Day 1: Experimental Design
Selection of Constituents and Analytical Methods

Mostly excerpted from:
Burton, G.A. Jr., and R. Pitt. *Stormwater Effects Handbook: A Tool Box for Watershed Managers, Scientists, and Engineers*. CRC Press, Inc., Boca Raton, FL . 2002. 911 pages
Freely available at:
http://unix.eng.ua.edu/~rpitt/Publications/BooksandReports/Stormwater%20Effects%20Handbook%20by%20%20Burton%20and%20Pitt%20book/MainEDFS_Book.html

Plus excerpts from various recent research projects

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- **Experimental design covers several aspects of a monitoring program.**
- **The most important aspect of an experimental design is being able to write down the study objectives and why the data are 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 are the data that is to be collected in defining the needed answer?**

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1) Establish clear study objectives and goals (hypothesis to be tested, calibration of equation or model to be used, etc.);

2) Initial site assessment and preliminary problem identification;

3) Review historical site data. Collect information on the physical conditions of the system to be studied (watershed characteristics, etc.), estimate the time and space variabilities of the parameters of interest (assumed, based on prior knowledge, or other methods).

4) Formulate a conceptual framework (e.g., the EPA ecological risk framework);

5) Determine optimal assessment parameters. Determine the sampling plan (strata and relationships that need to be defined), including the number of samples needed (when and where, within budget restraints).

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6) Establish data quality objectives (DQO) and procedures needed for QA/QC during sample collection, processing, analysis, data management, and data analyses;

7) Locate sampling sites;

8) Establish field procedures, including the sampling specifics (volumes, bottle types, preservatives, samplers to be used, etc.).

9) Review QA/QC issues;

10) Construct data analysis plan by determining the statistical procedures that will be used to analyze the data (including field data sheets and laboratory QA/QC plan); and finally,

11) Study implementation.

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During the past several decades, it has become apparent from numerous water and sediment quality assessment studies that no one single approach (e.g., chemical-specific criteria) can be routinely used to accurately determine or predict ecosystem health and beneficial use impairment associated with stormwater discharges in urban areas.

By 1996, 12 states were using biological indicators, and 27 states were developing local biological indicators. The use of biological indicators are much more widespread now.

This presentation focusses on water quality constituents; later presentations will address monitoring of other components.

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Early EPA Description of Integrated Approach to Assess Receiving Water Quality

Control Approach:	What It Provides:	What It Doesn't Provide:
Chemical-Specific	Human health protection Complete toxicology Straightforward treatability Familiarity with control Persistency coverage Regulatory ease	All toxicants present Bioavailability Interactions of mixtures (e.g., additivity) Poor trend analysis Accurate toxicology (false assumptions) Actual and direct evaluations of receiving water beneficial use impairments
Toxicity	Aggregate toxicity All toxicants present Bioavailability Accurate toxicology Good trend analysis Lab or *in situ* testing	Human health protection Complete toxicology (few species may be tested) Simple treatability Persistency coverage
Bioassessments	Actual receiving water effects Trend analysis Severity of impact Total effect of all sources	Critical flow effects Straightforward interpretation of results Cause of impact Differentiation of sources Habitat and site variation influence

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Select Constituents that may Affect Local Beneficial Uses

- Flooding and drainage: debris and obstructions affecting flow conveyance are parameters of concern.
- Biological integrity: habitat destruction, high/low flows, inappropriate discharges, polluted sediment (SOD and toxicants), benthic macroinvertebrate and fish species impairment (toxicity and bioaccumulation of contaminants) 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 parameters.
- 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.

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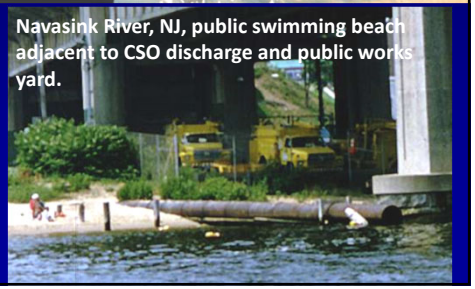
Urban Wildlife and Sewage Contamination

Potential health effects due to exposure to pathogens in urban receiving waters.



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Typical Urban Receiving Water Problems

Photos of Coyote Creek, San Jose, CA

Extremes in Flows

Urbanization causes extremes in flows; extended dry periods and short periods of higher flows in many areas. In the arid west, urbanization increases dry weather flows in intermittent streams due to excessive irrigation.

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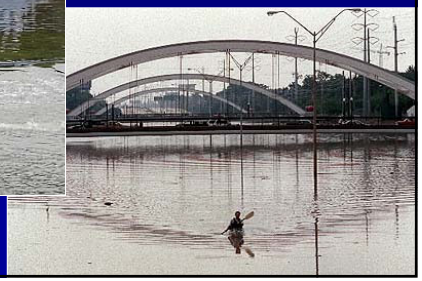
WI DNR photo



Photos from *Houston Chronicle*.

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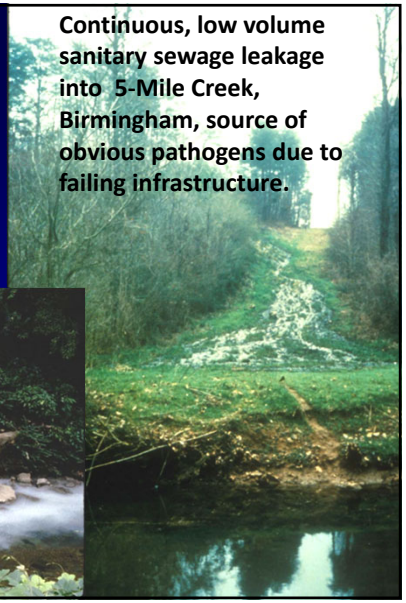
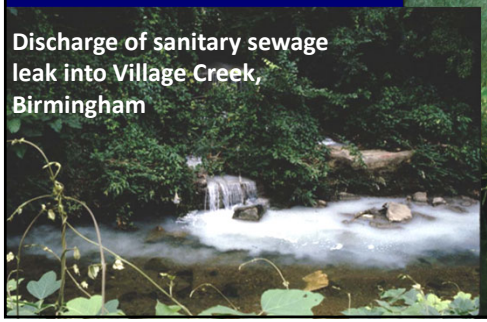
Failing Infrastructure



Continuous, low volume sanitary sewage leakage into 5-Mile Creek, Birmingham, source of obvious pathogens due to failing infrastructure.



Discharge of sanitary sewage leak into Village Creek, Birmingham

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	Drainage	Biological life and integrity	Non-contact recreation	Swimming and other contact recreation	Water supply	Shellfish harvesting and other consumptive fishing uses
debris and obstructions (channel conveyance capacity)	X					
habitat destruction (channel stability, sediment scour and deposition)		X				X
high/low flows (rates and durations)		X	X	X		X
aesthetics, odors and trash			X	X		
safety (bank condition, garbage)			X	X		
public access			X	X		
inappropriate discharges		X	X	X	X	X
benthic macroinvertebrate species present		X	X			X
fish species present		X				X
polluted sediment (SOD and toxicants)		X				X
toxicity and bioaccumulation of toxicants		X				X
health related water quality standards (especially microorganisms and toxicants)				X	X	X
wet weather quality (toxicants, nutrients, DO, temperature, alkalinity, and hardness)		X				X

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Primary constituents are underlined and should be analyzed for most all samples. Others can be analyzed less often as screening tests. In all cases, the common constituents should also be analyzed for all samples.

- Toxicants (organic toxicants such as: pesticides, herbicides, and PAHs; metallic toxicants such as: zinc, copper, lead, cadmium, arsenic, and mercury) and toxicity tests (such as: Microtox screening test, plus other *in-situ* and laboratory toxicity tests)
- Microorganisms (indicator bacteria and selected pathogens such as: fecal coliforms, *E. coli*, enterococci, and *Pseudomonas aeruginosa*)
- Nutrients (ammonia, TKN, nitrates, TP, phosphates)
- Common constituents, added to all water quality investigations (pH, conductivity, turbidity, suspended solids, COD)

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Review of Historical Site Data

As in any environmental assessment process, historical site data should be reviewed initially. Municipal, County, Regional, State and Federal information sources of public information may be available concerning:

1. pre-development water quality, fisheries, and flow conditions
2. annual hydrological conditions vs. development
3. business and industrial categories (e.g., municipality);
4. historical hazardous spills, large quantity toxicant releases and storage

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Stormwater Constituents and Benchmarks Listed in the US EPA 2015 MSGP (Multi-Sector General Permit)

Pollutant	Benchmark
Suspended Solids	100 mg/L
Aluminum	750 µg/L
Copper	9 µg/L (hardness = 60 mg/L); 28.5 µg/L (hardness = 200 mg/L)
Lead	45 µg/L (hardness = 60 mg/L); 213 µg/L (hardness = 200 mg/L)
Zinc	80 µg/L (hardness = 60 mg/L); 230 µg/L (hardness = 200 mg/L)
Chemical Oxygen Demand	120 mg/L
Phosphorus, Total	2 mg/L

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Constituents Selected based on Regulated Numeric Effluent Limits (Examples from a Site Discharge Permit)

	Constituents that have exceeded the benchmark values, benchmark value (# exceeding benchmark value/total number of samples prior to current sampling season)	Constituents that have a likelihood of exceeding the benchmark values during future monitoring, benchmark value (# exceeding benchmark value/total number of samples prior to current sampling season)
Outfall 008	Copper,14 µg/L (2 of 19) TCDD, 2.8 X 10^{-8} µg/L (2 of 19) Lead, 5.2 µg/L (8 of 19) Mercury, 0.13 µg/L (4 of 19)	Cadmium (0 of 19) Iron (no data, based on recent observations at other site locations) Gross beta, 50 pCi/L (0 of 5) Manganese (no data, based on recent observations at other site locations) Nitrite plus nitrate, 8 mg/L (0 of 19) Radium 226 plus 228, 5 pCi/L (0 of 3)
Outfall 009	Cadmium, 4 µg/L (1 of 31) Copper, 14 µg/L (3 of 31) TCDD, 2.8 X 10^{-8} µg/L (9 of 31) Gross alpha radioactivity, 15 pCi/L (1 of 7) Lead, 5.2 µg/L (7 of 31) Mercury, 0.13 µg/L (5 of 31) Oil and grease, 15 mg/L (1 of 31) pH, between 6.5 and 8.8 (1 high of 26)	Antimony, 6 µg/L (0 of 31) Iron (no data, based on recent observations at other site locations) Manganese (no data, based on recent observations at other site locations) Radium 226 plus 228, 5 pCi/L (0 of 4) Sulfate, 250 mg/L (0 of 31) Zinc (only if the 008 benchmark value of 159 µg/L was applicable at 009)

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Monitored Parameters

32-44 parameters are analyzed at **every** surface water outfall during **every** storm that produces runoff.

Over **250** parameters are analyzed at **every** outfall at least **once** annually.

bis (2-Chloroethyl) ether	Fluoranthene
bis (2-ethylhexyl) Phthalate	Fluorene
bis(2-Chloroethoxy) methane	gamma-BHC (Lindane)
bis(2-Chloroethoxy)methane	Gross Alpha Analytes
bis(2-Chloroethyl)ether	Gross Beta Analytes
bis(2-Chloroisopropyl) ether	Hardness
bis(2-Ethylhexyl)phthalate	Hardness as CaCO3
Boron, dissolved	Hardness as CaCO3, dissolved
Bromodichloromethane	Hardness, dissolved
Bromoform	Heptachlor
Bromomethane	Heptachlor epoxide
Bromomethane (Methyl Bromide)	Hexachlorobenzene
Butyl benzylphthalate	Hexachlorobutadiene
Butylbenzylphthalate	Hexachlorocyclopentadiene
Cadmium, dissolved	Hexachloroethane
Calcium	Indeno(1,2,3-cd)pyrene
Calcium, Dissolved	Iron
Carbon Tetrachloride	Iron, dissolved
Cesium 137	Isophorone
Cesium-137	Lead, dissolved

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Data Quality Objectives and Quality Assurance Issues

For each study parameter, the precision and accuracy needed to meet the project objectives should be defined. After this is accomplished, the procedures for monitoring and controlling data quality must be specific and incorporated within all aspects of the assessment, including sample collection, processing, analysis, data management and statistical procedures.

When designing a plan one should look at the study objectives and ask:

- how will the data be used to arrive at conclusions?
- what will the resulting actions be? and
- what are the allowable errors?

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Example Outline of a Comprehensive Stormwater Study

Step 1. What's the Question?
For example: Does site runoff degrade the quality of the receiving stream ecosystem?

Step 2. Decide on Problem Formulation:
Candidate experimental designs can be organized in one of the following basic patterns:

1. **Parallel watersheds (developed and undeveloped)**
2. **Upstream and downstream of a city**
3. **Long term trends**
4. **Preferably most elements of all of the above approaches combined in a staged approach**

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 3. Project Design

1. Qualitative watershed characterization

Establish degree of residential, commercial, and industrial area to predict potential stressors. Typically, elevated solids, flows and temperatures are stressors common to all urban land uses.

The following lists typical problem pollutants that may be associated with each of these land uses:

1) Residential: nutrients, pesticides, fecal pathogens, PAHs and metals
2) Commercial: petroleum compounds, metals
3) Industrial: petroleum compounds, other organics, metals,
4) Construction: suspended solids

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 3. Project Design (continued)

2. Stream characterization

A. Identify potential upstream stressor sources and potential stressors. Photograph and describe sites.

B. Survey upstream and downstream (from outfall to 1 km minimum) quality. Record observations on physical characteristics including: channel morphology (pools, riffles, runs, modification), flow levels, habitat (for fish and benthos), riparian zone, sediment type, organic mater, oil sheens, and odors. Record observations on biological communities, such as waterfowl, fish eating birds or mammals, fish, benthic invertebrate, algal blooms, benthic algae, and filamentous bacteria.

C. Identify appropriate reference site upstream and/or in a similar sized watershed with same ecoregion.

D. Collect any historical data on water quality and flows.

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 3. Project Design (continued)

3. Select Monitoring Parameters

A. Habitat Evaluation. Should be conducted at project initiation and termination. Includes Quantitative Habitat Evaluation Index (QHEI), bed instability survey (bed lining materials and channel cross-sectional area changes), aesthetic/litter survey, inappropriate discharges (field screening), etc.

B. Stressors and their indicators:

1) Physical: flow, temperature, turbidity. Determine at intervals throughout base to high flow conditions.

2) Chemical: conductivity, dissolved oxygen, hardness, alkalinity, pH, nutrients (nitrates, ammonia,

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 3. Project Design (continued)

2) Chemical: conductivity, dissolved oxygen, hardness, alkalinity, pH, nutrients (nitrates, ammonia, ortho-phosphates), metals (cadmium, copper, lead, and zinc) and immunoassays (pesticides and polycyclic aromatic hydrocarbons) and/or toxicity screening (Microtox). The necessity of doing nutrients, metals, and organics will be dependent on the watershed characteristics. Determine at intervals throughout base to high flow conditions.

3) Biological: benthic community structure (e.g., RBP), fish community structure and tissue residues (confirmatory studies only). Benthic structure should be determined at the end of the project. Sediment bioaccumulation potential can be determined using the benthic invertebrate, *Lumbriculus variegatus*.

4) Toxicity: short-term chronic toxicity assays of streamwater, outfalls, and sediment. Sediment should be sampled during base flow conditions and tested prior and after a high flow event. Water samples should be collected during base flow and during pre-crest levels. Expose test chambers with and without sunlight simulating light (containing ultraviolet light wavelengths) to detect PAH toxicity. *In situ* toxicity assays should be deployed in the stream for confirmatory studies during base and high flow periods.

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 3. Project Design (continued)

4. Data Quality Objectives. Determine the kinds of data needed and the levels of accuracy and precision necessary to meet the project objectives. These decisions must consider that there typically is a large amount of spatial and temporal variation associated with runoff study parameters. This requires additional resources for adequate quantification.

5. Triggers and Tiered Testing. Establish the trigger levels or criteria which will be used to determine when there is a significant effect, when the objective has been answered, and/or when additional testing is required. Appropriate trigger levels may include significant differences based on 95% confidence intervals; high toxicity in test sample; exceedance of a biotic integrity, sediment, or water quality criteria; exceedance of a hazard quotient.

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 3. Project Design (continued)

6. Sampling Station Selection. Select the study sites, such as upstream reference sites, outfall(s), and downstream impacted sites. In the selection of the upstream/reference and downstream sites, consider flow dynamics, stressor sources, and reference habitat similarities.

7. Quality Assurance Project Plans (QAPP). It is essential that the quality of the project be ensured with adequate quality assurance and quality control measures. This will include routine laboratory and field documentation of operator and instrumentation performance, chain-of-custody procedures, adequate sample replication, QA/QC samples (blanks and spikes, etc.), performance criteria, and ensuring data validity. Appropriate experimental design (study design and sampling efforts) are also critical components of a QAPP.

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 4. Project Implementation (Routine Initial Semi-Quantitative Survey)

1. Base Flow Conditions

A. Habitat Survey (e.g., Qualitative Habitat Evaluation Index)

B. Benthic RBP

C. Test water and sediment from all test sites for short-term chronic toxicity with two species.

D. Establish spatial and diurnal variation (YSI 6000 for several weeks, plus grab samples or time composites).

E. Set up automatic stream samplers/monitors, stream depth gauges, and rain gauges.

F. Establish local contacts to oversee field equipment and provide rain event notification.

G. Conduct field screening survey at outfalls to identify sources of dry weather flows.

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Example Outline of a Comprehensive Stormwater Study (continued)

2. High Flow Conditions

A. Confirm that the samplers and monitors are operational. Collect grab samples if necessary (for microbiological and VOC analyses, for example).

B. Deploy *in situ* toxicity test assays.

C. Measure flow and note staff gauge depth, using manual or automatic samplers and flow recorders. Repeat flow measurements at intervals of 0.5 to 1.0 ft stream depth intervals as the stream rises, noting time and depth. Focus on first flush to crest period.

D. Measure D.O., temperature, turbidity, conductivity, and stage at each station following each flow measurement. establish spatial variance. May use continuous recording water quality sondes.

E. Collect flow-weighted composited (or combine many discrete) samples for other analyses.

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 4. Project Implementation (Routine Initial Semi-Quantitative Survey) (continued)

3. Sample Analyses.

A. Filter, preserve and chill samples, as required.

B. Deliver samples to analytical laboratories with chain of custody forms.

C. Initiate toxicity testing and other chemical and microbiological analyses within required time period since sample collection.

D. Document QA/QC.

4. Follow-Up (Post-Event) Monitoring

A. Check *in situ* assay chambers at 24 and 48 and at 7 and 14 days if deployed.

B. Conduct benthic assessment

C. Conduct qualitative habitat evaluation index (QHEI), noting bed load movement

D. Collect fish for tissue residue analyses.

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 5. Data Evaluation

1. Plot flow vs. physical and chemical analysis results.
2. Statistically compare responses/loadings during base, first flush, and post-crest conditions. This will provide a characterization of flow dynamics and its affect on stressor profiles.
3. Statistically compare stations (instantaneous, mean periods) for significant differences and correlations.
4. Calculate and compare physical, chemical and toxicity (using Toxicity Units) loadings. This will show the relative load contribution of stressors from reference (upstream) vs. impacted (downstream) reach.
5. Identify magnitude and duration of trigger exceedances.
6. Identify sources of uncertainty.
7. Identify potential sources of pollutants and stressors.
8. Determine literature value thresholds for key stressors on key indigenous species.

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 6. Confirmatory Assessment (Optional Tier 2 Testing)

1. Repeat Steps 2 and 3 using Tier 1 information to select fewer test parameters with increased sampling frequency and/or select more descriptive methods. Increased sampling will better quantify the magnitude and duration of stressor dynamics. Expanded sampling will better document the quality of the receiving water. More definitive testing could include:

- Short-term chronic toxicity testing with additional species (lab and *in situ*),
- Increased testing of toxicants,
- Characterizing fish, plankton, periphyton, or mussel populations,
- Measuring assimilative capacity via long term BOD and SOD testing,
- Measure productivity with light/dark bottle BOD *in situ* tests

2. Conduct Toxicity Identification Evaluation (TIE) study of water, outfalls, and/or sediment to determine contribution of each stressor to total toxicity. This information can better determine which stressors are important to control and can also identify sources of toxicity.

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 6. Confirmatory Assessment (Optional Tier 2 Testing) (continued)

3. Conduct bioaccumulation testing of site sediments. Some pollutants, such as highly chlorinated organic compounds (e.g., chlordane, DDT, PCBs, dioxins) are readily bioaccumulated, yet may not be detected using the above study design. The EPA has a benthic invertebrate 28 day assay to measure sediment bioaccumulation potential. Also controlled bioaccumulation tests may be used.

4. Indigenous Biological Community Characterization and Tissue Analysis. More in-depth quantification of benthic and/or fish community structure on a seasonal basis will better identify significant ecological effects. Tissue sampling of fish for contaminants will provide information on bioaccumulative pollutants and potential food web or human health effects from consumption.

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Example Outline of a Comprehensive Stormwater Study (continued)

Step 7. Project Conclusions

1. List probable stressors.
2. Document trigger exceedances.
3. Discuss relative contribution of stressors(s) to ecosystem degradation. Support documentation may include:
   - Literature threshold values,
   - Criteria exceedances,
   - Toxicity observed (from TIE, photo-activation, or *in situ* assays)
   - Bioaccumulation factors and potential for food web contamination

4. Provide recommendations for stressor reduction and ecosystem enhancement.
5. Include suggestions on habitat improvement, flow reduction, turbidity removal and reduced siltation.

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Basic Study Approach

Experimental designs can be organized in one of the following basic patterns:

1. Parallel watersheds (developed and undeveloped)
2. Upstream and downstream of a city
3. Long-term trend

Preferably, most elements of all of the above approaches can be combined in a staged approach

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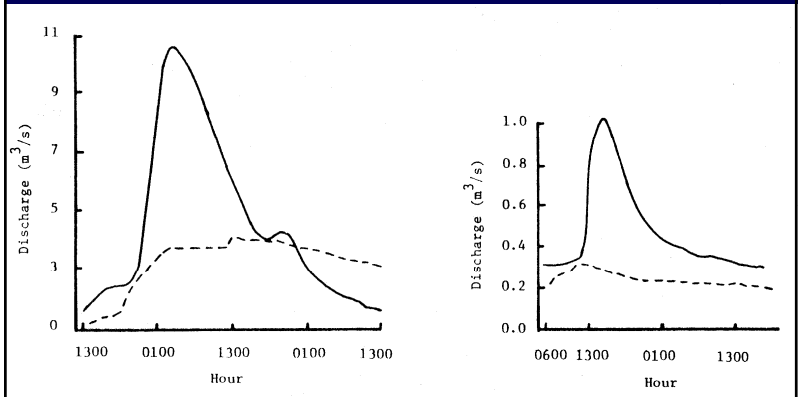
Parallel Stream Study (control and reference stream)



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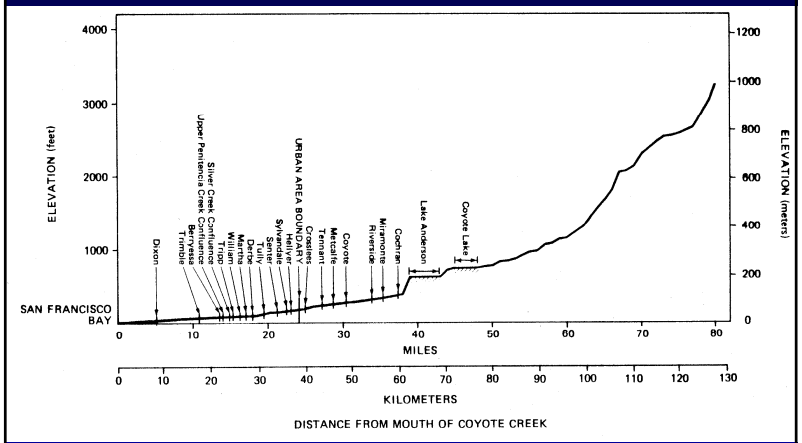
Longitudinal Trend Study (above and below city)



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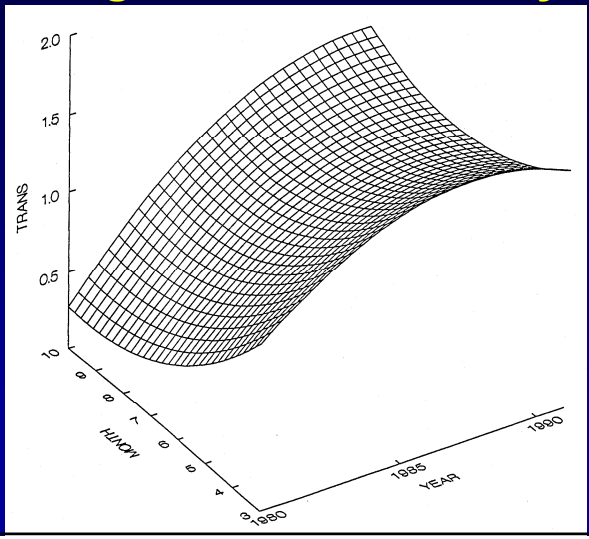
Long-Term Trend Study



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Example Sampling Guidance from *Standard Methods*

Determination	Container (plastic or glass)	Min. Sample Volume mL	Sample Type (grab or composite)	Preservation	Maximum Storage Recommended/ Regulatory
Acidity	P, G(B)	100	G	Refrigerate	24h/14d
Alkalinity	P, G	200	G	Refrigerate	24h/14d
BOD	P, G	1000	G	Refrigerate	6h/48h
Boron	P	100	G, C	None required	28d/6months
Bromide	P, G	100	G, C	None required	28d/28d
Carbon, organic, total	G	100	G, C	Analyze immediately; or refrigerate and add H_3PO_4 OR H_2SO_4 TO pH<2	7d/28d
Carbon dioxide	P, G	100	G	Analyze immediately	Stat/N.S.
COD	P, G	100	G, C	Analyze as soon as possible, or add H_2SO_4 to pH<2; refrigerate	7d/28d
Chloride	P, G	50	G, C	None required	28d
Chlorine, residual	P, G	500	G	Analyze immediately	0.5h/stat
Chlorine, dioxide	P, G	500	G	Analyze immediately	0.5 h/N.S.
Chlorophyll	P, G	500	G, C	30 d in dark	30d/N.S.
Color	P, G	500	G, C	Refrigerate	48h/48h
Conductivity	P, G	500	G, C	Refrigerate	28d/28d
Cyanide: Total	P, G	500	G, C	Add NaOH to pH>12, refrigerate in dark	24h/14d;24h if sulfide present

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Example Water Volume Requirements for Different Analytes using Special Small Volume Analyses

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)	**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-, NO2-, NO32-, SO42-, and PO42-)	**25 mL**	**yes**	
cations (Li+, Na+, NH4+, K+, Ca2+, and Mg2+)	**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**

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Quality Control/Quality Assurance: Use of Blanks to Minimize and to Identify Errors

There are many types of blanks that should be used in monitoring programs:

- 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.

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Quality Control/Quality Assurance
Use of Blanks to Minimize and to Identify Errors (continued)

- 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.

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Quality Control

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 method detection limit (MDL) of the procedure. The precision of the results should be within the values shown on the following table.

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 the table. The known addition concentration should be between 5 and 50 times the MDL (or 1 to 10 times the expected sample concentration).

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
Carbamate pesticides	50 - 150	40	20

Quality Control (continued)

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). The use of certified standards, that are traceable to National Institute of Standards and Technology (NIST) standard reference materials, at least once a day should be used. 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. At least 5% of the total analytical effort should be for 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 carry over, baseline drift of the instrument, and impurity of the reagents.

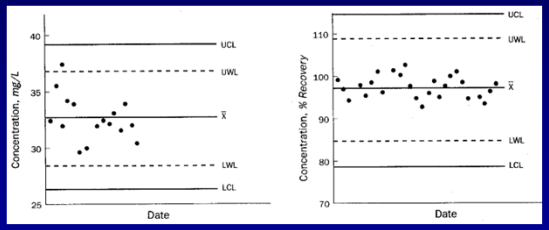
Quality Control (continued)

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. 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. At least 5% of the samples should have duplicate analyses, including the samples used for matrix interferences (known additions), while other guidance may suggest more duplicate analyses. The previous table presents the acceptable limits of the precision of the duplicate analyses for different parameters.

Quality Control (continued)

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.



This figure 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 approximately 1 out of 20 samples will exceed the limits, on average.

Quality Control (continued)

Carrying out a QA/QC program in the laboratory is not inexpensive. It can significantly add to the analytical effort:

- 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,
- at least 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.

Identifying the Needed Detection Limits and Selecting the Appropriate Analytical Method

The selection of the analytical procedure is dependent on a number of factors, including (in order of general importance):

- appropriate detection limits
- freedom from interferences
- good analytical precision (repeatability)
- minimal cost
- reasonable operator training, needed expertise, disposal of used reagents and safety of the method (a great concern when volunteers are used to conduct the monitoring program).

Besides the factors listed above, another consideration is whether the analyses should/can be conducted in the field, or in the laboratory. These factors can be grouped 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.

Based on numerous Monte Carlo analyses, if the analyte has an expected narrow range of concentrations (a low COV), then the detection limit can be greater than if the analyte has a wider range of expected concentrations (a high COV). These guidelines are as follows:

- If the analyte has a low level of variation (a 90th to 10th percentile range ratio of 1.5, or a COV of <0.5), then the estimated required detection limit is about 0.8 times the expected median concentration.

- If the analyte has a medium level of variation (a 90th to 10th percentile range ratio of 10, or a COV of about 0.5 to 1.25), then the estimated required detection limit is about 0.23 times the expected median concentration.

- Finally, if the analyte has a high level of variation (a 90th to 10th percentile range ratio of 100, or a COV of about >1.25), then the estimated required detection limit is about 0.12 times the expected median concentration.

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Summary of Quantitative QA Objectives (MDL and RPD) Required for an Example Stormwater Characterization Project

Constituent	Units	Example COV category	Example Median Conc.	Calculated MDL Requirement	Calculated Precision 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 CaCO3	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 CaCO3	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%

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Summary of Quantitative QA Objectives (MDL and RPD) Required for an Example Stormwater Characterization Project (continued)

Constituent	Units	Example COV category	Example Median Conc.	Calculated MDL Requirement	Calculated Precision Requirement
sodium	mg/L	low	2	1.5	<10%
potassium	mg/L	low	2	1.5	<10%
Microtox™ toxicity screening	I20 or EC50	medium	I20 of 25%	I20 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%

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Comparisons of Field and Laboratory Analytical Methods

Field Analytical Methods		Conventional Laboratory Methods	
Advantages	Disadvantages	Advantages	Disadvantages
Minimal change in sample character because no transport and storage.	Difficult to control environmental variables affecting analytical measurements and working conditions.	Good control of laboratory working conditions and use of in-place hazardous waste management.	Need to preserve samples and conduct analyses in prescribed period of time.
Opportunity to collect replacement sample if questionable results, or if sample is damaged.	Individual samples usually analyzed separately with more time required per sample.	Can analyze several samples in one batch.	Results may not be available for an extended time after sample collection.
Results generally available soon after sample collection.	Additional time needed to set up equipment and standardize procedure for each location.	More precise equipment generally used for analyses, and less time to set up for analyses.	Minimal opportunity to re-sample due to errors.
Continuous in-situ monitors result in large numbers of observations with fine resolution.	Analytical hazardous waste (and sharps) management may be a problem.	Easier to conduct and meet QA/QC requirements.	Generally more expensive and sample numbers are therefore limited.
	Many field analytical reagent sets are sensitive to storage conditions that may be difficult to meet.	Usually much lower limits of detection.	Sample storage space-consuming and requires logging system for sample tracking.
	Documentation can be incomplete and hazards not described.		
	Generally poorer limits of detection and limited working range.		
	Some of the most sensitive tests are very complex with analytical errors common.		

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Potential Use of Field Test Kits for Water Quality Analyses

Water Quality Parameter	Example Water Quality Objectives Associated with Aquatic Life Beneficial Uses (short-term exposures)	Expected Coefficient of Variation (COV) Category	Estimated Needed MDL	Suitable Field Measurement Methods Providing Estimated Needed MDL
Zinc	<120 µg/L	Medium	28 µg/L	No available field method could approach this desired MDL. The lowest MDL found was about 140 µg/L for Zn. Most of the field test methods also require toxic (cyanide) reagents.
Copper	<13 µg/L	Medium	3 µg/L	No available field method could approach this desired MDL. The lowest MDL found was about 100 µg/L for Cu.
Lead	<65 µg/L	Medium	15 µg/L	The HACH LeadTrak system has a MDL of about 5 µg/L, although it is a time consuming test and relatively expensive. The Metalyzer 3000 and Palintest SA-1000 both have lead MDLs of about 5 µg/L and would therefore be suitable, but are expensive instruments.
Microtox screening test	n/a: indicative of toxicants that may be present (such as pesticides), desire low value; I20 of <25%.	Medium	I20 of 6%	Deltatox (expensive instrument, but field portable).
Hardness	Narrative (want moderate to hard water conditions to reduce effect of some toxicants), would like to detect hardness to at least 50 mg/L.	Low	40 mg/L	HACH Digital Titrator and CHEMetrics EDTA titration methods would both likely be suitable field methods.
Alkalinity	n/a (would like moderate to high levels of alkalinity to reduce effects of some toxicants), would like to detect alkalinity to at least 25 mg/L.	Low	20 mg/L	Field titration methods available, but not evaluated.
Ammonia	<3.8 mg/L (2.5 X chronic at 30°C)	Low	3 mg/L	All 4 field test kits investigated have limits of detection better than this estimated needed MDL. However, one requires refrigeration, and others contain mercury in waste.
Nitrates	n/a (rarely toxic to aquatic life in natural streams, but indicative of potential eutrophicaiton problems in nitrogen limited streams), would like to detect NO_3 to at least 1 mg/L.	Low	0.8 mg/L	The La Motte and CHEMetrics nitrate tests, and likely the HACH low range nitrate test, can meet this MDL objective. Sharps and cadmium containing wastes are common with these methods.

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Potential Use of Field Test Kits for Water Quality Analyses (continued)

Water Quality Parameter	Example Water Quality Objectives Associated with Aquatic Life Beneficial Uses (short-term exposures)	Expected Coefficient of Variation (COV) Category	Estimated Needed MDL	Suitable Field Measurement Methods Providing Estimated Needed MDL
Phosphates	Narrative, <25 µg/L to prevent eutrophication.	Low	20 µg/L	Numerous phosphate field test kits are available, although not reviewed by Day (1996). It is expected that there are several that can meet these performance objectives.
Suspended solids	Narrative: <100 mg/L settleable fraction to prevent of smothering of streambed.	Large	12 mg/L	No field instruments known for measuring suspended solids (requires drying ovens and analytical balance), but can predicted/tracked using turbidity.
COD	n/a (indication of organic matter), would like to be <5 mg/L.	Medium	1 mg/L	No field instruments known for measuring COD (requires digestion).
pH	Between 6.5 and 9 desired (harmless to fish in this range).	Very low	Readable to 0.3 pH units	All of the pH electrode methods investigated should meet this readability objective, but the pH paper methods are not likely suitable.
Conductivity	n/a (variation should be minimal), would like to determine conductivity at 100 µS/cm.	Low	80 µS/cm	All three conductivity probes investigated had limits of detection about equal to this objective and would be suitable.[3]
Turbidity	Narrative: <50 NTU increase above background conditions.	Large	6 NTU	The HACH portable nephelometer, or the Horiba HU-10 and YSI *in-situ* probes can measure turbidity in the field, although these are all moderate to very expensive options.
DO	>5.0 mg/L	Low	Readable to 0.25 mg/L	Most modern field DO meters could be used to meet these objectives.
Temperature	Narrative (variation from natural conditions should be minimal).	Low	Readable to 0.5 °C	Most modern field DO meters also have temperature readouts and would be suitable, alternatively simple pocket thermometers could be used.

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The analyses that may be possible to conduct using field test kits that meet basic sensitivity requirements include:

Conventional Constituents:
- hardness (using field titration equipment)
- alkalinity (using field titration equipment)
- turbidity (possible using moderately expensive field nephelometer, or expensive *in-situ* recording probes)
- pH (easily conducted using electrodes, or expensive *in-situ* recording probes)
- conductivity (easily conducted using electrodes, or expensive *in-situ* recording probes)
- DO (easily conducted using electrodes, or expensive *in-situ* recording probes)
- temperature (easily conducted using electrodes, thermometers, or expensive *in-situ* recording probes)

Nutrients:
- ammonia (several simple field test kits available)
- nitrates (several simple field test kits available)
- phosphates (several simple field test kits available)

Toxicants:
- lead (but difficult, time consuming, or expensive)
- toxicity screening (expensive instrument)

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- In many cases, it is not practical to conduct field measurements at the time of sample collection due to the time needed to setup equipment, standardize the procedures, and conduct the individual constituent analyses at each sampling location.

- However, it may be very reasonable to use these field methods in a temporary field laboratory when conducting sampling in remote areas. In this case, samples collected over a short period of time (such as during the day) can be analyzed together, minimizing the time requirements.

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Typical List of Standard and Modified Methods for Wet Weather Flow Analyses

Parameter	Method
PHYSICAL ANALYSES	
Color, Spectrophotometric	EPA 110.3
Conductance, Specific Conductance	EPA 120.1
Particle size analysis by Coulter Counter and sieves	Coulter method
pH, Electrometric	EPA 150.1
Residue, filterable, gravimetric, dried at 180 °C	EPA 160.1
Residue, non-filterable, gravimetric, dried at 103-105 °C	EPA 160.2
Residue, total, gravimetric, dried at 103-105 °C	EPA 160.3
Residue, volatile, gravimetric, ignition at 550 °C	EPA 160.4
Turbidity, nephelometric	EPA 180.1
INORGANIC ANALYSES	
Hardness, Total (mg/L as CaCO3), Titrimetric EDTA	EPA 130.2
Aluminum, arsenic, cadmium, chromium, copper, iron, lead, nickel, and zinc	EPA 200.9
Chloride, fluoride, nitrate, nitrite, phosphate, and sulfate	EPA 300.0
Ammonium, calcium, lithium, magnesium, potassium, and sodium	EPA 300.0 modified
Alkalinity, titrimetric (pH 4.5)	EPA 310.1

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Typical List of Standard and Modified Methods for Wet Weather Flow Analyses (continued)

Parameter	Method
ORGANIC ANALYSES	
Chemical Oxygen Demand, colorimetric	EPA 410.4
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
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,Trichlorophenol, and 2,4,6-Trichlorophenol	EPA 625 modified
TOXICITY ANALYSES	
Microtox™ 100% toxicity screening analysis (using reagent salt for osmotic adjustments)	Microtox method

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Reporting Results Affected by Detection Limits

- Reporting chemical analysis results should be clear, based on the measured detection limits and QA/QC program.
- Concentrations below the IDL (instrument detection limit) 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 (method detection limit) 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.

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Reporting Results Affected by Detection Limits (continued)

- As noted in the discussions on statistical analysis methods, 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 available results in many left-censored data (such as >25% 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 (the sign method can be used with reduced power).
- From a statistical (and engineering) viewpoint, it would be better if all concentrations determined by the analytical procedure be reported, even if they are below the designated "formal" detection limit, set using an extreme 99% confidence limit.

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Reporting Results Affected by Detection Limits (continued)

Suggested Analytical Detection Limits for Stormwater Monitoring Programs to Obtain <5% Non-detects

	Residential, commercial, industrial, freeway	Open Space
Conductivity	20 µS/cm	20 µS/cm
Hardness	10 mg/L	10 mg/L
Oil and grease	0.5 mg/L	0.5 mg/L
TDS	10 mg/L	10 mg/L
TSS	5 mg/L	1 mg/L
BOD_5	2 mg/L	1 mg/L
COD	10 mg/L	5 mg/L
Ammonia	0.05 mg/L	0.01 mg/L
NO_2+NO_3	0.1 mg/L	0.05 mg/L
TKN	0.2 mg/L	0.2 mg/L
Dissolved P	0.02 mg/L	0.01 mg/L
Total P	0.05 mg/L	0.02 mg/L
Total Cu	2 µg/L	2 µg/L
Total Pb	3 µg/L (residential 1 µg/L)	1 µg/L
Total Ni	2 µg/L	1 µg/L
Total Zn	20 µg/L (residential 10 µg/L)	5 µg/L

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Conclusions

- There can be many constituents included in an urban stormwater study.
- These are selected to meet specific project requirements (supplement biological monitoring, characterize runoff, evaluate controls, meet regulatory requirements, etc.)
- Conventional laboratory QA/QC protocols are well established.
- However, larger errors and uncertainties are usually associated with poor sample collection practices (methods and effort)

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