confirmed in 2,000 cases at a shellfish associated outbreak in Australia and at several outbreaks associated with contaminated drinking water.

Fleisher (1991) reevaluated this marine swimming beach data and concluded that the limitation for enterococci promulgated by the EPA in 1986, based on the Cabelli, *et al.* (1982) study, (35 per 100 mL, geometric mean for 5 equally spaced samples over a 30-day period, for both fresh and saline water) was too severe, due to minor adjustments of the observed data. He was also especially concerned with the use of a single criterion based on pooled data, while the data from the individual sites indicated very different probabilities of gastroenteritis among swimmers at Boston compared to New York and Lake Pontchartrain (which were similar). He also reported that previous studies found bacteria indicator, and possibly pathogen, survival to be inversely correlated with salinity. He therefore concluded that any relation between enterococci and disease causing pathogens may be site specific, possibly related to water salinity. This EPA enterococci criterion for swimming waters was based on an “acceptable” rate of gastroenteritis of 19 cases per 1,000 swimmers, the same rate upon which the fecal coliform criterion (200 MPN/100 mL) was based. It is interesting to note that Fleisher later participated in additional epidemiological studies in the UK and concluded that 33 fecal streptococci (essentially enterococci)/100 mL was the threshold of increased risk for gastrointestinal illness for swimmers (Kay, *et al.* 1994).

Dufour (1984a) also reviewed a series of studies conducted at freshwater swimming beaches from 1979 to 1982, at Tulsa, OK, and at Erie, PA. Only enterococci, *E. coli*, and fecal coliforms were monitored, based on the results of the earlier studies. Table 3.4 shows the correlation coefficients for these three bacterial parameters and gastrointestinal disease.

Table 3.4. Correlation Coefficients for Bacterial Parameters and Gastrointestinal Disease (Fresh Water Swimming Beaches)

	Highly Credible Gastrointestinal Illness	Total Gastrointestinal Illness	Number of Study Units
Enterococci	0.774	0.673	9
E. coli	0.804	0.528	9
Fecal coliforms	-0.081	0.249	7

These results are quite different than the results from the marine studies, in that both enterococci and E. coli had high correlation coefficients between the bacterial levels and the incidence of gastrointestinal illness. However, the result was the same for fecal coliforms, in that there was no association between fecal coliform levels and gastrointestinal illness. Dufour (1984b) concluded that enterococci would be the indicator of choice for gastrointestinal illness, based on scientific dependability. *E. coli* could also be used, if only fresh waters were being evaluated. Fecal coliforms would be a poor choice for monitoring the safety of bathing waters. However, he concluded that numeric standards should be different for fresh and saline waters because of different dieoff rates for the bacteria and viruses for differing salinity conditions.

Other studies examined additional illness symptoms associated with swimming in contaminated water, besides gastrointestinal illness, and identified other potentially useful bacterial indicators. Seyfried, *et al*. (1985), for example, examined swimming beaches in Toronto for respiratory illness, skin rashes, plus eye and ear problems, in addition to gastrointestinal illness. They found that total staphylococci correlated best with swimming associated total illness, plus ear, eye and skin illness. However, fecal streptococci and fecal coliforms also correlated (but not as well) with swimming associated total illness. Ferley, *et al*. (1989) examined illnesses among swimmers during the summer of 1986 in the French Ardèche river basin, during a time when untreated domestic sewage was entering the river. They examined total coliforms, fecal coliforms, fecal streptococci and *Pseudomonas aeruginosa* and *Aeromonas Spp*, but only two samples per week were available for each swimming area. The total morbidity rate ratio for swimmers compared to nonswimmers was 2.1 (with a 95% confidence interval of 1.8 to 2.4), with gastrointestinal illness the major illness observed. They found that fecal streptococci (FS) was the best indicator of gastrointestinal illness. A critical FS value of 20 MPN/100 mL indicated significant differences between the swimmers and nonswimmers. Skin ailments were also more common for swimmers than for nonswimmers and were well correlated with the concentrations of fecal coliforms, *Aeromonas Spp* and *Pseudomonas aeruginosa*. They noted that a large fraction (about 60%) of the fecal coliforms corresponded to *E. coli*, and that their definition of fecal streptococci essentially was what North American researchers termed enterococci.

Koenraad, *et al*. (1997) investigated the contamination of surface waters by *Campylobacter* and its associated human health risks. They reported that campylobacteriosis is one the most frequently occurring acute gastroenteritis diseases in humans. Typical investigations have focused on the consumption of poultry, raw milk, and untreated water as the major sources of this bacterial illness. Koenraad, *et al*. (1997) found that human exposures to *Campylobacter* contaminated surface waters is likely a more important risk factor than previously considered. In fact, they felt that *Campylobacter* infections may be more common than *Salmonella* infections. The incidence of campylobacteriosis due to exposure to contaminated recreational waters has been estimated to be between 1.2 to 170 per 100,000 individuals. The natural habitat of *Campylobacter* is the intestinal tract of warm-blooded animals (including poultry, pigs, cattle, gulls, geese, pigeons, magpies, rodents, shellfish, and even flies). It does not seem to multiply outside of its host, but it can survive fairly well in aquatic environments. It can remain culturable and infective for more than 2 months under ideal environmental conditions. Besides runoff, treated wastewater effluent is also a major likely source of *Campylobacter* in surface waters. Sanitary wastewater may contain up to 50,000 MPN of *Campylobacter* per 100 mL, with 90 to 99% reductions occurring during typical wastewater treatment.

Many of the available epidemiological studies have been confined to healthy adult swimmers, in relatively uncontaminated waters. However, it is assumed that those most at risk would be children, the elderly, and those chronically ill, especially in waters known to be degraded. Obviously, children are the most likely of this most-at-

risk group to play in, or by, water. Alexander, *et al.* (1992) therefore specifically examined the risk of illness associated with swimming in contaminated sea water for children, aged 6 to 11 years old. This study was based on parental interviews for 703 child participants during the summer of 1990 at Blackpool beach, UK. Overall, 80% of the samples at the Blackpool Tower site and 93% of the samples at the South Pier site failed to meet the European Community Standards for recreational waters. All of the 11 designated beaches in Lancashire (including Blackpool beach), in the northwest region of England, continually fail the European directive imperative standards for recreational waters. During this study, statistically significant increases in disease were found for children who had water contact, compared to those who did not. Table 3.5 shows the prevalence and rate ratios for these symptoms. Diarrhea and loss of appetite had strong associations with the water contact group, while vomiting and itchy skin had moderate associations. No other variables examined (household income, sex of the child, sex of the respondent, general health, chronic or recurring illness in the child, age of the child, foods eaten, including ice cream, other dairy products, chicken, hamburgers, shellfish, or ice cubes, acute symptoms in other household members, presence of children under 5 in the household, and other swimming activities) could account for the significant increases in the reported symptoms for the children who had water contact.

Table 3.5. Illness Symptoms for Children Exposed to Sewage Contaminated Sea Water (Alexander, *et al.* 1992)

	Prevalence for water contact group, n=455 (%)	Prevalence for non-water contact group, n=248 (%)	Rate Ratio	Strength of Association
Vomiting	4.2	1.6	2.6	Moderate
Diarrhea	7.9	2.4	3.3	Strong
Itchy skin	5.1	2.8	1.8	Moderate
Loss of appetite	4.0	1.2	3.3	Strong

Other risk factors, in addition to exposure to sewage contaminated swimming waters, was investigated by Fleisher, *et al.* (1993). People visiting beaches for recreation are frequently exposed to additional risks for gastroenteritis disease, especially related to foods that are eaten. Picnic lunches and food purchased at swimming beaches may contain improperly prepared or inadequately stored foods, including food that may be especially risky including sandwiches having mayonnaise, chicken, eggs, hamburgers, and hot dogs. They found that non-water related risk factors confounded the relationships between gastroenteritis and fecal streptococci densities. They also found that fecal coliform and fecal streptococci densities changed rapidly in time and location at swimming beaches, requiring many more water sample evaluations than are typically obtained during most epidemiological studies.

Hong Kong Swimming Beach Study

Swimming beach studies were conducted in Hong Kong during the summers of 1986 and 1987 (Cheung, *et al.* 1990). This was a significant study in that it was one of the first major epidemiological investigations that has been conducted in subtropical waters. The Hong Kong swimming beach criteria, adopted in 1981, set the following objective: “The level of E. coli should not exceed 1,000 per 100 mL, calculated as the running median of the most recent five consecutive samples.” Beaches that did not meet this objective for 60% of the time in any year were closed to swimming.

The results of this study can be compared to the more common temperate area studies as an indication of the usability of recreation water quality criteria for a broader range of conditions. More than 18,700 responses were obtained from beachgoers on nine beaches. Water samples were collected every two hours at the nine beaches under study. The samples were analyzed for *E. coli*, *Klebsiella* spp., fecal streptococci, fecal coliforms, staphylococci, *Pseudomonas aeruginosa*, *Candida albicans*, and total fungi. E. coli only represented 57% of the fecal coliforms (much lower than reported elsewhere). Beachgoers were recruited on selected weekends and given initial interviews. Follow-up telephone interviews were obtained 7 to 10 days afterwards. The beachgoers spent an average of 3.5 hours at the beach, and swimmers spent an average of 1.3 hours in the water (much longer than reported in colder climates). The beaches studied were affected to varying degrees by nearby submarine sewage outfalls, agricultural runoff (pig farming) or by storm drains discharging across the beaches.

The overall symptom rates for gastrointestinal, ear, eye, skin, respiratory, fever, and total illness were significantly higher for swimmers than for non-swimmers. Many of the rates were also higher at "barely acceptable" beaches than at "relatively unpolluted" beaches. The increased risk of swimmers developing highly credible gastrointestinal illness (HCGI) was 5 times greater than for non-swimmers. The increased risk for swimmers in developing gastrointestinal (GI), eye, skin, and total illness was 2 to 4 times greater than for non-swimmers. The incubation period for the gastrointestinal symptoms in Hong Kong were similar to those reported for the U.S., indicating a possible similar causative agent (Norwalk virus and rotavirus virus originating from human sewage being suspected). Children under 10 years of age were also found to have significantly higher symptom rates for GI, HCGI, skin, respiratory, fever, and total illness than older swimmers. *Escherichia coli* was found to be the best indicator of swimmer illness (especially gastroenteritis and skin symptoms). Staphylococci measurements were recommended as a supplement to *E. coli*, especially for ear, respiratory and total illness. They contrasted this finding with typically better correlations between enterococci and health risks at U.S. beaches. They concluded that it may not be appropriate to adopt another country's water contact recreation water quality criteria, especially if they are vastly separated geographically. Differences may be due to differences in the immune state of the populations and the indicator-illness relationships. Geometric mean densities of 180 *E. coli* per 100 mL and 1,000 staphylococci per 100 mL were found to be the thresholds for differentiating "barely acceptable" and "relatively unpolluted" beaches. These observations were used to develop new swimming beach standards for Hong Kong, as shown in Table 3.6. This new classification scheme was in place in 1988.

Table 3.6. Classification of Hong Kong Beaches Based on Swimming Associated Health Risk Levels

Rank	Swimming associated gastroenteritis and skin symptom rate (per 1,000 swimmers)	Seasonal geometric mean *E. coli* density (per 100 mL)	Number of swimming beaches in category during 1988
Good	0	24	9
Acceptable	10	180	19
Barely acceptable	15	610	7
Unacceptable	>15	>610	7

Cheung, *et al.* 1990.

Sydney Beach Users Study

This study examined problems associated with sewage contaminated swimming beaches (from CSO discharges and ocean outfalls of treated sewage) (Corbett, *et al.* 1993). They interviewed almost 3,000 beach goers at 12 beaches during 3 months in late 1989 and early 1990. Follow-up telephone interviews were conducted about a week later concerning incidence of illness. During the 41 days of sampling, 461 samples were analyzed for fecal coliforms and fecal streptococci. Of these samples, 67% failed to meet New South Wales Department of Health water quality criteria.

Swimmers were almost twice as likely as nonswimmers to report symptoms, but the prevalence of respiratory symptoms in people aged 15 to 25 was high, irrespective of swimming status or pollution level. The incidence of respiratory, fever, eye, ear, and other problems increased with increasing bacterial counts. Fecal streptococci counts were worse predictors of the swimming risk than the fecal coliform counts. Gastrointestinal symptoms were not related to either the fecal coliforms or fecal streptococci counts monitored. Those who swam for longer than 30 minutes were more than 4 times as likely to develop gastrointestinal symptoms compared to nonswimmers or those who swam for shorter periods. Luckily, children playing near and in urban streams are not likely to have such prolonged submerged exposures, and gastrointestinal problems may not be as serious as other water contact problems. The risk of respiratory, ear, and eye symptoms accounted wholly for the increases in illness observed. They reported that enteroviruses can cause respiratory symptoms and can persist in marine sediments and waters for many months.

Table 3.7 shows the percentages of swimmers who reported various illness symptoms after swimming in waters having varying bacterial contamination levels. Increasing levels of contamination increased the health risks for all symptoms, except for gastrointestinal symptoms. Table 3.8 shows the odds ratios (and associated 95% confidence intervals) for illness at different levels of fecal coliform contamination. Above 1,000 cfu/100 mL fecal coliforms, the associations for these illnesses are all strong, while they are at least moderate for all levels shown, compared to the nonswimmers. However, most of the confidence intervals were quite large, indicating large variability in the observations, as expected.

Table 3.7. Percentages of Beachgoers Reporting Symptoms (Corbett, et al. 1993)

Illness	Did not swim (n=915)	Swam, low pollution (n=1770)	Swan, high pollution (n=154)	Total sample (n=2839)
Vomiting	0.9	1.0	0.6	0.9
Diarrhea	2.2	3.7	3.2	3.2
Cough, cold, flu	10.2	17.3	23.4	15.3
Ear infection	1.3	3.9	5.8	3.2
Eye infection	1.0	2.4	3.9	2.0
Fever	1.1	1.8	5.2	1.7
Other	4.7	8.0	13.0	7.2
Any condition reported	16.5	26.9	35.7	24.0
Attended a doctor	3.5	4.3	8.4	4.3
Took time off work	2.6	4.6	6.5	4.0

Table 3.8. Odds Ratios (OR) of Swimmers Reporting Health Problems for Different Levels of Fecal Coliform Bacteria (Corbett, *et al.* 1993)

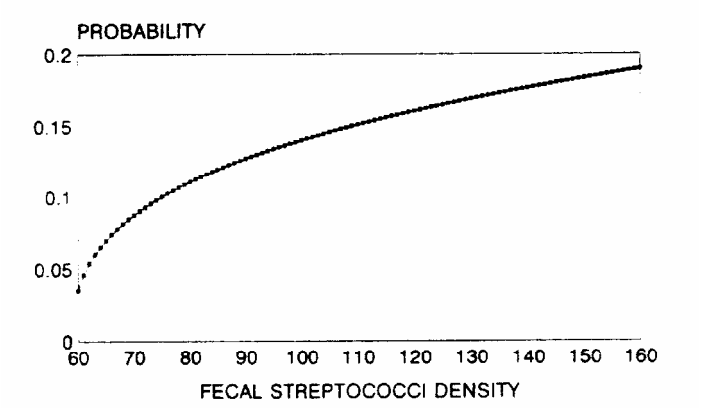
Illness	10 – 300 cfu/100 mL		300 – 1000 cfu/100 mL		1000 – 3000 cfu/100 mL		>3000 cfu/100 mL	
	OR	CI of OR	OR	CI of OR	OR	CI of OR	OR	CI of OR
Any symptom	2.9	1.7 – 5.1	3.8	2.1 – 7.1	5.2	1.7 – 16.0	5.9	3.0 – 11.5
Cough	2.4	1.5 – 3.8	2.0	0.9 – 4.4	4.2	1.2 – 14.6	6.9	3.3 – 14.1
Ear symptoms	4.3	1.1 – 16.2	8.6	1.7 – 43.2	8.5	0.8 – 97.6	7.4	1.3 – 43.3
Eye symptoms	6.3	1.3 – 30.8	9.7	1.5 – 63.7	8.7	1.0 – 72.8	na	na
Fever	2.1	0.6 – 7.0	4.7	1.0 – 22.5	9.0	1.9 – 43.5	na	na
Any gastrointestinal symptom	4.6	1.9 – 4.9	3.1	0.7 – 13.0	3.4	0.7 – 18.0	na	na

UK Swimmer/Sewage Exposure Study

Another recent swimmer/sewage exposure study was conducted in the UK, reported by Kay, *et al.* (1994) and by Fleisher, *et al.* (1996). This study was unique in design and was able to develop dose-response relationships and critical exposure levels for a few illnesses associated with swimmer exposures to sewage contaminated waters. Adult volunteers (1528 study participants) were studied over four seasons from 1989 through 1992. After arriving at the beach, healthy volunteers were randomized into bather and nonbather groups with the duration and place of individual exposure being rigorously controlled. All of the study locations met European Community mandatory bacteriological marine bathing water quality criteria and were therefore not excessively contaminated.

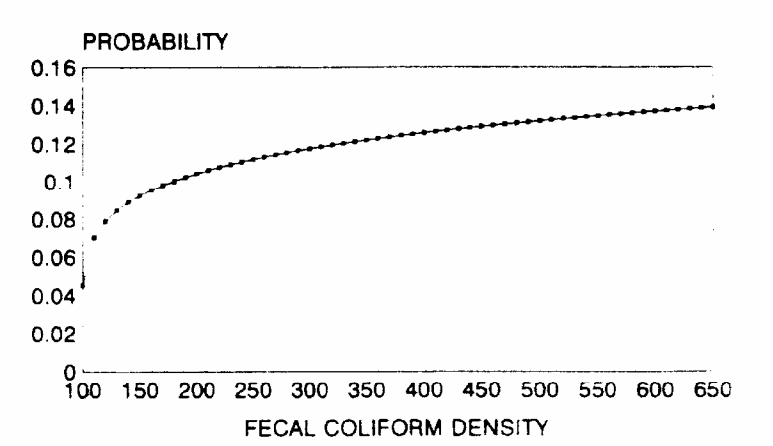
The researchers found a clear dose-response relationship between increasing levels of fecal streptococci and increased risk of acquiring acute febrile respiratory illness. Only bathers exposed to the highest quartile of exposure (51 to 158 FS /100 mL) showed a statistically significant increase in risk compared to the non bathers. The odds ratio (OR) was 2.65 (moderate association), with a 95% confidence interval of 1.19 – 5.48 for acute fibrile respiratory illness and fecal streptococci. There was a clear dose-response relationship among the bathers. In

addition, exposure to increased levels of fecal coliform organisms was found to be predictive of ear ailments among bathers. Figures 3.2 and 3.3 show the derived dose-response relationships for swimmers acquiring disease related to bacteria density in the swimming water.



Note. The plot is derived from logistic regression Model 2. Table 2. Results have been adjusted for age, gender, and household illness. Density = fecal streptococci/100 ml.

Figure 3.2. Bathers' probability of acquiring acute febrile respiratory illness through exposure to increasing levels of fecal streptococci (Fleisher, *et al*. 1996).



Note. The plot is derived from logistic regression Model 2, Table 4. Results have been adjusted for prior bathing and prior ear infection. Density = fecal coliform/100 ml.

Figure 3.3. Bathers' probability of acquiring ear infections through exposure to increasing levels of fecal coliforms (Fleisher, *et al*. 1996).

Thresholds of exposure to indicator organisms, below which bathers were at no excess risk of illness relative to nonbathers, were estimated to be 60 fecal streptococci organisms/100 mL for febrile respiratory illness and 100 fecal

coliform organisms/100 mL for ear ailments. These threshold levels are quite low and are commonly exceeded in most urban streams. No dose-response relationships or threshold levels were found for any of the indicator organisms (total coliforms, fecal coliforms, fecal streptococci, total staphlococci and *Pseudomonas aeruginosa*) and eye or skin ailments. They concluded that the use of a single illness or indicator organism for establishing swimming criteria in marine waters is incorrect.

Santa Monica Bay Project

This study was the first large-scale epidemiological study in the U.S. to investigate possible adverse health effects associated with swimming in ocean waters affected by discharges from separate storm drains (SMBRP 1996). This was a follow-up study after previous investigations found that human fecal waste was present in the stormwater collection systems (*Water Environment & Technology* 1996b, *Environmental Science & Technology* 1996b, and Haile, *et al.* 1996).

During a four month period in the summer of 1995, about 15,000 ocean swimmers were interviewed on the beach and during telephone interviews one to two weeks later. They were queried concerning illnesses since their beach outing. The incidence of illness (such as fever, chills, ear discharge, vomiting, coughing with phlegm, and credible gastrointestinal illness) was significantly greater (from 44 to 127% increased incidence) for ocean goers who swam directly off the outfalls, compared to those who swam 400 yards away, as shown on Table 3.9. As an example, the rate ratio (RR) for fever was 1.6, while it was 2.3 for ear discharges, and 2.2 for highly credible gastrointestinal illness comprised of vomiting and fever (HCGI). The approximated associations were weak for any of the symptoms, and moderate for the others listed. Disease incidence dropped significantly with distance from the storm drain. At 400 yards, and beyond, upcoast or downcoast, elevated disease risks were not found. The results did not change when adjusted for age, beach, gender, race, socioeconomic status, or worry about health risks associated with swimming at the beach.

Table 3.9. Comparative Health Outcomes for Swimming in Front of Storm Drain Outfalls, Compared to Swimming at least 400 Yards Away (from SMBRP 1996)

Health Outcome	Relative Risk	Rate Ratio	Estimated Association	Estimated No. of Excess Cases per 10,000 Swimmers (rate difference)
Fever	57%	1.57	Moderate	259
Chills	58%	1.58	Moderate	138
Ear discharge	127%	2.27	Moderate	88
Vomiting	61%	1.61	Moderate	115
Coughing with phlegm	59%	1.59	Moderate	175
Any of the above symptoms	44%	1.44	Weak	373
HCGI-2	111%	2.11	Moderate	95
SRD (significant respiratory disease)	66%	1.66	Moderate	303
HCGI-2 or SRD	53%	1.53	Moderate	314

These interviews were supplemented with indicator and pathogen bacteria and virus analyses in the waters. The greatest health problems were associated with times of highest concentrations (*E. coli* >320 cfu/100 mL, enterococcus > 106 cfu/100 mL, total coliforms >10,000 cfu/100 mL, and fecal coliforms > 400 cfu/100 mL). Bacteria populations greater than these are common in urban runoff and in urban receiving waters. Symptoms were found to be associated with swimming in areas where bacterial indicator levels were greater than these critical counts. Table 3.10 shows the heath outcomes associated with swimming in areas having bacterial counts greater that these critical values. The association for enterococcus with bloody diarrhea was strong, and the association of total coliforms with skin rash was moderate, but nearly strong.

Table 3.10. Heath Outcomes Associated with Swimming in Areas having High Bacterial Counts (from SMBRP 1996)

Indicator (and critical cutoff count)	Health Outcome	Increased Risk	Risk Ratio	Estimated Association	Excess Cases per 10,000 Swimmers
E. coli (>320 cfu/100mL)	Earache and nasal congestion	46% 24%	1.46 1.24	Weak Weak	149 211
Enterococcus (>106 cfu/100 mL)	Diarrhea w/blood and HCGI-1	323% 44%	4.23 1.44	Strong Weak	27 130
Total coliform bacteria (>10,000 cfu/100 mL)	Skin rash	200%	3.00	Moderate	165
Fecal coliform bacteria (>400 cfu/100 mL)	Shin rash	88%	1.88	Moderate	74

The ratio of total coliform to fecal coliform was found to be one of the better indicators for predicting health risks when swimming close to the storm drain. When the total coliforms were greater than 1,000 cfu/100 mL, the strongest effects were generally observed when the total to fecal coliform ratio was 2. The risks decreased as the ratio increased. In addition, illnesses were more common on days when enteric viruses were found in the water.

The percentage of survey days exceeding the critical bacterial counts were high, especially when closest to the storm drainage, as shown on Table 3.11. High densities of *E. coli*, fecal coliforms and enterococcus were observed on more than 25% of the days, however, there was a significant amount of variability in observed counts in the water samples obtained directly in front of the drains. The variability and the frequency of high counts dropped considerable with distance from the storm drains. Upcoast bacteria densities were less than downcoast densities probably because of prevailing near-shore currents.

Table 3.11. Percentages of Days when Samples Exceeded Critical Levels (from SMBRP 1996)

Bacterial Indicator	0 yards	1 to 100 yards upcoast	1 to 100 yards downcoast	400+ yards upcoast
E. coli (>320cfu/100 mL)	25.0%	3.5%	6.7%	0.6%
Total coliforms (>10,000 cfu/100 mL)	8.6	0.4	0.9	0.0
Fecal coliforms (>400 cfu/100 mL)	29.7	3.0	8.6	0.9
Enterococcus (>106 cfu/100 mL)	28.7	6.0	9.6	1.3
Total/Fecal coliform ratio ≤5 (and total coliforms >1,000 cfu/100 mL)	12.0	0.5	3.9	0.4

The SMBRP (1996) concluded that less than 2 miles of Santa Monica Bay's 50 mile coastline had problematic health concerns due to the storm drains flowing into the Bay. They also concluded that the bacterial indicators currently being monitored do help predict risk. In addition, the total to fecal coliform ratio was found to be a useful additional indicator of illness. As an outcome of this study, the Los Angeles County Department of Health Services will post new warning signs advising against swimming near the outfalls ("Warning! Storm drain water may cause illness. No swimming"). These signs will be posted on both sides of all flowing storm drains in Los Angeles County. In addition, county lifeguards will attempt to warn and advise swimmers to stay away from areas directly in front of storm drain outlets, especially in ponded areas. The county is also accelerating their studies on sources of pathogens in stormwater.

Proposed New California Recreational Area Bacteria Standards

In November of 1997, the State of California proposed new bacterial criteria for fresh and saltwater recreational areas (DHS 1997). These criteria are heavily based on the Santa Monica Bay study described above. The criteria documents state that:

> "a protocol should be developed that sets forth procedures for closing recreational waters and beach areas whenever significant amounts of rainfall results in urban runoff that enters recreational waters and beach areas.
>
> Ocean beaches that are subject to urban runoff should be closed for a minimum of 72 hours following significant rain to allow wave action to dissipate microbiological contamination, unless sampling and analysis indicates that earlier reopening is appropriate, or local health agencies have ample data and experience with the location to determine appropriate actions.
>
> Other beaches that are subject to significant urban runoff (e.g., via storm drains) should be closed until sampling by and/or experience of local health agencies indicate reopening is appropriate.
>
> Bays or other ocean water areas with poor water circulation may require a longer time to recover." (DHS 1997)

Similar wording was also provided relating to swimming in freshwaters. Indicator organisms should include total and fecal coliform bacteria, at a minimum. Enterococci can also be added as an indicator. They felt that monitoring for specific pathogens (such as *Giardia* or *Cryptosporidium*) is costly and doesn't appear to be reliable. They could be monitored if done in conjunction with the other required monitoring efforts, especially in response to specific needs. Levels indicating a need for additional attention (they suggested conducting sanitary surveys to identify and correct the sources of contamination) in both salt waters and freshwaters are:

Total coliforms:	1,000 per 100 mL (single sample), or
	1,000 per 100 mL, in more than 20 percent of the samples at any sampling station, in any 30-day period [Title 17 California Code of Regulations, Section 7958]
Fecal coliforms:	200 per 100 mL, or
	200 per 100 mL, based on the log mean of at least 5 equally spaced samples in a 30-day period (EPA 1986)

In addition, when the local health officer considers enterococcus monitoring for supplemental information, the following levels are also recommended:

Enterococcus (salt water):	35 per 100 mL (single sample), or
	35 per 100 mL, based on the log mean of at least 5 equally spaced samples in a 30-day period.
Enterococcus (freshwater):	33 per 100 mL (single sample), or
	33 per 100 mL, based on the log mean of at least 5 equally spaced samples in a 30-day period.

Freshwater swimming areas could also be monitored for *E. coli* to provide additional supplemental information. In that case, the following level indicating a need for more attention is also provided:

E. coli:	126 per 100 mL (single sample), or
	126 per 100 mL (log mean of samples over a 30-day period (EPA 1986)

Salt water beach closure is recommended when sampling indicates any of the following conditions, when confirmed within 24 to 48 hours:

Total coliforms:	10,000 per 100 mL (17 California Code of Regulations, Section 7958)
Total coliforms:	5,000 per 100 mL, if the coliform index (the ratio of fecal to total coliform counts, times 100) is 20, or more
Fecal coliforms:	1,000 per 100 mL

When enterococcus monitoring is also used, the following closure level is recommended:

Enterococcus: 104 per 100 mL (EPA 1986)

Freshwater recreational areas should be closed whenever any of the following conditions are exceeded, when confirmed within 24 to 48 hours:

Total coliforms: 10,000 per 100 mL
Fecal coliforms: 400 per 100 mL (EPA 1986)

When enterococcus or *E. coli* monitoring is also used, the following closure level is recommended:

Enterococcus: 61 per 100 mL (EPA 1986)
E. coli: 235 per 100 mL (EPA 1986)

Reopening of a closed recreational area is appropriate when two successive samples taken at least 24 hours apart are below the closure levels. If a swimming area is closed due to contamination by urban stormwater runoff, the following wording for warning signs is suggested: "Warning! Closed to swimming. Beach/swimming area is contaminated by stormwater runoff/sewage and may cause illness."

Exposure to SSO Contaminants through Drinking Water

The National Research Council conducted an intensive review of the use of waters of impaired quality for groundwater recharge (Andelman, *et al.* 1994). Included in this book was a review of the use of stormwater, treated municipal wastewater and irrigation return flows to recharge groundwater for eventual use as a drinking water supply. The following is a summary from that book, describing these potential human health risks.

Various chemical and bacteriological health risks were examined. The major risks were identified as originating from pathogenic organisms, disinfection byproducts for water that have undergone disinfection to reduce the threat from the pathogens, synthetic organic chemicals, and inorganic chemicals. Assessments are therefore needed to identify the potential risks associated with this reuse. These assessments contain four major components: hazard identification, dose-response assessment, exposure assessment, and risk characterization. The NRC committee reviewed available epidemiological studies that had investigated the use of degraded waters for recharge and as eventual drinking water supplies.

Table 3.12, summarized from the NRC report, lists the health effects of known chemicals found in WWF. The health effects shown are not meant to be comprehensive, but are the problems that the drinking water standards are intended to protect against. The EPA carcinogen classifications are as follows:

A = sufficient evidence for humans
B1 = limited evidence for humans and sufficient evidence in experimental animals
B2 = inadequate/limited evidence for humans, sufficient evidence in experimental animals
C = limited evidence in experimental animals with no human data
D = inadequate or no data
E = sufficient evidence for noncarcinogenicity

The concentrations presented are summarized from the EPA's Nationwide Urban Runoff Program (NURP) (EPA 1983) and show the percentage of samples where the toxicant was detected and the range of the detected values. Further information is given in Chapter 5 on stormwater characteristics. The maximum contaminant level (MCL) is the drinking water standard established by the EPA. Also shown (in parentheses) is the concentration associated with a cancer risk of 1 in a million, the generally recognized negligible risk level. The present background cancer occurrence rate in the U.S. is 25%. This 10^{-6} risk level, associated with a lifetime exposure to a chemical, will

increase the risk of getting cancer from 250,000 in 1 million to 250,001 in 1 million (Andelman, *et al.* 1994). The reference dose is the estimated daily dose that is likely to be without an appreciable risk of deleterious effects during a lifetime (expressed as mg of ingested chemical per day per kg of body weight). Most of the listed toxicants exceed the MCL limits and the negligible risk levels (highlighted in bold).

Table 3.12. Health Effects of Toxicants Found in WWF (Andelman, *et al.* 1994 and EPA 1983)

Chemical	Health Effects: Human	Health Effects: Animal/In Vitro	EPA Carcinogen classification	Reported frequency of detection (%) and observed concentrations in stormwater (μg/L) (EPA 1983, NURP)		Max. contaminant level (MCL) μg/L (10^{-6} cancer risk)	Reference dose (mg/kg/day)
Pesticides:							
Lindane		Morphological changes of kidney and liver cells	C	15	0.007 – 0.1	0.2	0.0003
Chlordane		Liver hypertrophy (regional)	B2	17	0.01 – 10	0.2 (0.03)	0.00006
Polyaromatic hydrocarbons:							
Fluoranthene		Nephrapathy; increased liver weight; hematologic alterations; clinical effects (increased SGPT levels)		16	0.3 – 21	-	0.04
Other organics:							
Pentachlorphenol		Liver and kidney pathology, feto-maternal toxicity	B2	19	**1** – **115**	1 (0.3)	0.03
Inorganics:							
Antimony	Gastrointestinal effects	Liver and kidney effects	D	13	2.6 – **23**	6	0.0004
Arsenic	Skin (hyperpigmentation, keratosis); vascular complications; neurotoxicity; liver injury	Reproductive/developmental effects; chromosomal effects	A	52	**1** – **51**	50 (0.000002)	0.0003
Beryllium	Contact dermatitis; pulmonary effects	Skeletal effects; genotoxicity	B2	12	**1 – 49**	4 (0.008)	0.005
Cadmium	Pulmonary and renal tubular effects; skeletal changes associated with effects on calcium metabolism	Reproductive/teratogenic effects; effects on myocardium	D	48	0.1 – **14**	5	0.0005
Chromium	Renal tubular necrosis	Genotoxicity	D	58	1 – **190**	100	0.005
Cyanide	Nausea, confusion, convulsion, paralysis, coma, cardiac arrhythmia, respiratory stimulation followed by respiratory failure		D	23	2 – **300**	200	0.022
Mercury	Nervous system effects; kidney effects	Genotoxicity	D	10	0.6 – 1.2	2	0.0003
Nickel	Contact dermatitis	Reproductive effects; genotoxicity	D	43	1 – **182**	100	0.005
Selenium	Nail changes; hair loss; skin lesions; nervous system effects	Reproductive effects, genotoxicity		11	2 – **77**	50	0.005
Zinc	Gastrointestinal distress; diarrhea	Poor growth	D	94	10 - 2400	-	0.3

Microorganisms of concern in drinking waters may include many different types of pathogens, including bacteria, viruses, and parasites. These are excreted from infected hosts and enter sanitary sewage. Stormwater and urban receiving waters can become contaminated with these pathogens, as noted earlier. Andelman, *et al.* (1994) reviewed waterborne disease outbreaks in the U.S. from 1971 through 1990. The most common identified causative agents were *Giardia*, chemical poisoning, and *Shigella* species. During this period, the causative agents in more than 50% of the outbreaks were not able to be identified. However, reviews of past outbreaks found that the Norwalk virus (causing acute nonbacterial gastroenteritis) was the likely cause of about 40% of the outbreaks from 1976 through 1980 that had no prior identified cause. The difficulty or inability to identify many of the viruses and parasites (such as *Cryptosporidium*) is the likely reason why they are not listed as a more common cause of illness from drinking contaminated water.

Dose-response information is usually determined by exposing volunteers to different doses of the microorganisms of interest. Normally, this data does not include special problems for special at-risk individuals. Table 3.13 (as reported in the NRC committee report) shows infective dose information for several pathogens. Table 3.14 shows the probability of infection of ingestion of 100 mL of water for various levels of contamination. As will be shown in Chapter 5, the levels of these microorganisms in stormwater can be much greater than the values shown on this table (enteriviruses of 100 to 3000 pfu/100 L, for example was reported by Olivieri, *et al.* 1977). Of course, ingestion of untreated or undiluted stormwater is rare.

Table 3.13 Values Used to Calculate Risks of Infection, Illness, and Mortality from Selected Enteric Microorganisms (Andelman, *et al.* 1994).

	Probability of infection from exposure to one organism (per one million)	Ratio of clinical illness to infection (%)	Mortality rate (%)	Secondary spread (%)
Campylobacter	7,000			
Salmonella typhi	380			
Shigella	1,000			
Vibrio cholerae	7			
Coxsackieviruses		5 – 96	0.12 – 0.94	76
Echoviruses	17,000	50	0.27 – 0.29	40
Hepatitis A virus		75	0.6	78
Norwalk virus			0.0001	30
Poliovirus 1	14,900	0.1 – 1	0.9	90
Poliovirus 3	31,000			
Rotavirus	310,000	28 – 60	0.01 – 0.12	
Giardia lamblia	19,800			

Table 3.14. Probability of Infection from Ingestion of 100 mL of Water Contaminated with Viruses or Protozoa

Levels in ingested water (per 100 L)	Exposure per 100 mL	Estimated risk of infection in exposed population
Rotavirus		
0.01 pfu	1.0×10^{-5}	6.2×10^{-6}
0.13 pfu	1.3×10^{-4}	6.0×10^{-5}
Echovirus		
0.01 pfu	1.0×10^{-5}	2.0×10^{-8}
0.13 pfu	1.3×10^{-4}	2.7×10^{-7}
Giardia		
0.49 cysts	4.9×10^{-4}	9.8×10^{-6}
0.89 cysts	8.9×10^{-4}	1.88×10^{-5}
1.67 cysts	1.77×10^{-3}	3.3×10^{-5}
3.3 cysts	3.3×10^{-3}	6.6×10^{-5}
Cryptosporidium		
0.75 oocysts	7.5×10^{-4}	1.5×10^{-5}
5.35 oocysts	5.35×10^{-3}	1.1×10^{-4}

Craun, *et al*. (1997) conducted evaluations of waterborne disease outbreaks from public water supplies and found that coliform bacteria monitoring is likely adequate to protect against bacterial and viral illness, but not for protozoa associated illness. Coliform bacteria monitoring has been used for many years to assess the microbiological quality of drinking waters. Except for a few strains, coliforms are not considered pathogenic. They are not very specific to fecal contamination, as most species of coliforms are free-living in the environment. Tap water having no coliforms has generally been thought to be free of agents likely to cause waterborne disease. However, Craun, *et al*. (1997) found that disease outbreaks (especially associated with *Giardia* or *Cryptosporidium*) have occurred in water systems that have not violated the maximum contaminant levels for total coliforms. The 1989 Coliform Rule for drinking waters states that systems collecting fewer than 40 samples per month may have no more than one total coliform positive sample (per 100 mL of water) per month, systems collecting more samples must have fewer than 5% of their samples positive for total coliforms. When Craun, *et al.* (1997) reviewed information from reported waterborne disease outbreaks from 1983 to 1992, they found that coliforms were detected during most of the outbreaks that were caused by bacteria, viruses, and unidentified agents, but they were found only during few of the outbreaks caused by protozoa. As an example, the 1993 Milwaukee *Cryptosporidium* outbreak (the largest documented waterborne disease outbreak in the U.S., with 400,000 cases of illness reported) occurred even though the MCL for coliforms was not violated. It is known that total coliforms are more susceptible to disinfection during water treatment than some protozoa. They concluded that "microbiological monitoring alone (for total coliforms and other indicator organisms for pathogens) cannot safeguard the public against waterborne disease. Emphasis must also be given to source water protection (watershed control programs, better control of wastewater discharges, and wellhead protection programs) and adequate water treatment and operation. The 1989 coliform rule with its more stringent requirements (periodic sanitary surveys, procedures for *E. coli* testing, and extra samples to evaluate water quality after positive total coliform results) and other USEPA regulations (e.g. the Surface Water Treatment Rule, and the pending Enhanced Surface Water Treatment Rule) are all important for reducing the risks of waterborne disease."

1986 EPA Guidance for Recreational Waters, Water Supplies, and Fish Consumption

A recreational water quality criterion can be defined as a "quantifiable relationship between the density of an indicator in the water and the potential human health risks involved in the water's recreational use." From such a definition, a criterion can be adopted which establishes upper limits for densities of indicator bacteria in waters that are associated with acceptable health risks for swimmers.

The Environmental Protection Agency, in 1972, initiated a series of studies at marine and fresh water bathing beaches which were designed to determine if swimming in sewage-contaminated marine and fresh water carries a health risk for bathers; and, if so, to what type of illness. Additionally, the EPA wanted to determine which bacterial indicator is best correlated to swimming-associated health effects and if the relationship is strong enough to provide

a criterion (EPA 1986: *Ambient Water Quality Criteria for Bacteria - 1986*, EPA 440/5-84-002, U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Washington, DC., NTIS access #: PB 86-158-045). Many of the above described U.S. studies were conducted as part of these EPA sponsored research activities. The quantitative relationships between the rates of swimming-associated health effects and bacterial indicator densities were determined using standard statistical procedures. The data for each summer season were analyzed by comparing the bacteria indicator density for a summer bathing season at each beach with the corresponding swimming-associated gastrointestinal illness rate for the same summer. The swimming-associated illness rate was determined by subtracting the gastrointestinal illness rate in nonswimmers from that for swimmers.
The EPA's evaluation of the bacteriological data indicated that using the fecal coliform indicator group at the maximum geometric mean of 200 organisms per 100 mL, as recommended in *Quality Criteria for Water* would cause an estimated 8 illness per 1,000 swimmers at freshwater beaches.

Additional criteria, using *E. coli* and *enterococci* bacteria analyses, were developed using these currently accepted illness rates. These bacteria are assumed to be more specifically related to poorly treated human sewage than the fecal coliform bacteria indicator. The freshwater equations developed by Dufour (1984b) were used to calculate new indicator densities corresponding to the accepted gastrointestinal illness rates.

It should be noted that these indicators only relate to gastrointestinal illness, and not other problems associated with waters contaminated with other bacterial or viral pathogens. Common swimming beach problems associated with contamination by stormwater include skin and ear infections caused by *Psuedomonas aeruginosa* and *Shigella*. National bacteria criteria have been established for contact with bacteria and are shown in Table 3.15. State standards usually also exist for fecal coliform bacteria. Typical public water supply standards (Alabama's are shown) are as follows:

(i) Bacteria of the fecal coliform group shall not exceed a geometric mean of 2,000/100 mL; nor exceed a maximum of 4,000/100 mL in any sample. The geometric mean shall be calculated from no less than five samples collected at a given station over a 30-day period at intervals not less than 24 hours. The membrane filter counting procedure will be preferred, but the multiple tube technique (five-tube) is acceptable.

(ii) For incidental water contact and recreation during June through September, the bacterial quality of water is acceptable when a sanitary survey by the controlling health authorities reveals no source of dangerous pollution and when the geometric mean fecal coliform organism density does not exceed 100/100 mL in coastal waters and 200/100 mL in other waters. When the geometric mean fecal coliform organism density exceeds these levels, the bacterial water quality shall be considered acceptable only if a second detailed sanitary survey and evaluation discloses no significant public health risk in the use of such waters. Waters in the immediate vicinity of discharges of sewage or other wastes likely to contain bacteria harmful to humans, regardless of the degree of treatment afforded these wastes, are not acceptable for swimming or other whole body water-contact sports.

Standards for fish and wildlife waters are similar to the above standard for a public water supply, except part (i) has different limits: "Bacteria of the fecal coliform group shall not exceed a geometric mean of 1,000/100 mL on a monthly average value; nor exceed a maximum of 2,000/100 mL in any sample." Part (ii) is the same for both water beneficial uses.

The EPA full body contact recreation water quality criteria are as follows:

Marine waters: "Based on a statistically sufficient number of samples (generally not less than 5 samples equally spaced over a 30-day period), the geometric mean of the enterococci densities should not exceed 35 per 100 mL." (EPA 1986)

Fresh waters: "Based on a statistically sufficient number of samples (generally not less than 5 samples equally spaced over a 30-day period), the geometric mean of the bacterial densities should not exceed one or the other of the following (Note that only one indicator should be used. The regulatory agency should select the appropriate indicator for its conditions.):

E. coli, at a concentration of 126 per 100 mL, or
Enterococci, at a concentration of 33 per 100 mL." (EPA 1986)

Table 3.15. U.S. EPA Water Quality Criteria for Swimming Waters

	Marine Waters	Fresh Waters
Main EPA research reference	Cabelli 1983	Dufour 1984b
Acceptable swimming associated gastroenteritis rate (per 1,000 swimmers)	Increase of 19 illnesses per 1,000 swimmers	Increase of 8 illnesses per 1,000 swimmers
Comparable fecal coliform exposure	200 fecal coliforms/100 mL	200 fecal coliforms/100 mL
Steady state geometric mean indicator density	35 enterococci/100 mL	33 enterococci/100 mL, or 126 *E. coli*/100 mL
Single sample limits:		
Designated bathing beach area	104 enterococci/100 mL	61 enterococci/100 mL, or 235 *E. coli*/100 mL
Moderate full body contact recreation	124 enterococci/100 mL	89 enterococci/100 mL, or 298 *E. coli*/100 mL
Lightly used full body contact recreation	276 enterococci/100 mL	108 enterococci/100 mL, or 406 *E. coli*/100 mL
Infrequently used full body contact recreation	500 enterococci/100 mL	151 enterococci/100 mL , or 576 *E. coli*/100 mL

EPA 1986

Water Environment & Technology (1997) reported the new EPA BEACH (Beaches Environmental Assessment, Closure, and Health) program to help states strengthen recreational water quality monitoring programs. During the summer of 1995, state and local governments reported closing or issuing warnings for 4,000 beaches because of suspected dangerous conditions associated from wastewater and stormwater contamination of swimming areas. A new testing method for *Escherichia coli* and enterococci bacteria was introduced that gives results in 1 day instead of the typical 2 days testing period. They also reported that these bacteria better correlate with human health risks. The EPA will survey state and local health and environmental directors about the quality of freshwater and marine recreational areas and post the results on a new Beach Watch Web site (http://epa.gov/OST/beaches) by the summer of 1998.

Other Human Health Risks Associated with Protozoa and other Microorganisms

Protozoa became an important public issue with the 1993 *Cryptosporidium*-caused disease outbreak in Milwaukee when about 400,000 people become ill from drinking contaminated water. Mac Kenzie, *et al*. (1994) prepared an overview of the outbreak, describing the investigation on the causes of the illness and the number of people affected. They point out that *Cryptosporidium*-caused disease in humans was first documented in 1976, but had received little attention and no routine monitoring. *Cryptosporidium* now is being monitored routinely at many areas and is the subject of much research concerning its sources and pathways. At the time of the Milwaukee outbreak, both of the city's water treatment plants (using water from Lake Michigan) were operating within acceptable limits, based on required monitoring. However, at one of the plants (which delivered water to most of the infected people), the treated water experienced a large increase in turbidity (from about 0.3 NTU to about 1.5 NTU) at the time of the outbreak that was not being well monitored (the continuous monitoring equipment was not functioning, and values were only obtained every 8 hours). More than half of the residents receiving water from this plant became ill. The plant had recently changed its coagulant from polyaluminum chloride to alum and equipment to assist in determining the correct chemical dosages was not being used. The finished water had apparently relatively high levels of cryptosporidium because some individuals became ill after only drinking less than 1 L of water. *Cryptosporidium* oocysts have often been found in untreated surface waters, and it was thought that *Cryptosporidium* oocysts entered the water treatment supply before the increase in turbidity was apparent. Mac Kenzie, *et al.* (1994) point out that monitoring in the United Kingdom has uncovered sudden, irregular, community-wide increases in cryptosporidiosis that were likely caused by waterborne transmission. They also stated that the source of the *Cryptosporidium* oocysts was speculative, but could have included cattle feces contamination in the

Milwaukee and Menomonee Rivers, slaughterhouse wastes, and human sewage. The rivers were also swelled by high spring rains and snowmelt runoff that may have aided the transport of upstream *Cryptosporidium* oocysts into the lake near the water intakes.

The Journal of the American Water Works Association has published numerous articles on protozoa contamination of drinking water supplies. Crockett and Haas (1997) describe a watershed investigation to identify sources of *Giardia* and *Cryptosporidium* in the Philadelphia watershed. They describe the difficulties associated with monitoring *Cryptosporidium* and *Giardia* in surface waters because of low analytical recoveries and the cost of analyses. Large variations in observed protozoa concentrations made it difficult to identify major sources during the preliminary stages of their investigations. They do expect that wastewater treatment plant discharges are a major local source, although animals (especially calves and lambs) are likely significant contributors. Combined sewer overflows had *Giardia* levels similar to raw sewage, but the CSOs were much less than the raw sewage for *Cryptosporidium*. LeChevallier, *et al*. (1997) investigated *Giardia* and *Cryptosporidium* in open reservoirs storing finished drinking water. This gave them an opportunity to observe small increases in oocyst concentrations associated from nonpoint sources of contamination from the highly controlled surrounding area. They observed significantly larger oocyst concentrations at the effluent (median values of 6.0 *Giardia*/100 L and 14 *Cryptosporidium*/100 L) in the reservoirs than in the influents (median values of 1.6 *Giardia*/100 L and 1.0 *Cryptosporidium*/100 L). No human wastes could influence any of the tested reservoirs and the increases were therefore likely caused by wastes from indigenous animals or birds, either directly contaminating the water, or through runoff from the adjacent wooded areas.

A Management Training Audioconference Seminar on *Cryptosporidium* and Water (MTA 1997) was broadcast in May of 1997 to familiarize state and local agencies about possible *Cryptosporidium* problems that may be evident after the EPA's Information Collection Rule begins in July of 1997. This regulation will require all communities serving more than 100,000 people to monitor their source water for *Cryptosporidium* oocysts. If the source water has more than 10 *Cryptosporidium* oocysts per liter, then the finished water must also be monitored. It is likely that many source waters will be found to be affected by cryptosporidium. The reviewed one study that found the percentage of positive samples of *Cryptosporidium* in lakes, rivers, and springs was about 50 to 60% and about 5% in wells. In contrast, the percentage of samples testing positive for *Giardia* was about 10 to 20% in lakes and rivers, and very low in springs and wells.

Special human health concerns have also been recently expressed about *Pfiesteria piscicida*, a marine dinoflagellate that apparently is associated with coastal eutrophication caused by runoff nutrients (Maguire and Walker 1997). This organism has gathered much attention in the popular press, usually called the "cell from hell" (Zimmerman 1998). It has been implicated as causing symptoms of nausea, fatigue, memory loss, and skin infections in south Atlantic coastal bay watermen. *Pfiesteria* and *Pfiesteria*-like organisms have also been implicated as the primary cause of many major fish kills and fish disease events in Virginia, Maryland, North Carolina, and Delaware. In August of 1997, hundreds of dead and dying fish were found in the Pocomoke River, near Shelltown, Maryland, in the Chesapeake Bay, prompting the closure of a portion of the river. Subsequent fish kills and confirmed occurrences of *Pfiesteria* led to further closures of the Manokin and Chicamacomico Rivers. The Maryland Department of Health and Mental Hygiene also presented preliminary evidence that adverse public health effects could results from exposure to the toxins released by *Pfiesteria* and *Pfiesteria*-like organisms. The increasing numbers of fish kills of Atlantic menhaden (an oily, non-game fish) motivated Maryland's governor to appoint a Citizens *Pfiesteria* Action Commission. The Commission conveyed a forum of noted scientists to examine the existing information on *Pfiesteria*. The results of the forum were adopted by the Commission and included in its final report (available on the Maryland Department of Natural Resources' website: http://quantum.gacc.com/dnr/Hot/contents.html).

Pfiesteria has a complex life cycle, including at lease 24 flagellated, amoeboid, and encysted stages. Only a few of these stages appears to be toxic, but their complex nature makes them difficult to identify by nonexperts (Maguire and Walker 1997). *Pfiesteria* spends much of its life span in a nontoxic predatory form, feeding on bacteria and algae, or as encysted dormant cells in muddy sediment. Large schools of oily fish (such as the Atlantic menhaden) trigger the encysted cells to emerge and excrete toxins. These toxins make the fish lethargic, so they remain in the area where the toxins attack the fish skin, causing open sores to develop. The *Pfiesteria* then feed on the sloughing

fish tissue. Unfortunately, people working in the water during these toxin releases may also be affected (Zimmerman 1998).

Researchers suggest that excessive nutrients (causing eutrophication) increase the algae and other organic matter that the *Pfiesteria* and Atlantic menhaden use for food. The increased concentrations of *Pfiesteria* above natural background levels increase the likelihood of toxic problems. Maguire and Walker (1997) state that other factors apparently involved include stream hydraulics, water temperature, and salinity. They feel that *Pfiesteria* is only one example of the increasing threats affecting coastal ecosystems that are experiencing increased nutrient levels. Most of the resulting algal blooms only present nuisance conditions, but a small number can result in human health problems (mostly as shellfish poisonings). The increased nutrient discharges are mostly associated with agricultural operations, especially animal wastes from large poultry and swine operations. In the Pocomoke River watershed, the Maryland Department of Natural Resources estimates that about 80% of the phosphorus and 75% of the nitrogen load is from agricultural sources. Urban runoff may also be a causative factor of eutrophication in coastal communities, especially those having small enclosed coastal lagoons or embayments, or in rapidly growing urban areas. Zimmerman (1998) points out that the Chesapeake Bay area is one of the country's most rapidly growing areas, with the population expected to increase by 12 percent by the year 2010.

SSO Discharges Along The Cahaba River, Near Birmingham, AL

Many of the local municipal wastewater treatment plants in Jefferson County, Alabama, have experienced very large wet weather associated SSO discharges. In addition, many of the smaller treatment facilities were operating rather poorly. A court settlement was reached in September, 1996, requiring modifications to the collection and treatment systems. Some of these modifications have been accomplished, while others will be completed by 2007. The historical effects of these overflows and poor treatment has been dramatic. During dry summer months, for example, we have measured the contributions of (poorly) treated sewage in the Little Cahaba River (a tributary to our local water supply) to be about 25% of the total river flow. During wet weather, some of the SSO discharges at the treatment plants have been greater than 10 times the facility capacity. The most recent SSO discharges at the treatment plants have been solely associated with I/I during heavy rains exceeding the facility's treatment capacity, except for one event associated with a power failure.

During a recent reporting period (from November 1995 to September 1997), 315 SSO discharges have been reported in Jefferson County. Most of these have occurred at relief points along 5 collection systems, but 84 were reported at 4 local treatment facilities. These are shown on Table 3.1.

Table 3.1. Volume and Number of SSO Events at WWTPs along the Cahaba River, AL

Treatment plant and collection system	Plant capacity (MGD)	# of SSOs at plant/yr	Volume of SSOs at plant (MG/yr)	Average SSO volume at plant (MG)	# of SSOs in collection system per year	Volume of SSOs in collection system (MG/yr)	Average SSO volume in collection system (MG)	Max. SSO volume (MG)	Total SSO as a % of annual plant discharge
Turkey Creek	4	4	47	13	11	small	small	25	3.2
Cahaba	12	14	250	18	27	152	6	80	9.2
5-mile	20	0	0	0	66	190	3	52	2.6
Village	60 (340 peak for wwf)	20	580	29	6	small	small	264	2.7
Valley	65	6	64	10	12	small	small	33	0.3

There are 40 NPDES permits for municipal wastewater disposal in the Cahaba River basin for which relatively detailed information is available. These plants range from 0.01 to 12 MGD. A number of these small facilities have undergone modifications in recent years to better accommodate wet weather flows. These modifications have

typically included detailed I/I studies and collection system repairs, surge tanks for short-term storage of wet weather flows, and expansion of the treatment plant capacities.

Jefferson County SSO Settlement

Fresh domestic sewage has a slightly soapy or oily odor, is cloudy and contains recognizable solids, often of a considerable size. Stale sewage has a pronounced odor of hydrogen sulfide, is dark gray, and contains smaller but occasionally recognizable solids. The change from fresh to stale requires 2 to 6 hours at a temperature of 20^{o}C, with the time depending primarily on the concentration of organic matter. As it ages, its pH tends to drop because of the production of organic acids by bacterial metabolism. When the wastewater is treated aerobically or undergoes natural stabilization, these acids are oxidized to carbon dioxide and water and the pH will rise.

The Cahaba River, a 190-mile river that flows from a mountainside near Springville (about thirty-five mile northeast of downtown Birmingham). According to Mike Bolton of the Birmingham News in his series about the Cahaba River (entitled *A River in Crisis*), "The Cahaba River begins as a trickle from a mountainside….The river is so vulnerable here that scratching the earth with a walking stick or kicking over a single stone can alter its course…. More than 190 miles to the southwest in rural Dallas County, the same Cahaba – here a wide, rolling river that once allowed steamboat navigation – empties into the Alabama River and ceases to be." The river drains 1,870 square miles of St. Clair, Jefferson, Shelby, Bibb, Tuscaloosa, Chilton, Perry and Dallas counties. Under the latest ADEM regulations, parts of the Cahaba River have been classified as an Outstanding Alabama Water (OAW), which means that the water quality criteria for the river is more stringent than that of many other water bodies in Alabama. Prior to its classification as an OAW, the Cahaba River was classified, depending on the location along the waterway, as either a 'Public Water Supply,' 'Swimming' or 'Fish & Wildlife,' classifications that it still maintains in the Birmingham metropolitan area. This river, however, is not just used for recreation. It is the source of approximately 50% of the drinking water for the Birmingham metropolitan area. It supplies water for about one-half million people. It also is the discharge point for wastewaters from many industries and municipal wastewater treatment plants. On an average day in 1996, 26 million gallons of treated sanitary wastewater, 16 million gallons of that from the Birmingham area, are discharged to the Cahaba by 24 municipal and 16 privately owned sewage treatment plants. There are also more than one hundred industries that have one 176 outfalls to the Cahaba or its tributaries.

The Clean Water Act provides relief for people who are adversely affected by the discharge of pollutants into a water of the U.S. Violators of the Clean Water Act, including those who violate their permit conditions, may be subject to a civil penalty not to exceed $25,000 per day for each violation. This penalty shall be determined by the court after considering the seriousness of the violation(s), the economic benefit (if any) resulting from the violation, history of violations, good-faith efforts to comply, and the economic impact of the penalty on the violator. This penalty does not include the cost for correcting the violation if it has not been corrected at the time of the lawsuit. Whenever a municipality is sued under the Clean Water Act, the State automatically becomes a party in the suit. This provision is there to ensure that the State is motivated to monitor municipal discharges.

On November 11, 1993, three citizen plaintiffs, R. Allen Kipp, Jr., Edward E. Angwin and Betsy B. Angwin, filed a complaint with the U.S. District Court, Northern District of Alabama Southern Division, alleging that Jefferson County was in violation of the Clean Water Act because they have discharged pollutants without the required NPDES permits (as sanitary sewer overflows) and have violated the NPDES permits that they do possess (bypassing the treatment plants with part of the plant influent during times of high flow). The Cahaba River Society filed its Motion to Intervene and Complaint in Intervention on March 9, 1994, and the EPA filed its complaint with the court on December 6, 1994. All three citizen plaintiffs are recreational users of the Cahaba River, as well as users of the drinking water provided from it. The Angwins also live and own property along the Cahaba. According to Mike Bolton in his series *A River in Crisis*, "Plastic grocery bags and trash bags hang eight feet high in trees along the river. Bends in the river look like landfills because of jams of old tires, car batteries, orange and white roadside construction barrels, plastic bottles, milk cartons, foam coffee cups, plastic swimming pools and tennis balls."

Alabama Department of Environmental Management (ADEM) records have shown that many of the violations continued after the lawsuit was filed. During January through March 1995 (the heaviest flooding season and a year after the suit was filed), Jefferson County released 271 million gallons of raw or partially treated sewage into the Cahaba. Jack Swann, head of Jefferson County Environmental Services, has acknowledged that there are releases of

untreated or partially treated sewage, but he questions whether the problem is as great as painted by the Cahaba River Society and the citizen plaintiffs. “These releases are done only during high flow periods,” Jack Swann said to the *Birmingham News*. “The river is running flooded by then. This sewage is far more diluted than it usually is. It’s almost clear.” “This influx of sewage causes numerous problems,” said Randy Haddock, field director of the Cahaba River Society. “One is the amount of nutrients and toxins it adds to the water. It causes algae blooms that release oxygen during the day and remove oxygen at night. That results in greatly varying levels of oxygen in the water and that lower swing can hurt aquatic wildlife.” EPA and ADEM say the upper 100 miles of the Cahaba are unsafe for swimming, but no signs are posted to warn swimmers. The other problem in the Cahaba in the Jefferson-Shelby county area is that in the summer, the volume of water withdrawn for drinking water is approximately equal to the total flow of the river. On some days, flow over the Highway 280 dam is negligible and the only water that is in the river below the dam is treated sewage. According to Haddock, “the river below the dam virtually goes dry for weeks at a time during the summer months, and that means no oxygenated water flowing downstream.”

The treatment plants listed in the following table, Table 3.2, are the plants owned by Jefferson County, along with their design treatment capacities:

Table 3.2. Jefferson County Wastewater Treatment Plants

LOCATION	FLOW CAPACITY (MGD)
Village Creek Wastewater Treatment Plant, Ensley	60
Valley Creek Wastewater Treatment Plan, Bessemer	65
Turkey Creek Wastewater Treatment Plant, Pinson	4
Warrior Wastewater Treatment Plant, Warrior	0.1
Prudes Creek Wastewater Treatment Plant, Graysville	0.6
Leeds Wastewater Treatment Plant, Leeds	10
Trussvile Wastewater Treatment Plan, Trussvile	4
Cahaba River Treatment Plant, Hoover	16
Five Mile Creek Wastewater Treatment Plant, Fultondale	20

Much of the problem with the county’s sewage treatment is not the capacity or capability of the treatment plant itself. The plants are generally overloaded only during heavy rains and flooding due to inflow and infiltration into the collection system. Design inflow and infiltration values are quickly exceeded in the system due to cracks in old underground sewage collector lines that encourage water to leak into the lines. “Eventually, the volume of water coming to the plants is so great, all they can do is pass it through a screen to remove the bigger objects like plastics, tampons, cigarette butts and condoms,” said Haddock to the *Birmingham News*. In order not to damage the collection system and the treatment plant, engineered bypasses have been installed.

Bypasses are defined under the Clean Water Act as “any diversion of wastewater away from or around a secondary treatment facility in order to limit the flow directed to such facilities or portions thereof….” Automatic bypasses are defined as “a wastewater collection system relief valve, flap gate or other device that operates automatically during periods of high flow when the collection line is surcharged and which allows untreated wastewater to be diverted to a receiving stream without reaching a wastewater treatment plant.” Jefferson County has the ability to do both types of bypassing during periods of high flow. They have flap gates to relieve excess pressure and volume in the collection system when necessary and they have the ability to divert part of the flow leaving the preliminary treatment directly to the disinfection unit before discharging a combination of treated and untreated sewage to the receiving water. “Flap valves serve the function of preventing the sewer system from being damaged,” Swann explained. “Without them, it would blow the system apart. It would blow the tops off manholes. It’s not pretty and not something we’re proud of. We haven’t installed flap gates in the past 20 years, and we’ve eliminated 45 to 50 of them in recent years.” Haddock responds by saying, “When the influx of water becomes too great, the flap gates open and stay open days at a time.” Several of the largest sewage treatment plants frequently exceed their Clean Water Act pollutant discharge permits. In addition, bypasses of untreated wastes at this plants are so great that one unnamed ADEM official called them “the worst in the state in terms of frequency and volume.” The US Fish and Wildlife service has cited bypass problems as a major reason for the chemical and biological decline of Cahaba over the past 20 years. Among the sites mentioned as engineered/automatic bypass locations are four sewer overflow points or flapgates near Tarrant, Pinson, and Hoover. In Tarrant, the wastewater sometimes enters at Barton Branch

and Tarrant Springs of Alabama Highway 79. Two other flapgates are at Horsepens, located in Hoover at the intersection of Interstates 65 and 459 (in the areas of Bent River Road), and at Hurricane Branch.

The County decided to settle the lawsuit out of court and the attorneys for both sides, along with representatives of the regulatory agencies, negotiated a three-phase settlement that included termination dates for bypassing. Jefferson county's existing sewer system suffers from many serious problems. The primary action of the settlement is the Remedial Action Plan (RAP). The RAP was developed to end illegal sewage bypassing and overflows by replacing or renovation decaying sewer lines in older neighborhoods, expanding capacity of the collection system and treatment plants, and renovating the county's treatment plans so they will come into compliance with the County's NPDES permits under the Clean Water Act. A time table, Table 3.3, was established for the elimination of sewer bypassing in various sections of the county's system.

Table 3.3. Sewer Bypass Termination Dates.

DATE	PLANTS AND SYSTEMS
2001	Cahaba, Leeds, Trussville systems and plants
2002	Barton & Tarrant Branches flapgates
2003	Village Creek Treatment Plant
2004	Village Creek system
2005	Valley & Five Mile Creek Treatment Plants
2006	Village Creek system east, Five Mile system, Valley Creek system
2007	Turkey Creek, Prudes Creek, Warrior systems and plants

The goal of the first phase is to identify the scope, time frame, methodology and resources needed for evaluation of the condition of the collection system, sources of inflow and infiltration, and development of remedial measures. Preliminary work will begin in this phase on the Preliminary Sewer System Analysis, the Inflow & Infiltration Plan, the Sewer System Evaluation Plan, the Capacity Analysis Plan, the Comprehensive Performance Evaluation Plan, the Water Quality Monitoring Plan, and the Waste Treatment System Capital Improvement Plan. Studies to show the location and magnitude of the problem is a part of the second phase of the RAP. This will include determining where the system is deteriorated, where stormwater is entering the collection system, and what the remaining capacity is at the treatment plants, as compared to needs. This phase will see the production of Infiltration/Inflow Analysis Reports, Sewer System Evaluation Survey, Capacity Analysis Reports, Capacity Improvement Schedules, Comprehensive Performance Evaluation Reports, and Performance Evaluation Plans. All documents generated under this settlement must be approved by ADEM and EPA Region IV. After they are approved, they must be available for public review at the Birmingham Public Library.

In March, 1997, the Environmental Services Department of Jefferson County presented the report "Comprehensive Performance Evaluation and Hydraulic Analyses: Jefferson County Wastewater Treatment Plants" for public review. This report evaluated the performance of each of the nine Jefferson County Wastewater Treatment Plants (WWTPs) to determine the treatment capacity and performance of each of the WWTPs and identify needed items for improvement. This report covered the results of Comprehensive Performance Evaluations (CPEs) for five of the WWTP and hydraulic analyses for the remaining four. The results contained in this report are discussed below.

The Village Creek Wastewater Treatment Plant, a 60 MGD conventional, two stage activated sludge plant with both anaerobic and aerobic sludge digestion, does not have sufficient capacity for sludge digestion and utilization and it does not have sufficient capacity in times of high flow due to inflow and infiltration. The Valley Creek Wastewater Treatment Plant, a 65 MGD step-feed, two-stage activated sludge plant with two stage anaerobic sludge digestion, needs to upgrade its sludge digestion and stabilization facility and, like the Village Creek WWTP, does not have sufficient capacity during high flow periods. The Turkey Creek Wastewater Treatment, a 4.0 MGD extended aeration plant, does not have sufficient capacity to adequately dry sludge, disinfect the effluent during periods of high flow and to hydraulically pass peak flow volumes through the headworks facilities of the plant. The Warrior WWTP, a 0.1 MGD extended aeration, plant, was not identified as having any problems. The Prudes Creek WWTP, a 0.6 MGD extended aeration plant, also was not identified as having any problems. The Leeds WWTP, a 2 MGD plant, like the Warrior and Prudes Creek plants, was identified as having no problems with capacity. The new Trussville WWTP, a 4 MGD plant, is not predicted to have capacity problems when construction is complete. The Cahaba River WWTP, a 16 MGD activated sludge plant, is currently under construction to upgrade its capacity and the upgrade is expected to remove any capacity problems that the plant will encounter.

The general part of this report explicitly outlines the problem for all the Jefferson County plants: wet weather flow. The plants do not have sufficient capacity to treat a volume of sewage and rainwater which is three to four times greater than the design maximum. The collection system studies begun over the past two years have provided hard data which supports the position of Cahaba River Society that meaningful efforts to correct today's sewer problems in Jefferson County must begin with an intensive I&I correction program. Peak flow reductions of fifty percent or more may well be possible with this program, since results similar to these have been seen recently in Nashville, Indianapolis and other cities with serious I&I problems.

The goal of the third phase of the sewer settlement is the implementation of sewer rehabilitation and replacement as necessary and the collection of the data required by the Water Quality Monitoring Program. The third phase is only now beginning. Another part of the sewer settlement was a Waste Treatment System Capital Improvement Plan to identify all ongoing and proposed sewer system projects. The question of whether, when, and where to provide sewer service in the Upper Cahaba Basin are some of the most important that local public officials address today. Before it can be determined which combination of wastewater management alternatives are best, the present and future uses of land in the basin must be taken in account. Some of the more promising alternatives are the following:

- Advanced wastewater treatment
- "Cluster" system
- Flow augmentation
- Relocation of points of discharge
- Minimization of waste flow
- Reuse of treated wastewater

Advanced wastewater treatment is the most direct mean of minimizing of water pollution, but many times it is not a panacea. Model simulations in the Cahaba River Basin have indicated that even the most highly sophisticated treatment system would not preserve all the Cahaba's waters. The growth in the area and the need for additional drinking water for the Birmingham metropolitan area prevent this from being the solution, although it may be incorporated into a final solution. These facilities are very expensive to build and operate. "Cluster system" collect wastewater and transport it to a neighborhood treatment facility. Cluster systems are usually considered to be neighborhood septic tanks serving no more than a few dozen homes. Flow augmentation is dilution that may not be the "solution to pollution," but, unfortunately, in streams with low flow and that receive waste discharges, there are very few solutions. Various sources of stream flow have been mentioned as possibilities in the Upper Cahaba Basin, including diversion from the Coosa River Basin, construction of flow augmentation dams in the area, and decreasing or removing the drinking water intake from the river. Relocation, or piping, of raw and treated wastes in the Cahaba is another mentioned possibility that offers several advantages. All treated wastes introduced upstream of the Water Works Board intake have an effect on the quality of the water supply and mean higher drinking water treatment costs. Relocation is also a way to discharge the treated wastewater into a receiving water with a better assimilative capacity. Water conservation to reduce wastewater flow is an attractive idea that unfortunately is not always feasible because of the need to get all the citizens to participate. The final alternative is the reuse of treated water. Water reuse is becoming more attractive in areas where there is not sufficient water and is being investigated locally by the Birmingham Water Works Board for their Riverview Treatment Plant because they are planning to double its capacity currently without the ability to increase the flow of their discharge. If they are not allowed to increase their discharge, the alternative is to use the treated water to irrigate a timberland, an alternative they are seriously considering. The other choice is to use the water to irrigate golf courses or landscape plants.

Unfortunately for the Cahaba River advocates, they feel that they get very little support from county leaders in maintaining a clean river. Mary Buckelew, president of the Jefferson County Commission, said many of the county's problems are overblown by the media. "People get these feelings that you can't go near the river, like if you go there, you might die. They envision toilet paper hanging all around the river," Buckelew said. "We're slowly but surely getting our act together. We need to do that (better control sewage discharges) in such a way that we don't kill business." Swann said the county is working on the problem "We've spent in excess of $500 million in the past 20 years repairing, enlarging and improving our sewage system and plants. The question is, how good do we want

them to be? It's like roads. Do we want to pour 12 inches of concrete and never have a pothole and pay $2 for a gallon of gasoline to pay for roads like that?"

The Washington-based nonprofit environmental group American Rivers has named the Cahaba River as one of the Top 10 most endangered rivers in North America. With census figures showing 780,000 people living in the Cahaba watershed today and projections of more than 1.4 million people living in the watershed by 2050, Jefferson and Shelby counties are forced to look at the future. The Birmingham Water Works board has proposed their own watershed protection ordinance solely to protect the drinking water for approximately half of the metropolitan area's population. The Water Quality Monitoring Program being implemented by Jefferson County will collect data on rainfall and inflow and infiltration as well as data on the water quality (pH, fecal coliforms, turbidity, specific conductance, and dissolved oxygen) in the streams receiving the discharge from their sewage treatment plants. The other problem affecting the Cahaba River is the huge amounts of stormwater runoff from development in Birmingham area which has eroded the banks significantly. Floods also can leave the river muddy for weeks at a time, making fishing virtually impossible. To alleviate part of this problem and to prevent paying large fines to the U.S. Treasury, the County is developing a Supplemental Environmental Project (SEP) which will include the following:

- greenways along the river's edge
- Ruffner Park expansion by 300 acres
- Bayview Lake nature preserves
- Countywide Master Plan
- purchase of streamside land for conservation easements
- restoration of streambanks in older, urban areas
- creation of Black Warrior-Cahaba Rivers Land Trust

This project is designed not only to preserve the river's integrity, but also to provide protected recreational areas for the use of Jefferson County citizens.

Evidence of Sewage Contamination of Urban Streams Due to Inappropriate Discharges to Storm Drains

The following case studies present summaries of various studies conducted throughout the U.S. that investigated contamination of urban streams by illicit discharges that were only supposed to be receiving stormwater discharges.

Nationwide

A number of issues emerged from the individual projects of the U.S. EPA's Nationwide Urban Runoff Program (NURP) (EPA 1983). One of these issues involved illicit connections to storm drainage systems and was summarized as follows in the Final Report of the NURP executive summary: "A number of the NURP projects identified what appeared to be illicit connections of sanitary discharges to stormwater sewer systems, resulting in high bacterial counts and dangers to public health. The costs and complications of locating and eliminating such connections may pose a substantial problem in urban areas, but the opportunities for dramatic improvement in the quality of urban stormwater discharges certainly exist where this can be accomplished. Although not emphasized in the NURP effort, other than to assure that the selected monitoring sites were free from sanitary sewage contamination, this BMP (Best Management Practice) is clearly a desirable one to pursue." The illicit discharges noted during NURP were especially surprising, because the monitored watersheds were carefully selected to minimize factors other than stormwater. Presumably, illicit discharge problems in typical watersheds would be much worse. Illicit entries into urban storm sewerage were identified by flow from storm sewer outfalls following substantial dry periods. Such flow could be the result of direct "illicit connections" as mentioned in the NURP final report, or could result from indirect connections (such as contributions from leaky sanitary sewerage through infiltration to the separate storm drainage). Many of these dry-weather flows are continuous and would therefore also occur during rain induced runoff periods. Pollutant contributions from the dry-weather flows in some storm

drains have been shown to be high enough to significantly degrade water quality because of their substantial contributions to the annual mass pollutant loadings to receiving waters.

Washtenaw County (Ann Arbor), MI

From 1984 to 1986, Washtenaw County, Michigan, dye-tested 160 businesses in an effort to locate direct illicit connections to the county stormwater sewerage (Murray 1985; Schmidt and Spencer 1986; Washtenaw County 1988). Of the businesses tested, 61 (38%) were found to have improper storm drain connections. The Huron River Pollution Abatement Program was the most thorough investigation of such improper connections. Beginning in 1987, 1067 businesses, homes and other buildings located in the Huron River watershed were dye tested. The following results were reported. Illicit connections were detected at 60% of the automobile related businesses inspected, including service stations, automobile dealerships, car washes, and auto body and repair shops. All plating shops inspected were found to have improper storm drain connections. Additionally, 67% of the manufacturers tested, 20% of the private service agencies, and 88% of the wholesale/retail establishments tested were found to have improper storm sewer connections. Of 319 homes dye tested, 19 were found to have direct sanitary connections to storm drains. The direct discharge of rug cleaning wastes into storm drains by carpet cleaners was also noted as a common problem. Several surveys, beginning as early as 1963, identified bacterial and chemical contamination of the Allen Creek storm drainage system. Studies in 1963, 1978 and 1979 found that discharges from the Allen Creek storm drain contained significant quantities of fecal coliform and fecal streptococci. The 1979 study also documented high pollutant loads of solids, nitrates and metals. A large number of inappropriate storm drain connections originating from businesses were found, especially within automobile related facilities. Chemical pollutants, such as detergents, oil, grease, radiator wastes and solvents were causing potential problems.

The elimination of these storm drain connections prevented thousands of gallons of contaminated water from entering the Huron River from the Allen Creek storm drainage system annually. Eight sampling locations along the main stem and major lateral branches of the storm drainage system were established and monitored for 37 chemicals during rain events. From 1984 to 1986, 32 (86%) of these chemicals showed a decrease in concentrations while only 2 (5%) showed an increase. In spite of this improvement, chemical concentrations in the stormwater discharges at the Allen Creek outfall were still greater than those from the control station much of the time.

Fort Worth, TX

This program has been underway since June of 1985 (Falkenbury 1987). Investigations to date indicate few direct connections from industries to storm drains. Storm runoff, in addition to illegal dumping, accidental spills and direct discharges into the street or adjacent creeks seem to account for the majority of the contaminants entering the storm drainage system. Major problems stemmed from septic tanks, self-management of liquid wastes by industry and construction of municipal overflow bypasses from the sanitary sewer to the storm drains. The success of this program was judged by a decline in the number of undesirable features at the target outfalls. An average of 44 undesirable observations per month were made in 1986 (522 total), compared to an average of 21 undesirable observations per month in 1988.

Inner Grays Harbor, WA

In 1987, an inspection of the 90 urban stormwater outfalls draining into Inner Grays Harbor in Washington revealed 29 (32%) flowing during dry weather (Beyer, *et al*. 1979; Pelletier and Determan 1988). A total of 19 outfalls (21%) were described as suspect, based on visual observation and/or anomalous pollutant levels, as compared to those expected in typical urban stormwater runoff characterized by NURP. At least one storm drain system was later found to receive a residential sanitary sewage connection which has since been corrected. This drain exhibited no unusual visual characteristics, but was found to have atypical pH and total suspended solids levels. Notably, fecal coliform levels were within the typical range expected for stormwater.

Sacramento, CA

A Sacramento, California, investigation of urban discharges identified commercial as well as domestic discharges of oil and other automobile related fluids as a common problem based on visual observations (Montoya 1987). Montoya found that slightly less than half the water discharged from Sacramento's stormwater drainage system was not directly attributable to precipitation. Most of this water comes from unpermitted sources, including illicit and/or inappropriate entries to the storm drainage system.

Bellevue, WA

During the Bellevue, Washington Urban Runoff Project baseflows as well as stormwater from two residential urban basins were monitored (Pitt 1985; Pitt and Bissonnette 1984). The areas included in this study, Surrey Downs and Lake Hills, are about 5 km apart and each covered an area of about 40 ha. Both were fully developed, with predominantly single family residences. No septic tanks were present in either area and the storm drainage systems were thoroughly mapped and investigated to ensure no non-stormwater discharges to storm drainage systems or obvious illegal discharges. The Bellevue, Washington, NURP project also summarized the reported incidents of intermittent discharges and dumpings of pollutants into the local storm drainage system. During a three year period of time, about 50 citizen contacts were made to the Bellevue Storm and Surface Water Utility District concerning water quality problems. About 25 percent of the complaints concerned oil being discharged into storm drain inlets. Another important category of complaints was for aesthetic problems, such as turbid or colored water in the creeks. Various industrial and commercial discharges into the storm drainage system were detected. Concrete wastes flushed from concrete trucks at urban job sites were a frequently occurring problem. Cleaning establishment discharges into creeks were also a common problem. Vehicle accidents also resulted in discharges of gasoline, diesel fuel, hydraulic fluids, and lawn care chemicals into the storm drain inlets.

Boston, MA

A field screening program was conducted to determine the relative levels of contamination at various locations in the Stony Brook drainage system (Metcalf and Eddy 1994). During eight days of dry-weather sampling, numerous inappropriate discharges of sanitary sewage into the drainage system were identified using the investigative procedures developed by Pitt, *et al.* (1993) and a modified flow chart approach.

Minneapolis/St. Paul, MN

Water Environment & Technology (1996a) reported that the fecal coliform counts decreased from about 500 counts/100 mL to about 150 counts/100 mL in the Mississippi River after the sewer separation program in the Minneapolis and St. Paul area of Minnesota. Combined sewers in 8,500 ha were separated during this 10-year, $332 million program.

Toronto, Ontario

The Toronto Area Watershed Management Strategy Study (TAWMSS) monitored and characterized both stormwater and baseflows (Pitt and McLean 1986 and GLA 1983). The project involved intensive monitoring in two test areas. The Emery catchment area, located near the City of North York, covered approximately 154 ha with predominantly “medium” industrial land uses (processing goods for final consumption). The Thistledown catchment, located in the City of Etobicoke, covered approximately 39 ha with residential and commercial land uses. During cold weather, the increases in dissolved solids were quite apparent in baseflows and snowmelt for both study catchments. This increase was probably caused by high chlorides from road salt applications. In contrast, bacteria populations were noticeably lower in all outfall discharges during cold weather. Nutrient and heavy metal concentrations at the outfalls remained fairly constant during cold and warm weather. Either warm- or cold-weather baseflows were responsible for most of the yields for many constituents from the industrial catchment. These constituents included runoff volume, phosphorus, total Kjeldahl nitrogen, chemical oxygen demand and chromium. Important constituents that had high yields in the baseflow from the residential/commercial catchment included total solids, dissolved solids, chlorides, and fecal coliform and *Pseudomonas aeruginosa* bacteria.

Gartner Lee and Associates, Ltd. conducted an extensive survey of dry-weather flows in storm drainage systems in the Humber River watershed (Toronto) in an attempt to identify the most significant urban runoff pollutant sources. About 625 outfalls were sampled two times during dry-weather, with analyses conducted for many pollutants, including organics, solids, nutrients, metals, phenols, and bacteria. About 59% had dry-weather flows, and about 33% of the outfalls were discharging at rates greater than 1 L/sec. The dry-weather flows were found to contribute significant loadings of nutrients, phenols, and metals, compared to upstream conditions. About 10 to 14 percent of the outfalls were considered significant pollutant sources. Further investigations identified many industrial and sanitary sewage non-stormwater discharges into the storm drainage. An apartment building with the sanitary drains from eight units illegally connected to the storm drainage system was typical of the problems found. Other problem

areas were found in industrial areas, including yard storage of animal hides and yard runoff from meat packing plants.

Ottawa, Ontario

Visual inspection of stormwater pipes discharging to the Rideau River (Ontario) found leakage from sanitary sewer joints or broken pipes to be a major source of storm drain contamination (OME 1983). A study of the lower Rideau River in the Regional Municipality of Ottawa-Carleton was conducted to establish the causes of bacteriological water quality degradation in the urbanized reach of the river and to analyze the impacts of future urbanization. Earlier programs had identified and corrected many cross-connections between sanitary sewers and stormwater sewers. Bacteriological water quality improved, but swimming standards at beaches were still not obtained.

Birmingham, AL

During the development of the methods to investigate inappropriate discharges, a three-mile section of Village Creek in Birmingham, AL, was selected for field verification of the test methods (Pitt, *et al.* 1993, Pitt and Lalor 1998). The drainage area for this section of the creek contains about 4500 acres. Residential land use comprises approximately 88% of the total area, commercial land use approximately 8%, and industrial land use less than 1%. The majority of the drainage area is serviced by sanitary sewers, but some septic tanks are also used. A total of 65 stormwater outfalls were located. Outfall diameters ranged from 2 inches to 12 feet, excluding open ditches. All sites were visited at least 8 times during the field investigation period. Of these 65 outfalls, 48 (74%) were always dry, 6 (9%) had flow intermittently, and 11 (17%) were always flowing. Eighteen direct unpermitted discharges to the creek from nearby industries and commercial areas were also located; 10 (56%) were always dry, 6 (33%) had intermittent flow, and 2 (11%) were always flowing. The dry weather flows from two of the 65 outfalls were found to be mostly sanitary sewage, while the flows from another nine were predominately washwaters. The remaining outfalls with dry weather flows were mostly affected by natural waters (most likely groundwater infiltration) or leaking domestic water.

Periodic stream surveys of tributaries of the Cahaba River in the Birmingham area (mostly the Little Cahaba River, upstream of Lake Purdy) during summer months have found that the small river contained about 1/3 treated sewage from upstream poorly operated municipal treatment facilities (since corrected), septage from failing septic tanks, and SSO discharges.

During this EPA sponsored project investigating SSO discharges being conducted by Lalor, *et al*. (this report) at UAB, sewage, through SSOs and poorly operating septic tanks, were found to make up about 25% of the dry weather flows in the small, completely urbanized stream in Homewood, AL, being studied. However, sewage contributions in the much larger, and much less urbanized 5-mile Creek are very small (on a percentage standpoint), although SSOs exist in the urbanized area. These streams are still being evaluating, including future human health risk assessments associated with these discharges.

Summary of Inappropriate Sanitary Sewage Discharges into Urban Streams

In many cases, sanitary sewage was an important component (although not necessarily the only component) of the illicit discharges affecting urban receiving waters. From a human health perspective (associated with pathogens), it may not require much raw or poorly treated sewage to cause a receiving water problem. However, at low discharge rates, the DO receiving water levels may be minimally affected. The effects these discharges have on the receiving waters is therefore highly dependent on many site specific factors, including frequency and quantity of sewage discharges and the creek flows. In many urban areas, the receiving waters are small creeks in completely developed watersheds. These creeks are the most at risk from these illicit discharges. In Tokyo (Fujita 1998), for example, numerous instances were found where correcting inappropriate sanitary sewage discharges resulted in the urban streams losing all of their flow. In cities that are adjacent to large receiving waters, these discharges likely have little impact (such as DO impacts from Nashville CSO discharges on the Cumberland River, Cardozo, *et al.* 1994). The presence of pathogens from raw, or poorly treated sewage, in urban streams, however, obviously presents a potentially serious public health threat. Even if the receiving waters are not designated as water contact recreation, children are often seen playing in small city streams.

Section 4 - Collecting the Data Needed for Site Specific Risk Assessments of SSOs

Selection of Analytes

The pollutants selected to be analyzed should ideally be determined based on the actual problems being considered. Without having that information, the initial list of parameters to be monitored has to be based on best judgment. The parameters to be monitored can be grouped into general categories, depending on expected beneficial use impairments, as follows:

- flooding and drainage: debris and obstructions affecting conveyance are parameters of concern.

- biological integrity: habitat destruction, high/low flows, inappropriate discharges, polluted sediment (sod and toxicants), and wet weather quality (toxicants, nutrients, DO) are key parameters.

- non-contact recreation: odors, trash, high/low flows, aesthetics, and public access are the key parameters.

- swimming and other contact recreation: pathogens, and above listed non-contact parameters, are key.

- water supply: water quality standards (especially pathogens and toxicants) are key parameters.

- shellfish harvesting and other consumptive fishing: pathogens, toxicants, and those listed under biological integrity, are key parameters.

SSO discharges, dry weather discharges, base flows in receiving waters, sediments, and biological specimens may all need to be sampled and analyzed to obtain a complete understanding of receiving water effects from SSO discharges.

Priorities for Analyses

An initial monitoring program needs to include the above key parameters. However, as the receiving water study progresses, it is likely that many locations and some beneficial uses may not be found to be problems. This would enable a reduction in the list of parameters to be routinely monitored.

The list of constituents for monitoring at primary monitoring stations, in order to appropriately evaluate the SSO affects on the above beneficial uses, should include the following:

Primary list (for routine analysis of all samples):

- pathogens, including protozoa, *Pseudomonas aeruginosa,* and *shigella*, plus viruses, and *E. Coli*.
- toxicants, including partitioned metals (lead, copper, cadmium, and zinc using graphite furnace atomic adsorption spectrophotometer, or other methods having comparable detection limits), partitioned organics (PAHs, phenols, and phthalate esters using GC/MSD with sim, or HPLC), herbicides, and insecticides (using gc/ecd or immunoassays); suggest routinely using toxicant screening method, such as Microtox™, for possible guidance in modifying specific list of toxicants.
- nutrients, including phosphates, total phosphorus, ammonia, Kjeldahl nitrogen, and nitrate plus nitrite, and partitioned TOC.
- partitioned COD.
- additional conventional parameters affecting fates and effects of pollutants in receiving waters, including hardness, alkalinity, pH, specific conductivity, particle size analyses, turbidity, suspended solids (SS), volatile suspended solids (VSS), and dissolved solids (TDS).

Secondary list (in addition to above listed analyses at selected critical locations):

- selected additional metallic toxicants (such as arsenic and mercury and possible screening using mass spec/mass spec) and selected additional organic toxicants (such as VOCs).
- long-term NBOD and CBOD (for k rates and ultimate BOD)
- particulate organic carbon (POC)
- major cations and anions

Sediment analyses:

- particle size distributions of sediment
- acid volatile sulfides (AVS) in sediments
- toxicants and nutrients by particle size
- BOD and COD (and possible POC) by particle size
- interstitial water analyses for key parameters, especially pathogens, DO, pH, and ORP, plus others, volume permitting

Partitioned analyses of the toxicants in runoff and in the receiving water is very important, as the form of the pollutants will have great effects on their fate and treatability. Conventional assumptions that only filterable toxicants have a toxic effect on receiving organisms is not always correct. Particulate forms of toxicants that accumulate in receiving water sediments and can have great effects on the distributions and types of macroinvertebrates, for example. Recent tests in Wisconsin have also shown that stormwater that was treated by sedimentation did not produce any fish mortality, while untreated stormwater produced nearly 100% mortality of test fish after about two weeks of exposure. Obviously, particulate forms of toxicants are more likely to settle out in the receiving waters and contaminate sediments, but they are also capable of high removal rates through relatively simple sedimentation and filtration practices (Pitt, *et al.* 1995).

The sorption of nonpolar organic compounds onto particulates is highly dependent on the organic's K_{ow} (octanol partition) coefficient and the amount of particulate organic carbon in the water (Novtony and Olem 1994). Figure 4.1 shows this relationship. Most heavy metals and organics in stormwater are almost completely associated with particulates, but some exceptions exist, as noted by Pitt, *et al.* (1995), including: bis(2-chloroethyl) ether (up to 50% filterable), 1,3-dichlorobenzene (up to 100% filterable), hexachloroethane (up to 90% filterable), napthalene (up to 80% filterable), anthracene (up to 25% filterable), benzyl butyl phthalate (up to 33% filterable), fluoranthene (up to 100% filterable), and pyrene (up to 100% filterable). The K_{ow} value is between 10^3 and 10^5 for these compounds (Novotny and Olem 1994), and the volatile suspended solids of stormwaters is mostly less than 25 mg/L. Figure Y.99 therefore indicates that the particulate fraction of compounds having these K_{ow} values in water having these relatively low VSS concentrations should be about 0 to 50%, with corresponding filterable fractions from 50 to 100%. It is therefore important to monitor the particulate and filterable fractions of these pollutants, along with the VSS (if POC values are not available).

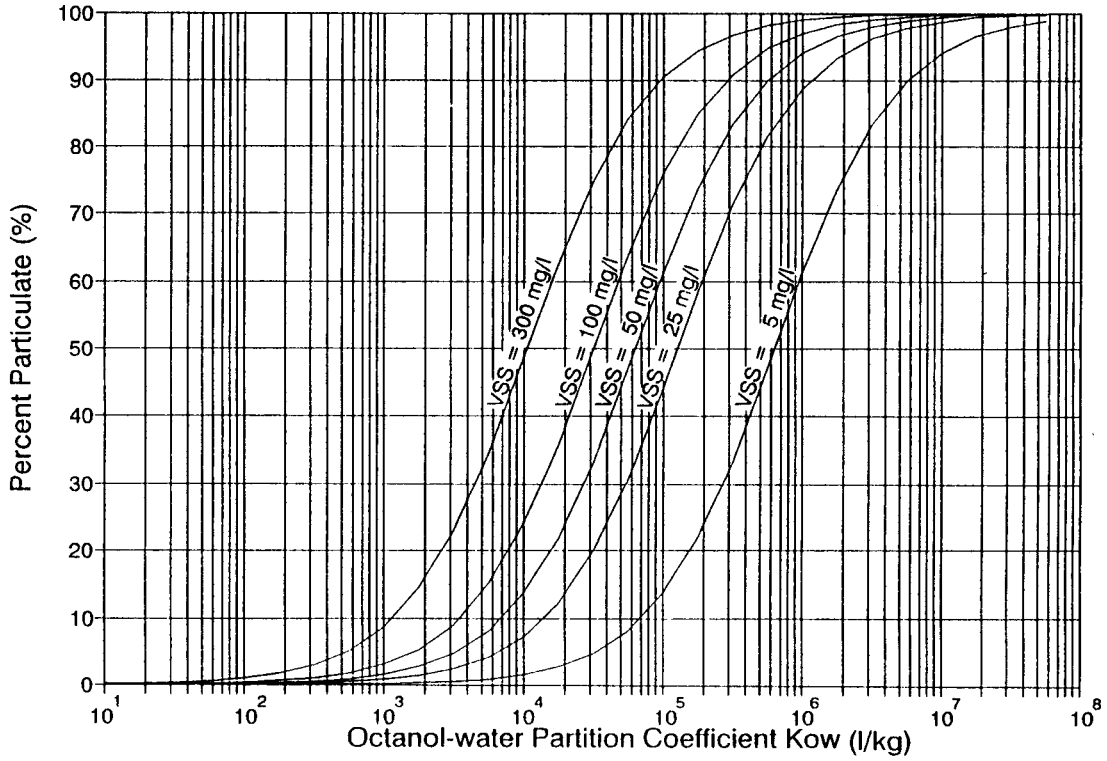


Figure 4.1. Relationship of dissolved and total concentrations of organic priority pollutants related to the octanol partitioning number and volatile suspended solids content of runoff (Novotny and Olem 1994).

The sampling requirements will vary for each parameter, based on the concentration variations observed. In most cases, one year of data (about 15 to 35 events for most areas) will be sufficient to confirm the total monitoring effort needed. For most parameters (assuming a cov of about 1), about 50 events will need to be monitored to obtain an emc value with a 25% error. However, some parameters will have a smaller cov value and will therefore require fewer observations. When sufficient data is obtained for a parameter, that parameter can be taken off the primary parameter list (for analysis for all events) and placed on a secondary list for periodic (seasonal) monitoring.

Additional in-stream measurements are needed and should be conducted as part of any receiving water impact study. These would include: do, temperature, debris and obstructions, habitat conditions, high/low flow variations, inappropriate discharges, polluted sediment (sod and toxicants), odors, trash, aesthetics, and public access.

Selection of Analytical Methods

Environmental researchers need to be concerned with many attributes of numerous analytical methods when selecting the most appropriate methods to use for their analysis. The main factors that affect the selection of an analytical method include: cost, reliability, and safety. These items can be subdivided into many categories including:

- capital cost, costs of consumables, training costs, method development costs, age before obsolesce, age when needed repair parts or maintenance supplies are no longer available, replacement costs, other support costs (data management, building and laboratory requirements, waste disposal, etc.).

- sensitivity, interferences, selectivity, repeatability, quality control and quality assurance reporting, etc.
- sample collection, preservation, and transportation requirements, etc.
- long-term chemical exposure hazards, waste disposal hazards, chemical storage requirements, etc.

Most of these issues are not well documented in the literature for environmental sample analyses. Aspects of analytical reliability have received the most attention in the literature, but most of the other aspects noted above have not been adequately discussed for the many analytical alternatives available, especially for field analytical methodology. It is therefore difficult for a water quality analyst to decide which methods to select, or even if a choice exists.

The selection of the appropriate analysis procedure is dependent on the use of the data and how false negatives or false positives would affect water use decisions or regulatory questions. The QA objectives for the method detection limit (MDL) and precision (RPD) for the compounds of interest have been shown to be a function of the anticipated median concentrations in the samples (Pitt and Lalor 1996). The MDL objectives should generally be about 0.25 of the median value for sample sets having typical concentration variations (COV values ranging from 0.5 to 1.25), based on many Monte Carlo evaluations to examine the rates of false negatives and false positives. The precision goal is estimated to be in the range of 10 to 100% (Relative Percent Difference of duplicate analyses), depending on the sample variability. Table Y.4 lists the typical median stormwater runoff constituent concentrations and the associated calculated MDL and RPD goals, for a typical stormwater monitoring project.

Table Y.4. Summary of Quantitative QA Objectives (MDL and RPD) Required for Example Stormwater Sample Analyses

Constituent	**Units**	**Example COV category[1]**	**Example Median Conc.**	**Calculated MDL Requirement**	**Calculated RPD Requirement**
pH	pH units	very low	7.5	must be readable to within 0.3 unit	<0.3 unit
specific conductance	μmhos/cm	low	100	80	<10%
hardness	mg/L as $CaCO_3$	low	50	40	<10%
Color	HACH units	low	30	24	<10%
Turbidity	NTU	low	5	4	<10%
COD	mg/L	medium	50	12	<30%
suspended solids	mg/L	medium	50	12	<30%
Particle size	size distribution	medium	30 μm	7 μm	<30%
alkalinity	mg/L as $CaCO_3$	low	35	30	<10%
chloride	mg/L	low	2	1.5	<10%
nitrates	mg/L	low	5	4	<10%
sulfate	mg/L	low	20	16	<10%
calcium	mg/L	low	20	16	<10%
magnesium	mg/L	low	2	1.5	<10%
sodium	mg/L	low	2	1.5	<10%
potassium	mg/L	low	2	1.5	<10%
Microtox® toxicity screening	I_{20} or EC_{50}	medium	I_{20} of 25%	I_{20} of 6%	<30%
chromium	μg/L	medium	40	9	<30%
copper	μg/L	medium	25	6	<30%
lead	μg/L	medium	30	7	<30%
nickel	μg/L	medium	30	7	<30%
zinc	μg/L	medium	50	12	<30%
1,3-dichlorobenzene	μg/L	medium	10	2	<30%
benzo(a) anthracene	μg/L	medium	30	8	<30%
bis(2-ethylhexyl) phthalate	μg/L	medium	20	5	<30%
butyl benzyl phthalate	μg/L	medium	15	3	<30%
fluoranthene	μg/L	medium	15	3	<30%
pentachlorophenol	μg/L	medium	10	2	<30%
phenanthrene	μg/L	medium	10	2	<30%
pyrene	μg/L	medium	20	5	<30%
Lindane	μg/L	medium	1	0.2	<30%
Chlordane	μg/L	medium	1	0.2	<30%

[1]

COV value:	Multiplier for MDL:	RDL Objective:
<0.5 (low)	0.8	<10%
0.5 to 1.25 (medium)	0.23	<30%
>1.25 (high)	0.12	<50%

from: Pitt and Lalor 1996

The environmental researcher also must be concerned with sampling issues, in addition to the analytical costs. Most environmental research efforts are not adequately supported to provide the necessary numbers of samples needed for

statistically reliable results. Costly recommendations are therefore commonly made based on too small of an analytical investment. The number of samples needed to simply characterize a water quality constituent can be estimated based on the expected variability of the constituent and on the allowable error of the result. As an example, 40 samples are needed for a commonly found coefficient of variation of 0.8, and an allowable error of 25% for the calculated constituent mean. If only 10 samples are evaluated, the error increases to a possibly unusable 100% level. Analyses of toxicants of great interest in many research activities currently can cost many hundreds of dollars per sample for a short list of organic and heavy metal compounds. A simple effort to adequately characterize the conditions at a single location can therefore cost more than $25,000. Clearly, there is a great need to be able to afford to collect and analyze a sufficient number of samples. The following discussion therefore presents several methods of collecting some of the needed data, including continuous *in-situ* monitors, and simple field test kits. Additional information on laboratory analyses for water samples can be found in Appendix D. Microbiological analysis methods, many modified specifically for use with polluted waters, are described in Appendix E.

Use of Field Methods for Water Quality Evaluations

There are many problems with current environmental sampling and analysis programs that can be met by conducting water quality evaluations in the field, especially if continuous, *in-situ* procedures are used. Foremost among these problems is the need to collect many samples in order to obtain the desired accuracy of the characteristics of interest. Other concerns involve inadvertent changes that may affect the sample characteristics between sample collection and analysis. The high cost of analyzing trace levels of organic and metallic toxicants using conventional laboratory procedures is also restrictive.

The following discussion is divided into aspects associated with conventional field test kits (which cover a wide variety of chemical parameters), and continuously recording *in-situ* instrumentation (which have generally quite narrow capabilities).

Continuous *In-Situ* Monitoring

One way to collect adequate data is to use simple field analytical methods, preferably continuously recording *in-situ* analyses. These methods allow a great amount of data to be collected without sample collection, transportation, or laboratory problems. However, new problems arise, specifically related to long-term reliability and costs of the instrumentation. Many of these instruments are currently available, but they are restricted to a few of the common constituents (usually temperature, conductivity, dissolved oxygen, and pH, plus turbidity on a few units) and can cost from three to seven thousand dollars. The newest and most reliable units can be placed in a waterbody and left unattended for several weeks to months before requiring service. They can continuously record these constituents over this time with very high resolution, enabling a much greater understanding of the dynamics of the pollutant behavior in the waterbody. Unfortunately, the constituents capable of currently being continuously and automatically monitored do not include many having the most interest.

In-situ monitors give continuous and relatively rapid results, in contrast to typical field test kits which require time and patience to evaluate the chemical parameters of interest. Unfortunately, these are all relatively costly instruments. However, their capabilities cannot be matched using other procedures. These instruments can be separated into two general categories. *In-situ* probes, having real-time display capabilities, but with limited data logging capabilities, are designed for real-time monitoring. The other category includes continuously recording probe units that are designed for long-term unattended operation. Examples of both types have been available for than 20 years.

In-situ *Direct Reading Probes*

The simplest direct reading probes that perform their analyses *in-situ*, with no sample preparation, include the classical series of field instruments from YSI, such as their DO probe and SCT (salinity, conductivity, and temperature) probe. These are very robust instruments that have been in use by many institutions for decades. The original models of the DO probes did require practice to replace the membranes and they required relatively frequent (but simple) re-calibration. Newer YSI models, especially utilizing the pulse current probe, exhibit much slower drift and are designed for long-term unattended operation.

Other direct reading instrumentation includes pH and ORP instruments. These generally are more sensitive to storage conditions and require frequent maintenance or calibrations. Some of the newer dry pH electrodes are very robust and much more reliable and easier to use. Ion selective electrodes (ISE) are sometimes included in this category and various equipment vendors offer them as options for their direct reading *in-situ* probes. It is suggested that careful and frequent evaluations be made of any electrode equipped equipment (especially pH and ISE) to ensure that the instrument is operating properly and that the probe is not dried out or damaged by oils or detergents.

Some direct reading *in-situ* probes are also available that have several parameter measurement capabilities. Most of these units are designed for long-term unattended operation, but somewhat less expensive versions are also available that have minimal data logging capabilities and are designed for real-time measurements. The Horiba U-10, for example, was evaluated by Day (1996). It costs about $2,500 from Hazco (800-332-0435, catalogue # B-H020001) and can simultaneously measure conductivity, temperature, salinity, dissolved oxygen, turbidity, and pH. Hazco also rents the Horiba U-10. It is especially useful for real-time profiling of shallow lakes and small urban streams. Relatively few probes offer turbidity which is helpful when examining light penetration and algal activity. Solomat and YSI also have hand-held instruments having similar capabilities as the Horiba U-10.

Other instrumentation is also available that can monitor hydrocarbon conditions in water on a real-time basis. The Turner 10-AU field fluorometer with “oil in water” optics is extremely sensitive and is used with no sample preparation. It can be used in a flow-through mode to map hydrocarbon concentrations in real time. It can also be used as a stand-alone instrument for long-term unattended operation, if properly housed. This instrument costs from $8,000 to $16,000, depending on housing, data logging and filter options, and is therefore not likely to be readily available. This instrument is also used for fluorescent tracer analyses (using Rhodamine WT) for primary calibration of water flow equipment. It can also be used for limited real-time chlorophyll *a* analyses, when using appropriate optics and filters.

The *Petrosense* hydrocarbon probe from FCI Environmental is also available for real-time hydrocarbon analyses. This instrument costs about $7,000 and has a slower response time (about 5 minutes) and is not nearly as sensitive (about 100 μg/L, as xylene) as the fluorometer. It can also be used in real time to monitor “total” hydrocarbons in water, with no sample preparation. It quantifies hydrocarbons by measuring changes in optical properties caused by hydrocarbon adsorption onto an exposed fiber optic.

An important chemical pollutant category that is not represented with any real-time instrumentation is heavy metals. Samples require digestion in order to release all of the particulate-bound heavy metals for analysis. In addition, most metals are not amenable to real-time analyses. Some colorimetric procedures, such as the diethyldithiocarbamate copper method (as available from La Motte) or the bicinchonate copper method (as available from HACH), could be conducted on a real-time basis with an automated chemical mixing and analysis procedure. Current research at the University of Alabama at Birmingham (in conjunction with the General Physics Institute of the Russian Academy of Sciences and Alabama Laser) that is sponsored by the National Science Foundation has developed and demonstrated a laser-based instrument that may be capable of continuous heavy metal analyses in water (Pitt, *et al*. 1996). This instrument is extremely sensitive, as it is based on atomic fluorescence. The use of lasers enables the specific wavelengths most critical for analysis to be precisely used in the instrument. In addition, automated digestion of the samples may also be possible.

Continuously Recording and Long-Term In-Situ *Measurements of Water Quality Parameters*

Several classical instruments have long been available to measure various water quality parameters with unattended instruments for relatively long periods of time. Hydrolab and YSI have long offered equipment that could monitor dissolved oxygen, pH, temperature, and conductivity unattended. The early instruments were plagued with stability problems and were usually most suited for unattended operation over a period of only about a day. This was still a major break-through, as it enabled diurnal fluctuations of these important parameters to be accurately and relatively conveniently obtained.

Currently available equipment, in contrast, has been demonstrated to be capable of unattended operations for longer than a month. These are relatively expensive instruments that can cost up to $7,000 each, depending on options

selected. Examples of equipment currently available include the 803 probe series from Solomat which can have up to 8 sensors installed. These may include pH, ORP, DO, temperature, conductivity, depth, ammonium, nitrite, and other ions by ISE. Several meters and data loggers are available for hand-held real-time measurements, or for long-term unattended operation.

YSI also offers several *in-situ* probe instruments. The 6000 series probe is self-contained, measuring and logging up to 9 separate parameters simultaneously, including DO, conductivity, temperature, pH, depth, ORP, nitrate, ammonium, and turbidity. The rapid pulse DO and self-wiping turbidity sensors enable very long unattended operations (up to 45 days), with minimal fouling or drift. Hazco (800-332-0435) sells the YSI 6000 basic probe (catalogue # B-6001) for about $7,000. The unit without the depth sensor is about $500 less.

These unattended instruments are capable of collecting high resolution (typically every 15 minute observations) data over long periods. This is extremely useful in receiving water studies affected by stormwater. Even though few dissolved oxygen problems have ever been associated with stormwater, these probes are unexcelled in documenting the exposure periods and gross variations in receiving water conditions over many separate storm events. This data is very important when used in conjunction with *in-situ* toxicity test chambers that are exposed for relatively long periods of time. In addition, the YSI self-contained probes with rapid-pulse DO sensors (so the probes don't consume oxygen themselves) can be used in light and dark chambers to conveniently obtain necessary data pertaining to sediment and water photosynthesis and respiration.

Field Test Kits

Field test kits cover a wide range of instrumentation and methods. They range from very simple visual comparator tests which use, colored paper, colored solutions in small vials, or color wheels, to match against the color developed with the test. The least expensive tests use small droppers or spoons to measure reagents into a reaction tube where the color is developed. More sophisticated tests use small filter colorimeters to more precisely measure the color developed during the test. HACH also offers continuous wavelength field spectrophotometers that are capable of measuring a wide variety of chemical parameters using a single instrument. La Motte has a filter colorimeter that contains several filter sets, also enabling many different chemical analyses to be conducted with the one instrument. HACH also has a field titration kit that is also very flexible. These multi-parameter instruments are usually superior to the simple dedicated test kits because of the increased sensitivity and precision that is achievable with the better equipment. They of course cost more. If only one or two parameters are to be monitored in the field, then it may be hard to justify the added cost of the better instruments. However, if the best quality data is needed, then the cost may be justified, especially if more than a few parameters are to be measured.

Also included in the category of field test kits are very sophisticated methods that are laboratory instrumentation and procedures that have been miniaturized and simplified. Some of these tests even meet the EPA reporting requirements for NPDES permit compliance. However, some of the field procedures skip certain sample clean-up or digestion steps that would be impractical to conduct in the field and are therefore not suitable for compliance monitoring. It is important to check with the field equipment suppliers and the reviewing regulatory agency to verify the current status of a field method for various reporting purposes. Many of the spectrophotometer and titration methods fall into this category of simplified laboratory methods. Several new instruments are also available that permit sensitive and precise heavy metal (especially copper and lead) analyses in the field. However, these instruments are expensive (equipment costs of $2,000 to $4,000 and per sample costs of $5 to $15). They are also not sensitive to particulate-bound metals (which may be an advantage, depending on study objectives).

The biggest difficulty with almost all of these field test kits is that they require time to evaluate the water sample. Continuous and *in-situ* monitors eliminate field analytical time. Some of the simple *in-situ* monitors are included in this test kit discussion (such as conductivity meters, pH meters, and DO meters), while the more complex continuously recording units were discussed previously. Even though these field test kits enable personnel to evaluate samples at the point of collection, that may not be desirable. Lalor (1993) and Pitt, *et al.* (1994) found that test kit performance was greatly enhanced by bringing the collected samples to a temporary "laboratory" for analyses. This greatly increased sample analytical through-put, as many of the test kits enabled multiple samples to be analyzed at one time. This is especially critical if sampling locations are widely spaced and the alternative is to analyze many parameters at each location before moving to the next sampling location. It may take more than an

hour to conduct a relatively few chemical tests at each location, including setting up equipment and re-standardizing procedures. However, if many samples are being collected in a small area, the equipment can be left in one place and simultaneous sample analyses would be possible in the field. Indoor facilities should be sought, as protection from weather, available electricity, good lighting, and water, enhance analytical performance. Make sure that adequate ventilation is available, however, wherever the tests are conducted. Many of the field test kits are not well labeled, especially concerning hazardous materials in the kit that require special protection and disposal practices.

Safety issues, along with test kit performance, have been recently examined (Pitt, *et al*. 1994; Pitt and Lalor 1996; Day 1996). The test kit evaluations were based on "fatal flaws" of the alternative equipment available for each parameter category. In the most recent series of tests conducted by Day (1996), 50 test kits were subjected to preliminary evaluations with half further subjected to more detailed tests. His results are summarized in the following discussions. Safety hazards, cost, poor detection limits, matrix interferences, limited concentration ranges, poor response factors, and complexity of the test kits were all reasons for rejection. The "easiest" to conduct test and the "best" test in each category were then identified, after rejecting those kits that were much more expensive than alternatives in each category. The comparison of field screening equipment is a somewhat objective process. Some parameters of interest are easily quantified; other features that should be evaluated require more objective evaluation techniques.

Section 5 - Where and How to Sample

There are numerous water quality sampling needs associated with a SSO investigation. The following elements should be considered:

- fluctuations in water quality with time at critical locations, including different flow phases (dry-weather flows, snowmelts, flows during rain events, etc.), as well as seasonal and diurnal variations in these characteristics, and
- interstitial water and sediment quality conditions (at least seasonally).

Additional water sampling may also be needed to characterize other potential sources of pollutants affecting the receiving water. This will require stormwater outfall sampling, in addition to possible source area sampling.

These different sampling locations and objectives require different types of sampling. Automatic samplers can be used in many situations, and with their internal computer controls they are capable of many different sampling modes. Composite and discrete sampling are both possible, in time or flow-weighted mode. Automatic samplers can also be set to start sampling based on raingage information, water stage, or flow. Manual sampling should also be considered in many situations, along with semi-automatic sampling devices that can be placed at many locations in the drainage area. Finally, monitoring of water flow rates and rainfall intensities are also required in many receiving water monitoring projects. These different sampling procedures are discussed in this section.

Safety Considerations

Water and sediment sampling may expose field personnel to hazardous conditions. Obviously, water hazards (high flows, deep pools, soft sediments, etc.) are of initial concern. In many stormwater assessment studies, sampling during rainy weather in streams that may undergo rapid velocity and depth changes is necessary. Great care must be taken when approaching a stream in wet weather, as steep and slippery banks may cause sliding into the water. Always sample in pairs and have adequate safety equipment available. At a minimum, this will include:

- throw rope
- inflatable life vests
- nylon covered neoprene waders (that offer some floatation, even when swamped)
- 2-way radio or cellular phone
- weather radio

If the conditions warrant (such as with steep and slippery stream banks), the sampler personnel should be tied together, with an attachment to a rigid shore object. In all cases, only go into the stream if absolutely necessary. Try to collect all samples from shore, especially if during heavy rains. Be extremely cautious of changing weather and stream conditions and cancel sampling when hazardous conditions warrant. Never enter a stream where your footing is unstable or if the water is too deep (probably more than 2 feet deep) or fast (probably more than 2.5 ft/sec). Always enter the water cautiously and be prepared to make an efficient retreat if you feel insecure.

Other hazardous conditions may also occur when working near urban streams. Sharp debris in the water and along the streams require that protective waders be worn at all times while in the stream. No one should enter the water bare-footed. Poison ivy, poison oak, and ticks thrive along many stream banks, requiring long pants and shirts. When in the field during sunny weather, sun screen and a hat is also a necessity. In many parts of the country, especially in the southeast, special caution is also required concerning snakes. Water moccasins are very common and coral snakes may also be present along urban streams in some areas. Again, waders offer some protection, but care must be taken when moving through thick underbrush where visibility is limited.

These cautions are necessary and are basically common sense. However, the greatest dangers associated with field sampling are likely to arise from loose running dogs, weird people, and automobiles (dangers which are not restricted to stream sampling).

Sampling Locations

Specific sampling locations are determined based on the objectives of the study and site specific conditions. Obviously, safety is a prime consideration, along with statistical requirements expressed in the experimental design. In all cases, the sample must represent the conditions being characterized.

Paired analyses are the most efficient sampling strategy. This can be simply sampling the influent and effluent of a control structure, outfalls of test and control watersheds, comparable stream habitats in test and control streams, or even the same stream sampling location, but at different seasons. Paired sampling can eliminate much variability, as many influencing factors are assumed to remain constant, enabling effects to be more easily seen. Obviously, if the expected differences are expected to be large between the two elements in the pair, and the background random variability is small, many fewer sampling pairs are needed to identify a statistically significant difference in the observations. Great care must be taken to select correct pairs, as the random variability can easily be greater than expected. The statistical analysis chapter presents methods to determine the sampling effort for paired testing.

One example of likely inefficient paired sampling is sampling above and below an outfall in a stream. In almost all cases, the stream pollutant loads and flows are much greater than a single outfall discharge. Therefore, the differences expected in stream water quality upstream versus downstream of an outfall would be very small and very difficult to detect. Exceptions may occur with large point source outfalls discharging during very low flow conditions, or near the headwaters of fairly small, pristine streams. Otherwise, one large number is basically subtracted from another large number (with both having a certain amount of uncertainty) to determine the effects of a relatively small discharge. If this sampling strategy needs to be employed, make sure that the outfall discharge is also well characterized.

If loadings, or stormwater concentrations of runoff from different land uses in a watershed are needed, then a sufficient number of examples need to be monitored. Many watersheds have several distinct land uses in their drainage area. It is important that a sufficient number of the land uses are adequately monitored in order to make an adequate mass balance. An example of marginal benefits for increasing sampling locations is given in the statistical analysis chapter.

The actual location of sampling is somewhat dependent on the type of sampler to be used. However, in all cases, the sample taken must be representative of the flow to be characterized. Permanently mounted automatic or semi-automatic samplers are most restricted in their placement, as security and better access is needed than with manual grab sampling. With manual sampling, less equipment is generally being carried to the sampling location (some type of manual dipper sampler, plus sample bottles, for example), while automatic samplers require a relatively large sample container, a multi-bottle sampler base, and batteries and other maintenance and cleaning supplies to be periodically carried to the sampler. Weekly visits to automatic samplers, at least, are typically needed for maintenance. In all cases, access during rains must be provided to all stormwater sampler locations. Manual stormwater sampling takes place during the rains, of course, while automatic samplers may need to have their bottles switched during rains, or other checks made. Therefore, dangerous locations, such as requiring steep ascents down clayey stream banks need to be avoided, for example.

Permanently mounted samplers must have their intakes located to represent flow conditions. This is much easier with relatively small urban streams or outfalls compared to larger receiving waters. Wide, shallow, and fast flowing streams are the most difficult to adequately sample. Great distances may be required before flows from individual discharges are completely mixed in these situations. Thomann and Mueller (1987) presents the following USGS equation that can be used to estimate the distance needed before complete mixing occurs (for a side-stream discharge):

$$L_m = (2.6\ UB^2)/H$$

where U is the stream velocity in ft/second
B is the average stream width in feet, and
H is average stream width in feet

As an example, about 2,000 meters (6,700 feet) may be required before complete mixing occurs for a stream that is 12 meters (40 feet) wide, 1.5 meters (5 feet) deep, and flowing at 2.4 meters/sec (8 ft/second). For a more typical urban stream with a 3 meter (10 feet) width, 0.6 meter (2 feet) depth, and flowing at 0.9 meters/sec (3 ft/second), the mixing length would be about 120 meters (390 feet). Half of these distance would be needed if the discharge is located at the centerline of the stream (such as may occur for a diffuser for an industrial outfall). ASTM (1995) in standard D 3370 states that a distance of 1 to 3 miles below a tributary is usually sufficient to obtain complete mixing. They also suggest that samples be taken at least ½ mile below dams or waterfalls to allow entrained air to escape.

These distances may be too great for many practical reasons, including the typical presence of numerous, and fairly closely spaced outfalls along an urban creek (every several hundred feet). If it is not possible to site the sampler intake where the water will be well-mixed, then several sample intakes may be needed to obtain a composite sample across the stream. This can be accomplished by using several submerged pumps at different locations feeding a central large container. Automatic samplers are also restricted to a vertical height from the water surface to the sampler pump of about 7 meters (since most use a peristaltic pump located on the sampler and therefore pull the water sample using vacuum suction). If the sampler height is greater than this critical height, a submerged pump operated in the same manner can also be used to solve this problem. The automatic sampler would then sample from a large container that the submerged pumps are discharging into. In most cases, the submerged pumps would run continuously (therefore need on-site AC power or solar charged batteries) and the flow-weighted sampler would be programmed to appropriately sample from the composite container, based on measured flows in the stream. The excess flow from the multiple pumps would overflow the composite container. The sample velocity in the sampler lines must be at least 100 cm per second to minimize particulate settling in the sampling lines. Care must also be taken to select a pump and sampler line that will not contaminate the samples (stainless steel, Teflon™, or appropriate plastic) and be easy to clean in the field.

A Grundfos Redi-Flo2 pump and converter is available with a 300 foot polyurethane hose on a convenient reel that can be used to deliver a water sample to a central location within reach of an automatic sampler. These pumps are available from Forestry Suppliers, Inc. (800-543-4203, catalogue #76328 for pump, hose, and reel, and #76333 for needed voltage converter, for a total cost of about $4500). Hazco (800-332-0435) also sells (and rents) the Redi-Flo2 pump and converter for about $2100 without a hose (catalogue #B-L020001 for converter and #B-L020005 for 150 motor lead and pump). A Teflon lined polyethylene hose is available from Hazco for about $3.25 per foot, with support cable (catalogue # A-N010041 and #C-L020009). This pump has an adjustable pumping rate of between 100 mL/min to 9 gal/min and can pump against a head of about 250 feet. However, this pump should be operated at least at 4.5 gal/min to meet the 100 cm/second criteria to minimize particulate settling in the ¾ inch ID hose. Low pumping rates from a submerged pump can also lead to “sand jamming”, in addition to preventing an adequate sample from being obtained.

A less expensive alternative is the XP-100 pump, also available from Forestry Suppliers (#76216 for XP-060 pump and #76230 for control box, for a total cost of about $525). This is an adjustable rate pump and can deliver the needed 100 cm/sec pump rate through a 3/8 inch tubing against a head of about 30 feet, or less. This pump operates from a 12V DC power supply and has a limited service life, compared to the Grundfos pump. It may be useful for temporary installations having limited head, but needing several pumping locations across a stream.

Obviously, care will also be needed to locate the sampler intakes to minimize induced scour of sediments and to prevent clogging from debris. All submerged pumps can quickly fail if the pump draws coarse particles into the pump, but doesn’t have enough velocity in the sample line to discharge most of them completely through the sample line. If the intake is located on a creek bottom, the water entering the sampler intake will likely scour sediment from the surrounding area. Locating the sampler intake on top of a small anchored concrete slab in the creek will minimize scour. Elevating the sampler intake above the creek bottom will also minimize scour, but would present an

obstruction to flows and would easily catch debris. Elevating the intake would be important to obtain a better sample if the flow is vertically stratified. In some cases, sampler intakes can be successfully located on the downstream side of a bridge piling or pier. Do not locate the sample intake near any treated wood structure if heavy metals or organics are to be sampled.

Locating a sampler intake in an outfall pipe presents other problems. Because the pipe is likely to be smaller than a receiving water, horizontal differences in water quality should not be a problem. However, vertical differences may occur. The sampler intake also presents a greater obstruction to the pipe flow and therefore has a greater tendency to catch debris. To ensure a well-mixed water sample, the intake can be placed in an area that has turbulent flow. This may decrease volatile components in the water sample, but typical automatic samplers are inappropriate for collecting samples for volatile analyses anyway. Locating the intake on the downstream side of a flow monitoring flume would help obtain a mixed sample. In addition, added obstructions (bricks and concrete blocks) can be cemented to the pipe above the sampling location to induce well-mixed conditions during low to moderate flows.

Manual sampling is much more flexible and can be modified to better represent the flow conditions at the time of sampling. Obviously, multiple dips across a stream, and at multiple depths will result in a better representation of the stream than a single sampling location. Special manual samplers (described later) are needed to collect depth-integrated samples that may be needed for sediment transport studies.

The advantages of manual sampling compared to automatic sampling are off-set by the time frame that is represented in the sample. A grab sample taken at a single time will not be as representative of a storm event as an automatic sampler taking sub-samples from many time periods during the event, even considering multiple versus single sampling points. A single sampling location will be subjected to varying conditions during the storm, including variable horizontal and vertical variations. However, if a single sampling location is consistently biased compared to the cross-section of the stream, then that needs to be recognized and corrected. Therefore, it is necessary to observe conditions in the stream during the sampling times as much as possible to detect any potential bias. A bias may be caused by currents or nearby discharges, for example, and may be visually observed if colored or turbid water is indicating current conditions near the sampler. A hand-held *in-situ* probe that can measure turbidity (such as sold by YSI, Solomat, or Horiba) would be extremely helpful in checking flow variations near the sampler intake. These probes can also be very helpful during manual grab sampling to measure the likely flow variabilities during the time of sampling. Other parameters are usually available on these probes (such as conductivity, temperature, DO, pH, and specific ions) that would also be helpful in these field checks.

Automatic Water Sampling Equipment

Automatic water samplers that are commonly used for stormwater monitoring are available from ISCO and American Sigma, amongst others. These manufactures have samplers that have very flexible programming capabilities specifically designed for stormwater sampling and are designed for priority pollutant sampling. A simpler automatic sampler is the Masterflex self-contained composite sampler (from Forestry Suppliers, Inc., for about $1,500). This sampler is restricted to composite sampling only on a time-increment basis and there is little control over the sample volumes that can be obtained. However, it may be a worthwhile option for simple sampling needs.

The American Sigma (800-635-4567) samplers are an excellent example of a highly flexible automatic sampler. They have an integral flow meter option and can directly connect to a liquid level actuator or a depth sensor. The depth sensor is placed in the storm drainage upstream of a flow monitoring device (such as a weir or flume, or any calibrated stage-discharge relationship can be used). The flow indicators can control sample initiation and/or sampling frequency. A raingage is also available that can be directly connected to the sampler. Rainfall data can therefore be logged by the sampler, along with flow information and sampling history. Rainfall can also be used to trigger sample initiation. A solar panel is also available to keep the sampler's battery charged. Several sample bases and sample bottle options are also available. Single bottle composite sample bases are available having glass or polyethylene bottles from 2.5 to 5.5 gallons in volume. Up to four one gallon glass or polyethylene bottles can also be used to obtain composite samples over segments of the runoff event. In addition, several 24 bottle options are

also available, with 575 mL or 1 L polyethylene bottles, or 350 mL glass bottles. American Sigma also has several AC powered samplers that are refrigerated.

ISCO (800-228-4373) also offers a complete line of automatic water samplers that have been used for stormwater sampling for many years. Flow meter and raingage options are available, along with numerous sample base and sample bottle options. ISCO also has several AC powered refrigerated samplers. The new ISCO 6100 sampler (about $8,000, with bladder pump and special bottle rack for 40 mL VOC bottles) is especially designed to obtain samples for volatile analyses. Samples are directly collected in capped 40 mL VOC vials in the sampler, with minimal loss of volatile compounds. Very few volatile hydrocarbons have ever been detected in stormwater, so this sampler (and VOC analyses) would probably only be used for specialized studies where VOCs are expected (such as in commercial areas with older dry cleaners and near gasoline stations).

Sigma and ISCO also have new automatic samplers that interface with continuously recording water quality probes that can be used to control sampling during critical periods, irrespective of time or flow. McCrone (1996) describes American Sigma's options for using numerous probes (such as conductivity, DO, temperature, ORP, and pH). The sampler can be programmed to collect a special sample when any of these monitored parameters meets a pre-set criterion. ISCO has a new sampler series that interfaces with the YSI 6000 water quality probes, allowing specific water quality conditions to also trigger sampling (similar to Sigma's list, plus turbidity).

If a refrigerated sampler cannot be used (due to lack of AC power), ice may be used if sample chilling is needed. Ice is placed in the central cavity surrounded by the sample bottles in the sampler base. The ice needs to be placed soon before an expected storm event, as it will generally melt within a day. The placement of any sampler in a cool location (such as in a manhole) is much preferred over placement in a small shelter that may heat excessively in the summer. In most cases, chilling stormwater during sample collection is not used due to lack of AC power and the inconvenience of using ice. If the sampler is located in a cool location and the samples retrieved soon after the storm has ended, few problems are expected. Bacteria sampling, for example, requires manual sampling to ensure sterile equipment and to minimize storage problems. VOC analyses have also previously required manual sampling, but the new VOC sampler from ISCO can be used for automatic sample collection. The use of probes to measure pH, ORP, and temperature *in-situ* also reduces the need for manual samples for these parameters. Therefore, it is possible to conduct a stormwater sampling program using automatic samplers that doesn't require AC powered refrigerated samplers, if supplemented with manual sampling for microorganism determinations, and if the samples are retrieved soon after the event has ended. Some analyses may not be available using automatically collected samples, and other options may need to be used to supplement the automatic sampling. In all cases, special storage tests can be used to determine the likely errors associated with long storage in the samplers, with and without chilling.

Required Sample Line Velocities to Minimize Particle Sampling Errors

Typical sample lines are Teflon™ lined polyethylene and are 10 mm in diameter. The water velocity in the sample line is about 100 cm per second, enabling practically all sediment to be transported to the sample containers. Bed load sampling equipment is usually needed to adequately collect samples of bed load at outfalls, however. Table 5.1 shows the particle sizes that would be lost in vertical sampling lines at a pumping rate of 30 and 100 cm/second.

Table 5.1. Losses of Particles in Sampling Lines

	30 cm/sec flow rate		100 cm/sec flow rate	
	Critical settling rate (cm/sec)	Size range (μm, for ρ = 1.5 to 2.65 g/cm^3)	Critical settling rate (cm/sec)	Size range (μm, for ρ = 1.5 to 2.65 g/cm^3)
100% loss	30	2,000 - 5,000	100	8,000 - 25,000
50% loss	15	800 - 1,500	50	3,000 - 10,000
25% loss	7.5	300 - 800	25	1,500 - 3,000
10% loss	3.7	200 - 300	10	350 - 900
1% loss	0.37	50 - 150	1	100 - 200

A water velocity of 100 cm/sec (about 3 ft/sec) would result in very little loss of stormwater particles. Particles of 8 to 25 mm would not be lifted in the sample line at all at this velocity, but these sized particles would not fit through the openings of the intake or even fit in most sample lines. They are also not present in stormwater, but may be a component of bedload in a stream, or gravel in the bottom of a stormdrain pipe, requiring special sampling. Very few particles larger than several hundred micrometers occur in stormwater and these should only have a loss rate of 10% at the most. Most particles in stormwater are between 1 and 100 μm in diameter and have a density of between 1.5 and 2.65 g/cm^3. Even at 30 cm/sec, these particles should experience insignificant losses. A pumping rate of about 100 cm/sec would add extra confidence in minimizing particle losses. ASTM (1995) in method D 4411 recommends that the sample velocity in the sampler line be at least 17 times the fall rate of the largest particle of interest. As an example, for the 100 cm/sec example above, the ASTM recommended critical fall rate would be about 6 cm/sec, enabling a particle of several hundred micrometers in diameter to be sampled with a loss rate of less than 10%. This is certainly adequate for most stormwater sampling needs.

Automatic Sampler Line Flushing

Automatic samplers generally go through three phases when activated to collect a sample. First, the sample line is back-flushed to minimize sample cross-over and to clear debris from the sample intake. Next, the sample is collected. Finally, the sample is back-flushed again before going into a sleep mode to await the next sampling instruction. It can require several minutes to cycle through this process. A volume of 1850 mL of water fills a 10 mm (3/8 inch) diameter sample line that is 7.5 meters (25 feet) long. If a sample volume of 350 mL is to be collected for each sample interval, the following total volume of water is pumped by the sampler for each sample instruction:

back-flush line:	1850 mL
fill tube:	1850 mL
collect sample:	350 mL
back-flush line:	1850 mL

This totals about 6,000 mL of water to be pumped. Typical automatic samplers have a pumping rate of about 3500 mL per minute for low head conditions (about 1 meter). It would therefore require about 1.7 minutes to pump this water. With pump reversing and slower pumping speeds at typical pumping heads, this could easily extend to 2 minutes, or more. If the sampler collects 3 liters of sample instead of 350 mL, then another minute can be added to this sampling time for one cycle.

This sampler cycle time requires various decisions to be made when setting up and programming a sampler, especially for flow-weighted composite sampling. The most important decisions relate to selecting the sampling interval that can accommodate expected peak flows and the sample volume needed for the smallest events to be sampled. Sample storage in the samplers is limited, further complicating the issue. The samplers are generally programmed to sample every 15 minutes to 1 hour for time-compositing sampling, or for an appropriate sample volume increment for flow-weighted sampling. If each sample increment is 0.25 L, a total of 40 sub-samples can therefore accumulate in a 10 L composite sample container.

Time or Flow-Weighted Composite Sampling

Automatic samplers can operate in two sampling modes, based on either time or flow increments. The sample bases can generally hold up to 24 bottles, each 1 L in volume. A single sample bottle of up to about 20 L is generally available for compositing the sample into one container. These bottle choices and the cycle time requirements of automatic samplers restrict the range of rain conditions that can be represented in a single sampler program for flow-weighted sampling. It is important to include samples from small rains (from about 0.01 to 0.2 inch) in a stormwater sampling program because they are very frequent and commonly exceed numeric water quality criteria, especially for fecal coliform bacteria and heavy metals. Moderate sized rains (from about 0.2 to 3 inches) are very important because they represent the majority of flow (and pollutant mass) discharges. The largest rains (greater than about 3 inches) are important from a drainage design perspective to minimize flooding problems. It is very difficult to collect a wide range of rain depths in an automatic sampler using flow-weighted sampling. Conflicts occur between needing to have enough sub-samples during the smallest event desired (including obtaining enough sample volume for the chemical analyses) and the resulting sampling frequency during peak flows for the largest sampling event desired. As an example, consider the following problem:

- desired minimum rain to be sampled: 0.15 inch in depth, 4 hour runoff duration, having a 0.20 Rv (volumetric runoff coefficient)
- largest rain desired to be sampled: 2.5 inch in depth, 12 hour runoff duration, having a 0.50 Rv
- the watershed is 250 acres in size and 3 samples, at least, are needed during the smallest rain

The calculated total runoff is therefore:

- minimum rain: 0.10 (0.15 in) (250 ac) (ft/12 in) (43,560 ft^2/ac) = 13,600 ft^3.
- maximum rain: 0.50 (2.5 in) (250 ac) (ft/12 in) (43,560 ft^2/ac) = 1,130,000 ft^3.

The average runoff flow rates expected are roughly estimated to be:

- minimum rain: (13,600 ft^3/4 hr) (hr/3600 sec) = 0.95 ft^3/sec.
- maximum rain: (1,130,000 ft^3/12 hr) (hr/3600 sec) = 26 ft^3/sec.

Using a simple triangular hydrograph, the peak flows are estimated to be about twice these average flow rates:

- minimum rain: 1.9 ft^3/sec.
- maximum rain: 53 ft^3/sec.

Actual peak flow rates are obviously related to the watershed time of concentration and other factors of the watershed and drainage system, but this triangular hydrograph has been found to roughly estimated high flows during small and moderate rains. It is certainly not an adequate procedure for drainage design, however. As the smallest storm is to be sampled three times during the runoff period, the volume of flow per sub-sample is simply: 13,600 ft^3/3 ≅ 4,500 ft^3.

Therefore, the total number of samples collected during the maximum rain would be: 1,130,000 ft^3/4,500 ft^3 ≅ 250 samples.

If the minimum sample volume required was 1 L, then each sub-sample could be as small as 350 mL. This would result in about 1 L of sample during the minimum storm, but it result in about 90 L during the maximum storm (obviously much larger than the typical 10 to 20 L container). During the estimated high flow conditions of the largest storm, a sub-sample would be collected every: 4,500 ft^3 per sample/53 ft^3/sec ≅ 85 seconds.

If the sampler required 2 minutes to collect 350 mL, the sampler would not complete its cycle before it was signaled to collect another subsample. This would result in the sampler pump running continuously during this peak time. Since the peak flow period is not expected to have a long duration, this continuous pumping may not be a serious problem, especially considering that about 250 samples are being collected. The biggest problem with this setup is the large volume of sample collected during the large event.

This problem was solved during numerous stormwater monitoring projects (including Pitt and Shawley 1982 during the Castro Valley, CA NURP project, and Pitt 1984 during the Bellevue, WA NURP project) by substituting a large container for the standard sample base and installing the sampler in a small shelter. The large container can be a large steel drum (Teflon™ lined), a stainless steel drum, or a large Nalgene™ container, depending on the sample bottle requirements. In order to minimize handling the large container during most of the events, a 10 L glass jar can be suspended inside to collect all of the sub-samples for the majority of the events. The jar would overflow into the large container for the largest events. Glass bottles are used in the sampler when organics are to be analyzed, with the assumption that the short period of storage in the glass would not adversely affect the metal concentrations. The

small shelter should be well vented to minimize extreme temperatures, as it is difficult to ice the large container. Obviously, the sampling stations need to be visited soon after a potential runoff event to verify sample collection, to collect and preserve the collected sample, and to clean the sampler to prepare it for the next event.

Alternatives to using a large sample base in order to accommodate a wide range of runoff events include:

- use time-compositing instead of flow-weighted sampling,
- use two samplers located at the same location, one optimized for small events, the other optimized for larger events, or
- visit the sampling station during the storm and re-program the sampler, switch out the bottles, or manual sample.

The most common option is the last one which is expensive, uncertain, and somewhat dangerous. Few monitoring stations have ever used multiple samplers, but that may be the best all-around solution, but at an increased cost. The first option above, using time-compositing instead of flow-weighted sampling, should be considered.

The Wisconsin Department of Natural Resources conducted a through evaluation of alternative sampling modes for stormwater sampling to determine the average pollutant concentrations for individual events (Roa-Espinosa and Bannerman 1995). Four sampling modes were compared at outfalls at five industrial sites, including: flow-weighted composite sampling, time-discrete sampling, time-composite sampling, and "first-flush" sampling during the first 30 minutes of runoff. Based on many attributes, they concluded that time-composite sampling at outfalls is the best method due to simplicity, low cost, and good comparisons to flow-weighted composite sampling. The time-composite sampling cost was about ¼ of the cost of the time discrete and flow-weighted sampling schemes, for example (but was about three times the cost of the first-flush sampling only). The accuracy and reproducibility of the composite samples were all good, while these attributes for the first-flush samples were poor.

It is important to ensure that the time-weighted composite sampling include many sub-samples. It would not be unusual to have the automatic samplers take samples every 10 minutes for the duration of an event. If the minimum sample volume needed is 1L and the shortest rain to be sampled is 30 minutes, then each subsample would need to be about 350 mL. The total volume collected would be about 50L (144 samples) if a storm lasted 24 hours. The sampler would have to have an enlarged container (as in the above flow-weighted example), or the sampler would have to be visited about every 5 hours if a 10L composite sample container was used.

Another important attribute of time-compositing sampling is that intermittent discharges and other short-term high concentration flows would be more readily detected (Newburn 1988). Flow-weighted composite sampling may allow very long periods to be unrepresented in the sample, while time-composite sampling can be adjusted to include relatively short sampling periods. Long periods between sampling periods could allow short-period episodes to be missed. However, sampling periods that are too short may result in almost continuous pumping activity that may exceed the continuous duty cycle of the sampler, resulting in frequent maintenance. Pump tubing should be carefully inspected and frequently replaced in any case, especially considering the gritty nature of stormwater. A new option is the use of *in-situ* probes attached to the sampler that can be used to trigger sampling during unusual water quality shifts.

Automatic Sampler Initiation and the use of Telemetry to Signal or Query Sampler Conditions

Automatic sampling equipment is typically located semi-permanently in the field and is set to automatically begin sampling for a pre-determined set of conditions. The most common method to start samplers is to use a stage indicator. This simple device, available from most sampler manufactures, may be a float switch (as from American Sigma) or an electronic sensor that shorts out when wet (ISCO). These devices plug into the sampler at the flow sensor connection. If flow monitoring is simultaneously being monitored, a cable Y connection is available to allow both connections. The stage sensor is typically placed slightly above the base flow water elevation (in a pipe, open channel, or creek). It is difficult trying to sample small events that may not cause a large-enough stage elevation increase to trip the indicator. False alarms are also common when the sensor is placed too close to the base flow water elevation. In addition, the base flow water stage changes seasonally, requiring constant modifications in the sensor location. If the channel or pipe is normally dry, then these problems are significantly reduced, as the sensor can be placed on the bottom of the drainage way or pipe. Flow-weighted sampling schemes can eliminate the use of

sensors all together. In this case, some water may collect in the sample container during base flow conditions, however. Frequent visits to the sampler is needed to empty and clean the sample container.

Another method used to initiate sampling is to trip the equipment using a local raingage. Pitt and McLean (1986) used a raingage to initiate sampling at an industrial site in Toronto, while simultaneously monitoring flow. A tipping bucket raingage was used and three trips (about 0.03 in. of rain) of the raingage within a few hours was usually used to initiate sampling.

In all cases, the use of telemetry (radio, telephone, or cellular phone) is extremely useful in minimizing false trips to a remote sampler by automatically signaling that samples have been collected. Campbell Scientific of Logan, Utah (801-753-2342), supplies many options allowing remote inquiring or automatic signaling to indicate sampler status. It is also possible to phone a monitoring station and immediately determine if a sampler is operating, and to download or observe instantaneous or compiled rain, flow, or continuous *in-situ* water quality monitoring information. The use of telemetry is extremely important when many remote systems are being operated by a small group. It should be considered an integral part of all sampling and monitoring programs where high reliability and good quality data is needed. There are potential problems with RF interference between cellular phones and some monitoring equipment, so care must be taken to use an external antenna, to electronically shield the monitoring equipment, and to thoroughly test the equipment.

An early example of an automatic stormwater monitoring program using telemetry to excellent advantage was the Champaign/Urbana NURP study conducted in the early 1980s (EPA 1983). The Universität Gesamthochschule in Essen, Germany has also recently used standard telemetry equipment components and specialized software in CSO monitoring in Dortmund to inquire concerning monitoring station and flow status (Wolfgang Geiger, personal communication). Numerous municipalities and state agencies in the U.S. have also installed telemetry coupled monitoring stations using relatively inexpensive components, including cellular telephone service and solar powered battery chargers. This has eliminated most of the concern about the availability of remote utility installations. Cooling collected samples still requires AC powered chillers, or ice. For remote installations with a small sampling crew, it is impractical to ice the sampler in anticipation of a rain, but that is possible when the samplers are more accessible. It would be more important to recover the samples from the samplers as soon as possible after the event. This is made much more practical, especially with remote samplers, when telemetry is used to inquire about the sampler status.

Retrieving Samples

Each sampler site will need to be visited soon after the runoff event to retrieve the sample for delivery to the laboratory. The storage time allowed in the sampler before collection should be determined from a special holding-time study conducted in conjunction with the analytical laboratory. Stormwater samples can usually withstand longer holding times without significant degradation than implied from standard laboratory method descriptions. This is especially important when organizing sample deliveries to the laboratory after hours (which can happen frequently).

General Manual Sampling Procedures

The following paragraphs summarize the procedures needed for manually collecting water and sediment samples from a creek or small stream.

1. Fill out the sample sheet and take photographs of the surrounding area and the sampling location. Conduct any *in-situ* analyses (such as stream flow measurements, along with dissolved oxygen, pH, temperature, conductivity, and turbidity measurements in the water).

2. Use a dipper sampler to reach out into the flow of the stream to collect the sample. Slowly lower the sampler onto the water, gently rolling the top opening into the flow. Be careful not to disturb the bottom sediments. Submerge the sampler lip several inches into the water so floating debris are not collected. Lift out the sampler and pour the water into a compositing container (such as a churn sample splitter). Several samples should be collected in the area of concern and composited.

3. Each water subsample can be poured into a large clean container during this sampling period. At the end of the sampling period, this composite sample is mixed and poured into the appropriate sample bottles (with preservatives) for delivery to the analytical laboratory.

Microbiological sampling requires special sampling techniques. ASTM (1995) in standard D 3370 describes the grab sampling procedures that must be used for collecting samples that will be analyzed for bacteria. The samples need to be glass and sterile. If the sample contains chlorine, then the sample bottle must contain thiosulfate so any residual disinfection action will be destroyed. The bottle lid is removed and the bottle is placed under flowing water and filled to about ¾ of its capacity. Care must be taken when handling the bottle and lid (including not setting them down on any surface and not touching any part of the upper bottle portion) to minimize contamination. Do not rinse the bottle with the sample or submerge it under water.

Sampling sediment can be difficult. The simplest method is to use a lake bottom sampler. Specifically, a small Eckman dredge sediment sampler, which is typically used for sand, silt, and mud sediments, is usually most useful. Corer samplers are generally not as successful for stream sediments. An exception is the freezing core sampler, where liquid CO_2 is pumped inside a stainless steel tube (with the bottom end sealed with a point) to freeze sediment to the outside of the tube. Again, the sediment would have to be at least several inches deep. In all cases, multiple sediment samples would have to be obtained and composited. Any water samples should be obtained first, as the sediment sampling will create substantial disturbance and re-suspension of sediment in the water column. All sampling equipment must also be constructed of non-contaminating materials. Stainless steel, polypropylene, or Teflon™ are the obvious choices.

Dipper Samplers

The simplest manual sampler is a dipper sampler. Markson (at 800-858-2243) sells a dipper sampler that has a 1 L polyethylene beaker on the end of a two piece, 4 m pole (catalogue # MK34438 for about $60). They also sell units on 1 and 2 m poles and with 500 mL capacities. These samplers can only obtain samples from the surface of the water. If subsurface samples are needed, then samplers having closure mechanisms need to be used, as described below. A dipper allows sampling of surface waters away from the immediate shoreline and from outfalls or sewerage pipes more conveniently than by using other types of samplers. Dippers are commonly used to sample small discharges from outfalls, where the flow is allowed to directly pour into the sampler. ASTM (1995) in standard D 5358 describes the correct stream water sampling procedure using a dipper sampler. The dipper needs to be slowly lowered into the water on its side to allow the water to flow into the sampler. The dipper is then rotated to capture the sample and lifted from the water. Care needs to be taken to prevent splashing or disturbing the water. The sample is then poured directly into the sample bottles, or into a larger container for compositing several dipped samples.

Submerged Water Samplers with Remotely Operated End Closures

There are numerous historical and modern designs of samplers that can take water samples at specific depths. These all have a way to remotely operate closures in a sample container. The sampler capacities usually range from 0.5 to up to 3 L. Older designs include the Kemmerer and Van Dorn samplers (*Standard Methods* 1995). These samplers have a tube made of metal or plastic and end closures made of plastic or rubber. All Teflon™ units are available to minimize sample contamination. Newer designs commonly used for small lakes or streams are similar to the Van Dorn design. This design allows unhindered flow through the sample container before closure, enabling faster equilibrium with surrounding waters. These samplers are also available in horizontal models (for shallow water) or vertical models. Several of the vertical units can be used on a single line to obtain water samples from various depths simultaneously. A weighted messenger slides down the line that the samplers are attached to, striking a trigger mechanism that closes the end seals. If multiple samplers are used, the trigger releases another messenger that slides down to the next sampler to close that sampler and to release another messenger. A vertical alpha end-closure 2.2 L sampler (polyurethane end seals and transparent acrylic cylinder) is available from Forestry Suppliers, Inc. (800-647-5368) as catalogue # 77244, with messenger #77285, for a total cost of about $450. Several of these samplers can be installed on a line for simultaneous sampling at various depths. Forestry Suppliers, Inc., also sell a 1.2 L Teflon™ Kemmerer vertical bottle sampler (catalogue # 77190) for about $800. A water sample collected with this sampler only contacts Teflon™.

Another surface operated design is a sampler that contains a 1L glass bottle on the end of a long pole (such as catalogue #53879 from Forestry Suppliers, Inc. at about $400). A stopper is spring loaded and is attached to a wire extending to the other end of the pole. The bottle end is lowered to the desired sampling depth and the wire is then pulled to fill the bottle. After a short period to allow the bottle to fill, the wire is released, resealing the bottle. This sampler was designed specifically for collecting water samples for Winkler titrations for DO analyses at sewage treatment plants. The bottle is initially full of air before the water enters the bottle and aeration may elevate the DO reading. If the bottle is prefilled with clean water, it is difficult to assume that the desired water sample will replace the water in the bottle. This sampler type may be useful for collecting sub-surface samples for bacteriological analyses, however, that should be collected in glass bottles with minimal handling.

A newer alternative is a Teflon™ tube sampler that contains a wire activated sealant mechanism and flow-through design. This overcomes the above limitations of the bottle sampler and still allows direct sampling at a specific depth. The AMS Cable Control Liquid Sampler is available from Forestry Suppliers, Inc. (catalogue # 77623), and costs about $550.

Depth-Integrated Samplers for Suspended Sediment

Suspended sediment is usually poorly distributed in both flowing and quiescent water bodies. The sediment is usually in greater concentrations near the bottom, as shown in Figure 5.1 (ASTM 1995). Larger and denser particles are also predominantly located in lower depths. Flowing water in a sinuous stream also distributes the suspended sediment horizontally as shown in Figure 5.2 (ASTM 1995). Collecting representative samples in these situations for sediment analyses is therefore difficult. Because most of the pollutants in stormwater are associated with the particulates, this unequal distribution of sediment also affects the ability to collect representative samples of many pollutants. Depth-integrating sampling is commonly done in small upland streams (Gordon, *et al*. 1992). Sampling in smaller and more turbulent flows (such as in sewerage or at outfalls during moderate to large storms) is not as severely affected by sediment stratification.

Figure 5.1. ASTM 1995, fig 1, pg. 204

Figure 5.2. ASTM 1995, fig 2, pg. 205

As shown in Figure 5.1, clay and silt-sized particles are generally well mixed across a stream cross-section, depending mostly on water mixing conditions near discharges, etc., and not on gravity. ASTM (1995) states that the concentrations of particles smaller than about 60 μm in diameter will be uniform throughout the stream depth. However, larger particles will be more affected by gravitational forces and may not be represented well with typical sampling procedures. Conventional water samplers may be used to represent all of the sediment in flowing water (floating material, suspended sediment, and bed load), if the water is very turbulent and capable of mixing the sediment of interest. ASTM refers to these locations as “total-load” stations, allowing the collection of all sediment greater than about 2 mm in diameter. These are generally located at outfalls or other free-falling locations.

Automatic samplers (or any pumped sampler) may disproportionately collect particulates if the intake velocities vary significantly from the water velocity. Isokinetic sampling requires that the sampler intake be pointed directly into the flowing water and that the velocity in the intake is the same as the flowing water. The water and sediment streamlines will therefore be parallel in this situation and a sample representative of the flowing water will be obtained. If the sample intake velocity is greater than the water velocity, water will be drawn into the sampler, while heavier particles will tend to flow past. This effect is most evident for heavier particles (larger and denser) than for lighter particles. Berg (1982) reports that particles approaching 100 μm in diameter with densities of 2.65 gm/cm^3 have less than a 20% sampling error when the velocities are not matched. Almost all stormwater and stream suspended particulates are smaller and have a lighter density than this and would therefore generally follow the flow streamlines. These particles would therefore not be significantly affected by this possible problem.

Large sized (larger than several hundred micrometers in diameter) suspended sediment measurements may be important for receiving water studies, especially in areas having flash flood flows in sandy soil regions (such as the southwest U.S.). The depth integrated sampler, as described by Gordon, *et al*. (1992), is designed to obtain a sample continuously as the sampler is lowered vertically through the water column at a constant velocity. This sampler was developed during the 1940s, and used glass milk bottles along with a home-made unit. These units vary significantly from commercial grab samplers that have remotely operated valves in that they have air vents to allow the air in the sample bottle to uniformly escape as the sample bottle fills with water. The home-made unit has a narrow mouthed bottle mounted on a rod with stabilizing fins. The mouth of the bottle is fitted with a 2-holed stopper. The top hole has a long flexible tube (which could extend above the water surface for most streams) to act as an air outlet, while the bottom hole has a rigid tube extending at least an inch to act as an intake. The intake nozzle should have a sharp front edge, with a narrow tubing thickness (less than 1/16 inch) and have an inner diameter of 5 to 6 mm (3/16 or ¼ inch) (ASTM 1995, standard D 4411).

When collecting a depth-integrated sample, the sampler needs to stand to the side and downstream of the sampling area to minimize disturbance (Gordon, *et al*. 1992). The rod is lowered vertically through the water column at a constant rate at about 0.4 times the stream velocity. Detailed vertical sampling rates are presented by ASTM (1995) in standard D 4411 for the series of older depth-integrated samplers. The sampler is lowered at this constant rate from the surface of the stream to the stream bottom, and then reversed and brought back to the surface at the same rate. The sampler does not collect samples within several inches of the stream bottom. Moving sediment near the bottom is usually included in the bed-load sample, which requires other sampling methods. The sample bottle should be between 2/3 and ¾ full after sample collection. If it is full, then the sampler did not represent the complete stream depth and the sample should be discarded and the sample collected again, at a faster vertical rate. If the sampler is less than 2/3 full, another vertical sample pass can be collected. After the sample is collected, the sample is poured from the sampler into a sample bottle. It is possible to mount an appropriate sample bottle directly to the sampler, and sample transfer would therefore not be needed.

Several vertical samples will normally need to be collected across the stream, as the coarser suspended sediment is likely highly variable in both time and space (ASTM 1995). The location and number of sampling verticals required at a sampling site is dependent primarily on the degree of mixing at the cross section.

Bed-Load Samplers

Bed load is the material that travels in almost continuous contact with the stream bed (ASTM 1995). The bed load material moves when hit by another moving particle, or when water forces overcome its resisting forces. Bed load is sampled by using a trapping sampler located on the stream bottom. The simplest bed load samplers are box or basket samplers which are containers having open ends facing upstream. Bed load material bounces and rolls into the sampler and is trapped. Other types of bed load samplers consist of containers set into the sediment with slot openings about flush with the sediment surface. The bed load material falls through a slot and is then trapped. Slot widths and lengths can be varied to represent various fractions of the bed load actually moving in the stream. The errors associated with sampling bed load are greater than with sampling suspended sediment because the larger particles move more irregularly under the influence of gravitational forces and are not well mixed in the water.

Bed load may be important when characterizing stormwater sediment discharges. In northern areas where sands are used for ice control, relatively large amounts of sand material can be transported along the drainage system as bed load. At the Monroe St. detention pond site in Madison, the bed load accounted for about 10% of the total annual sediment loading. This fraction was much greater during the spring when most of the sand was flushed from the drainage area.

Conventional water samplers may not adequately collect bed load material. A slot sampler placed in a drilled hole in the bottom on a discharge pipe can effectively collect this material. However, the slot dimensions and placement exposure times usually need to be determined by trial and error. In addition, several bed load samplers should be used in close proximity because of the varied nature of bed load transport. Bed load samplers that are full upon retrieval may not represent actual conditions. If full, then the slot widths should be reduced and/or the exposure time should be shortened. The slot length should be as long as possible for the container lid, as bouncing bed load

particles may jump over openings that are too short. In addition, the slot widths should be at least ¼ inch wide, as narrower slots will filter out large materials. Basket samplers are probably most applicable in streams, where the opening width is a small fraction of the stream width. Again, several samplers need to be used in close proximity and the best exposure period needs to be determined by trial.

Sediment Samplers

Analyzing urban stream sediment is normally a necessary aspect of a receiving water investigation. As noted previously, heavy metal and organic toxicants are of most interest in sediments. COD (along with TOC, DOC, etc.) concentrations and sediment interstitial water pH, ORP, and DO conditions are also of interest. Contaminated stream sediments likely impart the most important impairments to aquatic life in urban areas (after direct habitat destruction and frequent high flows). Benthic microorganisms especially suffer, with resulting adverse effects on other life forms that rely on them for food. Sediment accumulates relatively high concentrations of many problem pollutants, especially toxic organic compounds and heavy metals. Even through the short-term BOD of stormwater is not very high (BOD_5 of about 25 mg/L), the long-term BOD (BOD_{90} of about 250 mg/L) is high and resulting accumulations of organic debris in urban streams create anaerobic sediment conditions (Pitt 1979). The sediments therefore undergo chemical transformations of many of the trapped pollutants. Collecting and analyzing these sediments and interstitial water is therefore necessary when examining stream benthic organisms.

Numerous sediment samplers are available. Two general categories include core samplers (which can obtain samples that can be analyzed by depth) and surface grab samplers (which only collect surface sediment). ASTM (1995) standard 4823 contains much information concerning core sampling in unconsolidated sediments that is applicable to urban streams. ASTM standard E 1391 also presents additional useful information concerning the sampling of sediment for toxicological testing. The preferred sampling method is to use core samplers whenever possible. However, they collect relatively little sediment and represent only a very small area. In addition, it may be difficult to retain samples in the samplers for retrieval in some types of bottom conditions (especially sandy sediment).

Grab samplers only collect samples from the surface layers of the sediment (10 to 50 cm in depth, at maximum). They also greatly disturb the sediment that is being sampled. However, they are much easier to use than corers under a wide variety of conditions. The most common grab sampler is probably the Ponar sampler. It comes in a standard size and a “petite” size that weighs substantially less and is more practical for urban streams. The Ponar sampler is useful for sand, silt, and clay sediments and can be used in relatively deep water or shallow waters. It has a flexible cover over a top screen that helps to minimize the loss of fines during sampling, while allowing water to be displaced with sediment during sampling. Forestry Suppliers, Inc. (at 800-543-4203) sells a petite 6” x 6” Wildco Ponar bottom dredge (catalogue # 77250 for about $450) and a larger 9” x 9” Wildco Ponar bottom dredge (catalogue # 77249 for about $800). The Peterson grab sampler is similar to the Ponar, but doesn’t have a screened top plate. It is heavy and is more suitable for deeper water and harder clay bottoms than the Ponar sampler. Because of its weight, it requires the use of a winch. Cole Parmer (at 800-323-4340) sells a Petterson dredge sampler (catalogue # H-05472-00 for about $1,000). An Ekman sampler is also commonly used in small urban streams and ponds, but is limited to sampling soft bottoms. Forestry Suppliers, Inc. sells a light 6” x 6” Wildco-Ekmann bottom dredge (catalogue # 77251 for about $350, including line, messenger, and case). Cole Parmer also sells a larger 9” x 9” Ekman dredge (catalogue # H-05470-10 for about $600).

Corer samplers can penetrate the sediment by as much as 2 meters, but that is rarely necessary (or possible) in urban stream studies. Their most important advantage is that samples collected by corers can be separated by depth for analyses. A useful type of corer sampler is the freezing core sampler. All of the freezing core samplers rely on CO_2 (either as a liquid or a solid - dry ice). The use of CO_2 must be carefully evaluated and minimized in consideration of its role as a greenhouse gas. Pitt (1979) devised a freezing core sampler to collect profiles in sandy deposits of catchbasins which would also work well in shallow streams. This sampler was a 19 mm diameter stainless steel tube, with a stainless steel point attached to one end. This was pushed into the sediment. A length of flexible 6 mm copper tubing was then inserted into the free end of the stainless probe (which is above the water depth), extending to the bottom of the stainless probe. The other end of the copper tubing was attached to a high pressure hose and to a valve on a CO_2 fire extinguisher. The fire extinguisher was modified with a valve in place of the standard squeeze release, and with an internal “delivery” tube that extended to the bottom of the fire extinguisher. This enabled liquid

CO_2 to be delivered to the probe sampler, instead of gaseous CO_2 from the top of the fire extinguisher tank (the fire extinguisher is kept upright during operation). The valve was opened slightly and a continuous flow of CO_2 was delivered to the stainless steel probe. Care must be taken to turn off the flow of CO_2 at the fire extinguisher if it appears that a jam has occurred inside the probe (such as from ice forming due to water inside the probe sampler). The vaporization of the liquid CO_2 quickly chills the stainless steel probe and freezes the sediment sample to the outside of the tube. In operation, the CO_2 is allowed to flow for about one minute, but this can be changed depending on specific conditions and desired sample thickness. The stainless steel probe is then removed from the sediment (with the sediment frozen to the outside) after the CO_2 flow is terminated and the copper tube is withdrawn. The probe with frozen sample is then laid on a stainless steel tray and the sample is removed by section and bottled separately, according to desired depth. A flame torch can be used to gently heat the probe uncovered by sample to allow the easier removal of the sample. It may be difficult to separate the sample into precise segments unless the sample is allowed to warm slightly first.

Another version of a freezing core sampler suitable for deeper water use was described by Spliethoff and Hemond (1996). They developed two versions of core samplers using dry ice within a probe that was used to measure the history of heavy metal contamination in an urban lake. One sampler was made of a 96 cm length of 7.6 cm diameter aluminum tubing. The bottom half of the tube was cut away lengthwise, and a flat aluminum plate was welded to act as a freezing surface. Stabilizing fins were also attached, along with weights to control penetration. PVC was also used to insulate the sampler where sample was not wanted. The sampler nose piece was of solid aluminum. A screw cap was fitted to the other end which had a vent hole drilled in it. Another sampler was also constructed by Spliethoff and Hemond that allowed longer samples to be obtained. This sampler was made using a 125 cm length of 7.6 cm square Extren tubing (a fiberglass reinforced resin). One side of the square tubing was machined off and an aluminum plate was attached to act as a freezing surface. A point-shaped lead weight was attached to one end and a cap with gas relief valve was attached to the other end. They used a slurry of dry ice and denatured ethanol to act as a coolant in both samplers. The samplers were dropped from the lake surface to test the penetration depth. The samplers were then retrieved, filled with the coolant mixture, and dropped again. After about 15 minutes, the CO_2 bubbles reaching the lake surface subsided and the corers were then retrieved. The samplers were then cleaned of unfrozen sediment and filled with warm lake water to help in releasing the frozen sample from the sampler. The frozen samples were sealed in plastic wrap and transported to the lab in dry ice filled coolers where they were separated into segments for analysis.

The above described freezing core samplers result in relatively undisturbed cores for analyses, plus they enable effective sampling in conditions where sample retention using conventional core samplers is difficult (unconsolidated coarse textured sediment). ASTM (1995) in standard D 4823 describes many other types of core samplers. The most common sampler is the open tube sampler with a core catcher. This sampler is commonly used in shallow waters where it is manually pushed into the sediment. When the desired penetration depth is reached, the sampler is carefully withdrawn. A leaf core catcher is commonly used to help retain the sample in the corer. The leaves separate and fold against the inside walls of the sampler when the corer penetrates the sediment. The leaves fold closed when the sampler is withdrawn, holding the sample in the corer. Plastic liners are also commonly used inside the sampler, simplifying core removal from the corer. The liners usually have plastic end caps that can be placed on the liner ends, holding the cores inside until analyses. These conventional core samplers are most effective with clayey sediments. Sandy sediments tend to easily wash out of most corers upon retrieval, irrespective of the core catcher used. ASTM (1995) mentions excavating around a core sampler and sliding a flat plat under the bottom of the corer before retrieval in shallow water to capture most of the sample. Forestry Suppliers, Inc. sells the Wildco hand core sediment sampler that is 2” in diameter and 20” long, made of stainless steel with a plastic core liner tube and eggshell catcher (catalogue #77258 for about $340). Extra plastic liners are also available (catalogue # 77260) for about $12 each. They also sell stainless steel liners and core catchers (catalogue # 77303 for the stainless steel liner for about $70 each and catalogue # 77304 for the stainless steel eggshell sample catcher for about $40 each).

Interstitial Water Samplers

The conventional method of collecting interstitial water (pore water) samples is extracting the water from collected sediments. However, it is difficult to extract sufficient water volume from collected sediment samples. Interstitial water chemistry can also change significantly after 24 hours of storage (ASTM 1995, standard E 1391, section 10).

ASTM (1995) also notes that recommended storage times of sediments containing heavy metals ranges from two to seven days. The sediments should be stored at 4^{o}C and not frozen. Specific storage time limits is best determined from site specific evaluations. The extraction of interstitial water from sediments must be accomplished within a relatively short time after sediment collection.

ASTM (1995) states that centrifugation of sediments and sediment squeezing are the only two methods that are likely to result in large volumes of interstitial water for normal toxicity analyses. Suction and *in-situ* samplers are not likely to result in sufficient water volumes. ASTM recommends that sediments be centrifuged at 10,000 x g for 30-minutes for toxicity testing of interstitial waters.

ASTM does state that *in-situ* suction techniques or equilibrium dialysis are the likely optimal methods for collecting interstitial water resulting in the least chemical changes. However, the equilibrium methods most often require a one to two week equilibrium period, although periods of only several hours have been used. The use of pore water suction methods have been used to measure dissolved oxygen in interstitial water in urban streams. Galli (1997) used a simple aquarium aeration stone attached to a plastic tube and a hand operated pump to carefully extract enough water for analysis.

It is important to work with the analytical laboratory to determine the least amount of sample needed because of the difficulty of obtaining large amounts of pore water for chemical analyses. As an example, the use of an anodic stripping voltammeter is suitable for direct analyses (undigested) of heavy metals in interstitial water using only about 5 mL of water for lead, copper, and zinc simultaneously, instead of about 50 mL typically required. Organic analyses may be conducted using about 250 mL of water, using the methods previously described, instead of the typically required 1 L sample sizes, but with loss of sensitivity. The use of an automated water analyzer (such as the TrAAcs 2000 analyzer from Bran+Luebbe) can dramatically reduce the needed water volume for conventional nutrient analyses. Ion chromatography also requires only a very small amount of sample for complete cation and anion analyses. Microtox™, from Microbics, is also a very useful indicator of toxicity and only requires a very small amount of sample (about 1 mL). Bacteria tests can also be conducted using small sample volumes, if the bacteria densities are high, as likely in contaminated urban streams.

Special porewater samplers (commonly called peepers) were developed by Hesslein (1976) to collect sediment porewater for chemical analyses. These devices are made from plexliglass and are about 10 to 15 cm wide and 45 to 60 cm long, with one end tapered to a point. The main body is made of 20 mm thick stock and has numerous deep and wide slots (not cut through) spaced 1 cm apart, that hold about 5 to 10 mL of water each. The slots should not extend any closer than about 20 mm from the edge, to prevent cracking of the thinner cover piece. A nylon screen having 75 μm apertures is placed over this thick piece and is then covered with a thinner sheet of plexliglass that is 6 mm thick. This cover piece has identically located slots cut through the material and has countersunk holes matching tapped holes in the main body. For use, the cavities in the main body are filled with distilled or de-ionized water, covered with the nylon screen and then the two plexiglass pieces are screwed together using plastic screws, sandwiching the nylon screen. The unit is then pushed into the stream or lake sediment, gently pushing down on the unit until resistance prevents further penetration, leaving about 5 slots above the sediment/water interface. The unit is left in place until equilibrium is established, and is then removed. The unit may require up to two weeks for equilibrium to become established when using small aperture screenings (such as 0.45 or 2 μm membrane filter material). This long period is not feasible in urban streams due to security problems, and the typically frequent high flows that could damage the sampler. The use of larger aperture screening dramatically shortens the needed exposure time, but also requires greater care to prevent changes to the captured water. The samplers need to be taken immediately to the laboratory where the water is immediately analyzed. It is also possible to remove the samples from the slots in the field (using a syringe and needle), transferring the water into sealed and full bottles (such as small VOC vials). Four or five peepers located close together can provide a 20 to 50 mL composite sample of porewater in 1 cm depth increments for chemical analyses. As noted above, carefully selected analyses methods can result in many different analyses for this water. In this Birmingham SSO (sanitary sewer overflow) evaluation project being conducted by UAB, *enterococci*, *E. Coli*, total coliform bacteria, Microtox™ toxicity screening, heavy metals (copper, lead, and zinc), major ions, and nutrients are being analyzed on most of the porewater samples. Changes in porewater chemical and bacteriological quality can then be used to calculate diffusion coefficients for conservative pollutants, as described by Greb and Garrison (1988), and kinetic rate coefficients.

In-situ chemical analyses of interstitial water are also possible. The University of Alabama at Birmingham is currently using YSI 6000 monitoring probes to continuously monitor interstitial water pH, ORP, conductivity, DO, and temperature in urban streams as part of this EPA sponsored SSO impact research project. These instruments are capable of unattended operation for several weeks. The probe end of the instrument is wrapped with a nylon screen having 150 μm apertures. Equilibrium should be obtained within a few hours using this large aperture. The instrument can be placed vertically with the probe end buried several hundred mm in the sediment in slow moving streams for short periods. The instrument is completely buried horizontally for longer periods or for higher flows. The use of a direct readout (hand-held readout from YSI, or a portable computer) is useful in determining equilibrium times during preliminary trials. The available turbidity probe is also used to indicate the effects of placement of the probe by measuring the exchange of water in the probe chamber. A similar unit placed simultaneously in the water column can be used to measure the lag time of any chemical changes (such as conductivity) in response to storm events and to directly determine diffusion coefficients.

Flow Measurements to Supplement Water Quality Monitoring

Measuring stream velocities (V) and discharges (Q) are an important component of receiving water studies to determine the effects of SSOs. SSO discharges at the outfalls may also be needed. Stream flow measurements can be made using one of three basic methods briefly discussed here: (1) drift method, (2) current meter method, and (3) tracer method. Outfall discharges are best made using a flume inserted in the flow path, but most are made by only monitoring water level and applying Manning's formula to predict velocity and discharge.

Urban Hydrology

Basic watershed characteristics need to be known in order to understand stream flow conditions. These include topography (watershed divide plus stream and land slopes), drainage efficiency (stream orders, and types of artificial drainage system), and to a lesser extent in urban areas, soil characteristics (disturbed or compacted, age since development, type of ground cover, soil texture, etc.). It is important that characteristics throughout the watershed be evaluated when studying streams. Only looking at characteristics adjacent to the stream is very misleading, as urban drainage systems are very efficient transporting systems, capable of carrying water and pollutants to the stream from locations far away. These topics are beyond the scope of this report, but several good books are available that describe urban hydrology and associated drainage design (including McCuen 1989, ASCE 1992, Debo and Reese 1995, and Wanielista, *et al*. 1997).

The routing of pollutants through a watershed is a complex issue which is also beyond the scope of this report. One of the most important goals of a monitoring effort is collecting representative samples. In many cases, pollutant routing can affect pollutant concentration distributions. At outfalls, or in receiving waters, stormwater pollutant concentrations are random, with little of the observed variations being explainable by normal parameters (such as time since the event started, or by rain depth). As noted previously by Roa-Espinosa and Bannerman (1995), obtaining many discrete sub-samples over the event duration likely results in a composite sample that has pollutant concentrations very similar to a flow-weighted composite sample. However, if collecting samples from a relatively small homogeneous area (such as a paved parking area), high concentrations of practically all pollutants are commonly observed near the beginning of the rain.

This "first-flush" phenomenon is most prevalent for rain events of constant intensities and for small drainage areas. As a drainage area size increases (or as the surfaces become more complex, such as in a residential area), multiple first-flush waves travel through the drainage system, arriving at a single downstream location at different times. This moderates obvious concentration trends with time during the event. Also, as the rain intensity varies throughout an event, the washoff of pollutants at the sources also varies. Peak washoff occurs during periods of peak rain energy (high rain intensity). Therefore, periods of high concentrations may also occur later in a rain, as high rain intensities occur. Generally, lighter (more soluble) hydrocarbons and the smallest particles will "always" show a first-flush of high concentrations from small paved areas, while larger particulates and heavier hydrocarbons will wash off more effectively with high rain energies which may occur randomly during a rain.

Sampling strategies must therefore consider these possible scenarios. The most effective sampling (but most expensive) is flow-weighted composite sampling throughout the entire storm event. However, compositing many

discrete subsamples that are collected throughout the event is likely to result in similar concentration values. If sampling a small critical source area (such as a gas station, or convenience store), it may be useful to obtain an initial sample during the first few minutes of the event, and a composite over the later portions of the event. In all cases, it would be difficult to justify analyzing many individual discrete samples collected throughout an event.

Stream Flow Monitoring

Flow monitoring in streams and other open channels is usually a necessary component of receiving water investigations. Flow estimates need to be made whenever any in-stream measurements are made, or samples collected, for example. In addition, continuous flow monitoring equipment must be periodically calibrated using manual procedures. The following paragraphs briefly describe several common manual flow monitoring procedures.

Drift Method

The drift method is simply watching and timing debris floating down the stream. This velocity is then multiplied by the estimated or measured stream cross-sectional area to obtain the stream discharge rate. Of course, this method is usually the least accurate of available flow estimation methods. The accuracy can be improved by choosing drift material that floats barely under the stream surface (such as an orange). Do not use material that floats high in the water (such as Styrofoam debris, for example), as they will be strongly influenced by winds. Drift measurements made in the center of a stream will tend to be the highest stream velocities, so the values need to be reduced (by roughly 0.6, but highly variable) to better represent average stream flow rates.

Current Meter Method

The most traditional method of flow measurements is by using a current meter. This method requires at least two people (one person should never be working alone near a stream anyway), a current meter, and simple surveying equipment. The stream discharge is measured at a selected cross section, usually selected along a relatively straight stretch (about 10 stream widths downstream from any major bends). If the stream discharge is being used to calibrate a stage recorder for continuous flow monitoring, the cross section being measured must not be affected by back-water conditions. If the selected cross section is in the vicinity of sampling and will not be used to calibrate a flow equation but will be used to determine the instantaneous current conditions at the time of sampling, then back-water influences and affects from meanders need to be included in the measurements.

In order to calibrate a flow or discharge model (especially the Manning's equation), the stream is assumed to have normal flow, where the water surface is parallel with the stream bottom. This is unusual under real stream conditions, where actual water surface profiles exist. In this case, the Manning's equation can still be used, but by substituting the friction slope for the water surface (or stream bed) slope. The friction slope is elevated above the water surface by the velocity head ($v^2/2g$). It is therefore easy to adjust the surveyed water surface slope to the friction slope by adding the velocity heads at the upstream and downstream locations. The calibration procedure usually involves calculating the Manning's roughness factor (n) in the stream stretch.

Biological monitoring is normally conducted during relatively low flow periods, whereas the Manning's equation was developed for channel design for large, rare events. The Manning's equation is a conservative design formula (when using the published roughness coefficients). It is not an analysis method and it must be used with care during low flow conditions. During low flows, the roughness coefficient is usually much greater than during high flows, for example, requiring equation calibration at different stream stages.

Current meter flow monitoring requires that the stream be divided into several sections. About 10 sections that are from 1 to several feet wide are usually adequate, depending on overall stream width. The depth of the stream is measured at each section edge, and the water current velocity is measured in a vertical profile in the center of each section. The average velocities in each section are multiplied by the section areas to obtain the discharge rates for each section. These are then summed to obtain the stream discharge. Table 5.2 is an example calculation for a section on Cahaba Valley Creek, in Shelby County, AL, that is used as a field demonstration site for UAB hydrology classes. Figure Y.37 is a cross sectional diagram of this site, also showing the flow profile distributions. It is interesting to note that the peak water velocity for this stream section is seen to be near the bottom of the stream, close to the middle, but off-set. This is in contrast to the typically assumed velocity profile where the peak velocity is very near the top of the stream (and near the center). This observed profile has been commonly encountered at this

monitoring location. Figures Y.12 through Y.15 are photographs of a UAB hydrology class obtaining current measurements at this location.

Table 5.2. Example Calculation for Flow and Current Measurements

Section Interval (ft)	Midpoint, distance from shore (ft)	Depth at Midpoint (ft)	Section Area (ft^2)	Velocity at 0.2 depth (ft/sec)	Velocity at 0.8 depth (ft/sec)	Average Velocity (ft/sec)	Discharge (ft^3/sec)
0 - 1	0.5	0.21	0.2	0	0	0	0
1 - 3	2	0.74	1.5	0.3	0.4	0.4	0.6
3 - 5	4	1.42	2.8	1.1	1.6	1.4	3.9
5 - 7	6	1.70	3.4	1.8	2.0	1.9	6.5
7 - 9	8	1.93	3.9	1.5	2.5	2.0	7.8
9 - 11	10	1.94	3.9	1.4	2.5	2.0	7.8
11 -13	12	1.79	3.6	2.0	3.0	2.5	9.0
13 - 15	14	1.54	3.1	1.5	2.2	1.9	5.9
15 - 17	16	1.19	2.4	0	0	0	0
17 - 18.5	17.75	0.46	0.7	0	0	0	0
total			26			1.6	42

HereHere

Figure Y.37 Cross-Section of Stream Velocities at Cahaba Valley Creek, Shelby County, AL

Figures Y.12 - 15 (photographs of class taking stream measurements)

Stream discharge monitoring is obviously a multi-person job, both from a safety standpoint and in order to take the actual measurements. A safety throw rope should always be ready, and great care should be exercised when working in a fast moving and/or deep stream. If a stream has too great a velocity (especially greater than about 2.5 ft/sec), or too deep, then current measurements should be conducted from a bridge, or cable system, and personnel should not be allowed to enter the water. Urban streams are also known for hidden debris and very soft bottoms. As in all work in urban streams, waders are necessary to minimize water contact and to prevent injuries from sharp objects. Riparian plants (such as poison oak and poison ivy) and slippery banks can also present additional hazards near streams.

A suitable current meter is obviously needed for a stream discharge study. Direct reading digital meters, instead of older audible counter meters where the operator must count clicks that are related to the water velocity, are now most commonly used. The current meter should be able to measure to 0.1 ft/set, have a threshold velocity of at least 0.2 ft/sec, and preferably have an averaging mode in addition to an instantaneous mode. The meter should also be capable of measuring in very shallow water and next to the stream bottom (within a few inches deep). The readout should also be selectable between metric and U.S. customary units. The meter must be re-calibrated at least every year, preferably in the manufacture’s tow tank or in an open channel test facility. Numerous hand-held current

meters are available. Forestry Suppliers, Inc. (800-543-4203) has several different mechanical models, as listed below:

Swoffer Model 2100-1514 (#94161)	0.1 to 25 ft/sec	1% accuracy	$2,300
Handheld Flowmeter (#94303)	0.5 to 25 ft/sec	± 0.5 ft/sec accuracy	$700
Gurley Model 625 Pigmy (#94993)	0.05 to 3 ft/sec	audible counter	$1,320
Gurley Model 625 Pigmy (#94983)	0.05 to 3 ft/sec	digital indicator	$2,600
Gurley Model D622F Meter (#94982)	0.2 to 32 ft/sec	digital indicator	$2,940

All of these current meters meet the desirable performance criteria, except for the much less expense flowmeter. Newer portable meters are available that have no moving parts, typically using sonic pulses and doppler measurements of reflected sound waves from moving particles in the water.

An engineering level, rod, and tape are also needed to measure the water surface slope between adjacent cross sections when calibrating the Manning's equation. Cloth tapes are suitable for measuring the stream widths, and rigid (but thin) rules are useful for measuring water depth at the stream sections. When measuring water velocities with a current meter, the operator must stand to the side and behind the meter and ensure that no turbulence from their legs (or from others) affects the measurements.

Tracer Method

The most precise method of stream current measurements is through the use of tracers. This method is especially important when measuring flows in areas having karst conditions where surface waters frequently lose and/or gain substantial flows to and from underground flows. A single upstream dye injection location and multiple downstream sampling stations through the study area are used in this situation. Tracers are also needed if there is an obviously large fraction of inter-bed flow, or if the stream flow is very turbulent. The flow in very shallow streams, especially when the stream is cobble-lined, is also very difficult to monitor with current meters, requiring the use of tracers. Another common use of tracers is when measuring the transport and diffusion of a discharge into a receiving water. Hydraulic detention times in small ponds and lakes can also be determined using tracers. Orand and Colon (1993) state that the use of tracers for water discharge measurements is not a new concept. They admit that the use of current meters is usually much simpler and therefore more common. However, current meters are not applicable in many situations, as noted above. As an example, they routinely use a field fluorometer with continuously recording output to measure the discharge of very turbulent mountain streams that would not be possible with current meters.

Unfortunately, tracers are rarely useful for continuously monitoring flows, but they can be used for instantaneous flow determinations, or for calibrating conventional continuous flow monitoring equipment in actual installations. Dave Owens of the USGS in Madison, WI, (personal communication) recently installed several different flow monitoring devices in a single storm drain pipe for comparison (Figures Y.88-CC). A unique aspect of these tests was the use of continuous dye injection and downstream water sampling that was automatically activated when rainfall started. The samples were then brought to the laboratory for fluorometric determinations and actual flow values. These actual flows were than compared with the flows indicated by the different flow monitoring equipment.

Figures Y.88-CC (Dave Owens flow monitoring set-up photographs)

Brassington (1990) lists the desired traits for a tracer. He states that an ideal tracer should be detectable in very small concentrations, it should not be naturally occurring (if an artificial tracer is being used), it should exhibit conservative behavior, it should be safe to use and produce no harmful environmental effects, and should be relatively inexpensive and readily available. Three main classifications of tracers are generally used. Dyes give a specific and distinctive color to the water that can be detected easily. Chemicals, especially naturally occurring salts, can be effectively used if a discharge into a receiving water has a unique water chemistry and the tracer study's objectives is to determine the behavior of the discharge. Mechanical tracers can also be used to tag the water, much

like the drift method described previously. However, the most common mechanical tracer is a spore of *Lycopodium*, a club moss (Brassington 1990). The spores can be dyed and used to measure the surface and groundwater interactions in complex systems.

The most efficient tracer is a naturally occurring one. Johnson (1984) concluded that using naturally occurring materials (such as salinity, turbidity, temperature, or other suspended or dissolved materials) allows much more data to be collected and is usually relatively inexpensive (compared to using artificial tracers). In order to use a natural tracer, the material must be conservative, be highly soluble under a variety of conditions, not be amenable to sorption or precipitation or degradation, be linear with mixing, and be present in greatly contrasting concentrations in the two water bodies that are mixing. The tracer must also be easily and cheaply analyzed. In many cases, specific conductivity can be used. Specific conductivity is especially useful when examining fresh water inflows into saline receiving waters. Field, *et al.* (1994) described the use of specific conductivity to measure the effectiveness of a combined sewer overflow (CSO) capture and control device in Brooklyn, New York. In this example, the CSO (which had a specific conductivity of about 1,000 μS/cm, and a standard deviation of about 250 μS/cm) was contrasted with Fresh Creek water (which had a specific conductivity of about 20,600 μS/cm, and a standard deviation of about 2,600 μS/cm). Standard conductivity meters were used to trace the CSO water as it displaced the Fresh Creek water in the treatment facility during rains, and to measure the leakage of Fresh Creek water into the treatment facility between rains, as shown in Figure Y.83. The mass (M) of the tracer is equal to the water volume (V) times the concentration (P). It does not matter that there is no adequate conversion for specific conductivity to be expressed as a mass, as specific conductivity concentrations were shown to be linearly related to dilution with the receiving water. A Monte Carlo mixing model was used to calculate the unknowns in this diagram, considering the variabilities of the concentrations in the two water bodies. Stable isotopes have recently been successfully used as tracers by some researchers having access to sensitive mass spectrophotometers, if the waters being distinguished have a sufficiently different source (Sangal, *et al.*1996). Ratios of major ions have also been successfully used to identify different waters, especially in groundwater studies (Hounslow 1995).

Figure Y.83 fig 1, Field et al 1994 (fresh creek)

In most cases, naturally occurring tracers cannot be effectively used because of their non-conservative behavior, insufficient concentration contrasts, or expense of analyses. Commercially produced fluorescent dyes have been available for many years and have been extensively used for water tracer analyses. Fluorescein (a green fluorescent dye) has been used since the late 1800s, for example, but is not very stable in sunlight. However, it is still commonly used in visual leak detection tests and to visually trace discharge connections (such as determining if floor drains are connected to the sanitary wastewater lines or the storm drain system). Figure Y.04 shows fluorescein being used to trace sanitary sewage connections to a storm drainage system.

Figure Y.04 (slide of green outfall in Boston)

Rhodamine B was used in the 1950s for water tracing in Chesapeake Bay because it was more stable in sunlight than fluorescein, but it readily adsorbed to sediments making quantitative measurements difficult (Johnson 1984). Forestry Suppliers, Inc. (800-543-4203) sells liquid, and compressed tablets and cakes of Rhodamine B and fluorescein for visual tracer work (but not near water intakes). Bottles of 200 tablets of either dye, having a total weight of about 10 oz., or a 3” donut, also weighing 10 oz., of either dye costs about $35.

The most common artificial tracer currently used is Intracid Rhodamine WT dye, a 20% (by weight) stock of dye in water and other solvents having a specific gravity of 1.2. It is available from Crompton and Knowles (Reading, PA, 215-582-8765), at about $400 per 10 L . It is greatly diluted before use in the working stock solution for continuous dye injection studies. Chemical and laboratory suppliers also sell much more dilute mixtures (but at a much greater cost per unit of dye). Forestry Suppliers, Inc. sells a one gallon bottle of Rhodamine WT, unspecified dilution, (catalogue #92969) for about $100, and bottles of 200 compressed Rhodamine WT tablets (catalogue # 92991) (weighing 11 oz.) for about $36.

Rhodamine WT was specifically developed in the 1960s for water tracing applications and is much superior for quantitative work compared to the earlier dyes. It is generally easier to detect in much lower concentrations, less toxic, has lower sorption to particles and exhibits slower decay. Even though it is very expensive by volume, its very low detection limit (about 0.01 ppb of the 20% stock solution) and conservative behavior makes it very cost effective.

Even though Rhodamine WT is generally thought to have a very low toxicity level, the USGS limits its concentrations at water supply intakes to 10 ppb (Johnson 1984). The biggest toxicity problem associated with Rhodamine WT is apparently associated with reactions with very high concentrations of nitrates. In all cases, it is important to contact local drinking water and state water regulatory agencies when planning a dye tracer study. The largest concern is probably associated with complaints of red water.

The Corps of Engineers (Johnson 1984) has published a comprehensive description of the use of water tracing using fluorescent dyes. This report stresses monitoring inflows into reservoirs, with information applicable for a wide range of surface water conditions, including small streams, large rivers, and lakes. He reports that no significant decay of Rhodamine WT is likely to occur due to chemical or photochemical decay for conditions found in natural waters. However, high chlorine levels (several mg/L, as found in many drinking waters) can cause significant decay during long exposure tests (10s of hours). As an example, Johnson reports that chlorine concentrations of 5 mg/L in tests run over 20 hours caused about a 5% decay of fluorescent activity. If operating in urban areas, where the chlorine concentrations may be periodically high or turbidity variable, it is important to test decay and sorption of the dye. This is best done by using actual receiving water collected at the time of the tracer study as the dilution water when preparing the dye standards. These standards should be compared to standards using proper laboratory dilution water (preferably prepared using ion exchange, and/or reverse osmosis, as laboratory distilled water can contain very high chlorine levels).

Johnson (1984) states that total fluorescent decay of Rhodamine WT is probably about 0.04/day, from both sorption and photochemical decay. Almost all of this loss is likely associated with sorption. The sorption of Rhodamine WT onto particles, according to Orland and Colon (1993), had less than a 7% effect on the measured stream discharges (over-estimated) in water having suspended solids concentrations ranging from 200 to 2,000 mg/L (particle diameter $<200\mu m$).

Johnson (1984) also reports the effects of pH, temperature, and salinity on the fluorescence of Rhodamine WT. The most serious problem with precise measurements is that the fluorescent intensity decreases with increasing temperature, requiring temperature corrections. This change is a decrease in fluorescence by about 5 percent for every 2°C increase in temperature. If collecting discrete samples that are brought back to the laboratory for analysis, the samples and the standards can be kept at the same temperature for analyses, eliminating this problem. *In-situ* fluorescent measurements require temperature corrections (available as an option in the Turner Designs 10-AU, for example). It is recommended that discrete samples also be periodically collected, along with the continuous field measurements, for temperature controlled laboratory analyses to confirm the automatic corrections.

The pH of the receiving water affects the sorption of the Rhodamine WT to organic material. Below a pH value of 5.5, the carboxyl acid group of the dye becomes protonated, increasing adsorption. Johnson (1984) reviewed studies that showed that humic sediment solutions of 2.0 and 20 g/L and 100 ppb Rhodamine WT caused 18 and 89 percent decreases in fluorescence, respectively. The high humic concentrations lowered the pH values of the water, plus increased the organic content of the water. In similar solutions using a Kaolinite clay, the fluorescent losses were only 11 and 23 percent. These clay concentrations are very high (2,000 and 20,000 mg/L) and would be only likely

to occur in construction site runoff in urban areas. The very high associated turbidity of these samples would also greatly complicate fluorescent measurements. The samples would likely have to be clarified (by centrifuge or filtering) before measurements.

The most commonly used fluorescent measurement instrumentation is the older and obsolete Turner model 111 fluorometer that is still available in many laboratories, and the newer Turner Designs (408-749-0994) model 10-AU fluorometer. Both of these instruments are filter fluorometers and very sensitive. The Turner Designs 10-AU is a much superior unit for field measurements, as it is designed to operate by 12 volt batteries, has newer and more stable electronics, a wider dynamic range, and has a water resistant case. It is also suitable for laboratory measurements. The Turner Designs unit also has a flow-though cell, plus built-in temperature correction and data logging options, which are convenient for field use.

The downstream dye concentrations should be measured over a long period and at many locations across the stream to obtain the best flow estimate. In practice, an automatic water sampler is used to obtain samples, or manual grab samples are obtained, at the downstream location for laboratory analyses, or less commonly, a flow-through fluorometer is used to measure the dye concentrations on a real-time basis. If manual sampling is used, then subsamples can be obtained from several locations across the stream for compositing. If a flow-through instrument is used, the intake can be moved to various locations across the stream to investigate mixing conditions. In all cases, the downstream location should be well beyond the predicted fully-mixed area. Variations in dye concentrations observed are therefore assumed to be associated with flow variations in the stream.

Background fluorescence in the water must be determined before and during the test. During some tests, we have detected residual background fluorescence. In receiving waters affected by sanitary sewage (such as from raw overflows, inappropriate connections, leaks, septic tank influences, and treated effluent), background fluorescent can be very high due to detergents in the water. Almost all of this interference is eliminated by using specific Rhodamine WT filter sets in the fluorometer. The use of the actual water being tested as the injection water diluent during a continuous test reduces background problems, as does the highly selective optics available for Rhodamine WT analyses. However, background water samples need to be collected for analyses before any dye is added to the water. In addition, it is a good idea to periodically collect upstream water during the test to check for changing background conditions (especially important when conducting a tracer test in a sanitary sewer where background water quality can change dramatically over a relatively short period of time). If turbidity levels vary greatly during the test, Johnson (1984) recommends that the samples be filtered or centrifuged prior to analysis. Continuous dye analyses in the field does not allow a correction for turbidity (like the built-in temperature correction option available from Turner Designs), but periodic grab samples analyzed in the laboratory after turbidity reduction enables these effects to be determined.

The careful calibration of fluorometers is critical because of their great sensitivity. Calibration solutions from about 0.1 to 500 ppb should be used. These concentrations are in relation to the 20% stock solution. Two sets of calibration solutions need to be prepared. The initial laboratory series is prepared using laboratory grade clean water, and another set needs to be prepared using the receiving water. As noted previously, if using distilled water, ensure that the chlorine concentrations are very low. Never use tap water. De-ionized water (at 18 meg-ohm resistance) is probably the best. Preparing such low concentration standards requires a great deal of care, especially when withdrawing the stock and making the initial dilution. Needless to say, the largest hazard associated with working with Rhodamine WT is the mess that it can make. The stock solution is stratified in the shipping container, requiring stirring, but trying to stir or shake the stock container is a challenge, as it is heavy and minor spills or leaks are a great nuisance.

It is recommended that the amount of dye needed for the test be withdrawn from the stock shipping container, including the minor amount needed for preparing the standards. This will be only a very small amount, usually only a few hundred mLs for a slug dose test, or a few liters, if conducting a continuous injection experiment in an urban stream. This aliquot doesn't have to be perfectly representative of the stock solution. The goal is to withdraw the amount needed without spilling any, with minimal mixing. The initial dilution is usually made using 10 mL of the stock diluted in a liter of dilution water, using a volumetric flask. The 10 mL of stock is very dark and viscous, making it almost impossible to measure with a standard pipette. Many people weigh the initial amount, correcting

for the 1.2 specific gravity, but unless the aliquot was from a well-mixed stock container, the specific gravity can be quite different. An automatic pipette (capable of handling viscous fluids) is probably better, as volume dilutions are being measured during the test. Serial dilutions are then usually made, making weaker and weaker standards. The strong concentrations foam when violently mixed, making it difficult to accurately fill the volumetric flasks to calibration marks.

Analytical chemists do not approve of serial dilutions, as errors are easily compounded, but the nature of Rhodamine WT and the great dilutions needed would otherwise require measuring very small quantities of stock. Using a 1 μL pipette and a 1 L volumetric flask would only produce a 1 ppm (1,000 ppb) solution, by volume. At least a second (serial) dilution would still have to be made to obtain a 1 ppb concentration, and a third dilution to obtain a fraction of a ppb standard. Inaccuracies associated with serial dilutions are probably less of a problem than trying to pipette such small amounts.

Fluorescent analyses can be conducted in the field or in the laboratory. *In-situ* (flow-through) dye analyses (for which the Turner Designs 10-AU is specifically designed) can be much more efficient than collecting water samples and bringing them back to the laboratory for analyses. However, a combination approach is usually best, where periodic samples are collected and brought to the laboratory for temperature controlled analyses for comparison to the *in-situ* values. The *in-situ* analyses allow immediate evaluation of the sampling program, especially when the dye is being used at proper concentrations making it nearly invisible to the eye, or if complex hydraulics (such as in an estuary with strong currents) prohibit easy prediction of the flow path. However, using a fluorometer in flow-through mode presents special problems. Johnson (1984) stresses the need to ensure that all water connections are air tight to prevent bubbles from entering the flow path. In addition, the pump should be located above the light cell to decrease bubbles from leaky pump seals. The intake of the water delivery system should also be screened to decrease the chance of sand and other debris from scratching the instrument optics.

The two main types of dye injection include instantaneous or continuous releases. Instantaneous dye releases are much more efficient in the use of dye. The amount of dye quickly added to the water usually results in a visible dye cloud that can be manually followed easily. In addition, no special dye injection equipment is required, as the dye is simple poured quickly into the waterbody. However, continuous releases of dye, especially in conjunction with *in-situ* analyses, is necessary when simply tracking the dye is challenging. Continuous dye releases require substantially more dye and usually more field personnel, but changing conditions can be easily measured.

Thomman and Mueller (1987) present a USGS method used to estimate the amount of Rhodamine WT dye needed for an instantaneous release experiment. The amount is usually much less than needed for a continuous release experiment. They also present several methods to evaluate the observations to obtain estimates of flow, diffusion coefficients, and recovery of dye.

Continuous release rates of dye are dependent on the desired downstream concentration of dye, the concentration of the dye being released, the injection rate, and the estimated stream discharge. Figure Y.48 shows a basic mass balance for a discharge into a river or stream. This can be easily applied to a dye injection experiment, with the dye being considered as the effluent being discharged into the receiving water.

Figure Y.48 (Fig 2.9, pg. 51, Thomman and Mueller)

The mass balance for this situation is:

upstream mass + effluent mass = downstream mass, or:

$Q_u s_u + Q_e s_e = Qs$

where Q_u = upstream flow rate
s_u = upstream concentration
Q_e = effluent discharge (or dye injection) rate
s_e = effluent (or dye injection solution) concentration
Q = resulting downstream discharge rate (equal to $Q_u + Q_e$)
s = resulting downstream concentration

Solving for Q, the downstream discharge rate:

$$Q = (Q_u s_u + Q_e s_e) / s$$

If the background concentration (s_u) is zero (as desired in a tracer experiment), this further reduces to:

$$Q = Q_e (s_e / s)$$

where (s_e / s) is the dilution ratio of the dye

Therefore, the stream discharge (Q) is the ratio of the concentration of the dye injection solution (s_e) to the measured downstream dye concentration (s), multiplied by the dye injection rate. As an example, assume the following conditions:

Q_e = 10 cm^3/sec
s_e = 1.0 (injection dye solution concentration, given arbitrary concentration of 1.0)
s = 12 ppm_{vol} compared to injection concentration (average dye concentration from numerous samples collected).

The average value for s is 12 ppm and the calculated stream discharge rate is therefore:

$$Q = Q_e (s_e / s) = 10\ cm^3/sec\ (1.0/12 \times 10^{-6}) = 830{,}000\ cm^3/sec$$

This is equal to 830 L/sec, or about 29 ft^3/sec (cfs). As noted in this example, the absolute concentration of the injection solution is not needed to be known, as long as calibration solutions are made using the injection solution and the receiving water.

The injection solution needs to be discharged at a constant rate, made much easier by using a special metering pump (as supplied by Turner Designs, for example, or a battery operated peristaltic pump available from Cole-Parmer). In all cases, someone needs to be at the injection site during the duration of the experiment to ensure that the discharged dye is well mixed and that constant pumping of the injection solution is occurring by periodically measuring the time needed to fill an appropriate graduated cylinder (retain some of the solution from the filled cylinder for use in later calibration solutions, and dump the remainder of the material from the cylinder when finished timing). The injection solution samples should be analyzed to detect variations in injection dye concentration during the study period.

Fortunately, as evident from the above equation, everything is relative to the injection concentration, or the mass of dye used, with tracer work. The stock solution concentrate is never directly used in dye studies because the intense color would make the injection plume visible for a large downstream distance, the high 1.2 specific gravity affects the plume buoyancy, and because of the difficulty in precisely pumping very small dye injection rates. The stock is therefore greatly diluted (by about 10 to 100 times) to create an injection solution to minimize these problems. When conducting a continuous injection experiment, one measures the ratio in concentrations between the injection dye stream and the resulting receiving water concentration. This initial dilution therefore causes a loss of sensitivity and therefore requires more dye to be used in a continuous injection experiment. In small urban streams, this loss of efficiency is not too serious. When conducting a large-scale injection experiment, specific gravity adjustments are usually made and close to full-strength dye is injected to minimize costs. In a slug discharge test, much less dye is usually needed, and the full amount of tracer dye is introduced into the water as rapidly as possible (within a few

seconds). During instantaneous tests, the strength of the dye solution is not important, only knowing the mass of the dye used is needed. Therefore, the small amount of dye needed can be effectively diluted in a several gallon container that can be rapidly poured into the stream in a very short period to initiate the test.

Experimental conditions needed for various estimated stream discharges can be pre-determined by knowing the injection pump rates available and the sensitivity of the fluorometer. A Cole-Parmer Masterflex peristaltic pump can supply a wide range of dye injection rates, depending on the pump rotational speed and the size of tubing used. With #13 tubing, the pump can be set to deliver between 0.2 and 0.5 mL/sec. Number 16 tubing has a useful range of between 2.0 and 8.0 mL/sec, while #18 tubing can be used between 10 and 40 mL/sec. A Turner model 111 fluorometer has a range of sensitivity from less than 1 to more than 150 ppb Rhodamine WT, depending on the sensitivity setting. The newer Turner Designs model 10-AU has a much wider dynamic range. The combination of these settings allows a wide range of flow rates to be measured. Table Y.75 illustrates some of the flow rates that can be measured using some of these combinations. The downstream concentrations shown on this table are in relation to the injection concentration, which should be diluted at least by ten times compared to the 20% stock solution. Therefore, the downstream concentration of 10 ppb shown may actually be closer to 1 ppb of the 20% stock. Intermediate downstream concentrations should be targeted to ensure that variations in stream flow can be accommodated. If a needed injection rate is too low, it may be unstable. The concentration of the dye being injected should then be decreased so a higher pumping rate can be used.

Table Y.75. Stream Discharge Rates (cfs) that can be Measured for Different Experimental Conditions

Injection rate (mL/sec)	Downstream conc. = 50 ppb	Downstream conc. = 25 ppb	Downstream conc. = 10 ppb	Downstream conc. = 1 ppb
0.3	0.21 cfs	0.42 cfs	1.1 cfs	11 cfs
0.5	0.35	0.71	1.8	18
2	1.4	2.8	7.1	71
10	7.1	14	35	350
20	14	28	71	710
30	21	42	110	1100

As an example, consider a stream having an estimated discharge rate of 25 cfs and the target downstream concentration is 25 ppb (compared to the injection dye strength which is diluted ten times from the 20% stock solution; the actual downstream dye concentration is therefore about 2.5 ppb which would be about mid-scale on the most sensitive setting for a Turner model 111 fluorometer). An injection rate of about 20 mL per second will therefore be required. Therefore 2 mL of 20% stock will be used per second, or 120 mL of stock per minute of the test, or 7.2 L of stock per hour of the test, a large amount of dye. The injection duration is dependent on the duration of the steady flow period to be monitored. This should be long in comparison to the flow duration from the injection location to the monitoring location to minimize sampling problems. The sampling location must be located far enough downstream to ensure complete mixing. This length (in feet) can be estimated using the equation previously presented, from Thomann and Mueller (1987):

$$L_m = (2.6\ UB^2)/H$$

where U is the stream velocity in ft/second
B is the average stream width in feet, and
H is average stream depth in feet

As an example, the discharge rate is estimated to be 25 cfs, the stream velocity is estimated to be about 1 ft/sec, the stream width about 25 feet, and the depth about 1 foot. The “complete mixing” length is therefore about 1600 feet. About half of this distance would be needed if the dye injection point is located at the centerline of the stream. The travel time needed (if injected at mid-stream) is about 13 minutes, at least. Therefore, an hour-long injection period would not be unusually long, requiring about 7 L of 20% Rhodamine WT dye, for this example.

Outfall Flow Monitoring

Monitoring of flows in storm drainage systems is typically done to supplement stormwater sampling activities. In most cases, flow monitoring equipment available from the same vendor that supplied the automatic water samplers is selected. The flow sensors typically measure depth of flow in the sewerage and apply the Manning's equation to calculate the flow rate and discharge. Unfortunately, the Manning's equation was developed as a design equation and not as an analysis equation. It was not intended for accurate measurements for shallow flows and does not consider debris that accumulates in sewerage. A better approach is to use a control section in the sewerage and calibrate a stage-discharge relationship. The ultimate solution is to use a special pre-fabricated manhole that contains a flume. Plasti-Fab (503-692-5460) offers many options of manhole and flume sizes and types for a broad range of sites and conditions. A less expensive alternative (and more suitable for temporary installations) is a manhole flume insert. These are available from Plasti-Fab and from Badger Meter (918-836-8411). These are installed in the discharge sewer line from a manhole, causing a backwater in the manhole that provides an accurate stage-discharge relationship that can be measured. Acoustical flow meters (measuring water surface distances from a reference location above the water using reflected sound) or bubbler flow meters (measuring the depth of water above the sensor based on hydrostatic pressure) are usually used to measure the water depth. If the storm sewer line is debris and obstruction free, the Manning's equation can be used, but a site-specific stage-discharge relationship must be developed and calibrated over a wide range of depths. Flow calibration is most effectively conducted using Rhodamine WT dye as a tracer, as described previously.

Many flow measurement equipment vendors are also offering simultaneous stage and velocity sensors. The velocity sensors directly measure the flow rate of the water, reducing the need for a stage-discharge relationship. The two major types of velocity sensors are the time-of-transit flow meter and the Doppler flow meter. Time-of-transit flow meters uses acoustical signals directed diagonally across the water flow path to a receiver. The acoustical signal travel time can be very accurately predicted. Any difference between the predicted and measured travel time is associated with the water motion. Accusonic (508-548-5800) is one vendor of these devices that have been reliably used in large conduits. A series of three Accusonic sensors is placed in each of three parallel 10ft x 15ft CSO outfalls in Brooklyn, NY, as part of the Fresh Creek CSO treatment study (Field, *et al.* 1995). The three sensor and receiver pairs in each outfall are placed in three vertical zones in each outfall, representing three layers of flow that can measure the severe backwater conditions due to daily tides. As an example, the individual sensors can measure tidal flows entering the bottom of the outfall and any floating CSO discharging on top of the saline receiving water.

Doppler velocity sensors are more commonly used in small storm and sanitary sewer lines. These reflect acoustic signals off of particles flowing towards the sensors. The signals reflect off of the fastest moving particles and signal processing then determines the average water velocity. Several vendors sell Doppler units which are constantly improving in accuracy and ease of use. ADS Environmental Services, Inc. (800-633-7246) maintains many large-scale flow monitoring networks around the world using their Doppler velocity and ultrasonic level sensors. ISCO (800-228-4373) also sells a Doppler unit that can be used in conjunction with their automatic water samplers. Unidata America (503-697-3570) sells the Starflow ultrasonic/Doppler flow meter that is very compact and can be used in small open channels and sewer and drainage lines.

Rainfall Monitoring as Part of SSO Investigations

Rainfall data is very important when monitoring receiving water effects of SSO discharges. As an example, the volume and duration of the SSO is normally directly related to the rainfall depth and duration. The hydrology texts listed previously all contain excellent summaries of rainfall aspects of importance in runoff studies. An especially important reference on rainfall depth measurements and interpretation is the *National Engineering Handbook Series* (Part 630, Chapter 4, Storm Rainfall Depth) published by the USDA (Soil Conservation Service, SCS, now the Natural Resources Conservation Service, NRCS), commonly referred to as NEH-4. This is available from the Consolidated Forms and Distribution Center, 3222 Hubbard Road, Landover, Maryland 20785. Placement and selection of raingages are described in these references, along with calculating and interpreting watershed-wide rainfall. This brief section summarizes several important aspects of rainfall monitoring not usually discussed in available reference texts, especially selecting the proper raingage network density, placing the raingages correctly, and the need for calibration.

Raingages suitable for urban area rainfall monitoring are available from many sources. A new small and self-contained weather station is available from Hazco (800-332-0435) that contains sensors for wind speed, wind direction, temperature, relative humidity, dew point, barometric pressure, and rainfall. It has a built-in data logger for up to six months of recording and is even available with a modem for connection to a cellular telephone for telemetry. The cost is about $8,500 (catalogue # B-W010010M) with a modem and $6,600 (catalogue # B-W010010) without a modem. Tipping bucket recording raingages and data loggers, standard 8" raingages, and wind screens, are available without the other sensors for several sources, including Qualimetrics, Inc. (800-824-5873) and Global Water (916-638-3429).

An example of the other extreme in rainfall monitoring is the "Clear View" raingage from Cole-Parmer (800-323-4340) that is only about $35 (catalogue # H-03319-10). This is a non-recording raingage (having a 4" funnel diameter) requiring manual readings of the rain depth. Many other types of "garden store" type accumulative rainfall gages are also available. As noted below, relatively few recording raingages (for accurate rainfall intensity measurements and start and end rain times) are probably needed for most urban catchment studies. However, numerous non-recording gages should be placed throughout the study area to indicate rainfall variations, especially for small rains.

Determining Watershed Averaged Rainfall Depths

Three methods are most commonly used to determine representative watershed-wide rainfall amounts from several point observations. These include the station-average method, the Thiessen polygon method, and the isohyetal method. These methods are briefly described in the following paragraphs.

Station-Average Method

The simplest and easiest method of estimating watershed-wide rainfall amounts is simply to compute the numerical average of all observed values in the watershed. Only those raingages physically located in the watershed of interest are usually considered. This method yields good estimates if most of the following conditions occur: if the watershed has little topographical relief, if a sufficient number of raingages are present, if the raingages are reasonably uniformly distributed throughout the area, and if the individual rain depths observed for the different raingages do not vary widely from the overall mean. The most important criterion is the need for a large number of raingages uniformly distributed throughout the area.

Thiessen Polygon Method

The Thiessen method uses a weighted average for the raingage network, based on the area assumed to be represented by each raingage. Closely spaced raingages have smaller weightings than do raingages spaced further apart. The area weightings generally do not consider topography, or other watershed characteristics, although the polygons can be manually adjusted to account for these potential effects, with experience. The area represented by each station is assumed to be the area that is closer to it than to any other station. These areas are determined by drawing connecting lines between all adjacent raingages. These connecting lines are then bisected. The perpendicular bisectors then describe a polygon surrounding each raingage. Figure Y.39 is a simple illustration of the construction of the polygons surrounding each raingage. Figure Y.40 is an example of a Thiessen polygon system for the Toronto, Ontario, metropolitan area which has 35 raingages over an area of about 4,000 km^2. These polygons were prepared using the SYSTAT computer program.

Figure Y.39 (simple polygons)

Figure Y.40 (Toronto polygons)

Results from the Thiessen polygon method are usually assumed to be more accurate than those obtained by the simple station-average method because it accounts for non-uniform distributions of stations. Raingage measurements from surrounding areas are also used in the analysis. The polygons also do not change for different rains, unless data is missing from one or more raingages. The weightings therefore are relatively constant, making the calculations reasonably simple after the polygons are initially determined and measured.

Isohyetal Method
This is the most complex method for determining rainfall depths over a watershed and is usually considered the most accurate. It was rarely used before the common availability of computers that simplified the necessary calculations. In contrast to the Thiessen polygon method, the isohyetal method requires extensive calculations for each individual rain event. In this method, contours of equal precipitation depth are constructed over the watershed. The construction of the contours can consider the presence or topographic or lake effects. The averaged precipitation over the entire area is computed by multiplying the area enclosed between adjacent isohyetal lines by the average rain depth values of the two adjacent isohyetal lines. Figure Y.41 is an isohyetal map (rain depths in mm) for a single rainfall over the Toronto area, using data from 46 raingages. This map was also prepared using SYSTAT.

Figure Y.41 (Toronto isohyetals)

The Toronto raingage network density resulted in small differences between the three averaging methods because of the large number of raingages available. The use of the 35 raingages over the 4,000 km^2 area was dense (one raingage per 114 km^2) compared to available raingage networks in most urban areas. The resulting errors in using the simple averaging method or the Thiessen polygon method, compared to the isohyetal method, were all less than 1 mm in rain depth for rains of just a few mm in depth to over 25 mm in depth.

Rain Monitoring Errors
There are several common aspects of rainfall monitoring that lead to measurement errors. Most of these errors result in decreased rainfall values compared to true conditions. These include too few raingages for the area, poor placement of the raingages, wind effects, splashing of rain out of the gage during high intensity rains, tipping rate of tipping bucket raingage not keeping up with high intensity rains, and calibration errors. These problems can usually be identified when reviewing the data. Hopefully the errors can be corrected during the monitoring period, otherwise the collected rain data may not be usable.

The easiest method to identify questionable rainfall data is by comparing the site data with data collected from nearby and independent raingage locations. Residual analyses (differences between the site data and surrounding data) may indicate a consistent bias. This may be expected if there is a good reason for the bias (such as topographic differences or nearby large water bodies). The residuals also need to be examined for changes with time. This pattern should also be random, with no obvious trends or abrupt changes. In all cases, a recording raingage (especially a tipping bucket raingage) needs to have a standard raingage located in close proximity. The total rainfall recorded between observation times of the standard raingage is adjusted based on the standard gage readings. These adjustment factors should be reasonably consistent. Another way to check raingage data is by comparing the watershed rainfall quantity with the stream flow quantity. This relationship should follow a reasonable rainfall-runoff pattern, with no abrupt deviations. Finally, recording raingages need to be periodically calibrated against different artificial rain intensities. The measured rainfall causing a tip of the bucket in a tipping bucket raingage should remain constant for a wide range of rain intensities. This quantity should also not change abruptly with time without good reason (such as a lightning strike, vehicle striking the raingage mounting pier, etc.).

Needed Raingage Density

One of the most common problems with rainfall monitoring is simply not having enough raingages in the watershed. Typical guidance for appropriate raingage densities do not consider the likely errors associated with too few gages located in relatively small urban watersheds. The absolute number of raingages is probably more important than the simple raingage density. In all cases, multiple raingages are needed, even in the smallest study area. The number of raingages required depends on local conditions (Curtis 1993). Areas of higher rainfall variability require a greater number of raingages to adequately estimate rainfall over a watershed. As an example, mountainous areas will require more gages than flat lands, and areas subject to convective storms will require more gages than areas subject to frontal type storms.

The spatial variability and intended use of the data should be used in determining the needed number of raingages. Typical guidance for flat terrain indicates raingage spacing of about 25 to 30 km, while this spacing is reduced to 10 to 15 km for mountainous areas. Most monitored urban watershed areas are quite small: almost all are less than 100 km^2, and typically less than 10 ha in area. These small areas seem to justify only a single raingage. Wullshleger, *et al.* (1976) made one of the earliest recommendations for the number of raingages needed in small urban runoff catchments. They found about one gage needed in 0.5 to 1 km^2 watersheds, and about 12 gages for larger 25 km^2 watersheds. However, multiple raingages are needed in all monitored watersheds. This should include a tipping bucket raingage and a single standard raingage, at least, for the smallest area, if rain intensities are to be monitored. When the study area increases, and if smaller rains are of interest, the number of raingages must be increased to compensate for the increased variation in the rain depth throughout the area. These additional raingages can be additional pairs of tipping bucket and standard raingages, or by simple accumulative (garden-store type) raingages, if intensities are not needed.

The *National Engineering Handbook Series* contains a simple chart, shown here as Figure Y.49, that can be used to estimate the 90% confidence limits of a rainfall located a specific distance from a raingage. As an example, if the measured rainfall at a raingage is 2 inches, the 90% confidence limit in rain depth for a location 0.5 mile away can be estimated as:

- the “plus error” is about 0.8 inches, or 2.8 inches for the upper limit, and
- the “minus error” is assumed to be about one-half of this amount, or 0.4 inches, with a lower limit of 1.6 inches.

Figure Y.49 (fig. 4-4 NEH, pg 4-11)

The NEH also contains a nomograph (Figure Y.94) that can be used to estimate the watershed average rainfall depth, based on the size of the watershed, the number of raingages, the annual average precipitation depth and the storm rainfall depth of concern. The example shown on this figure is for a watershed of 200 acres in area, having 2 raingages. The annual rainfall is about 33 inches and the rain of interest is 5 inches. The average error is estimated to be about ± 12 %, or ± 0.6 inches.

Figure Y.94 (Fig. 4-6. NEH pg. 4-15).

Lei and Schilling (1993) studied the rainfall distribution in two urban watersheds located in Essen, Geramany. The catchment had an area of 34 km^2 and was represented by 17 raingages. Rainfall data for five summers (1980-1984) were analyzed. They only examined rains that had all stations represented and that had at least 0.5 mm of rain. They

compared catchment-wide averaged rain depth using subsets of the complete raingage network against the data from all 17 raingages as a reference. Figure 14 shows the basin-wide runoff volume errors that would result if only one rain gage was used in rainfall-runoff modeling. It shows that relative errors of computed runoff volume decreased with increasing rain depth. Rains greater than about 8 mm had about ± 20% errors in modeled runoff volume with a single rain gage over the 34 km^2 drainage area. However, smaller rains could have rain depth errors up to 250% with only a single rain gage.

Figure 14. Relative Runoff Volume Errors While Using One Rain Gage in Essen. (Ref. Lei and Schilling. *Urban Storm Drainage*. 1993)

Ciaponi, *et al.* (1993) studied rainfall variability in the 11.4 ha Cascina Scala experimental urban catchment watershed in Pavia, Italy for a 3 year period. Two rain gages separated by 310 m were used in this study. During this period, 233 storm events were selected for analysis, all being greater than 1 mm in depth. The following list shows the percentage differences between the rain depths measured at the two monitoring locations for three rain depth categories:

- for 1 mm < h < 5 mm (135 storms) the average error was 31%.
- for 5 mm < h < 20 mm (75 storms) the average error was 10 %.
- for h > 20 mm (23 storms) the average error was 8 %.

These results show that the rainfall monitoring variations over even a very small watershed and with two closely spaced raingages can be quite large for small rain depths (<5 mm), with the differences decreasing for larger rains.

The National Weather Service guideline (Curtis 1993) used to determine the minimum number of gages required in a local flood warning system is:

$$N = A^{0.33}$$

where A is the basin area in square miles. As an example, a 10 mi^2 watershed would require at least 2 rain gages, while a 100 mi^2 watershed would require at least 5 raingages.

Figure 16 shows the expected coefficients of variation for different raingage numbers and watershed sizes (Curtis 1993). For a fast responding watershed, a coefficient of variation (the standard deviation divided by the mean) goal of 0.10 would require about 6 raingages for a 50 mi^2 watershed, while a 500 mi^2 watershed would require about 13 raingages for the same COV of observed rain depths in the watershed. Average and slow responding watersheds would require slightly fewer raingages for the same watershed areas.

Figure 16. Areal Rainfall Accuracies for Fast Responding Watersheds.

Rodda, *et al*., (1976) presented recommendations (Tables 3 and 4) for the minimum numbers of raingages required for small and moderately-sized watersheds and for larger watersheds. Table 3 shows the number of raingages needed for observations of daily rain depth totals and for monthly rain depth totals.

Table 3. Recommended Minimum Numbers of Raingages Needed in Small and Medium-Sized Watersheds

Area (mi^2)	Daily	Monthly	Total
1	1	2	3
2	2	4	6
8	3	7	10
16	4	11	15
31	5	15	20
47	6	19	25
63	8	22	30

Table 4. Recommended Minimum Number of Raingages Needed for Large Watersheds

Area (mi^2)	Number of Raingages
10	1
100	2
500	3
1000	4
2000	5
3000	6

According to Chow (1964), one raingage per 625 mi^2 is the minimum needed for general climatological purposes, while for hydrologic purposes, each study basin should have at least one raingage per 100 mi^2. However, one raingage per 1 mi^2 was recommended for the analysis of thunderstorms.

Pitt and McLean (1986) investigated rainfall distributions in the Toronto area as part of the Humber River pilot watershed study. Rainfall data was available for 35 raingages over an area of about 4,000 km^2. This high number of raingages allowed sensitivity calculations to be made to determine the appropriate number of raingages that may be needed. Numerous random subsets of these raingage data was used to analyze potential errors associated from using fewer raingages for 46 rains. Figure Y.39 shows the likely errors for different numbers of raingages over this area. The largest rains (>25 mm) had the smallest rainfall variations over the area and therefore had the smallest errors for a specific number of raingages. The smallest rains (<5 mm in depth) had much greater errors because their variations were much greater throughout the area. This plot shows that the errors would be very large (several hundred percent in error) for all rains with only one raingage for the complete area. The errors somewhat leveled off after about 12 raingages were used. However, the rain depth errors for the largest rain category would remain greater than 10% even for 25 raingages, and the smallest rains may still have about 50% errors associated with this large number of raingages.

The small catchment monitoring effort by Pitt and McLean (1986) in Toronto illustrated the need to include multiple raingages in even very small areas. The two urban watersheds monitored were 39 and 154 ha in area and were located about 3 km apart. Rainfall was monitored at one of the areas only and the rainfall at the airport several km away was used for comparison. Part way through the monitoring program, a large deviation was noted between the local and airport monitored rain depths. The local raingage was then re-calibrated, with a 40% increase in the volume needed for a single bucket tip. This of course had a significant effect on the rainfall quantity monitored and much time was spent in identifying why and when the raingage had changed so much since its initial calibration. After much analyses using surrounding rainfall data and investigating the history of the specific raingage, it was determined that the raingage used had a historical problem with the bearings and several repairs had been made in an attempt to correct the problem. Unfortunately, the raingage calibration was found to be highly variable, and all of the locally monitored data was therefore questionable and not used. Thankfully, the Toronto raingage network had six other raingages surrounding the two study areas within a few km. These data were extensively evaluated, including examining the storm tracks across the city during all monitored rains to derive suitable rain depth and intensity values for the storms of interest. This additional analysis required much additional time, but thankfully was possible because of the additional raingage data. This problem could have been prevented with the use of a standard raingage

located next to the tipping bucket raingage for more frequent checks on the calibration factor. Non-recording raingages could also have been located in several locations in the small test watersheds to indicate variations throughout the drainage. Both of these options would have cost a small fraction of the additional cost associated with the additional detailed rainfall analyses required during this project and would have alerted the field personnel of the rainfall monitoring problem much sooner.

Proper Placement of Raingages

Precipitation measurements are greatly influenced by wind. Careful placement and shielding of raingages are both necessary to reduce wind-induced errors. The upward movement of air over a raingage reduces the amount of precipitation captured in a raingage. Proper placement is needed to minimize wind induced turbulence (and to minimize rain shadow effects) from nearby obstructions.

Linsley, *et al.*, (1958) concluded that reliable measurements of wind-induced errors are difficult because of problems involved in determining the actual amounts of precipitation reaching the ground. They reported that wind induced errors during rainfall monitoring exceed about 10% for winds greater than about 8 mph, for both shielded and unshielded raingages. This error increases to about 20% during 20 mph winds. Shielded raingages perform slightly better, with a wind induced error about 3% less than for an unshielded raingage during 10 mph winds, and about 5% less during 20 mph winds. The effects of winds on snowfall is much greater, with shielded gages having about half the magnitude of errors as unshielded gages when monitoring snowfalls. Snowfall errors (all under-reported) for unshielded gages may be about 50% for 10 mph winds and increase to about 70% for 20 mph winds. Various types of wind shields have been used, but the Alter shield (loose hanging vanes in a circle around the raingage) has been adopted as a standard in the United States. Its open and flexible construction provides less opportunity than solid shields for snow buildup, and the flexible design allows wind movement to help keep the shield free from accumulated snow and ice.

Raingage exposure and placement is very important to reduce rainfall measurement errors. The higher the raingage is located above the ground, the greater the wind error. It is therefore best to locate the raingage on level ground, definitely avoiding roof installations and steep hillsides. Linsley, *et al.*, (1958) and Shaw (1983) both recommend a partially sheltered site. Brassington (1990) stated that the raingage should be located at a distance that is at least twice the height of surrounding obstructions: the vertical angle from the raingage to the top of the surrounding trees and buildings should be no greater than 30°. Also, Shaw (1983) recommended that a turf wall be used in over-exposed locations where natural shelter is rare. A surrounding small grassed embankment decreases wind turbulence around the raingage which can inhibit raindrops from falling into an unprotected gage. The turf wall should form a circle having an inside diameter of about 3 m, and built up to the top of the raingage. The inside wall should have vertical walls, while the outside should have a slope of about 1 to 4. The inner area must be drained to the outside to prevent flooding. Raingages must also be placed level. If, a raingage is inclined 10 degrees from the vertical, it will catch 1.5% less than it should due to a decreased opening area exposed to the rain. In addition, if a raingage is inclined slightly toward the wind, it will catch more rain than the true amount.

Proper Calibration of Raingages

The standard U.S. Weather Bureau raingage is a non-recording, but accumulating raingage that has an 8 inch diameter funnel opening. The opening directs the water into a measuring tube that has $1/10^{th}$ of the cross-sectional area of the gage opening. The depth of accumulated rain in the measuring tube is therefore ten times the depth of rain that fell since the gage was last checked. This gage is usually used to measure the 24-hr total rain depths, usually read at 8 AM each day. This standard gage should be located adjacent to any recording rain gage to check the total amounts of rain that has fallen during the observation period.

A tipping bucket rain gage is the most common type of rain gage that measures rainfall intensity. This gage has an internal tipping mechanism that fills with water from the funnel connected to the standard 8 inch diameter opening. The tipping mechanism is balanced to dump its contents after a specific amount of water has accumulated (usually 0.01 inch). Upon dumping, another small bucket rises to collect the next increment of rainfall. Each tipping motion is recorded on an event recorder, along with its time. Rainfall intensity is therefore related to the rate of tips per time period.

Tipping bucket raingages must be periodically calibrated by measuring the number of tips associated with a specific amount of water slowly introduced into the raingage. The calibration water much be introduced in a rate comparable to the rate of rainfall of interest. Several rainfall rates should be checked over the range of interest. This calibration should be conducted in the field with the gage installed, at least every six months. As noted previously, tipping bucket rain gages are most accurate for small to moderate rain intensities. Significant rain can be missed during the time that the tipping action is moving and before the other bucket is in place. Heavy rains also tend to hold the buckets in intermediate positions for long periods, preventing the rain from accumulating in the buckets. The use of a standard accumulating raingage is therefore highly recommended adjacent to any recording raingage.

Table Y.75 shows the water delivery rate to a tipping bucket raingage needed for calibration for different equivalent rainfall intensities, assuming a standard 8 inch opening. The rates needed to calibrate a tipping bucket raingage for the smallest rainfall intensities shown on this table are very low and would require special low flow pumps. As an example, a Masterflex® portable pump can pump from 0.06 to 1100 mL/min, depending on pump head, tubing size, and pump speed (available from Forestry Suppliers, catalog #76899, model 7570-10 variable speed pump with rechargeable battery, and #76888 pump head with #16 tubing, for 0.80 to 320 mL/min, at a total cost of about $900). This pump can therefore be used for all of the rainfall intensity calibrations listed on Table Y.75. Of course, other available peristaltic pumps can also be used for this calibration, depending on the flow rates available.

Table Y.75 Water Delivery Rates for Recording Raingage Calibration (standard 8 inch opening)

Rainfall Intensity (mm/hr)	Rainfall Intensity (inches/hr)	Water Delivery Rate for Calibration (mL/min)
2	0.078	1.1
5	0.20	2.7
10	0.39	5.4
25	0.98	14
50	2.0	27
100	3.9	54
200	7.9	110

When the rainfall intensity becomes large, the tipping bucket mechanism cannot keep up, with a decreased amount of rain recorded. As an example, Ciaponi, *et al.* (1993) used a peristaltic pump to calibrate two raingages in an urban test watershed in Pavia, Italy. The calibrations showed that the raingages could accurately measure rainfall intensities at 44 mm/hr (the lowest rate calibrated with the pump) with errors less than 1%. However, at rain intensities of about 250 mm/hr, the errors were about 10%, and at 400 mm/hr, the errors increased to about 15%. The measured rain intensities were all less than the actual intensities due to missing rain during the tipping time of the individual buckets. Of course, very few rains would be expected to have prolonged large intensities that would cause errors greater than about 10%. However, short duration very high rain intensities are much more likely and accurate rates in these high intensity ranges may be needed. Therefore, care must be taken when calibrating raingages to use appropriate water delivery rates that correspond to a wide range of rainfall intensities.

Section 6 - Special Field and Laboratory Tests Needed to Locally Calibrate a SSO Risk Assessment Model

Description of the Sites Studied

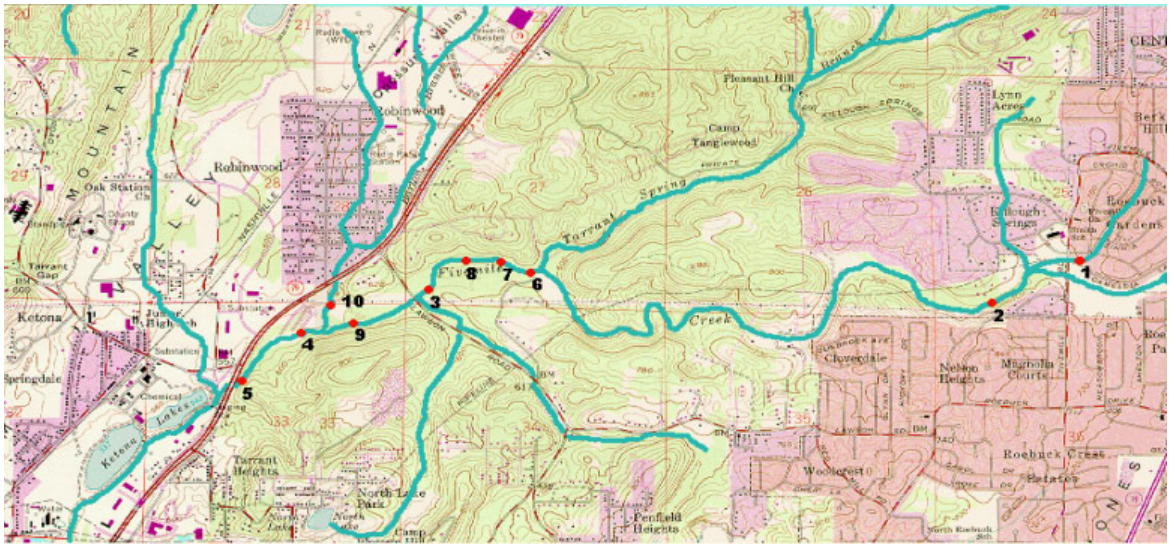
There are several sites where samples will be taken. The sites are located in and along two urban streams in the Birmingham, AL, area. These sites were chosen to allow for overland, upstream, in-stream, and downstream samples near known SSO locations which could be easily obtained. Diagrams of these sites are shown in Figures 1, 2, and 3.

Five Mile Creek

Figure 2. Five Mile Creek Sampling Locations

Figure 1 depicts the Five Mile Creek area and the 10 sampling sites along an approximate 3 mile reach from Five Mile Creek Road (sample location 1) to Highway 79 (sample location 5). Five Mile Creek is located in North Birmingham. It is surrounded by industrial and suburban development. Sampling locations for Five Mile Creek are described as follows:

1 - Bridge on Five Mile Creek Road
2 - 1000 feet downstream from confluence of Five Mile Creek with 2 secondary streams



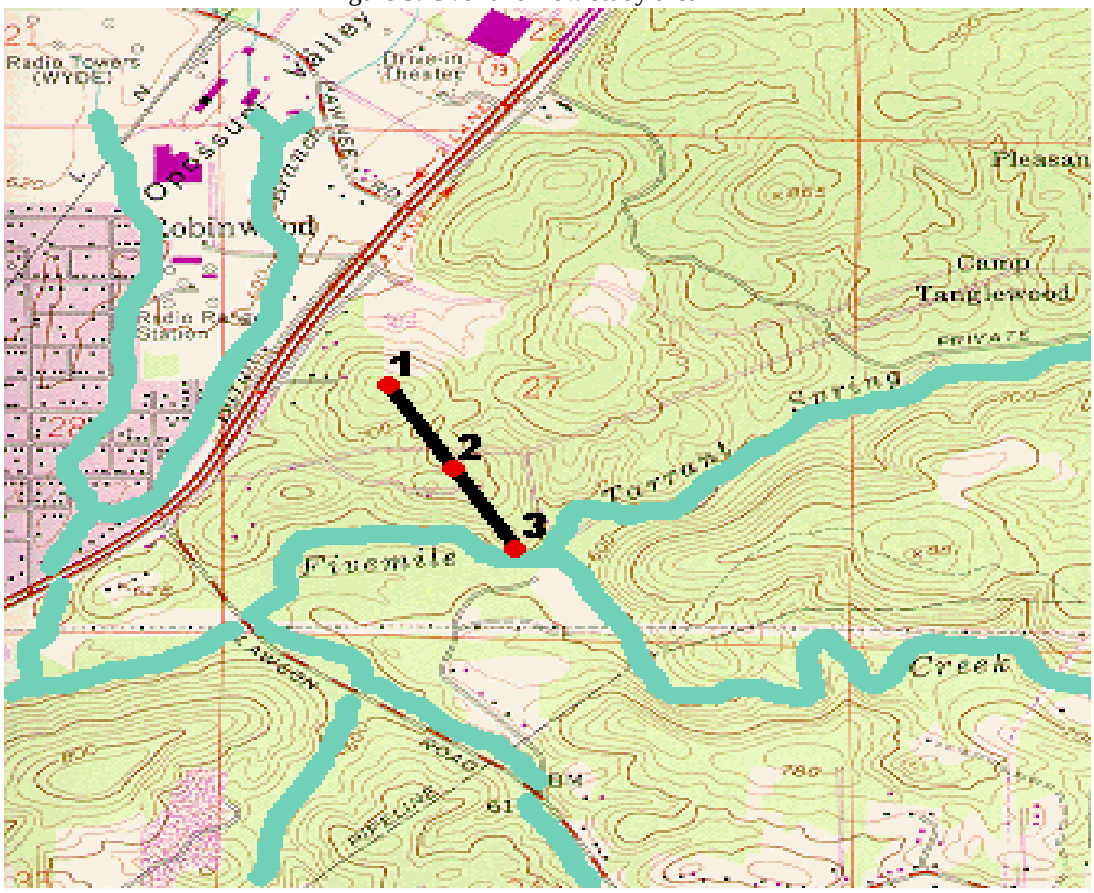
3 - Bridge on Lawson Road
4 - Below flap gate on Highway 79
5 - Bridge on Highway 79
6 - 500 feet upstream from overland flow discharge
7 - 5 feet downstream from overland flow discharge
8 - 100 feet downstream from overland flow discharge
9 - 1000 feet downstream from Lawson Road
10 - Flapgate near Highway 79

Overland Flow Sampling Site

The overland flow/continuous discharge SSO site is located near sampling site 7 in Figure 1 (enlarged in Figure 2). In order to evaluate the effects of overland flow on SSO characteristics, several hillside sampling locations will be tested, including:

1 - Top of hill
2 - Middle of hill
3 - Bottom of hill

Figure 3. Overland flow study area



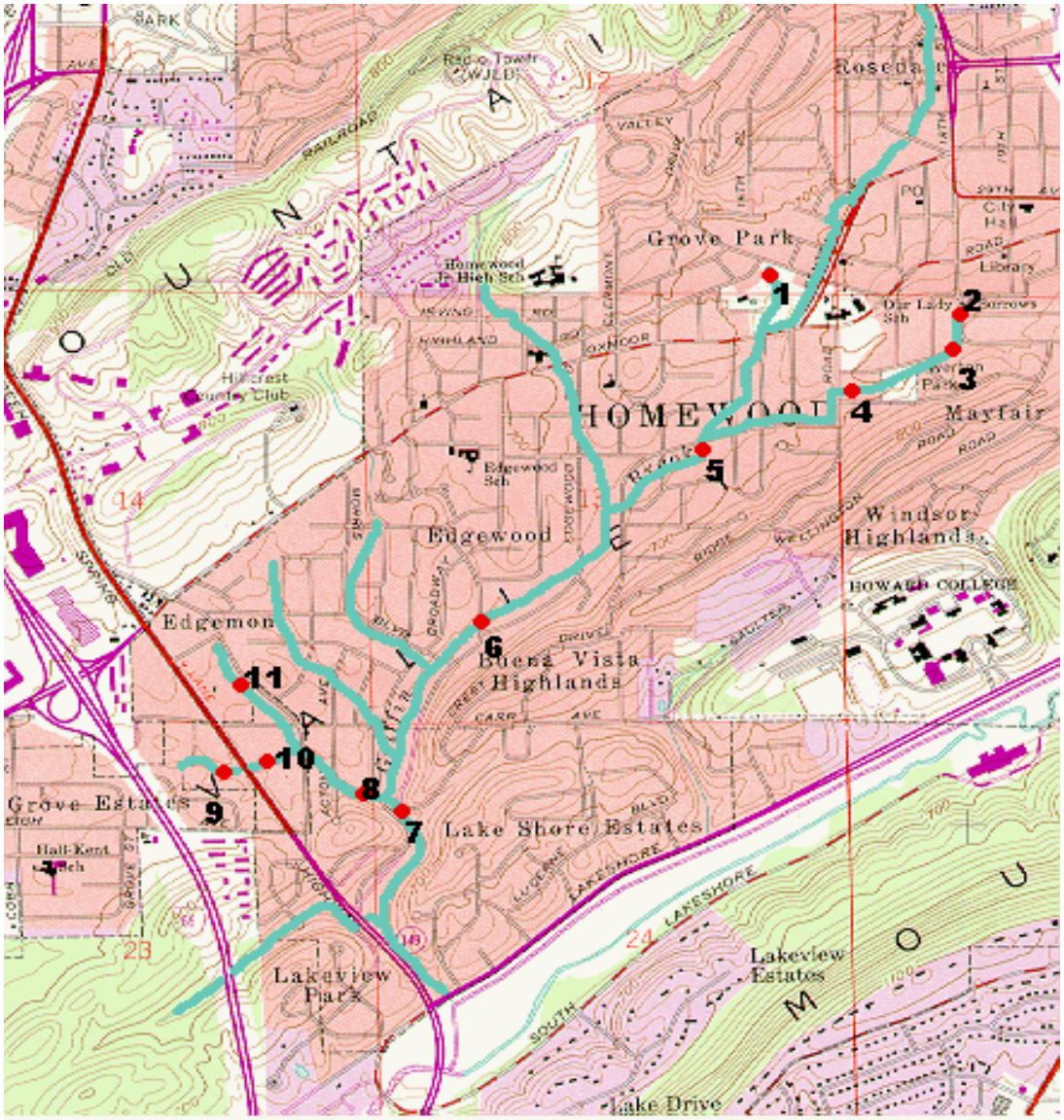
Griffin Brook

Figure 3 shows the sampling sites along Griffin Brook, which empties into Shades Creek. This location represents a small, fully developed watershed, having a first-order stream. Griffin Brook is located within Homewood, a suburb located in the southern Birmingham area. The Griffin Brook test reach is approximately 2.5 miles from sampling location 2 to sampling location 7. Sampling locations are described as follows:

1 - Upstream of studied discharges
2 - 150 feet upstream of discharge #1
3 - 15 feet downstream of discharge #1
4 - 1000 feet downstream from discharge #1
5 - Confluence of secondary stream with Griffin Brook
6 - Intermediate site between discharge #1 and discharge #2

7 - Downstream of all sites
8 - 1000 feet downstream from discharge #2
9 - 75 feet above discharge #2
10 - 5 feet below discharge #2

Figure 4. Griffin Brook study area



Bacteria and Other Pathogen Dieoff Tests

XXXXXXXXXXX from J.G., D.N. ???? XXXX How can you do a die-off test if the organisms are already dead or deactivated?? XXXXXX
The biological die-off studies will utilize standard methods for all biological parameters except for cryptosporidium oocysts and giardia cysts. In the biological die-off study for this project dialysis bags will be used to contain

deactivated or formalin preserved organisms. The dialysis bags allow water, nutrients, and gases to pass through them, yet do not allow particles larger than 0.2 microns to pass.

Photosynthesis and Respiration of Sewage Contaminated Waters

The aim of this experiment was to examine the acclimation time of the effects of a sewage discharge to a receiving water, and to measure the photosynthesis and respiration (P/R) rates for several mixtures of sewage and receiving waters. Previous studies (Pitt 1979) have shown that the results of five-day biochemical oxygen demand (BOD_5) tests may be inaccurate due to the acclimation time of the microbes to the waste, i.e., acclimation may not be relatively short compared to the traditional five-day test period for BOD_5, especially for unusual mixtures of waste and receiving waters. The use of continuously recording water quality sondes enabled collection of water quality data over a fourteen-day period during this field study. Traditional measurements of P/R rates are performed using light and dark bottles over a short period of time, usually several hours, and with little replication. This short period data is then used to construct a dissolved oxygen curve for a one-day cycle, for the light and dark bottles, from which P/R calculations are made. Again, with the continuously recording sondes, several curves can be constructed over multiple days having variable weather, providing far more useful results than the traditional method.

The YSI 6000UPG sonde is a multi-parameter water quality monitor manufactured by YSI Incorporated, Yellow Springs, OH. The 6000UPG was used to measurement the following parameters during this series of tests: dissolved oxygen, specific conductance, temperature, pH, ORP (oxidation reduction potential), depth, and turbidity. The 6000UPG can be left unattended in the field for approximately 45 days, depending upon the frequency of data logging and which parameters are being recorded. The instrument is constructed of PVC and stainless steel, and is 3.5 inches in diameter and 19.5 inches in length. It weighs approximately 6.5 pounds, with batteries. The sonde is capable of interfacing with an IBM PC compatible computer. In addition, a software package, Ecowatch for Windows, is available for sonde set-up, data acquisition, and data presentation/analysis. The performance specifications provided by the manufacturer for each sensor used are given in Table 1 (YSI Inc. 1996).

Table 1. YSI6000 Specifications

Parameter	Sensor Type	Range	Accuracy	Resolution
Dissolved Oxygen	Rapid Pulse – Clark-type, polarographic	0-200 % air saturation	± 2 % air saturation	0.1 % air saturation
Conductivity*	4 electrode cell with autoranging	0-100 mS/cm	±0.5 % of reading + 0.001 mS/cm	0.01 mS/cm
Temperature	Thermistor	-5-45 °C	± 0.15 °C	0.01 °C
pH	Glass combination electrode	2-14 units	± 0.2 units	0.01 units
ORP	Platinum ring	-999-999 mV	± 20 mV	0.1 mV
Turbidity	Optical, 90° scatter, mechanical cleaning	0-1000 NTU	± 5 %	0.1 NTU
Depth – Medium	Stainless steel strain guage	0-61 m	± 0.12 m	0.001 m
Depth – Shallow	Stainless steel strain guage	0-9.1 m	± 0.06 m	0.001 m

* Report outputs of specific conductance (conductivity corrected to 25 °C)

There are several biological processes occurring in receiving waters that were apparent during the monitoring during these tests. During the daylight hours, photosynthetic organisms, such as algae, use energy derived from the sun to produce ATP (adenosine triphosphate) and NADPH (reduced nicotine adenine dinucleotide phosphate), reactions that generate oxygen. Then, the energy (ATP) and reducing power (NADPH) are used to fix carbon dioxide (CO_2) into carbohydrate (Alberts 1994). Simultaneously, photosynthetic organisms and any other aerobic organism, such as fish and certain types of microorganisms, use oxygen to breakdown carbohydrates for energy. This process occurs during the daylight and nighttime hours. Therefore, there is a constant drain on levels of dissolved oxygen in the water that must be replenished by photosynthesis and/or exchange with the atmosphere. The net effect of these processes is that the dissolved oxygen level in the water rises during the daylight and falls at night. In addition, the pH of typical receiving waters is governed by the carbonic acid/bicarbonate/carbonate buffering system (Welch 1992). Increases in the dissolved CO_2 concentration causes corresponding decreases in pH, and vice-versa. Therefore, the pH increases during the daytime hours because CO_2 is being fixed by photosynthetic organisms and is thereby removed from the water. Then, at night, pH drops because atmospheric CO_2, and CO_2 being produced by respiration, increase the concentration of CO_2 in the water. The DO and pH sonde probes therefore directly

measured these changes. In addition, changes in temperature, ORP and specific conductance were also observed. Turbidity also changed, but was not directly related to experimental conditions.

The YSI 6000 sondes were used to evaluate *in-situ* photosynthesis and respiration rates of different mixtures of raw sewage and fresh water. The sondes were calibrated for the following experimental parameters on May 9: depth, specific conductance, dissolved oxygen, turbidity, pH, oxidation reduction potential (ORP), and temperature, according to instructions provided by the manufacturer. The sondes were also programmed to acquire data in unattended mode for 2 weeks at 15-minute intervals. The program was set to begin at 12:00 noon, on May 10.

Raw sewage was obtained at the Riverview Sewage Treatment Plant on the morning of May 10. The Birmingham Water Works Board (BWWB) operates this plant and permission to obtain the sewage was granted by Joel Rhaly of the BWWB. The sample was obtained by grabs with a dipper at the plant headworks before the bar screen. The sample was placed into four, two gallon, carboys and capped tightly for transport.

The site for this experiment was a small lake on private property located in Shelby County, AL, to ensure security for the sondes. The fresh water for diluting the sewage was taken from this lake. Four different mixtures of sewage and fresh water: 0/100%, 33/67%, 67/33%, and 100/0% (sewage/fresh water) were prepared in their respective test chambers. The lake rarely, if ever, received sanitary sewage.

The test chambers were 5-gallon clear plastic bags containing 15 liters of the test water mixture. The sondes were placed into the test chambers, and the bags were fastened to the sonde body by duct tape and large rubber bands, after removing as much air as possible. The test chambers and sondes were placed on the lake bottom in approximately one to two feet of water near the shore. The test chambers were anchored in place by looping a rope that was anchored at both ends, through the bracket on the exposed end of the sonde (Figure 3). The sondes were removed and the data was downloaded on May 21 at approximately 10:00 AM. The following paragraphs describe the measured test parameters.

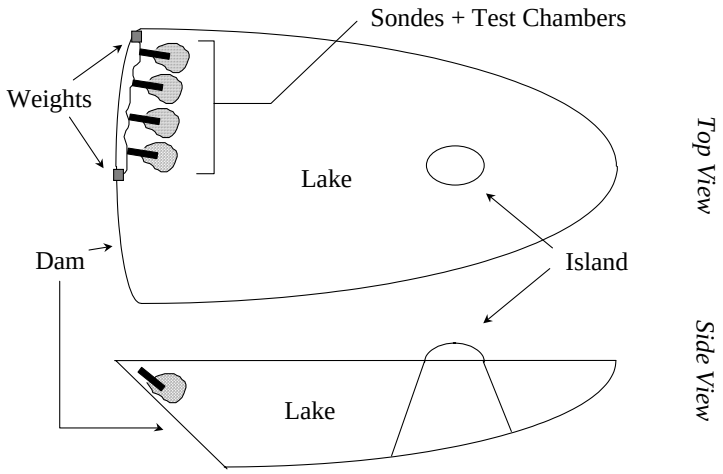


Figure 3. Sonde locations and experimental setup.

Temperature

The temperature results showed that the long-term trend was towards higher temperatures; this is consistent with a typical Spring. The range on day 1, 5/10/97, was 20-23^{o}C; and the range on day 10, 5/20/97, was 23-25^{o}C. A diurnal variation of about 3-4^{o}C was also observed; again, typical for the day/night solar cycle. It is important to note that the last two days, 5/19/97 and 5/20/97, were overcast with scattered heavy rains and variable winds, and therefore the diurnal temperature variation was less than for days with full sun. The graph of temperature data also shows that the results for each of the four probes were quite consistent, except that the 33% sewage chamber does not reach as

high of a daily peak as the others (Figure 15). It is possible that differences in the biologic processes occurring within the different test chambers could account for temperature differences, i.e., color, associated with increased algal growth, would have also affected the maximum temperature obtained. The large amount of green biomass observed in the 33% sewage chamber may have acted to moderate the extreme temperature levels found in the other chambers that did not have such a large algal biomass.

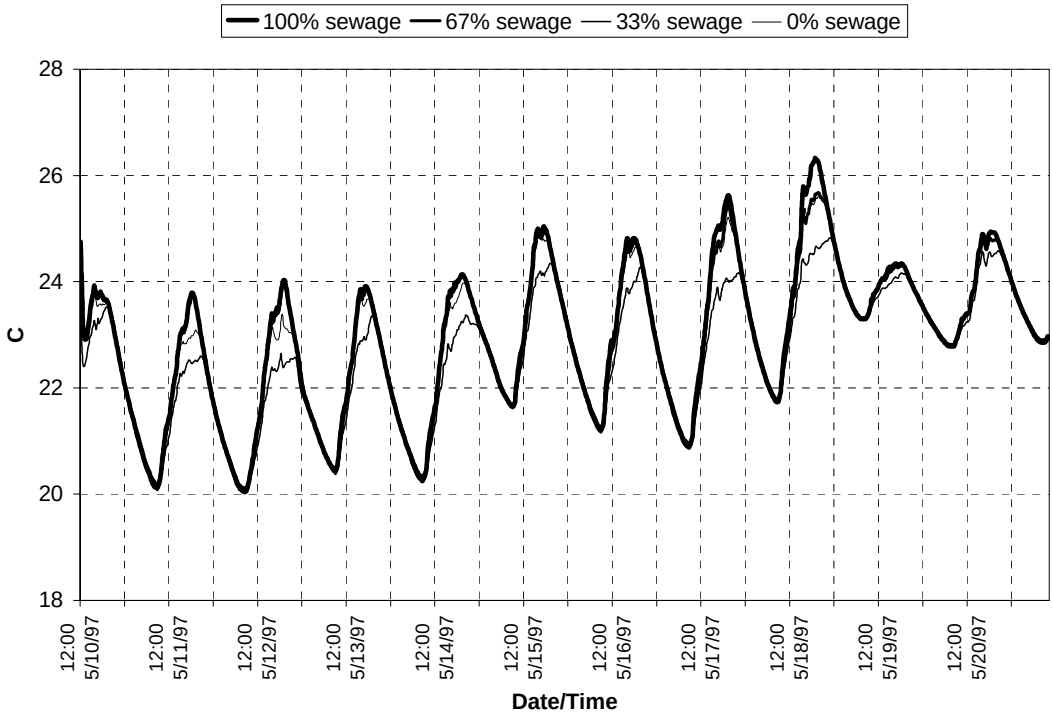


Figure 15. Temperature data for all four probes over ten day experiment.

Specific Conductance

The specific conductance results were also as expected (Figure 16). The 100% sewage test chamber had the highest specific conductance, and the incremental change for each dilution was approximately equal. This is expected because the dilutions were of equal increments, and sewage has higher specific conductance than the lake water because of the increased ionic strength of sewage. It is also interesting to note that the 0% sewage chamber seemed to trend upward throughout the length of the experiment. One possible explanation could be that the organisms were dying off over time and releasing the ions that were sequestered within the living cells.

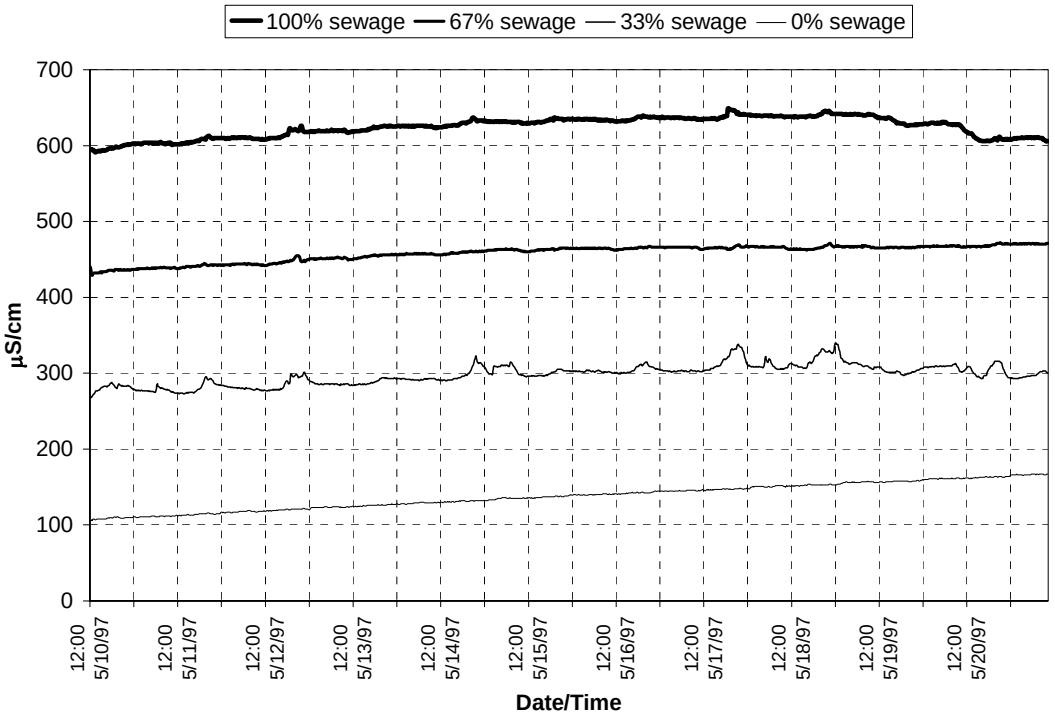


Figure 16. Specific conductance data for all four probes over ten day experiment.

pH

The pH results were also as predicted (Figure 17). There was a diurnal variation, at least in the test chambers that had photosynthesis occurring: in the chamber with 33% sewage (daily pH change ≅ 1 to 2, after day 7) and in the chamber with 0% sewage (daily pH change ≅ 0.25). This is due to the change in carbon dioxide concentrations from photosynthesis (removal of dissolved carbon dioxide) and respiration (addition of dissolved CO_2). An increase in dissolved carbon dioxide causes the pH to decrease from the formation of more carbonic acid, while removal of dissolved carbon dioxide increases pH.

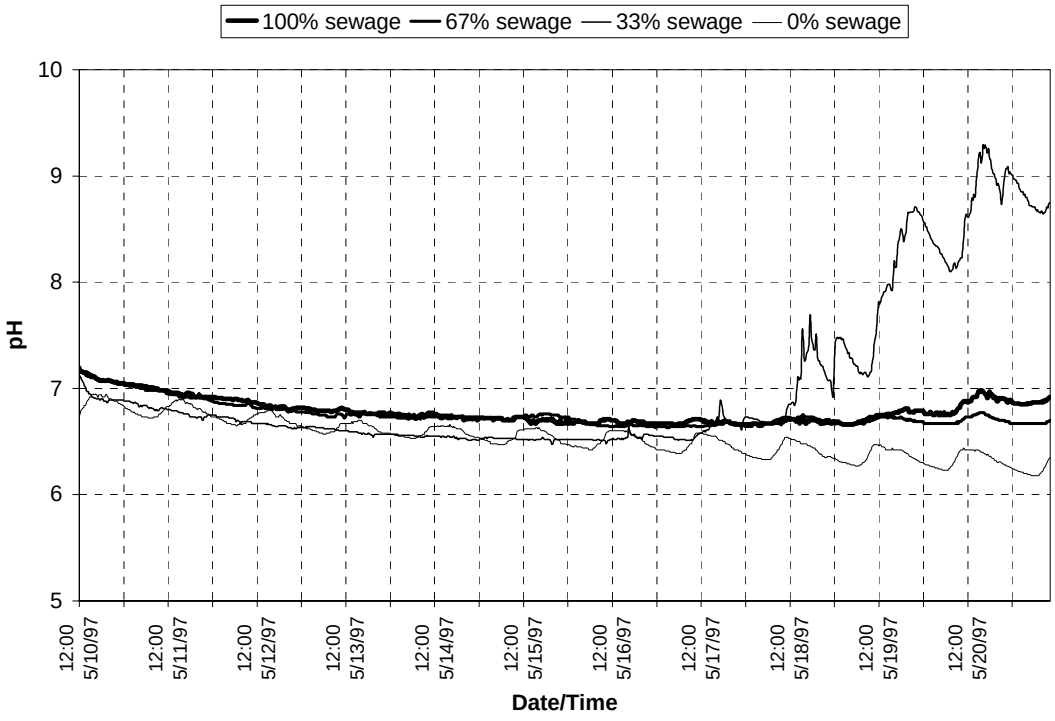


Figure 17. pH data for all four probes over ten day experiment.

Oxidation Reduction Potential

The results for this parameter were also as expected (Figure 18). The test chambers with high oxygen demand, and corresponding reducing environment (67 and 100% sewage), dropped rapidly to less than -400mV within the first few hours of the experiment and stayed there. The ORP in the 33% sewage chamber was similar to the 67 and 100% sewage chambers for the first five days, but then began to climb, reaching positive ORP values by day 6. This result is well correlated with the DO data, showing that after an initial acclimation period, the algae and other microorganisms began to respire and photosynthesize. The 0% sewage chamber showed a definite diurnal trend and stayed above 300mV, two factors that correlate well with the diurnal DO cycle resulting from photosynthesis and respiration.

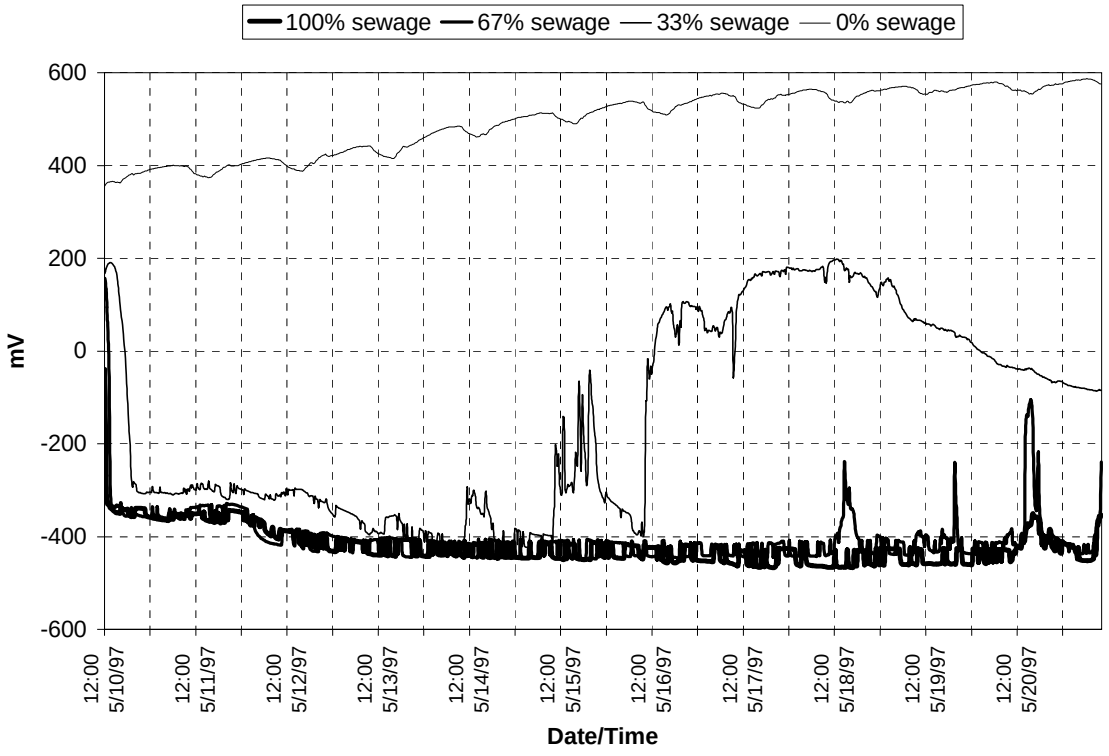


Figure 18. Oxidation reduction potential data for all four probes over ten day experiment.

Turbidity

The results of the turbidity measurements (Figure 19) were also as predicted. The turbidity was highest in the 100% sewage and decreased with decreasing concentrations of raw sewage. There was a general downward trend in turbidity in all of the test chambers, most likely due to settling after the initial experimental set up. There were also several upward spikes in the turbidity data, possibly indicating turbulence in the lake from wind, etc. There was a large storm event in the area during the last two days of the experiment.

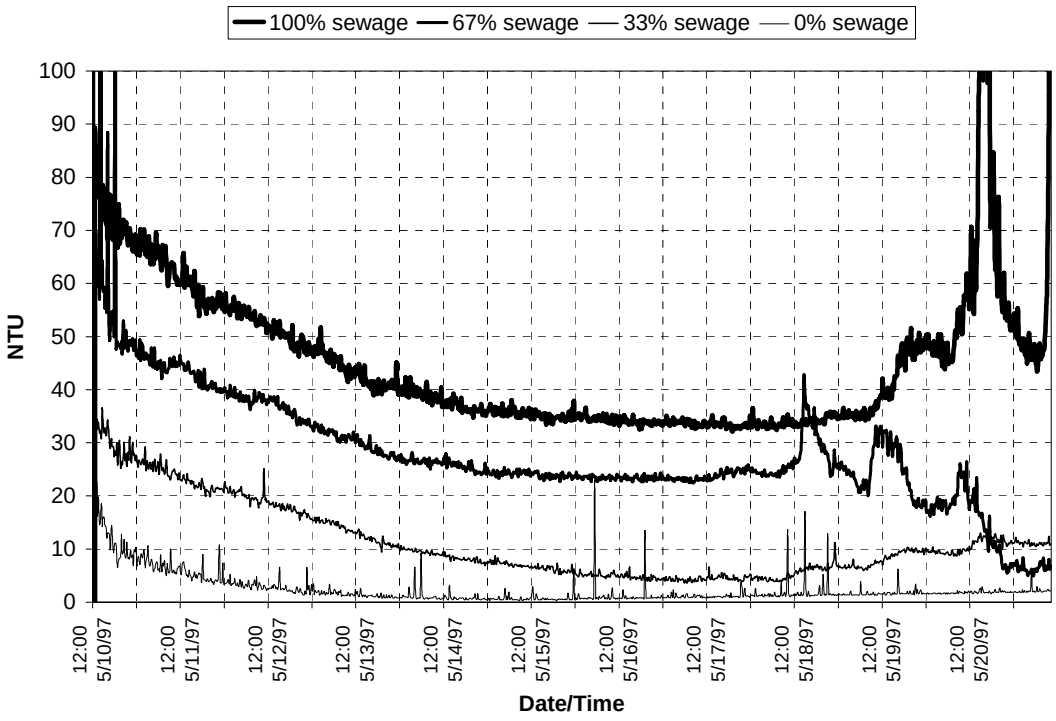


Figure 19. Turbidity data for all four probes over ten day experiment.

Dissolved Oxygen

DO was extensively studied for this experiment (Figure 20). This data was used to calculate photosynthesis and respiration rates for the microorganisms in the test chambers. The 0% sewage test chamber contained a five-day biochemical oxygen demand, BOD_5, of approximately 2.5 mg/L, therefore there was a general downward trend in dissolved oxygen levels over the ten day period of the experiment. This result is typical for a eutrophic lake. The owner used the lake for sport fishing and had been fertilizing the lake regularly in an attempt to produce larger fish.

Typically, a water body that has not previously been exposed to a given waste exhibits an acclimation period. This acclimation period is characterized by the time required for the new environmental conditions, introduced by the waste, to cause selection of organisms that are more tolerant to the pollutants in that particular waste. In addition, some microorganisms can actually adapt to new environmental conditions, but this requires expression of new enzymes that can use the waste as substrate. This process also takes time, as expression of genes for alternative metabolic pathways is not immediate. The water body where this study was conducted rarely, if ever, received sanitary sewage. In this case, an acclimation period was expected. However, if the water body had received regular discharges of sewage, this acclimation phenomenon would most likely not be observed. The 33% sewage chamber had initial anoxic conditions, but after acclimating for approximately five days, there was a diurnal photosynthesis/respiration variation observed. Indeed, the DO levels in this chamber were supersaturated during the daylight hours, as photosynthesis rates were very high. When this chamber was pulled at experiment's end, there was a large amount of green biomass, indicating the presence of photosynthesizing organisms. The 67% sewage test chamber stayed at anoxic DO levels, as expected. However there was an increase in DO on 5/16 and 5/17. Possibly, the organisms in this chamber began photosynthesizing after acclimating to the sewage, but the oxygen demand of the waste quickly drove the DO levels to anoxic levels shortly thereafter. The 100% test chamber stayed anoxic throughout the experiment, as anticipated.

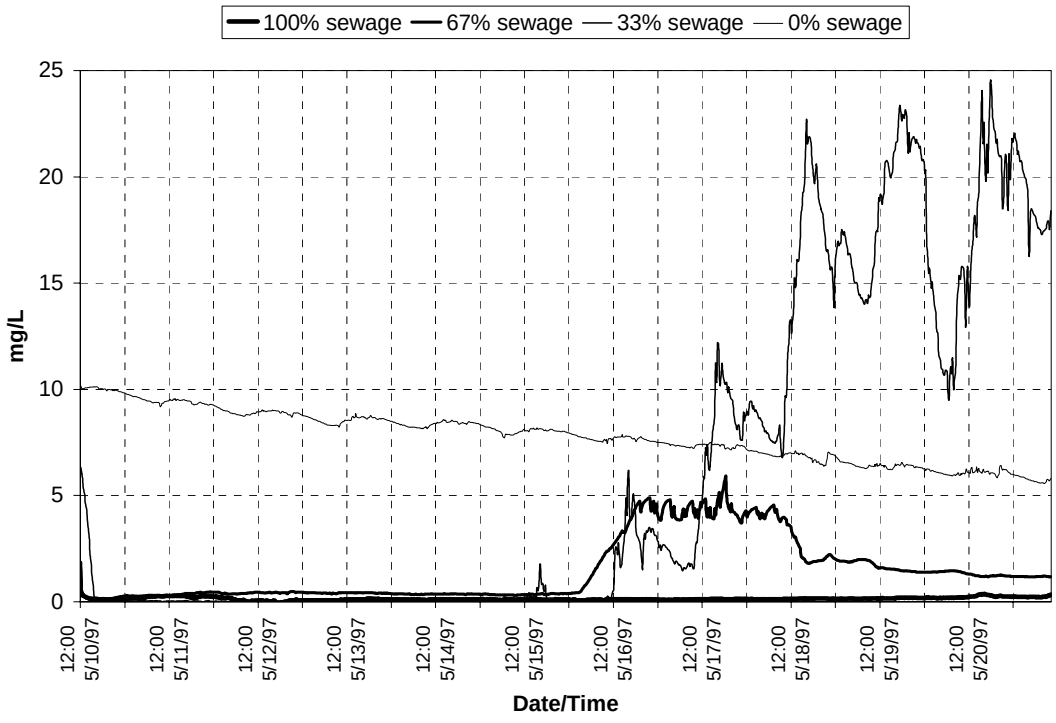


Figure 20. Dissolved oxygen data for all four probes over ten day experiment.

The rates of photosynthesis and respiration were analyzed using the following methods. First, after analyzing the data for the entire length of the experiment, it was determined that the data from only the last five days would be used to calculate rates of photosynthesis and respiration; these days occurred after the acclimation period. An analysis of the dissolved oxygen data given on Figure 20 showed that the rates of photosynthesis and respiration

would be impossible to determine from the 67% and 100% sewage samples because the DO levels were essentially zero. Therefore, the methods were applied only to the 0% and 33% sewage samples. In the future, further experiments should be done to examine sewage dilutions between the 0% and 33% level. In most cases, receiving water mixtures of SSOs and receiving waters would only contain a relatively small volume of sewage. Plots were then created of the 0% and 33% sewage results for this five day period, as shown on Figures 21 and 22.

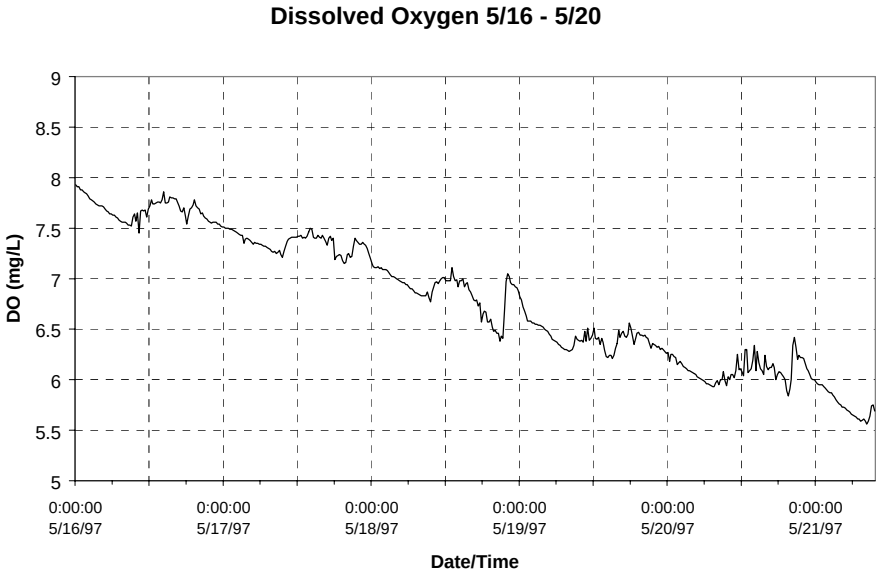


Figure 21. Dissolved oxygen data for 0% sewage.

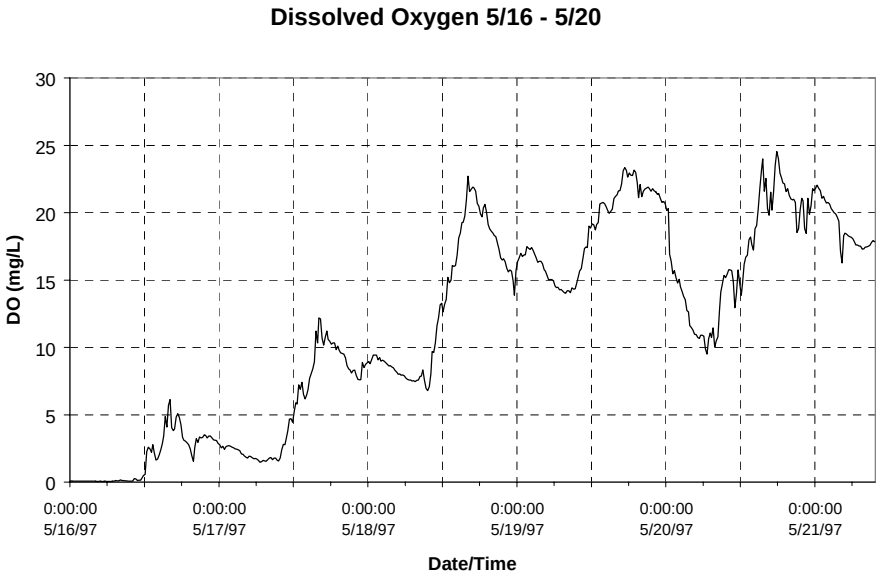


Figure 22. Dissolved oxygen data for 33% sewage.

Finally, these plots were inspected visually, and lines were drawn on positive slope portions and negative slope portions of the graphs. The positive slopes (occurring during daylight hours) were measured and assigned as values of p_{net} (photosynthesis minus respiration). The units were mg DO/L·hr. Then, the negative slopes (occurring at nighttime) were measured and calculated and assigned as values of R (respiration). These values are shown on Table 8, columns 2 through 5.

Table 8. Values calculated for p_{net}, R, and P

	Pnet (mg/L·hr)		R (mg/L·hr)		P (mg/L·hr)	
date	0%	33%	0%	33%	0%	33%
16-May	0.0496	0.8072	-0.0378	-0.2186	0.0874	1.0258
17-May	0.0390	1.1925	-0.0354	-0.2623	0.0744	1.4548
18-May	0.0496	1.9822	-0.0708	-0.5247	0.1204	2.5069
19-May	0.0354	0.7632	-0.0417	-0.9328	0.0771	1.6960
20-May	0.0378	1.0494	-0.0667	-0.4334	0.1044	1.4828
mean	**0.0423**	**1.1589**	**-0.0505**	**-0.4744**	**0.0927**	**1.6333**
std. dev.	**0.0068**	**0.4927**	**0.0169**	**0.2849**	**0.0195**	**0.5456**
COV	**0.1609**	**0.4252**	**-0.3348**	**-0.6006**	**0.2098**	**0.3340**

The R rate was then subtracted from the P_{net} rate to obtain an hourly photosynthesis rate, as shown on Table 8, columns 6 and 7. The rates of both respiration and photosynthesis are much higher in the 33% than in the 0% sewage due to the high amount of biomass present; the 33% sewage chamber was bright green when removed from the lake, indicating the presence of high numbers of photosynthesizing microorganisms.

The next step in determining the photosynthesis rate was to apply the daily average DO model (Thomann and Mueller 1987). The respiration rate is assumed constant throughout the day. The hourly rates determined previously were multiplied by 24 hours to give a respiration rate in units of mg/L·day. The photosynthetic oxygen production is assumed sinusoidally distributed over the photoperiod (f) from 6:00am to 7:00pm for these conditions, or f = 13 hr. The following equation is then used to determine the estimated daily averaged photosynthetic oxygen production rate (p_a):

$$p_a = p' \times \frac{2(t_2 - t_1)/T}{\cos(\pi \bullet t_1 / f) - \cos(\pi \bullet t_2 / f)}$$

where:

$p' = p_{net} + R$
$t_1 = 4$ (10:00am - 6:00am)
$t_2 = 12$ (6:00pm - 6:00am)
T = 24 hr

These results are given in Table 9.

Table 9. Calculated values for the estimated daily averaged photosynthetic oxygen production rate (p_a)

	0% Sewage				33% Sewage			
	p_{net}	respir	p'	p_a	p_{net}	respir	p'	p_a
Date	(mg/L·day)	(mg/L·day)	(mg/L·day)	(mg/L·day)	(mg/L·day)	(mg/L·day)	(mg/L·day)	(mg/L·day)
5/16/97	1.1900	0.9067	2.0967	1.0617	19.3732	5.2469	24.6201	12.4668
5/17/97	0.9350	0.8500	1.7850	0.9039	28.6195	6.2963	34.9158	17.6801
5/18/97	1.1900	1.7000	2.8900	1.4634	47.5720	12.5926	60.1646	30.4652
5/19/97	0.8500	1.0000	1.8500	0.9368	18.3165	22.3868	40.7033	20.6107
5/20/97	0.9067	1.6000	2.5067	1.2693	25.1852	10.4026	35.5878	18.0204
mean	**1.0143**	**1.2113**	**2.2257**	**1.1270**	**27.8133**	**11.3850**	**39.1983**	**19.8486**
std. dev.	**0.1633**	**0.4056**	**0.4670**	**0.2365**	**11.8257**	**6.8380**	**13.0934**	**6.6300**
COV	**0.1609**	**0.3348**	**0.2098**	**0.2098**	**0.4252**	**0.6006**	**0.3340**	**0.3340**

The photosynthesis rates for the 33% sewage were extremely high and variable, ranging from 12 to 30 mg/L·day; and the rates for the 0% sewage were typical, approximately 1 to 2 mg/L·day. Local values of approximately 1 to 4

mg/L·day have been observed during previous experiments with light and dark bottles in Lake Purdy and the Cahaba River (other student projects, Environmental Sampling and Experimental Design class, UAB).

The use of the sonde, with the rapid-pulse DO sensor, allowed these simple experiments to be conducted. Conventional P/R measurements using light and dark bottles would not be sensitive to the relatively long acclimation period noted for raw sewage discharges into waters that rarely receive SSOs. In areas having more consistent SSOs, the acclimation period would not be as long. In addition, the long-duration experiment enabled us to observe variations in the P/R rates corresponding to different weather conditions and other factors. The use of only a single random P/R value (which would be obtained using conventional light/dark bottle tests) could result in errors approaching 100%.

Interaction of Water Column Pollutants and Contaminated Sediments and Interstitial Waters

Exchange between Surface and Interstitial Waters

There are five processes that affect the pollutant exchange between the water column and the sediment interstitial water: 1) hydrodynamics, currents and wave action; 2) resuspension/erosion of sediments; 3) flocculation, settling speeds, and deposition; 4) sorption of chemicals to sediments; and 5) flux/diffusion of chemicals from the water column to interstitial water, and vise versa (Lick 1996). The most important processes, or those that contribute most to chemical exchange, in a stream such as Five Mile Creek, are those that promote turbulent mixing of the water column and the interstitial water. Therefore, it was expected that sediments with large particle sizes will exchange at a high rate due to the large pore size, allowing rapid mixing.

The use of real time interstitial water quality measurements enables one to examine the dynamic interactions of surface and interstitial water. These continuously recording instruments were used to monitor both the interstitial and surface water quality in a segment of Five Mile Creek. The study examined the exchange of water and the degradation of interstitial water due to poor water quality flowing over its surface. It was expected that differences in sediment particle size between the monitored sites will impact exchange, i.e., sites having larger, well-graded sediment particles will allow more rapid and complete exchange between the interstitial water and the stream water than smaller sediment particle sizes.

Five Mile Creek is a typical Alabama steam that has been impacted by sanitary sewer overflows (SSOs). In fact, the site for this study is near a site of continuous raw sewage discharge to the creek. At this site, raw sewage, at a rate of several liters per minute flows over approximately three hundred feet of ground before discharging into the creek. The flow in the creek ranged from approximately two to ten cubic meters per second, depending upon dry versus wet weather conditions. Four sondes were deployed: two upstream and two downstream of the discharge point. In addition, at each upstream and downstream site, one sonde was located on the creek bottom and the second sonde was buried under approximately six inches of sediment. The sondes were protected from large particles by placing them inside 75 μm aperture nylon mesh bags. The sondes were anchored to the bottom by a chain attached to cinder blocks which were then attached to a tree to prevent the sondes from being washed down stream during high flows.

Ten days into the experiment it was discovered that a large rain event had caused such an increase in flow in the creek that the buried sondes were pulled up out of the sediment by the force of the water. Therefore, the sondes were re-buried, and moved to other locations where the sediment characteristics were different. The new sites had generally smaller sediment particle sizes that the previous sites (Figure 2).

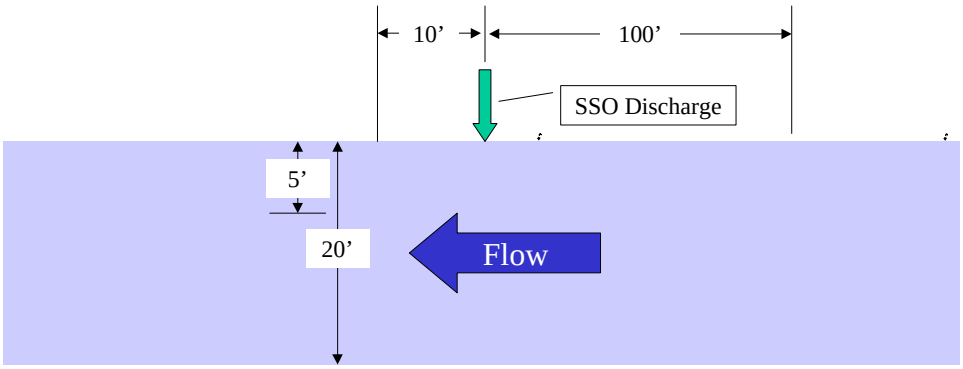


Figure 2. Deployment from June 25 to July 9 (14 days).

The YSI6000 sondes enabled an examination of the lag time response from the surface to interstitial water, and vice versa, for multiple parameters. In addition, it was expected that the relatively long deployment time would allow an investigation of traditional parameters over a longer period of time than has been done historically. For example, typical *in-situ* dissolved oxygen experiments are performed over one twenty-four hour period, to examine diurnal variations. These instruments enabled acquisition of data over multiple twenty-four hour periods. Furthermore, it was expected that the data could be correlated with meteorological conditions, such as cloud cover and rain events, due to the length of deployment.

The exchange of water between the surface and interstitium was examined by applying Thomann and Mueller’s (1987) model of thermal exchange between water layers to the temperature data collected. Moreover, visual inspection of graphical representations of the other water quality parameters were used to examine the effects of meteorological events.

There were no detectable differences between the upstream and downstream water quality data, in relation to the continuous SSO location. The background levels of pollutants in the creek masked the smaller SSO discharge effects. The differences in the flow rates of the SSO discharge (several liters per minute) and the creek (2 to 10 cubic meters per second) were high, causing great dilution. However, the data from the buried sondes was used to compare interstitial water characteristics at the two sites based upon different sediment characteristics. The downstream site, with larger sediment particle sizes will be referred to as the coarse sediment site, and the upstream site, with smaller sediment particle sizes will be referred to as the fine sediment site.

Figures 4-a, b and Figures 5-a, b show the data that was acquired from June 25 to July 9. The first set of figures shows the data collected both in the water column and in the sediment at the fine sediment site. The temperature plot shows a definite lag time between changes in the water column and the sediment interstitial water, approximately six hours from peak to peak at the fine sediment site and approximately two hours at the coarse sediment site. This characteristic is the basis for the exchange model that is presented later. As expected, the data collected at this site corresponds to typical sediment characteristics, i.e., the dissolved oxygen, oxidation-reduction potential, and turbidity data is much lower in the sediment than in the water column. Dissolved oxygen and oxidation-reduction potential are consistent with values associated with an anaerobic, or anoxic, environment. The second set of figures shows the data collected at the coarse sediment site. The data here is similar to, but not as extreme as, the data from the fine sediment, i.e., the values for dissolved oxygen, oxidation-reduction potential, and turbidity are lower than the water column values; however, these data are not ‘flatlines’ like the fine sediment data. This is to be expected as the larger sediment particle size, and associated larger pores, allow increased exchange between the water and sediment, especially when flow disturbances, such as rain events and associated runoff, are occurring. Note the

turbidity change in the interstitial water on July 1, figure 5-b. The larger sediment particle sizes allow passage of the fine particles that create turbidity into the interstitial water.

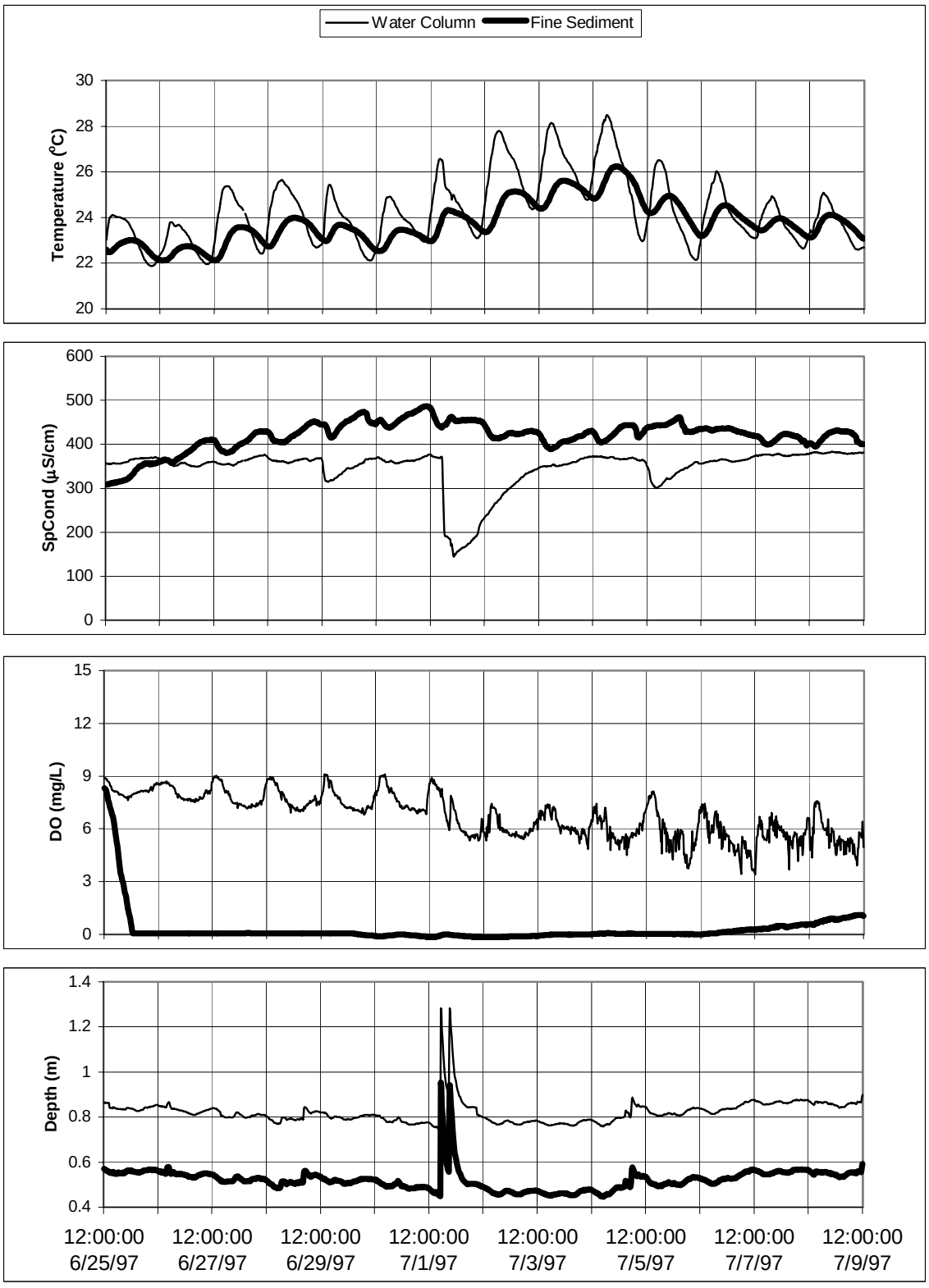
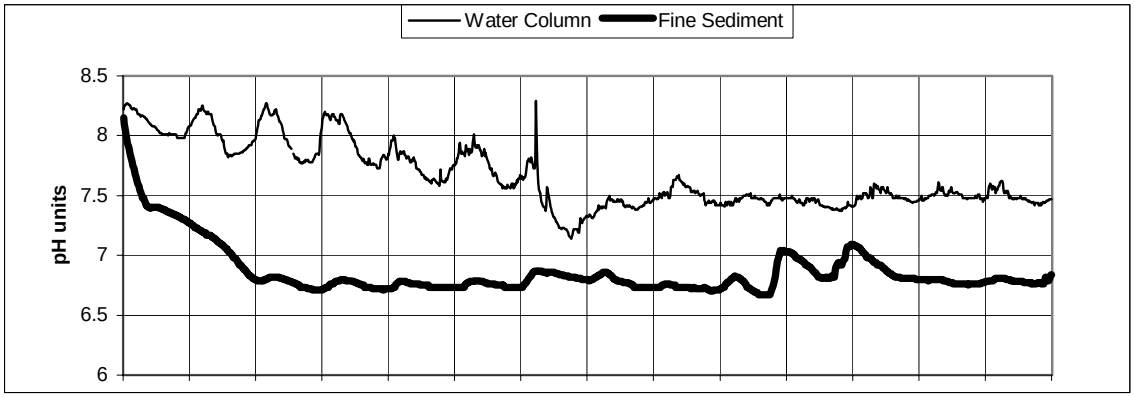
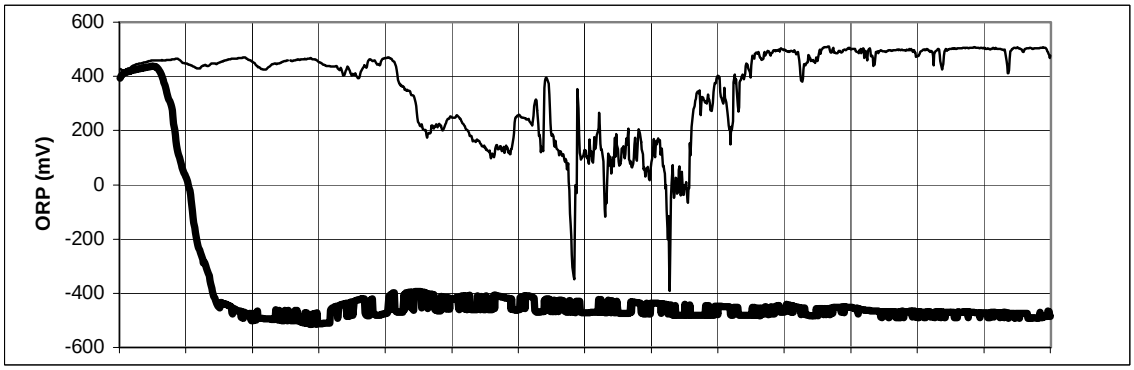
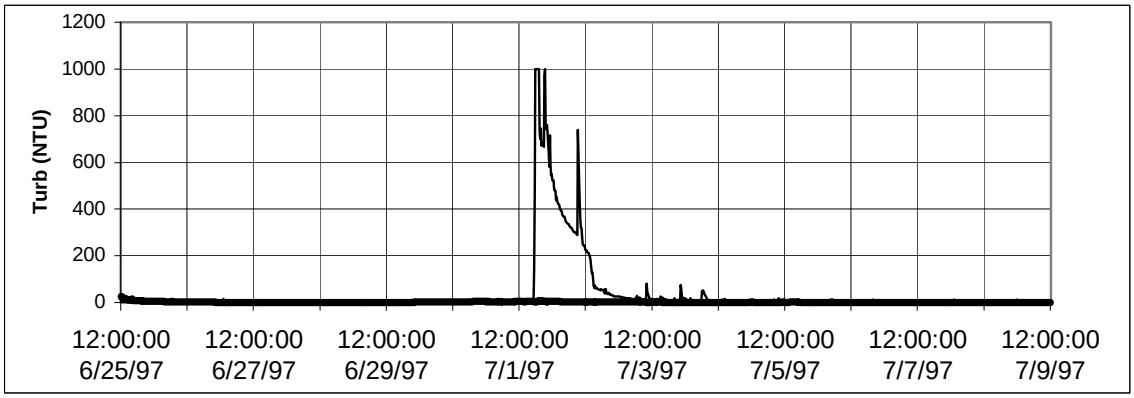


Figure 4-a. Plots of temperature, specific conductance, dissolved oxygen, and depth at fine sediment location.


Water Column
Fine Sediment
pH units
8.5
8
7.5
7
6.5
6


ORP (mV)
600
400
200
0
-200
-400
-600


Turb (NTU)
1200
1000
800
600
400
200
0
12:00:00 6/25/97
12:00:00 6/27/97
12:00:00 6/29/97
12:00:00 7/1/97
12:00:00 7/3/97
12:00:00 7/5/97
12:00:00 7/7/97
12:00:00 7/9/97

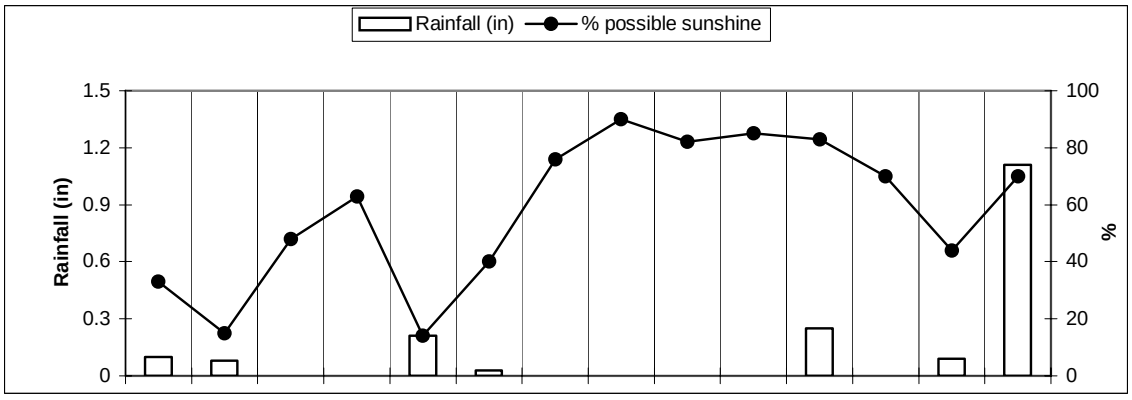

Rainfall (in)
% possible sunshine
Rainfall (in)
1.5
1.2
0.9
0.6
0.3
0
%
100
80
60
40
20
0

Figure 4–b. Plots of pH, oxidation-reduction potential, turbidity, and meteorology at fine sediment location.

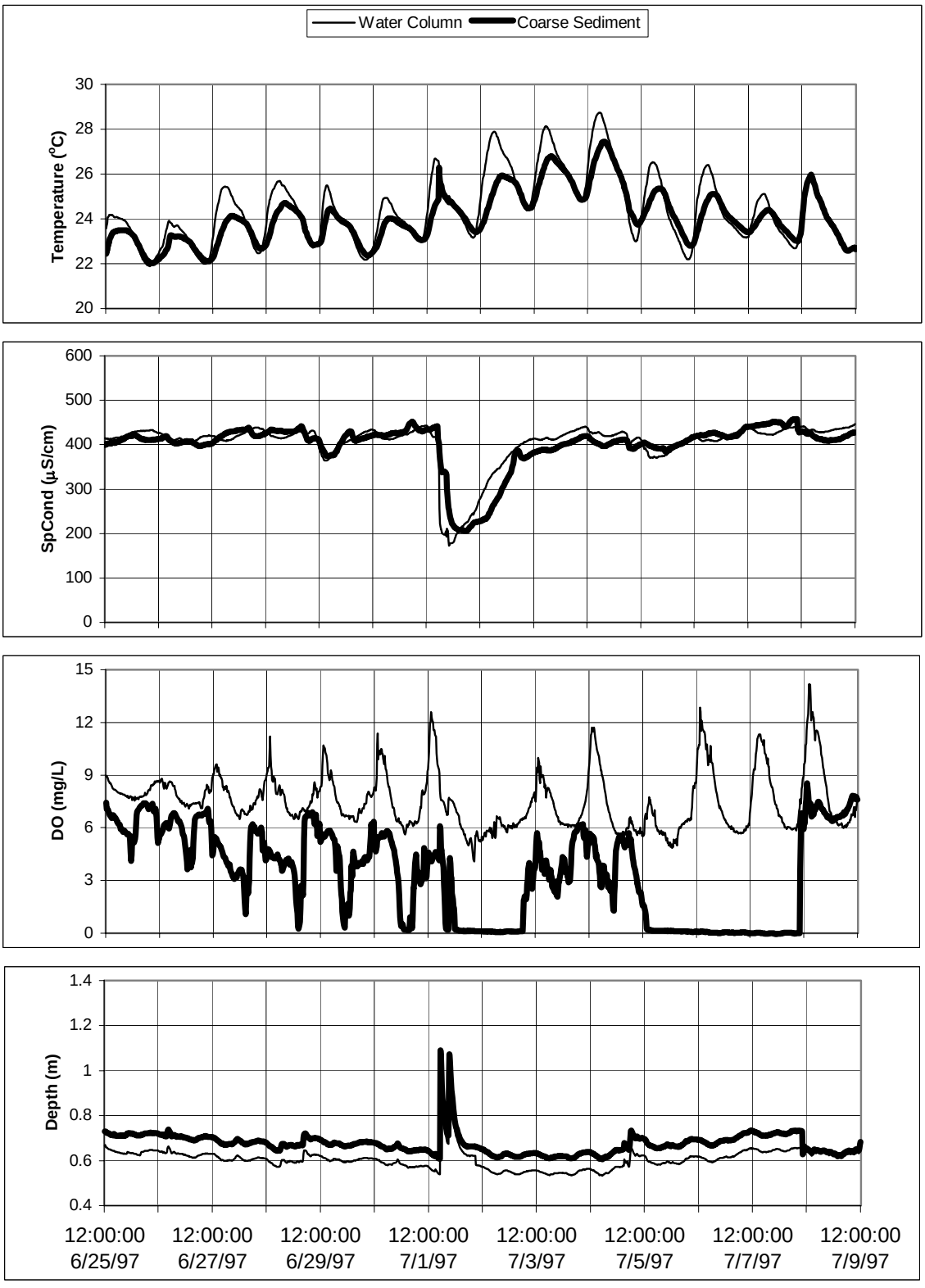

Water Column
Coarse Sediment
Temperature (°C)
30
28
26
24
22
20
SpCond (µS/cm)
600
500
400
300
200
100
0
DO (mg/L)
15
12
9
6
3
0
Depth (m)
1.4
1.2
1
0.8
0.6
0.4
12:00:00 6/25/97
12:00:00 6/27/97
12:00:00 6/29/97
12:00:00 7/1/97
12:00:00 7/3/97
12:00:00 7/5/97
12:00:00 7/7/97
12:00:00 7/9/97

Figure 5-a. Plots of temperature, specific conductance, dissolved oxygen, and depth at coarse sediment location.

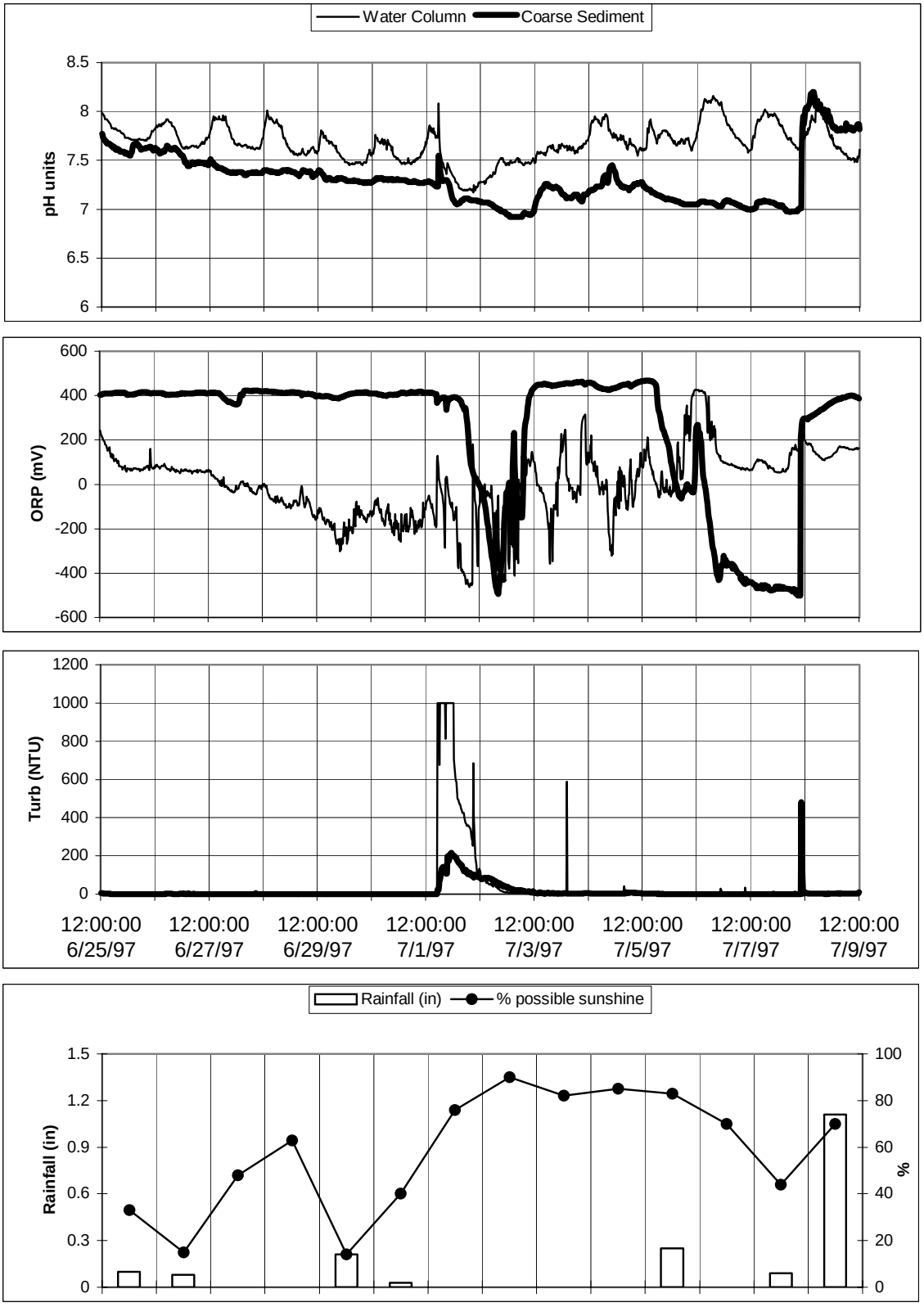

Water Column
Coarse Sediment
pH units
8.5
8
7.5
7
6.5
6
ORP (mV)
600
400
200
0
-200
-400
-600
Turb (NTU)
1200
1000
800
600
400
200
0
12:00:00 6/25/97
12:00:00 6/27/97
12:00:00 6/29/97
12:00:00 7/1/97
12:00:00 7/3/97
12:00:00 7/5/97
12:00:00 7/7/97
12:00:00 7/9/97
Rainfall (in)
% possible sunshine
Rainfall (in)
1.5
1.2
0.9
0.6
0.3
0
%
100
80
60
40
20
0

Figure 5–b. Plots of pH, oxidation-reduction potential, turbidity, and meteorology at coarse sediment location.

These data also show diurnal fluctuations in temperature, dissolved oxygen, and pH. The temperature fluctuation corresponds well with the day/night solar cycle and associated heating and cooling. The dissolved oxygen and pH data correlate with changes in photosynthesis and respiration rates occurring as a result of the day/night solar cycle also. Table 2 shows the diurnal fluctuations for these three parameters, and the means, standard deviations, and coefficients of variation. Note that the variations (COV) for dissolved oxygen and pH are much higher than the variations for the temperature. This is likely due to the fact that temperature is highly dependent upon sunlight, and the variations are mostly due to cloud cover. However, the dissolved oxygen and pH conditions, even though partially influenced by photosynthesis and therefore sunlight conditions, are also dependent upon other chemical process occurring in the stream, hence the higher variation. In addition, the dissolved oxygen maximums and variations at the coarse sediment site are higher than those at the fine sediment site because of the increased water velocity and turbulence in this riffle area, i.e., there is more exchange of oxygen with the atmosphere under these conditions.

Table 2. Diurnal ranges (differences between daily maximum and minimum values) in temperature, dissolved oxygen, and pH statistics at all sites.

	Temperature				Dissolved Oxygen				pH			
Date	water col.	fine sed.	water col.	coarse sed.	water col.	fine sed.	water col.	coarse sed.	water col.	fine sed.	water col.	coarse sed.
6/26	1.94	0.89	2.01	1.27	1.08	0.41	1.60	2.79	0.29	0.31	0.29	0.12
6/27	3.41	1.47	3.44	2.02	1.83	0.01	3.10	4.02	0.45	0.29	0.34	0.17
6/28	3.23	1.26	3.23	2.04	2.06	0.04	4.69	5.12	0.43	0.09	0.42	0.05
6/29	2.75	1.02	2.78	1.64	2.11	0.01	4.20	6.62	0.31	0.07	0.33	0.10
6/30	2.79	1.00	2.77	1.67	2.29	0.17	5.12	5.77	0.43	0.06	0.31	0.05
7/1	3.63	1.36	3.69	3.24	2.97	0.16	6.97	5.95	0.97	0.14	0.74	0.45
7/2	4.69	1.77	4.73	2.52	2.11	0.14	3.09	0.16	0.36	0.08	0.35	0.17
7/3	3.77	1.23	3.72	2.33	1.98	0.11	4.03	5.62	0.29	0.05	0.21	0.34
7/4	3.72	1.42	3.94	2.60	2.64	0.10	5.91	4.95	0.17	0.13	0.40	0.37
7/5	3.62	1.99	3.56	2.80	3.88	0.05	2.75	5.57	0.09	0.37	0.37	0.23
7/6	3.88	1.65	4.22	2.33	3.69	0.15	8.00	0.14	0.23	0.28	0.56	0.07
7/7	1.84	1.06	1.95	1.19	3.53	0.33	5.65	0.12	0.17	0.10	0.44	0.09
7/8	2.43	1.00	3.31	2.98	3.89	0.51	8.34	8.57	0.17	0.06	0.52	1.23
mean	**3.21**	**1.32**	**3.33**	**2.20**	**2.62**	**0.17**	**4.88**	**4.26**	**0.34**	**0.16**	**0.41**	**0.26**
std. dev.	**0.82**	**0.34**	**0.80**	**0.64**	**0.90**	**0.16**	**2.05**	**2.70**	**0.22**	**0.11**	**0.14**	**0.32**
COV	**0.26**	**0.26**	**0.24**	**0.29**	**0.34**	**0.92**	**0.42**	**0.63**	**0.66**	**0.73**	**0.34**	**1.20**

A further examination of Figures 4 and 5 yields a correlation between the meteorological data and the water quality data, i.e., the duration, frequency, and magnitude of runoff events is apparent. The meteorological data was obtained from NOAA, National Oceanographic and Atmospheric Administration, records collected at Birmingham International Airport. The data collected in the stream shows that the probe is capable of detection and study of water quality changes occurring due to WWF events. From the meteorological data, it is apparent that a rain event occurred at the airport on June 30 and July 1. The sonde data shows a large corresponding fluctuation in specific conductance, depth, and turbidity in the water column at both sites on July 1. The peaks are almost immediate, then return to previous levels within one to two days depending upon the parameter. Figures 6 and 7 are plots of these three parameters expanded around the time of the rain event.

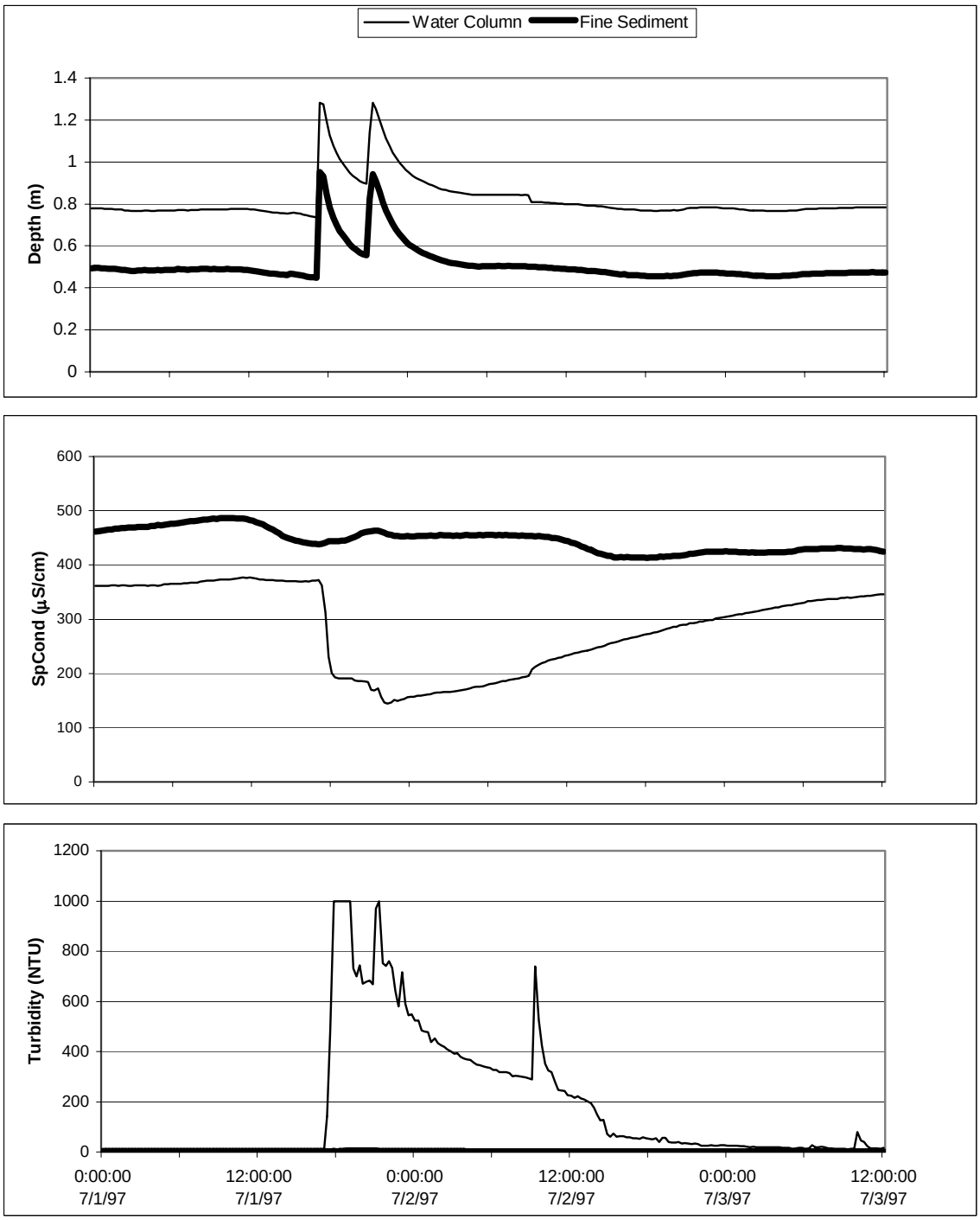


Figure 6. Event plots of depth, specific conductance, and turbidity at fine sediment site.
(Note: The maximum range of the turbidity probe is 1,000 NTU.)

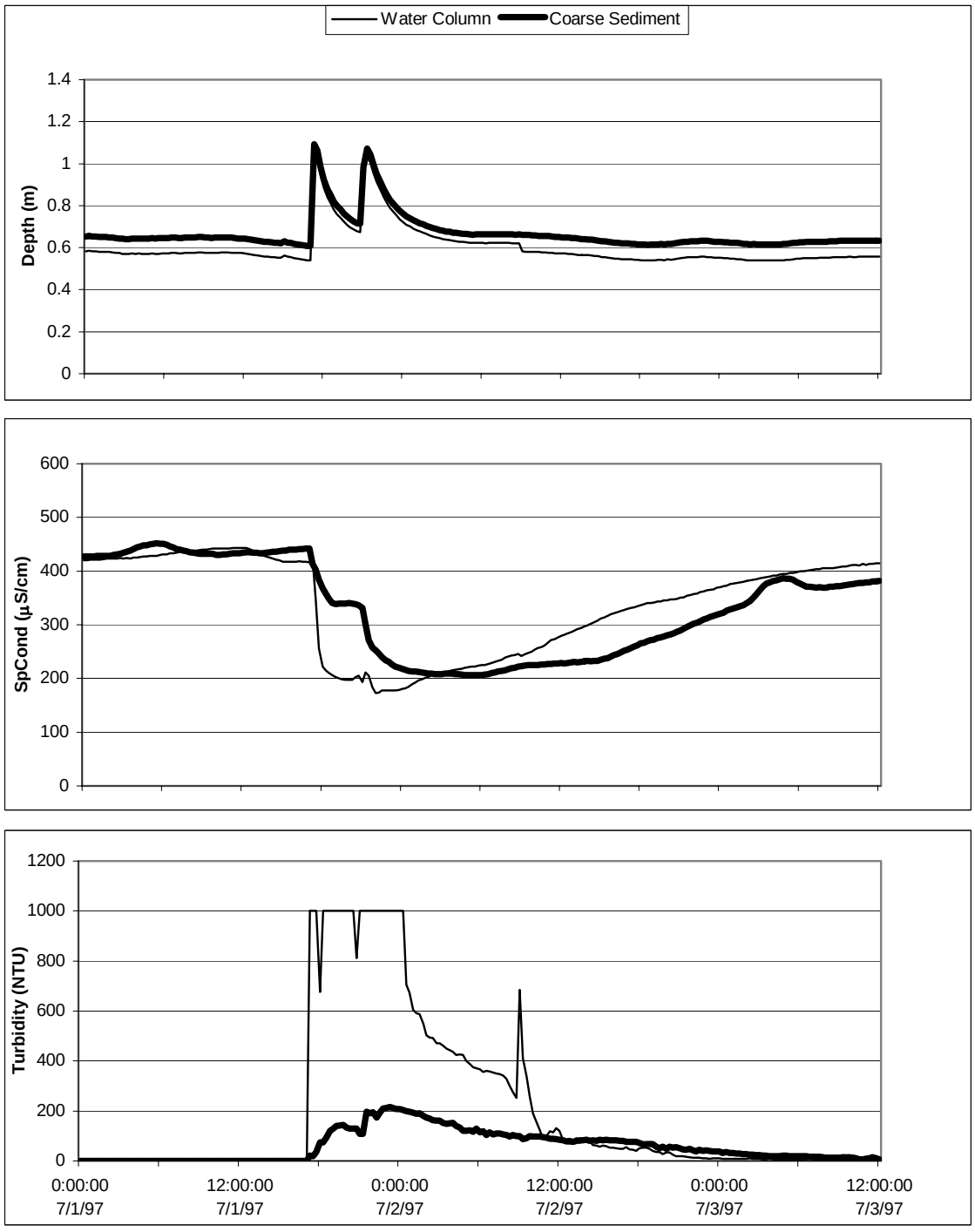


Figure 7. Event plots of depth, specific conductance, and turbidity at coarse sediment site.

Table 3. Values for Magnitude of Change and Time to Return to Baseline for Depth

Sonde location	magnitude of change (m)	time to return to baseline (hr)

	Peak 1	Peak 2	Peak 1*	Peak 2
Water column	0.6	0.4	na	12
Fine sediment	0.55	0.4	na	12
Water column	0.5	0.4	na	12
Coarse sediment	0.5	0.4	na	12

***Values are not available as the second hydrograph peaked before the first had receded.**

Table 4. Values for Magnitude of Change and Time to Return to Baseline for Specific Conductance

Sonde location	magnitude of change (μS/cm)	time to return to baseline (hr)
Water column	210	42
Fine sediment	Not obvious	Not obvious
Water column	260	44
Coarse sediment	230	46

Table 5. Values for Magnitude of Change and Time to Return to Baseline for Turbidity

Sonde location	magnitude of change (NTU)	time to return to baseline (hr)
Water column	>1000	30
Fine sediment	0	0
Water column	>1000	30
Coarse sediment	210	30

The data in Tables 4 and 5 again show the differences in exchange occurring in the two different sediment types. The interstitial water at the coarse sediment site changes with the water column, albeit at a reduced magnitude, while the interstitial water at the fine sediment site shows no change.

Exchange Model

The data collected for this experiment was used to apply the thermal exchange model (Thomann and Mueller 1987). This model is generally used to examine the long-term exchange between the epilimnion and the hypolimnion layers of a lake, two distinct and separate layers found in thermally stratified lakes. This model was applied to the Five Mile Creek data. In this case, the two layers are not the hypolimnion and epilimnion in a lake, but the fast-flowing water column and the slow-moving interstitial water. These are also two distinct, separate layers. Additionally, the lake model tracks exchange over a period of months, or seasons, while the applied stream model is examining changes occurring over a period of hours. Figure 8 is a schematic representation of the terms used in the applied thermal exchange model, given in equations 1 and 2.

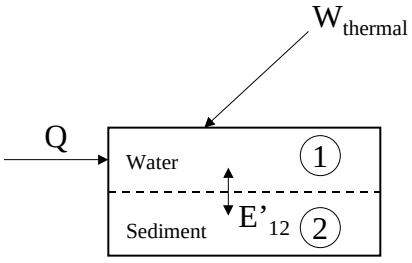


Figure 8. Thermal exchange modeling system.[3]

Thomann and Mueller used the following equations to calculate the exchange rate between the two lake layers.

$$E'_{12} = V_2 \frac{\Delta T_2}{\Delta t}\left(\frac{1}{T_1 - T_2}\right) = \frac{V_2}{\Delta t}\left[\frac{T_2(t+½) - T_2(t-½)}{T_1(t) - T_2(t)}\right]$$

$$E_{12} = \frac{E'_{12}\overline{Z}_{12}}{A_{12}} = \frac{V_2\overline{Z}_{12}}{A_{12}\Delta t}\left(\frac{\Delta T_2}{\Delta T} = \tau\right) = \frac{V_2\overline{Z}_{12}}{A_{12}}\left(\frac{\tau}{\Delta t}\right)$$

(Equations 1 and 2)

where:

$\overline{Z}_{12}$ is the average depth of the two layers,

E'_{12} is the bulk vertical mixing coefficient (L^3/T),

E_{12} is the vertical dispersion coefficient (L^2/T),

t is time (days),

A_{12} is the area of the interface between the two layers,

T_1 and T_2 are the temperature in layers 1 and 2 respectively,

ΔT_2 is the difference in temperatures in layer 2 after time, t,

ΔT is the difference in temperatures between layers 1 and 2,

and $\tau = \Delta$ in sediment temperature/ water – sediment temperature.

From these equations, with the appropriate conversion factors, one can obtain a vertical dispersion coefficient in cm^2/s. Since the model, as used by Thomann and Mueller, is applied to a lake with known layer volumes, our model, with unknown layer volumes in the stream, due to stream flow, was modified to calculate a relative exchange rate, or E_r. Therefore, the results expressed here are not an absolute exchange rate, given in terms of length per unit time, rather the rate is relative to the volume of the two layers. However, since the hydraulic characteristics in the stream reach at the two sonde locations are similar i.e., the unit volumes and exchange areas are analogous, comparisons can be made between the relative exchange at the two sites. Equation 3 is modified from Equation 2, and was used to calculate relative thermal exchange, E_r.

$$E_{12} = \frac{V_2\overline{Z}_{12}}{A_{12}}\left(\frac{\tau}{\Delta t}\right)$$

$$E_{12}\frac{A_{12}}{V_2} = \overline{Z}_{12}\left(\frac{\tau}{\Delta t}\right)$$

$$\frac{E_{12}A_{12}}{V_2} = E_r = \frac{depth \times \tau}{\Delta t}$$

(Equation 3)

Since the volumes and areas at the two sites are analogous at any point in time, i.e., stream flow conditions are the same, the relative exchange rate (E_r) can be compared between the two. Table 6, shows some example calculations.

Table 6. Example calculations of E_r (relative thermal exchange)

		Water		Sediment								
date	time	depth (m)	temp (C)	depth (m)	temp (C)	Δt (s)	T1 (C)	T2 (C)	ΔT2	ΔT	τ	E_r
6/25	12:00	0.666	23.57	0.73	22.45							
6/25	12:15	0.67	23.74	0.729	22.54							
6/25	12:30	0.662	23.83	0.729	22.63							
6/25	12:45	0.659	24.07	0.726	22.73							
6/25	13:00	0.658	24.08	0.725	22.83	3600	23.83	22.64	0.38	1.19	0.32	5.91E-05
6/25	13:15	0.656	24.12	0.724	22.92							
6/25	13:30	0.654	24.18	0.722	23.01							
6/25	13:45	0.652	24.18	0.72	23.1							
6/25	14:00	0.651	24.18	0.72	23.17	3600	24.13	23.00	0.34	1.13	0.30	5.47E-05

An examination of the plots showing relative thermal exchange, Figures 9 and 10, yields some interesting results. First, the temperature during the daylight hours on both plots is higher in the water column than in the interstitial water. Then, during the nighttime hours the temperature is higher in the interstitial water than in the water column. Therefore, since heat is transferred from high to low temperature, the process of thermal exchange is being driven by the water column during the day, and by the interstitial water during the night. Therefore, since the model is tracking exchange from the water column to the interstitial water, exchange is positive during the day, and negative at night. This is to be expected, as the thermal properties of the interstitial water are much more stable than that of the water column because the sediment is isolated from ambient temperature changes, unlike the water column, which interfaces directly with the air and absorbs the bulk of the solar radiation. Second, approximately every twelve hours the thermal exchange curve approaches an asymptotic relationship. This is because the exchange model, when the two temperature curves cross, yields an E_r value of zero or infinity.

In addition, it is interesting to compare the differences in thermal exchange between the coarse and fine sediments. The coarse sediment graph is similar to the graph of the trigonometric function cotangent, while the fine sediment graph resembles the graph of the secant function. Furthermore, there is much more scatter in the plot for the coarse sediment site. This is because, as expected, the larger pore size allows much more rapid and thorough exchange with the overlying water column. Whereas, the fine sediment site generally yields values for relative thermal exchange rate clustered around zero. Again, this is because the smaller pore size limits the exchange of water here, and the process is driven more by radiant heat transfer, a much slower process, than by mixing of the water column and interstitial water as occurs at the coarse sediment site.

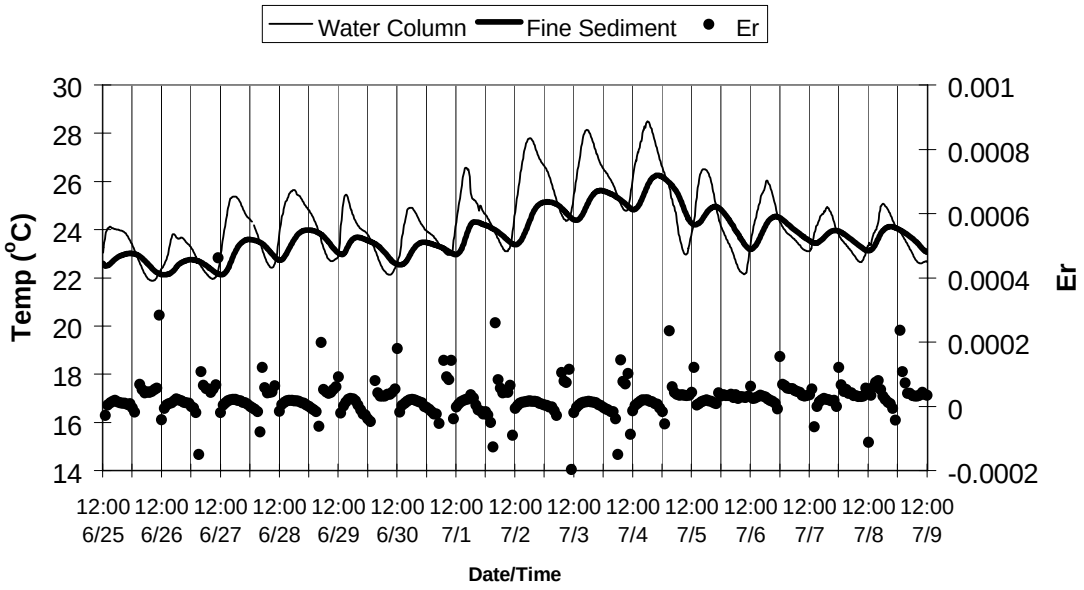


Figure 9. Temperature and relative thermal exchange at the fine sediment location

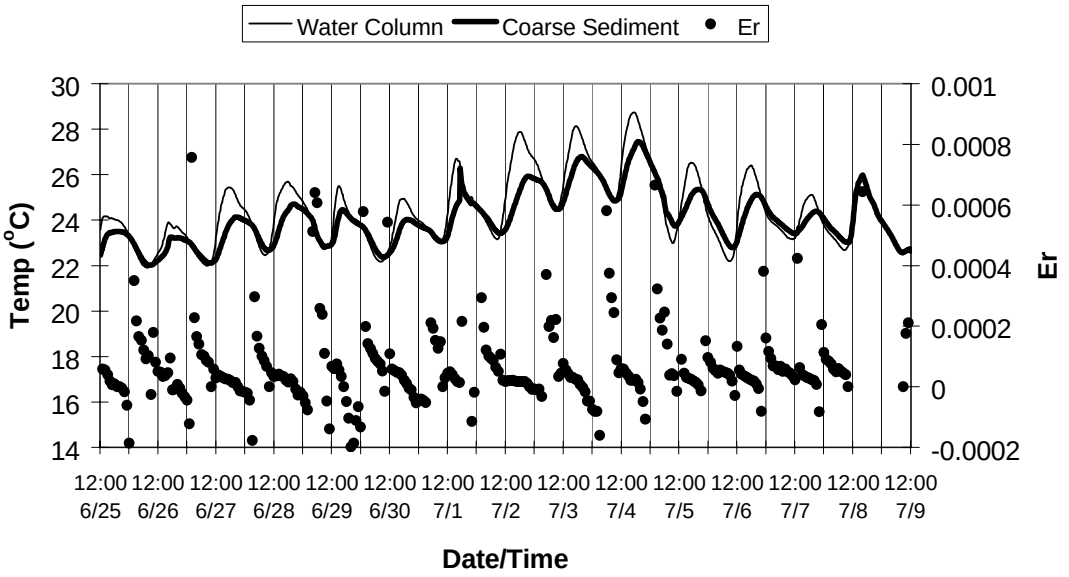


Figure 10. Temperature and relative thermal exchange at the coarse sediment location

More interesting than the rate of thermal exchange, is the rate of chemical exchange between the water column and the sediments. Therefore, scatter plots were also constructed to further investigate the chemical exchange processes occurring in the creek. These plots were examined to determine if any gross pattern exists between the data values in the water column versus those from the interstitial water. From these plots and intuition, it was determined that of those monitored, the specific conductance parameter would be best suited for monitoring chemical exchange between the water column and sediment interstitial water. The specific conductance plots are presented in Figures 11 and 12. The runoff event that occurred in the stream is seen in the coarse sediment plot, indicated by the loop structure in the lower left corner of Figure 12. The fact that this structure is not present in the fine sediment plot, Figure 11, is a further indication that exchange is much slower at this site. Notice that the interstitial water specific conductance values at the fine sediment site are clustered around higher values of specific conductance. This again shows that the dilution effects that occurred in the water column during the event (the line of lower values dropping below 150 in the water column) are not correspondingly present in the interstitial water.

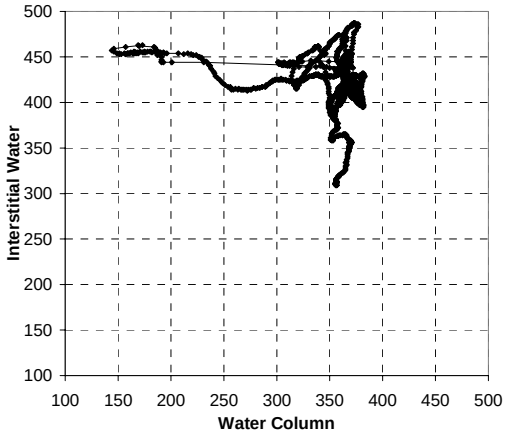


Figure 11. Fine sediment site specific conductance.

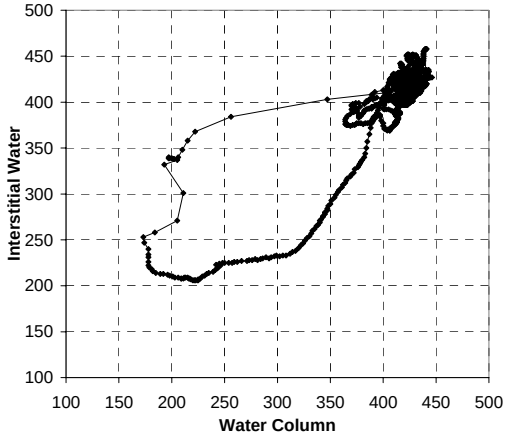


Figure 12. Coarse sediment site specific conductance.

The thermal exchange model was applied to the specific conductance data to attempt to analyze the rate of chemical (water) exchange. The results are similar to the thermal exchange, i.e., the rate of relative exchange was much higher and more variable in the coarse than in the fine sediment. Again, in the coarse sediment, the much more rapid process of turbulent mixing is occurring as opposed to the slower process of diffusion, which is the driving force in the fine sediment because smaller pore sizes limit turbulent mixing. Figures 13 and 14 are similar to those constructed for relative thermal exchange, except that specific conductance data were substituted for temperature data.

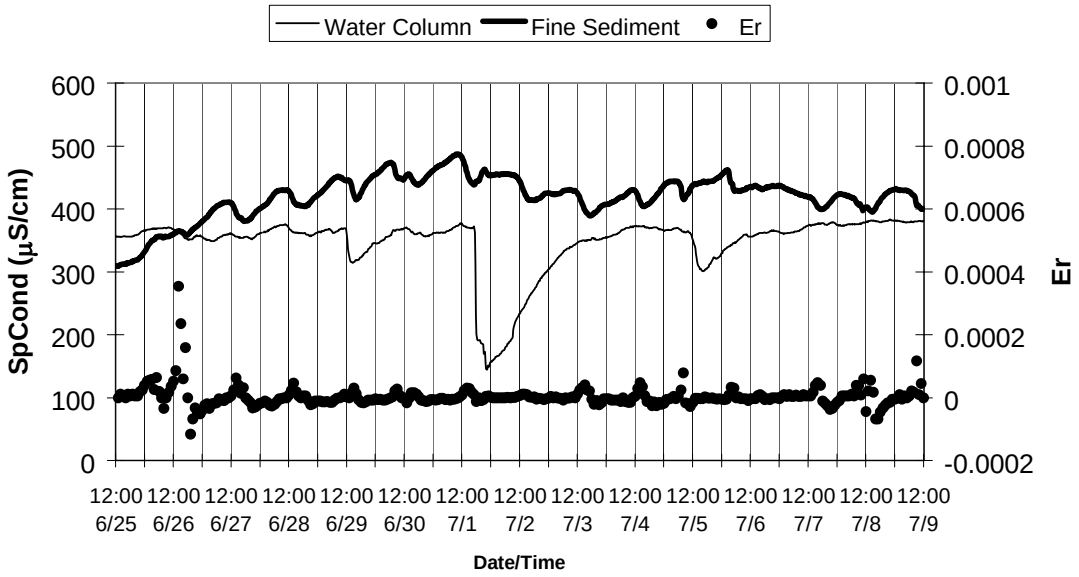


Figure 13. Specific conductance and relative chemical exchange at the fine sediment location

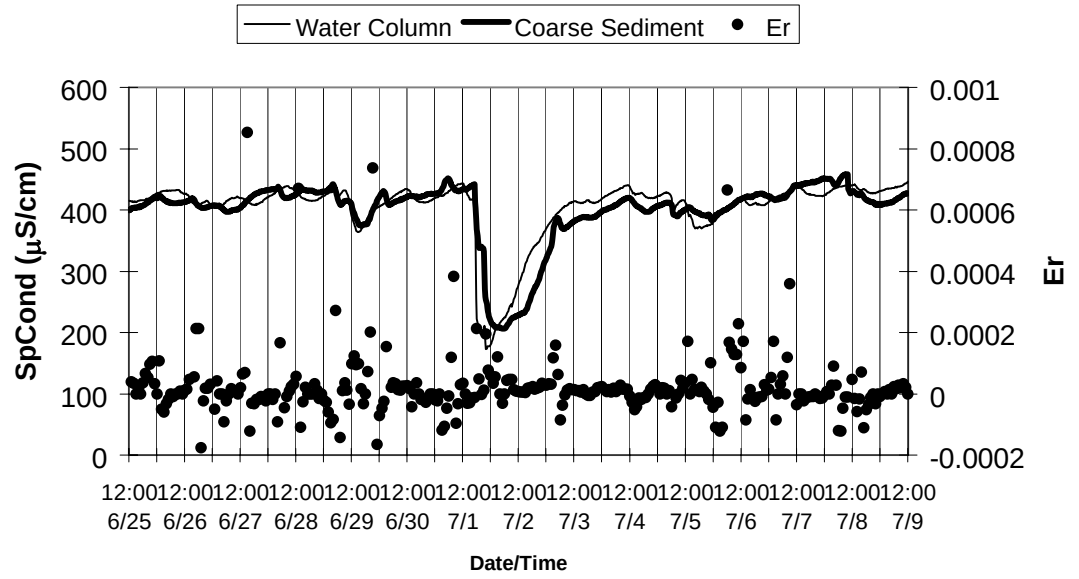


Figure 14. Specific conductance and relative chemical exchange at the coarse sediment location

Table 7 shows the summary statistics: means, standard deviations, and coefficients of variation, calculated for both relative thermal and relative chemical exchange rates. These values also indicate the differences between the exchange rates. Note that the values for the coefficients of variation, COV, are higher at the coarse sediment site than at the fine sediment site, indicating an increased rate of exchange. The COV is obtained by dividing the standard deviation into the mean, with larger values indicating higher variation within the sample group.

Table 7. Statistics For Relative Exchange Rates

Parameter	Sediment	Mean	Std. Dev.	COV

	Type			
Temperature	Fine	2.12×10^{-5}	1.03×10^{-4}	5
	Coarse	1.39×10^{-4}	1.28×10^{-3}	9
Specific Conductance	Fine	2.79×10^{-6}	3.33×10^{-5}	12
	Coarse	1.81×10^{-6}	2.54×10^{-4}	140

The use of the continuously recording sondes, especially with the rapid pulse DO sensors, enabled realtime interstitial water quality changes to be made. These measurements are especially important for sensitive parameters that are not possible to accurately measure in collected samples (especially ORP). The continuous measurements showed that interstitial water within fine sediments was basically isolated from the overlying water column and the quality of the interstitial water was therefore affected by sediment quality. The coarse sediments, however, allowed a relative free exchange of water between the overlying water and the interstitial water, with much less of an influence of sediment quality on interstitial water quality.

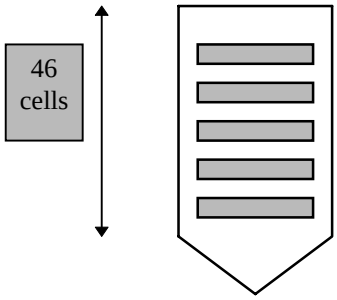
Interstitial Water Measurements

XXXXX more from Wynn Echols report XXXXXX

Peepers

Peepers, diagrammed below, consist of 46 cells of approximately 8 mL each. The cells are covered with a 75 micron nylon screen which will hold water, but allow diffusion of soluble pollutants and silts.

Figure 5. Peeper Diagram



The peepers are machined from Delrin™. The peepers are washed with concentrated nitric acid, rinsed with deionized water, and all cells filled with Reverse Osmosis quality water (18 Mohms resistivity). The cells are then sealed with the 75 micron nylon screen membrane. The prepared peepers are then brought to the field (keeping them horizontal to minimize water loss) and carefully pushed into the soft deposits of the stream bed, leaving a few of the uppermost cells above the sediment surface, at least.

The vertical distance of cells is approximately two feet. This array of cells allows investigation of the effect of depth on interstitial water chemistry and biology. The peeper is placed in the sediment and allowed to equilibrate for a period of time, usually at least 2 hours. After this period, the peeper is removed from the sediment and carefully rinsed with clean water to remove any superficial sediment from the cell coverings. In order to extract the water samples from the cells, a small hole is made in the mesh covering with a sharp object, allowing a 10 mL plastic syringe to withdraw the sample water. The water is then transferred to a small storage vial and sealed and brought to the laboratory for analysis.

Measurement of Frequency, Duration, and Magnitude of WWF Events

This study was conducted to examine the utility of the sondes as a tool for monitoring the duration, frequency, and magnitude of wet weather events. Short term, or runoff induced, pollution effects can be studied in detail using these instruments. The long deployment time and continuous monitoring capability of the YSI6000 enables acquisition of data for multiple events, i.e., as many as occur during the time of deployment. The sonde can be programmed to record stream depth, turbidity, and specific conductivity, all good indicators of a wet weather event.

The sonde data shown above for the sediment experiments indicated a large change in depth, specific conductivity, and turbidity in the water column at both sites on July 1 at 5:00pm. The depth and turbidity values increase and the specific conductivity values decreased simultaneously at the beginning of the event. The rise period for all of the parameters was very rapid, and the peaks occurred very early in the runoff event. They then returned to the previous levels within one to two days, depending upon the parameter. The data acquired for water depth is obviously the parameter that best correlates to runoff hydrographs. Examining the changes in depth that occurred at about 5:00pm on July 1 (figures 1, 2 and table 2) shows that there was an approximate 0.5 m increase in the stream depth. There were actually two separate runoff hydrographs that were spaced about 3 hours apart. The turbidity and specific conductance measurements did not distinguish between these two separate, but close peaks. The turbidity and specific conductance data also substantiate the presence of a runoff event, but with an additional perspective on the duration of the potential effects from elevated turbidity levels and decreased specific conductance.

The flow in Five Mile Creek rapidly changes with rain conditions, especially considering that the watershed is relatively large (many square miles). However, the water quality was degraded long after the water levels decreased to base flow conditions. The turbidity remained elevated for about 30 hours and the specific conductivity remained depressed for about 40 hours, although the hydrograph response was completed in about 12 hours. These longer periods of water quality degradation were likely caused by degraded groundwater recharge waters entering the creek, or by degraded small volume surface flows. In any case, the water was severely affected for periods of about three times the runoff duration (from 2 to more than 3 days). Because of the common rains in Alabama (rains occurring about every 3 to 5 days, and moderate rains similar to that which was monitored occurring about every 10 to 15 days), the degraded water quality associated with the WWF could affect the creek for 10 to 20 percent of the time. In addition, several days of exposure to degraded conditions may be common, instead of the several hours of exposure to degraded conditions typically assumed for WWF effects.

The use of continuously recording sondes, especially those capable of long-term monitoring of depth, turbidity, and specific conductivity, are therefore very useful in indicating the frequency, magnitude, and duration of WWF degradation on in-stream water quality. If located upstream and downstream from a major SSO discharge point, these devices can also continuously measure the magnitude of the SSO flows in relation to the receiving water flow. The SSO location where the sondes were located for this demonstration did not cause any measurable difference in the sonde parameters (DO, temperature, specific conductivity, pH, ORP, turbidity, or water depth) because of its relatively small flow in relation to the large creek flow.

Development of Organic Extraction and Analysis Methods for Urban Stream Sediments Affected by SSOs

The sediment samples were extracted using EPA method 3545 (Accelerated Solvent Extraction). The extract was further cleaned using gel permeation chromatography, capturing the fraction associated with the mass range of interest. A measured volume (5 mL) of a sediment sample was mixed with sodium sulfite to dry the sample. The same volume of sample was simultaneously dried to determine the moisture content of the sample. The sample/sodium sulfite mixture was then mixed with clean sand to fill the volume of the extraction vessel on the Dionex ASE (Accelerated Solvent Extractor). Up to 24 samples can be extracted automatically. Each sediment sample is extracted with methylene chloride at high pressure for 15 minutes. The collected extract is then slightly reduced in volume using a Savant AS-160 SpeedVac, under vacuum and cold conditions to minimize loss of volatile sample portions. The extracts must be further cleaned before GC/MSD analyses because of the high organic content of many of the sediment samples of interest. The reduced sample extract is cleaned using an OI Analytical AutoPrep gel permeation chromatography (GPC) unit. The GPC discards portions of the sample extract containing much of the unresolvable heavy hydrocarbons, leaving the PAHs and phenols, plus other compounds of interest, in the extract. The collected extract from the GPC is then reduced in volume on the Savant SpeedVac to the final analytical volume (2 mL). The final extracts are then stored in a freezer until they are analyzed using the Hewlett Packard 5890 Series II GC, having a mass spectrophotometer detector and auto sampler. The mass range of the mass spectrometer detector on the GC used in these analyses was optimized for the 40 – 550 atomic mass unit (AMU) range.

The method development activities involved analyzing many (about 60) sediments affected by urban runoff and SSO processes. The objective was to obtain a wide variety of sediments to represent the range of conditions that

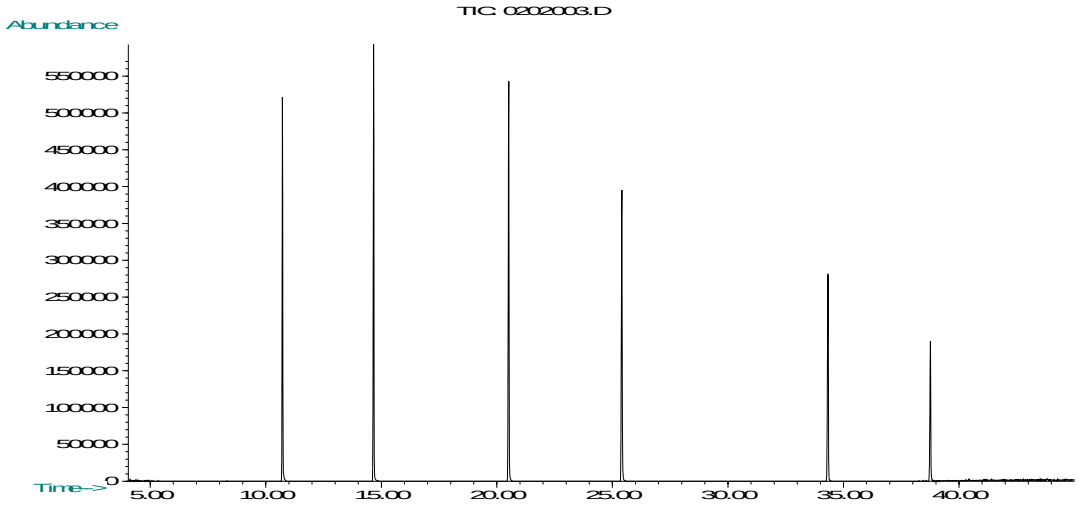
may be encountered in the field. Detailed stream sediment analyses will be conducted in the second project year. The sediments ranged in texture from grainy sand to an extremely fine silt or sludge. Color ranged from clear quartz/white sand to red clay and black sludge. Multi-colored sheens were observed on a few samples. Odor of the sediment samples ranged from no detectable odor to a scent of nutrient rich potting soil to clearly discernible diesel or other petroleum compounds to sulfur and sewage. The most striking feature of the test sediments analyzed as part of the methodology development activities was the wide range of physical characteristics such as texture, color, and odor, and their correlation with the organic analyses results.

Several classes of compounds were observed to be present including non-specific heterocyclic compounds such as low molecular weight (less than 550 AMU) fulvic and humic compounds, sulfur, sulfur compounds, phenols, phthalate esters, petroleum compounds, oxygenated (weathered) petroleum compounds, alkanes, alkenes, heterocyclic aromatic compounds, polycyclic compounds, polycyclic aromatic hydrocarbons, and steroids. In one sample all of the above were found. From the samples that have been analyzed as part of the method development activities, there is an apparent association between physical characteristics and amount of organic material in the sediment. Sandy or coarse sediments with a light color have lower amounts of organic materials and as texture becomes finer, or colors darker, the level of organic compounds increases.

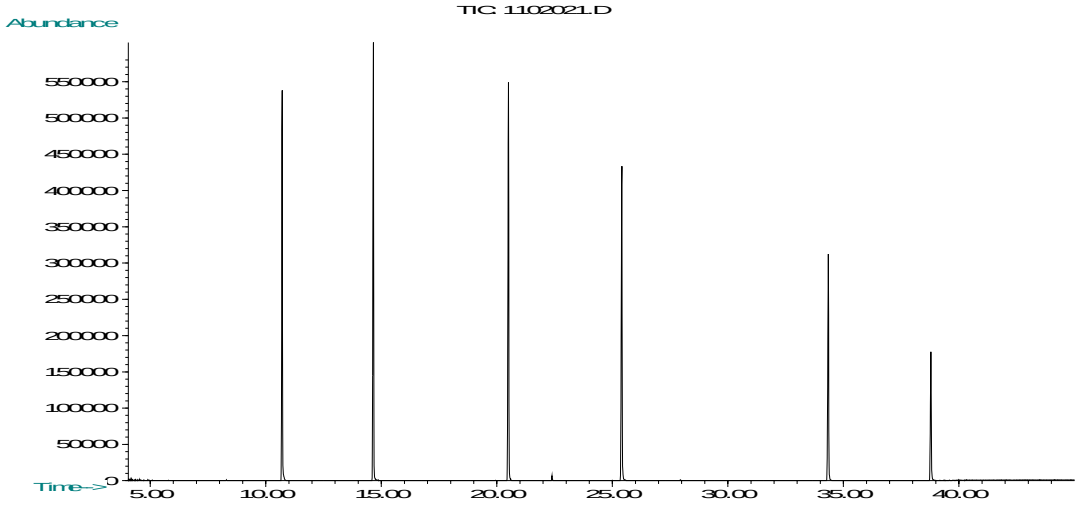
The following four chromatographs illustrate the range of conditions encountered. Chromatograph 1 is a blank for comparison purposes. The six peaks in the blank are in all chromatographs at the same concentration (6428 μg/kg) and serve as internal standards for quantitative purposes. Chromatograph 2 is from a coarse sand/quartz sample. There is very little difference between chromatographs 1 and 2. No detectable organic compounds were observed in the sample represented by chromatograph 2.

In contrast, chromatograph 3 is from a clay sample with a red-gray color. The peaks eluting in the 15-22 minute range in chromatograph 3 are alkanes associated with petroleum compounds. The large hump eluting from 30 minutes to the end of the run contains non-specific humic and fulvic compounds, with individual polycyclic aromatic hydrocarbons, phthalate esters, steroids and their degradation products as individual peaks superimposed on top of the humic hump.

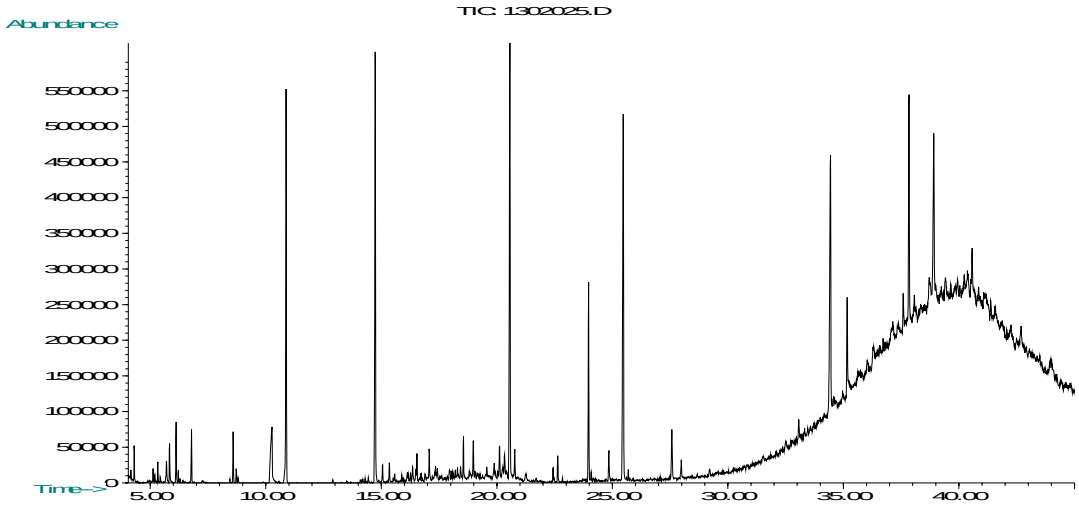
Chromatograph 1. Instrument blank with six internal standards



Chromatograph 2. Coarse sand/quartz sediment sample

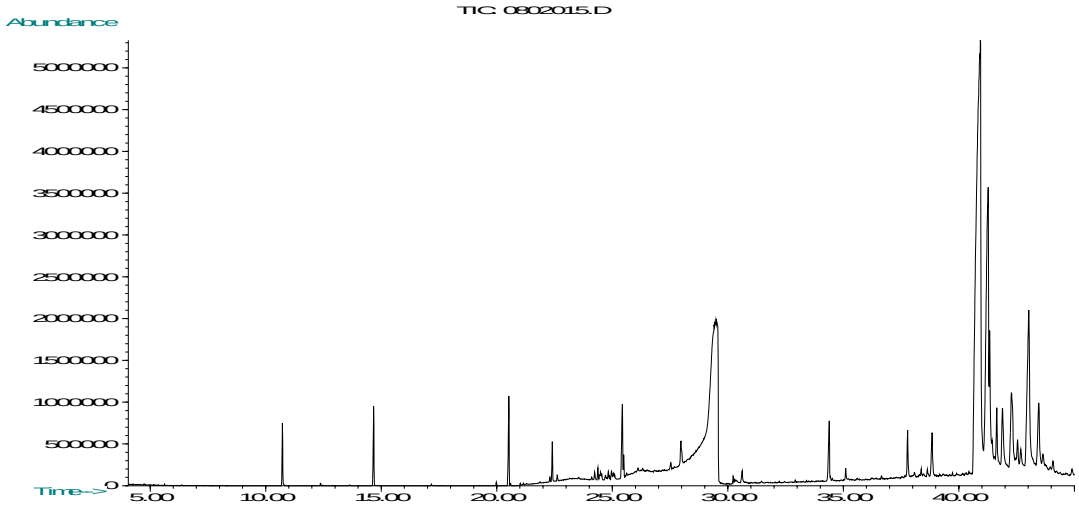


Chromatograph 3. Fine grained, red-gray clay sediment sample



Chromatograph 4 is from a black, very fine grained sludge-type sample, which has a distinct odor of petroleum and sewage. Notice that the large peaks at 29.5 minutes and at 41 minutes are two to ten times the intensity of the internal standards. The “fronting” peak eluting from 21 to 29.5 minutes is a combination of sulfur, sulfur compounds, and a fluorinated sulfur compounds. The large peak at 41 minutes and the large peaks after are steroids associated with sewage followed by poly- and heterocyclic hydrocarbons.

Chromatograph 4. Very fine-grained, black sludge sediment sample



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Appendix A –Other Urban Sources of SSO Contaminants and Fates after Discharge into Receiving Waters

Other Potential Urban Sources of Pathogens, Besides SSOs

Pathogens Observed In Urban Waters

Table C-1 summarizes the pathogenic bacteria biotypes that have been observed in the urban portion of the Rideau River in Ottawa, Ontario (Pitt 1984). The occurrence of Salmonella biotypes is low and their reported density is less than one organism/100mL. *Pseudomonas aeruginosa* are frequently encountered at densities greater than ten organisms/100mL, but only after rains. As a comparison, Tables C-2 and C-3 show typical pathogenic bacteria biotype concentrations found in raw sanitary wastewaters and in urban runoff. Table C-4 summarizes the occurrence of various pathogenic types found in urban stormwaters at various sites. The observed ranges of concentrations and percent isolations of these biotypes vary significantly from site to site and at the same location for different times. However, it is seen that many of the potentially pathogenic bacteria biotypes can be present in urban stormwater runoff. Table C-5 lists the pathogenic bacteria biotypes that affect mammals and birds and that can be transmitted by contaminated water. Many of these biotypes, of course, are rare but this table does demonstrate the wide range of possible diseases that can be transmitted by polluted waters.

Table C-1. Pathogenic Bacteria Biotypes found in the Rideau River, Ottawa, Ontario (from Pitt 1984)

Table C-2. Typical Pathogenic Bacteria Biotypes found in Sanitary Wastewaters (from Pitt 1984)

Table C-3. Typical Pathogenic Bacteria Biotypes found in Urban Stormwaters (from Pitt 1984)

Table C-4. Occurrence of Various Pathogenic Types Found in Urban Stormwaters at Various Sites (from Pitt 1984)

Table C-5. Pathogenic Bacteria Biotypes that Affect Mammals and Birds that can be Transmitted by Contaminated Water (from Pitt 1984)

Many potentially pathogenic bacteria biotypes may be present in urban receiving waters. Because of the low probability of ingestion of this water, many of the potential human diseases associated with these biotypes are not likely to occur. The pathogenic organisms of most concern in urban waters are therefore usually associated with skin

infections and body contact. The most important biotype causing skin infections would be *Pseudomonas aeruginosa*. This biotype has been detected frequently in most urban runoff studies in concentrations that may cause potential infections. However, there is little information associating the cause and effect of increased Pseudomonas concentrations with increased infections. Shigella may be present in urban runoff and receiving waters. This pathogen, when ingested in low numbers, can cause dysentery.

Potential Effects of Specific Pathogens found in Urban Waters

Most of the comprehensive urban runoff studies that examined bacteria, and especially pathogens, were conducted in the late 1960s to the early 1980s. These early references are summarized in the following paragraphs.

The fecal coliform test is not specific for any one coliform type, or groups of types, but instead has an excellent positive correlation for coliform bacteria derived from the intestinal tract of warm blooded animals (Geldreich, *et al*. 1968). The fecal coliform test measures *Escherichia coli* as well as all other coliforms that can ferment lactose at 44.5^{o}C and are found in warm blooded fecal discharges. Geldreich (1976) found that the fecal coliform test represents over 96 percent of the coliforms derived from human feces and from 93 to 98 percent of those discharged in feces from other warm blooded animals, including livestock, poultry, cats, dogs, and rodents. The variations in the specific fecal coliform bacteria biotypes are related to both fecal moisture content and diet. Moisture and diet may also affect the variety of bacteria biotypes found in the fecal coliform populations from different animal groups. In many urban runoff studies, all of the fecal coliforms were *E. coli* (Quresh and Dutka 1979). Fecal strep. bacteria are all of the intestinal Streptococci bacteria from warm blooded animal feces (Geldreich and Kenner 1969). The types and concentrations of different bacteria biotypes varies for different animal sources. Qureshi and Dutka (1979) found that pathogenic bacteria biotypes are present in southern Ontario urban runoff and are probably from several different sources.

Van Donzel, *et al*. (1967) reviewed water-borne disease outbreak information for 1946 to 1960. Almost 26,000 cases were listed for almost 230 known outbreaks in the United States and Puerto Rico. At least 29 of these outbreaks, involving more than 9,000 cases, were associated with stormwater runoff caused by either runoff washing human and animal feces or sewage into wells, springs, streams, small reservoirs, and open water mains, or by widespread flooding of individual and public water systems. Several authors, however, did not think that urban runoff may present a significant health problem. Olivieri, *et al*. (1977a) did not believe that urban runoff constitutes a major health problem because of the large numbers of viable bacteria cells that must be consumed to establish an infection. For urban runoff, it may be impossible to consume enough bacteria cells to establish the infective dose.

The Presence and Effects of Salmonella in Urban Waters

Salmonella has been reported in some but not all urban stormwaters. Oureshi and Dutka (1979) frequently detected Salmonella in southern Ontario stormwaters. They did not find any predictable patterns of Salmonella isolations as they were found throughout the various sampling periods. Olivieri, *et al*. (1977a) found Salmonella frequently in Baltimore runoff, but at relatively low concentrations and required sample concentration. Typical concentrations were from five to 300 Salmonella organisms/ten liters. The concentrations of Salmonella were about ten times higher in the stormwater samples than in the urban stream receiving the runoff. They also did not find any marked seasonal variations in Salmonella concentrations. Field, *et al*. (1976) also stated that Salmonella were frequently found in most Baltimore urban runoff samples. Almost all of the stormwater samples that had fecal coliform concentrations greater that 2000 organisms/100 mL had detectable Salmonella concentrations. About 27 percent of the samples having fecal coliform concentrations less than 200 organisms/100 mL had detectable Salmonella.

However, quite a few urban runoff studies did not detect Salmonella. Schillinger and Stuart (1978) found that Salmonella isolations were not common in a Montana subdivision study and that the isolations did not correlate well with fecal coliform concentrations. Environment Canada (1980) stated that Salmonella were virtually absent from Ottawa storm drainage samples in 1979. They concluded that Salmonella are seldom present in significant numbers in Ottawa urban runoff. The types of Salmonella found in southern Ontario were *S. thompson* and *S. typhimurium* var *copenhagen* (Qureshi and Dutka 1979).

Olivieri, *et al.* (1977b) stated that the primary human enteric disease producing Salmonella biotypes associated with the ingestion of water include *S. typhi* (typhoid fever), *S. paratyphi* (paratyphoid fever), and Salmonella species

(salmonellosis). These biotypes are all rare except for Salmonella. The dose of Salmonella required to produce an infection is quite large (approximately 105 organisms). The salmonellosis health hazard associated with water contact in urban streams is believed to be small because of this relatively large infective dose. If two liters of stormwater having typical Salmonella concentrations (ten Salmonella organisms per/ten liters) is ingested, less than 0.001 of the required infective dose would be ingested. If a worse case Salmonella stormwater concentration of 10,000 organisms/ten liters occurred, the ingestion of 20 liters of stormwater would be necessary for an infective dose. They stated that the low concentrations of Salmonella, coupled with the unlikely event of consuming enough stormwater, make the Salmonella health hazard associated with urban runoff small.

Geldreich (1965) recommended a fecal coliform standard of 200 organisms/100 mL because the frequency of Salmonella detection increased sharply at fecal coliform concentrations greater than this value. Setmire and Bradford (1980) stated that the National Academy of Sciences recommended a fecal coliform standard of 70/100 mL in waters with shellfish harvesting to restrict Salmonella concentrations in edible tissues. Field, *et al.* (1976) concluded that the use of indicator bacteria to protect Salmonella ingestion is less meaningful in stormwater runoff than in other waters.

Marron and Senn (1974) pointed out the possibility of dogs transmitting salmonellosis. They did not feel that this constitutes a serious public health threat, but people should be aware of the possibility of infection and direct contact with dog feces should be minimized.

The Presence and Effects of Staphylococci in Urban Waters

Staphylococcus aureus is an important human pathogen as it can cause boils, carbuncles, abscesses, and impetigo on skin on contact. Olivieri, *et al*. (1977b) stated that the typical concentrations of Staphylococci are not very high in urban streams. They also stated that there was little information available relating the degree of risk of staph. infections with water concentrations. They concluded that *Staph. aureus* appears to be the most potentially hazardous pathogen associated with urban runoff, but there is no evidence available that skin, eye, or ear infections can be caused by the presence of this organism in recreational waters. They concluded that there is little reason for extensive public health concern over recreational waters receiving urban storm runoff containing staph. organisms.

The Presence and Effects of Shigella in Urban Waters

Olivieri, *et al.* (1977b) stated that there is circumstantial evidence that Shigella is present in urban runoff and in urban receiving waters and that it could present a significant health hazard. Shigella species causing bacillary dysentery are one of the primary human enteric disease producing bacteria agents present in water. The infective dose of Shigella necessary to cause dysentery is quite low (10 to 100 organisms). Because of this low required infective dose and the assumed presence of Shigella in urban waters, it may be a significant health hazard.

The Presence and Effects of Streptococcus in Urban Waters

Streptococcus faecalis and atypical *S. faecalis* are of limited sanitary significance (Geldreich 1976). Streptococcus determinations in urban runoff are most useful for identifying the presence of *S. bovis* and *S. equinus* that are specific indicators of non-human, warm blooded animal pollution. However, it is difficult to interpret fecal strep. data when their concentrations are lower than 100 organisms/100 mL because of the ubiquitious occurrence of *S. faecalis* var. *liquifaciens*. This biotype is generally the predominant strep. biotype occurring at low fecal strep. concentrations.

The Presence and Effects of *Pseudomonas Aeruginosa* in Urban Waters

Pseudomonas aeruginosa was reported to be the most abundant pathogenic bacteria organism in urban runoff and streams (Olivieri, *et al.* 1977b). This pathogen is associated with eye and ear infections and is resistant to antibiotics. *P. aeruginosa* concentrations in urban runoff are at significantly greater concentrations (about 100 items) than the values associated with most bathing beach studies. Cabelli, *et al*. (1976) stated that *P. aeruginosa* is indigenous in about 15 percent of the human population. Swimmer's ear or other *P. aeruginosa* infections may, therefore, be caused by trauma to the ear canals associated with swimming and diving, and not exposure to *P. aeruginosa* in the bathing water.

Environment Canada (1980) stated that there is preliminary evidence of the direct relationship between very low levels of *P. aeruginosa* and an increase in incidents of ear infections in swimmers. They stated that a control level for this Pseudomonas biotype of between 23 and 30 organisms/100 mL was considered. Cabelli, *et al.* (1976) stated that *P. aeruginosa* densities greater than 10 organisms/100 mL were frequently associated with fecal coliform levels considerably less than 200 organisms/100 mL. *P. aeruginosa* densities were sometimes very low when the fecal coliform levels were greater than 200 organisms/100 mL. An average estimated *P. aeruginosa* density associated with a fecal coliform concentration of 200 organisms/100 mL is about 12/100 mL. They further stated that *P. aeruginosa* by itself cannot be used as a basis for water standards for the prevention of enteric diseases during recreational uses of surface waters. They recommended that bathing beaches be temporarily closed until the *P. aeruginosa* concentrations return to a baseline conditions.

The Presence and Effects of Other Pathogens in Urban Waters

Candida albicans is a yeast found in Ottawa area receiving waters (Environment Canada 1980). This yeast can cause oral, cutaneous, and vaginal mycosis. Other potential health problems associated with urban waters might be from histoplas-mosis and cryptococcosis that are associated with accumulations of guano at various bird roosts in or near areas of human habitation (Locke 1974).

E. coli and *Vibro cholerae* are disease producing pathogens associated with the ingestion of water. The cholera pathogen is quite rare, but *E. coli* is more common in urban waters. The required infective dose of both of these pathogens is about 108 organisms (Olivieri, *et al.* 1977b).

Dog feces are capable of transmitting many diseases, including leptospirosis, brucellosis, toxoplasmosis, tuberculosis and other diseases. However, these problems are quite rare and do not indicate a serious public health threat. Visceral larval migrans (VLM) is the most serious disease associated with dog feces. This mostly affects children under four years of age who ingest the bacteria through ingestion of feces or contaminated soil. Symptoms include blindness.

Viruses may also be important pathogens in urban waters. Very small amounts of a virus are capable of producing infections or diseases, especially when compared to the large numbers of bacteria organisms required for infection (Berg 1965). The quantity of enterroviruses which must be ingested to produce infections is usually not known (Olivieri, *et al.* 1977b). Viruses are usually detected at low levels in urban receiving waters. They stated that even though the minimum infective doses may be small, the information available indicates that stormwater virus threats to human health is small. Because of the low levels of virus necessary for infection, dilution of viruses does not significantly reduce their hazard.

CSO Bacteria Observations

Table A-5 presents some typical combined sewer overflow bacteria concentrations, as reported in the literature. The fecal coliform concentrations in combined sewer overflows are seen to range from about 2 x 10XXX to a high of about 2 x 10XXXX fecal coliform organisms/100 mL. The separate stormwater fecal coliform bacteria observations are at the low end of this reported range. Typical combined sewers can therefore have 100 to 1,000 times the fecal coliform concentrations as separate stormwater. A study by Burn and Vaughan (1966) in Detroit and Ann Arbor, Michigan, found that the total coliform densities in sanitary sewage were always about three to 15 times greater than those found in urban runoff. The fecal coliform densities in the sanitary sewage were about 90 times the stormwater values. They found that the fecal coliform to fecal strep. ratios in combined sewage was always greater than three, while this ratio was equal to or less than one in stormwater. They concluded that the bacteria densities for the combined sewer overflows were at least ten times greater than those reported for the stormwaters alone.

Table A-5. CSO Bacteria Concentrations (from Pitt 1984)

The Regional Municipality of Ottawa-Carleton (1972) noted the early Ottawa activities in correcting stormwater and sanitary sewage cross-connections. Since that time, many combined sewer overflows have also been eliminated from the Rideau River. Loijens (1981) stated that as a result of sewer separation activities, only one overflow currently remained active as of 1981. During river surveys in 1978 and 1979 in the vicinity of this outfall, increased bacteria levels were not found. Gore and Storrie/Proctor and Redfern (1981c) stated that there is currently no evidence that combined sewer overflows are causing the elevated fecal coliform bacteria levels in the river. Environment Canada, (1980) however, stated that high, dry weather bacteria density levels, especially when considering the fecal coliform to fecal strep. ratio, constitutes presumptive evidence of low volume sporadic inputs of sanitary sewage from diverse sources into the downstream Rideau River sectors.

Sources of Bacteria in Stormwater

High bacteria populations have been found in sidewalk, road, and some bare ground sheetflow samples (collected from locations where dogs would most likely be "walked"), as shown in Table 2.14. The Regional Municipality of Ottawa-Carleton (1972) recognized the importance of rooftop, street surface, and field runoff in contributing bacteria contaminants to surface waters in the Ottawa area. Gore and Storrie/Proctor and Redfern (1981c) also investigated various urban bacteria sources affecting the Rideau River. They examined dry weather continuous coliform sources, the resuspension of contaminated river bottom sediments, exfiltration from sanitary sewers, and bird feces. These sources were all considered in an attempt to explain the relatively high dry weather coliform bacteria concentrations found in the river. They concluded, however, that stormwater runoff is the most probable source for the wet weather and continuing dry weather bacteria Rideau River concentrations. The slow travel time of the river water usually does not allow the river to recover completely from one rainstorm before another begins.

Table 2.14 Source Area Bacteria Sheetflow Quality Summary (means)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/ Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets	Land-scaped	Un-developed	Freeway Paved Lane and Shoulders
Fecal Coliforms (#/100 mL)												
Residential:	85 (3) <2 (4) 1400 (5)	250,000 (5)	100 (5)		600 (5)			11,000 (5)	920 (4) 6,900 (5)	3300 (5)	5400 (3) 49 (4)	1500 (9)
Commercial	9 (4)	2900 (3) 350 (4) 210 (1) 480 (7) 23,000 (8)										
Industrial:	1600 (5)	8660 (8)	9200 (5)	18,000 (5)	66,000 (5)	300,000 (5)		55,000 (5)	100,000 (5)			
Fecal Strep (#/100 mL)												
Residential:	170 (3) 920 (4) 2200 (5)	190,000 (5)	<100 (5)		1900 (5)		1800 (5)		>2400 (4) 7300 (5)	43,000 (5)	16,500 (3) 920 (4)	2200 (9)
Commercial:	17 (3)	11,900 (3) >2400 (4) 770 (1) 1120 (7) 62,000 (8)										
Industrial:	690 (5)	7300 (5)	2070 (5)	8100 (5)	36,000 (5)	21,000 (5)		3600 (5)	45,000 (5)			
Pseudo, Aerug (#/100 mL)												
Residential:	30,000 (5) 50 (5)	1900 (5)	100 (5)		600 (5)		600 (5)		570 (5)	2100 (5)		
Industrial:		5800 (5)	5850 (5)	14,000 (5)	14,300 (5)	100 (5)		3600 (5)	6200 (5)			

References:
(1) Bannerman, *et al*. 1983 (Milwaukee, WI) (NURP)
(3) Pitt 1983 (Ottawa)
(4) Pitt and Bozeman 1982 (San Jose)
(5) Pitt and McLean 1986 (Toronto)
(7) STORET Site #590866-2954309 (Shop-Save-Durham, NH) (NURP)
(8) STORET Site #596296-2954843 (Huntington-Long Island, NY) (NURP)
(9) Kobriger, *et al.* 1981 and Gupta, *et al*. 1977

Street surfaces have been identified as potential major sources of urban runoff bacteria in many locations. Pitt and Bozeman (1982) found that parking lots, street surfaces, and sidewalks were the major contributors of indicator bacteria in the Coyote Creek watershed in California. Gupta, *et al*. (1981) found high concentrations of fecal coliforms at a highway runoff site in Milwaukee. This site was entirely impervious and located on an elevated bridge deck. The only likely sources of fecal coliforms at this site were bird droppings and possibly feces debris falling from livestock trucks or other vehicles.

Several studies have found that the bacteria in stormwater runoff in residential and light commercial areas were from predominantly non-human origins (Qureshi and Dutka 1979). Qureshi and Dutka (1979) found that there may be an initial flush of animal feces when runoff first develops. However, the most important bacteria source for runoff is the feces bacteria that have been distributed generally in the soils and on the surfaces of the drainage area. Geldreich and Kenner (1969) stated that the fecal coliforms in stormwater are from dogs, cats, and rodents in city areas, and from farm animals and wildlife in rural areas. The most important source, however, may be feces bacteria that are distributed in the soil and not the fresh feces washing off the impervious surfaces.

Some studies have investigated vegetation sources of coliform bacteria. For example, Geldreich (1965) found that the washoff of bacteria from vegetation does not contribute significant bacteria to the runoff. They also found that most of the bacteria on vegetation is of insect origin.

Geldreich, *et al*. (1980) found that recreation activities in water bodies also increase the fecal coliform and fecal strep. concentrations. These organisms of intestinal origin will concentrate in areas near the shore or in areas of stratification.

Fennell, *et al.* (1974) found that open dumps containing domestic refuse can be a reservoir of Salmonella bacteria that can be spread to nearby water bodies by foraging animals and birds.

When a drainage basin has much of its surface paved, the urban runoff bacteria concentrations can be expected to peak near the beginning of the rainfall event and then decrease as the event continues. Initial high levels of bacteria may be associated with direct flushing of feces from paved surfaces. These feces are from dogs defecating on parking lots and street areas and from birds roosting on rooftops. When a drainage area has a lot of landscaped areas or open land, relatively high bacteria concentrations in the urban runoff may occur throughout the rain event.

Water Body Sediment Bacteria

Matson, *et al*. (1978) studied the effects of river and lake sediments as a source of bacteria to the water column in Connecticut. They found that resuspended sediments in shallow waters can elevate the water column bacteria concentrations significantly. They stated that the physical resuspension of shallow water sediments is increased by elevated river discharges, wind induced turbulence, dredging, motorboats, swimming, walking, and wading and normal activities of aquatic microorganisms. The magnitude of sediment resuspension varies with the intensity of the mechanisms involved, and the water depth to the sediment. They stated that during stable river flows, the water bacteria populations are relatively constant, but during periods of high flows, sediment organisms can be scoured from the benthic surfaces and mixed into the water column. After peak discharges, water borne microorganisms resettle downstream, which increases those sediment bacteria populations. Geldreich, *et al.* (1980) also studied bacteria interactions between sediment and water. They found that the sediment-water interface of a water body is an attractive habitat for a variety of different bacteria involved in different biochemical processes. Shallow bottom sediments attract a variable bacteria population because of the physical and chemical requirements that can be satisfied there, in contrast to the more limited conditions available in the water or buried in the sediments.

Davis (1979) stated that bacteria contamination of waterways during and following storm events is a function of the stream sediment bacteria concentrations, the concentrations of bacteria in soils adjacent to

the stream (and source areas in an urban watershed), and the stream velocities. Davis further stated that stream sediments can contain greater densities of coliform bacteria on a number per unit weight or volume basis than the water body itself; the concentrations of bacteria in the top two inches of mud can be 100 to 1,000 times greater than the concentrations of the bacteria in the water. He reported fecal coliform sediment concentrations up to 100 organisms per gram of sediment and that the suspended sediments can be a major source of bacteria contamination. Geldreich, *et al.* (1980) stated that sediment bacteria concentrations can be as high as 3,000 to 15,000 organisms per square meter of particulate surface. Pitt and Bozeman (1979), in a study of an urban lake in Oakland, California, found fecal coliform sediment concentrations that ranged from one to 35,000 organisms per gram and averaged about 1,000. McSwain (1977) found that in a rural study in North Carolina, total and fecal coliform concentration increases were more related to bottom sediment disturbances than to stream bank flushing.

Soil Bacteria Sources

Van Donsel, *et al*. (1967) stated that soil bacteria pollution may occur from direct defecation by livestock, pets, and wild animals, by malfunctioning or overflowing septic tank systems or by flooding of sewerage systems. Much of the total coliform indicator bacteria organisms in urban areas, however, are not from these sources. Geldreich, *et al*. (1968) found that in a Cincinnati urban runoff study, direct fecal contamination accounted for less than 10 percent of the total coliform bacteria present in the stormwater. The remaining coliforms (which were non-fecal in origin) were assumed to be contributed from soil erosion. Therefore, soil can contain large numbers of both non-fecal and fecal coliform bacteria. Because rain water contains very small bacteria concentrations, urban runoff becomes contaminated with bacteria when the rain water contacts contaminated surfaces. In wilderness areas, runoff has very little fecal coliform bacteria, while runoff from agricultural areas or urban areas can have varying amounts of fecal coliform bacteria. Seidler (1979) found that the movement of fecal coliform bacteria in saturated soils were extremely rapid. Soil can add appreciable fecal and non-fecal coliform bacteria to rain runoff. Casserly and Davis (1979) found that coliform types in urban soils were the same as they found in urban runoff, indicating a strong interaction between polluted soils and contaminated urban runoff. Davis (1979) found that irrigated soils, with high humic content, can yield greater amounts of bacteria. Evans and Owens (1972) found that the concentrations of *E. Coli* and Enterococci in stormwater runoff were affected by the soil bacteria concentrations.

Evans and Owens (1973) reported that bacteria was more likely to erode than the particulate matter in the soil. Davis (1979) found that the leaching action of rain on soil bacteria was quite erratic. The most important factors affecting bacteria concentrations in runoff were found to be the concentrations of the bacteria in soils. They reported total coliform concentrations in soils ranging from 200 to more than 500,000 total coliform organisms per gram. Fecal coliform soil concentrations ranged from less than 20 to about 300 organisms per gram and fecal strep. soil concentrations ranged from less than 20 to about 1,000 organisms per gram.

Effects of Wildlife on Water Bacteria Concentrations in Urban Areas

Several studies have been conducted which examined the effects of large migratory or permanent waterfowl populations on the bacteria quality of water bodies. A study at the Montezuma Bird Refuge in New York (Have 1973) found inconsistent relationships between the bird populations and the total coliform, fecal coliform, and fecal strep. counts. Peak populations of 70,000 geese and 100,000 ducks frequent this 1,000 acre refuge. In fact, they found that the concentrations of the non-pathogenic bacteria in the two major streams flowing into the refuge were greater than in the water flowing out of the refuge. The specific conductance of the inflowing water was also greater than the outflowing water. The effluent did have higher concentrations of phosphorous and nitrogen. They concluded that the settling effect of the quite waters in the refuge may help explain the improvement in the quality of water leaving the refuge.

Brierley, *et al.* (1975) studied the Rio Grande Refuge in New Mexico. This refuge supports bird populations of more than 10,000 Sandhill cranes, 2,000 Canada geese, more than 8,000 snow geese, and more than 25,000 ducks from October to early March along ten miles of river channel. The water flowing into this bird refuge area along the Rio Grande River has high concentrations of suspended sediments and bacteria. The bacteria concentrations seem to correlate directly with the high sediment concentrations. The

presence of the large number of birds apparently does not affect the concentrations of the bacteria that were investigated (total heterotrophic bacteria, fecal and total coliforms, and Enterococci). Most of the birds use a single large pond at the end of their winter habitat. The draining of this pond at the end of their season did not seem to significantly change the bacteria population of the receiving channel water. The bird habitat pond, in fact, had decreased concentrations or bacteria during and following the period of maximum use. They concluded that the bacteria originated in upstream areas before it reached the refuge.

In a study at Lake Wingra in Wisconsin (Geldreich 1980), intermittent high fecal coliform counts during the late summer and early fall were found to be due to a combination of wastes from mallard ducks and the local weather. They reported that fecal coliforms in the sand due to duck defecation multiplied during the first week after deposition and then die-off occurred. Bacteria in these near-lake sands were transported into the water primarily by stormwater runoff erosion and by the foot traffic of abthers when going into the water.

Oplinger (1977) studied the effects of waterfowl populations on the water quality of a small creek park in Pennsylvania. They felt that increasing waterfowl populations and the declining water quality were related and threatened the health and welfare of both the waterfowl and the human watershed users.

Figley and Vandraff (1974), in a study of suburban parks in New York state, noted that mallard ducks are especially attracted to suburban lagoon developments. They felt that urban concentrations of semi-wild ducks may be detrimental, by serving as the focal points for outbreaks of infectious avian diseases and as a reservoir of diseases that could be transmitted to migrating wildfowl.

A study by Fennell, *et al*. (1974) examined the effects of about 500 roosting gulls on a one million cubic meter storage reservoir. Salmonella were usually found in the reservoir waters but never in the incoming water. They also found close correlations between the number of gulls and the degree of bacteria contamination. The sources of Salmonella appeared to be household and other refuse from dumps where the gulls were foraging. When the gulls left, after bird scaring fireworks were used, the Salmonella and other bacteria concentrations almost immediately decreased. The bacteria concentrations remained at low levels for a period of five weeks until the fireworks were stopped; the birds were allowed to return, and the bacteria concentrations in the reservoir immediately increased.

It is evident that birds can have varying effects on the bacteria concentrations in waterbodies. Large refuges do not seem to be severely affected by the wildlife populations. In fact, the ponding of waters in refuges appears to improve the water quality through sedimentation. Waterfowl frequenting smaller bodies of water, especially creeks and small lagoons, appear to have the potential for substantially increasing the water bacteria concentrations.

Gore and Storrie/Proctor and Redfern, (1981a) summarized the results of studies made to determine the effects of birds roosting on bridges over the Rideau River in Ottawa on river bacteria concentrations. They found that the birds on the bridges could have a statistically significant impact on fecal coliform concentrations, especially during the low summer flows. Measured concentration increases of fecal coliform bacteria downstream from the Queensway Bridge was found to be about 300 fecal coliform organisms/100 mL.

Urban Wildlife Feces Bacteria Contributions

Table B.3 lists samples (mostly from mammals and birds with some soil, sediment, and river samples) where specific bacteria types were not generally found. The presence or absence of certain bacteria types in environmental samples can be a very important factor in identifying the bacteria sources (feces from which animals). As an example, *Streptococcus bovis* and *S. equinus* have not been found in human feces by several projects. (These types, however, are the predominant fecal strep. type found in livestock feces.) Their absence in a sample indicates the probable absence of livestock feces contamination, considering their dieoff.

Table B.3. Negative Wildlife Sources of Specific Bacteria Biotypes (from Pitt 1984)

Table B.4 lists the feces samples in which different bacteria types were found, along with their relative concentrations. Geldreich and Kenner (1969) stated that the absence of fecal strep. bacteria indicates the absence of warm blooded fecal pollution. The presence of *Streptococcus faecalis* indicates human fecal contamination. *S. faecalis* far outnumbers *S. inulinaceus* in sewage and in sewage polluted waters, even though *S. inulinaceus* is in great abundance in fresh feces (Bartley and Slanetz 1960). *S. faecalis* var. *liquefaciens* is ubiquitous as it is present in almost all samples tested (Geldreich and Kenner 1969; Bartley and Slanetz 1960). *S. mitis* and *S. salivarious* are considered sensitive indicators of human pollution when they are found (Seidler 1979). *S. bovis* and *S. equinus* are nearly ideal non-human mammal fecal indicators (Seidler 1979). They have rapid die-off rates (much faster than fecal coliform die-offs) and are the most sensitive bacteria in the fecal strep. category. Their presence indicates recent livestock pollution (Feacham 1975; Geldreich 1976; Bartley and Slanetz 1960; Geldreich and Kenner 1969).

Table B.4. Sources of Wildlife Bacteria Biotypes (from Pitt 1984)

Table B-5 summarizes the bacteria concentrations observed in feces samples from different mammals and birds. Drake, *et al*. (1961) found a wide variation in the coliform content of some wild and domestic animal feces. Coliform bacteria were present in small numbers or were absent for some feces, such as from rabbits, shrews, deer, elk, some squirrels, and many birds. Mouse, ranging from absent to very large numbers. They also stated that coliform bacteria were not found in some carnivores (shrews) but were present in large number in the carnivores (coyotes and bears). They also found no significant differences in the fecal coliform content of different animals of the same species that were collected in different areas. However, feces from different species of animals collected in the same area could have large differences in their fecal coliform concentrations. They also noted that some mammals (coyote, bear, some gophers, and some squirrels) had coliform concentrations in the feces that were similar to human coliform concentrations. Animals with soft or moist feces (man and many domestic animals such as cows, dogs, and pigs) had very high numbers of coliform bacteria (many thousands to millions of coliform bacteria per gram). The feces of other animals, especially those with hard or dry feces, may contain few or no coliform bacteria.

Table B.5 Bacteria Concentrations in Mammal and Bird Feces (from Pitt 1984)

Geldreich (1976) summarized a study that showed the variations in fecal strep. bacteria concentrations in human feces from different locations. Feces collected from humans living in Cincinnati had concentrations more than five times greater than samples collected from healthy people in Nagpur, India (13 million and 2 million fecal strep. organisms per gram, respectively). He also reported that fecal strep. densities in farm animal, cat, dog, mice, and chipmunk feces samples were in the order of millions of organisms per gram. Rabbit feces fecal strep. concentrations, however, may be several orders of magnitude lower than those found in other animals. It is interesting to note that the Ottawa waterbird feces samples were reported to have the largest total coliform, fecal coliform, and fecal strep. concentrations when compared to all other

samples reported (except for the fecal strep. dog feces concentrations). Gull feces generally have the highest fecal coliform concentrations in their feces, followed by Ottawa pigeons, ducks, dogs, sheep, and humans.

Feces Discharges From Wildlife

Table B-6 summarizes reported discharges of feces from different mammals and birds. These discharges are expressed in grams per animal per day and vary quite widely. Animals can deposit substantial quantities of feces in an urban area, depending upon the animal's population. Geldreich (1976) stated that major contributions of bacteria in urban communities are from fecal discharges from cats, dogs, and rodents. These feces are deposited on soil, asphalt, and cement. He stated that the one-half million dogs in New York City deposit about 150,000 pounds of feces on the streets, sidewalks, and park areas per day. Significant populations of rodents may also contribute large amounts of fecal material in urban areas. Fortunately, very little of this fecal bacteria likely enters receiving waters. Faust (1976), in an agricultural watershed in the Rhode River near Chesapeake Bay, found that only about one percent of the fecal coliform bacteria deposited by cattle in the watershed was washed into the receiving waters. Sometimes the yields (application rates) were higher, with high values around 5 percent and on one occasion reaching 25 percent. They concluded that fecal coliform discharges can be substantial from a watershed that has the equivalent of about one cow per two hectares. Evans and Owens (1973), from a study in Scotland, stated that most of the bacteria in the runoff water came from the soil. They found that the soil bacteria washoff yield was only about one-tenth of one percent of the estimated total soil bacteria population. They felt that the maximum annual discharge of bacteria from the contaminated soil would only be about 0.15 percent of the total soil bacteria population.

Table B.6. Discharges of Feces from Mammals and Birds (from Pitt 1984)

Mammal and Bird Populations and Bacteria Discharges in Urban Areas

Table B-7 summarizes the expected populations of mammals and birds in the lower Rideau River watershed. There are other domestic and wild animals in this watershed (such as other birds and rodents) but their population estimates are not available. It is estimated that about 16,000 dogs and the same number of cats live in this watershed, corresponding to approximately one dog or cat for every other house. The waterbird estimates are based upon actual population counts made along the river.

Table B.7. Expected Populations of Mammals and Birds in the Ottawa Urban Area (from Pitt 1984)

Table B-8 is an estimate of the total annual bacteria discharges from these mammals and birds based upon these population estimates, the fecal discharges, the application factors, and the bacteria concentrations in the feces. The total estimated discharges are two to three orders of magnitude greater than what is expected in the annual urban runoff bacteria yield. This large difference may be associated with bacteria die-off or by laboratory analysis procedures. For example, if the urban runoff samples were not completely mixed

before analysis, each reported bacteria count could actually be associated with many organisms from a clump of feces.

Table B.8. Estimated Relative Bacteria Yields from Different Urban Animal Sources in the Ottawa Area (Pitt 1984)

As a rough estimate, the values in Table B-8 may all be considered to be affected by the same die-off rates and analytical measurement methods. The percentage contributions associated with each animal may, therefore, be reasonably valid. The major source of fecal coliforms in the Rideau River is expected to be pigeons (when using the high Ottawa pigeon fecal coliform values), followed by dogs and ducks. The other sources shown would all contribute less than a total of five percent. Dogs are expected to contribute almost half of the river total coliform organisms, while pigeons on the bridges and ducks on the river make up most of the remainder. Dogs are expected to contribute almost all of the river fecal strep. bacteria, with ducks on the river contributing to less than five percent. Pitt and Bozeman (1979) found that the lake birds can contribute a significant amount of fecal strep. bacteria to a lake refuge in the middle of an urban area. However, urban runoff components contribute much more bacteria during wet weather conditions.

It is interesting to compare these calculated estimates of fecal coliform contributions with those reported elsewhere. Faust and Goff (1977) reported 10XXXto 10XXX fecal coliforms discharged per hectare per year in the Chesapeake Bay area from cultivated lands, forests, and pastures. These values are about ten to 100 times the estimated urban area yields for the lower Rideau River watershed.

Protozoa Sources in Urban Watersheds

States, *et al.* (1997) examined *Cryptosporidium* and *Giardia* in river water serving as Pittsburgh's water supply. They collected monthly samples from the Allegheny and Youghiogheny Rivers for two years. They also sampled a small stream flowing through a diary farm, treated sanitary sewage effluent, and CSOs. Table XXX4 summarizes their observations. The CSO samples had much greater numbers of the protozoa than any of the other samples collected. No raw sewage samples were obtained, but they were assumed to be very high because of the high CSO sample values. The effluent from the sewage treatment plant was the next highest, at less than half of the CSO values. The diary farm stream was not significantly different from either of the two large rivers. The water treatment process appeared to effectively remove *Giardia*, but some *Cryptosporidium* was found in the filtered water. Settling the river water seemed to remove some of the protozoa, but the removal would be not adequate by itself.

Table XXX4. Observed *Giardia* and *Cryptosporidium* in the Pittsburgh, PA, area (States, *et al.* 1997)

Samples	*Giardia* cysts			*Cryptosporidium* oocysts		
	Number of samples	Occurrence (%)	Geometric mean of detectable samples (#/100 L)	Number of samples	Occurrence (%)	Geometric mean of detectable samples (#/100 L)
CSOs	5	100	28,700	5	80	2,010
Sewage treatment plant effluent	24	83	664	24	33	924
Dairy farm stream	24	55	82	24	82	42
Allegheny River	24	63	34	24	63	31
Settled Allegheny River water	24	8	29	24	29	12
Filtered Allegheny River water	24	0	0	24	21	0.5
Filter backwash water	24	8	59	24	38	328
Youghiogheny River	24	54	118	24	63	58

States, *et al.* (1997) also reviewed prior *Giardia* and *Cryptosporidium* monitoring data, as summarized in Table XXX5. Raw drinking water supplies were shown to have highly variable levels of these protozoa, typically up to several hundred *Giardia* cysts and *Cryptosporidium* oocysts per 100 L and were found in 5 to 50% of the samples evaluated. Conventional water treatment appeared remove about 90% of the protozoa.

Table XXX5. Observed *Giardia* and *Cryptosporidium* In Raw Water Supplies and in Treated Water (States, *et al.* 1997)

Samples	*Giardia* cysts			*Cryptosporidium* oocysts		
	Number of samples	Occurrence (%)	Geometric mean of detectable samples (#/100 L)	Number of samples	Occurrence (%)	Geometric mean of detectable samples (#/100 L)
Rivers, streams, and lakes in 17 states (Rose, *et al.* 1991)	257	16	3 (average)	257	55	43 (average)
Drinking water samples (Rose, *et al.* 1991)	36	0	0	36	17	0.5 to 1.7 (range)
Raw surface water supply samples at 72 water treatment plants (LeChevallier and Norton 1995)	262	45	200	262	52	240
Finished drinking water from above plants (LeChevallier and Norton 1995)	262	4.6	2.6	262	13.4	3.3
Raw surface water supply samples at 66 water treatment plants (LeChevallier, *et al.* 1991a)	85	81	277	85	87	270
Filtered drinking water from above plants (LeChevallier, *et al.* 1991b)	83	17	4.5	83	27	1.5
Finished water samples from 33 conventional water treatment plants (Hancock, *et al.* 1996)	55	5 presumptive 2 confirmed	2 to 5 presumptive (range) 2 confirmed	55	7 presumptive	1 to 26 presumptive (range)
Existing data on finished water from 130 U.S. water treatment plants (Rosen, *et al.* 1996)	1237	4.9	na	1237	7.1	na

Fate of SSO Contaminants in Receiving Waters

Fate of Bacteria and other Pathogens

The survival of discharged bacteria into receiving waters is an important issue. Very little direct consumption or contact of WWF usually occurs. However, when the WWF is discharged into a larger receiving water, consumption or contact may occur after the rain event has ended. The Rideau River Stormwater Management Study (Ottawa, Ontario) examined the die-off of fecal coliform bacteria in the Rideau River (Droste and Gupgupoglu 1982; Environment Canada 1980; Gore and Storrie/Proctor and Redfern 1981b and 1981c). They found that the 90 percent die-off for Rideau River fecal coliforms was about two days. Because of the long travel time on the Rideau River and short interevent times of rains in the area, the effects of bacteria discharges from stormwater from one storm can affect the river concentrations during the next storm. The persistence of fecal coliforms and the slow river velocities cause downstream beach bacteria concentrations to seldom, if ever, regain true low background bacteria concentration levels. Environment Canada (1980) reported significant increase in coliform concentrations in recently excreted moist feces.

Seidler (1979) stated that the sources of Salmonella bacteria can determine their survival. This is probably true for most types of bacteria because the different bacteria sources usually determine the specific bacteria biotypes found in the feces. Different bacteria types can have quite different die-off rates.

Factors affecting bacteria survival in WWF have been found to be quite variable and site specific. Geldreich, *et al.* (1968) found that no significant differences in survival of urban runoff bacteria could be related to the chemical constituents present. Water temperature, however, did have a strong influence on urban runoff bacteria survival. Geldreich, *et al.* (1980) found in a Kentucky study that when copper sulfate was applied as an algicide in a reservoir, sharp declines in fecal coliform densities occurred. The standard plate count densities, however, sharply increased. They found that the survival of urban runoff bacteria was longer near the bottom of the reservoir than in shallower waters. They also found that reduced dissolved oxygen concentrations near the sediments was not detrimental to bacteria survival. Faust and Goff (1978) found that high clay concentrations in the Rhode River in the Chesapeake Bay area extended the survival of fecal coliform bacteria.

Many studies reported the effects of temperature on WWF bacteria die-off. Geldreich, *et al.* (1968), in a series of lab tests, found that stormwater bacteria persisted at higher concentrations under winter water temperature conditions (10^oC) than they did for summer water temperature conditions (20^oC). There were some differences in survival for the various specific types of stormwater bacteria, but this trend seemed typical. Van Donzel, *et al*. (1967) found that fecal strep. did not survive as long as fecal coliform bacteria during the summer months, while in the autumn there was little difference in their survival times. In the winter and spring, the fecal strep. survived much longer than the fecal coliforms. Seidler (1979) found that Salmonella survived for longer periods of time in colder water temperatures. McSwain (1977) reported that coliform bacteria were able to multiply in bottom sediments at a rate regulated by stream temperature. They reported another study that found significant enteric bacteria concentration increases at temperatures above 16^oC, but that little or no growth occurred below 10^oC. The conditions affecting bacteria survival in water appear to be site and bacteria specific. Many of the differences are probably associated with the specific bacteria biotype present and with the water temperature. Chemical constituent concentrations do not appear to be a factor, except when they are present at very low concentrations.

Table B-2 summarizes reported 90 day die-off rates for different stormwater bacteria types. Fecal coliform die-off values varied from less than one day to about 13 days, but can be considered quite fast. Fecal strep. die-off values, however, were longer than the fecal coliform die-off rates. Some of the Streptococcus bacteria types had long survival rates, while others had short survival rates. The forms likely to be associated with agricultural activities (*S. bovis* and *S. equinus*) all are shown to have much shorter survival times than more common urban Streptococcus types (*S. faecalis*).

Table B-2. Bacteria Die-off Rates (from Pitt 1984)

Survival of Bacteria in Soil

Because of the importance of soil bacteria as a potential source of WWF bacteria, their survival in the soil after deposition is important. If an area has long interevent times between rain events, soil bacteria survival would have to be quite long in order for the soil to be a significant urban runoff bacteria source. However, in areas having frequent rains, soil bacteria survival is less important (assuming that it is greater than the interevent period). Many site conditions have been reported to influence soil bacteria survival. Van Donsel, Geldreich, and Clarke (1967) found that sunlight, temperatures, rainfall, soil moisture, pH, organic matter, and the presence of other microorganisms all affect the survival of total coliforms, fecal coliforms, and fecal strep. soil bacteria. They also reported that feces bacteria deposited on dry soils are relatively immobilized and subject to the specific site conditions. After-growth of soil bacteria (increasing populations without new deposition) may account for some of the seasonal variations in runoff bacteria counts. If the soil has not been recently contaminated, the runoff would have an immediate supply of microorganisms from the soil. Contamination of the receiving waters would be out of proportion to the true sanitary history of the area. They also stated that non-fecal coliforms reappeared after fecal organisms declined. They were also present in much higher concentrations after fecal bacteria die-off than before the soil was contaminated.

Both after-growth and decline of bacteria in soils have been reported. Soil coliforms exhibit after-growth following rainstorms and exhibit rapid declines during freezing weather. If very warm weather follows a rain, a very large increase in soil coliform bacteria was noted, while the increase was much less if cool weather followed a rain. They also found declining bacteria soil populations if the soil was dry. Alternate freezing and thawing at exposed winter sites caused significant morality of soil coliform bacteria. Evans and Owens (1972) reported that *E.Coli* and Enterococci showed 90 percent reductions after about two or three months in soils. Van Donzel, Geldreich, and Clarke (1967) reported prolonged persistence of other bacteria types. Various strains of Salmonella were found to exist for long periods of time (nine months for *S. typhimurium*). It is not uncommon for soil bacteria to survive for up to 200 days after inoculation.

Indicators of the Source of the Bacteria

Geldreich (1965) found that the ratio of fecal coliform to fecal strep. bacteria concentrations may be indicative of the probable fecal contamination source. In fresh human fecal material and domestic wastes, he found that the fecal coliform densities were more than four times the fecal strep. densities. However, this ratio for livestock, poultry, dogs, cats, and rodents was found to be less than 0.6. As a generality, he stated that fecal coliform to fecal strep. ratios greater than four indicate that the bacteria pollution is from domestic wastes, which are composed mostly of human fecal material, laundry wastes, and food refuse. If the ratio is less than 0.6, the bacteria is probably from livestock or poultry in agricultural areas or from stormwater runoff in urban areas. He further found that agricultural and stormwater runoff can be differentiated by studying the types of fecal strep. bacteria found in the water samples.

Many researchers have therefore used these ratios as indicators of the likely source of the fecal matter contamination (in order to differentiate human sewage sources from animal sources). These ratios must be used with caution, however, because of the effects of in-stream travel times and the different die-off rates of the bacteria (Geldreich and Kenner 1969). Geldreich and Kenner (1969) stressed that samples must be taken at the wastewater outfalls and only apply the ratio for situations where the waste is relatively “fresh.”. At these locations, domestic waste, meat packing wastes, stormwater discharges, and feedlot drainage contain large numbers of fecal organisms recently discharged from warm blooded animals. Once these organisms are diffused into the receiving stream, however, differential rates caused by water temperature, organic nutrients, toxic metals, and adverse pH values may alter the relationship between the indicator organisms. This ratio should only be applied within 24 hours following the discharge of the bacteria from the animal.

Feachem (1975) examined how these ratios could be used with bacteria observations taken over a period of time. Because the fecal coliform and fecal strep. bacteria die-off rates are not the same, the ratio gradually changes with time. He found that bacteria is predominantly from human sources if the FC/FS ratios are initially high (greater than four) and then decrease with time, while non-human bacteria sources would result in initially low fecal coliform to fecal strep. ratios (less than 0.7) which then rise with time.

Table B-1 summarizes the observed fecal coliform to fecal strep. bacteria population ratios in the Rideau River study area (Pitt 1984). These ratios are separated into source area sheet-flow and puddle samples, Rideau River water samples and water samples collected at the swimming beaches. The source area sheet-flow and puddle samples contain the most recent pollution, while the river segment and beach samples contain “older” bacteria. The initial source area samples all have ratios of less than 0.7. However, the river averages range from 0.5 to 1.2 and the beach samples (which may be “older” than the river samples) range from 1.7 to 2.8. These ratios are seen to start with values less than 0.7 and increase with time. Based on Feachem’s (1975) work, this would indicate that the major bacteria sources in the Rideau River are from non-human (not CSOs or SSOs) sources. Periodic high bacteria ratios in the river and at the beaches could be caused by the greater die-off rate of fecal strep. as compared to fecal coliform bacteria. The observed periodic high Rideau River FC/FS ratios (which can be greater than four) may therefore be from old, non-human fecal discharges and not from fresh human fecal discharges associated from CSOs or SSOs.

Table B-1. Fecal Coliform to Fecal Strep. Bacteria Population Ratios in the Rideau River Study Area (Pitt 1984)

In order to determine the sources of fecal pollution, studies could be conducted to measure population densities of several Streptococcus biotypes. *S. bovis* and *S. equinus* are only associated with non-human animals. They are the predominant fecal strep. biotypes found in livestock and are also common in dog, cat, rodent, and bird feces, but are not found in human feces. They also have a very rapid die-off rate, so samples would have to be obtained near the time and place of discharge and their analyses would also have to be started immediately. *S. faecalis* is the predominant human fecal strep. biotype and usually indicates human contamination. It may also be found in feces from other animals, however. *S. mitis* and *S. salivarius* are considered more sensitive human indicators, but may be more difficult to analyze. Therefore, if *S. bovis, S. equinus, S. equinus* and *S. faecalis* biotypes are monitored in a comprehensive sampling program, the presence of sanitary sewage flows into the receiving water may be determined.

Fate of Toxic Chemicals

Rubin (1976) discussed the forms and reactions that may occur for heavy metals discharged to natural water systems. Metals in natural waters may be soluble, colloidal or suspended. Soluble metals are defined as being less than 1 μm in size; while suspended metals are greater than 100 μm in size. Colloidal metals are intermediate in size. Using these definitions, settleable materials are also included in the suspended size fraction. (Similarly, filterable forms of pollutants are sometimes defined as those that can pass through a 0.45 μm filter, while non-filterable forms can not). Rubin further stated that the suspended and colloidal particles may consist of individual or mixed metals in the form of their hydroxides, oxides, silicates, sulfides or as other compounds. They may also consist of clay, silica or organic matter to which metals are bound by adsorption or ion exchange, or as a complex. The soluble metals may be un-ionized organo-metallic chelates, organic ions, or complexes of these chelates or ions. Because of various reactions within the water, (physical, chemical or biological) there may be dynamic interactions among the various particle sizes and chemical forms. When incoming metals mix with receiving water bodies, several types of potential interactions can take place. The pH and redox potential (oxidation reduction potential, or ORP) are very important in controlling solubility and agglomeration and, therefore, sedimentation of a metal. The pH of the water system also affects the bonding of the metals to insoluble carriers which influences adsorption, ion exchange and co-precipitation. The oxidation reduction potential can also radically affect the ionic form of the metal. Iron and manganese are the most responsive metals to redox changes, with lower redox potentials favoring the divalent (+2) iron and manganese valence states. These valence states are also much more soluble than the more oxidized (+3) states. Redox potential and pH will both affect the stability of certain transition metal chelates (Rubin 1976).

The presence of inorganic ions can form complexes with the metals that can increase the solubility of the metals. As an example, as salinity is increased, more manganese becomes dissolved rather than suspended. The opposite can happen with other complexes, where metal carbonates and sulfides typically have limited solubilities.

Organic complexing agents in natural waters include humic and fulvic acids. These can form stable metal humics and fulvics that are soluble in fresh waters. Adsorption and ion exchange can also bind metals to insoluble particulates, especially in flowing waters with large quantities of clay and soil. Much of the material that the metals interact with involve organic materials that originated from aquatic organisms. Other aquatic organism effects on metal solubilities include changes in pH and redox by various biochemical processes. These in turn affect soluble metal concentrations and metal accumulations in sediments. Aquatic organisms can also concentrate many metals in their tissues (bioaccumulation).

Rubin (1976) also discussed the importance of oxidation reduction reactions at the sediment-water interface. This interface can have a large redox gradient, depending upon the mixing, diffusion and the extent of biological activity. Intense redox activity can occur at the sediment-water interface because of deposition and accumulation of organic matter: diffusion of oxygen down into the sediment interstitial waters can then create a large redox gradient. Organic sediments generally contain large quantities of reduced material, especially sulfides. Since most heavy metal sulfides tend to be rather insoluble, it is clear

that interactions in the heterogeneous sulfide systems can be an important process where trace metals are retained or released from the soluble phase (Rubin 1976).

Gambrell and Patrick (1977) stated that metals are present in soils and sediments in many chemical forms that differ greatly in their bioavailability. Some metals are bound within the crystalline structure of the sediments and soils and are essentially unavailable to biota. However, metals dissolved in soil solutions, or in interstitial or surface waters, are considered readily available to biota. Also, metals weakly adsorbed to the solid mineral or organic colloidal phase by ionic exchange mechanisms are also readily available. Between the unavailable and readily available metal forms are a number of forms that are potentially available. As discussed previously, the potential solubility, and therefore availability, of various metal forms are strongly dependent upon the pH and oxidation reduction conditions and, of course, the specific chemical compound. In reduced sediment conditions (low redox potential), the formation of stable and insoluble metal sulfide precipitates is important in limiting the mobility and bioavailability of most metals. Humic materials in reduced environments are characterized by large molecular weights and greater structural complexity. These characteristics increase the metal retention capacity and the metal bonding stability of insoluble humic materials. If these reduced sediments are subjected to dredging, scouring during high flows, or by benthic organism activities, many of these insoluble organics are more likely to become soluble. This is especially true for copper, lead, and cadmium complexes. As an example, Gambrell and Patrick (1977) found that as the redox potential was increased from strongly reducing to well oxidized levels, insoluble organic bound cadmium was transferred to more available soluble and exchangeable forms. They also stated that a reduction in metal availability by the formation of insoluble organic complexes in reduced sediments may be offset to some extent by an increase in soluble or organic acids which maintain some metals in solution as soluble organic complexes. These various redox and pH mechanisms affect various metal complexes differently. As an example, lead solubility is enhanced by low pH levels, but is little affected by changes in oxidation reduction conditions.

Tables 5.1 through 5.3 summarize the importance of various environmental processes for the aquatic fates of some urban runoff heavy metals and organic priority pollutants, as described by Callahan, *et al*. (1979). Photolysis (the breakdown of the compounds in the presence of sunlight) and volatilization (the transfer of the materials from the water into the air as a gas or vapor) are not nearly as important as the other mechanisms for heavy metals. Chemical speciation (the formation of chemical compounds) is very important in determining the solubilities of the specific metals. Sorption (adsorption is the attachment of the material on to the outside of a solid and absorption is the attachment of the material within a solid) is very important for all of the heavy metals shown. Sorption can typically be the controlling mechanism affecting the mobility and the precipitation of most heavy metals. Bioaccumulation (the uptake of the material into organic tissue) can occur for all of the heavy metals shown. Biotransformation (the change of chemical form of the metal by organic processes) is very important for some of the metals, especially mercury, arsenic and lead. In many cases, the discharge of mercury, arsenic or lead compounds in forms that are unavailable can be accumulated in aquatic sediments. They are then exposed to various benthic organisms that can biotransform the material through metabolization to methylated forms which can be highly toxic and soluble.

Tables 5.1, 5.2, and 5.3

Tables 5.2 and 5.3 summarize various environmental fates for some of the toxic organic pollutants found in typical urban runoff and/or receiving waters; mainly various phenols, polycyclic aromatic hydrocarbons (PAHs) and phthalate esters. Photolysis may be an important fate process for phenols and PAHs but is probably not important for the phthalate esters. Oxidation or hydrolysis may be important for some phenols. Volatilization may be important for some phenols and PAHs. Sorption is an important fate process for most of the materials, except for phenols. Bioaccumulation, biotransformation and biodegradation is important for many of these organic materials.

Bioaccumulation of Toxic SSO Pollutants in Aquatic Organisms

Bioaccumulation can be an important fate mechanism for many urban runoff constituents. In addition, bioaccumulation can significantly alter the biological community by bioconcentrating toxic materials to critical (lethal) levels. Rubin (1976) listed five major mechanisms by which aquatic organisms can assimilate metals. These are particulate ingestion of waters (such as polluted sediments) containing suspended metals from the water, ingestion of food, solubilization and assimilation through secretion of biological chelating or complexing agents, incorporation into physiological systems and ion exchange, and sorption on tissue and membrane surfaces. The uptake of metals by aquatic organisms usually reduces the metal concentrations in the waters surrounding the organisms and will increase the sediment concentrations through waste secretion and settling. In addition, burrowing benthic organisms can increase the concentrations of the constituents at a greater depth than would likely occur by sedimentation alone. The accumulation of the metal in an organism is expressed as the concentration factor (the concentration in the tissue divided by the concentration in the water, or sediment). This concentration factor is affected by many physical and biological factors. These include duration of exposure, the salinity or water hardness, the concentration, and temperature (Neff, *et al*. 1978). Effects of these physical factors vary for each metal. Biological factors are also important along with the actual form of the metal. There is no clear relationship between organism weight and tissue heavy metal concentration for all species and metals.

Phillips and Russo (1978) pointed out that the toxic response for bioaccumulation is internally determined and that the organisms can adapt to various conditions. They summarized the relative hazards of metals to humans by their occurrence in the eatable portions of fish and shell fish. Arsenic has a high hazard rating from oral ingestion by humans, along with high hazard ratings for bioaccumulation tendencies in marine fish and shellfish. However, arsenic has a low tendency to accumulate in freshwater fish muscle. Cadmium also has a high hazard rating for direct human ingestion and a high rating for marine shellfish accumulation. Chromium has a low hazard level to humans in all categories and copper is high only for bioaccumulation by marine shellfish. Iron has high hazard ratings for freshwater and marine fish muscle and marine shellfish accumulation. Lead has a high hazard rating for direct human ingestion and a high rating for bioaccumulation in marine shellfish. Mercury, specifically the methylmercury form, has a high hazard rating for all mechanisms considered, while zinc only has a high hazard rating for marine shellfish bioaccumulation.

In many cases, metals are accumulated and concentrated up the food chain. However, not all metals experience higher bioaccumulations in the upper parts of the food chain and other mechanisms besides eating are involved with heavy metal bioaccumulation. The EPA (1978) stated that animals take up varying amounts of toxic elements with their food and with air as well as by licking and grooming, soil ingestion and other activities. They further stated that only a relatively small percentage of the ingested toxic elements are incorporated into the animal’s organs, while the remainder is excreted in animal wastes.

The different tissues and different organisms accumulate different levels of the toxicants, based upon many factors that are not well understood. Neff, *et al*. (1978) pointed out that tissue heavy metal concentrations also show seasonal variations due to changes in solutions, temperatures, or biological condition and physiological state of the animals. Phillips and Russo (1978) further stated that most metals, unlike mercury, are not accumulated in the eatable portions of fish and do not represent a threat to consumers unless the fish are entirely eaten. They also stated that most fish are capable of accumulating most metals from both their diet and from the water (from various membrane surfaces, particularly the gills). In most cases, the relative contributions from these two source mechanisms are not well understood. Because food can be an important source of heavy metals to fish, the toxicity and accumulation values derived in laboratory tests, where the metals are exposed to the fish only through their ambient water, may be misleading. Phillips and Russo also reported, from summarizing past studies, that very few age related trends are apparent in heavy metal bioaccumulation.

Neff, *et al*. (1978) stated that there is very little evidence of the direct accumulation and assimilation of sediment-bound heavy metals by benthic invertebrates. The main reason for this is the difficulty in conducting controlled laboratory tests or *in-situ* analyses. In most cases, the exposure to a fish to a test sediment that has been contaminated with a heavy metal will also contaminate the overlaying waters. Even low concentrations of dissolved metals will significantly contribute to metal uptake by the animals and

confuse attempts to quantify accumulations of metals from sediments. Neff, *et al.* (1978) further stated that deposit feeding benthic invertebrates can contain significant amounts of unassimulated sediment heavy metals in their digestive tracts. Therefore, whole-body analyses can greatly overestimate metal accumulation in the tissues of these animals. In addition, they stated that many of the heavy metals are known micro-nutrients for animals. These include iron, manganese, copper, zinc, cobalt, vanadium, chromium and sodium. Therefore, aquatic organisms have natural mechanisms for accumulating these elements from dilute solutions. Phillips and Russo (1978), from earlier studies, stated that benthos accumulate more metals from water than from the sediment. Benthos can metabolize and change the chemical form of some metal compounds into soluble, and sometimes more toxic forms. Benthic organisms themselves are not important sources of metals to fish, but they can increase the metal content of overlaying waters by disturbing the metals concentrated in the sediments.

Neff, *et al*. (1978) stated that the rate of accumulation of the metals in benthic invertebrates varies substantially. Zinc, copper, cadmium and lead are accumulated rapidly and are retained for a long time in animal tissues, while thallium and ruthenium are accumulated very slowly from solutions. Phillips and Russo (1978) stated that shellfish can accumulate many metals much more rapidly than fishes can. Potentially dangerous metals in shellfish include cadmium, arsenic, mercury, lead, silver, and various radioisotopes.

The chemical analysis of plant tissues usually does not indicate whether the elements detected have been taken up by the plant and incorporated into the plant tissue, or whether they only have been deposited on the plant surface as a result of air pollution (EPA 1978). Air pollutants that may be deposited on the plants are usually insoluble oxides and would not affect the plant growth, while elements that are taken into the plant through its root system have a greater biological availability. Ray and White (1976) have studied the use of vascular plants for monitoring heavy metal pollution.

Fates of Heavy Metals

Arsenic

Callahan, *et al.* (1979) stated that all of the potential environmental fates, except for photolysis, can be important for arsenic. Bioaccumulation of arsenic, however, is limited because of its toxicity: the organism usually dies before the bioaccumulation of the material can reach high magnitudes. Arsenic can also be metabolized by organisms to form trivalent arsenicals. Arsenic can be adsorbed onto clays, iron oxides, inorganics and either remain suspended or accumulate in sediments. The EPA (1976) stated that compounds of arsenic are ubiquitous in nature, insoluble in water and occur mostly as arsenides and organic arsenopyrites. Arsenics exist in the trivalent (+3) and pentavalent (+5) states as either organic or inorganic compounds. The trivalent inorganic arsenicals are more toxic than the pentavalent forms both to mammals and aquatic species. Most arsenic forms, however, are toxic to humans. Phillips and Russo (1978) stated that arsenic may be bacterially methylated, much like mercury, to form highly toxic methylarsenic or dimethylarsenic. These methylated forms of arsenic are very volatile and are readily oxidized to less toxic forms.

In a survey of 130 natural receiving water quality monitoring stations, the EPA (1976) reported that the ranges of observed arsenic values was 5 to 336 μg/L, with a mean value of 64 μg/L. Durum (1974) reported that a survey of 728 USGS water samples resulted in a range of 10 to 1,100 μg/L with a median value of less than 10 μg/L. The maximum value was found in the southeastern region of the U.S. The median and minimum values were similar for all areas of the country. The southwestern and northwestern parts of the country had the lowest maximums observed (10 and 30 μg/L respectively) while the New England region had a maximum value of 60 μg/L and the central states had a maximum value of 140 μg/L.

Phillips and Russo (1978) reported that arsenic is accumulated by fish from both water and food, but the concentration factors are quite low. Arsenic in fish tissue is concentrated in the fish fat. The muscle tissue also accumulates arsenic, but the biological half-time has been reported to be only 7 days in green sunfish. Shellfish, however, concentrate arsenic to a much greater extent than fish, Marine organisms contain more arsenic than fresh-water forms. Unfortunately, arsenate present in the tissues of consumable seafood is

rapidly converted to arsenite following death, a much more poisonous form (Phillips and Russo 1978). The EPA (1976) reported that even though arsenic is accumulated in aquatic organisms, it is not progressively concentrated along a food chain.

Phillips and Russo (1978) reported that arsenic concentrations in fish collected from various Wisconsin waters was typically less than 1 μg/g. Young and adult bluegills placed in ponds treated with sodium arsenite, a herbicide, contained arsenic levels similar to the concentration of arsenic in the pond (0.3 to 9 mg/L) after 16 weeks exposure. They also reported that arsenic concentrations in mature fish muscle were about 60 percent of whole fish arsenic concentrations. However, immature bluegills obtained arsenic concentrations almost twice the adult concentrations. The EPA (1978) reported that arsenic concentrations for freshwater fish are usually below 1 μg/g wet weight, with concentrations of 0.5 μg/g for bluegills and 0.07 to 0.15 μg/g for trout. They also reported on a study that incubated rainbow trout eggs in water containing various concentrations of sodium arseniate or arsenic trioxide. A similar accumulation pattern was observed for both arsenic compounds. The embryos accumulated up to 2.5 μg/g arsenic after 40 days exposure to only 0.05 mg/L of arsenic. This corresponds to a bioconcentration factor of 50. Interestingly, concentrations as high as 50 mg/L arsenic did not reduce egg survival, but concentrations less than 5 mg/L decreased survival because the higher arsenic concentrations reduced growths of fungus on the fish eggs. In another study, Phillips and Russo (1978) report that arsenic was rapidly accumulated in largemouth bass from both food and water sources, but the arsenic was rapidly eliminated after the exposure was terminated. The arsenic concentrations necessary to control aquatic vegetation would not result in arsenic concentrations in bass considered dangerous to human consumers. Average arsenic bioaccumulations in various freshwater fish species in the Southeastern United States are reported as 0.5 μg/g. However, liver oil from the fish averaged almost 40 μg/L arsenic.

Lake Michigan plankton and benthic organisms were found to contain about 6 μg/g arsenic. Leland and Luoma (1979) have also summarized many past studies of heavy metal bioaccumulation. They reported a range of arsenic tissue concentrations in benthic invertebrates ranging from less than 1 to 1,300 μg/g and a range of arsenic concentrations in zooplankton from 700 to 2,400 μg/g. Neff, *et al.* (1978) also reviewed many bioaccumulation studies and found that the bioconcentration factors for macroinvertebrates were usually greater than for other organisms. Concentration factors ranged from 300 to 3,300 for arsenic in macroinvertebrates. Leland and Luoma (1979) also reported another study that examined trace metal uptake by invertebrates in laboratories. They found that arsenic uptake by snails was similar to the arsenic concentrations in the sediment, rather than in the water.

Arsenic can also accumulate in aquatic vegetation. The EPA (1976) reported on a previous study in a Wisconsin lake that had water concentrations ranging from 100 to 450 μg/L arsenic. The concentration of arsenic in the bottom mud was about 200 μg/g. A sample of cladophora contained more than 1,200 μg/g arsenic and fresh shoots of mature Myriophyllum sp. stems contained as much as 550 μg/g arsenic.

Cadmium

Callahan, *et al.* (1979) stated that in most unpolluted waters, the majority of cadmium will exist as the hydrated divalent cation. In polluted waters, complexes with organic materials will be the most important cadmium forms. The affinity of ligands for cadmium follows the order of humic acids greater than carbonates, carbonates greater than hydroxides and hydroxides greater than both chlorides and sulfates. Adsorption of cadmium onto organics, clays, hydrous iron and manganese oxides is also important in polluted water. Cadmium is also strongly bioaccumulated. Durum (1974) stated that concentrations of the carbonate and hydroxide forms of cadmium, with pH values equal to or less than 7, are relatively high and that the USPHS standard of 10 μg/L may occur in many stable water systems, including both surface and groundwaters. Pitt and Amy (1973) studied the solubility of cadmium in street dirt, along with other metals, and found that in typical urban runoff concentrations, soluble cadmium values of less than 1 μg/L occurred in moderately hard water (hardness equal to 50 mg/L) after an exposure of 25 days. This soluble fraction was 14 percent of the total cadmium in the mixture. Wilber and Hunter (1980), in an urban receiving water study in Lodi, New Jersey, found that with most low flows in the Saddle River, the cadmium was mostly dissolved. However, during wet weather conditions, most of the cadmium was associated with particulates.

Durum (1974) in the nationwide USGS study of water quality conditions that analyzed 727 samples, observed an overall range of cadmium of less than one to as much as 130 μg/L. The nationwide minimum and median values for all regions of the country were all less than 1 μg/L, except in New England where the median value was 2 μg/L. The maximum observed value of 130 μg/L was found in the southwest. A maximum value of 90 μg/L was observed in the southeast, and maximums of 40, 21 and 32 μg/L were observed for the central, northwest and New England areas respectively.

Phillips and Russo (1978) reported that very little cadmium is accumulated in the eatable portions of fish. However, shellfish are capable of accumulating extremely high levels of cadmium in eatable portions. Cadmium is readily available through both food and water to marine and freshwater organisms. Either source can result in toxic symptoms by fish. The fish tissues appear to reach cadmium equilibrium after about 2 to 5 months exposure. Soft water usually results in higher cadmium bioaccumulations in fish than when in hard waters. Cadmium uptake also increases with increasing water temperature and decreasing salinity. Neff, *et al*. (1978) studied cadmium concentrations in a relatively unpolluted Illinois stream system. Cadmium was found in all components of the aquatic system. Fish and sediment cadmium concentrations were similar, but aquatic insects had cadmium concentrations higher than the sediments. There was, therefore, no indication of food chain cadmium magnification.

Leland and Luoma (1979) reported a study that observed museum fish specimens that had been collected over a 40-year period which did not detect any chronological accumulation of cadmium. Phillips and Russo (1978) also noted another study where cadmium was not detected in any fish samples collected in Wisconsin. Fish samples, however, collected from the Iowa River did contain low concentrations of cadmium. Another study exposed rainbow trout to high cadmium concentrations and found that most of the cadmium in the gills were rapidly lost when the fish were returned to clean water. However, almost no cadmium was lost from the kidney. In another study, cadmium concentrations in the gills of bluegills greater than 150 μg/g almost always killed the fish. Three spine sickleback experienced concentration factors from 500 at the lowest cadmium water concentrations to about 0.5 at the highest cadmium water concentrations. The water concentrations ranged from 1 μg/L to 100 mg/L and all were lethal. The EPA (1978) reports that cadmium concentrations of more than 0.1 μg/g in goldfish were evident from samples from the Hudson River.

Neff, *et al*. (1978) reported on another study that examined the accumulation of cadmium by freshwater snails. It was found that the initial cadmium uptake rate for the snails was higher in hard water than in soft water, but the total amount of cadmium accumulated in the snails was greater for soft water environments. Leland and Luoma (1979) reported bioconcentration factors of more than 500 for cadmium in crayfish after exposures of 1 mg/L of cadmium for about 1 week. Spehar, *et al*. (1978) reported that cadmium concentrations in invertebrates increased with increasing water concentrations and were as much as 30,000 times greater than the water cadmium concentrations. Insect and snail body cadmium concentrations of 1 to 10 μg/g occurred with water concentrations of 1 μg/L, while the insect and snail cadmium concentrations increased to 100 to 200 μg/g when the water concentration was increased to 300 μg/L. Neff, *et al*. (1978) reported macroinvertebrate cadmium concentration factors of 82,000 to 182,000.

Phillips and Russo (1978) reported a study that found that the feces of migratory waterfowl contained high levels of cadmium. It was felt that waterfowl can contribute significant quantities of cadmium to the Illinois lake that was studied. In another study, cadmium was found to increase in concentration moving from water to fish to sediment to invertebrates in an Illinois stream. It was found that aquatic insects contained the highest cadmium level possibly due to their close association with the sediment. Rolfe, *et al*. (1977) found significant retention of cadmium in predator protozoa in another Illinois stream study.

Ray and White (1976) examined cadmium bioaccumulation in aquatic plants. Bioaccumulation factors from 1 to 260 were observed for various plants and plant parts in clean water systems, while the range in polluted water was only 0.2 to 2. Plant tissue cadmium concentrations ranged from about 0.5 to 6 μg/g. Leland and Luoma (1979) reported sphagnum moss cadmium concentrations of 1 to 2 μg/g. DePinto, *et al*. (1980) reported a study that found cadmium rapidly taken up by algae. The algae was also a more efficient

collector of the cadmium than the sediments. The EPA (1978) reported a study that found cadmium concentrations being greater in the roots of aquatic plants than in the plant shoots. They concluded that roots can take up large quantities of cadmium from solutions, but there are restrictions to cadmium movement through the plant.

Chromium

Phillips and Russo (1978) stated that in water, trivalent (+3) chromium exists as a complex, colloid or precipitate, depending on pH. The more toxic hexavalent (+6) chromium form is usually present only as an ion. Pitt and Amy (1973) found that the solubility of chromium associated with street dirt in moderately hard water was about 4 μg/L or about 0.3 percent of the total chromium in the mixture.

The EPA (1976) found, in a nationwide survey of 1,577 analyses, an overall observed chromium concentration range of 1 to 112 μg/L, for 386 samples that had detectable chromium concentrations. The mean value for the positive test samples was 9.7 μg/L. Durum (1974) reported that a USGS survey of 728 samples resulted in an overall range of chromium of less than 1 to a maximum of 19 μg/L. The median observed value was less than 1 μg/L.

Phillips and Russo (1978) reported on a study in New Zealand that showed that chromium was concentrated through a simple food chain of sediment to bacteria to tubificid worms. They also reported a study in Wisconsin that showed typical chromium concentrations in fish were less than 1 μg/g. Fish exposed to chromium in water can bioconcentration chromium nearly 100 times. Fish, however, were shown to rapidly eliminate chromium when returned to clean water. Therefore, chromium is not likely to accumulate in fish tissue if only exposed to intermittent high chromium concentrations. Chromium is apparently accumulated in fish through the gills and eliminated through the feces. Phillips and Russo (1978) also reported another study of rainbow trout that showed hexavalent chromium bioaccumulations when the chromate water concentration was greater than 10 μg/L. The chromium continued to accumulate for at least 30 days. An equilibrium concentration of chromium in rainbow trout appears to be reached rapidly.

Rubin (1976) reported chromium concentration factors of about 10 for fish and more than 250 for mollusks. Leland and Luoma (1979) reported chromium concentrations of 1.8 to 4.6 μg/g in aquatic sphagnum moss plants.

Copper

The EPA (1976) stated that copper occurs as a natural or native metal and in various mineral forms, such as cuprite and malachite. Callahan, *et al*. (1979) stated that copper in unpolluted waters is mostly a carbonate complex and in polluted waters forms complexes with organic materials. Pitt and Amy (1973) found that inorganic copper is mostly found with valence states of plus one and plus two in natural water systems near neutral pH values. The common inorganic copper forms at these pH conditions are copper sulfide, oxide, hydroxide, cyanice, sulfate and iodide. Phillips and Russo (1978) stated that divalent copper ion (+2) and its hydroxides are believed to be the toxic copper forms for fish. Alkalinity and pH are believed to be the major factors controlling copper speciation. Callahan, *et al*. (1979) stated that copper speciation with organics is most important in polluted waters. The adsorption of copper can reduce is mobility and enrich suspended and settled sediments. Copper is absorbed onto organics, clay minerals, hydrous iron and manganese oxides. They also reported that copper is strongly bioaccumulated.

Wilber and Hunter (1980), in a study of an urban river in Lodi, New Jersey, found that the readily available copper (at a pH of about 7) was about 13 percent of the street dirt and runoff solids total copper content. Pitt and Amy (1973) found that the copper solubility of street dirt was about 160 μg/L, or about 36 percent of the total copper in the mixture, with moderately hard water conditions.

The EPA (1976) found that about 74 percent of the more than 1,500 copper analyses in nationwide waters had detectable copper concentrations, with an average value of 15 μg/L and a maximum observed value of

280 μg/L. Goldschmidt (1958) reported a range of copper concentrations near the estuary of the Mississippi River of 1 to 15 μg/L. He also reported a concentration range of 9 to almost 400 μg/L observed in three Connecticut lakes, and a range of 65 to 600 μg/L for 25 municipal water supplies throughout the country.

Phillips and Russo (1978) reported that copper is bioaccumulated by fresh water and marine fish, shellfish and aquatic insects. They also found that chronic symptoms in fish start to develop very soon after copper bioaccumulation rises above background levels. They also reported on a study conducted in a New Zealand river that confirmed the potential for copper being concentrated as it moves through a simple food chain consisting of metal enriched sediments to bacteria to tubificid worms.

Phillips and Russo (1978) reported that rainbow trout tissue copper concentrations ranged from 1.7 to 12.9 μg/g when the trout was collected in a hatchery with a pristine water supply. Bluegill was also found to accumulate copper when the water concentrations were greater than 40 μg/L. This concentration also resulted in decreased larval survival for bluegills. In another study, bullheads were found to accumulate copper at all water concentrations exceeding 27 μg/L. Rubin (1976) reported copper concentration factors of about 60 for fish, 1,500 for mollusks and about 160 for macrophytes.

Phillips and Russo (1978) reported on a study that found clams and tubificid worms, along with another benthic organisms, containing higher copper concentrations than either omnivorous or carnivorous fish. Neff, *et al*. (1978) found that concentration factors for macroinvertebrates were higher than for almost all other test organisms. The concentration factors ranged from 2,400 to 3,500. In another study, Phillips and Russo (1978) summarized that insects in a heavy polluted mine stream contained as much as 6,400 μg/g copper. They also reported another study's conclusion that mayflies and stoneflies were more resistant to copper pollution than fish, and that their copper accumulation reflected copper water exposure. Neff, reported another study that showed that copper tolerant worms accumulated copper more rapidly than non-tolerant worms.

DePinto, *et al*. (1980) reported a study that showed rapid copper bioaccumulation in algae when the resultant algae concentrations were greater than sediment copper concentrations. Ray and White (1976) reported copper concentrations in various aquatic plants sampled in polluted and unpolluted reaches of an urban creek. Plant concentrations in an unpolluted stream reach ranged from about 3 to 200 μg/g and from about 13 to 240 μg/g for other algae and plant species in the polluted reach. The approximate copper bioconcentration factors ranged from about 1 to 20 in the clean stream reach and about 0.1 to 4 in the polluted reach of the stream. Leland and Luoma (1979) reported sphagnum moss copper concentrations of 13 to 540 μg/g.

Iron

Phillips and Russo (1978) stated that the soluble ferrous form of iron (+2) is readily oxidized to the insoluble ferric, or trivalent (+3) state in most natural surface waters. A substantial fraction of iron in natural waters is therefore associated with suspended solids. The EPA (1976) stated that the ferrous form can persist in waters void of dissolved oxygen, and originates usually from anaerobic groundwaters or from mine drainage. Iron can exist in natural organometallic, humic, and colloidal forms. Black or brown “swamp waters” may contain iron concentrations of several milligrams per liter in the presence or absence of dissolved oxygen, but this iron form has little effect on aquatic life because it is complexed and relatively inactive chemically or physiologically.

Pitt and Amy (1973) found that the solubility of iron in street dirt was about 50 μg/L, or much less than 1 percent of the total iron in a mixture with a moderately hard receiving water. They also stated that the principle inorganic iron forms, with neutral pH water conditions, are iron oxide, hydroxide, sulfate, nitrate and carbonate.

Phillips and Russo (1978) reported that iron is concentrated to a considerable degree by some marine organisms, with most of the iron being accumulated in the gills. Iron was also found to concentrate as it moved through a simple food chain from sediment to benthic worms.

Phillips and Russo (1978) reported that whole bluegill iron concentrations averaged about 150 μg/g from a South Carolina reservoir. While carp from Austria was found to have iron tissue concentrations ranging from about 7 to 40 μg/g. The gill iron concentrations of this carp was almost 15,000 μg/g. The concentrations of iron on the gills were similar to the iron concentrations in the suspended sediments, suggesting that the metals were on particles embedded on the gill surfaces. Rubin (1976) reported iron bioconcentration factors of about 200 for fish and more than 3,600 for macrophytes. Phillips and Russo (1978), in reviewing many studies, were not able to find any age related iron increases. They also reported Lake Michigan benthos iron concentrations of about 1,800 μg/g. Leland the Luoma (1979) reported sphagnum moss iron concentrations of about 150 to 2,800 μg/g.

Lead

The EPA (1976) stated that most lead salts are of low solubility. Lead exists in nature mainly as lead sulfide (Galena). Other common natural forms of lead are lead carbonate (Cerussite), lead sulfate (Anglesite) and lead chlorophosphate (Pyromorphite). Stable complexes result from the interaction of lead with organic materials. The toxicity of lead in water is affected by pH, hardness, organic materials and the presence of other metals. The aqueous solubility of lead ranges from 500 μg/L in soft water to 3 μg/L in hard water. Durum (1974) stated that lead carbonate and lead hydroxide are soluble lead forms at pH vales of 6.5, or less, with low alkalinity conditions (less than 30 mg/L alkalinity). The soluble lead concentrations under these conditions can reach 40 to several hundred μg/L. If the alkalinity is greater than 60 mg/L and if the pH is near 8, however, the dissolved lead would be less than 10 μg/L. Callahan, *et al.* (1979) stated that lead carbonate and lead sulfate control lead solubility under aerobic conditions and normal pH values. Lead sulfide and lead ions, however, control lead solubility in anaerobic conditions. In polluted water, the organic complexes of lead are most important in controlling lead solubility. Phillips and Russo (1978) stated that most lead is probably precipitated in natural waters due to the presence of carbonates and hydroxides.

Pitt and Amy (1973) found that the solubility of lead in a street dirt mixture was about 40 μg/L, or about 3 percent of the total lead, in moderately hard water. Wilber and Hunter (1980) found that readily available lead was about 21 percent of the total lead in street dirt and runoff solids. They also found that under most low flow river conditions, most of the lead was dissolved, but under wet weather conditions, most of the lead was insoluble. Solomon and Natusch (1977) also examined the solubilities of lead associated with street dust. They found solubilities ranging from 500 to 5000 μg/L which was 0.03 to 0.3 percent of the initial mixture total lead concentration. However, the test mixture of street dirt with water was very high (1750 mg/L lead).

Rolfe and Reinbold (1977) found that about 46 percent of the total lead input in a test watershed remained airborne. The total input included gaseous and particulate vehicle emissions. About 5 percent of the total lead input to the watershed occurred with rainfall and about 60 percent occurred with atmospheric settleable solids. They found that about 80 percent of the lead in stream water was insoluble and associated with suspended solids, and only 3 percent of the lead input into the watershed exited the watershed in the stream. The streamflow accounted for the majority of all of the lead discharged from the watershed (about 7 to 8 percent of the total lead input).

Pitt and Amy (1973) reported that most inorganic lead in water systems near neutral pH conditions exist in the plus 2 or plus 4 valence states as lead sulfide, carbonate, sulfate, chromate, hydroxide, chloride or iodine.

Drumum (1974) reported lead concentrations in 727 nationwide samples. The reported range was less than 1 to 890 μg/L with a median value of 2 μg/L. The observed minimum values were all 1 μg/L, or less. The median values were all 1 μg/L, except for New England where the median value was 6 μg/L, and in the southeast where it was 4 μg/L. The maximum value of 890 μg/L was reported for New England. Maximum lead values of 84, 44, 34 and 23 μg/L were reported for the central, southeast, southwest and northwest regions of the country, respectively. The EPA (1976) reported a range of 1 to 10 μg/L as the natural mean

lead concentration of the world's lakes and rivers. In 1,500 analyses, less than 20 percent had detectable lead concentrations, with a reported mean value of about 20 μg/L and a maximum value of 140 μg/L.

Lead is present in all animals and as for many heavy metals, animals higher up in the food chain can bioaccumulate higher quantities of lead in their bodies (EPA 1978). Rolfe, *et al*. (1977) collected plant and animal tissues from terrestrial and aquatic urban areas. They found that most of the lead was concentrated in the soils, plants, animals and insects in the urban area or near high traffic volume rural highways. They found that the lead concentrations of aquatic organisms varied substantially within and between the urban and non-urban sectors of their test area near Champaign, Illinois. Lead concentrations in organisms from the urban sector were 10 to 20 times higher than those from the rural area. They, however, found no biological magnification of lead through the aquatic food chain, which conflicts with much of the published information. They found that biological lead concentrations were influenced by the amount of contact an organisms had with the polluted stream substrate. They therefore, concluded that external contact is a more important lead uptake mechanism that ingestion. They also found that the uptake rate and final lead body concentrations were proportional to the amount of lead in the water solution when the other lead sources were eliminated.

Phillips and Russo (1978) report that the Canadian Food and Drug limit for lead in fish food is 2 μg/g. They also report that most of the lead accumulated by aquatic animals is in the divalent form which increases with decreasing pH values. Neff, *et al*. (1978) reported that for an unpolluted Illinois stream, that lead concentrations in sediment and aquatic insects were similar and higher than in fish. Fish lead bioaccumulation concentrations, however, were greater than the water lead concentrations. Snails had the next highest bioaccumulations of lead. Again, there was no indication of food chain magnification of lead in this study area.

Rolfe, *et al.* (1977) reported body tissue lead concentrations in aquatic organisms in a rural stream near Champaign, Illinois, ranging from about 1.4 to 16 μg/g. Crayfish samples had concentrations of about 5.4 μg/g, mayfly nymphs had concentrations of about 10 μg/g and leaches and aquatic worms had concentrations of about 13 μg/g. They also found no biological magnification of lead in this food chain. Phillips and Russo (1978) reported that in a study conducted in New Zealand, bioconcentration of lead in a simple food chain did occur from sediments to bacteria to tubificid worms. Almost all studies showed higher lead concentrations in benthic invertebrates than in the sediments, however, predator fish typically had lower lead concentrations than the benthos. Fish usually have greater body lead concentrations than the water concentration. Therefore, the magnification of lead through a complete freshwater aquatic food chain is uncertain.

Phillips and Russo (1978) report that lead concentrations in fish livers greater than 50 μg/g and fish kidneys above 100 μg/g may indicate a history of unacceptable lead exposures. In another study, fish collected in Wisconsin typically had whole body lead concentrations less than 1 μg/g. Leland and Luoma (1979) reported on a study that examined Hudson River fish collected over a 30-year period, ending in 1975, showing no significant chronological lead increases.

Phillips and Russo (1978) report on a study that showed that most of the lead was still retained in rainbow trout after they had been returned to clean water. In another study, pumpkinseed sunfish bioaccumulated lead three times as much at a pH of 6.0 then at a pH of 7.5. The EPA (1978) reported that most freshwater fish contain at least 0.5 μg/g lead, with green sunfish containing as high as 16 μg/g lead.

Phillips and Russo (1978) summarized a report that discussed isopods that had accumulated lead from both food and water. The most lead-tolerant isopods were found to bioaccumulate the most lead in their tissue. Rolfe, *et al*. (1977) noted dramatic increases in lead concentrations in tubificid worms during a period of high urban runoff. However, they also found that the amount of lead transported by drifting stream invertebrates was insignificant in this south central Illinois watershed. Spehar, *et al*. (1978) reported that lead concentrations were as much as 9,000 times greater than corresponding lead concentrations in the water. With 1 μg/L lead water concentrations, the bioaccumulation factor was about 10 to 30 times for insects, snails and amphipods. With water concentrations of 600 μg/L, however, the bioaccumulation factor

was reduced to 2 to 3 times, with resultant insect, snail and amphipod concentrations of 1,000 to 2,000 μg/g. Neff, *et al*. (1978) found macroinvertebrate lead bioconcentration factors higher for almost all other organisms. These lead bioconcentration factors ranged from 7,000 to 100,000. Phillips and Russo (1978) reported a study conducted in a polluted Colorado stream where the insects contained up to 6,000 μg/g lead.

Rolfe, *et al*. (1977) studied the uptake of lead that was deposited on plants from atmospheric sources. They found a complete lack of lead uptake in these plants by this mechanism. Leland and Luoma (1979) report on a study that found 10 to 30 times more lead in algae grown on lead polluted snow, than in a control area. They also reported that duckweed lead bioconcentration factors were highest, when the lead concentrations in the water were the lowest. Ray and White (1976) reported lead concentrations from various aquatic plants collected from polluted and non-polluted streams. The plant tissue concentrations ranged from about 1 to 13 μg/g for some plants in the clean water and ranged from about 5 to 570 μg/g for other plants in the polluted stream reach. Leland and Luoma (1979) summarized feather moss lead concentrations ranging from 44 to about 310 μg/g and lead concentrations of 5 to about 30 μg/g for sphagnum moss. In a study of retention of lead in a bacterial food chain, Rolfe, *et al*. (1977) found that only 10 percent of the lead ingested by protozoa was retained in its cells and the remainder of the lead was found in a water-soluble form in the culture media.

Nickel

Wilber and Hunter (1980) found that the readily available nickel fraction of street dirt and runoff solids was about 4 percent at close to neutral pH conditions. Pitt and Amy (1973) found that the nickel solubility of street dirt solids, in a moderately hard water mixture, was about 30 μg/L or about 7 percent of the total nickel in the mixture.

Mercury

Phillips and Russo (1978) reported that inorganic mercury concentration, availability of inorganic mercury, pH, microbial activity and redox potential all affect mercury methylation rates. In general, more methylmercury is produced when more inorganic mercury is present. Chemical agents which precipitate mercury, such as sulfide, reduce the availability of mercury for methylation, but only when present in large quantities. At neutral pH values, the primary product of mercury methylation is monomethylmercury. Methylation can occur under both aerobic and anaerobic conditions, but more mercury is produced when more bacteria are present. Therefore, highly organic sediments which favor bacterial growth have a higher methylation potential than inorganic sediments. Methylmercury is also strongly accumulated by organisms. Fish accumulated more mercury as the temperature and mercury content of the sediment increased. Bacteria not only act as methylators of mercury, but also accumulate large amounts of mercury. However, sediment and water are probably the two most important mercury sinks. Conditions reducing the mercury content of overlaying waters, such as the accumulation of mercury by aquatic organisms, result in the mobilization of mercury from sediment. Virtually any mercury compounds discharged to water may become a bioaccumulation hazard if the environmental conditions are favorable for methylation. Other microbial conversions of mercury have also been reported. Some bacteria are capable of transforming mercuric ion and phenylmercuric acetate to volatile mercury. Under certain conditions, however, the most toxic form of methylmercury can be demethylated.

Callahan, *et al.* (1979) also stated that almost all of the environmental processes are important when determining the fate of mercury in aquatic environments. The EPA (1976) reported that typical mercury concentrations in 31 states with no known mercury deposits are typically less than 0.1 μg/L. Durum (1974) found that in 722 nationwide water analyses, the total mercury concentrations ranged from less than 0.5 to 6.8 μg/L, with a median value of less than 0.5 μg/L. He also reported dissolved mercury concentrations in 262 samples that ranged from less than 0.1 to a maximum of 4.3 μg/L, with a median value of less than 0.1 μg/L.

Essentially all animal tissues contain some mercury. Much information exists in the literature on mercury content of various animal tissues. In general, it is found that animals higher up in the food chain bioaccumulate higher amounts of mercury (EPA 1978). Methylmercury is bioconcentrated many times in fish and other aquatic organisms because of the rapid uptake of the methylmercury and the relative inability of the fish to excrete it from their tissues (EPA 1976). In addition, methylmercury appears to persist in the aquatic environment for sufficient time periods to allow uptake by aquatic organisms. Phillips and Russo (1978) reported a study that found more than 80 percent of the mercury that accumulated in mosquito fish was inorganic. Leland and Luoma (1979) also reported on studies that showed biomagnifications of 3 to 5 times for each step in a simple food chain. In a Georgia salt marsh food chain, plants had the lowest percentage of total mercury as methylated mercury. Herbivorous snails had the next highest percentage methylated mercury followed by benthic worms and mollusks, then crabs, fish and finally birds which had the highest percent of total mercury as methylated mercury in their tissues.

Phillips and Russo (1980) reported that fish can tolerate very high tissue concentrations of mercury. Fathead minnows exposed to about 0.1 μg/L methylated mercury obtained methylated mercury concentrations in their eatable portions greater than the Food and Drug Administration's action level (0.5 μg/g mercury) without suffering adverse affects. Rainbow trout were reported to accumulate up to 30 μg/g mercury without noticeable affects (about 60 times the FDA level). Phillips and Russo also reported that methylmercury is readily accumulated by fish both from food and from water. The biological halftime of methylmercury in fish is between 1 and 3 years. Leland and Luoma (1979) reported that a survey of museum fish collected over a period of 30 years indicated no detectable chronological accumulation of mercury in any species. The EPA (1976) reported concentration factors of 15,000 to 30,000 for methylmercury in fish with resultant tissue mercury concentrations of about 0.5 μg/g. Leland and Luoma (1979) also reported that sporadic feeding of mercury to trout resulted in much greater mercury tissue concentrations than continuous feeding. Phillips and Russo (1978) summarized a report that studied fathead minnows in methylmercury concentrations of 0.018 to 0.025 μg/L. The resultant minnow tissue concentrations ranged from 1.5 to 11 μg/g after 48 weeks of exposure. In another study, mercuric chloride uptake in fathead minnows increased as the water pH decreased, with a sharp increase in uptake at pH values below 7. In another study, fathead minnows accumulated more mercury when their food source was also raised in the test water.

Phillips and Russo (1978) reported on a study of waterfowl mercury accumulation that resulted in waterfowl breast tissue mercury concentrations ranging from about 0.5 to 8 μg/g. The waterfowl were sampled from a heavily polluted river. Fish and shellfish from highly polluted Minamata Bay in Japan contained 9 to 24 μg/g mercury (EPA 1978).

Aquatic plants accumulate mercury primarily by surface adsorption (EPA 1976). Leland and Luoma (1979) reported mercury plant tissue concentrations ranging from 0.08 to 0.14 μg/g in 23 aquatic plants collected in Finland, and a mercury range of 13 to 112 μg/g in sphagnum moss from northern Canada.

The concentrations of mercury in invertebrates varies over a wide range. Leland and Luoma (1979) stated that benthic organisms accumulated mercury in their tissues through ingestion of material in the sediments. This mercury is then transferred to their fish predators upon ingestion (EPA 1976). Leland and Luoma (1979) reported mercury concentrations in crayfish from Wisconsin ranging from 0.07 to about 0.6 μg/g.

Zinc

Durum (1974) stated that the solubility of zinc is less than 100 μg/L at pH values greater than 8, and less than 1,000 μg/L for pH values greater than 7, if there is a high concentration of dissolved carbon dioxide. Phillips and Russo (1978) stated that zinc sulfates and halides are soluble in water, but zinc carbonates, oxides and sulfides are insoluble. The EPA (1976) stated that zinc is usually found in nature as the sulfide. It is often associated with the sulfides of other metals, especially lead, copper, cadmium and iron. Callahan, *et al*. (1979) stated that zinc in unpolluted waters is mostly as the hydrated divalent cation (+2) but in polluted waters complexation of zinc predominates. Pitt and Amy (1973) reported that zinc is mostly found as the divalent form, as a sulfide, oxide, sulfate or hydroxide.

Wilber and Hunter (1980), in a study of an urban stream near Lodi, New Jersey, found that the readily available zinc in street dirt and runoff solids was about 17 percent of the total zinc. Most of the zinc in the river during low flow conditions was dissolved, while during wet weather it was mostly in the solid form. Pitt and Amy (1973) found that the solubility of zinc was about 170 μg/L, or about 8 percent of the total street dirt zinc, in a moderately hard water mixture.

Durum (1974) reported zinc concentrations in 727 nationwide water samples ranging from less than 10 μg/L to a maximum of 4,200 μg/L, with a median value of about 20 μg/L. The EPA (1976), in a nationwide survey of over 1,200 positive zinc results, found a mean value of 64 μg/L and a maximum value of about 1,200 μg/L.

Phillips and Russo (1978) summarized a report that found zinc had concentrated in the upper levels in a simple food chain consisting of sediment to bacteria to tubificid worms. They also reported that zinc is bioaccumulated in fish gills at a modest rate during chronic exposures, but rapidly during acutely lethal zinc exposures. In another study in Wisconsin, zinc concentrations in freshwater fish was found to range from 3 to more than 18 μg/g. Studies of zinc bioaccumulation in rainbow trout showed that eyes accumulated the highest concentrations, followed by gills, bone, intestine, liver, kidney and finally skin. Baseline zinc levels ranged from 400 μg/g for the eye to 1 μg/g for the stomach. In another study, zinc was shown to bioaccumulate in the intestine of goldfish, implying that zinc is excreted through the intestine (Phillips and Russo 1978). In general, zinc begins to accumulate in fish at about the concentration where it becomes quite chronically toxic to the fish. Whole fish zinc uptake was higher in hard water for three spine stickleback, even though the zinc toxicity was much lower under the hard water conditions. Much of the zinc in the gill area could be suspended particulates imbedded on the gills. The half-life for zinc in brown bullhead appears to be about 6 days, after removal to clean water. The zinc half-life in juvenile mosquitofish have, however, ranged from 2 to more than 200 days, depending upon the fraction of the total zinc in the system accumulated within the fish. Rubin (1976) reports bioconcentration factors for zinc in fish of about 230, about 2,300 for mollusks and more than 300 for macrophytes.

Phillips and Russo (1978) reported a study that showed that benthic organisms such as clams and tubificid worms contained higher zinc concentrations than either omnivorous or carnivorous fish. Neff, *et al*. (1978) reported that concentration factors for macroinvertebrates were higher than for other test organisms and ranged from about 150,000 to 300,000. They also found that zinc tolerant worms were less permeable to zinc and excreted it more rapidly than non-tolerant worms. Phillips and Russo (1978) also reported on a study conducted in a polluted Colorado river that showed zinc concentrations in insects of up to 10,000 μg/g. In another study, crayfish were found to bioaccumulate zinc through food, as their major source of zinc uptake.

Leland and Luoma (1979) reported zinc concentrations in feather moss ranging from 54 to more than 130 μg/g and from 26 to 40 μg/g in aquatic sphagnum moss. Ray and White (1976) reported zinc concentrations in various aquatic plants that were collected from polluted and unpolluted reaches of an urban creek. Zinc concentrations for plants in the clean reach of the creek ranged from about 100 to 3,000 μg/g and from about 500 to 6,000 μg/g for another plant species in the polluted stream reach. The concentration factors in the clean stream reach ranged from about 2 to 20 while they ranged from about 0.02 to 0.7 in the polluted reach.

Fates of Phenols and Chlorophenols

The EPA (1979) stated that the solubility of chlorinated phenols in water solutions is low, but increases when the pH increases. Phenoxide salts are also more soluble than the corresponding phenol in water with neutral pH conditions. Phenol may be biochemically hydroxylated to ortho and paradihydroxybenzenes and readily oxidized to the corresponding benzoquinones. These may in turn react with numerous components of industrial waters, sewerage or other waste streams such as mercaptans, amines, or the -SH, or -NH group of proteins. Phenol has also been shown to be highly reactive to chlorine in dilute solutions over a wide pH range. The chlorination of the phenol to toxic chlorophenols has been demonstrated under conditions similar to those used for disinfection of wastewater effluent.

Pentachlorinated Phenols (PCP)

PCPs is highly soluble in water (EPA 1979). PCPs can undergo photochemical degradation in solutions in the presence of sunlight, with subsequent formation of several chlorinated benzoquinones. Sodium-PCP can be decomposed directly by sunlight with the formation of numerous products. Micro-organisms have also been reported to metabolize PCPs. PCPs have also been reported to persist in warm and moist soils for a period of one year. Therefore, PCPs may also persist for a long time in urban creek sediments.

Bioconcentrations of PCP in aquatic life have been reported in the range of 13 to 1,000 for freshwater and marine invertebrates (EPA 1979).

2,4-Dimethylphenol (2,4-DMP)

2,4-DMP is slightly soluble in water. The EPA (1979) reported a study that showed a bioaccumulation of 2,4-DMP in carp of 16 to 17 mg/g for the whole fish after a 6-hour exposure to water concentrations of about 20,000 μg/L. The total carp content of 2,4-DMP was reduced to less than 10 μg after 1 hour and less than 5 μg after 3 hours after removal from the polluted water. Bluegill bioconcentration factors of 150 for 2,4-DMP were also observed. The half-life of 2,4-DMP in the bluegills was less than 1 day.

Fates of Polycyclic Aromatic Hydrocarbons (PAHs)

The PAH compounds found in urban runoff (most commonly anthracene, fluoranthene and phenanthrene) are formed by incomplete combustion when organic compounds are burned with insufficient oxygen. They are basically insoluble in water. These materials will be adsorbed onto suspended particulates and biota. The dissolved portion of these compounds can undergo direct photolysis at a rapid rate. Biodegradation and biotransformation by benthic organisms of PAH contaminated sediments is believed to be their ultimate fate (Callahan, *et al.* 1979).

There are no studies that have examined the carcinogenic risk associated with the ingestion of PAHs by humans. However, many animal studies have established the wide range of carcinogenicity of PAHs by skin contact and ingestion (Varanasi 1989). The concentrations of PAHs needed to produce cancers can be extremely low. As an example, the PAH concentration associated with a cancer risk level of 10^{-6} is only 9.7 X 10^{-4} μg/L. These low concentrations are not possible to routinely monitor, so “zero” PAH levels are usually set as objectives. Tissue damage and systemic toxicity has also been associated with PAH exposure (PHS 1981).

Because of the low solubility of PAHs in water, biological treatment has little benefit. However, because of their attraction to solids, physical solids separation processes can be very effective in reducing PAH concentrations (PHS 1981). It would be very difficult to sufficiently reduce PAH concentrations from contaminated water to remove the cancer risk associated with their long-term ingestion.

Benzo (a) Anthracene

Verschueren (1983) has summarized much information concerning benzo (a) anthracene. A major source of benzo (a) anthracene is gasoline, with an emission factor as high as 0.5 mg emitted in the exhaust condensate per liter of gasoline consumed. Wood preservative use may also contribute benzo (a) anthracene. The solubility of benzo (a) anthracene in water is about 10 to 45 μg/L. Biodegradation was not observed, but more than half was adsorbed onto waterborne particulates (including aggregates of dead plankton and bacteria) after just 3 hours exposure. Typical domestic sewage effluent values ranged from 0.2 to more than 1 μg/L (in heavily industrialized areas). During heavy rains, sewage concentrations of benzo (a) anthracene increased substantially to more than 10 μg/L. Reported raw sewage values were about 2 and 30 μg/L. Mechanical treatment of the sewage reduced the benzo (a) anthracene concentrations by about 80 percent, while biological treatment removed almost all of the benzo (a) anthracene, leaving less than 0.1 μg/L in the effluent. Oxonation reduced the benzo (a) anthracene concentrations by about 95

percent, while chlorination reduced the concentrations by about 50 percent. Benzo (a) anthracene was reported to be both carcinogenic and mutagenic.

Benzo (b) Fluoranthene

Verschueren (1983) has summarized limited information concerning benzo (b) anthracene. Benzo (b) anthracene is also found in gasolines, in addition to fresh and used motor oils. The automobile emission factor for benzo (b) anthracene is about 20 to 50 μg in the exhaust condensate per liter of gasoline consumed. It is also found in bitumen, an ingredient of roofing compounds. Benzo (b) fluoranthene was found in domestic wastewater effluent in concentrations of about 0.04 to 0.2 μg/L. Raw sewage concentrations were as high as 0.9 μg/L in areas of heavy industry. Typical sewage concentrations were about 0.04 μg/L, but increased to about 10 μg/L during heavy rains. Physical sewage treatment processes reduced benzo (b) anthracene concentrations by 50 to 80 percent, while biological processes allowed almost complete removal. Chlorination alone accounted for about a 33 percent reduction.

Water treatment reduced initial 0.15 μg/L benzo (b) anthracene concentrations by about 70 percent, mostly occurring after filtration. Sedimentation in a storage reservoir only slightly reduced the concentrations. The IARC (1979) has found sufficient evidence of carcinogenicity of benzo (b) anthracene in animals.

Benzo (k) Fluoranthene

Verschueren (1983) has summarized information concerning benzo (k) fluoranthene, as follows. Benzo (k) fluoranthene is found in crude oils, gasolines, and bitumen. Sewage sludges have been found to contain from 100 to 400 μg/L benzo (k) fluoranthene. Domestic sewage effluent can contain from 0.03 to 0.2 μg/L benzo (k) fluoranthene, while sewage in heavily industrialized areas may contain concentrations as great as 0.5 μg/L. During heavy rains, sewage concentrations of benzo (k) fluoranthene increased to more than 4 μg/L. Mechanical sewage treatment reduced concentrations of benzo (k) fluoranthene from 8 to about 2 μg/L. Biological treatment further reduced the concentrations to less than 0.1 μg/L. Chlorination alone reduced the concentrations by about 60 percent, from an initial value of about 70 μg/L.

Benzo (a) Pyrene

Verschueren (1983) has summarized much information concerning benzo (a) pyrene, as follows. Benzo (a) pyrene can be synthesized by various bacteria (including *Escherichia coli*) at a rate of about 20 to 60 μg per dry kg of bacterial biomass. It is also a potential leachate of asphalt and is present in oils and gasolines. Its solubility is about 3 μg/L. It can be degraded in soil that is inoculated with special bacteria, with as much as 80 percent destroyed after eight days. In natural estuarine waters, its degradation rate is only about 2 μg/L destroyed per 1,000 days. Its volatilization half-life is about 1,000 hours (40 days) in waters moving about 1 m/sec with winds of about 2 m/sec. The volatilization half-life extends to about 10,000 hours (400 days) for still water and calm air, and decreases to about 400 hours (20 days) for very violent mixing conditions. About 70 percent of a benzo (a) pyrene mixture, having an initial concentration of 3 μg/L, was adsorbed onto particles after three hours.

Verschueren (1983) also reported that benzo (a) pyrene is present in domestic sewage effluents at concentrations of about 0.05 μg/L and in raw sewage sludge at concentrations of about 400 μg/L. From 90 to 99 percent removal was found using activated carbon water treatment in waters having initial concentrations of 5 to 50 μg/L. Chlorination (6 mg/L Cl_2) also reduced initial concentrations of 50 μg/L benzo (a) pyrene by 98 percent. Mechanical wastewater treatment reduced benzo (a) pyrene concentrations by about 65 to 95 percent, and biological treatment further reduced these concentrations by another 50 to 99 percent. Bioaccumulation factors of benzo (a) pyrene in oysters, compared to water concentrations, varied from about 200 to 3000. The depuration half-life was about 18 days after the oysters were removed from contaminated water. Benzo (a) pyrene is a known carcinogen and mutagen.

Fluoranthene

Water solubility of fluoranthene is about 200 μg/L. It was the only PAH found in an EPA drinking water survey of 110 samples in 1977 (Harris 1982). Harris also reported that sedimentation processes was the most important removal mechanism for fluoranthene, with removals of about 65 percent. Biological treatment increased the removal to about 95 percent. Laboratory work indicated that biological degradation of fluoranthene is not significant, but that filtration readily removes fluoranthene.

Verschueren (1983) has also summarized much information concerning fluoranthene. Fluoranthene is found in crude oils, gasolines, motoroils and wood preservatives. It is found in the exhaust condensate of gasoline engines at a rate of about 1 mg per liter of gasoline consumed. It is found in domestic sewage effluents in concentrations of about 0.01 to 2.5 μg/L, and in raw sewage sludge at concentrations of up to about 1200 μg/L. In one case, sewage effluent had concentrations of fluoranthene of about 0.4 μg/L during dry weather, but increased to about 16 μg/L during heavy rains. Mechanical sewage treatment reduced initial fluoranthene concentrations of 3 to 45 μg/L by about 60 percent, and biological treatment further reduced the fluoranthene by another 80 percent. Water treatment reduced the raw water fluoranthene concentrations of 0.15 μg/L by about 50 percent by filtration, and by another 50 percent by chlorination. Storage in a reservoir reduced the fluoranthene concentrations by less than 10 percent. Oysters bioconcentrated fluoranthene by 700 to 10,000 times compared to the water concentrations. The depuration half-life was about 5 days after the oysters were placed in clean water. Several studies have shown that fluoranthene is a potent carcinogen which substantially increases the carcinogenic potential of other known carcinogens (EPA 1980).

Naphthalene

Naphthalene was one of many compounds investigated by the EPA's "reportable quantities" program. Naphthalene is the single most abundant component of coal tar, and is present in gasolines and insecticides (especially moth balls). Data indicates that naphthalene is only moderately toxic and would be readily removed by physical and biological treatment processes.

Howard (1989) also summarized much information concerning naphthalene. At about 32 mg/L, the solubility of naphthalene is quite high compared to other PAHs. Besides the potential sources mentioned above, naphthalene may also originate from natural uncontrolled combustion, such as forest fires, along with house fires in urban areas. However, vehicle emissions are probably the most significant urban source of naphthalene. In rapidly flowing streams, volatilization accounted for about 80 percent and sediment adsorption accounted for about 15 percent of the removal of naphthalene from the water column. In deeper and slower moving water, biodegradation (having a half-life of about 1 to 9 days) was probably the most important fate mechanism. Adsorption onto sediments is probably only a significant removal mechanism in waters having high solids concentrations and slow moving waters, such as in lakes. Photolysis degrades naphthalene in surface waters with a half-life of about 3 days, but is much less efficient at deeper waters. In 5 meter deep water, the photolysis half-life was about 550 days. The presence of algae can substantially increase the photolysis rate of naphthalene.

Howard (1989) reported that naphthalene in water biodegrades after a short acclimation period. Bacteria can only utilize soluble naphthalene, however. Biodegradation of sediment bound naphthalene is 8 to 20 times faster than in water. In heavily contaminated sediment, the biodegradation half-life is about 5 hours, but can be longer than 3 months in uncontaminated sediments. No anaerobic biodegradation of naphthalene in laboratory tests was observed after 11 weeks. Naphthalene is bioconcentrated to a moderate degree in aquatic invertebrates, but the depuration rate is quite rapid after removal to unpolluted water. Naphthalene is also readily metabolized by fish. Naphthalene is moderately adsorbed by soils and sediments, but at a much less extent than for other PAHs. It is weakly sorbed by sandy soils, and tests have found that less than one percent was sorbed by particulate matter in a variety of surface waters. The evaporation half-life of naphthalene in surface waters is about 5 hours for moderate current and wind conditions. The expected half-life of naphthalene in surface waters due to evaporation losses is expected to be about 50 hours in rivers and 200 hours in lakes.

Verschueren (1983) has also summarized much information concerning naphthalene. Additional major urban naphthalene sources mentioned included detergents, solvents, and asphalt. Microbial degradation rates were about 0.1 μg/L per day. Less than one percent of the naphthalene was sorbed to particles in water after 3 hours exposure. Ion exchange water treatment was close to 100 percent effective and the evaporation half-life of naphthalene was reported to be about 7 hours at a water depth of 1 meter. Bioaccumulation factors of oysters was about 5,000 compared to water concentrations, but the depuration half-life was about 2 days when moved to clean water. Carcinogenicity and mutagenicity tests were negative for naphthalene.

Phenanthrene

Verschueren (1983) summarized limited information concerning phenanthrene. Its solubility in water is relatively high for a PAH, being about 1,000 μg/L. It is found in crude oil, gasoline, and coal tar. Its emission factor in gasoline engine exhaust condensate is about 2.5 mg per liter of gasoline consumed. Carcinogenicity and mutagenicity tests were negative for phenanthrene.

Pyrene

Verschueren (1983) summarized some information concerning pyrene. Pyrene is found in crude oils, gasolines, motor oils, bitumen, coal tar, and wood preservatives. The emission factor of pyrene from gasoline engine exhaust condensates is about 2.5 mg per liter of gasoline consumed. Its solubility in water is about 160 μg/L. It was degraded in seawater by 85 percent from an initial concentration of 365 μg/L after 12 days. Pyrene is discharged in domestic wastewater effluents at concentrations of about 2 μg/L. In one study, dry weather raw sewage had pyrene concentrations of about 0.2 μg/L, while pyrene concentrations in raw sewage during a heavy rain increased to about 16 μg/L. Pyrene can be photo-degraded from soils by UV radiation. Chlorination at 6 mg/L chlorine for 6 hours decreased initial pyrene concentrations of 27 μg/L by about 25 percent. Mechanical wastewater treatment processes decreased pyrene concentrations by about 80 percent, and biological processes further decreased the pyrene concentrations by about 98 percent. Reservoir storage of river water decreased pyrene concentrations by about 25 percent. Filtration further decreased the concentrations by another 40 percent, and chlorination further decreased the pyrene concentrations by another 60 percent. Mutagenicity test results of pyrene were negative, but pyrene is considered a human carcinogen.

Fates of Insecticides

Chlordane

Chlordane is a non-systemic insecticide and its registered use has been cancelled by the EPA. The food chain concentration potential of chlordane is considered high. The EPA has also revoked chlordane residual tolerances in foods (Federal Register, Vol. 51, No. 247, page 46665, Dec. 24, 1986).

Verschueren (1983) summarized some information concerning chlordane. Its solubility in water is about 60 μg/L. The persistence of chlordane in water in sealed jars exposed to sunlight indicated a 15 percent decrease after 8 weeks. Chlordane was reduced by 75 to 100 percent from soils after 3 to 5 years. Bioconcentration of chlordane in algae was rapid and was as high as 100,000 compared to water concentrations. Bioconcentration factors of chlordane was 7300 in oysters, 100 in frogs, and about 1000 in goldfish. The depuration half-lifes of chlordane was about 4 weeks for the frog and goldfish, but was as long as 20 weeks in other fish.

Fates of Phthalate Esters

Butyl Benzyl Phthalate

Verschueren (1983) summarized some information concerning butyl benzyl phthalate. BBP is used chiefly as a plasticizer in polyvinylchlorides. It is not tightly bound to the plastic and is readily lost and enters aqueous solutions in contact with the plastic. Its solubility in water is about 3 mg/L. The typical average

concentration of BBP in natural U.S. waters is about 0.4 μg/L, but was reported to be as high as 4.1 μg/L. BBP does undergo biodegradation with relatively complete removals within one month. Biodegradation using activated sludge from a wastewater treatment plant was reported to be 99 percent effective after 48 hours. Biodegradation in natural river waters was about 80 percent effective after one week of exposure. Photodegradation and chemical degradation (through hydrolysis) of BBP is much less effective, with reported half-lifes of greater than 100 days. The bioconcentration factor of BBP was more than 650 for a bluegill. The depuration half-life was less than two days after removal to uncontaminated water.

Fates of Ethers

Bis (2-chloroethyl) Ether

Howard (1989) summarized information from various environmental fate references for bis (2-chloroethyl) ether. BCEE solubility in water is about 1 mg/L. It also was adsorbed at low values onto fine sand, implying that it would be highly mobile in soils and could leach rapidly to groundwaters. BCEE may degrade in soils, but acclimation may be necessary. The volatilization half-life of BCEE in streams and lakes was estimated to be about 4 days, while the volatilization half-life of BCEE in lakes was estimated to be about 180 days. Photolysis is not expected to be important, but biodegradation can reduce BCEE concentrations by 50 percent over 35 days. After acclimation, only 9 days was required to remove 50 percent of the BCEE by biodegradation. The bioconcentration factor of BCEE in bluegills was only about 11 after two weeks exposure, implying that bioconcentration of BCEE was probably not significant for aquatic organisms.

Verschueren (1983) also summarized some information concerning bis (2-chloroethyl) ether. BCEE is used as a fumigant, and as an ingredient in solvents, insecticides, paints, lacquers and varnishes. It is also formed by the chlorination of waters that contain ethers. Conventional water treatment removed about 80 percent of the BCEE, while activated carbon when added to conventional water treatment processes removed all of the BCEE.

Bis (2-chloroisopropyl) Ether

Basu and Bosch (1982), in their summary of the literature concerning BCIE, reported that hydrolysis is probably its most significant transformation process in aquatic systems. The overall half-life of BCIE was estimated to vary between 3 and 30 days in rivers and 30 to 300 days in lakes and groundwaters. Evaporation half-lifes in surface waters were estimated to be similar to the hydrolysis half-lifes. Leaching of BCIE is expected to be important in soils. They also reported that BCIE is unlikely to be significantly sorbed by plants.

Verschueren (1983) summarized limited information concerning bis (2-chloroisopropyl) ether. The solubility of BCIE was reported to be 1700 mg/L. Activated carbon treatment of contaminated water resulted in almost complete removal of BCIE. Conventional water treatment reduced the BCIE water content from 24 μg/L to below detection limits. BCIE was found not to be carcinogenic during rat tests (HEW 1979).

Fates of Other Organic Toxicants

1,3-Dichlorobenzene

The solubility of 1,3-DCP is about 125 mg/L and bacterial degradation disturbed the chemical ring structure within 96 hours (Verschueren 1983). Neal and Basu (1982) reviewed literature pertaining to the aquatic fate of 1,3-DCP. They reported that biotransformation is the most significant transformation process, with a half-life of about 580 days in a river system. Sedimentation and volatilization processes decrease 1,3-DCP concentration in half over about 1.5 days in rivers and 50 days in lakes.

Howard (1989) summarized many 1,3-DCP references. 1,3-DCP may be moderately to tightly adsorbed to soils, but leaching can occur. Biodegradation under aerobic conditions and volatilization from soil may be important. Adsorption of 1,3-DCP to sediment is a major environmental fate mechanism. 1,3-DCP is also

quite volatile from water, with a half-life of about 4 hours in moderately turbulent streams. It may biodegrade under aerobic conditions in water, but is not expected to degrade under anaerobic conditions (such as in polluted sediments). Bioconcentration factors of 90 to 740 have been reported. Hydrolysis, oxidation, and direct photolysis are not expected to be important fate mechanisms of 1,3-DCP in the aquatic environment.

Appendix B - Statistical Basis for Sampling

Determination of the Number of Samples Needed

The main areas where the use of statistics is important in wet weather flow studies is in designing the field experiments (specifically in selecting the specific experimental design for the experiments), determining the sampling effort, and in data evaluation. The following discussion is only intended as a summary of important issues in these areas. Some helpful tools are presented here and examples are given for their use. Important references that should be consulted for additional information on applied statistics include *Statistical Methods for Environmental Pollution Monitoring* (Gilbert 1987) which contains a good summary of sampling designs and methods to identify trends, unusual conditions, etc., *Statistics for Experimenters* (Box, *et al*. 1978) which contains detailed descriptions of basic statistical methods for comparing experimental conditions and model building, and *Statistics for Environmental Engineers* (Berthouex and Brown 1994) which contains clarifications for many statistical procedures that are commonly misused.

Experimental Design and Sampling Plans

The main objectives of most environmental monitoring studies may be divided into two general categories: characterization, and/or comparisons. Characterization pertains to quantifying a few simple attributes of the parameter of interest. As an example, the concentration of copper in the sediment near an outfall may be of concern. The most important question would be “What is the most likely concentration of the copper?” Other questions of interest include changes in the copper concentrations between surface deposits and buried deposits, or in upstream vs. downstream locations. These additional questions are considered in the second category, namely comparisons. Other comparison questions may concern relating the observed copper concentrations with criteria or standards. Finally, most researchers would also be interested in quantifying trends in the copper concentrations. These extend beyond the above comparison category, as trends usually consider more than just two locations or conditions. Examples of trend analyses would examine copper gradients along the receiving stream, or trends of copper concentrations with time. Another type of analysis related to comparisons is the identification of hot spots, where the gradient of concentrations in an area is used to identify areas having unusually high concentrations.

An adequate experimental design enables a researcher to efficiently investigate a study hypothesis. The results of the experiments will theoretically either prove or disprove the hypothesis. In reality, the experiments will tend to shed some light on the real problem and will probably result in many more questions that need addressing. In many cases, the real question may not have even been recognized initially. Therefore, even though it is very important to formally have a study hypothesis and appropriate experimental design, it is just as important to save sufficient study resources to enable additional unanticipated experiments. In this discussion, sampling plans and specific statistical tools will be briefly examined.

Experimental design covers several aspects of a monitoring program. The following list is a simple outline of a typical experimental design sequence:

- Clearly define objectives (hypothesis to be tested, equation or model to be used, etc.).
- Estimate the time and space variabilities of the parameters of interest (assumed based on prior knowledge,
  or other methods).
- Collect information on the physical conditions of the system to be studied (watershed characteristics,

etc.).
- Determine sampling plan (strata and relationships that need to be defined).
- Determine the statistical procedures that will be used to analyze the data (including field data sheets and laboratory QA/QC plan).
- Determine the number of samples needed (when and where, with budget restraints).
- Determine sampling specifics (volumes, bottle types, preservatives, samplers to be used, etc.).
- Carry out the sampling effort.
- Evaluate the data.
- Conduct follow-up monitoring that will be designed after initial activities.

The most important aspect is being able to write down the study objectives and why the data is needed. The quality of the data (accuracy of the measurements) must also be known. Allowable errors need to be identified based on how the information will change a conclusion. Specifically, how sensitive is the data that is to be collected in defining the needed answer?

All sampling plans attempt to obtain certain information (usually average values, totals, ranges, etc.) of a large population by sampling and analyzing a much smaller sample. The first step in this process is to select the sampling plan and then to determine the appropriate number of samples needed. Many sampling plans have been well described in the environmental literature. Gilbert (1987) has defined the following four main categories, plus subcategories, of sampling plans:

- Haphazard sampling. Samples are taken in a haphazard (not random) manner, usually at the convenience of the sampler when time permits. Especially common when the weather is pleasant. This is only possible with a very homogeneous condition over time and space, otherwise biases are introduced in the measured population parameters. It is therefore not recommended because of the difficulty of verifying the homogeneous assumption. This is the most common sampling strategy used when volunteers are used for sampling, unless the grateful agency is able to spend sufficient time to educate the volunteer samplers to the problems of this type of sampling and to specify a more appropriate sampling strategy.

- Judgment sampling. This strategy is used when only a specific subset of the total population is to be evaluated, with no desire to obtain “universal” characteristics. The target population must be clearly defined (such as during wet weather conditions only) and sampling is conducted appropriately. This could be the first stage of later, more comprehensive, sampling of other target population groups (multistage sampling).

- Probability sampling. Several subcategories of probability sampling have been described:

- simple random sampling. Samples are taken randomly from the complete population. This usually results in total population information, but it is usually inefficient as a greater sampling effort may be required than if the population was sub-divided into distinct groups. Simple random sampling doesn’t allow information to be obtained for trends or patterns in the population. This method is used when there is no reason to believe that the sample variation is dependent on any known or measurable factor.

- stratified random sampling. This may the most appropriate sampling strategy for most wet weather flow studies, especially if combined with an initial limited field effort as part of a multistage sampling effort. The goal is to define strata that results in little variation within any one strata, and great variation between different strata. Samples are randomly obtained from several population groups that are assumed to be internally more homogeneous than the population as a whole, such as separating an annual sampling effort by season, lake depth, site location, habitat category, rainfall depth, land use, etc. This results in the individual groups having smaller variations in the characteristics of interest than in the population as a whole. Therefore, sample efforts within each group will vary, depending on the variability of characteristics for each group, and the total sum of the sampling effort may be less than if the complete population was sampled as a whole. In addition, much additional useful information is likely if the groups are shown to actually be different.

- systematic sampling. This approach is most useful for basic trend analyses, where evenly spaced samples are collected for an extended time. Evenly spaced sampling is also most efficient when trying to find localized hot spots that randomly occur over an area. Gilbert (1987) present guidelines for spacing of sampling locations for specific project objectives relating to the size of the hot spot to be found. Spatial gradient sampling is a systematic sampling strategy that may be worthy of consideration when historical information implies a aerial variation of conditions in a river or other receiving water. One example would be to examine the effects of a point source discharge on receiving sediment quality. A grid would be described in the receiving water in the discharge vicinity whose spacing would be determined by preliminary investigations.

- Search sampling. This sampling plan is used to find specific conditions where prior knowledge is available, such as the location of a historical (but now absence) waste discharger affecting a receiving water. Therefore, the sampling pattern is not systematic or random over an area, but stresses areas thought to have a greater probability of success.

Box, *et al*. (1978) contains much information concerning sampling strategies, specifically addressing problems associated with randomizing the experiments and blocking the sampling experiments. Blocking (such as in paired analyses to determine the effectiveness of a control device, or to compare upstream and downstream locations) eliminates unwanted sources of variability. Another way of blocking is to conduct repeated analyses (such for different seasons) at the same locations. Most of the above probability sampling strategies should include randomization and blocking within the final sampling plans (as demonstrated in the following example and in the use of factorial experiments).

Example Use of Stratified Random Sampling Plan

Street dirt samples were collected in San Jose, CA, during an early EPA project to identify sources of urban runoff pollutants (Pitt 1979). The samples were collected from narrow strips, from curb to curb, using an industrial vacuum. Many of these strips were to be collected in each area and combined to determine the dust and dirt loadings and their associated characteristics (particle size and pollutant concentrations). Each area (strata) was to be frequently sampled to determine the changes in loadings with time and to measure the effects of street cleaning and rains in reducing the loadings. The analytical procedure used to determine the number of subsamples needed for each composite sample involved weighing individual subsamples in each study area to calculate the coefficient of variation (COV = standard deviation/mean) of the street surface loading. The number of subsamples necessary (N),depending on the allowable error (L), were then determined. An allowable error value of about 25 percent, or less, was needed to keep the precision and sampling effort at reasonable levels. The formula used (after Cochran 1963) was:

$$N = 4\sigma^2/L^2$$

With 95 percent confidence, this equation estimates the number of sub-samples necessary to determine the true mean value for the loading within a range of ±L. As to be shown in the following discussions, more samples are required for a specific allowable error as the COV increases. Similarly, as the allowable error decreases for a specific COV, more samples are also required. Therefore, with an allowable error of 25 percent, the required number of subsamples for a study area with a COV of 0.8 would be 36.

Initially, individual samples were taken at 49 locations in the three study areas to determine the loading variabilities. The loadings averaged about 2700 lb./curb-mile in the Downtown and Keyes Street areas, but were found to vary greatly within these two areas. The Tropicana area loadings were not as high, and averaged 310 lb./curb-mile. The Cochran (1963) equation was then used to determine the required number of subsamples in each test area. The data were then examined to determine if the study areas should be divided into meaningful test area groups.

The purpose of these divisions was to identify a small number of meaningful test area-groupings (strata) that would require a reasonable number of subsamples and to increase the usefulness of the test data by identifying important groupings. Five different strata were identified for this research: two of the areas

were divided by street texture conditions (good vs. poor) into two separate strata each, while the other area was left undivided. The total number of individual sub-samples for all five areas combined was 111, and the number of subsamples per strata ranged from 10 to 35. In contrast, 150 subsamples would have been needed if the individual areas were not sub-divided. Sub-dividing the main sampling areas into separate strata not only resulted in a savings of about 25% in the sampling effort, but also resulted in much more useful information concerning the factors affecting the values measured. The loading variations in each strata were re-examined seasonally and the sampling effort was re-adjusted accordingly.

Number of Samples Needed to Characterize Conditions

An important aspect of any research is the assurance that the samples collected represent the conditions to be tested and that the number of samples to be collected are sufficient to provide statistically relevant conclusions. Receiving water studies frequently include objectives to characterize various chemical, biological, and physical parameters of the waterbody itself, or influencing features (meteorological, discharges, watershed, etc.). An experimental design process can be used that estimates the number of needed samples based on the allowable error, the variance of the observations, and the degree of confidence and power needed for each parameter. An equation that can be used (after Cameron, undated) is as follows:

$$n = [COV(Z_{1-\alpha} + Z_{1-\beta})/(error)]^2$$

where n = number of samples needed

α= false positive rate (1-α is the degree of confidence. A value of α of 0.05 is usually considered statistically significant, corresponding to a 1-α degree of confidence of 0.95, or 95%.)

β= false negative rate (1-β is the power. If used, a value of β of 0.2 is common, but it is frequently ignored, corresponding to a β of 0.5.)

$Z_{1-\alpha}$ = Z score (associated with area under normal curve) corresponding to 1-α. If α is 0.05 (95% degree of confidence), then the corresponding $Z_{1-\alpha}$ score is 1.645 (from standard statistical tables).

$Z_{1-\beta}$= Z score corresponding to 1-β value. If β is 0.2 (power of 80%), then the corresponding $Z_{1-\beta}$ score is 0.85 (from standard statistical tables). However, if power is ignored and β is 0.5, then the corresponding $Z_{1-\beta}$ score is 0.

error = allowable error, as a fraction of the true value of the mean

COV = coefficient of variation, the standard deviation divided by the mean (Data set assumed to be normally distributed.)

This equation is only approximate, as it requires that the data set be normally distributed. However, if the coefficient of variation (COV) values are low (less than about 0.4), then there is likely no significant difference in the predicted sampling effort. This equation is only appropriate as an approximation in many cases, as normal distributions are rare (log-normal distributions are appropriate for most water quality parameters) and the COV values are typically relatively large (closer to 1). The presentation of the results and the statistical procedures used to evaluate the data need to consider the exact degree of confidence of the measured values.

Figure 3 (Pitt and Parmer 1995) is a plot of this equation showing the approximate number of samples needed for an α of 0.05 (degree of confidence of 95%), and a β of 0.2 (power of 80%). As an example, if an allowable error of about 25% is desired and the COV is estimated to be 0.4, then about 20 samples would have to be analyzed. The samples could be composited and a single analysis conducted, but this would not allow the COV assumption to be confirmed, or the actual confidence range of the concentration

to be determined. The use of stratified random sampling can usually be used to advantage by significantly reducing the COV of the sub-population in the strata, requiring fewer samples for characterization.

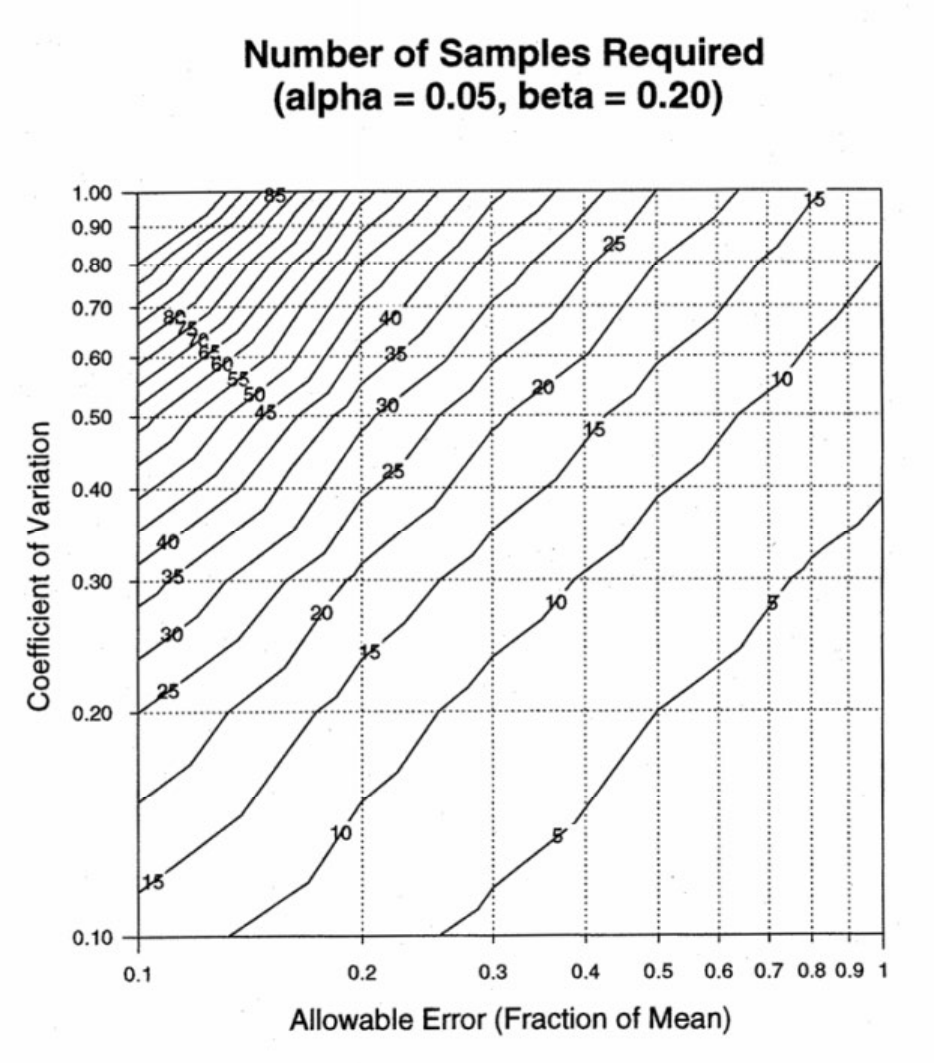


Figure 3. Sample Requirements for Confidence of 95% (α= 0.05) and Power of 80% (β= 0.20) (Pitt and Parmer 1995).

Errors

Unfortunately, there are many errors associated with a receiving water study. Errors associated with too few (or too many) samples for a parameter of interest is only one category. Sampling and analytical errors may also be significant and would add to these other errors. Hopefully, the collective sum of all errors is known (through QA/QC activities and adequate experimental design) and manageable. An important aspect of a monitoring program is recognizing the levels of errors and consider the resulting uncertainties in developing recommendations and conclusions.

Generally, errors can be divided into precision and bias problems. Both of these errors, either together or separately, have dramatic effects on the final conclusions of a study. Figure 4 (Gilbert 1987) shows the effects of these errors. Bias is a measure of how close the measured median value is to the true median

value, while precision is a measure of how “fuzzy” the median estimate is (the repeatability of the analyses and is used to determine the confidence of the measurements).

Errors in decision making are usually divided into type 1 (α: alpha) and type 2 (β: beta) errors:

α (alpha) (type 1 error) - a false positive, or assuming something is true when it is actually false. An example would be concluding that a tested water was adversely contaminated, when it actually was clean. The most common value of α is 0.05 (accepting a 5% risk of having a type 1 error). Confidence is 1-α, or the confidence of not having a false positive.

β (beta) (type 2 error) - a false negative, or assuming something is false when it is actually true. An example would be concluding that a tested water was clean when it actually was contaminated. If this was an effluent, it would therefore be an illegal discharge with the possible imposition of severe penalties from the regulatory agency. In most statistical tests, β is usually ignored (if ignored, β is 0.5). If it is considered, a typical value is 0.2, implying accepting a 20% risk of having a type 2 error. Power is 1-β, or the certainty of not having a false negative.

Example Showing Improvement of Mean Concentrations with Increasing Sampling Effort
Many stormwater discharge samples were obtained from two study areas during the Bellevue, Washington, Urban Runoff Program (Pitt 1984). The runoff from each drainage area was affected by different public works stormwater control practices and the outfall data were compared to identify if any runoff quality improvements were associated with this effort. This data offers an opportunity to examine how increasing numbers of outfall data decreased the uncertainty of the overall average concentrations of the stormwater pollutants. Table 3 shows how the accumulative average of the observed concentrations eventually become reasonable steady, but only after a significant sampling effort. As an example. The average on the first three observations would result in an EMC (Event-mean concentration) that would be in error by about 40%. It would require more than 15 samples before the average value is consistently less than 10% from the seasonal average value which only had a total population of 25 storm events, even with the relatively small COV value of 0.65.

Table 3. Event-Mean Concentrations for Series of Storm Samples in Bellevue, Washington (Pitt 1985)

Storm #	Lead Concentration (mg/L)	Moving Average Concentration (EMC)	Error from Seasonal Average (percent)
1	0.53	0.53	119
2	0.10	0.32	30
3	0.38	0.34	39
4	0.15	0.29	20
5	0.12	0.26	6
6	0.12	0.23	-3
7	0.56	0.28	16
8	0.19	0.27	11
9	0.38	0.28	16
10	0.23	0.28	14
11	0.20	0.27	11
12	0.39	0.28	16
13	0.53	0.30	24
14	0.05	0.28	16
15	0.26	0.28	16
16	0.05	0.27	10
17	0.05	0.25	5
18	0.39	0.26	8
19	0.28	0.26	8
20	0.10	0.25	5
21	0.29	0.25	6
22	0.18	0.25	4
23	0.31	0.25	5
24	0.10	0.25	2
25	0.10	0.24	0

Albert and Horwitz (1988) points out that taking averages leads to a tighter distribution. As shown above, the extreme values have little effect on the overall average, even with a relatively few observations (for a Gaussian distribution). The reduction in the standard deviation is proportional to $1/n^{0.5}$, for n observations. Even if the population is not Gaussian, the averages tend to be Gaussian-like. In addition, the larger the sample size, the more Gaussian-like is the population of averages.

Number of Samples Needed for Comparisons between Different Sites or Times

The comparison of paired data sets is commonly used when evaluating the differences between two situations (locations, times, practices, etc.). A related equation to the one given previously can be used to estimate the needed samples for a paired comparison (Cameron, undated):

$$n = 2\,[(Z_{1-\alpha} + Z_{1-\beta})/(\mu_1 - \mu_2)]^2\sigma^2$$

where:

α = false positive rate ($1-\alpha$ is the degree of confidence. A value of α of 0.05 is usually considered statistically significant, corresponding to a $1-\alpha$ degree of confidence of 0.95, or 95%)

β = false negative rate ($1-\beta$ is the power. If used, a value of β of 0.2 is common, but it is frequently ignored, corresponding to a β of 0.5.)

$Z_{1-\alpha}$ = Z score (associated with area under normal curve) corresponding to $1-\alpha$

$Z_{1-\beta}$ = Z score corresponding to $1-\beta$ value

μ_1 = mean of data set one

μ_2 = mean of data set two

σ = standard deviation (same for both data sets, same units as μ. Both data sets are also assumed to be
normally distributed.)

This equation is also only approximate, as it requires that the two data sets be normally distributed and have the same standard deviations. As noted previously, many parameters of interest in receiving water studies are likely closer to being log-normally distributed. Again, if the coefficient of variation (COV) values are low (less than about 0.4), then there is probably no real difference in the predicted sampling effort.

Figure 9 (Pitt and Parmer 1996) is a plot of this equation (normalized using COV and differences of sample means) showing the approximate number of sample pairs needed for an α of 0.05 (degree of confidence of 95%), and a β of 0.2 (power of 80%). As an example, twelve sample pairs will be sufficient to detect significant differences (with at least a 50% difference in the parameter value) for two locations, if the coefficient of variations are no more than about 0.5.

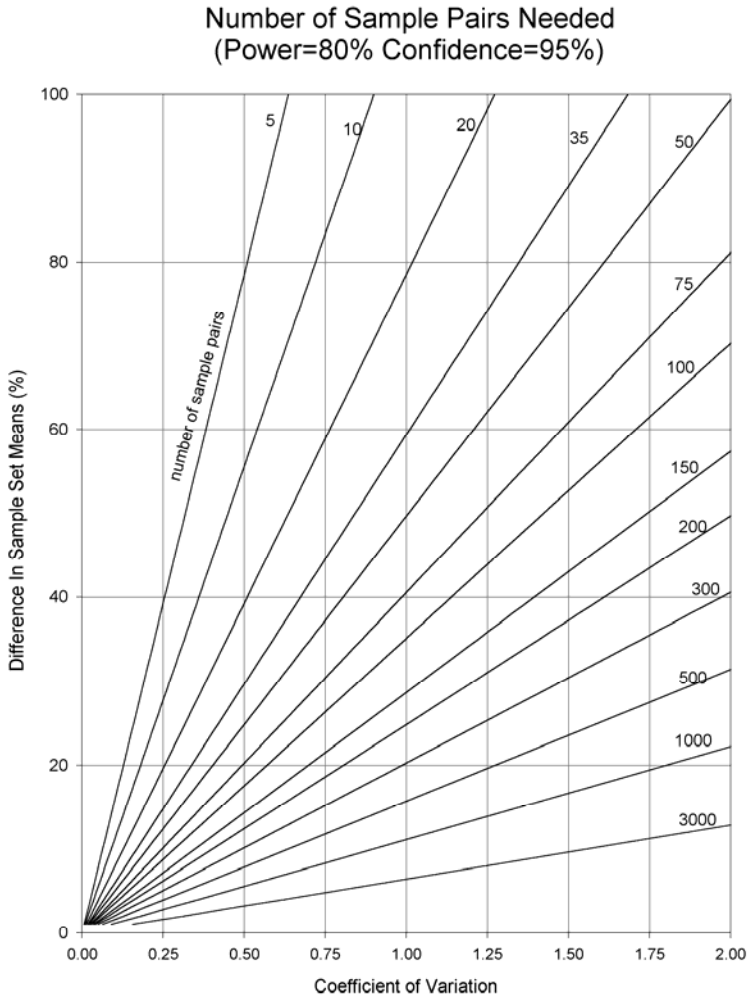


Figure 9. Sample Effort Needed for Paired Testing (Power of 80% and Confidence of 95%) (Pitt and Parmer 1995).

Need for Probability Information and Confidence Intervals

The above discussions presented information mostly pertaining to a simple characteristic of the population being sampled: the "central tendency", usually presented as the average, or mean, of the observations. However, much greater information is typically needed, especially when conducting statistical analyses of the information. Information concerning the probability distribution of the data (especially variance) was used previously as it affected sampling effort. However, many more uses of the probability distributions exist. Albert and Horwitz (1988) state that the researcher must be aware of how misleading an average value alone can be, because the average tells nothing about the underlying spread of values. Berthouex and Brown (1994) also point out the importance of knowing the confidence interval (and the probability) of a statistical conclusion. It can be misleading to simply state that the results of an analysis is significant (implying that the null hypothesis, the difference between the means of two sets of data is zero, is rejected at the 0.05 level), for example, when the difference may not be very important. It is much more informative to present the 95% confidence interval of the difference between the means of the two sets of data.

Data Analysis Methods

This discussion presents several interesting aspects of common statistical analyses of collected data from receiving water studies. Exploratory data analyses is a very useful tool for preliminary evaluations of historical data needed to help design data gathering experiments, and, it should also be used as the first step in evaluating newly collected data. The comparison of data from multiple situations (upstream and downstream of an outfall, summer vs. winter observations, etc.) is a very common experimental objective.

Similarly, the use of regression analyses is also a very common statistical tool for receiving water investigations. Trend investigations of water quality or biological conditions with time are also commonly conducted. The experimental design determines the location and conditions of the sampling for these statistical objectives, but several errors are commonly made when conducting the statistical evaluations of the collected data. Basic features and recommended procedures of these important statistical tests are therefore summarized in the following discussions.

Determination of Outliers

Outliers in data collection can be recognized in the tails of the probability distributions. Observations that do not perfectly fit the probability distributions in the tails are commonly considered outliers. They can be either very low, or very high values. These values always attract considerable attention because they don't fit the mathematical probability distributions exactly and are usually assumed to be flawed and are then discarded. Certainly, these values (like any other suspect values) requires additional evaluation to confirm that simple correctable errors (transcription, math, etc.) are not responsible. If no errors are found, then these values should be included in the data analyses as they represent rare conditions that may be very informative.

Analytical results less than the practical quantification limit (PQL) or the method detection limit (MDL) need to be flagged, but the result (if greater than the instrument detection limit, or IDL) should still be used in most of the statistical calculations. In some cases, the statistical test procedures can handle some undetected values with minimal modifications. In most cases, however, commonly used statistical procedures behave badly with undetected values. In these cases, results less than the IDL should be treated according to Berthouex and Brown (1994). Generally, the statistical procedures should be used twice, once with the LDV equal to zero, and again with the LDV equal to the IDL. This procedure will determine if a significant difference in conclusions would occur with handling the data in a specific manner. In characterizing studies, it is useful to report the frequency of detection (and the detection limit) and then present the basic descriptive statistics on only the detected values.

Similarly, unusually high values need to be critically examined to identify any possible errors. In most cases, the sample should be re-evaluated. It is difficult to reject wet weather constituent observations solely because they are unusually high, as wet weather flows can easily have wide ranging constituent observations. High values should not automatically be considered as outliers and therefore worthy of rejection, but as rare and unusual observations that may shed some light on the problem.

Exploratory Data Analyses

Exploratory data analyses (EDA) is an important tool to quickly review available data before a specific data collection effort is initiated. It is also an important first step in summarizing collected data to supplement the specific data analyses associated with the selected experimental designs. A summary of the data's variation is most important and can be presented using several simple graphical tools. *The Visual Display of Quantitative Information* (Tufte 1983) is a beautiful book with many examples of how to and how not to present graphical information. *Envisioning Information*, also by Tufte (1990) supplements his earlier book. Another important reference for basic analyses is *Exploratory Data Analysis* (Tukey 1977) which is the classic book on this subject and presents many simple ways to examine data to find patterns and relationships. Cleveland (1993 and 1994) has also published two books related to exploratory data analyses: *Visualizing Data*, and *The Elements of Graphing Data*.

Probability Plots

The most basic exploratory data analysis method is to prepare a probability plot of the available data. The plots indicate the possible range of the values expected, their likely probability distribution type, and the data variation. It is difficult to recommend another method that results in so much information using the data available. Histograms, for example, cannot accurately indicate the probability distribution type very accurately, but they more clearly indicate multi-modal distributions. The observations are ranked in ascending order and probability values are calculated for each observation using the following formula:

$$P = (i - 0.5)/n$$

where "i" is the rank position and "n" is the total number of observations. If 11 observations are available, the 6^{th} ranked value would have a probability of 0.50 (50%) using the above formula. The values and corresponding probability positions are plotted on special normal-probability paper. This paper has a y-axis whose values are spread out for the extreme small and large probability values. When plotted on this paper, the values form a straight line if they are Normally (Gaussian) distributed. If the points do not form an acceptably straight line, they can then be plotted on log-normal probability paper (or the data observations can be log transformed and plotted on normal probability paper). If they form a straight line on the log-normal plot, then the data is log-normally distributed. Other data transformations are also possible for plotting on normal-probability paper, but these two (normal and log-normal) usually are sufficient for most wet weather data analyses.

Generally, water quality observations do not form a straight line on normal probability paper, but do (at least from about the 10 to 90 percentile points) on log-normal probability paper. This indicates that the samples have a log-normal distribution and many parametric statistical tests can be used, but only after the data is log-transformed. These plots indicate the central tendency (median) of the data, along with their possible distribution type and variance (the steeper the plot, the smaller the COV and the flatter the slope of the plot, the larger the COV for the data). Multiple data sets can also be plotted on the same plot (such as for different sites, different seasons, different habitats, etc.) to indicate obvious similarities (or differences) in the data sets. Most statistical methods used to compare different data sets require that the sets have the same variances. Similar variances would be indicated by generally parallel plots on the probability paper.

Digidot Plot

Berthouex and Brown (1994) point out that since the best way to display data is with a plot, it makes little sense to present the data in a table. They highly recommend a digidot plot, developed by Hunter (1988) based on Tukey (1977), as a basic presentation of characterization data. This plot indicates the basic distribution of the data, shows changes with time, and presents the actual values, all in one plot. A data table is therefore not needed in addition to the digidot plot. A stem and leaf plot of the data is presented as the y-axis and the data are presented in a time series (in the order of collection) along the x-axis. The stem and leaf plot is constructed by placing the last digit of the value on the y-axis between the appropriate tic marks. The value 47 is represented with a 7 placed in the division between 45 and 50. Similarly, 33 is represented with a 3 placed in the division between 30 and 35. Values from 30 to 34 are placed between the 30 and 35 tic marks, while values from 35 to 39 are placed between the 35 and 40 tic marks. Simultaneously, the values are plotted in a time series in the order of collection. This plot can therefore be constructed in real time as the data is collected and obvious trends with time can be noted. This plot also presents the actual numerical data that can also be used in later statistical analyses.

Grouped Box and Whisker Plots

Another primary exploratory data analysis tool, especially when differences between sample groups are of interest, is the use of grouped box and whisker plots. Examples of their use include examining different sampling locations (such as above and below a discharge), influent and effluent of a treatment process, different seasons, etc. If the 75 and 25 percentile lines of the boxes do not overlap on different box and whisker plots, then the data groupings are likely significantly different (at least at the 95% level). When large numbers of data sets are plotted using box and whisker plots, the relative overlapping (or separation) of the plots can be used to identify possible groupings of the separate sets.

Scatterplots
According to Berthouex and Brown (1994), the majority of the graphs used in science are scatterplots. They stated that these plots should be made before any other analyses of the data is performed. Scatterplots are typically made by plotting the primary variable (such as a water quality constituent) against a factor that may influence its value (such as time, season, flow, another constituent like suspended solids, etc.). Grouped scatterplots (miniatures) of all possible combinations of constituents can be organized as in a correlation matrix. This arrangement allows obvious relationships to be easily seen, and even indicates if the relationships are straight-lined, or are curvilinear.

Correlation Matrices
Knowledge of the correlations between data elements is very important in many environmental data analyses efforts. They are especially important when model building, such as with regression analysis. When constructing a model, it is important to include the important factors in the model, but the factors should be independent. Correlation analyses can assist by identifying the basic structure of the model.

Another method to examine relationships between measured parameters is by using hierarchical cluster analyses. A tree diagram illustrates both simple and complex relationships between parameters. Parameters having short branches linking them are more closely related than parameters linked by longer branches. In addition, the branches can encompass more than just two parameters. The length of the short branches linking only two parameters are indirectly comparable to the correlation coefficients (short branches signify correlation coefficients close to 1). The main advantage of a cluster analyses is the ability to identify complex relationships that cannot be observed using a simple correlation matrix.

It is very important not to confuse correlation with causation. Many investigators make improper assumptions of cause and effect from their observations, especially if high correlations are found. It is extremely important that theoretical knowledge of the system being modeled be considered. If this knowledge is meager, then specific tests to directly investigate cause and effect relationships must be conducted.

Comparing Multiple Sets of Data
Making comparisons of data sets are fundamental objectives of many wet weather flow investigations. Different habitats and seasons can produce significant affects on the observations, for example. The presence of influencing factors, such as pollutant discharges or control practices, also affect the data observations. Berthouex and Brown (1994) and Gilbert (1987) present excellent summaries of the most common statistical tests that are used for these comparisons in environmental investigations. The significance test results (the α value) will indicate the level of confidence that the two sets of observations are the same. In most cases, an α level of less than 0.05 is used to signify significant differences between two sets of observations. Even if the α level is significant (less than 0.05), the pollutant reduction may not be very important. The importance of the level of pollutant reductions should also be graphically presented using grouped box plots indicating the range and variations of the concentrations at each of the sampling locations, as described previously.

The main types of comparison tests are separated into independent and paired tests. These can be further separated into tests that require specific probability distribution characteristics (parametric tests) and tests that do not have as many restrictions based on probability distribution characteristics of the data (nonparametric data). If the parametric test requirements can be met, then they should be used as they have more statistical power. However, if information concerning the probability distributions is not available, or if the distributions do not behave correctly, then the somewhat less powerful nonparametric tests should be used. Similarly, if the data gathering activity can allow for paired observations, then they should be used preferentially over independent tests.

In many cases, observations cannot be related to each other, such as a series of observations at two locations during all of the rains during a season. Unless the sites are very close together, the rains are likely to vary considerably at the two locations, disallowing a paired analysis. However, if data can be collected simultaneously, such as at influent and effluent locations for a (rapid) treatment process, paired tests can be

used to control all factors that may influence the outcome, resulting in a more efficient statistical analysis. Paired experimental designs ensure that uncontrolled factors basically influence both sets of data observations equally (Berthouex and Brown 1994).

The parametric tests used for comparisons are the t-tests (both independent and paired t-tests). All statistical analyses software and most spreadsheet programs contain both of these basic tests. These tests require that the variances of the sample sets be the same and do not vary over the range of the values. These tests also require that the probability distributions be Gaussian. Transformations can possibly be used to modify the data sets to these conditions. Log-transformations can be used to produce Gaussian distributions of most water quality data. Square root transformations are also commonly used to make the variance constant over the data range, especially for biological observations (Sokal and Rohlf 1969). In all cases, it is necessary to confirm these requirements before the standard t-tests are used.

Nonparametrics: Statistical Methods Based on Ranks by Lehman and D'Abrera (1975) is a comprehensive general reference on nonparametric statistical analyses. Gilbert (1987) presents an excellent review of nonparametric alternatives to the t-tests, especially for environmental investigations from which the following discussion is summarized. Even though the nonparametric tests remove many of the restrictions associated with the t-tests, the t-tests should be used if justifiable. Unfortunately, seldom are the t-test requirements easily met with environmental data and the slight loss of power associated with using the nonparametric tests is much more acceptable than misusing the t-tests. Besides having few data distribution restrictions, many of the nonparametric tests can also accommodate a few missing data, or observations below the detection limits. The following paragraphs briefly describe the features of the nonparametric tests used to compare data sets.

Nonparametric Tests for Paired Data Observations

The sign test is the basic nonparametric test for paired data. It is simple to compute and has no requirements pertaining to data distributions. A few "not detected" observations can also be accommodated. Two sets of data are compared and the differences are used to assign a positive sign if the value in one data set is greater than the corresponding value in the other data set, or a negative sign is assigned if the one value is less than the corresponding value in the other data set. The number of positive signs are added and a statistical table (such as in Lehman and D'Abrera 1975) is used to determine if the number of positive signs found is unusual for the number of data pairs examined.

The Wilcoxon signed rank test (not to be confused with the Wilcoxon rank sum test, which is for independent data observations) has more power than the sign test, but it requires that the data distributions be symmetrical (but with no specific distribution type). Without transformations, this requirement may be difficult to justify for water quality data. This test requires that the differences between the data pairs in the two data sets be calculated and ranked before checking with a special statistical table (as in Lehman and D'Abrera 1975). In the simplest case for monitoring the effectiveness of treatment alternatives, comparisons can be made of inlet and outlet conditions to determine the level of pollutant removal and the statistical significance of the concentration differences.

Friedman's test is an extension of the sign test for several related data groups. There are no data distribution requirements and the test can accommodate a moderate number of "non-detectable" values, but no missing values are allowed.

Nonparametric Tests for Independent Data Observations

As for the t-tests, paired test experimental designs are superior to independent designs for nonparametric tests because of their ability to cancel out confusing properties. However, paired experiments are not always possible, requiring the use of independent tests. The Wilcoxon rank sum test is the basic nonparametric test for independent observations. The test statistic is also easy to compute and compare to the appropriate statistical table (as in Lehman and D'Abrera 1975). The Wilcoxon rank sum test requires that the probability distributions of the two data sets be the same (and therefore have the same variances). There are no other restrictions on the data distributions (they do not have to be symmetrical, for example). A moderate number of "non-detectable" values can be accommodated by treating them as ties.

The Kruskal-Wallis test is an extension of the Wilcoxon rank sum test and allows evaluations of several independent data sets, instead of just two. Again, the distributions of the data sets must all be the same, but they can have any shape. A moderate number of ties and non-detectable values can also be accommodated.

Regression Analyses

Requirements for the Use of Regression Analyses

Regression analyses are also a very popular, but commonly misused, statistical analysis tool. All statistical packages and most spreadsheets also contain regression analyses routines. An excellent reference for regression analyses is *Applied Regression Analysis* by Draper and Smith (1981), while Berthouex and Brown (1994) have extensive discussions concerning misapplications and suggestions for proper use of regression analyses. Draper and Smith (1981) present the following requirements for proper use of regression analyses:

- the residuals are independent
- the residuals have zero mean
- the residuals have a constant variance (σ^2)
- the residuals have a normal distribution (required for making F-tests)

Residuals are the unexplained variation of a model and are calculated as the differences between what is actually observed and what is predicted by the model. Examination of the residuals should confirm if the fitted model is correct. The easiest method to confirm residual behavior is through graphical analyses. The examination of residuals applies to any model situation, not just regression models.

The Need for Graphical Analyses of Residuals

In all cases, graphical analyses of model residuals is necessary to confirm most of these requirements and to verify the use of the model. Berthouex and Brown (1994) list the following required residual graphical analyses for a regression model:

- Check for normality of the residuals (preferably by constructing a probability plot on normal probability paper and having the residuals form a straight line, or at least use an overall plot),
- plot the residuals against the predicted values,
- plot the residuals against the predictor variables, and
- plot the residuals against time in the order the measurements were made.

The residuals need to be random and have the same variance for all these plots. If the residuals spread out, then data transformations may be needed, or a weighted least-squares analysis may be needed. If a trend is evident, then a linear term should have been included in the model. If the residuals are curved, then a higher level model (if a polynomial) may be needed.

Simple lag plots can also be constructed to identify serial correlations of the residuals. In order to make lag-1 plots, the residuals are plotted against the preceding residual value. If the resulting plot has a negative slope, then the residuals are negatively serially correlated. If the resulting plot has a positive slope, then the residuals are positively correlated. Both of these behaviors are undesirable for residuals because it indicates that the measurements are not independent.

Problems with Interpreting Regression Analysis Results

Berthouex and Brown (1994) present a fascinating discussion on the coefficient of determination (R^2) commonly used to "verify" a regression model. The coefficient of determination is the proportion of the total variability in the dependent variables that the regression equation accounts for. An R^2 of 1.0 indicates that the equation accounts for all of the variability of the dependent variables. Unfortunately, a high R^2

value, even if the model is statistically significant, doesn't guarantee that the model has any predictive value.

Berthouex and Brown (1994) also show that having a low R^2 doesn't mean that the regression model is useless. The significance of the regression coefficients are highly dependent on the number of data observations. Highly significant equation coefficients are possible with a concurrent very low R^2 value if the number of data observations is large. The opposite is also true: a high R^2 value can occur with insignificant equation coefficients if only a few data observations are available. This leads to their comment that practical significance and statistical significance are not equivalent: a modest and unimportant true relationship may be established as statistically significant if a large number of observations are available. Conversely, a strong and important relationship may not be shown to be significant if only a few data are available. They therefore stress that great care needs to be expressed if a regression equation is to be used for predictions as it is not possible to determine how accurate predictions will be based on the value of R^2. They strongly suggest that the model (such as a regression equation) be evaluated by: (1) examining the data and resultant model residuals graphically (as described previously), and (2) by using the standard error of the estimate as a more useful measure of the prediction capability of the model instead of relying on R^2. The standard error of the estimate is computed from the variance of the predicted values using the model, so it is a more accurate indicator of the ability of the model to predict dependent variables.

Analysis of Trends in Receiving Water Investigations

The statistical identification of trends is very demanding. Several publications have excellent descriptions of statistical trend analyses for water quality data (as summarized by Pitt 1995). In addition to containing detailed descriptions and examples of experimental design methods to determine required sampling effort, Gilbert (1987) devotes a large portion of his book to detecting trends in environmental data and includes the code for a comprehensive computer program for trend analysis. Reckhow and Stow (1990) present a comprehensive assessment of the effectiveness of different water quality monitoring programs in detecting water quality trends using EPA STORET data for several rivers and lakes in North Carolina. They found that most of the data (monthly phosphorus, nitrogen, and specific conductance values were examined) exhibited seasonal trends and inverse relations with flow. In many cases, large numbers of samples would be needed to detect changes of 25 percent or less (typical for stormwater retro-fitting activities).

Spooner and Line (1993) present recommendations for monitoring requirements in order to detect trends in receiving water quality associated with nonpoint source pollution control programs, based on many years experience with the Rural Clean Water Program. These recommendations, even though derived from rural experience, should also be very applicable for urban receiving water trend analyses. The following is a general list (modified) of their recommended data needs for associating water quality trends with land use/treatment trends:

- Appropriate and sufficient control practices need to be implemented. A high level of participation/control implementation is needed in the watershed to result in a substantial and more easily observed water quality improvement. Controls need to be used in areas of greatest benefit (critical source areas, or in drainages below major sources) and most of the area must be treated.

- Control practice and land use monitoring is needed to separate and quantify the effects of changes in water quality due to the implemented controls by reducing the statistical confusion from other major factors. Monitor changes in land use and other activity on a frequent basis to observe temporal changes in the watershed. Seasonal variations in runoff quality can be great, along with seasonal variations in pollutant sources (monitor during all flow phases, such as during dry weather, wet weather, cold weather, warm weather, for example). Collect monitoring data and implement controls on a watershed basis.

- Monitor the pollutants affecting the beneficial uses of the receiving waters. Conduct the trend analyses for pollutants of concern, not just for easy, or convenient, parameters.

• Monitor for multiple years (at least 2 to 3 years for both pre- and post-control implementation) to account for year-to-year variability. Utilize a good experimental design, with preferable use of parallel watersheds (one must be a control and the other undergoing treatment).

Preliminary Evaluations before Trend Analyses are used

Gilbert (1987) illustrates several sequences of water quality data that can confuse trend analyses. It is obviously easiest to detect a trend when the trend is large and the random variation is very small. Cyclic data (such as seasonal changes) often are confused as trends when no trends exist (type 1 error) or mask trends that do exist (type 2 error) (Reckhow and Stow 1990; Reckhow 1992). Three data characteristics need to be addressed before the data can be analyzed for trends because of confusing factors. These include:

• Measure data correlations, as most statistical tests require uncorrelated data. If data are taken close together (in time or in location), they are likely partially correlated. As an example, it is likely that a high value is closely surrounded by other relatively high values. Close data can therefore be influenced by each other and do not provide unique information. This is especially important when determining confidence limits of predicted values or when determining the number of data needed for a trend analyses (Reckhow and Stow 1990). Test statistics developed by Sen can use dependent data, but they may require several hundred data observations to be valid (Gilbert 1987).

• Remove any seasonal (or daily) effects, or select a data analysis procedure that is unaffected by data cycles. The nonparametric Sen test can be used when no cycles are present, or if cyclic effects are removed, while the seasonal Kendall test is not affected by cyclic data (Gilbert 1987).

• Identify any other likely predictable effects on concentrations and remove their influence. Normally occurring large variations in water quality data easily mask commonly occurring subtle trends. Typical relations between water quality and flow rate (for flowing water) can be detected by fitting a regression equation to a concentration vs. flow plot. The residuals from subtracting the regression from the data are then tested for trends using the seasonal Kendall test (Gilbert 1987).

Statistical Methods Available for Detecting Trends

Graphical methods. Several sophisticated graphical methods are available for trend analyses that use special smoothing routines to reduce short-term variations so the long-term trends can be seen (Gilbert 1987). In all cases, simple plots of concentrations versus time of data collection should be made. This will enable obvious data gaps, potential short-term variations, and distinct long-term trends to be possibly seen.

Regression methods. A time-honored approach in trend analysis is to perform a least-squares linear regression on the quality versus time plot and to conduct a *t* test to determine if the true slope is not different from zero (Gilbert 1987). However, Gilbert (1987) points out that the *t* test can be misleading due to cyclic data, correlated data, and data that are not normally distributed.

Mann-Kendall test. This test is useful when missing data occur (due to gaps in monitoring, such as if frozen waters occur during the winters, equipment failures, or when data are reported as below the limit of detection). Besides missing data, this test can also consider multiple data observations per time period. This test also examines trends at multiple stations (such as surface waters and deep waters, etc.) and enables comparisons of any trends between the stations. This method also is not sensitive to the data distribution type. This test can be considered a nonparametric test for zero slope of water quality versus time of sample collection (Gilbert 1987). Short-term (such as seasonal changes) cycles and other data relationships (such as flow versus concentration) affect this test and must be corrected. If data are highly correlated, then this test can be applied to median values in each discrete time groupings.

Sen's nonparametric estimator of slope. Being a nonparametric test based on ranks, this method is not sensitive to extreme values (or gross data errors) when calculating slope (Gilbert 1987). This test can also be used when missing data occur in the set of observations. It is closely related to the Mann-Kendall test.

Seasonal Kendall test. This method is preferred to most regression methods if the data are skewed, serially correlated, or cyclic (Gilbert 1987). This test can be used for data sets having missing values, tied values, censored values (less than detection limits) or single or multiple data observations in each time period. The testing of homogeneity of trend direction enables one to determine if the slopes at different locations are the same, when seasonality is present. Data correlations (such as flow versus concentration) and dependence also affect this test and must be considered in the analysis.

The code for the computer program contained in Gilbert (1987) computes Sen's estimator of slope for each station-season combination, along with the seasonal Kendall test, Sen's aligned test for trends, the seasonal Kendall slope estimator for each station, the equivalent slope estimator for each season, and confidence limits on the slope.

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Appendix C - Specific Sampling Guidance

Sampler Materials

A major concern when samples are analyzed for trace contaminants is the use of sampling equipment that will have little effect on the sample characteristics. As previously noted, most modern automatic water samplers have been continuously improved over the years and current models are designed to have little effect on sample quality. Teflon™ lined sample tubing, special silicon peristaltic pump tubing, and glass sample bottles are all that contact the sample for automatic water samplers designed for monitoring toxicants. Careful selection of construction materials for manual samplers is just as important as for automatic samplers. Sediment samplers are available made with stainless steel to minimize sample contamination. Cole Parmer includes an extensive table in their standard catalogue that lists chemical compatibility with different materials, including many plastics, elastomers, metals, and non-metals. The effects listed include “no effect”, “minor effect”, “moderate effect”, and “severe effect, not recommended”. This guidance is mostly for material degradation and high concentrations of the chemicals, but it is useful when considering potential contamination problems.

Table Y.29 lists potential contaminants from some sampler materials (Cowgill 1988). It was found that extensive steam cleaning (at least 5 washings using steam produced from distilled water) practically eliminated all contamination problems. Cemented materials should probably be avoided, as is evident from this table. Threaded or bolted together sampler components are much preferable. ASTM (1995), in standard E 1391, recommends preconditioning samplers (plus test chambers and sample containers) before their first use. They summarized research that found that all plastics (including Teflon™) leached elements, but that this could be minimized with a 7 day leaching using a 1:1 solution of HCl and deionized water and than another 7 days in a 1:1 solution of HNO_3 in deionized water. Overnight soaking in these solutions was found to be adequate for glassware.

Extreme caution must be used when conducting preconditioning. Obviously, the solutions are corrosive and laboratory safety provisions are needed, including protection from fuming acid vapors. In addition, the solutions may very well damage the equipment or container. We have destroyed some sampling equipment (made of Delrin™) using these solutions, even though the guidance provided in compatibility charts indicated this would not happen. Obviously, testing should be conducted to ensure compatibility. In our case, the damage did not occur until the seventh and last day of the soaking with the 1:1 solution of HCl. Thin pieces (6 mm) of the Delrin™ did not show any damage, but the 20 mm pieces were destroyed (severe cracking and breaking). It is expected that the material batches were different (with the thicker sheet being a poorer grade) and the relatively thick pieces of plastics were machined and inherent material stress was present.

Table Y.29. Potential Sample Contamination from Sampler Material

Material:	Contaminant:
PVC - threaded joints	chloroform
PVC - cemented joints	methylethyl ketone, toluene, acetone, methylene chloride, benzene, ethyl acetate, tetrahydrofuran, cyclohexanone, organic tin compounds, and vinyl chloride
Teflon™	nothing
polypropylene and polyethylene	plasticizers and phthalates
fiberglass reinforced epoxy material (FRE)	nothing
stainless steel	chromium, iron, nickel, and molybdenum
glass	boron and silica

source: Cowgill (1988)

Pitt, *et al.* (1997) tested leaching potentials for many materials that may be used in sampling apparatus and also pilot-scale treatment units (Table Y.30). The most serious problems occur with plywood, including untreated wood. Attempting to seal the wood with Formica and caulking was partially successful, but toxicants were still leached. Fiberglass screening material, especially before cleaning, also causes a potential problem with plasticizers and other organics. PVC and aluminum may be acceptable sampling apparatus material, if phthalate esters and aluminum contamination can be tolerated. Clark, *et al.* (1997) used aggressive water (18 megohm water, prepared using ion exchange) when conducting his leaching tests. They were also conducted over a three day period (for worst-case conditions during treatability tests). The much shorter contact times associated with sampling (especially after the sampler has been rigorously cleaned) should result in minimal contamination problems when using sampling equipment that has been reasonable selected to avoid contamination of compounds of major interest.

Table Y.30. Potential Sample Contamination from Materials used in Sampler and Pilot-scale Treatability Test Apparatus

Material:	Contaminant:
untreated plywood	toxicity, chloride, sulfate, sodium, potassium, calcium, 2,4-dimethylphenol, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, phenol, N-nitro-so-di-n-propylamine, 4-chloro-3-methylphenol, 2,4-dinitrotoluene, 4-nitrophenol, alpha BHC, gamma BHC, 4,4'-DDE, endosulfan II, methoxychlor, and endrin ketone
treated plywood (CCA)	toxicity, chloride, sulfate, sodium, potassium, hexachloroethane, 2,4-dimethylphenol, bis(2-chloroethoxyl) methane, 2,4-dichlorophenol, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, phenol, 4-chloro-3-methylphenol, acenaphthene, 2,4-dinitrotoluene, 4-nitrophenol, alpha BHC, gamma BHC, beta BHC, 4,4'-DDE, 4,4'-DDD, endosulfan II, endosulfan sulfate, methoxychlor, endrin ketone, and copper (likely), chromium (likely), arsenic (likely)
treated plywood (CCA) and Formica	toxicity, chloride, sulfate, sodium, potassium, bis(2-chloroethyl) ether*, diethylphthalate, phenanthrene, anthracene, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, phenol*, N-nitro-so-di-n-propylamine, 4-chloro-3-methylphenol*, 4-nitrophenol, pentachlorophenol, alpha BHC, 4,4'-DDE, endosulfan II, methoxychlor, endrin ketone, and copper (likely), chromium (likely), arsenic (likely)
treated plywood (CCA), Formica and silica caulk	lowered pH, toxicity, bis(2-chloroethyl) ether*, hexachlorocyclopentadiene, diethylphthalate, bis(2-ethylhexyl) phthalate, phenol*, N-nitro-so-di-n-propylamine, 4-chloro-3-methylphenol*, alpha BHC, heptachlor epoxide, 4,4'-DDE, endosulfan II, and copper (likely), chromium (likely), arsenic (likely)
Formica and silica caulk	lowered pH, toxicity, 4-chloro-3-methylphenol, aldrin, and endosulfan 1
silica caulk	lowered pH, toxicity, and heptachlor epoxide
PVC pipe	N-nitrosodiphenylamine, and 2,4-dinitrotoluene
PVC pipe with cemented joint	bis(2-ethylhexyl) phthalate*, acenaphthene, and endosulfan sulfate
plexiglass and plexiglass cement	naphthalene, benzylbutyl phthalate, and bis(2-ethylhexyl) phthalate, and endosulfan II
aluminum	toxicity, and aluminum (likely)
plastic aeration balls	2,6-dinitrotoluene
filter fabric material	acenaphthylene, diethylphthalate, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, and pentachlorophenol
sorbent pillows	diethylphthalate, and bis(2-ethylhexyl) phthalate
black plastic fittings	pentachlorophenol
reinforced PVC tubing	diethylphthalate, and benzylbutyl phthalate
fiberglass window screening	toxicity, dimethylphthalate, diethylphthalate*, bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, phenol, 4-nitrophenol, pentachlorophenol, and 4,4'-DDD
Delrin™	benzylbutyl phthalate
Teflon™	nothing (likely)
glass	zinc (likely)

note: * signifies that the observed concentrations in the leaching solution were very large compared to the other materials. Not all of the heavy metals had been verified.
source: Clark, *et al*. (1997)

These tables indicate that care must be taken when selecting and cleaning sampling equipment. The use of Teflon™ reduces most of the problems, but it is quite expensive. Delrin™ is almost as effective, is somewhat less expensive, and is much easier to machine when manufacturing custom equipment. Both of

these materials are fragile and cannot withstand rough handling. They are therefore not appropriate for sediment sampling, but can be used to advantage in water samplers. Glass is not usable for most sampling equipment, but is commonly used in bench-scale tests and when storing and preparing samples. Glass presents a problem with heavy metals attaching to the glass walls, and zinc leaching out of the glass. It is a necessary material when analyzing organics, however. Stainless steel is preferred for most sediment samplers and for hardware for water samplers. Plastics should not be used if contamination by phthalate esters is to be avoided. Many adequate and inexpensive sampler apparatus can be made of plastics, especially if cements are not used. In all cases, careful cleaning and preconditioning has been shown to significantly reduce the concentrations of the contaminants in the leach water, stressing the need to thoroughly clean and condition the sampling equipment.

Cleaning Sampling Equipment

Minimum cleaning would include cleaning the samplers, including sampling lines, with domestic tap water immediately after sample retrieval. Components that can be taken to the laboratory (such as the containers in the automatic samplers) are washed using warm tap water and laboratory detergent (phosphate free), rinsed with tap, then distilled, and finally laboratory grade (18 megohm) water.

ASTM (1995) presents standard D 5088-90 covering the cleaning of sampling equipment. They recommend a series of washings, depending on the analyses to be performed. The first wash is with a phosphate-free detergent solution (with a scrub brush, if possible), followed by a rinse of clean (known characteristics) water, such as tap water. If inorganic analyses are to be performed (especially trace heavy metals), then the sample contacting components of the equipment need to be rinsed with a 10% solution of reagent grade nitric or hydrochloric acid and deionized water. The equipment is rinsed again. If organic analyses are to be performed (especially trace organic compounds by GC/MSD), then the sample contacting components of the equipment need to be rinsed with pesticide grade isopropanol alcohol, acetone, or methanol. The equipment is rinsed with deionized water and allowed to air dry. The cleaned equipment needs to be wrapped with suitable inert material (such as aluminum foil or plastic wrap) for storage and transport. If sample components cannot be reached with a brush, such as tubing, the cleaning solutions need to be recirculated through the equipment. Be careful of potentially explosive conditions when using alcohols or acetone. Intrinsically save sampling equipment that does not produce sparking with electronic contacts or from motors, or friction heat, should be used whenever possible. Obviously, work in a well-ventilated area and wear protective garments, including eye protection, when cleaning the sampling equipment with the acid or solvents.

ASTM also recommends that the equipment components that do not contact the sample be cleaned with a portable power washer or steam cleaning machine. If these are not available, then a hand brush needs to be used with the detergent solution.

Volumes to be Collected, Container Types, Preservatives to be Used, and Shipping of Samples

The specific sample volume, bottle type, and preservative requirements will be specified by the analytical laboratory used. *Standard Methods for the Examination of Water and Wastewater* (1995) lists the basic container requirements, minimum sample sizes, required preservative, and the maximum storage period before the analyses need to be conducted. Table Y.94 shows these guidelines. Care must be taken to handle the samples properly to ensure the best analytical results. Numerous losses, transformations, and increases in pollutant concentrations may occur if these guidelines are not followed. Some analyses should be conducted as soon as possible (within a few hours of sample collection, or preferably on-site or *in-situ*). These include: CO_2, chlorine residual, DO unless fixed, iodine, nitrite, ozone, pH, and temperature. ORP (oxidation reduction potential) is also in this category of required on-site analyses, even though not on this table. Parameters that need to be analyzed within 24-hours of sample collection (same day) include: acidity, alkalinity, BOD, cyanide, chromium VI (and other specific ionic forms of metals), taste and odor, and turbidity. Most of the nutrients need to be analyzed within 2 days. Many parameters can be stored for long periods of time, after preservation, specifically total forms of most heavy metals (6 months) and extracted organic compounds (30 days). In some cases, it may be possible to deviate from these guidelines if site-specific testing is conducted to demonstrate acceptable pollutant stability. The most important guidelines

are the bottle type and preservative. Some parameters may be able to undergo longer storage periods, but this must be tested for specific conditions. The required sample volumes are all much greater than needed for most modern laboratory procedures and may be reduced if shipping costs or sample storage facilities are of a concern. Make sure that extra sample is available to redo critical analyses if problems develop, however.

Table Y.94 Standard Methods Table 1060:I (containers, preserv, etc.) pg. 1-22 and 1-23

ASTM (1995) has also discussed sample requirements in standard D 3370. They describe how new glass bottles must be preconditioned before use by filling with water for several days. This conditioning time can be shortened by using a dilute solution of HCl. They also point out that polyethylene is the only suitable material for sample containers when low concentrations of hardness, silica, sodium, or potassium are to be determined. All sample containers must also be sealed with Teflon™ (preferred) or aluminum lined caps. The bottles must be washed using a similar protocol as described above for the sampling equipment. ASTM (1995), in standard E 1391, also recommended more stringent preconditioning of sample containers before their first use in critical toxicological testing. They summarized research that recommended the preconditioning of all plastic containers with a 7 day leaching using a 1:1 solution of HCl and deionized water and than another 7 days in a 1:1 solution of HNO_3 in deionized water. Overnight soaking in these solutions was found to be adequate for glassware.

In order to minimize problems, we recommend that all samples be shipped using overnight courier in ice chests, using “blue-ice” packs instead of water ice. The sample containers need to be separated from one another (such as in dividers) to keep them from banging each other and breaking. Sample lids also need to be taped on to minimize loosening. We generally conduct all filtering and preservation in the laboratory, as this lessens the severe problems associated with field filtration. Critical parameters (pH, DO, temperature) are analyzed *in-situ* or on site. If samples cannot be delivered to the laboratory within a day of collection, field filtration and preservation may be necessary.

The following example for calculating the water volume needed for laboratory analyses is based on the requirements of the UAB Environmental Engineering Laboratory. We have developed analytical modifications that require minimal amounts of sample to decrease shipping costs and storage problems, plus enabling small-scale treatability tests. Table 6 summarizes the sample quantities collected for each set of analysis. Also shown on this table is whether the sample is filtered or unfiltered (for constituent partitioning analyses). As an example, the metallic and organic toxicants are analyzed in both unfiltered and filtered sample portions in order to determine the amount of the pollutants associated with particulates and the amount that are considered “soluble”. Filtering is through 0.45 μm membrane filters (using all-glass filtering apparatus and filters that are found to have minimal affects on constituent concentrations). The sample volumes that needs to be delivered to the laboratory (where further filtering, splitting, and chemical preservation will be performed) and the required containers are as follows:

- three 500 mL amber glass containers with Teflon lined screw caps
- three 500 mL HDPE (high density polyethylene) plastic containers with screw caps

A total of 3 L of each water sample is therefore needed. In addition to the water samples, any collected sediment needs to be shipped in the following sample bottles:

- one 500 mL amber glass wide mouth container with Teflon lined screw cap
- one 500 mL HDPE (high density polyethylene) wide mouth plastic container

Table 6. Analytes And Water Volumes To Be Collected

Constituent	Volume (mL)	Filtered?	Unfiltered?
total solids	100 mL		yes
dissolved solids	100 mL	yes	
turbidity	30 mL	yes	yes
particle size (by Coulter Counter MultiSizer IIe)	20 mL		yes
conductivity	70 mL		yes
pH (also on-site or *in-situ*)	25 mL		yes
color	25 mL		yes
hardness	100 mL		yes
alkalinity	50 mL		yes
anions (F^-, Cl^-, NO_2^-, NO_3^{2-}, SO_4^{2-}, and PO_4^{2-})	25 mL	yes	
cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+})	25 mL	yes	
COD	10 mL	yes	yes
metals (Pb, Cr, Cd, Cu, and Zn)	70 mL	yes	yes
semi-volatile compounds (by GC/MSD)	315 mL	yes	yes
pesticides (by GC/ECD)	315 mL	yes	yes
Microtox™ toxicity screen	10 mL	yes	yes

If the samples are to be analyzed locally, the field collection bottles (such as the automatic sampler base with bottles) can be delivered directly to the laboratory for processing. If they are to be shipped, or delivered to a laboratory requiring that the samples be split and preserved before delivery, further processing is needed. Samples need to be split and individually preserved, as described in *Standard Methods*. A commercial sample splitter is available from Markson Scientific (800-858-2243) (catalogue # 6614K1455 at about $265 for a 14 L polyethylene churn sample splitter, with 4 and 8 L splitters also available). A sample splitter is also useful if numerous individual sampler bottles are to be combined as a composite. The appropriate sample volumes are poured into the splitter from the individual bottles, the composite sample is then agitated and drained into individual bottles for shipping or further processing.

Personnel should wear latex gloves and safety glasses when handling the samples. The sample jars should be filled completely with the sample and the caps screwed on securely, minimizing the amount of air space in the sample jars. Sample container lids need to be taped on (using black electrical tape after drying the bottle first) to reduce loosening of lid and loss of sample. Do not let the samples freeze. The chain-of-custody seal can then be applied over the sealing tape. The paper chain-of-custody seals are not adequate to seal the lids on the jars.

Pre-cleaned sample containers can be obtained from I-Chem (through Fisher Scientific at 800-766-7000), or Eagle Picher (at 800-331-7425). Fisher's catalog numbers and prices are as follows:

I-Chem #	Fisher #	Approx. Cost	Description
241 -0500	05-719-74	$35/case of 12	wide mouth amber 0.5 L glass jars with Teflon™-lined lids and labels
311 -0500	05-719-242	$68/case of 24	wide mouth 0.5 L HDPE jars with Teflon™-lined lids and labels

Eagle Picher sample containers are as follows:

122- 16A	case of 12 - $25	wide mouth amber 0.5 L glass jars with Teflon™-lined lids
151500WWM	case of 24 - $46	wide mouth 0.5 L HDPE jar with Teflon™-lined lids

Once the samples are split into the appropriate shipping bottles (and preserved, if needed), the sample container label should be filled out completely and then logged onto a shipping list for each shipping container. Shipping containers are usually plastic coolers. There needs to be adequate packing (preferably as many “ice” packs as can fit, plus bubble wrap) inside the shipping container to insure that the sample bottles do not rub or bang against each other enroute. Newspapers (flat, not wadded) can be placed on top of the samples and ice packs, directly under the lid, to further fill up any extra volume. Do not use packing peanuts (especially the water soluble type) to fill up space. Wrap glass bottles with bubble wrap. Use sufficient “blue ice” or other cooling packs to insure the coolers stay cool during shipment. Do not use water ice. The coolers must also be securely taped shut (seal the seams) to minimize leakage if a bottle breaks during shipment. The samples should be sent via overnight courier so they arrive before Friday (unless special arrangements have been made with the laboratory). Always call to schedule a sample shipment and fax a confirmation of the sample shipping information. Always keep a copy of any sample identification sheets and send the originals (by mail, not in the coolers). Include a shipping list (and copy of appropriate sampling forms) in an envelope taped to the outside of the cooler.

When the sample is collected, the bottle labels and chain-of-custody forms must be filled out. In many cases, additional field sheets containing site or sample information are also filled out. The typical information provided on a chain-of-custody form includes:

- The sampling location.
- The sample identification number.
- The type of test or analytical procedure.
- The name of the person who relinquishes the samples.
- The date and time of sample collection.
- The date and time when samples are relinquished.
- The name of the person who should receive the sampling results.

After the sediment and water sampling is completed, the sampling equipment must be cleaned using clean water and non-phosphate laboratory detergent and rinsed using clean water.

Handling Samples after Arrival in Laboratory

Once the samples arrive in the laboratory, they need to be logged in, sorted for further processing, and filtered and preserved, as needed, if not already. A reading of pH is conducted immediately when the samples arrive.

Within a day, chilled samples need to be filtered. Glass filters used for suspended solids analyses typically contain large amounts of zinc that easily contaminate samples, therefore, membrane filters need to be used. The filtered and unfiltered sample portions (for the stormwater example shown on Table 6) are then divided and preserved as follows:

- unfiltered sample in two 250 mL amber glass bottles (Teflon lined lids) (no preservatives) for total forms of toxicity, COD, and GC analyses (using MSD and ECD detectors).

- filtered sample in one 250 mL amber glass bottle (Teflon lined lids) (no preservative) for filtered forms of toxicity, COD, and GC analyses (using MSD and ECD detectors).

- unfiltered sample in one 250 mL high density polyethylene (no preservatives) for solids, turbidity, color, particle size, and conductivity.

- filtered sample in one 250 mL high density polyethylene (no preservatives) for anion and cation analyses (using ion chromatography), hardness, dissolved solids, and alkalinity.

- unfiltered sample in one 250 mL high density polyethylene (HNO_3 preservative to pH<2) for total forms of heavy metal, using the graphite furnace atomic adsorption spectrophotometer.

- filtered sample in one 125 mL high density polyethylene (HNO_3 preservative to pH<2) for filtered forms of heavy metal, using the graphite furnace atomic adsorption spectrophotometer.

All samples are chilled on ice or in a refrigerator at 4°C (except for the HNO_3 preserved samples for heavy metal analyses) and analyzed within the holding times shown below:

- immediately after sample collection and again upon arrival in the laboratory: pH
- within 24 hours: toxicity, ions, color, and turbidity
- within 7 days: GC extractions, solids, and conductivity
- within 40 day: GC analyses
- within 6 months: heavy metal digestions and analyses

Quality Control and Quality Assurance to Identify Sampling and Analysis Problems

Quality assurance and quality control (QA/QC) has been used in laboratories for many years to ensure the accuracy of the analytical results. Unfortunately, similar formal QA/QC programs have been lacking in field collection and field analysis programs. Without carefully planned and executed sample collection activities, the best laboratory results are meaningless. The chapter titled *Statistical Elements of Concern when Conducting a Receiving Water Investigation* discussed the necessary experimental design aspects that enable the magnitude of the sampling effort to be determined. It specifically showed how the sample collection and data analysis efforts need to be balanced with experimental objectives. That chapter stressed the need to have a well conceived experimental design to enable the questions at hand to be answered. This chapter presents additional detailed information needed to conduct a water sampling program. These two chapters therefore contain discussions pertaining to “good practice” in conducting a field investigation and are therefore fundamental components of a QA/QC program for field activities.

This section reviews some of the aspects of conventional laboratory QA/QC programs that must also be used in field investigations of receiving water problems. This is not a comprehensive presentation of these topics suitable for conventional laboratory use. This is intended only as a description of many of the components that should be used in field or screening analyses. It is also suitable as a description of the QA/QC efforts that supporting analytical laboratories should be using and to help the scientist or engineer interpret the analytical reports.

Use of Blanks to Minimize and to Identify Errors

Lewis (1988) states that blanks are the most effective tools for assessing and controlling contamination, which is a common source of error in environmental measurements. Contamination can occur from many sources, including during sample collection, sample transport and storage, sample preparation, and sample analysis. Proper cleaning of sampling equipment and sample containers, as previously described, is critical in reducing contamination. The use of appropriate materials that contact the sample (sampling equipment and sample containers especially) was also previously noted as being critical in reducing sample contamination. Field handling of samples (such as adding preservatives) may also cause sample contamination. During the Castro Valley urban runoff study, Pitt and Shawley (1982) found very high, but inconsistent, concentrations of lead in the samples. This was especially critical because the several months delay between sending the samples to the laboratory and receiving the results prevented repeating the collection or analysis of the suspect samples. After many months of investigation, the use of trip blanks identified the source of contamination. The glass vials containing the HNO_3 used for sample preservation were color coded with a painted strip. The paint apparently had a high lead content. When the acid was poured into the sample container in the field, some of it flowed across the paint strip, leaching lead into the sample. About one year of runoff data for heavy metals had to be discarded.

There are many types of blanks that should be used in monitoring programs. Lewis (1988) lists the following, along with their purpose:

- Instrument blank (system blank). Used to establish the baseline response of an instrument in the absence of the analyte. This is a blank analysis only using the minimal reagents needed for instrument operation (doesn't include reagents needed to prepare the sample). May be only ultrapure water.

- Calibration blank (solvent blank). Used to detect and measure solvent impurities. Similar to the above blank but only contains the solvent used to dilute the sample. This typically is the zero concentration in a calibration series.

- Method blank (reagent blank). Used to detect and measure contamination from all of the reagents used in sample preparation. A blank sample (using ultrapure water) with all reagents needed in sample preparation is processed and analyzed. This value is commonly subtracted from the analytical results for the samples prepared in the same way during the same analytical run. This blank is carried through the complete sample preparation procedures, in contrast to the calibration blank which doesn't require any preparation, but is directly injected into the instrument.

- Trip blank (sampling media blank). Used to detect contamination associated with field filtration apparatus and sample bottles. A known water (similar to sample) is carried from the laboratory and processed in the field in an identical manner as a sample.

- Equipment blank. Used to detect contamination associated with the sampling equipment. Also used to verify the effectiveness of cleaning the sampling equipment. A known water (similar to sample) is pumped through the sampling equipment and analyzed. Rinse water (or solvent) after the final equipment cleaning can also be collected and analyzed for comparison with a sample of the fluid before rinsing.

Quality Control

Standard Methods (1995) lists seven elements of a good quality control program: certification of operator competence, recovery of known additions, analysis of externally supplied standards, analysis of reagent blanks, calibration with standards, analysis of duplicates, and the use of control charts. These elements are briefly described below.

Certification of operators. Adequate training and suitable experience of analysts are necessary for good laboratory work. Periodic tests of analytical skill are needed. A test proposed by *Standard Methods* (1995) is to use at least four replicate analyses of a check sample that is between 5 and 50 times the MDL of the procedure. The precision of the results should be within the values shown on Table Y.39.

Table Y.39 Acceptance Limits for Replicate Samples and Known Additions

Parameter	Recovery of Known Additions (%)	Precision of Low-Level (<20 x MDL) Duplicates (± %)	Precision of High-Level (> 20 x MDL) Duplicates (± %)
Metals, anions, nutrients, other inorganics, and TOC	80 - 120	25	10
Volatile and base/neutral organics	70 - 130	40	20
Acid extractable organics	60 - 140	40	20
Herbicides	40 - 160	40	20
Organochlorine pesticides	50 - 140	40	20
Organophosphate pesticides	50 - 200	40	20
Carbonate pesticides	50 - 150	40	20

Source: *Standard Methods* (1995)

Recovery of Known Additions
The use of known additions should be a standard component of regular laboratory procedures. A known concentration is added to periodic samples before sample processing. This increase should be detected compared to a split of the same sample that did not receive the known addition. Matrix interferences are detected if the concentration increase is outside of the tolerance limit, as shown on Table Y.39. The known addition concentration should be between 5 and 50 times the MDL (or 1 to 10 times the expected sample concentration). Care should be taken to ensure that the total concentration is within the linear response of the method. *Standard Methods* (1995) suggests that known additions be added to 10% of the samples analyzed.

Analysis of External Standards
These standards are periodically analyzed to check the performance of the instrument and the calibration procedure. The concentrations should be between 5 and 50 times the MDL, or close to the sample concentrations (whichever is greater). *Standard Methods* (1995) prefers the use of certified standards, that are traceable to National Institute of Standards and Technology (NIST) standard reference materials, at least once a day. Do not confuse these external standards with the standards that are used to calibrate the instrument.

Analysis of Reagent Blanks
Reagent blanks also need to be periodically analyzed. *Standard Methods* (1995) suggests that at least 5% of the total analytical effort be reagent blanks. These blanks should be randomly spaced between samples in the analytical run order, and after samples having very high concentrations. These samples will measure sample carryover, baseline drift of the instrument, and impurity of the reagents.

Calibration with Standards
Obviously, the instrument needs to be calibrated with known standards according to specific guidelines for the instrument and the method. However, at least three known concentrations of the parameter should be analyzed at the beginning of the instrument run, according to *Standard Methods* (1995). It is also preferable to repeat these analyses at least at the end of the analytical run to check for instrument drift.

Analysis of Duplicates
Standard Methods (1995) suggests that at least 5% of the samples have duplicate analyses, including the samples used for matrix interferences (known additions). Table Y.39 presents the acceptable limits of the precision of the duplicate analyses for different parameters.

Control Charts
The use of control charts enables rapid and visual indications of QA/QC problems which can then be corrected in a timely manner, especially while it may still be possible to reanalyze samples. However, many laboratories are slow to upgrade the charts, losing their main benefit. Most automated instrument procedures and laboratory information management systems (LIMs) have control charting capabilities

built-in. *Standard Methods* (1995) describes a “means” chart for standards, blanks, and recoveries. A means chart is simply a display of the results of analyses in run order, with the ±2 (warning level) and ±3 (control level) standard deviation limits shown. At least five means charts should be prepared (and kept updated) for each analyte: one for each of the three standards analyzed at the beginning (and at least at the end) of each analytical run, one for the blank samples, and one for the recoveries. Figure Y.19 is an example of a means chart. The pattern of observations should be random and most within the warning limits. Drift, or sudden change, should also be cause for concern, needing immediate investigation. Of course, if the warning levels are at the 95% confidence limit (approximate ±2 standard deviations), then 1 out of 20 samples will exceed the limits, on average. Only one out of 100 should exceed the control limits (if at the 99% confidence limit, or approximate ±3 standard deviations).

Figure Y.19 (expand, based on figure 1020:1 control chart for means in 1992 standard methods)

Standard Methods (1995) suggests that if one measurement exceeds the control limit, the sample should be immediately reanalyzed. If the repeat is within acceptable limits, then continue. If the repeat analysis is outside of the control limit, then the analyses must be discontinued and the problem identified and corrected. If two out of three successive analyses exceed the warning limit, another replicate analysis is made. If the replicate is within the warning limits, then continue. However, if the third analysis is also outside of the warning limits, the analyses must be discontinued and the problem identified and corrected. If four out of five successive analyses are greater than ±1 standard deviation of the expected value, or are in decreasing or increasing order, another sample is to be analyzed. If the trend continues, or if the sample is still greater than ±1 standard deviation of the expected value, then the analyses must be discontinued and the problem identified and corrected. If six successive samples are all on one side of the average concentration line, and the next is also on the same side as the others, the analyses must be discontinued and the problem identified and corrected. After correcting the problem, *Standard Methods* (1995) recommends that at least half of the samples analyzed between the last in-control measurement and the out-of-control measurement be reanalyzed.

Standard Methods (1995) also points out that another major function of control charts is to identify changes in detection limits. Recalculate the warning and control limits (based on the standard deviations of the results) for every 20 samples. Running averages of these limits can be used to easily detect trends in precision (and therefore detection limits).

Carrying out a QA/QC program in the laboratory is not inexpensive. It can significantly add to the analytical effort. ASTM (1995) summarizes these typical extra sample analyses:

- three or more standards to develop or check a calibration curve per run,
- one method blank per run,
- one field blank per set of samples,
- one duplicate analysis for precision analyses for every 20 samples,
- one standard sample to check the calibration for every 20 samples, and
- one spiked sample for matrix interference analyses for every 20 samples.

This can total at least eight additional analyses for every run having up to 20 samples.

Checking Results

Good sense is very important and should be used in reviewing analytical results. Extreme values should be questioned, for example, not routinely discarded. With a complete QA/QC program, including laboratory and field blanks, there should be little question if a problem has occurred and what the source of the problem may be. Unfortunately, few monitoring efforts actually carry out adequate or complete QA/QC programs. Especially lacking is timely updating of control charts and other tools that can easily detect problems. The reasons for this may be cost, ignorance, or insufficient time. However, the cost of discarded

results may be very high, such as for resampling. In many cases, resampling is not possible and much associated data may be worth much less without necessary supporting analytical information. In all cases, unusual analytical results should be reported to the field sampling crew and other personnel as soon as possible to solicit their assistance in verifying that the results are valid and not associated with labeling or sampling error.

Standard Methods (1995) presents several ways to check analytical results for basic measurements, based on a paper by Rossum (1975). The total dissolved solids concentration can be estimated using the following calculation:

$$TDS = 0.6\ (alkalinity) + Na + K + Ca + Mg + Cl + SO_4 + SiO_3 + NO_3 + F$$

where the ions are measured in mg/L (alkalinity as $CaCO_3$, SO_4 as SO_4, and NO_3 as NO_3, not as N). The measured TDS should be higher than the calculated value because of likely missing important components in the calculation. If the measured value is smaller than the calculated TDS value, the sample should be reanalyzed. If the measured TDS is more than 20% higher than the calculated value, the sample should also be reanalyzed.

The anion-cation balance should also be checked. The milliequivalents per liter (meq/L) sums of the anions and the cations should be close to 1.0. The percentage difference is calculated by (*Standard Methods* 1995):

$$\%\ difference = 100\ (\Sigma\ cations - \Sigma\ anions) / (\Sigma\ cations + \Sigma\ anions)$$

with the following acceptance criteria:

Anion Sum (meq/L)	Acceptable Difference
0 to 3.0	± 0.2 meq/L
3.1 to 10.0	± 2 %
10.1 to 800	± 2 to 5%

In addition, Standard Methods (1995) states that both the anion and cation sums (in meq/L) should be 1/100 of the measured electrical conductivity value (measured as μS/cm). If either of the sums are more than 10% different from this criterion, then the sample should be reanalyzed. The ratio of the measured TDS (in mg/L) and measured electrical conductivity (as μS/cm) values should also be within the range of 0.55 to 0.70.

Detection Limits

There are several different detection limits that are used in laboratory analyses. Standard Methods (1995) states that the common definition of a detection limit is that it is the smallest concentration that can be detected above background noise using a specific procedure and with a specific confidence. The instrument detection limit (IDL) is the concentration that produces a signal that is three standard deviations of the noise level. This would result in about a 99% confidence that the signal was different from the background noise. This is the simplest measure of detection and is solely a function of the instrument and is not dependent on sample preparation. The method detection limit (MDL) accounts for sample preparation in addition to the instrument sensitivity. The MDL is about four times greater than the IDL because sample preparation increases the variability in the analytical results. Automated methods have MDLs much closer to the IDLs than manual sample preparation methods. An MDL is determined by spiking reagent water with a known concentration of the analyte of interest at a concentration close to the expected MDL. Seven portions of this solution are then analyzed (with complete sample preparation) and the standard deviation is calculated. The MDL is 3.14 times this measured standard deviation (at the 99% confidence level). The practical quantification limit (PQL) is a more conservative detection limit and considers the variability between laboratories using the same methods on a routine basis. The PQL is estimated to be about five times the MDL.

Reporting Results

Reporting chemical analysis results should be clear, based on the measured detection limits and QA/QC program. Concentrations below the IDL are not present with sufficient confidence to detect them as significantly different from the baseline random noise of the instrument. These should be reported as not detected (generally given a “U” qualifier in organic compound analytical reports). Concentrations of a parameter above the IDL, but below the MDL are present, but the confidence in the concentration value is less than 99% (can be given a “J” qualifier in organic analytical reports). Concentrations above the MDL indicate that the parameter is present in the sample and that the reported concentration is certain, at the 99% confidence level, or greater. Many other conditions may be present that degrade the confidence of the analytical results. These should all be carefully noted in the analytical report.

Non-detected (“left-censored”) values present special problems in analyzing data. If only a few (or most) of the observations are below the detection limit, these problems are not very serious. However, if the detection limit results in many left-censored data (say between 25 and 75% of the observations), statistical analyses are severely limited. It may not be possible to completely statistically evaluate the effectiveness of a treatment process, for example, if many of the effluent concentrations of a critical pollutant are below the detection limit, even if the influent concentrations are well above the MDL. The removal of the pollutant is obviously important and effective, but it is not possible to calculate the significance of the differences in the observed concentrations. From a statistical (and engineering) viewpoint, it would be better if all concentrations determined by the analytical procedure are reported, even if they are below the detection limits. The use of the qualifiers (such as U and J) along with the numeric values and obvious reporting of the MDL should serve as a warning for the limited use of these values. However, analytical chemists are justifiably concerned about the misuse of “non-detected” values and the availability of these values for statistical analyses will likely remain elusive.

Appendix D - Laboratory Analyses for Wet Weather Flow Samples

Conventional Laboratory Analyses

Table 7 lists the analytical methods typically used for analyzing wet weather flow (WWF) samples by the Environmental Engineering Laboratory at the University of Alabama at Birmingham. Several methods have been found to need modifications to effectively analyze WWF samples, especially if small sample volumes are only available (such as from porewater from stream sediments, from bench-scale treatability tests, or to reduce sample shipping costs). Modifications to the standard methods are described later and were necessitated because of the large particulate fractions of the organic toxicants which interfered with conventional extraction methods. Reducing the sample volumes (especially for the organic analyses) also significantly reduces the volumes of hazardous laboratory wastes generated.

Table 7. Table of Standard and Modified Methods

#	Parameter	Method
	PHYSICAL ANALYSES	
1	Color, Spectrophotometric	EPA 110.3
2	Conductance, Specific Conductance	EPA 120.1
3	Hardness, Total (mg/L as $CaCO_3$), Titrimetric EDTA	EPA 130.2
4	Particle size analysis by Coulter Counter Multi Sizer IIe	Coulter method
5	pH, Electrometric	EPA 150.1
6	Residue, filterable, gravimetric, dried at 180°C	EPA 160.1
7	Residue, non-filterable, gravimetric, dried at 103-105°C	EPA 160.2
8	Residue, total, gravimetric, dried at 103-105°C	EPA 160.3
9	Residue, volatile, gravimetric, ignition at 550°C	EPA 160.4
10	Turbidity, nephelometric	EPA 180.1
	INORGANIC ANALYSES	
11 - 19	Aluminum, arsenic, cadmium, chromium, copper, iron, lead, nickel, and zinc	EPA 200.9
20 - 25	Chloride, fluoride, nitrate, nitrite, phosphate, and sulfate	EPA 300.0
26 - 31	Ammonium, calcium, lithium, magnesium, potassium, and sodium	EPA 300.0 modified
32	Alkalinity, titrimetric (pH 4.5)	EPA 310.1
	ORGANIC ANALYSES	
33	Chemical Oxygen Demand, colorimetric	EPA 410.4
34 - 52	Aldrin, Chlordane-alpha, Chlordane-gamma, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Dieldrin, Endosulfan I, Endosulfan II, Endosulfan sulfate, Endrin, Endrin aldehyde, Endrin ketone, HCH-alpha, HCH-beta, HCH-gamma (Lindane), Heptachlor, Heptachlor epoxide, and Methoxychlor	EPA 608 modified
53 - 110	Acenaphthene, Acenaphthylene, Anthracene, Azobenzene, Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Benzo(a)pyrene, 4-Bromophenyl-phenylether, Bis-(2-chloroethyl)ether, Bis-(2-chloroethoxy)methane, Bis-(2-ethylhexyl)phthalate, Butylbenzyl phthalate, Carbazole, 4-Chloro-3-methylphenol, 2-Chloronaphthalene, 2-Chlorophenol, 4-Chlorophenyl-phenylether, Chrysene, Coprostanol, Dibenzo(a,h)anthracene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 2,4-Dichlorophenol, Diethyl phthalate, 2,4-Dimethylphenol, Dimethyl phthalate, Di-n-butyl phthalate, 2,4-Dinitrophenol, 2,4-Dinitrotoluene, 2,6-Dinitrotoluene, Di-n-octyl phthalate, Fluoranthene, Fluorene, Hexachlorobenzene, Hexachlorobutadiene, Hexachlorocyclopentadiene, Hexachloroethane, Indeno(1,2,3-cd)pyrene, Isophorone, 2-Methylnaphthalene, 2-Methylphenol, 4-Methylphenol, Naphthalene, Nitrobenzene, 2-Nitrophenol, 4-Nitrophenol, N-Nitroso-di-n-propylamine, N-Nitroso-diphenylamine, Pentachlorophenol, Phenanthrene, Phenol, Pyrene, 1,2,4-Trichlorobenzene, 2,4,5-Trichlorophenol, and 2,4,6-Trichlorophenol	EPA 625 modified
	Toxicity Analyses	
111	Microtox® 100% toxicity screening analysis (using reagent salt for osmotic adjustments)	Microbics method

Non-Standard and Modified Methods for WWF Samples

EPA Method 300 Modifications (Ion Chromatography)

For anions: Samples are filtered through C18 and cation exchange columns prior to analysis to remove interferences

For cations: This method covers the determination of the following inorganic cations: lithium, sodium, potassium, calcium, ammonium, and magnesium. Samples are filtered through C18 and anion exchange columns prior to analysis to remove interferences. Cation analytical column utilized is a Dionex Cation exchange column

Stormwater Sample Extractions for EPA methods 608 and 625 (GC/MSD/ECD Organic Toxicants)

1. Samples are extracted using a separatory funnel technique. This has been found to give the most reliable results, especially compared to solid phase extraction or critical fluid extraction methods, for stormwater samples (and most surface water samples). The problem with stormwater organics is that a substantial fraction of many of the organic compounds of interest are associated with particulates. This particulate fraction needs to be quantified, as stormwater has been shown to have significant effects on receiving water sediments. If emulsions prevent achieving acceptable solvent recovery with separatory funnel extraction, continuous extraction is used. The separatory funnel extraction scheme described below assumes a sample volume of 250 mL. Serial extraction of the base/neutrals uses 10 mL additions of methylene chloride, as does the serial extraction of the acids. Prior to the extraction, all glassware is oven baked at 300° C for 24 hours.

2. A sample volume of 250 mL is collected in a 400 mL beaker and poured into a 500 mL glass separation funnel. For every twelve samples extracted, an additional four samples are extracted for quality control and quality assurance. These include three 250 mL composite samples made of equal amounts of the twelve samples, and one 250 mL sample of reverse osmosis water. Standard solution additions consisting of 25 μL of 1000 μg/mL base/neutral spiking solution, 25 μL of 1000 μg/mL base/neutral surrogates, 12.5 μL of 2000 μg/mL acid spiking solution , and 12.5 μL of 2000 μg/mL acid surrogates are made to the separation funnels of two of the three composite samples and mixed well. Sample pH is measured with wide range pH paper and adjusted to pH > 11 with sodium hydroxide solution.

3. A 10 mL volume of methylene chloride is added to the separatory funnel and sealed by capping. The separatory funnel is gently shaken by hand for 15 s and vented to release pressure. The cap is removed from the separatory funnel and replaced with a vented snorkel stopper. The separatory funnel is then placed on a mechanical shaker and shaken for 2 min. After returning the separatory funnel to its stand and replacing the snorkel stopper with the cap, the organic layer is allowed to separate from the water phase for a minimum of 10 minutes, longer if an emulsion develops. The extract and any emulsion present is then collected into a 125 mL Erlenmeyer flask.

4. A second 10 mL volume of methylene chloride is added to the separatory funnel and the extraction method is repeated, combining the extract with the previously collected extract in the Erlenmeyer flask. For persistent emulsions, those with emulsion interface between layers more than one-third the volume of the solvent layer, the extract including the emulsion is poured into a 50 mL centrifuge vial, capped, and centrifuged at 2000 rpm for 2 min. to break the emulsion. Water phase separated by the centrifuge is collected from the vial and returned to the separatory funnel using a disposable pipette. The centrifuge vial with the extract is recapped before performing the extraction of the acid portion.

5. The pH of the remaining sample in the separatory funnel is adjusted to pH < 2 using sulfuric acid. The acidified aqueous phase is serially extracted two times with 10 mL aliquots of methylene chloride

as done in the previous base/neutral extraction procedure. Extract and any emulsions are again collected in the 125 mL Erlenmeyer flask.

6. The base/neutral extract is poured from the centrifuge vial though a drying column of at least 10 cm of anhydrous sodium sulfate and is collected in a 50 mL beaker. The Erlenmeyer flask is rinsed with 5 mL of methylene chloride which is then used to rinse the centrifuge vial and then for rinsing the drying column and completing the quantitative transfer.

7. The base/neutral extract is transferred into a 50 mL concentration vial and is placed in an automatic vacuum/centrifuge concentrator from Savant (Vacuum concentration is used in place of the Kuderna-Danish method). Extract is concentrated to approximately 0.5 mL.

8. The acid extract collected in the 125 mL Erlenmeyer flask is placed in the 50 mL centrifuge vial. Again, if persistent emulsions persist, the extract is centrifuged at 2000 rpm for 2 min. Water is drawn from the extract and discarded. Extract is poured through the 10 cm anhydrous sodium sulfate drying column and collected in the 50 mL beaker as before. The Erlenmeyer flask is then rinsed with 5 mL of methylene chloride which is then poured into the centrifuge vial and finally through the drying column.

9. The acid extract is then poured into the 50 mL concentration vial combining it with the evaporated base/neutral extract. The combined extract is then concentrated to approximately 0.5 mL in the automatic vacuum/centrifuge concentrator.

10. Using a disposable pipette, extract is transferred to a graduated Kuderna-Danish concentrator. Approximately 1.5 mL of methylene chloride is placed in the concentration vial for rinsing. This rinse solvent is then used to adjust the volume of extract to 2.0 mL. Extract is then poured into a labeled Teflon-sealed screw-cap vial and freezer stored until analysis.

Solid Phase Extraction of Organic Compounds

This method is for the extraction and concentration of semi-volatile compounds in the basic, acidic and neutral categories. The usable range of concentrations are from 1 to 250 μg per liter dependent on the individual compound. The matrix for samples prepared using this SOP is limited to water samples with less than 4 g/L solids. Expected precision and accuracy are 25% precision (determined from replicate matrix spikes), and a range of accuracy (as recovery ranging from detection to 125%) dependent on the particular compound.

A Waters SepPak 3 mL syringe containing 500 mg C_{18} material bonded to a spherical silica support sandwiched between Teflon or glass mat filters comprises the absorbent material. A Vacuum Elution device (VacElut) holds the SepPak in place via a female luer adapter. An adapter attached to the top of the SepPak holds a 100 mL reservoir above the SepPak. The VacElut device also routes wastes and collects final elution volume in a glass tube for future analysis.

Spikes for recovery and precision determination are necessary every 30 samples. Since 12 samples can be extracted in one batch run, 3 batches will result in a total of 36 extraction samples. The following pattern of spikes are necessary:

Sample Position	Batch 1	Batch 2	Batch 3
1	RO water	sample	sample
2	composite	sample	sample
3	composite + semivolatile surrogates & matrix spikes	sample	sample
4	composite + semivolatile surrogates & matrix spikes	sample	sample
5	composite + pesticide surrogates & matrix spikes	sample	sample
6	composite + pesticide surrogates & matrix spikes	sample	sample
7	sample	sample	sample
8	sample	sample	sample
9	sample	sample	sample
10	sample	sample	sample
11	sample	sample	sample
12	sample	sample	sample

Standards Needed

a. Source - Surrogate and matrix spikes are available from various vendors. The surrogates and matrix spikes are listed in the UAB QA document which lists method descriptions - Quality Assurance Project Plan. Use spikes undiluted.
b. Preparation - Typically spiking solutions are 1000 to 2000 μg/mL. In order to obtain a 100 μg/L spike in a 250 mL sample from a 1000 μg/mL solution inject 25 μL of the standard below the surface of the sample. For a 2000 μg/mL solution inject 12.5 μL.

Procedure

1. Empty VacElut reservoir.
2. Setup 12 collection tubes in VacElut device.
3. Setup 12 clean SepPaks with adapter and reservoir on VacElut device. Insure the VacElut is in the waste position.
4. Turn on vacuum pump.
5. Wash the SepPaks with 5 mL HPLC grade methanol.
6. Wash the SepPaks with 5 mL RO water.
7. Load the samples into the reservoirs with vacuum on full. (*NOTE* - if vacuum exceeds 30 inches Hg, bleed system and shut down pump)
8. After full volume of sample has been eluted through SepPak, allow to dry with vacuum on full for a minimum 20 minutes.
9. Switch VacElut to collect position and move to hood.
10. If there is any remaining water drops in sample container, add 1 gm sodium sulfate to sample container to absorb the water.
11. Move all sample containers and VacElut device to hood.
12. Insure all collection tubes on VacElut are in collection vials.
13. Introduce 3 mL methylene chloride into each sample container. Swirl methylene chloride to wash sample container walls and any sodium sulfate added.
14. Pour 3 mL methylene chloride wash into VacElut reservoir. Note: This step should be accomplished using a maximum 5 inches Hg vacuum. If methylene chloride does not flow smoothly, the SepPak cartridge is still wet. Increase vacuum and proceed, but note in extraction log that the SepPak elution with methylene chloride was not smooth.
15. Transfer collected eluant to a labeled amber glass vial.
16. Store vial in freezer until analysis.

Organic Extraction Methods for Urban Stream Sediments

The sediment samples were extracted using EPA method 3545 (Accelerated Solvent Extraction). The extract was further cleaned using gel permeation chromatography, capturing the fraction associated with the mass range of interest. A measured volume (5 mL) of a sediment sample was mixed with sodium sulfite to dry the sample. The same volume of sample was simultaneously dried to determine the moisture content

of the sample. The sample/sodium sulfite mixture was then mixed with clean sand to fill the volume of the extraction vessel on the Dionex ASE (Accelerated Solvent Extractor). Up to 24 samples can be extracted automatically. Each sediment sample is extracted with methylene chloride at high pressure for 15 minutes. The collected extract is then slightly reduced in volume using a Savant AS-160 SpeedVac, under vacuum and cold conditions to minimize loss of volatile sample portions. The extracts must be further cleaned before GC/MSD analyses because of the high organic content of many of the sediment samples of interest. The reduced sample extract is cleaned using an OI Analytical AutoPrep gel permeation chromatography (GPC) unit. The GPC discards portions of the sample extract containing much of the unresolvable heavy hydrocarbons, leaving the PAHs and phenols, plus other compounds of interest, in the extract. The collected extract from the GPC is then reduced in volume on the Savant SpeedVac to the final analytical volume (2 mL). The final extracts are then stored in a freezer until they are analyzed using the Hewlett Packard 5890 Series II GC, having a mass spectrophotometer detector and auto sampler. The mass range of the mass spectrometer detector on the GC used in these analyses was optimized for the 40 – 550 atomic mass unit (AMU) range.

Sample Clean-up

If clean-up procedures are necessary, the use of automated gel permeation chromatography (GPC) can be used. The GPC procedure utilizes an OI analytical Autoprep 500. Reduce or dilute the sample extract to 7 mL and place in the Autoprep sample vial. Run program 1 after stabilizing the GPC system and running a GPC calibration sample. The eluent from the run will be approximately 50 mL, which must be evaporated to 1 mL and diluted to a final volume of 2 mL.

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Comments Pertaining to Heavy Metal Analyses

Sample preparation is very critical for all metal analysis procedures. Typical sample preparation requires acid digestion using a combination of acids to reduce interferences by organic matter and to convert the metal associated with particulates (and colloids) to the free metal forms that can be detected. Nitric acid digestion with heat is adequate for most samples. However, hydrofluoric acid is also needed if the digestion is to completely release metals that may be tied up in a silica matrix. Unfortunately, hydrofluoric acid forms volatile compounds with some metals, resulting in their partial loss upon storage if not analyzed immediately. Most all of the stormwater heavy metals can be released from the particulates using just nitric acid, especially considering metal losses from using a hydrofluoric acid digestion. A nitric acid and perchloric acid mixture may be needed to digest organic material in the samples. Microwave-assisted digestion has become more common recently because of improved metal recovery, much faster digestion, and better repeatability.

Quality control and quality assurance activities require a substantial effort in most analytical laboratories. EPA analytical guidelines published in the Federal Register for the different tests specify the types and magnitude of QA/QC analyses. These analyses supplement the standardization efforts as they are used to measure the efficiency of the sample preparation and analysis procedures. Blanks are used to identify possible contamination problems, while matrix spikes added to the samples prior to any preparation steps indicate the efficiency of the complete analytical process. Spikes added to the samples prior to analyses are also used to identify interferences, mainly associated with other compounds in the sample. In heavy metal analyses, it is not uncommon to increase the sample analysis effort by an extra 50% for standards and QA/QC samples in production work. Method development activities would require even a greater additional analytical effort.

Special Analytical Methods and Sample Preparation Procedures for Identifying Specific Forms of Metals

Sequential extraction has been used to separate the metals in a sample into various forms (such as separating the fraction bound to organic material from the fraction bound to mineral particulates and to identify the fraction of the metals that may accumulate in aquatic organisms) (Florence and Batley 1980). Several types of sequential extraction procedures were summarized by Bott (1995) to identify the form of heavy metals that may exist in a water sample (Figures Y-55 from Figura and McDuffie 1980, Y-66 from Florence and Batley 1980, and Y-77 from Nurnberg 1985). These procedures are useful to supplement the Toxicity Identification Evaluation (TIE) scheme noted below if metals are found to be the causative agent for stormwater toxicity (highly likely). The TIE scheme resulted in sample components having specific toxicities. The most toxic sample components can then be subjected to further analyses to measure the toxicant concentrations. Organic analyses using GC/MSD or HPLC technology is very sensitive and can identify specific organic compounds present in the water. Unfortunately, the heavy metal analyses methods are only capable of measuring the total and filterable forms of each metal. However, heavy metals have greatly varying toxicities depending on their form. These sequential extraction procedures can result in a better understanding of the forms of the metals present in the sample and can identify the likely toxic forms present. These schemes typically separate the metals into functional categories, depending on the sample handling. As an example, Figure Y.66 shows a 0.45 μm filtration step to separate particulate from "soluble" forms. The soluble forms are further subjected to acetate buffer digestion (at pH 4.9) to identify labile forms of the metals, then to Chelex-100 extraction columns to identify forms that are sorbed onto inorganics or organics, and finally to UV digestion to identify the organic bound fraction. Anodic stripping voltammetric methods are available to further identify the oxidation state of many of the metals of interest and can result in much more information than if graphite furnace atomic adsorption spectrophotometry is used for the metal analyses with these schemes.

Figure Y.55 (fig 4 from Bott 1995)

Figure Y.66 (fig 3 from Bott 1995)

Figure Y.77 (fig 2 from Bott 1995)

Chemical-Based Toxicity Identification Evaluation of SSO Samples

An important aspect of a stormwater project is trying to identify the toxicants that are interfering with biological uses in the receiving water. Numerous toxicity identification evaluation (TIE) protocols have been used. Figure Y.88 is from Lopes and Fossum (1995) that was used in association with a stormwater toxicity study conducted in Phoenix, Arizona. Acute toxicity of stormwater was found to occur, especially to fathead minnows, and was likely to degrade the quality of the receiving water (the Salt River).

Figure Y.88 TIE protocol, Lopes and Fossum (1995)

This test protocol involved first conducting toxicity tests to identify stormwater that was toxic (>20% mortality after 24-hours). The toxic stormwater was then subjected to different extractions to selectively remove various pollutants from the stormwater, after which additional toxicity tests were conducted. The first extractions were with activated carbon to remove oil and grease. The water was then split by filtering through 0.45 and 0.7 μm filters and further treated to remove metals (by chelation extraction) and remove organics (by solid-phase extraction). This procedure enabled the pollutant phase causing the toxicity to be identified: particulate bound pollutants, filterable metals, or filterable organics.

Appendix E – Microbiological Analysis Methods

Quantifying Total Coliforms and *E. coli* in Water using the IDEXX Colilert-18 Method

Colilert-18 is used for the simultaneous detection, specific identification and confirmation of total coliforms and *E. coli* in water. It is based on IDEXX's patented Defined Substrate Technology® (DST™). It utilizes nutrient indicators that produce color and /or fluorescence when metabolized by total coliforms and *E. coli*. When the reagent is added to a sample and incubated, it can detect these bacteria at 1 CFU in 100 mL within 18 hours with as many as 2 million heterotrophic bacteria per 100 mL present. It is a most probable number (MPN) method.

Summary of Method

Colilert-18 utilizes nutrient indicators that produce color and /or fluorescence when metabolized by total coliforms and *E. coli.* When the colilert-18 reagent is added to a sample and incubated, it can detect these bacteria at 1 CFU in 100 mL within 18 hours with as many as 2 million heterotrophic bacteria per 100 mL present.

Interferences

If an inoculated Colilert-18 sample is inadvertently incubated over 22 hours, the following guidelines apply: No yellow color is a valid negative test. A yellow color after 22 hours is not valid and should be repeated or verified.
Some water samples containing humic material may have an innate color. If a water sample has some background color, compare inoculated Colilert-18 sample to a control blank of the same water sample.

Apparatus, Reagents and Materials

Quanti-tray sealer
water bath or incubator
20 or 200 Snap Paks of Colilert-18 reagent
quanti trays
6 watt 365 nm UV light
fluorescence comparator

Analysis Summary

This procedure requires a 100 mL sample which should be analyzed ASAP after sampling. Marine water samples must be diluted at least 10 fold with sterile fresh water. Do not dilute sample in buffered water for addition to Colilert-18, as the Colilert 18 is already buffered.

1. Turn the power switch on the quanti tray sealer to "ON" position.
2. Turn the Run/Park switch to "RUN". This will cause the sealer to extend the tray shelf.
3. Wait for the sealer to come up to operating temperature (about 10 minutes). Ready light will come on.
4. Carefully separate one snap pack from the strip taking care not to accidentally open the adjacent pack.
5. Tap the snap pack to ensure that all of the Colilert-18 powder is in the bottom part of the pack.
6. Open one pack by snapping back the top at the scoreline. CAUTION: Do not touch the opening of the pack.
7. Add the reagent to a 100 mL water sample in a sterile container.

8. Once the reagent is dissolved, pour this sample directly into the tray avoiding contact with the foil tab.
9. To prevent foam from causing overflows in the sealer, wait until foam subsides before sealing.
10. Lay the tray well-side down in the rubber insert being sure that it is properly aligned. NOTE: improper alignment in the rubber insert may destroy the tray and sample.
11. Keep hands, hair and clothing clear of tray shelf during sealing.
12. Press the seal button. In 15-20 seconds, the sealer will distribute the reagent/sample mixture in the tray wells, seal the wells and return the sealed tray. NOTE: Trapped air bubbles, empty or partially filled wells, and excess spillover do not affect the results of the quanti tray.
13. Park Mode: to retract the shelf into the sealer when not in use, put the Park/Run switch in the "PARK" position. The sealer will maintain temperature in the park mode with the power on.
14. Incubate for 18 hours at 35 ± 0.5°C.
15. Read the results at 18 hours. Compare each result against the comparator. If no yellow is observed, the test is negative. If the sample has a yellow color greater or equal to the comparator, the presence of coliforms is confirmed. If color is not uniform, mix by inversion and recheck. If yellow is observed, check vessel for fluorescence by placing a 6 watt 365 nm UV light within five inches of the sample in a dark room or box. Be sure the light is facing away from your eyes and towards the vessel. If fluorescence is greater or equal to the fluorescence of the comparator, the presence of *E. coli* is confirmed.
16. Count large and small positive wells and refer to the MPN table to find the most probable number

Quality control should be conducted on each lot of Colilert-18.
Inoculate 3 vessels of 100 mL sterile water with the following:

one with Quanti-Cult *E. coli* or American Type Culture Collection (ATCC) 25922 or 11775
one with Quanti-Cult *Klebsiella pneumoniae* or ATCC 31488
one with Quanti-Cult *Pseudomonas aeruginosa* or ATCC 10145 or 27853

Follow the regular Colilert-18 procedure. The following results should be observed:

Escherichia coli - yellow, fluorescent
Klebsiella pneumoniae - yellow, no fluorescence
Pseudomonas aeruginosa - clear, no fluorescence

Quantifying Enterococci in Water using the IDEXX Enterolert Method

Enterolert is used for the detection of enterococci such as *E. faecium*, *E. faecalis* in fresh and marine water. This product is based on Defined Substrate Technology® (DST™) and utilizes a nutrient indicator that fluoresces when metabolized by enterococci. When the reagent is added to the sample and incubated, bacteria down to one CFU in a 100 mL sample can be detected within 24 hours.

Interferences

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.

Apparatus, Reagents and Materials

Quanti-tray sealer
water bath or incubator
20 or 200 Snap Paks of Enterolert reagent
quanti trays

6 watt 365 nm UV light

Analysis Summary

This procedure requires a 100 mL sample which should be analyzed ASAP after sampling. Marine water samples must be diluted at least 10 fold with sterile fresh water.

1. Turn the power switch on the quanti tray sealer to "ON" position.
2. Turn the Run/Park switch to "RUN". This will cause the sealer to extend the tray shelf.
3. Wait for the sealer to come up to operating temperature (about 10 minutes). Ready light will come on.
4. Carefully separate one snap pack from the strip taking care not to accidentally open the adjacent pack.
5. Tap the snap pack to ensure that all of the Enterolert powder is in the bottom part of the pack.
6. Open one pack by snapping back the top at the scoreline. CAUTION: Do not touch the opening of the pack.
7. Add the reagent to a 100 mL water sample.
8. Once the reagent is dissolved, pour this sample directly into the tray avoiding contact with the foil tab.
9. To prevent foam from causing overflows in the sealer, wait until foam subsides before sealing.
10. Lay the tray well-side down in the rubber insert being sure that it is properly aligned. NOTE: improper alignment in the rubber insert may destroy the tray and sample.
11. Keep hands, hair and clothing clear of tray shelf during sealing.
12. Press the seal button. In 15-20 seconds, the sealer will distribute the reagent/sample mixture in the tray wells, seal the wells and return the sealed tray. NOTE: Trapped air bubbles, empty or partially filled wells, and excess spillover do not affect the results of the quanti tray.
13. Park Mode: to retract the shelf into the sealer when not in use, put the Park/Run switch in the "PARK" position. The sealer will maintain temperature in the park mode with the power on.
14. Incubate for 24 hours at 41 ± 0.5°C. The first 20 minutes must be in a water bath. The remainder can be done in an incubator or water bath.
15. Read the results at 24 hours by placing a 6 watt, 365 nm wavelength UV light within five inches of the vessel in a dark room or box. Be sure the light is facing away from your eyes and towards the vessel. Blue fluorescence indicates the presence of enterococci.
16. Count large and small positive wells and refer to the MPN table to find the most probable number

The following quality control procedure should be conducted on each lot of Enterolert. For each of the American Type Culture Collection (ATCC) bacterial strain listed below, streak the culture onto labelled TSA or Blood Agar plates and incubate at 35°C for 18-24 hours. For each bacterial strain, touch a sterile 1 μL inoculating loop to a colony and use it to inoculate a labeled test tube containing 5 mL of sterile deionized water. Close cap and shake thoroughly. For each bacterial strain, take a 1 μL loop from the test tube and use it to inoculate a labeled vessel containing 100 mL of sterile deionized water. These are your controls. Follow the Enterolert procedure above to test these controls. Compare test results to the expected results below:

Control	ATCC#	Expected result
Enterococcus faecium	35667	fluorescence
Serratia marcescens (gram -)	43862	no fluorescence
Aerococcus viridans (gram +)	10400	no fluorescence