

QUALITY ASSURANCE PROJECT PLAN
FOR THE
CHESAPEAKE BAY CITIZEN MONITORING PROGRAM
ALLIANCE FOR THE CHESAPEAKE BAY, INC.

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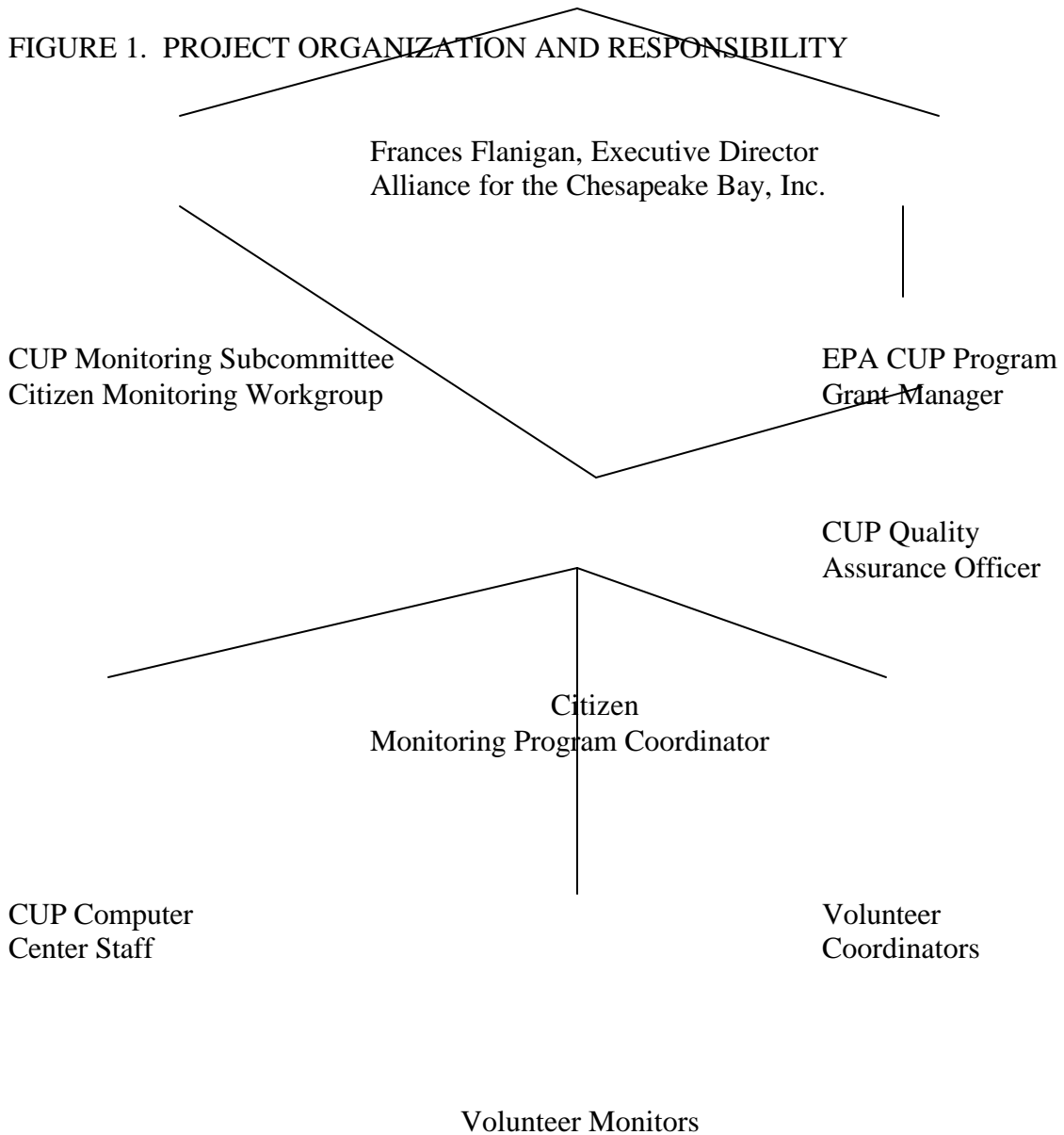
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PROJECT ORGANIZATION

FIGURE 1. PROJECT ORGANIZATION AND RESPONSIBILITY



The Citizen Monitoring Program Coordinator is responsible for generally organizing and overseeing the program, ordering equipment, providing replacements, and refill reagents. The coordinator manages the data, conducts quality control sessions and recruits and trains volunteers. The coordinator also edits the newsletter, carries out some data analysis, and writes reports on the results and status of the program. Other members of ACB staff help from time to time with training and QC sessions. These assistants are trained by the coordinator.

The Citizen Monitoring Workgroup of the CUP Monitoring Subcommittee provides direction to the program with input from relevant state and federal agency personnel.

Chesapeake Bay Computer Center personnel are responsible for seeing that the citizen monitoring data are stored correctly.

In order to manage the large network of volunteers, a watershed coordinator system was established as a way of decentralizing management tasks. Volunteer coordinators were recruited to manage groups of 10-12 volunteers. They relay equipment requests, troubleshoot, act as a liaison with the coordinator and help with data management.

PROJECT DEFINITION/BACKGROUND

The CBCMP was designed to involve stakeholders in the Chesapeake Bay restoration effort and to provide data as a supplement to state and federal databases. Volunteer efforts can add tremendously to the information that managers need but can't necessarily afford. The data collected in this project are used to assist in determining seasonal and temporal trends and evaluating the water quality status of selected tributaries to the Bay. These data supplement and enhance the data collected by the water quality monitoring programs in the Bay mainstem and tributaries supported by EPA and the states. Data collected by volunteers in the CBCMP have been used in a variety of ways including:

- Augmenting the Chesapeake Bay Program's mid-channel monitoring program.
- Chesapeake Bay Citizen Monitoring Program Report, USEPA, CUP/TRS 27/89 reported that comparisons made between water quality data collected by the states and by citizen monitors show consistent differences between shoreline, volunteer-collected measures and state mid-river measures of water conditions.
- Nitrate + Nitrite concentrations are being measured by the Conestoga River volunteers to track changes in the level of $\text{NO}_2 + \text{NO}_3$ out of the river's waters.
- CBCMP data on ammonia collected near Jordan Point on the James River have been used to reevaluate the permit of the Hopewell Regional Sewage Treatment Plant.
- Data being collected at nearshore sites will be used to evaluate submerged aquatic vegetation habitat.
- Salinity data on the Eastern Shore of Virginia have been used to locate good oyster habitat for aquaculture.
- Data have documented episodes of hypoxia in relatively shallow (9-10ft.) nearshore areas in St. Leonard's Creek, a tributary to the Patuxent River.
- Since 1992 citizen monitoring data have been included in Virginia's Water Quality Assessment Report to EPA and Congress. Given the distribution potential of the network's sampling sites it is anticipated that the data will be of particular value to local governments and jurisdictions throughout the Commonwealth.

- Water samples have been collected bi-monthly at 12 stations on The Patuxent since 1990 and five stations on the Piankatank since 1991 for analysis of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP).
- Data collected on three tributaries will be used to assess the Habitat of submerged aquatic vegetation (SAV). The five habitat requirements monitored are DIP, DIN, Chlorophyll a, light Attenuation and total suspended solids.
- Data collected bimonthly by the CBCMP at 12 sites on the Patuxent River will be used to compare nearshore data to mid-channel data collected by State personnel.

A volunteer monitoring program that delivers data of known quality can augment the baywide monitoring program and help to determine seasonal and temporal changes in Bay waters. It can aid in the evaluation of the water quality status of selected tributaries. A well-coordinated, long-term volunteer monitoring program can also promote active stewardship of natural resources by local residents; provide an early warning of problems in stormwater management, sediment control, and sewage contamination; and further the education of the general public and concerned public officials regarding the Bay. (See Appendix A, Resolutions on Citizen Monitoring).

PROJECT DESCRIPTION

One of the larger monitoring programs is the Chesapeake Bay Citizen Monitoring Program (CBCMP) designed and managed by the Alliance for the Chesapeake Bay, inc. (ACB). The CBCMP is a network of over 150 volunteers in Pennsylvania, Maryland and Virginia who are dedicated to collecting water quality data and information on tributaries to the Chesapeake Bay. This regional program was designed to determine the feasibility of including a permanent, Baywide citizen monitoring network among the long-term Bay management strategies of state and federal governments. Volunteers in this program learn to be stewards of their watershed and can foster this ethic in others while providing valuable information to supplement state and federal databases.

In 1985, funded by a Chesapeake Bay Program public participation grant from USEPA, the CBCMP began monitoring with some 35 volunteers at stations on tidal portions of the Patuxent River in Maryland and the James River in Virginia. A modified program began on the Conestoga River in Pennsylvania in 1986. Program directors were concerned with several questions: 1. Can citizens collect water quality data that meet rigorous quality control standards? 2. Does the data collected at nearshore locations reflect water quality in the river generally? 3. What are the most reliable sampling procedures, reporting formats, and data management systems for a volunteer program?

Volunteers in the CBCMP collect weekly water samples and perform tests with equipment and supplies provided by ACB. In tidal waters, parameters tested are dissolved oxygen (DO), pH, salinity (where appropriate), Secchi and water depth, and air and water temperature. Some also record daily precipitation and weather observations. These parameters are now considered to be the “core” program and were chosen for their ability to indicate overall water quality. Collecting data on these parameters is essential in studying the habitat of the Bay’s living resources. For example, striped bass, at certain stages, are very sensitive to pH and certain species of Bay clams require different levels of dissolved oxygen.

Today the program includes over 150 volunteers who sample water on the Lynnhaven, Elizabeth, James, York, Mattoponi, Pumunkey, Piankatank, Rappahannock, Potomac and Eastern Shore of Virginia; the Patuxent, Middle, and Severn in Maryland; and the Conestoga and Conodoguinet in Pennsylvania. The CBCMP has demonstrated that citizen volunteers can collect data that meet strict quality control standards. Sampling procedures, reporting formats, and a specialized computer data management system have been developed by the CBCMP and shared with groups across the country. The Implementation Committee of the Chesapeake Bay Program endorsed expansion of the CBCMP to meet other data needs of Bay managers and scientists and instructed its relevant subcommittees to report on ways citizen monitoring data can be used to provide a better understanding of the status of the nearshore habitat.

Over the years, as the program has matured, volunteers have taken on other monitoring tasks. Since excess nutrients have been found to be a major problem in the Bay, some monitors on the Upper James, Piankatank, Conestoga, and Patuxent Rivers were asked to participate in a nutrient sampling program. Monitors collect samples which are tested in a laboratory for dissolved inorganic nitrogen and dissolved inorganic phosphorus. These results will be used to study water quality necessary for the survival of submerged aquatic vegetation (SAV) and help target sites for restoration projects. The CBCMP will also work with managers to help collect information that will be useful in the development of tributary strategies to reduce nutrients in the rivers.

In Pennsylvania, volunteers have assisted in a riparian vegetation inventory of the Conodoguinet Creek watershed. The purpose of the inventory/mapping study was to utilize volunteer monitors to collect riparian vegetation data and land use information for a Geographic Information System (GIS). Pennsylvania volunteers also participated in an atmospheric deposition study in which rain samples from eight sites representing various land uses were collected and analyzed for nitrogen and triazine herbicides at a United States Geological Survey laboratory. This study will help answer questions concerning atmospheric deposition. Which reportedly contributes one third of the total nitrogen load reaching the Bay. In Virginia volunteers were recruited to participate in the Mattaponi and Pamunkey Integrated monitoring program in which they collect and identify macroinvertebrates as well as perform chemical analysis. This pilot project was designed to be filling in the gap between the tidal and non-tidal monitoring programs.

Other CBCMP activities include: an “SAV Hunt” conducted with the US Fish and Wildlife Service and the Chesapeake Bay Foundation to “groundtruth” the results of annual aerial photographs; general wildlife, Bottlenose Dolphin and Zebra Mussel monitoring programs in conjunction with the Virginia Department of Game and Inland Fisheries, and hands-on assistance with the Virginia striped bass restoration program and Maryland’s fish surveys.

The performance standard of volunteer efforts has been dedication to quality assurance and quality control (CA/QC). The acceptance and use of volunteer collected data has been dependent on the emphasis that the CBCMP placed on developing and adhering to a Quality Assurance Project Plan. The plan requires program coordinators to determine and verify the precision, accuracy, consistency and comparability of all data and volunteer performance. The Alliance has been instrumental in promoting the concepts of CA/QC throughout the volunteer monitoring community.

As the Chesapeake Bay Citizen Monitoring Program has become a model monitoring program for the nation, coordinators have begun networking with other groups throughout the nation interested in citizen monitoring. The Alliance

has provided guidance and technical assistance to other watershed groups who are interested in collecting valuable information in their watersheds.

The CBCMP was awarded the 1990 Water Conservationist of the Year award by the Virginia Wildlife Federation. In 1991, the CBCMP won a special merit award as part of Renew America's Searching for Success national awards program. The program is now listed in the Environmental Success Index, a descriptive collection of more than 1200 nationally verified and recognized environmental success stories.

Based on method comparisons and data results, the CUP Implementation Committee has endorsed the volunteer monitoring project and stated that the project:

- Has established the feasibility of instituting a network of citizen monitoring programs in the Bay region;
- Can deliver data of known quality and provide observational information about the area monitored;
- Has developed standardized sampling procedures, reporting formats and is working toward developing a data management system for volunteer programs; (since trained individual who is knowledgeable in environmental programs;
- Has public interest value and has increased the knowledge and understanding of the participants;
- Can provide guidance to private groups and state agencies who wish to undertake similar projects and;
- Has defined the essential requirements for undertaking a successful volunteer monitoring program.

MEASUREMENT QUALITY OBJECTIVES

Data of known quality collected by volunteers can augment the data being collected by the States and Federal agencies. The volunteers provide reliable and sustained sampling and observations at sites and at frequencies not currently covered by other Bay-wide monitoring programs. The constituents and characteristics measured in this program provide basic information about the water quality in the Lynnhaven and Broad Bay watersheds. These data track the seasonal changes typical in the Chesapeake Bay region as well as changes due to climatological variations and major pollution prevention efforts. The methods and equipment used were chosen based on cost, ease of use, and PARCC parameters. Considerable effort was made to determine method comparability between methods employed by the CUP monitoring program and the volunteer program. Methods comparison tests have been performed and degree of comparability has been determined. The units reported are the same as used in the CUP monitoring program.

Weekly collection of data increases the knowledge of variance associated with time series measurements of selected environmental variables and provides increased resolution and sensitivity to localized and short-term effects of events along tributary margins and in embayments.

Table 1 summarizes the CA objectives for data collected in estuarine waters. It should be noted that CA objectives for monitoring projects using volunteers are being established with this program and are subject to change when deemed desirable by consultation with the QAO and SBPO. It is obvious that water flowing past a given location on land is constantly changing in response to inflow, tidal cycle, weather, etc. This project is not designed to determine what water quality conditions are in the entire river, but, rather, to track the long term and seasonal variation in conditions at the particular site. This approach will hopefully provide information about localized habitats for living resources.

Volunteer monitors are expected to collect data and sample once a week throughout the year, which means a potential of 52 observations per site per year. However, it is assumed that some weeks will be missed for vacations, illness, and severe weather (wind, flooding, ice). Therefore, 48 observations per year will be considered to constitute a complete data set for a given site.

Most volunteers sample from their own property which means that if they drop out of the project that site will no longer be accessible. If data from that location is considered important to the overall program, an effort will be made to recruit a replacement nearby at a site with similar ecological characteristics. However, it is recognized that when working with volunteers this may not always be practical. It is also recognized that it is difficult to hire a volunteer. If it is determined that a monitor is unable to meet the PARCC parameters for this project, consideration will be given to allowing the person to continue if he or she wishes. The data set will be flagged in the computer files as being unacceptable for inclusion in data analyses.

DISSOLVED OXYGEN: This project was started as a pilot program to determine whether volunteers could collect data of known quality on characteristics and constituents of estuarine water quality. Simple and inexpensive equipment was tested and found to be satisfactory. The initial testing of methods for use in this program was conducted at the EPA Central Regional Laboratory, Annapolis, MD under the supervision of the Chesapeake Bay Program Quality Assurance Officer and various other chemists and technicians.

Testing kits from several manufacturers were compared with results obtained from Standard Winkler titrations and with YSI probes. The field was narrowed to two contenders based on accuracy and cost, HACH and LaMotte. The LaMotte kit proved to be more accurate than the HACH kit and was less expensive (See Table 2).

The bias in DO values determined with the LaMotte kit is reported at X mg/l. This was arrived at by carrying out a paired t analysis of the standard deviation of the mean difference between results of four paired measurements with the kit and a Standard Winkler titration.

The precision of dissolved oxygen measurements obtained with the LaMotte micro-Winkler kit is stated as X mg/l + 0.9 and was developed from a Precision Control Chart-Shewhart Construction Method (See Table 3 at end of this section). This chart is based on replicate samples taken by the monitoring coordinator over a period of time. It computed an upper warning limit of 0.68 and an upper control limit of 0.9. Monitors titrate two samples at each sampling time. They are instructed to do a third titration if the difference between the first two is greater than 0.6 mg/l. The two closer values are recorded on the data sheet. If values greater than 0.9 are reported with no third test done, the results are not entered in the database. If a volunteer reports values that are beyond the warning limit two weeks in a row, he or she is called to determine the cause of the problem. A site visit may be necessary.

The precision of the DO data reported by this program is based on methods of testing how well the group of monitors agrees with a given reference standard. At the first QC session, a YSI DO meter was used as a reference. The mean and standard deviation of the differences between the meter and individual monitors was 0.40 ± 0.263 mg/l for one group and 0.270 ± 0.237 mg/l for the other group. These values may be expressed as a ratio of the mean of the absolute differences to the baseline (meter reading): Group 1 – $4.7\% \pm 3.1\%$; Group 2 – $3.5\% \pm 2.8\%$.

At subsequent sessions, we have used the results obtained by the coordinator using a LaMotte kit as the reference standard. The ratios of the mean of individual measurements to the reference standard for four groups was $95\% \pm 2.4\%$, $92\% \pm 3.9\%$, $104\% \pm 1.5\%$, and $103\% \pm 4.9\%$. An Accuracy Tally Sheet for Shewhart Construction – Percent Recovery Method is provided in Figure 16, Appendix B. The above report ratios, which correspond to % Recovery (R), fall within the calculated warning limits of 86 - 118%R.

TABLE 2 COMPARATIVE TESTING OF DISSOLVED OXYGEN KITS

Standard Winkler	HACH	LaMotte
6.2 mg/l	8.0 mg/l	6.8 mg/l
6.25	8.0	6.8
6.2	8.0	
8.6	10.0	8.2
8.6	10.0	8.2
8.7	10.0	
8.3	10.0	

Mean and Standard Deviation

7.55 ± 1.160 9.14 ± 0.989 7.50 ± 0.700

YSI Meter	HACH	LaMotte
8.2	10.0	8.0
8.2	10.0	8.0
8.2	10.0	8.0

The titrating reagent used in Winkler titrations for dissolved oxygen is sodium thiosulfate. We were concerned about the results of inexperienced volunteers using this reagent under conditions that precluded titrating against a standard each time a test was conducted. Monitors were told to keep the reagents in their kit box in the dark and cool. They were cautioned about possible contamination and instructed in how to prevent it-never return any unused titrant to the storage bottle and thoroughly rinse all equipment after each use.

A standard protocol has been adopted to QC of DO reagents. A complete set of new reagents is sent to all monitors every 4 months. They are asked to do duplicate tests on the new and old reagents and record the results on the current data collection form. The reported results indicate that the reagent is stable over six months (See Appendix B, Methods Comparison Report).

TEMPERATURE MEASUREMENT: At the beginning of the project, 49 armored thermometers reading from -5°C to 45°C were calibrated using NBS calibrated thermometers. The field (LaMotte) thermometers were placed in three water baths: 1) 10 and ice bath; 2) large beaker of water that had been placed in a 20°C incubator overnight. At least two readings were taken in each thermometer (See Appendix C, Calibration Protocols).

The average difference between the “corrected readings” and readings of the certified thermometer over a range of $0\text{-}36^{\circ}\text{C}$ was $+0.190^{\circ}\text{C}$ (See Appendix D). Since the thermometers read in 0.5°C increments, we have concluded the error in any individual thermometer does not add sufficient bias to warrant the use of individual correction factors, or, for that matter, the use of any correction factor. A protocol has been developed to test all thermometers purchased for use in this project and a basis for rejection of those that do not pass the test is stated.

The reported precision (see Table 1) of temperature was derived from data collected at the first CCC sessions. Monitors used their individual thermometers to measure the temperature of ice water and a room temperature water bath. The mean and standard deviation for each group was calculated. The results for the room temperature bath showed that all groups were within 0.5°C of the mean. The ice water results were less precise primarily because it is difficult to stabilize temperature over a long period of time in an ice bath.

Subsequent CCC sessions have had the monitors reading the same thermometers in a room temperature bath using the coordinator’s reading as the reference standard. The ratios of the means to the reference standard for 8 groups of readings were 99, 97, 99, 96, 98, 98, 96, 99.

SALINITY DETERMINATION: Specific gravity hydrometers are used to determine salinity. These instruments are inexpensive and deliver consistent results for the trained observer. The first 40 hydrometers to be used were calibrated against a set of certified salinity hydrometers belonging to the State of Maryland and kept at EPA Central Regional Laboratory. Three salt concentrations were prepared and all hydrometers were read at all salt concentrations. Correction factors and conversion are necessary to go from specific gravity at 15° to salinity. The monitors record the specific gravity reading and the water temperature in the hydrometer jar. The correction and conversion to salinity is carried out by a computer program. Tables to carry out the conversion are included in Attachment 1, Citizen Monitoring Program Manual.

The accuracy reported for the hydrometric method of determining salinity is ± 0.82 parts per thousand (0/00). Precision of this method was determined in a manner previously described. At the first CCC sessions, monitors used their individual hydrometers to test four solutions of varying salt concentrations: 1) estuarine, 2) 4 o/oo, 3) 10 o/oo, and 4) 20 o/oo. Temperature was recorded for each measurement. The tables were used to correct for temperature and convert to salinity value. The mean and standard deviation

was calculated for each group and for each solution. All values were within a standard deviation of ± 0.9 o/oo.

At the CCC sessions, monitor' results were compared to those obtained by the coordinator. Ratios of the means of individual readings to the reference standard were 99%, 95%, 97%, 100%, and 92% for solutions of 10 and 20 o/oo. The ratios of the means for the solution of 0 o/oo (tap water) were 76% and 50%.

Having determined the accuracy of the thermometers and hydrometers used in this program, we have concluded that no great amount of error will be introduced in to the reported salinity value if the instrument readings are used directly, providing the thermometers and hydrometers have been calibrated according to the protocol in this plan.

An effort has been made to determine the comparability of the hydrometric method for determining salinity. Details of these efforts are included in Appendix B. These results indicate that the citizen monitoring groups using the hydrometers to measure salinity should get similar results, excluding human error. The refractometer and salinometer appear to get consistently lower readings than the other two methods.

pH DETERMINATION: Several color comparator kits for testing pH were looked at in the beginning of the program, and pH paper as well. All pH papers that were tested were deficient for use in estuarine water. The LaMotte wide-range kit was selected because it covered the full range of expected pH values and because of its demonstrated accuracy when compared with a laboratory calibrated pH meter.

TABLE 4 pH TESTING RESULTS

Water Tested	pH Meter	LaMotte Comparator
Aquarium	8.2 units	8.0 units
Spa Creek	8.0	8.0
Tap	6.3	6.0

Results obtained by monitors at the first CCC session were compared to measurements with an Orion field pH meter calibrated and loaned from EPA Central Regional Laboratory. The average of the differences between the individual readings and that of the meter was 0.56 ± 0.378 pH units with a range of 0.05 – 1.85 units.

Narrow range kits were compared with a Beckman pH meter over several months of data collection at Benedict Laboratory. The mean and standard deviation of the differences of 12 readings was 0.17 ± 0.096 pH units (See Appendix B).

LIMIT OF VISIBILITY: The Secchi disc lines were all attached to the disc and marked by the coordinator in tenths of meters in black indelible ink. Meter marks were indicated in red indelible ink. The accuracy or precision of the Secchi disc has not been determined. No information is available on accuracy of this method even though this instrument is widely used throughout the world and especially in the Chesapeake region.

NITRATE NITROGEN is measured with an octet comparator manufactured by LaMotte Company. Results obtained with this kit were compared with results obtained using an autoanalyzer at the EPA Central Regional Laboratory in Annapolis. The samples were taken from a sewage treatment plant effluent. The results in table 5 indicate that we can have confidence in data obtained with this kit when used properly and carefully.

TABLE 5 COMPARISON OF LAMOTTE COMPANY NITRATE COLOR COMPARATOR KIT WITH AN AUTOANALYZER

Sample	mg/l-Kit	mg/l-Autoanalyzer
Standard	0.5	0.5
Standard	0.9	1.0
Standard	2.0	2.0
Audit	3.0	3.22
06	4.0	4.22
07	4.0	3.96
08	10.0	10.0
04	4.0	4.54
05	4.0	4.69

In the winter of 1988-89, unusually low concentrations of nitrate led a volunteer to question the test procedure. The volunteer was issued new chemical reagents and a comparison with results using old reagents indicated that the cadmium reducing reagent is very sensitive to humidity. The reagent is now packaged in a bottle with a desiccant and the monitors are cautioned to store the reagent in a dry place and to avoid getting moisture in the container.

AMMONIA NITROGEN: Two LaMotte Company test kits that measure ammonia-nitrogen were evaluated for sensitivity and comparability. Kit Code #4795 has a range of 10.0 to 8.0. Higher values can be measured with diluted samples. Samples and standards were tested using both kits at the EPA Central Regional Laboratory in Annapolis. The same samples were run on an autoanalyzer at the same time and results compared.

TABLE I: Precision and Accuracy Objectives

PARAMETER	METHOD/RANGE	UNITS	SENSITIVITY*	PRECISION	ACCURACY	CALIBRATION
Temperature	Thermometer -5.0°C to +45°	°C	0.5°C	±0.5°C	±0.5°C	NBS certified Thermometer
pH	Color Comparator Wide-range Narrow-range	Standard pH units	0.5 units 0.1 units	±0.6 ?***	±0.4 ±.02	Orion Field pH meter Reckman pH meter
Salinity	Hydrometer	Parts per thousand (0/000)	0.1 0/000	±1.0	±0.82	Certified salinity hydrometer set
Dissolved Oxygen	Micro Winkler Titration	mg/l	0.1 mg/l	±0.9	±0.3***	Standard Winkler and YSI DO meter
Limit of Visibility	Secchi disk depth	Meters	0.05 m	NA	NA	NA

* Determined by the increments measurable with the stated method reflecting estimation where allowed.

** Lack of sufficient data at present.

*** Paired t analysis ($\alpha=0/05$, 3 d.f.) of the standard deviation of the mean difference between 4 paired determinations.

TABLE 6 COMPARISON OF AMMONIA TEST KITS WITH RESULTS OBTAINED WITH AN AUTOANALYZER

Sample Autoanalyzer Code #7418	NH ³ -N ppm
Standard 0.04	<0.02
Standard 0.10	<0.02
Standard 0.10	0.02
Standard 0.20	0.14
Standard 0.20	0.12
Standard 0.375	0.30
Standard 0.50	0.50
Standard 0.75	0.8
Standard 0.75	0.8
Standard 1.00	1.0
607-12F 0.532	0.5
607-13F 0.653	0.5
607-13F 0.653	0.6
607-14F 0.547	0.5

TABLE 3: PRECISION QUALITY CONTROL CHART (Shewhart Construction Method)

n	Sample No.	Replicate 1	Replicate 2	/dj/
1	6/18/85	7.0	6.6	0.4
2	6/26/85	7.8	8.0	0.2
3	7/3/85	11.0	10.0	1.0
4	7/22/85	7.2	6.6	0.6
5	7/29/85	6.6	6.2	0.4
6	8/2/85	7.0	7.0	0.0
7	8/12/85	3.6	3.6	0.0
8	8/19/85	3.8	3.4	0.4
9	9/3/85	4.8	4.4	0.4
10	9/9/85	5.8	5.8	0.0
11	9/16/85	4.4	4.4	0.0
12	9/24/85	7.8	7.7	0.1
13	9/30/85	6.6	6.4	0.2
14	10/7/85	10.0	10.1	0.1
15	10/15/85	7.2	7.0	0.2
16	10/22/85	4.6	4.8	0.2
17	10/30/85	7.8	7.8	0.0
18	11/5/85	8.8	8.8	0.0
19	11/19/85	8.4	8.4	0.0
20	11/23/85	10.2	10.0	0.2
21	12/3/85	7.8	7.4	0.4
22	12/10/85	13.0	12.6	0.0
23	12/17/85	7.6	8.0	0.4
24	12/30/85	12.6	12.2	0.4
25	1/6/86	12.2	12.8	0.6

Parameter: Dissolved Oxygen
 Analyst: K. Ellett
 Units: ppm
 Date Prepared: Jan. 15, 1986
 Method: Micro-Winkler Titration
 R: 0.272
 Instrument: LaMotte Chem Kit
 Up. Warning Limit: 0.68
 Conc. Range: 0-20+ O₂
 Up. Control Limit: 0.89

/dj/= 6.8
 $R=(/dj)/n= 0.272$
 Calc: UWL= 2.51 (R)= 0.6827
 UCL= 3.27 (R)= 0.5894
 (2.51 and 3.27 are constants for

TRAINING REQUIREMENTS AND CERTIFICATION

All volunteers are trained by the Citizen Monitoring Program Coordinator. Training sessions are two to three hours long and involve hands-on participation. Each volunteer is issued a kit and performs the tests individually. Any results out of range of the data quality objectives are rectified. Each volunteer is reevaluated at the subsequent quality control session.

DOCUMENTATION AND RECORDS

All data sheets are filled out in the field at the time of sampling (See Attachment 1, CBCMP Manual for data form). Volunteers make copies of the data sheets or record the data on spreadsheets then mail the original to their Local Watershed Coordinator or directly to the Citizen Monitoring Program Coordinator. Data sheets are archived for six years.

SAMPLING PROCESS DESIGN

Monitoring sites are located along the shores of the following major Chesapeake Bay tributaries: Lynnhaven, Elizabeth, James, York, Mattaponi, Pamunkey, Piankatank, Rappahannock, and Potomac Rivers in Virginia; Patuxent, Middle and Severn Rivers in Maryland; and the Conestoga River in Pennsylvania. Sites are also located on some rivers and creeks of the Eastern Shore of Virginia (See Appendix F, Tributary Site Maps).

Volunteers are sought who live on or near the water so that obtaining samples will be convenient. Taking samples from a boat is not encouraged because it is more difficult to locate the exact sampling site, bad weather can interfere with sample collection, and personal safety cannot be assured.

It is not always practical to pre-select precise sites in a voluntary program. However, the following criteria are used to locate sites:

- equally divided in the estuarine, transition and tidal fresh portions of a tidal river;
- above and below the mouth of any tributary running into the river;
- above and below major construction sites and sewage treatment plants;
- near a farm or animal holding facility that is instituting best management practices;
- on shore opposite a state monitoring site to allow for comparison of data sets.

The volunteers initially attend a training session. These sessions include the viewing of an introductory slide show followed by a demonstration and carrying out of the tests. Volunteers who are unable to attend a session are trained by the coordinator individually.

The monitoring sites were chosen by balancing the locations that meet the criteria listed above and locations where an individual lives and wishes to sample. Sites on the Patuxent River were chosen that would provide data from the estuarine, transition, and tidal-fresh portions of the river as well as providing data from some of the creeks off the mainstem of the river.

The water sample is obtained in a bucket that is rinsed twice with the water to be tested. The bucket is then gently filled about two-thirds full. This sample is used to determine water temperature, pH, dissolved oxygen, and salinity. (For complete sampling procedures, see the Chesapeake Bay Citizen Monitoring Program Manual, Attachment 1).

Samples for nutrient analysis are taken from selected sites the number of which was limited by the cost of laboratory analysis. Maryland monitors collect nutrient samples the 1st and 3rd weeks of the month except for November through February when the samples are collected only during the 1st week of the month. This schedule is the same as that of the Maryland Department of the Environment’s Patuxent monitoring program. Two nutrient sampling sites on the Patuxent were chosen for their locations above and below the effluent outfall of the Western Branch Sewage Treatment Plant. This will provide data on nutrient concentrations before and after the installation of a biological nutrient removal process at this plant. In Virginia nutrient samples are collected every other week and delivered to the state laboratory every 28 days. Nutrient sampling sites in Virginia were chosen for their location in or near SAV beds. Monitors began the nutrient sample filtering with 60cc syringes fitted with a 25mm filter holder and a 2.25cm glass microfibre filter to filter the sample water into autoanalyzer cups (or a 20ml bottle in Virginia). The filtering protocols were changed to using hand vacuum pumps to coincide with the state filtering protocols (See Attachment 1 for detailed protocols).

Parameters/Frequency

All volunteers in this program monitor at weekly intervals throughout the year. They measure 6 or 7 parameters. They are:

<u>METHOD</u>	<u>PARAMETER</u>
air temperature	armored thermometer
water temperature	armored thermometer
water clarity	Secchi disk
water depth	Secchi disk
dissolved oxygen	micro-Winkler titration kit
pH	color comparator
salinity (where appropriate)	hydrometer

Monitors report weekly accumulated rainfall if they have sufficiently clear space to install a rain gauge. In addition, information on weather and general observations about the site (live or dead organisms, debris, oil slicks, ice, odor, water color, anything unusual) is recorded on a data collection form and sent to the local project coordinator (See Attachment 1 for data form).

CRITERIA FOR SITE LOCATIONS:

(See Appendix G for Latitudes and Longitudes)

Nomini Creek Sites

001, 01, 01A, 02, 03, 04

This watershed was chosen for monitoring in conjunction with a pre and post BMP analysis. The undeveloped agricultural watershed was being assessed by deep well analysis in association with the Chesapeake Bay Program and the Virginia Tech. Division of Soil and Water Conservation Districts. The surface samples taken by the Citizen Monitoring Program will be compared to the subaqueous samples. Specific sites were chosen according to volunteer availability.

York-NERRS

10, 11, 12, 13, 18, 50

These sites were chosen for monitoring in conjunction with the National Estuarine Research Reserve Sites in Virginia. All are within the reserves or the buffer zones.

Upper Rappahannock

6, 7, 8, 9, 120, 121, 122, 123, 123A, 124, 125

These sites were chosen by Friends of the Rappahannock and were added to the Citizen Monitoring Program.

Piankatank/York/Corrotoman-Nutrient Sampling

126, 128, 130, 131, 133, 134, 135, 136

These nutrient sampling sites were chosen with regard to the VSWCB maps showing areas of SAV. Working with Save the Ole' Piankatank we recruited the volunteers in the SAV areas.

Piankatank

41, 43, 44, 52, 54, 98, 127, 129, 137

Volunteers for these sites were recruited with the help of Save the Ole' Piankatank in an effort to expand monitoring on the Piankatank. Sites were chosen according to the availability of volunteers.

Mattaponi/Pamunkey

138, 139, 140, 141, 142, 143, 144, 145

Monitoring on the Pamunkey began in conjunction with the NERRS site at Sweet Hall marsh in an effort to collect more data up and downstream from that site. Monitoring on the Mattaponi was started in conjunction with King William County in an effort to add

data to an ongoing study of the impacts of freshwater withdrawal. Volunteers were recruited with the help of the Mattaponi and Pamunkey Rivers Association.

The monitoring sites were chosen by balancing the locations that meet the criteria listed above and locations where an individual lives and wishes to sample. Sites on the Patuxent River were chosen that would provide data from the estuarine, transition, and tidal-fresh portions of the river as well as providing data from some of the creeks off the mainstream of the river.

The water sample is obtained in a bucket that is rinsed twice with the water to be tested. The bucket is then gently filled about two-thirds full. This sample is used to determine water temperature, pH, dissolved oxygen and salinity. (For complete sampling procedures, see the Chesapeake Bay Citizen Monitoring Program Manual, Attachment 1).

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pH
salinity (where appropriate)

PARAMETER

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Secchi disc
Secchi disc
micro-Winkler titration kit
color comparator
hydrometer

Monitors report weekly accumulated rainfall if they have sufficiently clear space to install a rain gauge. In addition, information on weather and general observations about the site (live or dead organisms, debris, oil slicks, ice, odor, water color, anything unusual) is recorded on a data collection form and sent to the local project coordinator. (See Attachment 1 for data form).

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Piankatank / York / Corrotoman – Nutrient Sampling

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These nutrient sampling sites were chosen with regard to the VSWCB maps showing areas of SAV. Working with Save the Ole' Piankatank, we recruited the volunteers in the SAV areas.

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41, 43, 44, 52, 54, 98, 127, 129, 137

Volunteers for these sites were recruited with the help of Save the Ole' Piankatank in an effort to expand monitoring on the Piankatank. Sites were chosen according to the availability of volunteers.

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Monitoring on the Pamunkey began in conjunction with the NERRS site at Sweet Hall marsh in an effort to collect more data up and downstream from that site. Monitoring on

the Mattaponi was started in conjunction with King William County in an effort to add data to an ongoing study of the impacts of freshwater withdrawal. Volunteers were recruited with the help of the Mattaponi and Pamunkey Rivers.

York

14, 16, 19, 20, 42, 47, 51

These sites were chosen in conjunction with the National Estuarine Research Reserve System in Virginia. Volunteers were recruited with the help of the York Chapter of the Chesapeake Bay Foundation. Of all the available volunteers, ones with access to sites nearest Goodwin Island Reserve were chosen.

James

21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 34, 35, 37, 38, 39, 40, 53, 59, 71, 96, 97

These pilot sites were chosen with regard to side of river, section of river (Freshwater Zone, Transition Zone, Lower Estuary) and availability of volunteers.

Lower Rappahannock

61, 63, 64, 65, 66

These sites were chosen for monitoring in order to compare pre and post construction data. Their locations were in close proximity to a SWCB monitoring buoy.

Middle Rappahannock

67, 68, 69, 70, 77, 78, 79, 80, 95, 99

These sites were chosen solely on the basis of volunteer availability in an effort to expand monitoring on the middle Rappahannock.

Elizabeth

72, 73, 74, 75, 76

These sites were chosen in conjunction with the Chesapeake Bay Youth Conservation Corps. Sites were chosen with regard to even distribution of publicly accessible sites on the Southern Branch of the Elizabeth River.

State Parks

737, 751, 765, 766, 770, 775, 852, 865, 870, 965

All seven riparian State Parks were selected for monitoring sites.

Eastern Shore

80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94

Volunteers were recruited with the help of the Citizens for a Better Eastern Shore and The Nature Conservancy. All available sites were chosen.

Several sites have become inactive since the program began in 1985. When monitors located on the lower James River dropped out of the program, they were not replaced because the then Virginia State Water Control Board felt that this portion of the river was adequately monitored by the state and because the water quality in this portion of the river was not severely impaired. They preferred to focus on that portion of the James between Richmond and Hopewell, which is heavily impacted by a regional STP.

The Virginia Water Control Board is concerned about ammonia concentrations in the upper James River estuary. Municipal point sources are estimated to contribute 90% of total ammonium loading and the dynamics of ammonium in the James is very much influenced by these inputs. Volunteer monitors at sites between Richmond and Hopewell added ammonia testing to their sampling schedule in June 1988. The volunteers' data documents the frequency and severity of violations of the State water quality criteria. This data may be used to evaluate the discharge permits as they come up for review.

Nutrient Analysis:

The purpose of this section is to discuss the control of analytical performance in the laboratory during analysis of field nutrient samples. It is assumed that a valid sample has been taken properly, preserved correctly if necessary, and that recording and reporting of results were done in a systematic and permanent manner. It must be recognized that quality control begins with the sample collection and does not end until the resulting data are reported. The laboratory control of analytical performance is only one vital link in obtaining valid data. A continuous rapport and conscientious use of quality control between field sampling, laboratory analyses, and management decisions are necessary to insure this validity. No individual should undertake to provide nutrient analytical data unless they are aware of the importance of using a comprehensive and systematic approach and are committed to making a conscientious effort to prepare reliable measurements. It is necessary to communicate the results of such measurements in a way that permits open inspection of their intrinsic weaknesses and strengths. This is one of the main objectives for precision and accuracy control. Data quality objectives for accuracy and precision are established for each parameter and are based on prior knowledge of the system and method validation. Studies using replicates, spikes, standards, calibrations, and recovery are made on a daily basis.

The Nutrients Laboratory precision assessment is based upon the results of replicate measurements made at concentration levels representative of the range observed in routine samples. Units are expressed in the ppm range. The frequency of replicate measurements shall be at the beginning of each bench worksheet for each parameter. These replicates are entered as standards for each daily run. Therefore, at least four replicates are run for each system. After the accumulation of approximately 30 sets of duplicates, new assessments for precision are calculated to reflect the current precision of the systems. This is done by replacement of the historical database with the most current data available. The end of the month's totals can be obtained on the Kaypro computer using the CCC software or the Lotus software on the IBM computer.

For accuracy, a representative portion of the sample lot is selected for spiking and the selected samples are analyzed, both unspiked and spiked, to measure recovery. One sample is spiked per analytical run with approximately twenty-four to fifty samples being run per day. After 25 new recovery measurements have been accumulated, the control limits are recalculated to reflect the current accuracy of the systems. This is done by calculating the average of the last three months recovery data and using it.

TABLE 2: Nutrient Analysis

Parameter	Holding Time	Cont. Req.	Det. Lev.	Volume	Acc/Precision	EPA Method
Ammonium	28 days	Nalgene Wide Mouth Bottle	.004 ppm	125 ml	± 2 st. dev.	350.1
Nitrate	28 days	Nalgene Wide Mouth Bottle	.002 ppm	125 ml	±2 st. dev.	353.2
Nitrite	28 days	Nalgene Wide Mouth Bottle	.002 ppm	125 ml	±2 st. dev.	353.2
Ortho Phosphorus	28 days	Nalgene Wide Mouth Bottle	.002 ppm	125 ml	±2 st. dev.	365.1

LABORATORY NUTRIENT ANALYSIS:

Accuracy and precision are considered out of control if the percent recovery of the Quality Control sample exceeds 2 standard deviations. If these control limits are exceeded in the Nutrients Laboratory, the analyst shall notify the laboratory supervisor at once. The laboratory supervisor and the analyst shall investigate the many possible causes of the problem. After the problem is corrected, the samples from that set are run again with duplicate spiked samples. Data obtained for the actual samples in a group determined as out of control are considered unreliable and are not reported out. When a Quality Control sample exceeds the warning limits (greater than ± 2 standard deviations), but is within the control limits, the analyst shall inform the laboratory supervisor and the procedure is inspected carefully. These results are reported.

In addition to the above procedures, the Nutrients Lab also adheres to the following:

- a. A percent efficiency is kept daily on the cadmium columns. This is done by recording the values of the 0.5 ppm standard with the NO_2 system and the NO_3 system. The numbers are divided and a percent figure is recorded.
- b. For all Chesapeake Bay samples, the slopes and intercepts are calculated and recorded.
- c. For all Chesapeake Bay samples, correlation coefficients are calculated and recorded. The correlation coefficient must be equal to or above 0.995. If the correlation coefficient is less than 0.995, the results are considered unreliable and are not reported out. The problem must be corrected and then the samples can be run again.
- d. Blanks are analyzed with each run to detect reagent or any system contamination. The blanks shall be in the form of de-ionized water.
- e. Daily performance, daily precision, and accuracy data can be plotted by means of quality control charts to determine if valid, questionable, or invalid data are being generated from day to day. Precision control charts are constructed from duplicate standard analyses, where as, accuracy control charts are constructed from spike samples. The Nutrients Lab uses X (mean) and R (range) charts for precision. The lab uses percent recovery charts for accuracy. These charts follow the guidelines set forth in the Bureau of Chemistry Quality Control Manual. A copy of the data sheets and the procedures for calculating control limits are found in Appendix X of the Bureau's manual. The control charts will be made and maintenance on a daily basis for all parameters. The control limits will be established for all parameters and used with each set of analysis as a basis for accepting or rejecting data. Possible causes of control chart problems may be found in Appendix X of the Bureau's manual.

See Appendix H for Laboratory Procedures, Control Charts and Worksheets.

DEPARTMENT OF CONSOLIDATED LABORATORY SERVICES (DCLS)
SAMPLE REJECTION PROCEDURE:

1. 1st Tier – Immediate Rejection

- a. Leaking or packaging that creates a hazard for employees.
- b. Broken or leaked sample.
- c. Labeling illegible for positive ID.
- d. Paperwork and sample do not match and can not be resolved.

Exception: Legal, priority, sediment, and tissue samples, notify the lab liaison or program manager and hold for 24 hours for the responsible person to resolve in person or by FAX. See #3.

- e. Delivered to DCLS in error (contact submitter for pick-up).

Exception: Legal, priority, sediment, and tissue samples, notify the lab liaison or program manager and hold for 24 hours for the responsible person to resolve in person or by FAX. See #3.

- f. Improper preservation.
- g. No paperwork or analysis request and inadequate information to contact customer. Sample will be held for 24 hours before rejection unless the holding time will be exceeded before analysis can occur.
- h. Required information not supplied (e.g. Incorrect Parameter Code).
- i. Wrong container for regulated samples.
- j. Samples submitted with the expectation that results will be used for private lawsuits.
- k. Samples received were greater than 4 degrees centigrade.

2. 2nd Tier – Separate and ask for labs input:

- a. Analysis not routinely performed by DCLS.
- b. Insufficient quantity.
- c. Improper packaging to preserve sample.

- d. Past time for analysis requirement/Holding time exceeded.
 - e. Nonsensical samples (e.g. goldfish liver).
 - f. Samples brought by a private citizen without prior consent by a lab manager.
 - g. All in Tier 3 that cannot be resolved.
 - h. Wrong container.
3. 3rd Tier – Non-replaceable samples: legal, priority, sediment, tissue, waste for spills; separate and store while trying to resolve with customer for 1 day (24 hours). No change on sample information will be made by DCLS personnel without a written request from the customer:
- a. Sample without paperwork.
 - b. Paperwork without sample.
 - c. Paperwork and sample do not match (multiple choices which the sampler may wish to resolve).
 - d. Labeling incomplete for ID for reporting.
 - e. Labeling on sample or paperwork illegible.
 - f. Left without proper chain-of-custody.

If samples are rejected, they are given a DCLS number, paperwork is so noted with reason, and steps are taken toward resolution, copied for data entry, and notification sent to Lab. A rejection report is mailed to the customer when sufficient information is available to do so. When appropriate, the rejection notice is accompanied with a new collection kit.

DCLS SAMPLE REJECTION CODES:

1A LEAKING

Leaking or packaging that creates a hazard for employees.

1B BROKEN

Broken or leaked sample.

1C ILLEGIBLE

Labeling illegible for positive ID.

1D PAPER DOES NOT MATCH SAMPLE

Paperwork and sample do not match and cannot be resolved.

1E NOT DCLS

Delivered to DCLS in error.

1F WRONG PRESERVATION

Improper preservation of sample.

1G NO DATA

No paperwork or analysis request and inadequate information to contact customer.

1H INADEQUATE INFORMATION

Required information not supplied (e.g. Incorrect parameter code).

1I WRONG CONTAINER

Wrong container for regulated samples.

1J PRIVATE LAWSUIT

Sample submitted with the expectation that results will be used for private lawsuits.

1K HOT

Samples received were greater than 4 degrees centigrade.

2A ANALYSIS NOT PERFORMED BY DCLS

Analysis not routinely performed by DCLS.

2B QNS

Insufficient quantity.

2C WRONG PACKAGING

Improper packaging to preserve sample.

- 2D HOLDING TIME EXCEEDED
Past time for analysis requirement/Holding time exceeded.
- 2E NONSENSICAL SAMPLE
Nonsensical sample (e.g. Goldfish liver).
- 2F PRIVATE CITIZEN SAMPLE
Private citizen sample without prior consent by a lab manager.
- 2G UNRESOLVED TIER 3
All in tier 3 that cannot be resolved.
- 2H WRONG CONTAINER
Wrong container.
- 3A NO PAPERWORK
Sample without paperwork.
- 3B NO SAMPLE
Paperwork without sample.
- 3C NON MATCHING DATA
Paperwork and sample do not match (multiple choices which the sampler may wish to resolve).
- 3D INCOMPLETE ID
Labeling incomplete for ID for reporting.
- 3E ILLEGIBLE
Labeling on sample or paperwork illegible.
- 3F IMPROPER CHAIN OF CUSTODY
Left without proper chain of custody.

SAMPLE HANDLING AND CUSTODY REQUIREMENTS

In all but the nutrient sampling, each monitor individually carries out all field and laboratory procedures. All relevant procedures are detailed in the Chesapeake Bay Citizen Monitoring Program Manual (Attachment 2). In Maryland, the nutrient samples are picked up and delivered to Chesapeake Biological Laboratory (CBL) bimonthly April through October and monthly November through March. Frozen samples are placed into an Igloo cooler and the temperature is monitored in the cooler hourly.

In Virginia, the samples are collected every other week and delivered to the Department of Consolidated Laboratory Services every 28 days. During transit, all samples are placed in a cooler with several blue ice packs. The temperature in the cooler is recorded at the start and at the end of the run and it remains below freezing. The samples are placed in the freezer of the labs as soon as they arrive.

(See Appendix I, VA DCLS Lab Sheet and VA DEQ sample bottle tag).

QUALITY CONTROL REQUIREMENTS

Calibration Procedures and Frequency:

All kits and equipment are checked twice a year at a quality control session. Any faulty equipment is replaced. The coordinator keeps all records on the maintenance and calibration of the kits and equipment. All data on calibration and comparability of equipment and reagents has been entered into a quality control log book.

Temperature: Armored thermometers reading from -5.0° Celsius to $+45.0^{\circ}$ Celsius are purchased from LaMotte Company. They are calibrated against NBS certified thermometers and correction factors are calculated for each thermometer. The NBS certified thermometers used were #3J6634, certified on 2/28/77 and #3J3461, certified on 1/28/77. The field thermometers are sufficiently accurate to make it unnecessary to carry out correction for each value of air and water temperature.

Salinity: Salinity is determined by the hydrometric method as described in Standard Methods for the Examination of Water and Wastewater. Hydrometers and hydrometer jars are obtained from Greers Ferry Glass, Inc. Experiments were performed to compare field hydrometers with a certified hydrometer set calibrated to read salinity directly. The certified set belongs to Maryland Department of the Environment and was used at the EPA Central Regional Laboratory, Annapolis, MD. Multiple paired readings of specific gravity and salinity were taken over a range of salt concentration with the field and certified hydrometers. Results were analyzed and a single regression equation was calculated to correct all field hydrometer readings. The specific gravity value is corrected for temperature of the water in the hydrometer jar and converted to salinity by equations stored in a computer program. Thermometers and hydrometers are checked for calibration once a year at a quality control session. Replacements are calibrated by the coordinator using simplified methods.

Limit of visibility: Secchi discs with black and white quadrants and measuring 8 inches (20 cm) in diameter are used to determine the limit of visibility. A nylon line approximately 4 m long and marked in black in 0.1 m increments is attached to each disc. Each one meter increment is marked in red. The discs are obtained from LaMotte Company. The Secchi disc is also used to determine water depth. When the Secchi depth is greater than the water depth at that particular reporting time, water depth is recorded as the same as the Secchi depth.

pH: Color comparator kits from LaMotte Company are used to determine pH. Volunteers are first issued wide range kits, ranging from 3.0 to 10.0. After a year's worth of data are collected and a general range of pH for the site is known, narrow range kits are supplied. These kits test for a narrow range of values (1.4 units) in 0.2 unit increments. When the color observed is between two colors on the comparator, the value is reported to the nearest 0.5 unit on the wide range or 0.2 unit on the narrow range comparator. Various indicator solutions are used depending on the pH range needed at a give site:

<u>pH units</u>	<u>Indicator Reagent</u>
3.0 – 10.0	Wide range
6.8 – 8.2	Phenol Red
7.2 – 8.6	Cresol Red
8.0 – 9.4	Thymol Blue

Results of pH determinations with wide range kits were compared with pH values obtained using an Orion field pH meter to calculate the precision of overall results reported. Results of a comparison of pH were determined with a narrow range kit and a Beckman pH meter.

Dissolved Oxygen: The test for dissolved oxygen is made using a water analysis kit which employs a modified Winkler titration method. The sample of water to be tested is collected with a minimum of contact with the air. Duplicate samples are collected and titrated. Manganese sulfate and alkaline potassium iodide solutions are added to the sample and mixed. A precipitate forms which is allowed to settle. With saline water a 10 minute contact time with the precipitate is required. The precipitate is a manganese hydroxide floc. Sulfuric acid is added and mixed until both reagent and precipitate dissolve. The sulfuric acid reaction frees iodine in proportion to the amount of oxygen present in the test sample. A portion of this solution is decanted to a test vial. A direct reading titrator (syringe) is used to titrate with sodium thiosulfate solution. Starch solution is added as the endpoint indicator. The concentration of dissolved oxygen, expressed in mg/l is read directly from the titrator scale in 0.2 mg/l increments.

LaMotte dissolved oxygen kits were compared to measurements with Standard Winkler titrations and with a YSI DO meter at the EPA Central Regional Laboratory and found to be satisfactory. Data quality were established using results from one operator using the kit over several months and taking duplicate samples each week. A quality control chart was constructed to determine the upper control limit and the upper warning limit for this method. (See Table 3).

Fresh chemical reagents are issued to monitors every six months. Upon receipt of the chemicals, monitors are asked to carry out comparison titrations with old and new reagents. These results are evaluated for each participant and compared to control limits established for the analysis and found to be within these limits.

Internal QC Checks:

Two quality control sessions are held per year. If a monitor misses both sessions, a site visit will be made to ensure that methods of sampling and competence of the monitor meet the project standards. Volunteers will be contacted by letter or phone when data is reported that appears to be incorrect. If the question cannot be cleared up by these methods, the coordinator will make a site visit to rectify the problem. If a volunteer does not attend at least one session per year, the coordinator will visit the site and test the volunteer on the procedures to make sure the individual is carrying out the procedures in the prescribed manner.

Data collected at the QC session is used to assess and update the accuracy and precision of the data collected in the program. Results and analyses from the QC sessions are stored by the coordinator.

Sensitivity of field tests does not merit collecting and testing samples from two closely sequential buckets of water. Likewise, the sensitivity of all tests, other than that for dissolved oxygen, does not justify carrying out duplicate tests or readings.

Two types of QC sessions are conducted. In the first kind, set up like a lab practical, the volunteers proceed through stations set up by the coordinator and read the equipment. In the second type of session, each volunteer reads his or her own equipment using the same sample of water. (See Guidelines for a Successful CC Session, Quality Control Session Instructions and Quality Control Audit Form, Appendix J).

PERFORMANCE AND SYSTEM AUDITS:

No performance and system audits beyond the described CCC sessions are planned for this project. The activities included in the CCC exercises basically constitute performance and system audits.

We attempt to go over the results recorded at a CCC session with the participants before they leave. A discussion of any difference in results obtained can clear up difficulties and differences in technique without embarrassing or putting a particular individual on the

spot. Defective equipment or outdated reagents can be replaced at that time. When it is not possible to go over the results at the CCC session, a copy of an individual's results compared to the reference standard is sent to each participant. The results obtained by the coordinator are used as a reference standard. It is necessary to contact monitors whose results were unacceptable by phone or in person. Results of all CCC sessions are recorded and kept by the coordinator. It would be possible to have the QAO conduct or observe a CCC session to fulfill a requirement for a system audit.

PREVENTIVE MAINTENANCE:

The major cause of missed observations in a volunteer program are: 1) equipment gets broken; 2) monitor runs out of reagent and replacements are not requested or do not reach the site before the next sampling time; 3) volunteer is ill, goes on vacation or gets too busy to sample at the regular time.

The coordinator should keep replacement equipment and reagents on hand at all times and send requested replacements by return mail. One can anticipate the amount of reagent needed for most tests and see that they are received by monitors before the current ones are used up. A replacement inventory of chemicals is kept up to date. Reagents are not stored more than six months.

It is assumed that all monitors will not be able to sample all of the weeks of the year. If someone plans to be away for an extended period of time, particularly in the summer, they are encouraged to find a reliable substitute to collect data. This backup monitor is trained by the coordinator.

The responsibility for deciding to take corrective action rests with the monitoring coordinator. Data collection forms are looked at by the watershed coordinators and the program coordinator as they are received. Changes may be made at this time to facilitate data entry.

Particular things to check are:

- Legibility
- Correct use of military clock
- Consistency of site # and monitor #
- Presence of site # and monitor #
- Decimal points, zero values
- Warning limit on DO values
- Conversion from inches to mm for rainfall

If any of the data is questionable, the monitor is contacted by phone and corrections are made. The only measurement for which there is an upper control limit and warning limit is the dissolved oxygen test. If a monitor reports duplicate values that are beyond the UCL two consecutive weeks or a third test has not been run, he or she will be contacted to see if the results can be corrected by more careful attention to reporting.

EQUIPMENT TESTING INSPECTION AND MAINTENANCE REQUIREMENTS

All equipment is tested and inspected at CCC sessions every six months. All chemicals are replaced and any equipment out of range of DQO's is replaced.

EQUIPMENT CALIBRATION AND FREQUENCY

All kits and equipment are checked twice a year at a quality control session. Any faulty equipment is replaced. The coordinator keeps all records on the maintenance and calibration of the kits and equipment. All data on calibration and comparability of equipment and reagents has been entered into a quality control log book.

Temperature: Armored thermometers reading from -5.0° Celsius to $+45.0^{\circ}$ Celsius are purchased from LaMotte Company. They are calibrated against NBS certified thermometers and correction factors are calculated for each thermometer. The NBS certified thermometers used were #3J6634, certified on 2/28/77 and #3J3461, certified on 1/28/77. The field thermometers are sufficiently accurate to make it unnecessary to carry out correction for each value of air and water temperature.

Salinity: Salinity is determined by the hydrometric method as described in Standard Methods for the Examination of Water and Wastewater. Hydrometers and hydrometer jars are obtained from Greers Ferry Glass, Inc. Experiments were performed to compare field hydrometers with a certified hydrometer set calibrated to read salinity directly. The certified set belongs to Maryland Department of the Environment and was used at the EPA Central Regional Laboratory, Annapolis, MD. Multiple paired readings of specific gravity and salinity were taken over a range of salt concentration with the field and certified hydrometers. Results were analyzed and a single regression equation was calculated to correct all field hydrometer readings. The specific gravity value is corrected for temperature of the water in the hydrometer jar and converted to salinity by equations stored in a computer program. Thermometers and hydrometers are checked for calibration once a year at a quality control session. Replacements are calibrated by the coordinator using simplified methods.

Limit of visibility: Secchi discs with black and white quadrants and measuring 8 inches (20 cm) in diameter are used to determine the limit of visibility. A nylon line approximately 4 m long and marked in black in 0.1 m increments is attached to each disc. Each one meter increment is marked in red. The discs are obtained from LaMotte Company. The Secchi disc is also used to determine water depth. When the Secchi depth is greater than the water depth at that particular reporting time, water depth is recorded as the same as the Secchi depth.

pH: Color comparator kits from LaMotte Company are used to determine pH. Volunteers are first issued wide range kits, ranging from 3.0 to 10.0. After a year's worth of data are collected and a general range of pH for the site is known, narrow range kits are supplied. These kits test for a narrow range of values (1.4 units) in 0.2 unit increments. When the color observed is between two colors on the comparator, the value

is reported to the nearest 0.5 unit on the wide range or 0.2 unit on the narrow range comparator. Various indicator solutions are used depending on the pH range needed at a give site:

<u>pH units</u>	<u>Indicator Reagent</u>
3.0 – 10.0	Wide range
6.8 – 8.2	Phenol Red
7.2 – 8.6	Cresol Red
8.0 – 9.4	Thymol Blue

Results of pH determinations with wide range kits were compared with pH values obtained using an Orion field pH meter to calculate the precision of overall results reported. Results of a comparison of pH were determined with a narrow range kit and a Beckman pH meter.

Dissolved Oxygen: The test for dissolved oxygen is made using a water analysis kit which employs a modified Winkler titration method. The sample of water to be tested is collected with a minimum of contact with the air. Duplicate samples are collected and titrated. Manganese sulfate and alkaline potassium iodide solutions are added to the sample and mixed. A precipitate forms which is allowed to settle. With saline water a 10 minute contact time with the precipitate is required. The precipitate is a manganese hydroxide floc. Sulfuric acid is added and mixed until both reagent and precipitate dissolve. The sulfuric acid reaction frees iodine in proportion to the amount of oxygen present in the test sample. A portion of this solution is decanted to a test vial. A direct reading titrator (syringe) is used to titrate with sodium thiosulfate solution. Starch solution is added as the endpoint indicator. The concentration of dissolved oxygen, expressed in mg/l is read directly from the titrator scale in 0.2 mg/l increments.

LaMotte dissolved oxygen kits were compared to measurements with Standard Winkler titrations and with a YSI DO meter at the EPA Central Regional Laboratory and found to be satisfactory. Data quality were established using results from one operator using the kit over several months and taking duplicate samples each week. A quality control chart was constructed to determine the upper control limit and the upper warning limit for this method. (See Table 3).

Fresh chemical reagents are issued to monitors every six months. Upon receipt of the chemicals, monitors are asked to carry out comparison titrations with old and new reagents. These results are evaluated for each participant and compared to control limits established for the analysis and found to be within these limits.

INSPECTION REQUIREMENTS FOR SUPPLIES

All equipment and supplies are ordered from original manufacturers. Each shipment is inspected upon arrival for unusual qualities or damage.

DATA ACQUISITION REQUIREMENTS

Site latitudes and longitudes are determined using USGS 7.5 minute quadrangle maps. Some site locations were based on VA DEQ site locations. Nutrient sampling sites were located using SAV maps in the 1992 Distribution of SAV in Chesapeake Bay, Virginia Institute of Marine Science, Orth.

DATA MANAGEMENT

Volunteers mail data sheets monthly either to the CBCMP coordinator or the local volunteer watershed coordinator. They are instructed to make a copy of the form and to send the original to the coordinator. They keep a copy in case the originals are lost and to facilitate discussion of any data. Specific gravity readings and water temperature in the hydrometer jar are recorded and conversion to salinity is carried out by computer. Duplicate DO results are recorded and the average is calculated by computer. Each sheet is reviewed for decimal point errors, site/monitor number or any other questionable results. Monitors are contacted by phone or mail to answer questions about data entries. Dissolved oxygen values at or above the upper control limit are not saved in the database. A monitor that reports dissolved oxygen values at or above the upper warning limit two weeks in a row is contacted and reminded of the protocol to conduct a third titration when the duplicates differ by greater than 0.6 mg/l. Replacement equipment and reagent requests are filled immediately.

The data are entered into a database using a specially designed software called CitMon*MAN. (See Attachment 2 for CitMon*MAN Manuel). Each quarter, the local watershed coordinators send data on disk and original data sheets to the CBCMP coordinator where it is checked for accuracy. The compiled data is then sent on disc to the Virginia Department of Environmental Quality and the Chesapeake Bay Program Office.

A data documentation plan is on file at the CUP Computer Center. Data are reported on a data collection form supplied to the monitors. (See Attachment 1 for data form). The monitors are instructed to make a copy of the form and to send the original to their watershed coordinator or the program coordinator once a month. They keep a copy in case of loss in the mail and to facilitate discussion of questions about the data reported. They either photocopy the original or record their results in their own record books.

Specific gravity readings and water temperature in the hydrometer jar are recorded and conversion to salinity is carried out by the computer. Duplicate DO results are recorded;

the average is computed and entered into the database. The watershed coordinator or the program coordinator looks over each form as it is received for decimal point errors, missing site and/or monitor numbers, and general questions or problems. Monitors are contacted by phone or mail to answer questions about data that appear to be in error. Dissolved oxygen values that are beyond the upper control limit are not entered into the database. A monitor that reports dissolved oxygen values at or above the upper warning limit two weeks running is contacted and reminded of the protocol to conduct a third titration when the duplicates differ by greater than 0.6 mg/l. Replacement equipment and reagent requests are filled immediately. Questions are answered by phone or mail.

Data are entered by the watershed coordinators or the program coordinator into a Paradox database using a Runtime version of Paradox named, CitMon*MAN, which was designed specifically for the CBCMP data. Data are mailed to the program coordinator on disk along with the original data collection forms. Data are then submitted to the CUP Computer Center and the Virginia Department of Environmental Quality in ACSII comma delimited format. (See Appendix K for Data File Example).

ASSESSMENT AND RESPONSE ACTIONS

The program coordinator is responsible for insuring that all monitors attend QC sessions twice each year. These sessions serve as performance and systems audits for monitors and equipment. Monitors with faulty sampling techniques are retrained, and if the problems persist, their data is flagged and denoted as questionable within the computerized data set. Faulty equipment is immediately replaced. If a monitor misses two QC sessions within a single year, then the program coordinator will make a site visit, evaluate the monitor and their equipment, and re-equip or retrain as necessary. Information from QC session is analyzed to determine if the data quality objectives are met. If the objectives are not met, then the program coordinator will decide if monitors should be trained to use an alternative method, equipment should be calibrated more frequently, or if monitors should stop measuring the parameter in question.

Performance and systems audits of laboratory data are the responsibility of the lab analyst and lab supervisor. Benchmarks of accuracy and precision are provided for each sample so that the program coordinator can evaluate these aspects of the laboratory analyses. Any laboratory procedure problems are reported to the lab supervisor, who investigates and corrects the problem. All field and laboratory activities may be reviewed by state and EPA quality assurance officers as requested.

REPORTS

The program coordinator prepares an annual report for the data collected during the preceding year (January-December). This annual report includes the total number of sites monitored, the data collected at each site, the number of samples collected at each site, and individual site locations. Additionally, the report lists the previous years QC

schedules and any adjustments in technique or equipment that were based on data collected at QC sessions. The number and type of analyses, technical reports, and data transfers are listed and summarized, and data users are identified. The annual report is distributed to all monitors, the Region III EPA office, Chesapeake Bay Program Office, Maryland DNR, Pennsylvania DEP, and Virginia DEQ. The citizen monitoring database is transferred quarterly to CBPO and Virginia DEQ.

DATA REVIEW, VALIDATION AND VERIFICATION REQUIREMENTS

Field data are reviewed by the individual monitors when samples are collected, by watershed coordinators as they are entered in the computer, and finally by the program coordinator when the complete data set is compiled. Laboratory data are reviewed by the lab analyst, lab supervisor, and program coordinator. The program coordinator makes the final decision about whether to accept or reject data. Data quality objectives are provided to data users so that they can assess data quality based on their individual needs.

VALIDATION AND VERIFICATION METHODS

The QC sessions that are held every six months serve as the only validation checks for all variables except nutrient parameters. Data are examined by the watershed coordinators, who flag nonsensical numbers and information gaps while entering data into the computerized data set. Additionally, there are automatic range-checks included within the CitMon*MAN computer program, so the program will not accept data entries outside the predetermined range. The program coordinator decides whether to accept or reject questionable data, prints the computerized data set, and checks the numbers against field data sheets to verify correct data review. If necessary, the program coordinator will contact monitors to determine if unusual measurements can be explained.

Monitors verify that they are collecting DO measurements within the acceptable level of precision by repeating the titration until they collect two measurements with 0.6 mg/l. Watershed coordinators check DO data at the time of data entry, and the program coordinator uses an error checking program to further verify that data meet the accepted level of precision.

For laboratory samples, the accuracy of the methodology is validated by spiking one sample for every 25-50 that are analyzed. The results of spiked samples are examined by the lab analyst, and the lab supervisor corrects any problems that are detected. New sample standard deviations are calculated after every 30 sets of duplicates that are analyzed. The lab analyst verifies that samples meet the accepted level of precision (2 SD). Benchmarks of accuracy and precision of laboratory samples are sent to the program coordinator for further verification, and are provided to data users.

Each laboratory sample has a chain of custody tag attached. The laboratory analyst verifies the proper chain of custody. Samples that did not go through the proper chain of custody are flagged when entered in the computer database by the program coordinator.

If validation and verification procedures indicate that there is a consistent problem with the data quality for a variable, then the program coordinator will decide if personnel should be retrained, a new method should be substituted for the present method, or if the variable should no longer be measured. Any changes in procedures or in the variables that are collected will be discussed in the annual report.

RECONCILIATION WITH DATA QUALITY OBJECTIVES

The results of all QC sessions are immediately analyzed to determine if they meet data quality objectives (DQO's). Consequently, the DQO's for most variables are evaluated every six months. The precision of DO and precision and accuracy of nutrient parameters are evaluated.

If an individual monitor does not meet DQO's, then their equipment will be calibrated, checked, and replaced if it is determined to be faulty. If the monitor's technique is incorrect, then they will be retrained. If they continue to use incorrect technique, then their data will be flagged in the computerized data set to indicate that it is not reliable.

If laboratory data does not meet DQO's then the laboratory supervisor will be informed so that the problem can be identified and corrected. Field and laboratory data that does not meet DQO's will be rejected. Chronic problems with meeting DQO's will be described in the annual report. Data users will be informed of data limitations.