CHAPTER IV

MAINSTEM & TRIBUTARY FIELD PROCEDURES

SECTION A

BACKGROUND AND DESCRIPTION

1. Management Objectives

The 1985 Chesapeake Bay Restoration and Protection Plan identified the need for restoration activities and a monitoring program to measure the success of these activities. On June 28, 2000, the Chesapeake Bay Program adopted a new Bay agreement, *Chesapeake 2000: A Watershed Partnership* to guide the management and restoration of the Bay. In this "C2K"document, Bay Program Partners agreed upon multiple objectives, one of which is "to achieve and maintain the water quality necessary to support the aquatic living resources of the Bay and its tributaries". Water quality monitoring data are necessary to assess these objectives.

2. Monitoring Objectives: The monitoring objectives for the Tidal Water Quality Monitoring Program are to:

2.1. Assess the habitat conditions for aquatic living resources and determine if these conditions meet tidal water quality criteria and standards designed to protect them from nutrient and sediment impacts;

2.2. Deduce the likely causes of nutrient and sediment impairments, and determine the best course of action necessary to meet the water quality criteria and standards;

2.3. Support continued refinement, calibration and validation of Chesapeake Bay Program models such as the Estuarine Water Quality Model and multi-species management models and;

2.4. Provide a long-term consistent set of data that is available for public and private research.

3. Sampling Design

3.1. The Chesapeake Bay Mainstem and Tributary Monitoring Program focuses on inorganic and physical parameters in the open and deep tidal waters of the Chesapeake Bay estuary. Staffs from the Maryland Department of Natural Resources (MDNR), Virginia Department of Environment (VDEQ), and Old Dominion University (ODU) collect surface to bottom discrete measurements at over 100 mid-channel stations. The timing and methods of sample collection are closely coordinated between Maryland and Virginia to permit consistent data presentations across the region. Phytoplankton samples are collected concurrently with water quality samples.

3.2. Twenty-two field and laboratory parameters are monitored, and include nutrients, suspended solids, dissolved oxygen, salinity, temperature and chlorophyll *a*. Field parameters are measured *in-vivo*, and discrete, grab samples are processed (i.e., filtered) immediately onboard and frozen. A complete listing of mainstem and tributary water quality parameters is provided in Table IV.1.

3.3. The number of grab samples taken and the depth at which they are taken varies among stations. At many stations, four samples will always be collected: surface and bottom, and either above and below pycnocline if one is present, at 1/3 and 2/3 the total depth, or above and below the pycnocline, depending on the presence or absence of a pycnocline. At other stations, only two samples (surface and bottom) are collected. The presence of a pycnocline and the sampling depths are determined according to the procedures found in Chapter IV Section C 2.4 and 3.3.

3.4. *Figure IV.1 Chesapeake Bay Mid-Channel Monitoring Stations,* is a map of water quality monitoring station

locations. Appendix A gives the lat/long coordinates and a description of each station. This information is also available electronically from the CIMS data hub under Water Quality Data - "Station Table".

4. Water Quality Parameters

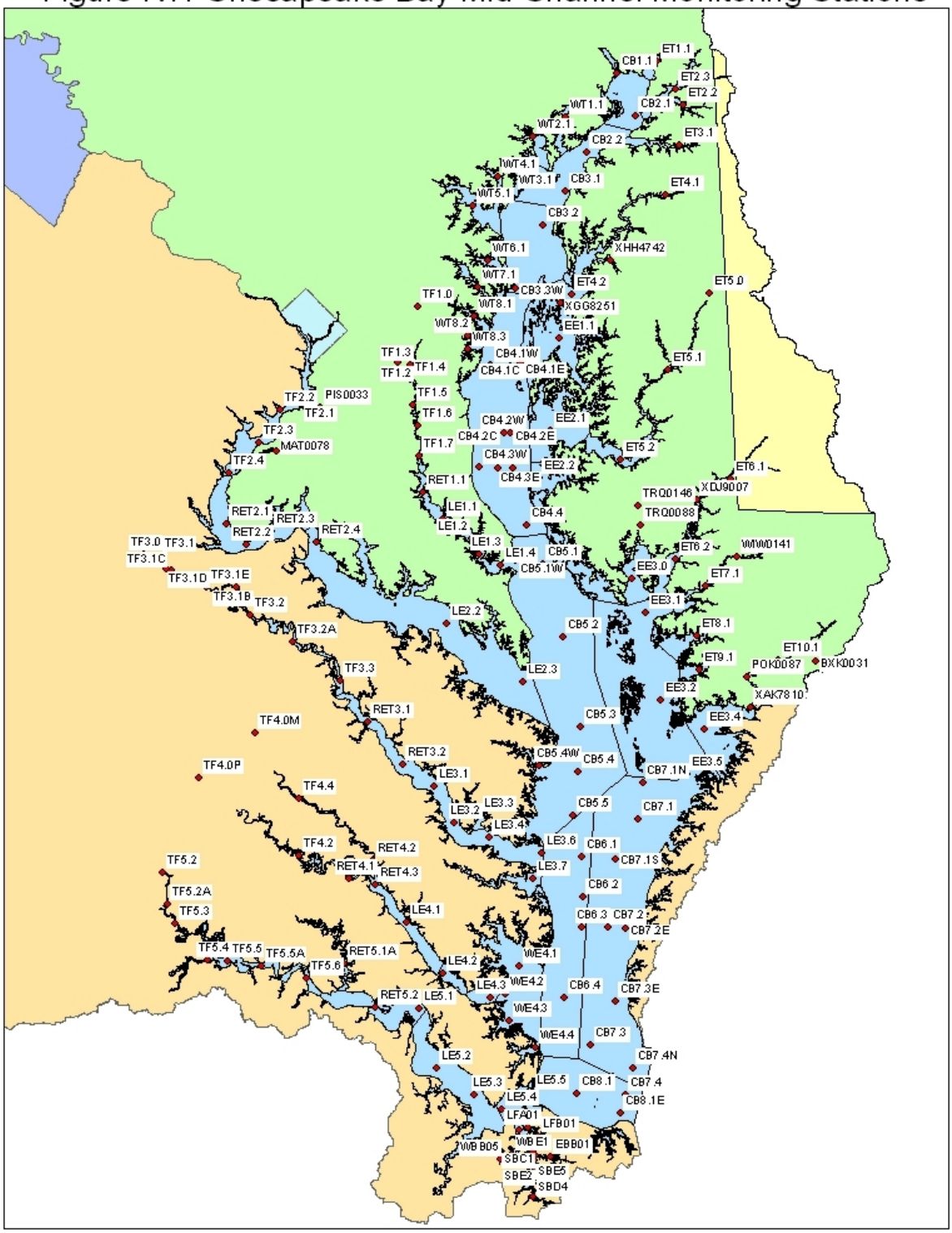
TABLE IV.1 Mainstem and Tributary WQ Parameters

Laboratory Parameters (mg/L)	In-situ Measurements
Total Dissolved Phosphorus (TDP)	Dissolved Oxygen (mg/L)
Dissolved Orthophosphate (PO_4F)	Temperature (°C)
Particulate Phosphorus (PP)	pH (su)
Nitrite (NO_2F)	Specific Conductance (µmhos/cm)
Nitrate + Nitrite ($NO_{23}F$)	Salinity (psu)
Ammonium (NH_4F)	Secchi Depth (m)
Total Dissolved Nitrogen (TDN)	Total Depth (m)
Particulate Nitrogen (PN)	Sample Depth (m)
Particulate Carbon (PC)	
Total Suspended Solids (TSS)	Photosynthetic Active Radiation (PAR), (µM = µmoles/second-meter^2)
Volatile Suspended Solids* (VSS)	
Chlorophyll *a* (CHLA) (µg/L)	
Pheophytin (PHEO) (µg/L)	
Dissolved Organic Carbon* (DOC)	
Silica* (SiF)	
*** Collected from a subset of stations**	

5. Map of Station Locations:

See *Figure IV.1 Chesapeake Bay Mid-Channel Monitoring Stations*.

Figure IV.1 Chesapeake Bay Mid-Channel Monitoring Stations



SECTION B

FIELD MEASUREMENT PROCEDURES

1. Sampling Sites
   1.1. Each fixed station has predetermined latitude and longitude coordinates. Locate the sampling location by GPS and position the vessel within 25 meters of that point. The engine may be turned off and the vessel either anchored or allowed to drift. Avoid drifting to shallower or deeper waters as this may result in real differences in water quality.

   1.2. Record the actual initial GPS coordinates on the field sheet or in the captain's log. If sampling conditions prevent collection of data at the predetermined coordinates, record the actual coordinates and depth in the "Details" field of the CIMS Event Table.

   1.3. The total depth measurement from surface to bottom may be done in several ways: from the vessel depth finder, the pressure sensor of the sonde, or calibrated markings on lines attached to the sampling equipment.

2. Weather Conditions
   Record weather and sea conditions at the time of sampling, i.e., cloud cover, air temperature, precipitation type, wind speed, wind direction, wave height and tidal current stage.

3. Physiochemical Profile

   3.1. An *in-situ* vertical profile is determined at every sampling station. The following parameters are measured from the bottom to the surface of the water column: water temperature, pH, dissolved oxygen, salinity, and secchi depth. The depth of each measurement and total depth are also measured. Light attenuation is measured at collocated phytoplankton monitoring stations.

   3.2. Equipment

      3.2.1. A multi-parameter, water quality instrument, such as a YSI or Hydrolab sonde.

      3.2.2. The instrument shall be equipped with the following sensors:

         3.2.2.1. Dissolved oxygen sensor,
         3.2.2.2. pH sensor,
         3.2.2.3. Thermistor (temperature sensor), and,
         3.2.2.4. Conductivity cell (salinity).

         Note: Some sondes have pressure sensors which may be used to determine sampling depth.

      3.2.3. The sonde must be outfitted with a data logger or computer to display the measurement values. If possible, record and store measurements electronically.

   3.3. Calibration: (See also Section II.C.2)

      3.3.1. Pre-cruise calibrations must be performed for dissolved oxygen (DO), pH, and conductivity to standardize

the response of each probe. Post-cruise calibration checks are performed to ensure that calibration was maintained over the course of sampling. For multiple day cruises, a daily, one-point DO calibration check is highly recommended.

3.3.2. Staff shall maintain logbooks for each instrument and/or sensor. The logbooks shall document all calibration, maintenance and servicing information.

3.3.3. Calibrations are performed indoors after the probes have stabilized to room temperature. Follow all manufacturer specifications for calibration and maintenance; fully document selected options in the calibration SOP.

3.3.4. If a post-calibration check does not meet acceptable tolerances, censor the corresponding data back to the last calibration check using the CIMS WQ problem code "V" (Sample results rejected due to QC criteria.)

If the post-calibration failure is due to an accident that occurred after sampling, qualify the data with the CIMS WQ problem code "F" (i.e., Post-calibration failure possible due to equipment damage after sampling, but data appear normal.)

3.3.5. *Conductivity*: The conductivity sensor must be calibrated against a reference solution, according to manufacturer's specifications. As a minimum, conductivity should be verified before and after each cruise.

3.3.6. *pH*: As a minimum, the pH sensor must be calibrated at the beginning and end of every cruise. Use two standard solutions of pH 4.0, pH 7.0 or pH 10.0 buffers, bracketing the expected values of pH. If the post-calibration drift is ± 0.2 pH units or more, censor the data with the CIMS WQ problem code "V" or report values with code "F".

3.3.7. *Dissolved oxygen (DO)*: The DO probe must be calibrated at the beginning and end of each multiple-day cruise according to manufacturer's specifications. Typically, Clark cell probes are calibrated against water-saturated air. Check the calibration at the beginning of each day.

If daily DO checks deviate by ≥ 0.30 mg DO/L from the expected value, the sensor must be recalibrated before using again. If a calibration check (daily or post-calibration) is ≥ 0.50 mg DO/L, censor all data corresponding back to the last calibration check using the CIMS WQ Problem Code "V".

3.3.8. *Thermistor*: Verify the accuracy of the thermistor reading at least once a year against a NIST certified thermometer over a range of temperatures. If the temperature is off by ≥ ± 1°C, have a service representative recalibrate the unit.

3.3.9. *Depth sensor*: Verify the accuracy of the sonde pressure transducer at the beginning of each sampling day at a known depth below the surface. The depth should be accurate to 0.2 meters, or the tolerance given by the manufacturer.

3.3.10. *LiCor Meter*: An annual calibration is recommended; every 2 years is required.

3.4. *In-situ* Data Collection (Multi-parameter sonde)

3.4.1. Record the total depth from surface to bottom from the vessel depth finder, a calibrated line or the sonde.

3.4.2. Take the surface reading at 0.5m (Md.) or 1.0m (Va.) below the surface. Take subsequent readings at 1m, 2m, and 3m depths below the surface, then at least every 2m intervals until 1m above the bottom.

3.4.3. Take measurements every meter if:

3.4.3.1. The station total depth is ≤10m deep,
3.4.3.2. The change in DO is ≥1.0 mg/L every 2 m, or,
3.4.3.3. The change in specific conductance is ≥ 1,000µmhos/cm every 2 m.

3.4.4. Lower the sonde to the desired depth, as displayed on the data logger or winch meter.

3.4.5. When all readings have stabilized, record the temperature, pH, DO, conductivity and salinity values on the field data sheet and in the data logger if available.

3.4.6. Repeat procedure for all required depths. Collect additional measurements at the calculated AP and BP depths if these depths were not included in the profile.

4. Pycnocline determination

The pycnocline is a region in which the water density changes appreciably with increasing depth and thus forms a layer of much greater stability than is provided by overlying surface waters. It is necessary to calculate the pycnocline in the field to determine the depths at which to collect grab samples.

The pycnocline calculated threshold value (CTV) is calculated using Equation IV.1. If the CTV is less than 500 micromhos/cm, then there is no discernible pycnocline. If the CTV is above 500 micromhos/cm, a pycnocline exists with boundaries at the first and last depths where the change in conductivity is greater than the CTV.

$$CTV = \frac{C_b - C_s}{D_b - Ds} \; x\, 2$$

Where:

C_b = bottom conductivity (micromhos/cm),
C_s = surface conductivity (micromhos/cm),
D_b = depth of bottom conductivity measurement (m),
D_s = depth of surface conductivity measurement (m),
CTV = calculated threshold value (micromhos/cm)

5. Secchi depth

5.1. Secchi depth is a measure of the transparency of a water column.

5.2. Equipment: A 20 cm Secchi disk, held by a non-stretchable line that is marked in tenths of meters.

5.3. Frequency: The Secchi depth is determined at each station.

5.4. Procedure:

5.4.1. The Secchi depth must be determined from the *shady* side of the boat during daylight hours.

5.4.2. Slowly lower the Secchi disk until it is no longer visible and note the depth using the markings on the line.

5.4.3. Slowly raise the Secchi disk until it just becomes visible and note the depth using the markings on the line.

5.4.4. Record the average of the two Secchi readings to the nearest 0.1 meter.

5.4.5. Do not wear sunglasses or any devices that shades the eyes while performing this procedure.

5.5. Quality Control - Secchi

5.5.1. If the range of measurements for the two readings is greater than 0.5 m, repeat the entire measurement process, raising and lowering the disk several times around the "disappearing" point.

5.5.2. If the disk hit the bottom and remains visible, record the depth reading and note this in the comment section.

5.5.3. Calibrate the markings on the Secchi line periodically against a metal meter stick.

6. Light Attenuation (PAR)

6.1. Equipment: Manufactured by LI-COR, Inc.

6.1.1. LI-192SA, flat cosine Underwater Quantum Sensor

6.1.2. LI-190SA, air (deck) reference sensor.

6.1.3. Data Logger (LI-1000 or LI-1400)

6.2. Parameters:

6.2.1. EPARU_Z: Downwelling PAR, measured underwater (µM, micromoles/second-meter^2 = µE, microEinsteins).

6.2.2. EPAR_S: PAR measured in air, on deck or pier, recorded concurrently with each underwater depth reading (µM).

6.2.3. SDEPTH: Sample depth at which PAR reading is recorded (meters).

6.3. Depths for Mid-Channel PAR

6.3.1. Record the initial PAR just below the surface. If wave action is too great, take the initial PAR at 0.5 m.

6.3.2. As a general rule, record subsequent measurements at 1 meter increments for mainstem stations and at 0.5 m intervals for tributary stations deeper than 2 m. This may be increased to 2 m if the water is clear and deep.

6.3.3. Increments of 0.25 m are recommended for stations ≤ 2 m, or if water is turbid or colored.

6.3.4. Measurements are recorded until the meter reads ≤10 % of the initial subsurface value or if the bottom is

reached.

6.4. PAR Procedure

6.4.1. PAR must be measured from the *sunny* side of a vessel or pier during daylight hours. Both the deck sensor and the submersed sensor must be placed away from the shadow of the vessel.

6.4.2. Check the sensor operation by connecting the deck sensor and underwater sensor to corresponding ports of the Li-Cor data logger, and turn the power on. Check battery level. Cover the sensor and check to see if the output is very near zero. Place the sensor under a light source to assure that it has a positive reading. A negative reading indicates that the polarity of the sensor is reversed (it is plugged into the cable backwards). A very positive or negative reading under darkness indicates a possible short in the cable or some other electrical short.

6.4.3. In the field, mount the deck sensor in a location which is level and unobstructed by shadows. Ensure that the sensors are positioned properly on the deck sensor mounting and the lowering frame. Connect deck sensor and underwater sensor to corresponding ports of the meter, and turn the power on.

6.4.4. Set the instrument averaging constant to display results from previous 10 or 15 seconds.

6.4.5. Lower the frame until the sensor is just below the surface of the water; simultaneously record the deck sensor and the underwater readings. If wave action prevents this, take a deeper reading ≤ 0.5 m. Determine the measurement depth using a calibrated pole, non-stretching rope or depth sensor.

6.4.6. Lower the frame and take subsequent measurements at depths appropriate to the monitoring location and purpose of the project. Allow the instrument output to stabilize, and then record both deck and underwater readings at each depth.

6.4.7. The simultaneous deck and submersed readings are stored by pressing “Enter”. Each record will be stored with a time stamp which will flash on the data logger readout. Record this time. All readings can be subsequently retrieved at the end of the cruise.

6.5. Quality Control

6.5.1. The deck cell should have the highest PAR value, and the underwater sensor output should decrease as the sensor is lowered to greater depths.

6.5.2. Periodically check that the two sensors are linear and not out of calibration with respect to each other.

6.5.3. Calibration of the sensors by LICOR, Inc. is recommended every year, and required every two years.

6.6. Reporting PAR

The CIMS database stores PAR values from the deck sensor and each underwater measurement. Report the values under the following method codes:

6.6.1. **EPARU_Z F01**: Flat cosine sensor LI-192SA
6.6.2. **EPAR_S F01**: Deck (reference) sensor LI-190SA
6.6.3. **SDEPTH**: Sample depth at which PAR reading is recorded, in meters

7. Documentation and Records

Field Data Sheets, Calibration and Maintenance Logs must permit a complete historical reconstruction of the data. See Chapter II.4 for detailed document control protocols.

8. Decontamination

8.1. *Multi-Parameter Sonde*: Rinse the sonde, probes and cable with tap water or DI water at the end of each sampling day. Cover with the storage cup containing ~ 1 inch of water to provide an air-saturated environment. For routine maintenance, follow the manufacturer's procedures.

8.2. *LiCor Sensors:* Rinse the underwater sensor and cable with tap or DI water at the end of each sampling day.

8.3. *Secchi Disk*: Clean the Secchi disk with a mild detergent solution at least once per month.

SECTION C

SAMPLING PROCEDURES

1. Sampling Schedule

1.1. The Maryland Department of Natural Resources (MDNR) and Virginia Department of Environmental Quality (VDEQ) collaborate to develop an annual sampling or "cruise" schedule to ensure that samples are collected by both groups within reasonably the same time. The cruise schedule is submitted to the EPA Project Officer and published on the Chesapeake Bay Program website at http://www.chesapeakebay.net/data/index.htm.

1.2. Weather and sea conditions permitting, all field measurements and sample collections for each mainstem cruise shall be completed during three days; and all field monitoring and sample collections for each tributary cruise shall be completed as closely as possible to the mainstem cruise dates.

1.3. Due to the large distance that must be covered in a single day of sampling, it is not practical to sample stations at a selected tidal stage. Instead, cruises shall begin on the designated date in the early morning and shall be completed by evening (usually 6 or 7 PM). Sampling should occur during daylight hours. In addition, all light dependent measurements, i.e., Secchi depth, light attenuation and fluorescence, must be measured during daylight hours.

2. Sampling Equipment

2.1. Collection bottles: Two to four pre-cleaned 4-liter polyethylene or Teflon bottles per sampling station.

2.2. Submersible pump or Hydrocast sampling system (General Oceanics Model 1016 Rosette, or equivalent.)

2.3. Laboratory sample bottles - Pre-cleaned and stored protected from contamination. Avoid using sample bottles previously used for high concentration samples.

2.4. Sample filter containers – Plastic bags, aluminum foil or plastic dishes, appropriate for the parameter

2.5. Filtration apparatus with vacuum pump. Syringe filters may be permitted for certain projects, but never for PC/PN.

2.5.1. *Chlorophyll* – Vacuum pressure < 10 in. Hg (< 5 psi).
2.5.2. *PC/ PN* – Vacuum pressure < 10in. Hg (<5 psi).
2.5.3. *TSS & Nutrients* – Unspecified

2.6. Filter Preparation – Whatman® GF/F, 0.7 µm pore size. Diameters other than those listed below may be used. See specific comments throughout the analytical methodology for concerns related to alternate sizes.

2.6.1. TSS & VSS: Whatman® GF/F, 47 mm

Rinse filters three times with DI and transfer them to weighing pans. For TSS only, place in a drying oven at 103-105°C for 1 hour. For combined TSS/VSS, combust at 550 °C for 15 minutes in a muffle furnace. Cool in a desiccator and weigh. For at least 10% of the samples[1], repeat the cycle of drying or combustion until a

[1] The CBP procedure deviates from Standard Methods, 20th edition, which requires re-drying and re-weighing 100% of the filters.

constant weight (± 0.05mg) is reached.

2.6.2. TSS only: Same as 2.6.1, without combustion at 550°C.

2.6.3. PN/PC: Whatman® GF/F, 13 or 25 mm diameter – Filters must be pre-combusted at 550°C.

2.6.4. Chlorophyll: Whatman® GF/F, 47mm diameter – Pretreatment is unnecessary.

2.6.5. Dissolved parameters: Filters must be pre-rinsed to remove trace elements. Alternatively, use TSS filtrate.

2.6.6. Particulate P: Use either TSS or other pre-rinsed filters.

2.7. Refrigerator/Cooler (4 ± 2°C) and/or freezer (-20 ± 2°C).

3. Reagents

3.1. Magnesium carbonate suspension for fresh water chlorophyll – Add 1 g of finely powdered $MgCO_3$ to 100 mL water.

3.2. Reagent water - ASTM Type II water, or equivalent.

3.3. Hydrochloric acid (HCl) solution for cleaning equipment – Prepare a 5% or 10% HCl (v/v) solution. Be sure to add concentrated HCl to the water.

3.4. Reagent-grade HCl for preserving liquid samples

4. Sample Collection

4.1. Collect samples after completing field measurements.

4.2. At stations where pycnocline sampling is designated, if a pycnocline is detected, samples are collected 0.5m (Md.) and 1.0 (Va.) m below the surface, 1.0 m above the upper boundary of the pycnocline, 1.0 m below the lower boundary of the pycnocline, and 1.0 m above the bottom to nearest 0.5 m. See Chapter IV, Section B.4 for pycnocline definitions and calculations.

4.3. If there is no discernable pycnocline at designated stations, collections will be made at 0.5 m (Md.) and 1.0 m (Va.) below the surface, at the closest profile depth above one third of the distance between the surface depth, 1.0 m, and the bottom sample depth, at closest profile depth below two thirds the distance between 1.0 m and the bottom sample depth, and 1.0 m above the bottom to the nearest 0.5 m.

4.4. At all other stations, samples are collected at the surface (0.5 m (Md.) and 1.0 m (Va.)) and 1m above the bottom.

4.5. Lower the submersible pump or Rosette to each sampling depth and fill one bottle per depth. Process the sample according to Section 5 below.

5. Sample Processing and Preservation

5.1. Sample processing and division for all samples should follow Figure IV.2. Filtration should be done immediately

after sample collection. If weather conditions are poor, it may be necessary to process samples on shore after sampling is completed.

5.2. Chlorophyll and pheophytin processing:

5.2.1. Filtration for chlorophyll should be done in subdued light as soon as possible after collecting the sample. Gently shake the sample and pour quickly into a graduated cylinder, measure and record the volume. Transfer the aliquot to the filter tower and apply the vacuum to concentrate the algae on the filter. Filter sufficient sample (100-1500 mL) to produce a green color on the filter pad. To avoid cell damage and loss of contents during filtration, do not exceed a vacuum of 10 in. Hg (≤ 5 psi), or a filtration duration greater than 10 minutes. Do not suck the filter dry with the vacuum; instead slowly release the vacuum as the final volume approaches the level of the filter and completely release the vacuum as the last bit of water is pulled through the filter. If sampling non-saline water, i.e., < 0.5 psu salinity, add 1mL of saturated $MgCO_3$ solution during the last few seconds of filtering. $MgCO_3$ is optional for higher salinity samples.

5.2.2. Remove the filter from the fritted base with tweezers, fold once with the particulate matter inside and place it in a Petri dish or other suitable container. Wrap the container in aluminum foil to protect the phytoplankton from light and store the filter at -20°C. Short term storage on ice is acceptable but samples should be stored at -20 °C as soon as possible.

5.2.3. Chlorophyll samples that cannot be concentrated immediately after collection may be held at 0 to 4°C in the dark for 4 hours before the plankton are concentrated, however any delay is strongly discouraged due to the possible growth of phytoplankton cells or degradation of pigments.

5.2.4. The filter may be stored in the dark at -20 ± 2°C for up to 28 days before extracting the pigments[2]. Studies have shown that extracts are stable for up to 3 months if they are extracted soon after collection (Wasmund, et al. 2006).

5.3. *Particulate Carbon and Particulate Nitrogen:* A 25-500 mL sample is filtered under a vacuum (≤10 in. Hg or ≤ 5 psi) through a 13 mm GF/F filter. Do not rinse the residue on the filter with DI. Store the filters in Petri dishes or foil pouches at -20 ± 2°C.

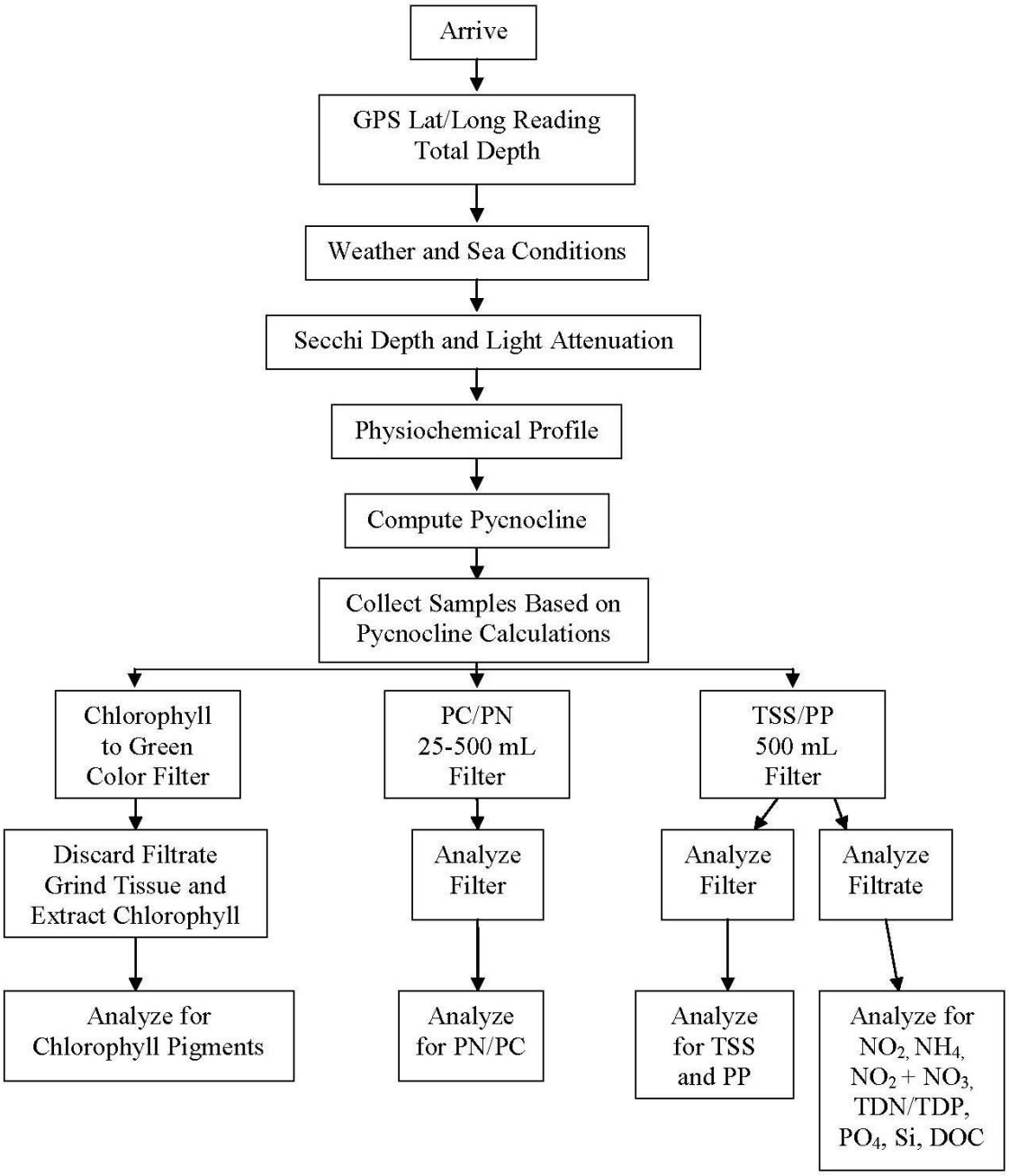
5.4. *Ammonia, Nitrite, Nitrite+ nitrate, Orthophosphate, Total Dissolved Nitrogen, Total Dissolved Phosphorus, Dissolved Organic Carbon, and Silicates:* Pour the filtrate from the particulate phosphorus and/or total suspended solids filtration into sample containers and store at -20 ± 2°C for laboratory analysis, except samples for silicate analysis must be stored at ≤ 6°C. Ammonium and DOC samples must be frozen immediately or, acidified to pH ≤2 and stored at ≤ 6°C. (Note: Acidify DOC samples with HCl to protect laboratory instruments.)

5.5. *Total Suspended and Volatile Solids*: A 50-1,000 mL sample is filtered under vacuum through prepared 47 mm GF/F filters. Rinse the residue on the filter three times with ~10 mL DI water to remove dissolved solids. Freeze or store filters at 4°±2°C. If the filtrate is to be used for dissolved parameters, dispense into sample containers prior to rinsing. If TSS filters are to be used for PP analyses, freeze at -20 ± 2°C.

5.6. *Particulate Phosphorus*: A 50-1000 mL sample is filtered under vacuum through a pre-rinsed 47 mm GF/F filter. Rinse the residue on the filter three times with ~10 mL DI water to remove dissolved solids. Store the filters in Petri dishes or foil pouches at -20 ± 2°C.

[2] Deviations from EPA Method 446.0 are: a) Filtration pressure of 10 in. Hg used instead of 6 in. Hg, b) Chlorophyll filters from tributary stations may be stored on ice for up to 24 hrs., c) Holding time for sampling extraction is 28 days instead of 24 days.

FIGURE IV.2 Field Measurements and Sample Processing



6. Quality Control Samples

6.1. Field Filtered Blank – A field filtered blank is an equivalent aliquot of reagent water that is processed and preserved exactly as are samples. If the concentration of an analyte exceeds the lowest standard in the calibration curve, field and/or laboratory contamination should be suspected and corrective action initiated. (See Chapter II for corrective actions.)

6.1.1. Mainstem cruises: One field filtered blank is recommended each day of the cruise; however, the required minimum is one for each 3-day cruise.

6.1.2. Tributary cruises: One field filtered blank is required per month, or alternatively, one filtered equipment blank per month.

6.2. Replicate Sample (S1, S2 & S3) – A replicate sample is a second (or third) discrete sample taken in quick succession, at the same location and depth as the first samples. Data from replicate samples may be used to estimate overall precision or to deduce sampling precision.

6.3. Field Split (FS1, FS2 & FS3) – One sample is collected and two (or 3) homogeneous subsamples are processed identically for all parameters.

6.3.1. Mainstem Monitoring: Collect a field split **or** a replicate sample once for every 20 samples.

6.3.2. Tidal Tributary Monitoring: Each sampling group should collect field splits once per month, from the surface and bottom depths of the station.

6.4. Sampling Equipment Blanks

6.4.1. Equipment blanks indicate the effectiveness of the sampling equipment cleaning procedure. The equipment blank is processed in the office laboratory after the equipment has been cleaned.

6.4.2. An equipment blank is required once per year or whenever new equipment is used for the first time.

6.4.3. The equipment blanks consist of ASTM Type II water that has been passed sequentially through each component of the sample processing and collection equipment, e.g., submersible pump and hose, Rosette bottles, sampling containers, churn splitter, filtration unit, etc.

6.4.4. An analysis of the unfiltered reagent grade water used to prepare the blanks maybe helpful in interpreting the results if contamination is found.

6.4.5. If the concentration of the equipment blank exceeds the lowest analytical standard in the calibration curve, prepare blanks of just the sampling equipment to isolate the cause of the contamination.

7. Documentation and Records

Field Processing Sheets and Laboratory Forms must permit a complete historical reconstruction of the data. A unique sample number or ID must be assigned to each sample collected and/or processed. See Chapter II.4 for additional document control protocols.

8. Decontamination

Filtration Units: At the end of each sampling day, clean the filtration units, flasks and graduated cylinders with a non-phosphate detergent, rinse with tap water then a final DI water rinse. For low level nutrient sampling, i.e., mainstem stations, rinse with 5-10% HCl between the tap and DI water rinses. If unable to use HCl during a multi-day cruise, soak or fill filtration equipment overnight in DI water.

References:

1. EPA Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices – 2nd Edition, Sept. 1997. (EPA/600/R-97/072)

[a]Method 440.0 Determination of Carbon and Nitrogen in Sediments and Particulates of Esturarine/Coastal Waters Using Elemental Analysis

[b]Method 446.0 *In Vitro* Determination of Chlorophylls *a, b,* c_1+c_2 and Pheopigments in Marine and Freshwater Algae by Visible Spectrophotmetry

2. Wasmund, Topp, Schories (2006). *Optimising the Storage and Extraction of Chlorophyll Samples*, OCEANOLOGIA, 48 (1), 2006. pp. 125-144.