WATER CHEMISTRY MONITORING PROCEDURES FOR CHESAPEAKE AND ATLANTIC COASTAL BAYS TRUST FUND PROJECTS

Prepared for

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1.0 GENERAL SAMPLING AND EQUIPMENT REQUIREMENTS

1.1 AUTOMATED VERSUS MANUAL STORM SAMPLING

The Department does not endorse one sampling method over another so long as the required samples are successfully taken at the appropriate positions on the storm hydrograph. Field sampling teams may elect to collect samples using a technique of their preference based on personnel availability, safety, budget, or facility with automated sampling equipment.

1.2 MINIMUM ELIGIBLE STORM AND SAMPLING ACCEPTABILITY CRITERIA

To maintain uniformity and comparability of data from captured storms, acceptable candidate storms will satisfy the following:

- be preceded by 48 hours of antecedent dry time, with dry time defined as < 0.05" of rain
- be 0.10" of rain in depth or greater within 24 hours

Two storms per calendar quarter will be captured, with one storm in any given month preferred. Two storms should not be monitored in a given month, unless all efforts to do otherwise have been unsuccessful.

Samples will be collected during the rising, peak, and falling limbs of the storm hydrograph. The rising limb is considered the portion of the storm runoff event where the stream stage is rising. Peak is the highest stage level of the stream. The falling limb is the portion of the storm where the stream stage is falling, usually when rainfall rate is slowing or it has ceased. The stage of the stream during storms may be logged using either electronic or manual means in order to determine appropriate sampling points on the hydrograph. It is helpful for field teams to have access to meteorological data as a secondary guide to determining optimal sampling points.

While flow logging at study waterways will be conducted by DNR, field sampling teams should employ an independent means of measuring stream stage since staff may not have immediate access to DNR data for the purposes of assigning samples to limbs after the fact.

1.3 BASEFLOW MONITORING GUIDANCE

Baseflow monitoring is performed in conjunction with storm monitoring, not as a substitute when storms are scant or have been difficult to capture in a given quarter. The antecedent dry time requirement will be 72 hours of less than a total of 0.05" of rain. Baseflow shall be taken during the first week of the quarter (provided antecedent dry time criterion has been met) and during the second week of the second month of the quarter. If criteria are not met during these time frames, then baseflow sampling will take place as soon as possible after the criteria are met.

1.4 SAMPLE HANDLING AND CHAIN OF CUSTODY PROCEDURES

Baseflow and storm runoff samples will, whenever practical, be kept refrigerated during the time period from immediately after sampling to relinquishing custody to laboratory personnel. During transport from the field and during intervals where samples are otherwise being processed by field staff, samples will be kept refrigerated or placed in coolers with sufficient ice to preserve them at 4° C. During storm sampling, automated samplers will be stocked with ice in the center of the bottle rack during sampling runs; the ice will be checked mid-run if the sampling run exceeds 24 hours.

Samples will be relinquished to laboratory personnel within 48 hours of sampling completion (if the sampling run exceeds 24 hours, and when practical, samples should be relinquished to the analytical laboratory within 24 hours of sampling completion). The completion time of sampling is defined as the end time of an automated sampling run or the time at which the last manual sample was obtained. The hold time set forth above is based on the shortest hold time available for the analysis of the collective parameters and is based on the requirement for nitrite and orthophosphate.

Chain of Custody (COC) forms (Figure 1-1), used for all samples, are a permanent record of transfer of sample custody from field staff to laboratory. Custom COC forms may be designed from analytical laboratory templates for time-saving and accuracy-assurance reasons. The COC form is the official analytical request for a given sample(s). Field staff should obtain a signed copy of the COC form from laboratory courier or staff upon sample relinquishment.

1.5 QUALITY CONTROL SAMPLES

Quality control samples will be analyzed according to the schedule provided in Table 1-1.

Table 1-1. Schedule of quality control sampling

Flow Type	**Blank**	**Duplicate**
Baseflow, all stations	Distilled water	Duplicate sample
Stormflow, all stations	Distilled water run through automated sampler tubing using sampler pump	Not applicable

For blank samples, house distilled water will be taken into the field and transferred to laboratory bottles onsite. When required, the distilled water will be passed through the same filtration apparatus as routine samples. For baseflow blanks, distilled water will be simply transferred from a distilled water stock bottle to laboratory submittal bottles. For storm monitoring blanks, distilled water will be transferred from the stock bottle to the laboratory bottles via automated sampler (when applicable) suction tubing using the manual sampling function of the sampler. The blank will be treated the same as and analyzed by the laboratory for the same parameters as the routine stream samples.

MARTEL ***CHAIN OF CUSTODY / SAMPLE INFORMATION FORM***

Martel Laboratories JDS Inc. • 1025 Cromwell Bridge Road • Baltimore, MD 21286 • (410) 825-7790 • FAX (410) 821-1054 Email: vk@martellabs.com

MARTEL Log # ______ Client Code ______	Sampler ______
Client Name/Phone/FAX ______	Project Name/# ______
Client Address ______	Contract/P.O Number ______
Invoice Address ______	Sample Turnaround Time ______

Station No./ Sample ID	Station Location	Matrix	Container Description/ Preservation Status	Potentially Hazardous?	# of Containers	Date	Time	Analyses Required/Comments

Transferred by:	Received by:	Date	Time	Cooler Receipt Information **(LAB USE ONLY)** Sufficient ice? - Yes/No If No, temp.= ________ Sample containers pres'd? - Yes/No If No, explain Custody Seal present/intact? - Yes/No Initials: Date:
Transferred by:	Received by:	Date	Time	
Transferred by:	Received by:	Date	Time	

Figure 1-1. Example of a laboratory Chain-of-Custody form

1.6 SAMPLE BOTTLE FILLING

Sample bottles that will be submitted to the laboratory for analysis should be filled to the bottle neck with sample. Leaving head space in the bottle facilitates mixing prior to analysis. Pre-preserved bottles are calibrated for a certain volume, so it is best not to either over-fill or under-fill the sample bottle.

1.7 SAMPLE FILTRATION

Onsite sample filtering is required for nitrogen and phosphorus parameters. Samples will be filtered through 0.45 μm filters using a manual filtration apparatus prior to laboratory submittal.

1.8 WATER QUALITY MEASUREMENTS

Water chemistry monitoring will also consist of measurements of in-situ, grab, or composite storm sample specific conductivity, water temperature, and pH with the goal of accurately reflecting stream conditions at the time of sampling.

1.9 SAMPLE CONTAINERS AND SIZES

Required bottle types and sample sizes for baseflow and stormflow monitoring are given in Table 1-2. For storm monitoring, mixing containers that contain composites of discrete samples that represent specific hydrograph limbs should be of sufficient size to distribute the required volumes to sample submittal bottles. The specific type and size of sample submittal bottles are dependent upon the requirements of the laboratory performing the analyses.

Table 1-2. Analytical requirements for Trust Fund monitoring (bottle sizes and minimum volumes will vary between laboratories)

Parameter	Analytical Method	Minimum Detection Limit*	Hold Time	Min. Volume	Bottle Type and Preservative
Ammonia as N	ASTM D6919-03	0.0016 mg/L	28 days	1 L	HDPE, H_2SO_4
Total Dissolved Phosphorus	EPA 365.1	0.006 mg/L	28 days	500 mL	HDPE, H_2SO_4
Total Dissolved Nitrogen	EPA 300.0 & SM 4500C	0.034 mg/L	7 days		
Particulate Phosphorus as P	EPA 365.1	0.0003 mg/L	28 days	N.A.	HDPE
Particulate Nitrogen as N	EPA 300.0 & SM 4500C	0.003 mg/L	28 days	N.A.	HDPE
Total Suspended Solids	SM 2540D	0.8 mg/L	7 days	1 L	HDPE
Nitrite-N	EPA 300.0	0.002 mg/L	48 hours		
Nitrite/Nitrate-N	EPA 300.0	0.003 mg/L	28 days		
Orthophosphate (PO_4)	SM 4500 PE	0.002 mg/L	48 hours		
Turbidity	SM 2130B	1 NTU	28 days		
Suspended Solids Concentration	ASTM D3977-97	0.8 mg/L	7 days	1 L	HDPE

* Analytical results should be reported as minimum detection limit (MDL) rather than reportable detection limit (RDL) or performance quantitation limit (PQL).

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2.0 SAMPLING EQUIPMENT DESCRIPTION AND MAINTENANCE

This section is applicable for storm runoff sampling via automated sampler and electronic flow logging equipment.

2.1 AUTOMATED SAMPLER

The sampler assembly consists of a keypad, pump, tubing, and sample bottle container that holds 24 plastic frames (to support disposable 1-Liter polyethylene liners) or plastic bottles. The 24 bottles will be used to contain the "discrete" samples that the sampler collects over the course of a storm event. Maintenance requirements consist of the following:

- checking integrity of the suction tubing to the anchor point,
- checking to see that suction tubing is securely attached to the pump tubing,
- ensuring that pump tubing is properly threaded through the distributor arm,
- running internal electronic maintenance cycle (includes internal CPU diagnostics and mechanical tests of sample pump and distributor arm), and
- making sure the distributor arm is securely attached to the frame.

Monthly maintenance checks will consist of running the sample pump to check for suction line integrity (so that the sampler will indeed sample). The suction line will be replaced biennially. The pump tubing will be replaced annually.

The sample delivery volume requires periodic recalibration. Once calibrated, the volume delivered tends to remain within 50 mL of the desired volume. Recalibration will be required when the volume delivered, for whatever reason, is consistently less than 800 mL rather than the full 1000 mL. Consistent volume deliveries below this level threaten minimum volume requirements for laboratory analysis. Recommended, but not necessary for autosampler volume recalibration, is a plastic, 1000-mL graduated cylinder. To gauge success of volume recalibration, use a plastic, 1000-mL graduated cylinder or a spare polypropylene discrete sample bottle, for example. If recalibration is performed in the field, use water brought to the field or a local water source (e.g., stream). If performed in the laboratory, place suction tubing in a bucket of water.

2.2 FLOW LOGGER

A continuously logging flowmeter (or stage logger) provides a long-term database of flow, as well as immediate access to stage and flow rate data with which to accurately select and composite discrete samples during storm event monitoring. The electronic data can be easily exported to ASCII (plain text) format and imported into spreadsheets and databases with little manipulation. The flow logger should have the capability of measuring stage at a resolution of at least 0.01 feet.

Maintenance tasks for this instrument include: ensuring that bubbler rate is at roughly 1 bubble/second and exchanging any desiccant canisters when the indicator shows moisture saturation. The 1 bubble/second bubble emanation rate enables accurate level measurements while conserving battery power.

Logger calibration should be checked at a variety of stages on a quarterly basis or if staff suspect a response issue has arisen. Pressure transducer and bubbler-type loggers are calibrated using a single point and should automatically hold calibration thereafter.

2.3 POWER SUPPLY

Automated sampler and flow logger manufacturers carry dedicated, portable supply packs that can be used with their instrumentation if connection to AC power is not practical in the field. Small power supply packs are useful for short-term deployments of equipment. Power supplies have a finite shelf-life and therefore should be checked periodically to determine if they continue to hold charge. Power supplies should be charged fully prior to deployment to avoid mid-sequence power interruption.

2.4 WATER QUALITY METER

Water quality meters come in a variety of configurations and are manufactured by several companies. The resolution of water quality meters per parameter should meet the following criteria: 0.1 pH units, 1 mS/cm^2 for specific conductivity, and 0.1 °C for temperature. Water quality meters should be rugged and field-deployable. Consult instrument manuals for recommended calibration frequency; however, as a guideline, each parameter (save temperature) should be checked and calibrated every three days when in use. Probes should be inspected and cleaned according to manufacturer recommendations.

An example calibration procedure is provided below. A sample of the calibration sheet is shown in Figure 2-1.

SONDE CALIBRATION SHEET

Sonde Make/Model ______________

SN # ______________________

	Pre-calibration[1]	Calibration[2]
Dissolved oxygen (DO)	________	________
Specific conductivity (SpCond)	________	________
pH (7)	________	________
pH (4/10)	________	________
Depth	________	________
ORP	________	________

Calibrated by: ________

Date: ________

Comments:

(1) Display reading before adjustment
(2) Display reading after adjustment

Figure 2-1. Sonde Calibration Form

1. Attach hand-held display and communication cable. Open

communication program to connect to the unit.

2. **Specific Conductivity** - Rinse with correct KCl solution and discard
3. Fill to above probe with KCl solution
4. Select specific conductivity from the list of parameters then select the correct calibration units.
5. Follow procedure to calibrate specific conductivity to the correct value.
6. **pH** - Rinse by adding a small portion of pH buffer, cap loosely, agitate, and discard.
7. Add enough pH buffer to cover all probes.
8. Select pH from the list of parameters and then select the number of points (usually 2). Follow manufacturer calibration procedure for pH.
9. Move on to next point calibration when prompted. Follow calibration procedure as above.
10. **Dissolved oxygen –** add approx. 20 ml of tap water to calibration chamber, cap loosely, agitate, and discard.
11. Add 1 cm of water to calibration chamber, orient sonde in an upright position, and cap loosely. Wait 15 minutes for air layer above water to saturate.
12. Select automated method of dissolved oxygen calibration that takes local atmospheric pressure into account.

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3.0 PROCEDURES FOR STORM RUNOFF MONITORING

3.1 AUTOMATED WATER CHEMISTRY MONITORING

Preparation for Storm

Equipment:

- automated samplers
- sample caps
- roll of suction tubing
- spare bubbler line
- project field notebook
- bags of ice
- chain of custody forms
- NiCd batteries
- 1-liter sampler bottles
- cable ties
- bike locks
- spare strainers

Notify contractor laboratory of intent to sample and provide approximate pickup or drop-off time for samples.

Determine approximate onset, duration, and amount of predicted rainfall by consulting meteorological services (e.g., Weather Channel broadcast or NOAA website).

Confirm that the samplers have clean bottles or Propak liners in the frames well before the onset of an anticipated storm.

Charge batteries fully prior to setting up for storm. Voltage should be 13.0 or greater. Plan on swapping in fresh batteries during the storm if the anticipated event is over 36 hours in duration.

Sampler Placement Guidance

Deploy the sampler in a secure location on stream bank, preferably near the location of staff plate and control structure (if any; Figure 3-1). Check to make sure the strainer is well-submerged in the water and firmly attached to a structure such as the staff gauge, DNR flow logger assembly, or separate piece of rebar. Minimize the amount of tubing within the water column so that a smaller target is presented for collection of debris and trash. Attach both the suction line and bubbler line to sampler. Set level on automated sampler to level shown on staff gauge. Repeat the process at other sites. Check for presence of bubbles from the bubble tube on power-up.

Sampler Programming

1. Attach bubbler line and suction tubing to sampler. Attach suction line to low-flow strainer in waterway.
2. Check that sampler is level.
3. Place ice in center of sampler.
4. Check for misalignment of bottles or liners to prevent snagging of distributor arm.
5. Program Sampler by setting sampling initiation time and inter-bottle interval time. Note: since the waterways are flashy, reduce bottle interval to as small an increment as possible while maintaining enough spread to capture the required three limbs. The overall sampling time should take into account period of rainfall plus estimated drain-out time of the catchment.
6. Secure sampler.
7. Attach and secure sampler covers. Be sure no tubing has been pinched between cap and sampler body. Align tubing in tubing access slots.
8. Enter sampler start time and bottle interval on field data sheet.

Compositing

For all sites, cap each discrete bottle if samplers and samples are to be moved to a different location for compositing.

Figure 3-1. Automated sampler placement.

1. Download sampler data.
2. Create hydrograph of continuous level data corresponding to storm.
3. Using cursor to show time of collection, determine one-liter bottles corresponding to rising, peak, and falling limbs of the storm hydrograph. Each limb shall consist of sufficient adjacent, one-liter bottles in order to obtain enough volume to fill laboratory bottles for analysis.
4. Label laboratory bottles to identify station, site, and storm date.
5. Cap and agitate each discrete sample bottle, and then pour the contents into a mixing container (clean, stainless steel bucket or four-liter jug, for example). After mixing, pour

sample into each laboratory bottle as needed, taking care to fill the laboratory bottles to the shoulder.

6. Repeat step 5 for remaining limbs.
7. Ice or refrigerate samples until pickup by the contractor laboratory.
8. Prepare chain of custody form.

For all samplers, remove used Propak liners and discard. Mount new liners by following directions printed on liners. If polypropylene bottles are used in the automated sampler, wash bottles and caps with detergent in tap water, and rinse three times with distilled water. Fill each bottle to the top with distilled water, cover with clean cap, and allow to sit for 48 hours. Empty water and allow to dry.

3.2 SUSPENDED SEDIMENT MONITORING

Preparation and Mounting of Siphon Samplers

Equipment:

- siphon samplers
- medium-duty flat head screwdriver
- project field notebook
- bags of ice
- chain of custody forms
- crest gauge logger
- one-liter Nalgene-type bottles (6)

Reference: Diehl, T. H. 2008. A modified siphon sampler for shallow water. United States Geological Survey, Reston, Virginia.

The siphon samplers, depending on design, have an array of six, removable, one-liter bottles attached. Copper tubing, with opening oriented downward, along with vent tubing, allows sample to enter the collection bottle at specific stage heights and prevents washout. The sampler apparatus also includes an attached, electronic crest gauge to record continuous level to correlate suspended solids concentration to stream stage.

The siphon sampler should be deployed for the same storms as the automated samplers so that the results from each sampling device can be directly compared.

Sampler Placement Guidance

The sampler design includes hooks or a strip of vertically-oriented small-diameter PVC to allow the sampler to be attached and detached from a fixed object in the stream. A two to three foot-length of rebar, sunk firmly into the stream bed is a good anchor for the siphon sampler. When deployed, the sampler simply attaches to or slides onto the rebar. The position of the sampler should be in the thalweg of a section of straight run or a riffle to allow increasing stage to fill higher-positioned sampler bottles.

1. Attach one-liter, labeled plastic bottles (6) to matching, labeled mountings. Screw in for tight fit, but do not over-tighten.
2. Launch level logger and attach to siphon sampler structure.
3. Insure that ends of copper nozzles are oriented straight down.
4. In stream, mount on vertical rebar piece in stream (Figure 3-2). Note distance between tip of lowest nozzle and water surface and record. Orient sampler so that the copper nozzles are facing upstream and the bottles downstream.
5. To keep the sampler stable and upright during storm flow, place three bricks (or another heavy object) on the shelf above the siphon bottles. Use a screw driver to tighten the pipe clamps around the bricks so the bricks don't shift.
6. Enter deployment date and time on field data sheet.

Figure 3-2. Siphon sampler

Siphon Sampler Retrieval

1. Loosen bricks on shelf above siphon bottles and set high on bank.
2. Remove siphon sampler and transport to truck with PVC tubing oriented horizontally (bottles should be vertical with copper nozzle side up so as to contain the water and not let water run back out).
3. Rinse excess sediment off outer surface of bottles using a wash bottle and distilled water.
4. Carefully unscrew each plastic bottle and set aside.
5. Transfer contents of each bottle to separate, labeled, laboratory bottles (one liter unpreserved) by alternately swirling and pouring bottle contents. Record % fill status of each of the sampler bottles on field data sheet in project binder.
6. Store samples on ice or in refrigerator to await transfer to laboratory.
7. Prepare chain of custody form.
8. Rinse out excess sediment with tap water with the aid of a brush and then rinse with distilled water.

Upon return from the field, siphon samplers should be well-cleaned and inspected for damage, so that any issues can be addressed immediately so that the samplers will be ready for redeployment for the next round of sampling. The siphon samplers collect a lot of debris and sediment and sometimes are toppled and buried during very high flow events. The best way to clean the sampler is to first remove gross silt accumulation using a garden hose. Wash any dirt out of the main PVC pipe. It is very important to wash out any sediment clogging the plastic vent tubing. The best way to do this is to lay the sampler nozzle-side down with the bottles off and force water through the copper tubing and out the vent tubing which is usually where sediment clogs form. Running water or a straightened coat hanger through the tubing should be sufficient to clear or break up any clogs. Inspect the sampler for loose pipe clamps and cable ties. The vent tubing should be running as straight up the main PVC pipe as possible. Inspect the lid mounts at the rubber stoppers for loss of integrity, (e.g., breaking, loose, missing silicone seal).

4.0 BASEFLOW MONITORING PROCEDURE

Equipment:

- project field data notebook
- water quality monitoring equipment (e.g., sonde or parameter-specific handheld units)
- sampling bottles
- cooler
- bags of ice
- chain of custody forms

Preparation

1. Inform analytical laboratory of possible sampling activities 24 hours prior to sampling and arrange pickup or drop-off time.
2. Calibrate sonde and any other necessary equipment (fill out calibration sheet).
3. Label sampling bottles.

On-site Monitoring

1. Measure instream water quality parameters (temperature, pH, specific conductivity, and dissolved oxygen) using calibrated sonde unit (be sure to submerge probe-end of sonde in the middle of stream where there is flow and wait for DO readings to stabilize before recording other readings). Record instream parameter results on field data sheets.
2. Record stream height (using staff gauge) on field data sheet.
3. Record air temperature on field data sheet.
4. Collect grab samples at the thalweg by immersing bottle mouth part-way into water column. Approach sampling point by walking upstream; orient bottle mouth so that it is facing upstream. For pre-preserved sample bottles, withdraw bottle from water before it fills completely so that no preservative backwashes into the stream.
5. Place samples in iced coolers.
6. Complete chain of custody forms. Confirm collection time, date, and sample ID are recorded accurately for each sample.
7. Transport samples to contractor laboratory or back to office for pickup by laboratory courier.

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APPENDIX

EXAMPLE FIELD DATA SHEETS

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STORM EVENT
STREAM MONITORING

CREW SET-UP | COMPOSITE | STATION | YEAR | MONTH | DAY

STORM DURATION (hr) | SAMPLE INTERVAL (min) | SAMPLE BEGIN | TIME

INSTREAM WATER QUALITY:

H_2O TEMP (C) | DO (mg/L) | pH | COND (mmhos) | AIR TEMP (C)

HYDROLAB CALIBRATION DATE: ______________ BY: ______________

HYDROGRAPH/COMPOSITE INFORMATION:

(1) RISING LIMB

Bottle | Time | Interval discharge (cf) | pH | Cond

(2) PEAK LIMB

Bottle | Time | Interval discharge (cf) | pH | Cond

(3) FALLING LIMB

Bottle | Time | Interval discharge (cf) | pH | Cond

TIME OF COMPOSITE ______________

					S	T	1					
					S	T	2					
					S	T	3					

COMMENTS ____

____

REVIEWED BY ______________ DATE: ______________

MONTHLY BASEFLOW STREAM MONITORING

CREW

YEAR_MONTH_DAY

WEATHER CONDITIONS/ COMMENTS

TIME

STAFF GAUGE HEIGHT (ft)

WATER QUALITY

H_2O TEMP (C)	DO (mg/L)	pH	COND (mmhos)	AIR TEMP(C)	RAINFALL

SONDE CALIBRATION DATE: ______________ BY: ______________

SAMPLE DATA COLLECTION: General Water Quality

Upstream

CREW

YEAR_MONTH_DAY

WEATHER CONDITIONS/ COMMENTS

TIME

STAFF GAUGE HEIGHT (ft)

WATER QUALITY

H_2O TEMP (C)	DO (mg/L)	pH	COND (mmhos)	AIR TEMP(C)	RAINFALL

SONDE CALIBRATION DATE: ______________ BY: ______________

SAMPLE DATA COLLECTION: General Water Quality

Downstream

SITE INSPECTION LOG

CREW			

TIME			

YEAR_MONTH_DAY					

	SITE 1		**SITE 2**	
	UPSTREAM	DOWNSTREAM	UPSTREAM	DOWNSTREAM
SITE COND.				
TEMP LOGGER				
Primary Device Cond.				
DOWNLOAD date				
Stage Level				
BATTERY Status (24 = 100%)				
Measured Level				
COMMENTS				

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