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Six Mile Creek Volunteer Monitoring Project

Workshop on Sample Collection, Chemical Analysis, and Flow

July 17, 2004, 9 AM - 12:30 PM, Bethel Grove Community Center

Goal
The goal of the workshop is to introduce concepts and techniques for collecting water samples, analyzing them for chemical and microbiological parameters, and calculating loads (amounts) of problem parameters such as phosphorus and sediment that are being delivered by Six Mile Creek to the southern end of Cayuga Lake.

Overview

The workshop is divided into an indoor and an outdoor segment.

Indoor segment, 9:00 - 10:30 AM
A. Principles of collecting and handling water samples for certified tests to determine concentrations of chemical, physical and microbiological parameters
B. Overview of certified water quality tests and what they tell about the hydrogeology of the stream, its fitness as a habitat for aquatic organisms, and sources of pollution
C. Portable test kits and meters for measuring chemical "vital signs" and documenting data quality assurance and control (QA/QC)
D. Principles of measuring flow and calculating pollutant loadings to the stream

Outdoor segment, 10:30 AM - 12:30 PM
A. Hands-on demonstration of how to collect and preserve water samples
B. Hands-on demonstration of how to measure chemical "vital signs:" Temperature, pH, dissolved oxygen, turbidity, alkalinity and conductivity
C. Demonstration of how to measure flow, channel elevation and suspended sediment

Introductions to topic areas

A. Principles of collecting and preserving water samples for certified analyses

Collecting water samples that are representative of the stream and preserving them so that they are not degraded prior to testing are the two most important considerations in a sampling plan.

Sample representativeness: For most purposes, the water in a stream can be assumed to be completely mixed and uniform with respect to the chemicals, sediment and bacteria that are in it. This assumption holds best for the water in the middle of the stream. Near the banks, on the surface and at the bottom, where mixing is less complete, the assumption of uniformity can break down. Water collected at the edge of the stream can have different concentrations of water quality indicators than water in the middle of the stream. To maximize the representativeness of a sample, wade to the middle of the stream and grab a sample at a depth about halfway between the surface and the bottom. Face upstream to avoid getting sediment you've stirred up. If the current is too strong, sample by lowering a bucket from a bridge. If there is no bridge near the sampling site, sample from the bank, reaching as far out into the stream as you can and remain safe.
Sample preservation: Conditions for preserving the sample during transport to the certified laboratory are referred to collectively as the "holding time." The single most important condition is to keep the sample ice-cold but not frozen. Cold temperatures slow down the bacterial and chemical reactions that degrade the sample. For some water quality tests, acid is added to the sample to lower the pH to less than 2, in order to further inhibit bacterial and chemical reactions. Examples of holding times for unacidified samples are: 48 hours for soluble reactive phosphorus, seven days for total suspended solids, and 14 days for alkalinity. Examples for acidified samples are: 28 days for nitrate plus nitrite and six months for total hardness.
Sampling frequency: In a typical monitoring program, water samples are collected eight times per year or twice per season. Ideally, seasonal samples are collected once under base flow conditions and once under high flow conditions, following a rainfall or snowmelt. Approximately 90% of the annual pollutant load is transported during the few days of the year when runoff is plentiful and flow is high. In order to estimate pollutant loadings as well as identify potential sources of pollution, it is important to sample under high flow conditions.

B. Overview of certified water quality tests

For monitoring purposes, water quality parameters can be prioritized roughly as follows:
1. Chemical "vital signs:" Temperature, pH, dissolved oxygen, alkalinity, turbidity, and conductivity. These parameters indicate whether a waterbody offers a good habitat for aquatic organisms, from single-celled algae to benthic macroinvertebrates and fish (see attachment B-1).
2. Common pollutants: The pollutants that affect the most waterbodies in the United States are phosphorus and nitrogen nutrients, sediment, and fecal bacteria. Note that these things are always present and are not considered pollutants unless their concentrations are too high. Excessive phosphorus or nitrogen nutrients can lead to algal blooms and other unwanted plant growth that stresses native ecosystems and may lower dissolved oxygen concentrations. Sediment can cover the stream bottom, preventing fish from spawning and suffocating aquatic insects that form a vital part of the food web. Excessive fecal bacteria make stream water unsafe to swim in or to drink without extensive disinfection. (See attachment B-2)
3. Toxic chemicals: These include metals such as lead and arsenic as well as organic chemicals such as pesticides and petroleum products. Toxic chemicals typically come

from a point source of pollution, such as a factory or an abandoned industrial site or landfill. While toxic chemicals tend to be less common than nutrients, sediment and fecal bacteria as water quality concerns, when present they pose an immediate risk to human health and the environment.

4. Hydrogeology: Under base flow conditions, when virtually all of the water in the stream is derived from groundwater, several water quality parameters reflect the natural hydrogeology of a stream, including pH, alkalinity, hardness, conductivity, total dissolved solids and chloride concentrations. When the stream is fed by runoff following a rain or snowmelt event, changes from baseline values indicate the impact(s) of the runoff on water quality. For example, increased chloride can be due to road salt, while decreased pH, alkalinity, hardness and conductivity can be caused by the dilution of calcium carbonate and other minerals by relatively soft rain water (see Attachment B-2).

Attachment B-1: New York State River Classifications and Water Quality Standards
Attachment B-2: Reports of water quality parameters in Fall Creek at the Cayuga Street bridge under relatively low flow conditions (5/25/04) and high flow conditions (3/5/04); samples collected by volunteers from the Fall Creek Watershed Committee Tompkins County SWCD staff and analyzed by the Community Science Institute Testing Lab

C. Measuring chemical "vital signs" with portable test kits and meters

The chemical "vital signs" of a waterbody can be measured using portable test kits and meters. With practice, the accuracy of the portable tests is quite good and approaches that of certified tests. Potential data users, e.g., government agencies, are generally willing to consider volunteer test kit data in their management decisions provided these data are accompanied by quality assurance and quality control (QA/QC) information which documents their scientific validity. QA/QC includes such things as keeping the glassware clean, replacing test chemicals once a year, checking to make sure batteries work, periodically performing tests on calibration standards, distilled water blanks, and duplicate samples, and occasionally splitting samples with a certified lab to verify results (see attachment C-1). Advantages of portable tests include savings on the cost of certified tests and the flexibility to test water samples at any time, without the need to coordinate with a lab or several other volunteers.

Unfortunately, while several "vital signs" can be measured conveniently and reliably using portable tests, most water quality parameters cannot. Test kits for nutrients such as phosphate, nitrate and ammonia, for example, rely on color comparisons that are subject to considerable variability, depending on such factors as available light and the perception of the person performing the test. Tests of other important parameters depend on equipment that is generally available only in a lab. Thus, measuring suspended sediments requires a balance accurate to 0.1 milligram, and measuring bacterial concentrations requires sterile conditions and temperature control. Volunteers can accomplish a great deal by monitoring the chemical and biological "vital signs" of a stream. They increase their effectiveness when, in addition to tracking "vital signs," they also team up with an independent lab to collect samples and monitor water quality impacts from nutrients, sediment, bacteria and toxics.

Attachment C-1: Summary of Quality Assurance and Quality Control Criteria for Volunteer Monitoring Data

D. Principles of stream flow and pollutant loads

Flow, which is also called discharge, is defined as the volume of water that moves past a transect across a stream in a given period of time. It is typically expressed in units of cubic feet of water per second. Flow is an important hydrologic characteristic of any stream. From a water quality perspective, flow is essential to calculating loads of nutrients, sediments and other pollutant parameters. Under the federal Clean Water Act, Total Maximum Daily Loads, or TMDLs, are used to regulate the amounts of pollutants that may be transported in or to an impaired waterbody. In order to calculate loads and determine whether they exceed mandated TMDLs, measurements of both stream flow and pollutant concentration are required.

Pollutant concentrations are typically measured in units of milligrams per liter. These units can be converted to other units, as necessary and convenient. For example, flow is often expressed in units of cubic feet per second. Thus, concentration might be expressed in units of pounds per cubic foot. To calculate load, we have:

Flow units = ft^3/sec

Converted concentration units = lbs/ft^3

Load = Concentration x Flow
= $lbs/ft^3 \times ft^3/sec$
= lbs/sec

Any units of load, in this case lbs/sec, are readily converted to other units, for example, lbs/day or kg/year -- whatever units make the most sense for the data user.

There are two USGS flow gauges on Six Mile Creek, and readings from the gauges are posted on the USGS web site in real time. In principle, USGS flow gauge readings can be combined with certified test results to calculate pollutant loads. Note, however, that USGS gauges measure flow only at the specific transects where they are located on the stream. Flow will tend to be lower at a sampling location upstream of a gauge; it will tend to be higher when the sampling location is downstream from the gauge.

It is possible to measure flow directly at the sampling location; however, obtaining accurate results is challenging, particularly when the water is high. A second approach is to estimate flow at the sampling location by assuming that flow is proportional to the drainage area above the sampling site. Flow is approximated as:

Flow at sampling site =
(Drainage area of sampling site) / (Drainage area at USGS gauge) x Flow at USGS gauge

New York State River Classifications & Water Quality Standards

(A brief overview—for more complete and up to date info, obtain a copy from NYS DEC)

New York State River Classifications

Class A Drinking, cooking, contact recreation (swimming), fishing, fish propagation and survival (aquatic life)
AA-Special: No discharge into water, no wastes or solids attributable to sewage, industrial, or wastes.
All other Class A: Can be treated to meet drinking water standards.

Class B Primary and secondary contact recreation, fishing, fish propagation and survival (aquatic life).

Class C Fishing, fish propagation and survival (aquatic life). Can be suitable for contact recreation, but may be limited.

Class D Fishing. Cannot support fish propagation due to natural conditions such as streambed and flow. Suitable for fish survival. Contact recreation may be limited.

New York State Water Quality Criteria for Surface Freshwater

Parameter	Class	Standard	Guideline for a Healthy Stream
PH	A,B,C	between 6.5-8.5	
	D	between 6.0-9.0	
DO	A-Special	6.0 mg/L	
	A, B, C	Trout spawning, 7.0 mg/L Trout waters, never < 5.0/L, daily ave. 6.0 Non-trout, never < 4.0 mg/L, daily ave 5.0	
	D	Not less than 3.0 mg/L	
Temperature		No standard	Trout, ≤ 70°F (21.1°C) Non-trout, <80°F(26.7°C)
Total phosphorus (P) *(multiply by 3 for ortho-phosphate)*		"None that will result In growths of algae, weeds, and slime that will impair uses" No numerical standard	> 0.05 mg/L impact likely > 0.1 mg/L impact certain (especially if slow moving area or upstream from lake)
Nitrate-nitrogen (NO_3-N)	A	10 mg/L	
	B, C, D	"None that will result in growths of algae, weeds, and slime that will impair uses"	Natural levels generally < 1 mg/L
Ammonia-nitrogen	(NH_3-N)	No standard	0.10 mg/L
Alkalinity		No Standard	0-5 mg/L endangered or critical 5-10 mg/L highly sensitive 10-20 mg/L sensitive 20 mg/L not sensitive
Chloride	A	250 mg/L	
	B, C, D	No standard	Natural levels generally <50 mg/l)
Conductivity	freshwaters	No standard	Generally 150-500 □S/cm, salt water much higher
Fecal Coliform	A, B, C, D	< 200 colonies/100 mL	
Turbidity	A, B, C, D	"No increase that will cause a substantial visible contrast to natural conditions"	
Suspended and settleable solids	A, B, C, D	"None from sewage, industrial wastes or other wastes that cause deposition or impair the waters for their best usages"	

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Test Report # [illegible]

Project: Volunteer Monitoring
Sample Field ID [illegible]
Sample Lab ID [illegible]
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HIGH FLOW

Client: Tompkins SWCD Contact name: Gordie Morgan
Address: Ithaca, NY
Telephone: 607-257-2340 Volunteer partnership Fall Creek Watershed Committee
Sampling location: Fall Creek at Cayuga Street Bridge
Sampling Date, Time: 3/5/04 2:05 PM Date and time of sample receipt: 3/5/04 4:30 PM
Sample received by: S. Penningroth

Water Quality Parameter	Result	Units	Date of Analysis	Standard Method	MDL	Remarks	Initials
Temperature	13 (C)	C or F		SM18: 2550 B	n/a		
pH	7.85	Unitless	3/5/04 [illegible]	SM18: 4500-H B	0.05		SMP
Conductivity	256	uS/cm	3/23/04	SM18: 2510 B	2		SMP
Alkalinity	67	mg CaCO/L	3/19/04	SM18: 2320 B	2		SMP
Total Hardness	129	mg CaCO/L	3/25/04	SM18: 2340-C	2		SMP
Ca-Hardness	96	mg CaCO/L	3/25/04	SM18: 3500-Ca D	2		SMP
(Total Hardness) - (Ca-Hardness)	33	mg CaCO/L	n/a		n/a		SMP
Chloride	26.7	mg/L	3/[illegible]	SM18: 4500-Cl C	2		SMP
Turbidity	304	NTU	3/5/04 [illegible]	SM18: 2130-B	0.1		SMP
Total solids (TS)	613	mg/L	3/5/04	EPA 1979: 160.3	20		SMP
Total suspended solids (TSS)	442	mg/L	3/[illegible]	EPA 1979: 160.2	2		SMP
(TS) - (TSS)	171	mg/L	n/a		n/a		SMP
Soluble reactive Phosphorus(SRP)^	30	ug/L	3/6/04	EPA 1979: 365.3	6		SMP
Total reactive phosphorus	147	ug/L	3/6/04	EPA 1979: 365.3	6		SMP
Total Phosphorus (TP)	320	ug/L	3/19/04	EPA 1979: 365.3	6		SMP
Ratio (TP-SRP)/TSS	0.66	ug/mg	n/a		n/a		SMP
Nitrate- + Nitrite-N	0.99	mg/L	3/24/04	EPA 1979: 353.3	0.014		SMP
Kjeldahl-Nitrogen	1.76	mg/L	3/19/04	SM18: 4500-Norg C	0.05*		SMP
Total Dissolved N**	2.75	mg/L	n/a		n/a		SMP
Ammonia-Nitrogen	0.11	mg/L	3/15/04	SM18:4500-NH3 B,C	0.05*	[illegible]	SMP
Organic Nitrogen***	1.65	mg/L	n/a		n/a		SMP
Chemical oxygen demand	111	mg/L	3/23/04	SM18: 5220 D	27		SMP
Dissolved oxygen	10.25	mg/L	3/[illegible]	SM18: 4500-O C	0.1	[illegible]	SMP
Total coliform/E. coli	14,600 / 6,382	Colonies/ 100 ml	3/5/04 [illegible]	SM18: 9222B, MI Agar	10		SMP

^Sample filtered within 4 hours of collection * Estimated Minimum Detection Limit **Total dissolved nitrogen = (Nitrate- + Nitrite-N) + (Kjeldahl-N)
*** Organic nitrogen = (Kjeldahl-N) - (Ammonia-N) [illegible]

Stephen M. Penningroth
Stephen M. Penningroth, Ph.D.
Technical Director

4/6/04
Date

ATTACHMENT B-2

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RELATIVELY LOW FLOW

Project: [illegible]
Sample Field ID: FCCb
Sample Lab ID: FCCb-052504

Client: [illegible] Contact name: [illegible]
Address: [illegible]
Telephone: [illegible] Volunteer partnership: [illegible]
Sampling location: Fall Creek at Cayuga Street Bridge
Sampling Date, Time: 5/25/04, 11:35 AM Date and time of sample receipt: 5/25/04, 3:40 PM
Sample received by:

Water Quality Parameter	Result	Units	Date Analyzed	Standard Method	MDL	[illegible]	Initials
Temperature	(17°C)[1]	°C		[illegible]	N/A		
pH	8.11	Unitless	5/25/04 7:30 PM	SM18: 4500-H B	0.05		SMP
Conductivity	250	[illegible]	6/23/04	[illegible]	[illegible]	See QC remarks	SMP
Alkalinity	95.7	mg CaCO3/L	6/18/04	[illegible]	[illegible]	See QC remarks	SMP
Total Hardness	117	mg CaCO3/L	6/24/04	[illegible]	[illegible]		SMP
Ca-Hardness		mg CaCO3/L		SM18: 3500-Ca D	[illegible]		
Chloride	16.4	[illegible]	6/23/04	[illegible]	[illegible]	See QC remarks	SMP
Turbidity	32.3	[illegible]	5/25/04 11:45 PM	SM18: 2130-B	[illegible]		SMP
Total solids (TS)	237	mg/L	5/27/04	EPA 1979: 160.3	[illegible]		SMP
Total suspended solids (TSS)	35.2	[illegible]	5/28/04	[illegible]	[illegible]		SMP
Total dissolved solids (TDS)		mg/L		[illegible]			
Soluble reactive Phosphorus (SRP)	32	[illegible]	5/26/04, 3:00 PM	[illegible]	1/2		SMP
Total reactive phosphorus		[illegible]		EPA 1979: 365.1	[illegible]		
Total Phosphorus (TP)	62	[illegible]	5/27/04	[illegible]	[illegible]		SMP
Nitrate + Nitrite-N	0.58	[illegible]	6/9/04	[illegible]	[illegible]		SMP
Kjeldahl-Nitrogen	0.70	[illegible]	6/18/04	[illegible]	[illegible]		SMP
Total Nitrogen	1.28	[illegible]	N/A		[illegible]		
Ammonia-Nitrogen	0.08	[illegible]	6/16/04	[illegible]	[illegible]		SMP
Organic Nitrogen	0.62	[illegible]	N/A		[illegible]		
Chemical oxygen demand	30	mg/L	6/25/04	SM18: 5220 D	[illegible]	See QC remarks	SMP
Dissolved oxygen	7.75	[illegible]	5/26/04, 12:15 AM	[illegible]		82% saturation	SMP
Total coliform/E. coli	32,150/1,100	Colonies/100 mL	5/25/04, 8:00 PM	SM18: 9223B, m-Agar	[illegible]		SMP
Total coliform		Colonies/100 mL		SM18: 9222B, m-Endo			
Fecal coliform		Colonies/100 mL		[illegible]			
Standard Plate Counts		Colonies/mL		SM18: 9215 B			

Estimated Minimum Detection Limit [illegible] Total Nitrogen = [illegible] Organic Nitrogen = (Kjeldahl-N) - (Ammonia-N)

[1] Client field measurement

Stephen M. Penningroth 6/30/04
Stephen M. Penningroth, Ph.D.
Technical Director
Date

Assuring the Credibility of Volunteer Data: Background

Summary of Quality Assurance and Quality Control Criteria for Volunteer Monitoring Data

QA/QC Level	BMI Sampling and Analysis	Chemical Testing with Portable Kits and Meters
A	1. Use net with 0.5-0.6 or 0.8-0.9 mm mesh. 2. Sample is a composite of 4 areas in a riffle, representing a total of about 1 square meter of the stream bottom. 3. Clean nets thoroughly of organisms between samples. 4. Attach Physical/Habitat survey. 5. Label sampling spots on sketches in Physical Survey.	General: 1. Clean sample bottles and glassware. 2. Collect according to standard procedures 3. Make sure reagents are less than one year old. 4. Analyze immediately or observe holding times. 5. Attach Physical/Habitat survey. Accuracy: • Calibrate test kits with standard and distilled water blank at beginning of testing (except DO kit, which does not require calibration). Repeat calibration standard at end of testing if more than 10 tests are performed. • Calibrate conductivity meter (standard and distilled water blank) and pH meter (standard only) every 10 analyses or at each new site, whichever is more frequent • Conduct super-saturation test for dissolved oxygen meter. 2.Precision: • Conduct one duplicate analysis for each chemical indicator per sampling day.
B	Same as Level A plus: 1. Collect and analyze two replicate samples from at least one site per sampling day. Similarity of at least 65% (Tier 3) or 75% (Tier 2) between replicates indicates satisfactory sample collection and analysis.	Same as Level A except: 1. Conduct duplicate analyses on 20% of samples or more per sampling day
C	Same as Level B plus: 1. Samples must be preserved in alcohol. 2. Once per sampling day, outside professional verifies analyses of two replicate samples. Goal is at least 65% (Tier 3) or 75% (Tier 2) similarity between outside professional's and volunteer group's results.	Same as Level B plus: Split one sample for every 20 samples analyzed **or** split one sample in every 30 day sampling period, whichever is more frequent. Send splits to an ELAP-certified lab for analysis.

Explanation of table: The quality assurance and quality control (QA/QC) criteria summarized in the table above were developed through the **Volunteer Monitoring Pilot Project**, a collaborative project of the Community Science Institute, the Hudson Basin River Watch, and the New York State Department of Environmental Conservation (NYSDEC) from 2001-2003. The Pilot Project demonstrated that when volunteers apply QA/QC criteria consistently, they make it possible for professional scientists to evaluate and use their results. To learn more about the Pilot Project, click on **Volunteer Monitoring Pilot Project: Executive Summary** and **Volunteer Monitoring Pilot Project: Final Report.**

What the table means: The credibility of any scientific data depends on following a specific protocol and then performing controls to show that the protocol actually works. In scientific jargon, following a specific protocol is referred to as "quality assurance" or QA, while performing controls to show the protocol works is referred to as "quality control" or QC. "QA/QC" refers to the entire process of demonstrating that data are credible.

Volunteer water quality monitoring generally involves two different types of protocols: 1) Benthic macroinvertebrate (BMI) sampling in stream riffles using kicknets followed by identification of insect orders and families, and 2) Chemical testing of stream or lake water samples using portable kits and meters. Three levels of QA/QC for volunteer monitoring data: Level A, level B and level C, were developed in the Volunteer Monitoring Pilot Project and are presented in the table above. Level C is the highest level of QA/QC for volunteers and consists of splitting samples with a certified lab, such as CSI.

If you are interested in a more detailed discussion of QA/QC concepts and their application to volunteer monitoring, click on **Documenting Scientific Credibility**.

HBRW Guidance Document: The Hudson Basin River Watch (HBRW), CSI's collaborator in the Pilot Project, is in the process of revising its Guidance Document for volunteer monitoring groups in New York State. The revised Guidance Document will incorporate the QA/QC criteria that were developed in the Volunteer Monitoring Pilot Project (see table, above). First produced in 2000 as a collaborative project of River Network, HBRW, and the New York State Department of Environmental Conservation, the HBRW Guidance Document contains excellent protocols for volunteer BMI and chemical monitoring in New York State. CSI uses the HBRW Guidance Document in its volunteer monitoring workshops. **For information on ordering the HBRW Guidance Document, contact Doug Reed, Hudson Basin River Watch, 3570 Route 29, East Greenwich, NY 12865, 518-677-5029, or <reed@netheaven.com.**

Split samples: CSI's certified lab splits samples with volunteer groups who wish to perform Level C QA/QC on their BMI and chemical results. For more information on the practical support CSI offers for the credibility of volunteer data, click on **Assuring the Credibility of Volunteer Data in Practice**.

Chemical Data Reporting Sheet

School/Group________________________________ River/Stream________________________________

Name of person(s) analyzing samples____Date analyzed______

Indicator	Calibration*			Sample Results (write in site & date, or sample #, in spaces below, for up to 5 samples)										Standard	Split*
		Standard												End of Testing*	
	Blank	Actual Value	Your Result	Result	Dup.*	Result	Dup.*	Result	Dup.*	Result	Dup.*	Result	Dup.*	Your Result	ELAP Result
Temperature °C	n/a	n/a	n/a												
pH	n/a														
Alkalinity (mg/L $CaCO_3$)															
Dissolved Oxygen (mg/L)	n/a	super-sat. test for meters													
% Saturation	n/a	n/a	n/a												
Nitrate-N* (mg/L)															
Orthophosphate* as PO_4 (mg/L)															
Conductivity (uS/cm)															
Other															
Other															

* Calibrate with blank & standard at start of testing. If 10 or more analyses per indicator per day (including duplicates), calibrate with standard at end of testing.
For QAQC Level A, analyze at least 1 duplicate per indicator per day. For QAQC Levels B & C, analyze at least 1 duplicate per 20% of samples per day.
For Tier 3 Nitrate-N and Orthophosphate, indicate under calibration that standard curve was used. Attach curve results.
For QAQC Level C, split one sample for every 20 samples analyzed or one in every 30 day period; send to ELAP lab.

Name, phone & email of person completing this sheet________________________________Date completed__________