

Operating
Procedures
and
Quality
Control Assurance
Program

for Water Quality
Monitoring Network

Ohio River Valley Water Sanitation Commission

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*as of June 30, 1984

Operating Procedures
and
Quality Control Assurance Program
for
Water Quality Monitoring Network

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Quality Assurance Policy

It is the policy of the Ohio River Valley Water Sanitation Commission (ORSANCO) that there shall be sufficient quality assurance conducted within its programs to demonstrate that environmental data generated, processed, or used is scientifically valid, defensible, and of known acceptable quality. The quality of data generated and used is consistent with regional and national program requirements.

The procedures manual which follows contains descriptions of various water quality monitoring network elements and their prescribed quality control measures for assuring adherence to the policy objectives as stated in Quality Assurance Program Plan, June, 1983.



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INTRODUCTION

The following procedures outline a program for quality control assurance for the ORSANCO river monitoring program. Essentially, the procedures are in conformance with those previously published in the Federal Register as referenced throughout this document. Elements of the program are: representative sampling, sampling devices and preservation of samples, shipment of samples, chain of custody, analytical procedures, quality control of data, and data reporting.

Representative Sampling

Initially, each sampling point is selected by making measurements with field instruments for temperature, pH, conductivity and dissolved oxygen (DO) (or other parameters as appropriate) at various points and depths across the river. Following the initial survey, representative points are chosen. This multipoint examination is performed periodically to ensure the continued validity of the selected point.

Sampling Devices and Preservation of Samples

The conventional "Ohio River" sampler, sometimes called the Sargent sampler, is used for routine grab sample collection. This sampler has a volume of about 3-4 liters and can accommodate two DO bottles when such samples are required. The sampler is made of cast aluminum with stainless steel fittings and weighted from the outside so that it may be used for metals sampling.

A set of plastic or glass bottles, sterile or nonsterile as required, and of appropriate volume, is supplied for each sampling location. Sample bottles are spiked with the appropriate preservative by laboratory personnel before the bottles are sent into the field, or by the sample collector at the time of collection, using prepackaged ampules of preservative. Reagents used for preservatives are checked for acceptable quality and freedom from contamination by a quality control officer. Methods of preservation for all samples adhere to guidelines suggested in the U.S. Environmental Protection Agency (US EPA) Handbook for Sampling and Sample Preservation of Water and Wastewater, 1982. All

samples requiring preservation are kept on ice at 4°C and shipped to the appropriate contract laboratory the same day they are collected. All samples requiring field filtration (i.e., dissolved trace metals) are filtered immediately after collection through a membrane filter (0.45µm). In cases where recommended holding times cannot be met, the laboratory quality control officer determines whether samples are to be analyzed or discarded.

Shipment of Samples

Shipping containers are coolers with impact-resistant outer coverings and fitted lids to maintain cooling efficiency. Ice needed for cooling is obtained locally. A standardized protocol for shipping the sample cartons to the laboratory in minimum time has been established.

Measurements which can be performed efficiently and accurately in the field are performed at the time of collection to reduce the number of shipping containers required. For such measurements, field instruments are calibrated by approved techniques specified by the manufacturer on each day of use. Such calibration data are permanently recorded in field notebooks. (Chapter II).

Arrangements have been made with local laboratories to perform those measurements requiring minimal holding times, i.e., coliform, 5-day BOD.

Chain of Custody

Using waterproof ink, the sample collector labels sample bottles with all pertinent information in an approved log form. The sample collector attests to the validity of the sample by signature on the bottle and in the log form.

All samples, having been duly recorded, are delivered by the sample collector to the authorized carrier for shipment to the receiving laboratory. At the receiving laboratory, all samples are delivered to the authorized laboratory personnel.

In special cases, such as enforcement cases where it is legally imperative that sample integrity be maintained, special chain of custody procedures will be followed as required to satisfy the parties involved.

Analytical Procedures

Analytical methods used for analysis of all samples conform to those methods cited in 40 CFR 136; "Guidelines Establishing Test Procedures for the Analysis of Pollutants".

In the event that an analytical variance is required, the request for the variance is made by the Commission executive director following the protocol prescribed in the CFR cited above.

The choice of methods for certain biological and microbiological examinations for which no official guidelines have been promulgated is made following advice from qualified authorities.

Quality Control of Data

- Quality control of analytical data is achieved by:
- a) routine calibration and maintenance of laboratory instruments and equipment;
 - b) routine verification of working standard curves;
 - c) determination of individual method precision and accuracy;
 - d) use of reference samples and blind samples to verify daily results;
 - e) use of reference samples and standards, as knowns or unknowns, as additional checks. (See Chapter IV.)

Reporting of Data

All data are reported using accepted reporting levels (Chapter III) and in a form suitable for computerized storage and retrieval. Sample data, along with quality control data, are sent by the analytical laboratory to the Commission office for review before computer entry and sample discarding. For storage and retrieval of data, the most recently distributed STORET parameter codes are used. (See Chapter III.)

Samples are not held longer than seven days after the data have been reported to the Commission, except for those samples involving chain-of-custody and enforcement actions.

Calibration and Quality Control of Data for Electronic Monitors

In general, the calibration of the instrument is performed according to the manufacturer's recommendations by a duly qualified representative of the

manufacturer or Commission (see Chapter V for a detailed description of procedures). All instruments are inspected, repaired as necessary, calibrated and standardized on a fixed schedule every two weeks or as needed to maintain integrity of the system.

The procedures used are as follows:

pH - Clean electrodes as necessary; calibrate using standard buffers at 4 and 7 to ensure linearity. When practical, a separate pH check may be run with a precalibrated field meter against a stream sample.

Temperature - Clean sensor; calibrate with a standard NBS-certified thermometer.

Dissolved oxygen - Clean sensor; standardize against a DO measurement using the Winkler method. When practical, a separate check may be made against an air-calibrated sensor.

Conductivity - Calibrate with standard conductivity solution at ± 200 and ± 1200 micromhos. When practical, a check may be made against an actual stream sample using a precalibrated field meter.

A record of maintenance for each electronic monitor is kept on file at Commission headquarters showing the date of maintenance and standardization with readings before and after calibration. Accumulated data are discarded (or flagged) if the maintenance update shows sensor drift of ± 5 percent from the true reading.

Specific instructions to the field personnel concerning safety, sample collection, preservation and shipment techniques and the use and protection of field equipment are contained in "Quality Control in Field Sampling and Analysis" (Chapter II).

CHAPTER I

RIVER CROSS-SECTION

The river cross-sectioning program is conducted to fulfill the following specific objectives at all of the monitoring stations covered by the Commission's Monitoring Strategy for the Ohio River and lower reaches of major tributaries:

1. to determine the variation in specified parameters in the river at each station;
2. to determine the adequacy of the electronic and manual sampling location, as representative of the dissolved oxygen, pH, conductivity and temperature of the river; and
3. to compare the electronic data with the observed river values at the time of cross-sectioning.

Procedure

The cross-sectioning of each of the electronic and manual sampling stations consists of performing dissolved oxygen, pH, conductivity and temperature measurements at three or more points across the river, depending upon the width of the river and other hydrologic factors. The depth measurements are made at five-foot intervals starting about 2 feet from the bottom and ending at 1 1/2 feet from the surface.

Measurements are made at the same location as each specific manual and automatic sampling point.

Measurements are also made on the water samples from intake lines to the electronic monitor, to determine if there are any changes in water quality, especially in the dissolved oxygen concentration, as the water flows through the intake line.

Electronic monitors and the instruments are calibrated before cross-sectioning and the DO probes are checked against Winkler titration.

Data Analysis

The cross-sectional data are analyzed by plotting the cross-sectional profile and performing a statistical analysis to find the variation of parametric values within the river and to compare these with values obtained in conventional monitoring fashion.

Cross-sectional Profile

Two dimensional charts are prepared which represent the cross-section of the river at all stations along the Ohio River and lower reaches of major tributaries. The profiles show the difference between the actual observed values and the overall average for parameters being observed.

Statistical Analysis

A. Discrepancies across the river

The coefficient of variation, or relative variation, is calculated in the following manner to determine the actual variation of parametric values in the river at all stations, because it is a measure of the dispersion of the average value of these parameters across the river:

$$CV = \frac{SD}{M} \times 100$$

where:

CV = coefficient of variation

SD = standard deviation

M = average value of a parameter

The CV value is a relative value which can be used for the purpose of comparing parameters.

B. Adequacy of the electronic and manual sampling locations

For the point where each routine chemistry manual sample is collected and the intake for each electronic monitor, the mean of the samples collected at that vertical section is compared with the range revealed by the 95 percent confidence interval.

Ninety-five percent confidence intervals are calculated as:

$$C_{195} = M_R \pm 1.96 \sqrt{R}$$

where:

M_R = overall averages of a parameter in the river

1.96 = confidence factor for 5 percent level of significance

\sqrt{R} = standard deviation of a parameter in the river

C. Comparison of electronic data and observed river value

The 95 percent confidence intervals calculated above are used to determine if the electronic data are within these limits.



CHAPTER II
QUALITY CONTROL IN FIELD SAMPLING
AND
FIELD ANALYSIS

This section of the Quality Control Assurance Program for the In-stream Monitoring Network is divided into two elements:

1. Safety in the Field
2. Sampling, Sample Handling and Preservation
 - a. Primary Routine Chemistry Monitoring Network
 - b. Organics Detection System (ODS) Network
 - c. Biological Monitoring Network

Safety in the Field

There are a number of situations that each person taking field samples will encounter at different locations, and each of these situations must be given full consideration and attention. At any sampling site, safety is a prime consideration. There is no short cut to safety. No water sample is worth the life or physical impairment of a field person.

If the sampling operation is conducted from a bridge and the vehicle must be parked either on the bridge or at the bridge approach, every precaution must be taken to minimize traffic hazards. Park the vehicle in the least hazardous place with safety flashers operating. Set out warning flags as appropriate. Take the sample as quickly as possible and perform the necessary operations as promptly as possible. Do not linger in the area. Be especially cautious in bad weather and during the early morning or twilight hours. If special or unusual conditions exist that the supervisor-in-charge does not know about, report them.

If the sampling operation is conducted from a restricted area (power plant, dam, etc.), check in with site personnel as appropriate. Do not assume that the guard knows that you are in the area. Register upon entering premises. If hard hats or life jackets are required, use them. Operate your vehicle with special care on the company grounds and park it where it will not be an inconvenience to company personnel or violate company rules.

Since many of the automatic monitors are installed in remote, isolated areas of power plants and water treatment plants, it is a good practice when visiting these sites to let local personnel know that you are in the area and should return within a specified period of time. Similarly, let the same persons know when you are leaving the area. By all means, police the area carefully after you have serviced the automatic monitor and have completed the required field analyses. If you observe any unsafe conditions such as electrical hazards, greasy catwalks, etc., report them to the local man in charge.

Sampling, Sample Handling and Preservation

PRIMARY (ROUTINE CHEMISTRY) NETWORK

The Commission's Routine Chemistry Monitoring Network consists of 38 stations, of which 24 are located on the Ohio River and 14 on lower reaches of the major tributaries. This network represents a nucleus of key locations above and below major population centers and industrial areas, and in critical sections of the relatively new higher level pools on the Ohio River. The stations were selected by the Monitoring Strategy Study Team from a compendium of potential sites recommended by the participating state agencies for satisfying their need with regard to statutory requirements.

The analytical parameters selected (along with those gathered in other monitoring elements), and the frequency of sampling (Table 1) are designed to provide sufficient information to appraise water quality conditions at each location and to provide for comparisons of quality with other sections of the river. Data reviews in the future may indicate that frequency of sampling should be altered, sampling sites moved, additional analyses added to the existing list, or that some analyses should be omitted. Meanwhile, it is the basic function of the field person to visit the sampling station at the scheduled time and secure the samples in the prescribed manner.

T A B L E 1

Analytical Schedule for
Primary Monitoring Network Stations¹

<u>Group 11</u> (Monthly)	<u>Group 21</u> (Quarterly)
Coliform, fecal ² , BOD ₅	All of Group <u>11</u>
Suspended Solids	plus:
Tot. Kjeldahl Nitrogen ³	Arsenic
Nitrite+Nitrate as N ³	Selenium
Ammonia as N ³	Silver
Tot. Phosphorus ³	Nickel
Sulfate	Chromium ⁶
Alkalinity ⁴	Barium ⁶
Cyanide	Sodium ⁶
Phenolics	
Total Hardness	
Cadmium	
Copper	
Iron	
Zinc	
Mercury	
Lead	
Manganese	
Magnesium	
COD ⁵	
DO	
pH	
Conductivity	
Temperature	

In addition to the laboratory analyses, each sample is analyzed in the field for temperature, dissolved oxygen, conductivity and pH.

-
- ¹ As prescribed by the Commission, May 12, 1983
- ² Fecal coliform will be analyzed at all stations May through October and at CORE stations
- ³ Nutrients will be analyzed at all stations May through October and at CORE stations all year.
- ⁴ All stations in Pennsylvania and at East Liverpool, OH
- ⁵ CORE stations only -- those monitored as part of the National Basic Water Quality Monitoring Network (see Table 2)
- ⁶ Main stem stations only

Sampling Schedules

The sampling schedule for the ORSANCO river routine chemistry monitoring network has been planned so that it should be possible to sample each of the selected sites once every month or more frequently using two full-time field representatives. Each field person is responsible for approximately one-half of the river, but the number of sites assigned to each person is not the same because of varying distances between sites. The sampling stations are shown in Table 2, which also indicates state-designated CORE stations in the US EPA National Basic Water Monitoring Network.

Samples are always taken at the designated site. If access to the site is not available (locked gate, high water, icy walkways, etc.), the sample may be taken at the nearest convenient point, and duly noted on the sampling report form.

Locations of Sampling Sites

Each sampling site in the monitoring network is located and briefly described in Appendix A. For example, the location of the South Pittsburgh station on the Monongahela River at mile point 4.5 is described as "intake to Western Pennsylvania Water Co. . . . tap on raw water line in pumping station of water works."

Securing the Sample

The basic sampling instrument used is the so-called Ohio River sampler. The original material used to construct the sampler was copper, because of ease of construction. At the time (mid-1930's) there was little concern about trace metals in surface waters. The bucket is currently made of aluminum with exterior weight in the form of lead plates, so that samples may be taken with no detectable metals contamination. The sampler is designed to accommodate collection of samples for dissolved oxygen measurement and/or bacteriological samples. The sampler also provides for a three-fold displacement of water in the DO bottles without aeration. Additional sample volume is secured at the same time to allow for other analyses.

In use, the sampler should have sufficient exterior weight attached to the outside of the bottom to submerge it promptly. In flowing water, an inadequately weighted sampler will float some distance with the current before sinking. Sufficient weight decreases the angle between the line and the vertical so that the depth accuracy is improved. To ensure that the sample is taken at the

MONITORING NETWORK
STATION LOCATION AND TYPE

Station Number	Location	River	Mile-Point	Station Type
1	Lock #3	Allegheny	14.5	Fish
2	*Oakmont, PA	Allegheny	13.3	Electronic & Manual
3	Pittsburgh Dept. of Water	Allegheny	7.4	Organics Detection System (ODS)
4	West Penn Water, Aldrich Plt.	Monongahela	24.5	ODS
5	Lock #2	Monongahela	11.2	Fish
6	*S. Pittsburgh Water Works	Monongahela	4.5	Electronic & Manual
7	West View Water Authority	Ohio	4.5	ODS
8	Dashields Locks & Dam	Ohio	13.3	Fish
9	*South Heights, PA	Ohio	15.2	Electronic & Manual
10	*Beaver Falls, PA	Beaver	5.3	Electronic, Manual & Fish
11	*East Liverpool, OH	Ohio	40.2	Electronic & Manual & ODS
12	New Cumberland L & D	Ohio	54.4	Fish
13	*Pike Island L & D	Ohio	84.2	Manual & Fish
14	Wheeling Water Dept.	Ohio	86.8	ODS
15	Shadyside, OH	Ohio	102.4	Electronic & Manual
16	*Hannibal L & D	Ohio	126.4	Manual & Fish
17	*Willow Island L & D	Ohio	161.8	Manual & Fish
18	Lock & Dam #2	Muskingum	5.8	Manual
19	Parkersburg, WV	Ohio	190.3	ODS
20	*Belleville L & D	Ohio	203.9	Manual & Fish
21	Racine L & D	Ohio	238.0	Fish
22	*Addison, OH	Ohio	260.0	Electronic & Manual
23	St. Albans, WV	Kanawha	38.3	ODS
24	Winfield L & D	Kanawha	31.1	Electronic & Manual
25	*Gallipolis L & D	Ohio	279.2	Electronic, Manual & Fish
26	*Huntington, WV	Ohio	306.9	Electronic, Manual, ODS & Fish
27	Kenova, WV	Ohio	315.8	Manual
28	*Louisa, KY	Big Sandy	20.3	Electronic, Manual & Fish
29	*Greenup L & D	Ohio	341.0	Manual & Fish
30	Portsmouth, OH, Water Works	Ohio	350.1	ODS
31	Lucasville, OH	Scioto	15.0	Manual
32	Meldahl L & D	Ohio	436.2	Manual
33	Cincinnati Water Works	Ohio	462.8	Electronic, Manual & ODS
34	Near Cincinnati, OH	Little Miami	7.5	Manual
35	*Covington, KY	Licking	4.5	Electronic, Manual & Fish
36	North Bend, OH	Ohio	490.0	Electronic & Manual (Elec. out in FY83)
37	Elizabethtown Bridge, OH	Great Miami	5.5	Manual
38	Markland L & D	Ohio	531.5	Electronic & Manual
39	*Louisville Water Co.	Ohio	600.6	Electronic, Manual & ODS
40	McAlpine L & D	Ohio	606.8	Fish
41	*West Point	Ohio	625.9	Electronic, Manual & Fish
42	Cannelton L & D	Ohio	720.7	Electronic & Manual
43	*Near Sebree, KY	Green	41.3	Manual & Fish
44	*Evansville Water Works	Ohio	791.5	Electronic, Manual & ODS
45	Uniontown L & D	Ohio	846.0	Manual & Fish
46	New Harmony, IN	Wabash	51.5	Electronic & Manual
47	Paducah Water Works	Ohio	953.0	Electronic, Manual & ODS
48	Smithland L & D	Ohio	918.5	Manual (Electronic in FY83)
49	Near Grand Rivers, KY	Cumberland	30.6	Manual
50	*At Rt. 60, KY	Tennessee	6.0	Manual & Fish
51	*Joppa, IL	Ohio	952.3	Electronic & Manual
52	Lock #53	Ohio	926.6	Fish

*Indicates CORE Station

desired depth, the sample line should be marked or knotted at regular intervals so that the sample collector can read the depth of the sampler below the surface.

The interior of the bucket must be kept scrupulously clean. After each sample, the bucket should be emptied and visually inspected for residual debris or oil films that may contaminate the next sample. If it is contaminated with oil or grease, clean with detergent and rinse thoroughly with water. Good field practice requires that the bucket be rinsed first with the sample being taken in order to avoid sample-to-sample contamination by abrupt changes in concentrations. In the case of Commission samples, however, where there are no dramatic changes in sample-to-sample concentrations because all samples are taken from the same surface waters, it is sufficient to use the previous sample as a rinse for the next sample. If the bucket is kept clean and emptied after each sample, it should not be necessary to obtain a preliminary rinse sample. In the unlikely event that an unusual condition is encountered when a sample is taken, e.g., a heavy oil slick or similar condition, the bucket must then be thoroughly cleaned with detergent and rinsed with water before taking the next sample.

Securing the Sample with the Use of the Ohio River Sampler

Place two clean, dry DO bottles in the spring clips mounted in the bottom of the bucket. Position the lid on the bucket so that the dip tubes on the underside of the lid are inserted into the open necks of the DO bottles. Fasten the lid securely in place with the pivoting wing nuts mounted on the flange of the bucket. Lower the bucket into the water to the depth of one to one and a half meters, and wait until bubbling ceases to ensure that the bucket is full. Retrieve the bucket, remove the lid and carefully remove the DO bottles. Promptly stopper the bottles and place in the sample cooler. If a large volume of sample is needed, pour the water remaining in the sample bucket (after removal of the DO bottles) into a larger container and repeat the sampling operation without the DO bottles. The auxiliary sample container should be a plastic container of about two-gallon capacity, fitted with a lid to prevent spillage. The auxiliary container must also be kept scrupulously clean and rinsed in the same manner as the sample bucket.

Protection of Samples, Dilute Solutions and Field Instruments from Freezing

In the spring, summer and fall months when weather temperatures are normal, no special temperature precautions for protection of the samples, various dilute solutions and instruments are required. In the winter months, however, when air temperatures are below freezing for extended periods of time, there is always the danger of sample and solution loss or instrument damage due to icing and freezing.

During freezing weather, remember that the following events may occur:

1. DO bottles, filled with water at the freezing temperature and exposed at sub-freezing ambient air temperatures, will freeze and crack.
2. Buffer solutions used for pH standardization will freeze.
3. Standard solutions used for conductivity standards will freeze.
4. Ampuled preservatives may freeze and crack the container.
5. pH electrodes may freeze and crack.

Take whatever precautions are required to forestall the freezing and icing events. Store equipment in insulated chests, in the heated rear of the van or in the heated passenger compartment of car or truck. Particularly use special care to protect the pH electrode, since any damage to this item is costly to repair.

It is suggested that the field work required after securing the sample (field measurements, sample preparation, etc.) be performed under a roof at the various sampling sites.

Preservation of Samples

After returning to the vehicle, mix the sample in the auxiliary container, either by stirring or inversion and aliquot the sample to the appropriate pre-washed bottles according to the determinations to be performed (Table 3). Any stirring device used to agitate the sample prior to aliquoting should be constructed of an inert plastic material.

TABLE 3 (continued)

<u>Parameter</u> ¹	<u>Container</u> ²	<u>Preservative</u> ^{3, 13}	<u>Maximum Holding Time</u> ⁴
Residue, Non-filterable (TSS) ¹	P,G	Cool, 4°C	7 days
Residue, settleable	P,G	Cool, 4°C	48 hours
Residue, volatile	P,G	Cool, 4°C	7 days
Silica	P	Cool, 4°C	28 days
Specific conductance ¹	P,G	Cool, 4°C	28 days
Sulfate ¹	P,G	Cool, 4°C	28 days
Sulfide	P,G	Cool, 4°C, add zinc acetate plus sodium hydroxide to pH >9	7 days
Sulfite	P,G	Cool, 4°C	Analyze immediately
Surfactants	P,G	Cool, 4°C	48 hours
Temperature ¹	P,G	None required	Analyze immediately
Turbidity	P,G	Cool, 4°C	48 hours
<u>Organic Tests</u> ⁶			
Purgeable halocarbons	G, Teflon-lined septum	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁷	14 days
Purgeable aromatics	G, Teflon-lined septum	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁷ HCl to pH <2 ¹⁰	14 days
Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁷	14 days
Adjust pH to 4-5 ¹²			

TABLE 3 (continued)

<u>Parameter</u> ¹	<u>Container</u> ²	<u>Preservative</u> ^{3, 13}	<u>Maximum Holding Time</u> ⁴
Phenols	G, Teflon- lined cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁷	7 days until extraction, 40 days after extraction
Benzidines	G, Teflon- lined cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁷	7 days until extraction, 40 days after extraction
Phthalate esters	G, Teflon- lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Nitrosamines ⁸	G, Teflon- lined cap	Cool, 4°C store in dark 0.008% Na ₂ S ₂ O ₃ ⁷	7 days until extraction, 40 days after extraction
PCB's	G, Teflon- lined cap	Cool, 4°C ⁹ pH 5-9	7 days until extraction, 40 days after extraction
Nitroaromatics and isophorone	G, Teflon- lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Polynuclear and hydrocarbons	G, Teflon- lined cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁷ store in dark	7 days until extraction, 40 days after extraction
Haloethers	G, Teflon- lined cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁷	7 days until extraction, 40 days after extraction
Chlorinated hydrocarbons	G, Teflon- cap	Cool, 4°C	7 days until extraction, 40 days after extraction
TCDD	G, Teflon- cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁷	7 days until extraction, 40 days after extraction

TABLE 3 (continued)

<u>Parameter</u> ¹	<u>Container</u> ²	<u>Preservative</u> ^{3, 13}	<u>Maximum Holding Time</u> ⁴
<u>Pesticides Tests</u>			
Pesticides	G, Teflon- lined cap	Cool, 4°C pH 5-9 ⁹	7 days until extraction, 40 days after extraction
<u>Radiological Tests</u>			
Alpha, beta and radium	P,G	HNO ₃ to pH <2	6 months

TABLE 3 NOTES

1. Parameters noted in Monitoring Strategy; additional parameters and requirements included for reference.
2. Polyethylene (P) or Glass (G).
3. Sample preservation should be performed immediately upon sample collection. For composite samples, each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.
4. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the NPDES permittee or monitoring laboratory has data on file to show that the specific types of samples under study are stable for the longer time. Some samples may not be stable for the maximum time period given in the table. A permittee or monitoring laboratory is obligated to analyze the sample within a shorter time if knowledge exists to show this is necessary to maintain sample stability.
5. Samples should be filtered immediately on-site before adding preservative for dissolved metals.
6. Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.
7. Should only be used in the presence of residual chlorine.
8. For the analysis of diphenylnitrosamine, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3^6$ and adjust pH to 7-10 s.u. with NaOH within 24 hours of sampling.

9. The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted with 72 hours of collection. For the analysis of aldrin, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$.
10. Maximum holding time is 24 hours when sulfide is present.
11. Sample receiving no pH adjustment must be analyzed within 7 days of sampling.
12. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.
13. When any sample is to be shipped by common carrier or sent by the U.S. Postal Service, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person sending the samples is responsible for ensuring such compliance. For the preservation requirements of Table 3, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following substances: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

Add the proper preservative to each portion as indicated in Table 3, but do not open the ampules containing the preservative solutions until immediately prior to use. Note that the constricted neck of the opened ampule restricts the flow and tapping the inverted ampule against the neck of the sample bottle may be necessary. Avoid scattering of the preserving solutions; if any of these fluids touch the skin or clothing, flush the area with water. An acid burn of any significance should have medical attention.

Shipment of Samples

All samples are to be shipped by a ground express carrier to ensure delivery to the laboratory within 24 hours. Any bus shipment, in which a transfer or similar problem is anticipated, is to be shipped by Greyhound's "Next Bus Out" service, where expedited shipment is guaranteed. All samples are to be shipped in insulated coolers packed with ice. Shipments arriving during the night are transferred to the laboratories at the start of business on the following day. The sample report form which accompanies each sample is the log-in document which the laboratory uses to indicate time of arrival at the lab.

Chain of Custody

Normally, the samples and analytical data obtained by the Monitoring Network do not possess the legal significance requiring a chain of custody protocol. In the event that a situation should arise in which such a formal procedure will be required, the chain of custody procedure recommended by the US EPA Region in which the situation arises will be used.

The field personnel should note, however, that proper identification of all samples is a vital necessity. Misidentified samples result in confusing data production. Unidentified samples or samples illegibly labeled are simply discarded in the laboratory, resulting in useless field work.

Analysis Techniques with Field Instruments

Four parameters must be measured as soon as possible after the sample is taken because of their instability. These are conductivity, pH, dissolved oxygen and temperature. Temperature and dissolved oxygen should be run as soon as possible after the sample is taken; pH and conductivity are not as critical but also require measurement in the field. Each of these measurements is affected by ambient air temperature and the necessary precautions and corrections for each must be observed.

The instruments supplied to the field representatives for these determinations have been selected by Commission staff as being the best suited for the measurements required.* However, the best evidence of suitability is performance under the varying and often adverse conditions of actual field use. The field personnel are urged to view these instruments critically for signs of fragility, instability, corrosion, chronic maintenance problems and other impediments to efficient field use.

Comments and observations regarding instrument malfunctions or desirable improvements are encouraged.

Temperature

The Fahrenheit thermometer should be used for calibration of the electronic monitors; the Centigrade thermometer should be used for reporting temperature of the grab samples at the time of collection.

For measurement of temperature of the grab sample, remove the DO bottle from the sampling bucket as soon as it is retrieved. Then, with the sample still in the bucket, immerse the stem of the thermometer at least three inches below the surface of the sample and wait about one minute for the temperature to equilibrate. Read the thermometer with the thermometer immersed in the sample. Do not remove the thermometer from the sample in order to read it more conveniently.

Report the temperature on the report form to the nearest 0.1°Centigrade.

Dissolved oxygen

The instrument supplied by the Commission for this measurement is the Weston and Stack Model 330 Dissolved Oxygen Analyzer, equipped with a Model 33 Lab Probe. The lab probe is designed with a built-in agitator to provide the necessary sample flow. Each field person must be familiar with the details of operation and routine maintenance prescribed in the instruction manual supplied with the instrument.

The DO meter should be standardized daily, or in the case of intermittent operation, before use. Use the standardization procedure outlined in the Weston and Stack Manual, employing the Winkler method. The "wet

*Field instruments specified herein may be replaced from time to time with differing models or brands as deemed appropriate.

bottle" standardization, which is not outlined in the Weston and Stack instruction manual, may also be used as follows:

1. Place about 100 ml of distilled water in a standard DO bottle; stopper and shake vigorously;
2. Remove the stopper and insert the probe, taking care not to wet the tip of the probe;
3. Note the temperature of the air phase in the bottle, as indicated on the Model 330 meter. Switch the meter to the high DO range and adjust the reading according to the following table:

<u>Temperature (°C)</u>	<u>Oxygen (mg/l)</u>
20	9.2
21	9.0
22	8.8
23	8.7
24	8.5
25	8.4
26	8.2
27	8.1
28	7.9

The probe is now standardized for future readings, but should be calibrated daily. An occasional check of the wet bottle against the Winkler calibration is recommended.

To obtain a DO reading on the sample, remove the DO bottles containing a fresh sample from the sampling bucket as soon as it is retrieved. Stopper the bottles and return to the vehicle. Insert the probe into the bottle and note the DO reading, using the high range scale, and reading the result to the nearest 0.1 mg/l. Also, note the sample temperature as indicated by the meter to check the sample temperature as observed with the glass-stemmed mercury thermometer. Record the result on the report form.

pH

The instrument used for the pH measurement is the Horizon Ecology Company Model 5995 Portable pH meter. As with other Commission field instruments, it is the responsibility of the field personnel to be familiar with the manufacturer's directions for use and maintenance of the meter.

Follow the manufacturer's instructions for standardization of the meter; however, to improve accuracy of readings, standardize the meter at two levels using both the pH 4.0 and pH 7.0 buffers. Discard the buffer solutions used for the standardizations; use fresh solutions each time the meter is standardized.

Abnormal instrument behavior, such as a wildly twitching needle, slow drift or erratic response may be indicative of various instrument failures, such as a cracked electrode, weak battery, loss of potassium chloride in the reference electrode, faulty electrical connection, etc. Such behaviors are most likely to be observed during the standardization operation. Refer to the instruction manual for troubleshooting or return the meter to the Commission for repairs.

Note the temperature of the sample and adjust the temperature °C compensator to the measured temperature. Pour an aliquot of the fresh grab sample into the vessel reserved for pH measurement, and with the meter on standby, rinse the electrode by gently raising and lowering the container several times. Discard that portion of the sample and pour a fresh aliquot into the vessel. With the meter on pH, immerse the electrode into the sample and read the pH to the nearest 0.1 unit. Record the result on the report form. Rinse the electrode with distilled water and store until the next sample.

Conductivity

The instrument used for the conductivity measurement is the Solu Bridge RRB-3 portable battery-operated meter, equipped with a CEL-VS 2 dip cell. Details of operation, maintenance and troubleshooting are contained in the manual supplied with the instrument.

The conductivity cell supplied with the instrument has a stated cell constant of 2.0. The cell is very stable, barring accident or sample damage, and does not require standardization. However, the cell should be checked daily with the two standard conductivity solutions supplied by the Commission. These solutions have conductivities of - 200 and - 1200 umhos/cm.

Pour the standard solution into the container reserved for conductivity readings. Place the cell in the solution and move it up and down vigorously under the liquid to ensure removal of air bubbles from the cell casing. Discard the solution, place fresh solution in the container and repeat the operation. Take the

conductivity measurement with the cell immersed in the solution to a point at least 0.5 inches above the uppermost air vent and no closer than 0.5 inches to the sides and bottom of the container. Apply the necessary temperature conversion for adjusting the reading to 25°C. Temperature compensation is necessary because the stated conductivity of the standard solutions implies reading at 25°C. The cell readings, with the 200 and 1200 umhos/cm standards should agree within \pm 3 percent.

If the cell constant appears to have changed, a new constant may be calculated following the procedure outlined in Standard Methods, 15th Edition, 1980, pages 70 and 72. A damaged cell should be replaced with a new one.

Using an aliquot of fresh grab sample, rinse the cell with one or more portions, as described in the previous paragraph. Measure the resistance of the sample using the proper temperature compensation as outlined in the manufacturer's manual. Record the result on the report form.

Special Samples

The sampling requirements for pesticides, radioactivity and organics in water are listed in Table 3. No listing has been made for sediment sampling, pending further discussion concerning available methods.

The analytical procedures to be used for special samples will be those recommended by the US EPA when and if a special sample program is initiated.

Use of Water Quality Report Form

A Water Quality Report Form (Figure 1) is used to record field data, to provide instructions for laboratory analysis and to record laboratory data. Instructions for completing the form follow.

Station Name

The station name should be entered on all forms used. Names for regular stations with ID numbers assigned should remain uniform.

Station ID Code

The station ID Code (Table 4) is the four-digit code used by the Commission to identify stations to the computer. The first digit is the station type code. It is used for routine grab samples. The second digit is a state code. The third and fourth digits are station

**ORSANCO WATER QUALITY
SAMPLE REPORT**

Station Name _____ Station I.D. Code

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 Stream _____ Mile Point _____ Collection Date & Time

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 Analysis Code _____ Analysis Exceptions _____
 Type Sample ☐ Routine Grab ☐ Other _____ Field Technician _____
 Comments: _____

River Conditions _____ Lab Number _____
 Date Received at Lab _____ Time _____
 Weather Conditions _____ Date Completed _____ Supervising Chemist _____

Left Column	Center Column	Right Column																																																																																																																																																																																																																												
<p><u>FIELD DATA</u></p> <p>F1A Water Temperature (C°) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F1B Conductivity (µmhos/cm) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F1C pH (su) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F1D Dissolved Oxygen (mg/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p><u>GENERAL</u></p> <p>F2A Flow (CFS) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F2C Suspended Solids (mg/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F2D Dissolved Solids (mg/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F2F Alkalinity (mg/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F2G Sulfate (mg/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F2K Total Hardness (mg/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p><u>NUTRIENTS</u></p> <p>F3A Total Phosphorus (P) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F3B TKN <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F3C Ammonia <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F3D Nitrate/Nitrite <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p>																																																																							<p align="center"><u>NON-ROUTINE</u></p> <table border="1" style="width: 100%; height: 100px;"> <tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr> <tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr> </table>																																																			<p><u>BACTERIOLOGICAL</u></p> <p>F5B Fecal Coliform (#/100 ml) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F5C BOD (mg/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F5D COD (mg/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p><u>GENERAL</u></p> <p>F2M Magnesium (mg/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F2N Sodium (mg/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F2R Phenolics (ug/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F2S Cyanide (ng/l) <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p><u>METALS (µg/l)</u></p> <p>F4C Cadmium <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F4E Copper <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F4F Iron <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F4G Lead <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F4H Manganese <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F4J Mercury <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td> </td><td> </td><td> </td><td> </td><td> </td></tr></table></p> <p>F4N Zinc <table border="1" style="display: inline-table; 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Figure 1: ORSANCO Water Quality Report Form for Routine Water Chemistry Analysis

TABLE 4

Station Codes for ORSANCO¹
Manual Monitoring Stations¹

Upper Ohio Region

Allegheny River at Oakmont, PA	1233
Monongahela River at South Pittsburgh, PA	1237
Ohio River at South Heights, PA	1201
Beaver River at Beaver Falls, PA	1242
Ohio River at East Liverpool, OH	1500
Ohio River at Wheeling, WV (Pike Island Dam)	1405
Ohio River at Shadyside, OH	1521
Ohio River at Willow Island, WV	1408
Ohio River at Hannibal Dam, OH	1423
Muskingum River near Marietta, OH	1531
Ohio River at Belleville Dam, WV	1421
Ohio River at Addison (Kyger Creek), OH	1510
Ohio River at Gallipolis Dam, WV	1422

Middle Ohio Region

Kanawha River at Winfield, WV	1450
Ohio River at Huntington, WV	1412
Ohio River at Kenova, WV (South Point, OH)	1523
Big Sandy River near Louisa, KY	1630
Ohio River at Greenup Dam, KY	1621
Scioto River at Lucasville, OH	1538
Ohio River at Meldahl Dam, OH	1511
Ohio River at Cincinnati, OH	1504
Little Miami River at Cincinnati, OH	1571
Licking River at Covington, KY	1634
Ohio River at North Bend, OH	1508
Great Miami River at Cleves, OH	1551
Ohio River at Markland Dam, KY	1600

Lower Ohio Region

Ohio River at Louisville, KY	1601
Ohio River at West Point, KY	1622
Ohio River at Cannelton Dam, IN	1721
Green River at Sebree, KY	1656
Ohio River at Evansville, IN	1703
Ohio River at Uniontown Dam, IN	1722
Wabash River at New Harmony, IN	1741
Cumberland River at Barkley Dam, KY	1645
Ohio River at Paducah, KY	1625
Ohio River at Smithland Dam, IL	1820
Tennessee River at Paducah, KY	1650
Ohio River at Joppa, IL	1821

¹Location description of each of these monitoring stations are in Appendix A.

identifiers. Forms and samples from locations where routine samples have not been collected will not use this column, but will have the stream and mile point identified. The code designations are as follows:

First Digit

0: indicates water users data, pre-1972 USGS data, or special reports from discharges data received during a demonstration project (1969-71).

1: indicates manual samples collected in accordance with the Commission's Monitoring Strategy.

Second Digit

This digit is a state code for sampling locations.

1 : New York
2 : Pennsylvania
3 : Virginia
4 : West Virginia
5 : Ohio
6 : Kentucky
7 : Indiana
8 : Illinois

Third Digit

This sampling point identification code relates to sampling location.

00-29 : Main stem Ohio River location
30-99 : Tributary location

Stream and Mile Point

This information may be omitted when station ID code is used.

Collection Data and Time

Numbers only should be used for the date, such as 7-01-76. For the time, military time, time zone, and daylight or standard time should be entered, for example, 1415 CDT.

Analysis Code

A two-digit code is to be used.

11 = monthly sample 21 = quarterly sample

Analysis Exceptions

Any exceptions to the standard analyses should be noted (identified by their codes) by marking add to the two-digit alpha numeric parameter code(s) and/or delete and the parameter code(s).

Type Sample

Either "routine grab" or other box should be checked and type sample specified in blank provided.

Field Technician

Form should be signed by person responsible for the collection and preservation of the sample.

Comments

This column is reserved for any comments or unusual conditions noted by sampler or special instructions to the laboratory.

River Conditions

Flow and general river conditions should be noted, as well as unusual conditions.

Weather

Weather conditions and approximate air temperature at time of sample collection should be noted.

Field Data

Field readings are recorded here on sheet.

Three copies of this form should accompany the sample to the laboratory. The laboratory will complete the form and forward it to the Commission. One copy should be forwarded to the Commission office by the field technician.

ORGANICS DETECTION SYSTEM (ODS) NETWORK

The Organics Detection System (ODS) is a network of detection and notification equipment located to protect major Ohio Valley water supplies, operated by personnel at cooperating water utilities and other sites. The network consists of 13 stations, ten on the Ohio River and one each on the Monongahela, Allegheny, and Kanawha Rivers. Each station utilizes one of the following gas chromatographic (GC) analytical instruments: an HNU 401 GC with a Spectra-Physics 4270 or Perkin-Elmer Sigma I microprocessor; a Varian 3700 GC with a Spectra-Physics 4100 microprocessor; or a Hewlett-Packard 5840 GC. (Table 5)

Currently, halogenated methanes, ethanes, ethylenes, propanes, and certain other volatile organic compounds which exhibit low water solubility and a vapor pressure greater than that of water are detected by the ODS.

Each day the operator at each station collects two 2-ounce nonchlorinated raw water samples and organic-free blanks which are headspace free. At that time, he/she also collects a 1 gallon solvent extractable sample of raw water for alert situations. An internal standard is spiked into an aliquot of one of the duplicate organic-free water blanks and run before the daily raw water analysis to insure that the system is operating properly. If extraneous organics appear or internal standard retention times change, these problems are resolved before initiating the raw water analysis.

An aliquot of one of the 2-ounce raw water samples is injected with the internal standard and run through the purgeable GC analytical procedure by the station's operator, in accordance with quality control procedures. If a significant concentration of one or more organics is noted in the raw water sample, another raw water aliquot obtained from the same sample bottle should be run to confirm its presence.

If a significant concentration of one or more organics is noted, the ODS station immediately notifies the Commission by telecopier.*

*A significant concentration has been defined by the Commission to be 10 times the previous day's detection or more than 25 ug/l.

TABLE 5

Analytical Schedule for ORSANCO Organics
Monitoring Network Stations

<u>Station Name</u>	<u>Sampling Frequency</u>	<u>Detectors Used</u>	<u>Compounds Detected</u>
Western Penn Water Co. Aldrich Plant	Daily	Coulson Conduc- tivity ¹ detector	Volatile organic compounds
Pittsburgh Water Treatment Plant	Daily	Coulson Conduc- tivity detector	Volatile organic compounds
West View Water Authority	Daily	Coulson Conduc- tivity detector; Photoionization detector ²	Volatile organic compounds and aromatic compounds
East Liverpool Water Works	Week Days	Coulson Conduc- tivity detector	Volatile organic compounds
Wheeling Water Treatment Plant	Daily	Coulson Conduc- tivity detector; Photoionization detector	Volatile organic and aromatic compounds
E.I. duPont deNemours & Co. Parkersburg	Daily	Flame Ionization detector ³	Volatile organic and aromatic compounds
Appalachian Power Company St. Albans	Week Days	Flame Ionization detector	Volatile organic and aromatic compounds
Huntington Water Corporation	Daily	Coulson conduc- tivity detector; Photoionization detector	Volatile organic and aromatic compounds
Portsmouth Water Treatment Plant	Daily	Coulson Conduc- tivity detector	Volatile organic compounds
Cincinnati Water Works	Daily	Coulson Conduc- tivity detector	Volatile organic compounds
Louisville Water Company	Daily	Coulson Conduc- tivity detector; Photoionization detector	Volatile organic compounds and aromatic compounds
Evansville Water Works	Daily	Coulson Conduc- tivity detector	Volatile organic compounds
Paducah Water Works	Daily	Coulson Conduc- tivity detector	Volatile organic compounds

¹Detection limit is 0.1 ug/l

²Detection limit is 0.1 ug/l

³Detection limit is 5-10 ug/l. Stations utilizing the FID are spill detection stations only and not low level detection stations.

An alert may be declared after consultation between Commission staff and the station GC operator. During an alert situation, the remaining 2-ounce raw water sample and 1-gallon solvent extractable sample are shipped by station personnel to a contract analytical laboratory for GC/MS confirmation. Otherwise, the duplicate samples are discarded the next day and the bottles are cleaned for subsequent usage.

BIOLOGICAL MONITORING NETWORK

The biological monitoring program consists of multi-agency cooperative fish population and tissue sampling at selected sites on the Ohio River main stem and seven of its major tributaries. Macroinvertebrate population sampling at 21 Commission-operated US EPA CORE network water monitoring stations is done to further augment state programs. (Table 6)

Quality assurance methods practiced in biological monitoring adhere to those recommendations in Standard Methods 14th ed.; the U.S. Department of Interior National Handbook of Recommended Methods for Water-Data Acquisition, Chapter 4; and the US EPA manual 600/4-78-043; Quality Assurance Guidelines for Biological Testing.

The primary concern in assuring the quality and utility of biological data for trend monitoring is in gathering the data in a manner consistent with that previously used so that results can be compared.

TABLE 6
BIOLOGICAL MONITORING STATIONS

Annual Macroinvertebrate Sampling Locations		Biennial Fish Population and Tissue Sampling**	
	<u>Mile</u>		<u>Mile</u>
Allegheny R. @ Oakmont, PA	13.3*	Allegheny R. @ Lock 3	14.5*
Monongahela R. @ Pittsburgh, PA	4.5*	Monongahela R. @ Lock 2	11.2*
Ohio R. near South Heights, PA	15.2	Ohio R. @ Dashields Lock	13.3
Beaver R. @ Beaver Falls, PA	5.3*	Beaver R. @ Beaver Falls, PA	5.3**
Ohio R. near E. Liverpool, OH	40.2	Ohio R. @ New Cumberland Lock	54.4
Ohio R. @ Pike Island Dam	84.2	Ohio R. @ Pike Island Dam	84.2
Ohio R. @ Hannibal Dam	126.4	Ohio R. @ Hannibal Dam	126.4
Ohio R. @ Willow Island Dam	161.8	Ohio R. @ Willow Island Dam	161.8
Ohio R. @ Belleville Dam	203.9	Ohio R. @ Belleville Dam	203.9
Ohio R. @ Addison, OH	260.0	Ohio R. @ Addison, OH	260.0**
Ohio R. @ Gallipolis Dam	279.2	Ohio R. @ Gallipolis Dam	279.2
Ohio R. @ Huntington, WV	306.9	Ohio R. @ Huntington, WV	306.9**
Big Sandy R. near Louisa, KY	20.3*	Big Sandy R. near Louisa, KY	20.3**
Ohio R. @ Greenup Dam	341.0	Ohio R. @ Greenup Dam	341.0
Licking R. @ Covington, KY	4.5*	Licking R. @ Covington, KY	4.5**
Ohio R. @ McAlpine Dam	606.8	Ohio R. @ McAlpine Dam	606.8
Ohio R. @ West Point, KY	625.9	Ohio R. @ West Point, KY	625.9**
Green R. near Seebree, KY	41.3*	Green R. near Seebree, KY	41.3**
Ohio R. @ Evansville, IN	791.5	Ohio R. @ Uniontown Dam	846.0
Tennessee R. near Paducah, KY	6.0*	Tennessee R. near Paducah, KY	6.0**
Ohio R. @ Joppa, IL	952.3	Ohio R. Dam #53	952.3

* From confluence with Ohio River.

** Fish tissue samples collected by state personnel.

CHAPTER III
PROTOCOL FOR QUALITY CONTROL OF DATA IN
CONTRACT LABORATORIES

State and Other Laboratories

Analytical services furnished by contract to the Commission, either by private consulting laboratories or by state laboratories, require the following procedures as a part of the laboratory's quality control effort:

1. Minimum Daily Quality Control

- A. After a standard reagent curve composed of a reagent blank and at least three standards has been prepared, a daily check of the standard curve is to be run using at least a reagent blank and one standard at mid-range of the working curve. Daily checks must be within ± 10 percent of the original curve.
- B. If 20 or more samples per day are analyzed, the working standard curve is verified by running an additional standard at mid-range every 20 samples. Checks must be within ± 10 percent of the original curve.
- C. At least one duplicate sample and one spike is run every 10 to 20 samples or with each set of samples to verify the precision of the samples. Checks must be within ± 2 standard deviations.

2. Routine, Non-daily Quality Control

- A. The laboratory must analyze a known reference sample (when available) once per quarter for the parameters measured. The measured value should be within ± 2 standard deviations of the known value as based upon the precision given in the approved method.

- B. The laboratory must analyze an unknown performance sample (when available) once per year for the parameters measured. Results must be within ± 2 standard deviations for precision in the approved methods. If problems do occur, appropriate technical consultation will be provided and a follow-up performance sample will be analyzed.
 - C. Standard deviation (σ) should be calculated and documented for all measurements being conducted.
- 3. If more than five persons are employed in the laboratory (other than the supervisor), one person will be appointed as the quality control officer, to be responsible for quality control techniques and programs.
 - 4. The quality control officer will keep a complete log of all quality control samples and data. All such information will be available for inspection.
 - 5. Other recommendations to the contract laboratories include:
 - a) the use of service contracts on analytical balances;
 - b) use of class S weights for periodic checks on balances;
 - c) use of an NBS-standardized thermometer to check thermometers in ovens, water baths, etc.;
 - d) color standards for spectrophotometer checks; and
 - e) use of quality control charts.

TABLE 7
PARAMETER, STORET CODES, AND REPORTING LEVELS

PARAMETER AND REPORTING UNITS	STORET AND PARAMETER CODE	REPORTING LEVEL
<u>BASIC PHYSICAL AND CHEMICAL</u>		
Temperature, °C	00010	.x
pH, Units	00400	.x
Dissolved Oxygen, mg/l	00300	x.x
Conductivity, micromhos	00095	x.
Turbidity, NTU	00070	x.
Flow, CFS	00060	
<u>GENERAL CHEMICAL</u>		
Acidity, mg/l as CaCO ₃	00435	x.
Alkalinity, mg/l as CaCO ₃	00410	x.
BOD, 5 day, mg/l	00310	x.
Cyanide, mg/l	00720	.xxx
Fluoride, mg/l	00950	.xx
Total Hardness, mg/l as CaCO ₃	00900	x.
Ammonia, mg/l	00610	.xx
Nitrate/Nitrite, mg/l	00630	.xx
Total Kjeldahl/N, mg/l	00625	.xx
Phenolics, mg/l	32730	.xxx
Total Dissolved Phosphorus, mg/l	00666	.xx
Total Phosphorous, mg/l	00665	.xx
Solids, dissolved, mg/l	70304	x.
Solids, suspended, mg/l	00515	x.
Sulfate, mg/l	00945	x.

TABLE 7 (continued)

PARAMETER, STORET CODES, AND REPORTING LEVELS

PARAMETER AND REPORTING UNITS	STORET AND PARAMETER CODE	REPORTING LEVEL
Sodium, mg/l	00929	.x
Potassium, mg/l	00935	.x
Silica, Dissolved, mg/l as SiO ₂	00955	.x
Calcium, Dissolved mg/l	00915	.x
Magnesium, Dissolved, mg/l	00925	.x
Magnesium, Total, mg/l	00927	.x
Total Organic Carbon, mg/l	00680	.x
<u>TRACE METALS</u>		
Arsenic, Total, mg/l	01002	.xxx
Arsenic, Dissolved, mg/l	01000	.xxx
Barium, Total, mg/l	01007	.xxx
Barium, Dissolved, mg/l	01005	.xxx
Cadmium, Total, mg/l	01027	.xxx
Cadmium, Dissolved, mg/l	01025	.xxx
Chromium, Total, mg/l	01034	.xxx
Chromium, Dissolved, mg/l	01030	.xxx
Copper, Total, mg/l	01042	.xxx
Copper, Dissolved, mg/l	01040	.xxx
Iron, Total, mg/l	01045	.xxx
Iron, Dissolved, mg/l	01046	.xxx
Manganese, Total, mg/l	01055	.xxx
Manganese, Dissolved, mg/l	01056	.xxx
Mercury, Total, mg/l	71900	.xxxx

TABLE 7 (continued)
PARAMETER, STORET CODES, AND REPORTING LEVELS

PARAMETER AND REPORTING UNITS	STORET AND PARAMETER CODE	REPORTING LEVEL
Mercury, Dissolved, mg/l	71890	.xxxx
Lead, Total, mg/l	01051	.xxx
Lead, Dissolved, mg/l	01049	.xxx
Nickel, Total, mg/l	01067	.xxx
Nickel, Dissolved, mg/l	01065	.xxx
Selenium, Total, mg/l	01147	.xxx
Selenium, Dissolved, mg/l	01145	.xxx
Silver, Total, mg/l	01077	.xxx
Silver, Dissolved, mg/l	01075	.xxx
Zinc, Total, mg/l	01092	.xxx
Zinc, Dissolved, mg/l	01090	.xxx
Trace Metals Not Listed		
<u>RADIOLOGICAL</u>		
Alpha, Total, pc/l	01501	.x
Alpha, Dissolved, pc/l	01503	.x
Alpha, Counting Error, pc/l	01502	
Beta, Total, pc/l	03501	.x
Beta, Dissolved, pc/l	03503	.x
Beta, Counting Error, pc/l	03502	
Radium, Total, pc/l	09501	.x
Radium, Total, Counting Error, pc/l	09502	
<u>BACTERIA</u>		
Coliform, Fecal, No/100 ml	31616	x.

TABLE 7 (continued)
PARAMETER, STORET CODES, AND REPORTING LEVELS

PARAMETER AND REPORTING UNITS	STORET AND PARAMETER CODE	REPORTING LEVEL
Coliform Fecal in Presence of Chlorine, No/100 ml		
Coliform, Total, No/100 ml	31501	x.
Coliform, Total, in Presence of Chlorine, No/100 ml		
Fecal Strep., No/100 ml	31671	x.
<u>ORGANICS</u>		
Pesticides and other organics	ug/l	.xx

TABLE 7 (continued)

ODS DATA

<u>Comp. #</u>	<u>Compound</u>	<u>STORET #</u>	<u>Reporting Level</u>
2	Methylene Chloride ug/l	34423	.x
3	Trichlorofluoromethane ug/l	34488	.x
21	1,1-Dichloroethylene ug/l	34501	.x
22	Bromochloromethane ug/l	77297	.x
4	1,1-Dichloroethane ug/l	34496	.x
5	Chloroform ug/l	32106	.x
6	1,2-Dichloroethane ug/l	34531	.x
7	1,1,1-Trichloroethane ug/l	34506	.x
8	Carbon Tetrachloride ug/l	32102	.x
9	Bromodichloromethane ug/l	32101	.x
10	1,2-Dichloropropane ug/l	34541	.x
12	Trichloroethylene ug/l	39180	.x
13	Dibromochloromethane ug/l	32105	.x
16	Bromoform ug/l	32104	.x
17	Tetrachloroethylene ug/l	34475	.x
19	Chlorobenzene ug/l	34301	.x
20	1,4-Dichlorobenzene ug/l	34571	.x

Analytical Method: GC analysis

US EPA Method: 601

TABLE 7 (continued)

Priority Pollutants and Respective Detection Limits

BASE/NEUTRAL FRACTION

		<u>STORET No.</u>	<u>Detection Limit</u>
1B	Acenaphthene	34205	5 ppb
2B	Acenaphthylene	34200	5 ppb
3B	Anthracene	34220	5 ppb
4B	Benzidine	34241	5 ppb
5B	Benzo(a)Anthracene	34526	5 ppb
6B	Benzo(a)Pyrene	34247	5 ppb
7B	3,4-Benzofluoranthene	79531	5 ppb
8B	Benzo(ghi)Perylene	34521	12 ppb
9B	Benzo(k)Fluoranthene	34242	5 ppb
10B	bis(2-Chloroethoxy)Methane	34278	5 ppb
11B	bis(2-Chloroethyl)Ether	34273	5 ppb
12B	bis(2-Chloroisopropyl)Ether	34283	5 ppb
13B	bis(2-Ethylhexyl)Phthalate	39100	5 ppb
14B	4-Bromophenyl Phenyl Ether	34636	5 ppb
15B	Butyl Benzyl Phthalate	79565	5 ppb
16B	2-Chloronaphthalene	34581	5 ppb
17B	4-Chlorophenyl Phenyl Ether	34641	5 ppb
18B	Chrysene	34320	5 ppb
19B	Dibenzo(a,h)Anthracene	34556	12 ppb
20B	1,2-Dichlorobenzene	34536	5 ppb
21B	1,3-Dichlorobenzene	34566	5 ppb
22B	1,4-Dichlorobenzene	34571	5 ppb
23B	3,3-Dichlorobenzidine	34631	5 ppb
24B	Diethyl Phthalate	34336	5 ppb
25B	Dimethyl Phthalate	34341	5 ppb
26B	Di-N-Butyl Phthalate	39110	5 ppb
27B	2,4-Dinitrotoluene	34611	5 ppb
28B	2,6-Dinitrotoluene	34626	5 ppb
29B	Di-N-Octyl Phthalate	34596	5 ppb
30B	1,2-Diphenylhydrazine (as Azobenzene)	34346	5 ppb
31B	Fluoranthene	34376	5 ppb
32B	Fluorene	34381	5 ppb
33B	Hexachlorobenzene	39700	5 ppb
34B	Hexachlorobutadiene	34391	5 ppb
35B	Hexachlorocyclopentadiene	34386	5 ppb
36B	Hexachloroethane	34396	5 ppb
37B	Indeno(1,2,3-cd)Pyrene	34403	12 ppb
38B	Isophorone	34408	5 ppb
39B	Naphthalene	34696	5 ppb
40B	Nitrobenzene	34447	5 ppb
41B	N-Nitrosodimethylamine	34438	5 ppb
42B	N-Nitrosodi-N-Propylamine	34428	5 ppb
43B	N-Nitrosodiphenylamine	34433	5 ppb
44B	Phenathrene	34461	5 ppb
45B	Pyrene	34469	5 ppb
46B	1,2,4-Trichlorobenzene	34551	5 ppb

Analytical Method: Extraction --> GC/MS

US EPA Method: 625

TABLE 7 (continued)

Polynuclear Aromatic Hydrocarbon (PAH's)

	<u>STORET No.</u>	<u>Detection Limit</u>
Acenaphthene ug/l	34205	x.
Acenaphthylene ug/l	34200	x.
Anthracene ug/l	34220	x.
Benzo (a) anthracene ug/l	34526	x.
Benzo (a) pyrene ug/l	34247	x.
Benzo (b) fluoranthene ug/l	34230	x.
Benzo (ghi) perylene ug/l	34521	x.
Benzo (k) fluoranthene ug/l	34242	x.
Chrysene ug/l	34320	x.
Dibenzo (a,h) anthracene ug/l	34556	x.
Fluoroanthene ug/l	34376	x.
Fluorene ug/l	34381	x.
Indeno (1,2,3-cd) pyrene ug/l	34403	x.
Naphthalene ug/l	34696	x.
Phenanthrene ug/l	34461	x.
Pyrene ug/l	34469	x.

Analytical Method: HPLC/GC

US EPA Method: 610



CHAPTER IV

MAINTENANCE AND SERVICE OF ELECTRONIC QUALITY MONITORS*

Introduction

A disciplined and rigorous maintenance program is the key to obtaining valid and useful data from the operation of automatic field instrumentation. For the electronic monitor, this program must be carried out with diligence to assure that:

1. an adequate flow of sample water is obtained through the flow system at all times (about 7 gallons per minute);
2. sensors are free of dirt and contaminants which may decrease their sensitivity or accuracy;
3. the electronic circuitry is functioning properly and with good stability;
4. the calibrations of the parametric systems and the recording equipment are maintained; and
5. functional failures of electromechanical and mechanical phases of the system are averted by preventive maintenance procedures.

Maintenance Schedules

Monitor station service calls for cleaning and operation checking will be required at a frequency determined by local stream conditions and influenced by seasonal variations in flow. Experience is essential to decide the exact need for attention at each monitor location in each season. However, optimum performance may require a 7- to 10-day schedule.

*Procedures outlined for maintenance and service of the electronic monitors are based on instructions furnished by Schneider Instrument Company, 8115 Camargo Road, Cincinnati, Ohio 45243.

Service Log

Field personnel will maintain a service log for each monitor. This record consists of an assembly of individual service call reports (Figure 2) containing pertinent comments relating to stream conditions and instrumentation problems. The log should also include records of repair work and basic calibration that may be done away from the monitor site.

The complete log is useful (a) in evaluation of unusual or questionable data, (b) for more accurate determination of cleaning requirements on a seasonal and location basis, (c) for anticipation of the need for sensor replacement, (d) as a troubleshooting tool, and (e) as a record of what has been done and what may have been neglected. The log is a means for better system performance and an aid in evaluating system data output.

Procedure for Routine Service

The procedure is subdivided into four categories for reference; however, there is no exact dividing line between areas of activity. The individual steps are arranged to permit the most orderly progression through the work and to minimize time required.

Initial Observation:

1. Before disturbing the monitor in any manner, read and record the panel meter indication for each parameter. Be certain to interpret the meter scale divisions properly.
2. Read and record the telemeter line current.
3. Open the telemeter cubicle and switch the test signal to the 0100 level. Do not leave the door open. (The telemeter output signal will automatically revert to the 1000 level upon the next recording of data by the microprocessor.)
4. Observe the flows through the effluent line. Make a record of any abnormal flow conditions.
5. Open the flow cell drawer; try to avoid causing any change in flow. Observe the flow through each cell and make a record of any abnormal flow conditions in particular flow cells.

Serv. by _____

MONITOR SERVICE CALL REPORT

Station # _____ Location _____ Date _____ Time _____ to _____

TEMPERATURE

Reading: Initial _____ After cleaning _____ After service _____

Calibration check: 0 adjust _____ FS Adjust _____

Water temperature measured with standard thermometer _____

Calibration (circle adjustments): R1 R2 R3a R3b R4 R5 R6 R7

CONDUCTIVITY

Reading: Initial _____ After cleaning _____ After service _____

Calibration check: 1/6 adjust _____ FS Adjust _____

Conductivity SS check 200 read _____ 1200 read _____

Calibration (circle adjustments): R1 R2 R3a R3b R4 R5 R6 R7

DISSOLVED OXYGEN

Reading: Initial _____ After cleaning _____ After service _____

Calibration check: 1/6 read _____ FS adjust _____

DO determined by Winkler titration _____

Calibration (circle adjustments): R1 R2 R3a R3b R4 R5 R6 R7

pH

Reading: Initial _____ After cleaning _____ After service _____

Calibration check: 7 adjust _____ FS adjust _____

7 buffer _____ 4 buffer _____

Calibration (circle adjustments): R1 R2 R3a R3b R4 R5 R6 R7

Time: _____

Telemeter check:

Test	ORP	Temp	Cond	pH	SRI	DO	DCL	DCL
------	-----	------	------	----	-----	----	-----	-----

Reading at monitor

Reading at
Central Station

Figure 2: Robot Monitor Service Form

Cleaning:

1. Remove the temperature/dissolved oxygen sensor assembly; the temperature sensor shares a flow cell with the dissolved oxygen sensor assembly. Observe the condition of the membrane and of the DO electrode. If unusual slime build-up or algae growth exists, note the condition on the service call report. The sensor systems are expected to get dirty and it will take some field experience to recognize the difference between normal and unusual conditions.
2. Gently wipe the DO electrode membrane with wet soft tissue; do not clean with any abrasive material or use any tool which may injure the membrane. Wipe and rinse the membrane repeatedly as required until it is entirely clean. A squirt bottle of distilled water (or tap water) may be useful.
3. Use wet tissue to clean thoroughly the entire body of the DO electrode, the temperature compensator, the temperature sensor, and the underside of the neoprene stopper. Clean the top of the sensor assembly with moist tissue and dry carefully with clean dry tissue.
4. Clean the temperature/dissolved oxygen flow cell using the plastic handled sponge mop provided for this use. Use the tubing brush provided to clean the outlet line from the flow cell.
5. Return the temperature/dissolved oxygen sensor assembly to its flow cell.
6. Remove the conductivity sensor assembly. Observe the condition of the vertical and horizontal bores in the conductivity cell. If unusual slime build-up or algae growth exists, note this condition on the service call report.
7. Clean the vertical and horizontal bores of the conductivity cell using wet 8mm tubing cleaner. For the low-range cell (K=1, black body), use a double strand, running the folded end into the cell. This cell has a platinum black surface which can be damaged by the sharp end of the wire of the tubing cleaner. Moving it slowly and gently, pass it into or through each bore several times. A squirt bottle of distilled water (or tap water) will be useful. Vigorous manipulation of the cleaner is not required and

may cause damage to the cell. Under no circumstances in the field should the conductivity cell be cleaned chemically, under power, or with any mechanical abrasive device.

8. Use wet tissue to clean thoroughly the entire body of the conductivity cell, the temperature compensator, and the underside of the neoprene stopper. Clean the top of the sensor assembly with moist tissue and dry with dry tissue.
9. Clean the conductivity flow cell and flow cell outlet line.
10. Return the conductivity sensor assembly to its flow cell.
11. Remove the pH sensor assembly. Observe the condition of the sensitive tip of the glass electrode and the orifice end of the reference electrode. If unusual slime build-up or algae growth exists, note conditions on the service call report.
12. Gently wipe the tips of the glass electrode and the reference electrode with wet soft tissue. Use extreme care when handling the glass electrode and avoid a twisting action during wiping; the glass ball tip can be twisted off very easily. A squirt bottle of distilled water (or tap water) may be useful.
13. Use wet tissue to clean thoroughly the entire bodies of the glass and the reference electrodes, the temperature compensator, the ground rod, and the underside of the neoprene stopper. Clean the top of the sensor assembly with moist tissue and dry carefully with clean dry tissue.
14. Check the electrolyte level in the reference electrode. If it is within 3/4 inch above the bottom of the reservoir, then refill to within 1/2 inch of the filler hole with Beckman #4787 reference electrode filler solution.
CAUTION: Use no other solution in the reference electrode.
15. Clean the pH flow cell and flow cell outlet line.
16. Return the pH sensor assembly to its flow cell.

17. Wait at least five minutes after the replacement of the last sensor assembly for transients to subside, then read and record the panel meter indication for each parameter. These readings are "after cleaning" and will provide some indication of the effect of sensor cleaning. However, it must be considered quite possible that some parameter values may have changed during the time between the initial reading and the completion of the sensor cleaning.
18. Turn the flow control valve in the flow cell drawer to the off position. Place the plastic basin on the flow at one side of the drawer to catch wastewater. Remove the cleanout plugs from the flow cells on that side one at a time and run the tubing brush through each line and into the inlet reservoir. The flow control valve can be opened briefly after each line is cleaned to flush it out. Replace the plug after each line is cleaned, tightening it only enough to prevent leaks. This can be done by hand. Repeat for the flow cells on the other side.
19. Open the flow control valve and adjust the flow to the proper rate.
20. After five minutes, review the parameter readings, comparing them to the "after cleaning" readings already recorded. Give special attention to the DO reading, since an increase may be an indication of inadequate flow before adjustment. If there is a change, record it on the service call report. The monitor sample flow must not drop to a borderline level between weekly cleanings. If such a situation should arise, the reason for flow decrease must be corrected.

Operation Checking:

1. For each analyzer the following steps should be performed:
 - a. Open the control access door on the front panel of the analyzer.
 - b. Press the push-button switch (left side of the sub-panel).
 - c. Put the toggle switch (right side of the sub-panel) in the **DOWN** position.

- d. Read the panel meter; it should indicate the reading of the low-scale calibration reference. Record this reading on the service call report. NOTE: The low-scale calibration reference point and the high-scale calibration reference point are marked on the front sub-panel of each analyzer as the labels for the front panel controls, R1 and R2, e.g., "Zero Adj" and "FS Adj".
- e. Put the toggle switch in the **UP** position with the push button switch pressed.
- f. The panel meter should indicate the reading of the high-scale calibration reference. Record this reading.
- g. If both references are checked perfectly, the operation and stability of the analyzer are verified.
- h. If either or both of the reference checks are off by less than 1/2 percent of full scale (1/64 inch on the meter scale), no adjustment is required, but it may be performed if it is desired to trim up the calibration. This is accomplished by adjusting the front panel calibration controls, R1 and R2, to cause the analyzer to read the references exactly, as follows in (i), (j), and (k).
- i. With the push button pressed and the toggle switch **DOWN** to read low-scale reference, adjust R1 until the panel meter indicates the low-scale reference exactly. Always adjust R1 first since it will affect both the low-scale and the high-scale readings equally. R2 will usually have a very small effect on the low-scale reading.
- j. With the push button pressed and the toggle switch **UP** to read the high-scale reference, adjust R2 until the panel meter indicates the high-scale reference exactly.
- k. Repeat (i) and (j) as required until both references can be read exactly without further adjustment of either control.

1. If the error noted in (h) is greater than 1/2 percent but less than 3 percent, follow the same adjustment procedure, but make a special note on the call report to watch the check of the analyzer on the next service call to see if a further shift of calibration occurs in the same direction.
 - m. If the error noted in (h) is greater than 3 percent of full scale, a troubleshooting check of the analyzer is needed.
2. Perform steps (a)-(m) to check the Temperature Analyzer.

The low-scale calibration reference is zero and the high-scale calibration reference is full scale.
3. Perform steps (a)-(m) to check the Conductivity Analyzer.

The low-scale calibration reference is 1/6 of full scale and the high-scale calibration reference is full scale.
4. Perform steps (a)-(m) to check the Dissolved Oxygen Analyzer.
 - a. The low-scale calibration reference is 1/6 of full scale and the high-scale calibration reference is full scale.
 - b. There is no R1 control on the dissolved oxygen analyzer.
5. Check the pH Analyzer as follows:
 - a. Open the lower analyzer cubicle drawer.
 - b. Remove the pH analyzer input coaxial cable from the connector on the rear left of the pH analyzer chassis deck. Replace it with the coaxial jumper and plug the pin on the jumper into the white test jack. This removes the pH glass electrode from the analyzer input and grounds the electrometer input without running the high-impedance circuit through the front panel switches.
 - c. Perform steps (a)-(m).

- d. The low-scale calibration reference is 7 and the high-scale calibration reference is full scale.
 - e. After check, or check and adjustment, remove the coaxial jumper and replace the input coaxial cable on the connector.
 - f. Close and fasten the lower analyzer cubicle drawer.
6. Perform steps (a)-(m) to check the Solar Radiation Intensity Analyzer.
- a. The low-scale calibration reference is zero and the high-scale calibration reference is full scale.
 - b. There is no R1 control on the solar radiation intensity analyzer.
7. Check the functioning of the telemeter transmitter by observing the transmission of a complete "line of data" in response to a call from the central station at Commission headquarters. This call may be a regularly scheduled station call, or may be a manually initiated call requested by telephone.

Make a record on the service call report of the reading of each parameter as that parameter is being transmitted. Include the time of transmission, so that later this line of data can be compared to the line logged at the central station to confirm satisfactory transmission.

Verification of the Dissolved Oxygen Reading

The importance of dissolved oxygen as a water quality parameter and the vulnerable nature of the dissolved oxygen electrode make it advisable to give this parametric system special attention during every service call. Care and patience are required to provide a validly calibrated and clean parametric system, but the extra care will be reflected in the data obtained.

1. After completion of the operation check for the dissolved oxygen analyzer and at least five minutes after the return of the dissolved oxygen sensor assembly to its flow cell, draw two water samples from that flow cell for Winkler titration.

2. Read and record the dissolved oxygen panel meter indication during the time that the BOD bottles are being filled. If there are slight fluctuations, try to record an average value. If any significant excursion in the reading (over 0.25 mg/l) occurs during this time, discard the samples and start over.
3. Prepare the samples and follow the Winkler titration procedure.
4. The average of the two titrations will be used as the titrated dissolved value for comparison with the analyzer reading recorded in step 2 above.
5. If this comparison is within one percent of full scale (approximately 0.25 mg/l), the system should be considered properly calibrated and no adjustments should be made.
6. If the titrated dissolved oxygen value is higher or lower than the analyzer reading by more than 0.25 mg/l, but not more than 1.0 mg/l, merely adjust R2, the full scale adjust control on the front sub-panel of the analyzer, by an amount which will cause the analyzer reading to agree with the titrated value. Note that this adjustment should not make the current reading agree with the titrated value; the dissolved oxygen level in the water may have changed in the time elapsed during the titration. The amount of the adjustment should be determined by noting the difference in values and adjusting the present analyzer reading by that percentage.

For example:

DO indication when sample was drawn = 7.0 mg/l
DO concentration determined by titration = 7.7 mg/l
Current DO indication = 8.0 mg/l
Required adjustment of indication = 10% of 8.0
= +0.8 mg/l

7. If the difference between the titrated value and the analyzer reading is greater than 1.0 mg/l, additional factors should be considered before making the decision either to adjust the analyzer or to replace the electrode. These factors are length of service, record of recent performance, and physical condition. Refer to the service log to determine the date of

installation of the electrode and note the comparison between the titrated value of dissolved oxygen and the analyzer reading for the last two service calls. If the period of use is less than ten weeks, but the recent service record indicates that the current discrepancy in reading is part of a developing trend (difference in the same direction and growing larger each week), the electrode should be replaced. There are other factors, some of which will be noticeable in a visual inspection, which will be cause for replacement of the electrode regardless of the past record.

8. If the electrode is not replaced, adjust R2 in the manner described in step 6.
9. If the electrode is replaced, it will be necessary to allow at least one hour of operation of the replacement electrode before attempting adjustment of the dissolved oxygen parametric system. Then steps 1 - 4 above should be repeated. After the titration is completed, R2 should be adjusted to cause the analyzer reading to agree with the titrated dissolved oxygen value as outlined in step 6.
10. After an adjustment of R2 (whether or not the electrode has been replaced), it will be necessary to reset the calibration references by adjusting R4 and R5. Press the push button switch, put the toggle switch in an UP position, and adjust R5 to cause the analyzer meter to read full scale.

Check Out

Close all drawers and doors and fasten them securely. All fasteners should be tightened; their purpose is to provide a compression of the gasket to seal the cubicles containing electronic equipment from dirt and moisture. Time saved by leaving the fasteners loose will be negligible, compared to the time needed to correct the extra service problems which this practice may cause.

Procedure for Monthly Calibration Checking and Preventive Maintenance

This procedure calls for all the work performed in the routine cleaning and operation checking plus additional cleaning of all parametric systems and cleaning and lubrication of some of the system hardware.

Preliminary Steps

1. Perform steps 1-6 of "Initial Observation".
2. Open the upper drawer of the analyzer cubicle and estimate the inside temperature; it should be about 105°F. Heaters located on subpanels at the two sides of the cubicle are thermostatically controlled to maintain this temperature. If it is noticeably higher or lower, check the setting of the adjustable thermostat near the top on the right side.
3. A service light in the cubicle is switched by limit switches operated by the analyzer drawers. It should go on whenever an analyzer drawer is opened. Replace the bulb if it does not. CAUTION: Do not use a bulb of higher power rating than 40 watts; it may create a hot-spot problem for the nearest amplifier.
4. Inspect all analyzers to see that all plug-in components are seated properly in their sockets.
5. Check the analyzer cubicle front panels to see that each analyzer is securely fastened in its plug-in position to assure good contact at the blue-ribbon connector.
6. Perform steps 1-20 of "Cleaning".
7. Remove the end plug from the inlet reservoir, using the adapter plate provided for this purpose. This is a steel plate, approximately 2 x 3 x 1/8 inches, which fits in the slot on the plug to permit removal of the plug with a small adjustable wrench. Use the plastic basin to catch any water that comes out of the reservoirs.
8. Clean the reservoir with the sponge mop. Open the flow valve briefly to flush the dirt into the basin. Replace the end plug.
9. Repeat steps 7 and 8 for the outlet header.
10. Inspect the effluent line and, if necessary, clean it with the pipe auger, using a piece of cloth wrapped around the tip of the auger.
11. Shut off the water flow at the service valve. Disconnect the inlet line from the monitor and

run the pipe auger through the line. Open the service valve briefly to flush the line. Reconnect the line to the monitor and open the service valve. Experience may indicate that this cleaning operation need not be performed monthly; however, it should at least be checked each time continually.

12. Open the flow control valve and adjust the flow to the proper rate.
13. After five minutes, review the parameter readings, comparing them with the "after cleaning" readings previously recorded. Give special attention to the DO reading, since an increase may be an indication of inadequate initial flow. If there is a change, record it on the service call report as the DO reading "after flow adjustment". However, consider that some change in parameters of the water sample may have occurred in the stream during the time required for the cleaning.
14. If the initial observation of the flow conditions or the change in DO reading after flow adjustment give cause to suspect a decrease in the incoming water supply since the last station visit, it may be advisable to check the supply line. In some cases, debris will accumulate in the line behind the service valve. Use of a mud-leg will alleviate, but not completely eliminate, this condition. Occasionally, it may be necessary to back flush the line or to remove the service valve for cleaning. A low flow situation must always be corrected promptly, since it will create other problems if ignored.
15. Inspect the tops of the sensor assemblies and the flow cell terminal board to see that all leads are securely fastened.
16. If the flow cell terminal board is not entirely clean, it should be brushed carefully with a stiff-bristled brush (such as a toothbrush) to remove all dirt or salt. Wipe, as required, with a clean dry cloth. Wipe the steatite standoff insulators with clean dry tissue.
17. Perform steps 1-7 of "Operating Checking".

At this stage the parametric systems should be in good operational condition and ready for a calibration check.

Calibration Checking

This procedure is for a simple calibration check of the complete parametric systems (sensors and analyzers) while they are in operation in the field. The primary purpose is to check the sensors, since the stability of the analyzers has already been certified by the operation check against the built-in references. The procedure is not as comprehensive as the initial or basic calibration, but is adequate to assure that system accuracy has been maintained.

The itemized procedure provides a guideline to accomplishing the work in the minimum time by checking all parametric systems simultaneously. It is presented for monitors having analyzers for temperature, conductivity, dissolved oxygen, pH, and solar radiation intensity.

1. All cleaning and operation checking has been completed in the steps outlined in "Preliminary Steps".
2. The temperature parametric system will be checked at one point only, the present stream temperature.
3. Place the standard thermometer in the temperature/dissolved oxygen flow cell. CAUTION: Remember to remove the thermometer to avoid breaking it, if the flow cell drawer is to be closed at any time.
4. The conductivity parametric system will be checked at a low-scale point approximately 1/6 of full scale, at mid-scale, and at full scale. This initial check, including a mid-scale point, will prevent the possibility of calibrating with badly contaminated standards or an unclean conductivity cell. If the initial check is satisfactory, calibration adjustments will be made using the low standard and the full-scale standard only.

For this procedure, it will be assumed that a 2400 micromho range is being checked, and that standard solutions of 2400, 1200, and 400 micromhos are available. NOTE: In the calibration of the conductivity parametric system, two portions of the same standard are employed. One is labeled a wash solution; the other, the primary standard. When a clean sensor is immersed into a wash, then into the

primary standard of the same value, the droplets of solution remaining inside the sensor are of approximately the same conductivity as the primary standard and, therefore, will not contaminate it. Wash solutions should be discarded and replaced when they deviate by more than 10 percent from the standard solutions.

5. Remove the conductivity sensor assembly from its flow cell, shake it briskly to remove water from the vertical and horizontal bores and dry it with tissue. Immerse the cell in the 400 micromho wash solution and swirl it to flush out the cell bores. Remove the assembly, shake it, dry it carefully, and insert it in the jar of 400 micromho standard solution. Put this test setup aside for at least five minutes to allow transients to subside, and proceed with the next step. NOTE: A low stool, bench, or table that can be placed beside the flow cell drawer will be convenient for placement of standard solution jars during their test use.
6. The pH parametric system will be checked at a pH of 7 and a pH of 4 only. Calibration adjustments will be made using only these two buffers. The Fischer pH 7 buffer solution varies in pH from 7.0 at 100°F and 77°F to 7.1 at 35°F. The Fischer pH 4 buffer can be considered to have a pH of 4.0 over the full temperature range.

Alternatively, a high pH buffer (9 or 10) may be used for an additional check after calibration adjustment; however, these high pH buffers are of questionable value for field service. Each has a high temperature coefficient and the variation of pH with temperature is not linear. The pH 10 buffer is much less stable than the 7 and 4 buffers. NOTE: Wash solutions are not required with the pH buffer solutions since the pH electrode assembly can be completely dried before being put into the buffer.

7. Remove the pH sensor assembly from its flow cell, dry it carefully and insert it in the jar of pH 7 buffer solution. Put this test setup aside for at least five minutes and proceed with the next step.
8. Draw two water samples from the dissolved oxygen flow cell for Winkler titration. Read and record the dissolved oxygen panel meter

indication during the time that the BOD bottles are being filled. If there are slight fluctuations, try to read an average value. If any significant excursion in the reading (over 0.25 mg/l) occurs during this time, discard the samples and start over. Add reagents and prepare the samples as instructed in Winkler procedure.

9. In the following steps all transfers of sensor assemblies from one solution to another must follow the procedures outlined in the preceding steps.
10. Read and record on the service call report the conductivity analyzer panel meter indication for the 400 micromho standard solution.
11. Transfer the conductivity sensor assembly through the 1200 micromho wash solution to the 1200 micromho standard solution. Put this test setup aside for at least five minutes.
12. Read and record on the service call report the pH analyzer panel meter indication for the pH 7 buffer solution. It is usually helpful to stir the buffer solution slightly with the electrode assembly about 30 seconds before taking the reading.
13. Remove the pH electrode assembly from the pH 7 buffer solution, dry it carefully with clean dry tissue and insert it in the jar of pH 4 buffer solution. Put this test setup aside for at least five minutes.
14. Add acid to the two Winkler samples.
15. Read and record the conductivity analyzer reading for the 1200 micromho standard solution.
16. Transfer the conductivity sensor assembly through the 2400 micromho wash solution to the 2400 micromho standard solution. Put this test setup aside for at least five minutes.
17. Titrate the two Winkler samples following procedure. If the results of the two titrations are within 0.25 mg/l of agreement, use the average of the two as the titrated dissolved oxygen concentration. If the results of the two titrations do not agree, it will be necessary to start over by drawing two new

samples. Record the results of the titrations on the service call report.

18. Read and record the pH analyzer reading for the pH 4 buffer solution.
19. Read and record the temperature indications of the standard thermometer and temperature analyzer.
20. Read and record the conductivity analyzer reading for the 2400 micromho standard solution.

At this stage, a set of data will have been acquired covering the existing calibration of all of the parametric systems measuring water parameters. The calibration information will be useful in evaluating the stream data obtained by the monitor since the last calibration check.

The calibration information can be summarized as follows:

<u>Parameter</u>	<u>Standard</u>	<u>Monitor</u>
Temperature	Standard thermometer reading of sample water	Analyzer reading of sample water
Conductivity	400 micromho standard solution	Analyzer reading
	1200 micromho standard solution	Analyzer reading
	2400 micromho standard solution	Analyzer reading
pH	pH 4 buffer solution	Analyzer reading
	pH 7 buffer solution	Analyzer reading

This comparison will determine if any parametric systems require calibration adjustment. A few general guidelines can be provided:

- a. Do not adjust calibration of a parametric system for which the analyzer readings are within 1/2 percent of agreement with the standards.
- b. If there is a difference of between 1/2 and 3 percent, adjust the calibration, note the adjustment on the service call report and watch future calibration checks of the parametric system to see if a trend develops. Slow deterioration of a sensor may be detected in this manner.

- c. If a difference of 3 to 10 percent exists, look for the reason before changing calibration as a last resort.
- d. If a difference of more than 10 percent exists, the cause must be determined and the fault corrected.

For conditions (c) or (d), the best aids for locating the trouble are: (a) the analyzer built-in reference check facility, (b) the service log, and (c) spare electrodes.

By referring to the service log, it can be determined whether any abnormal adjustments of the analyzer calibration controls, R1 and R2, have been made during the weekly operation checks since the last monthly calibration check. If not, and if the analyzer now checks the built-in calibration references (which were set immediately after the last calibration adjustment last month), then the analyzer must be in good order and is not a factor.

This means the "shift in calibration" is sensor oriented; that is, it is probably due to a change in the electrode, a defect in the temperature compensator, a poor connection in the sensor assembly wiring, or contaminated standard solutions or reagents. IMPORTANT: There is always the possibility that the previous calibration adjustment (last month) was incorrect because of poor standard solutions. A review of the service log will indicate whether any large changes were made in the other direction at that time.

The substitution of a spare electrode, known to be in working order, should always be one of the first measures used to isolate the trouble further. In most cases it will provide the solution.

Assuming that one or more parametric systems will require a calibration change, the adjustment procedures in steps 21-28 below should be followed. The precautions relating to drying of sensors, using wash solutions, allowing five minutes response time, etc., will always apply but will not be repeated in the instructions for the individual steps.

21. To adjust the calibration of the temperature parametric system:
 - a. Read the current indication of the standard thermometer in the temperature/dissolved oxygen flow cell, and simultaneously read the temperature analyzer panel meter.
 - b. If the water temperature is below 60°F, use R1 to adjust the analyzer reading to agree with the standard thermometer reading. If the water temperature is above 60°F, use R2 for the adjustment.
22. To adjust the calibration of the dissolved oxygen parametric system use the data already recorded as the basis for an adjustment of R2 as described in step 6 of "Verification of the Dissolved Oxygen Reading".
23. To adjust the calibration of the conductivity or turbidity parametric systems:
 - a. Transfer the sensor assembly to the low-scale standard solution.
 - b. Adjust R1 until the analyzer panel meter is correctly reading the low-scale standard solution.
 - c. Transfer the sensor assembly to the full-scale standard solution.
 - d. Adjust R2 until the analyzer panel meter is correctly reading the full-scale standard and the calibration adjustment is completed. If not, then repeat steps (b), (d) and (a) in sequence, until both standard solutions can be measured correctly without further adjustment.
24. To adjust the calibration of the pH parametric system:
 - a. Transfer the pH sensor assembly to the pH 7 buffer solution.
 - b. Adjust R1 until the pH analyzer meter reads 7.0.
 - c. Transfer the pH sensor assembly to the pH 4 buffer solution.

- d. Adjust R2 until the pH analyzer panel meter reads 4.0.
 - e. Return the sensor assembly to the pH 7 buffer solution. If the pH analyzer panel meter reading is 7.0, the calibration adjustment is completed. If not, then repeat steps (b), (c), (d) and (a) in sequence until both buffer solutions can be measured correctly without further adjustment.
25. After calibration adjustment, if the settings of R1 and/or R2 have been changed for any analyzer, the references R4 and R5 for that analyzer must be reset to correspond to the new calibration. NOTE: There are no R1 or R4 controls on the pH analyzer.

Perform the following procedure for the temperature, conductivity, dissolved oxygen, and turbidity analyzers:

- a. Press the push-button switch, put the toggle switch in the **DOWN** position and adjust R4 (top rear left on the chassis deck) to cause the analyzer panel meter to read the low-scale reference marked on the front sub-panel (above control R1).
 - b. Press the push-button switch, put the toggle switch in the **UP** position, and adjust R5 (top rear left on the chassis deck) to cause the analyzer panel meter to read full scale.
26. For the pH analyzer, follow the same procedure after removing the input coaxial from the connector at top rear on the analyzer chassis deck and replacing it with the coaxial jumper to ground (coaxial connector to white pin jack). Do not remove the jumper at this time.
27. Check each analyzer telemeter output by measuring between the orange jack and the white jack at the front on the analyzer chassis deck. Use a digital voltmeter or MV potentiometer. With the push-button switch pressed and the toggle switch **UP** (panel meter reading an accurate full scale), the voltage should be 1000 MV; if it is not, adjust by turning R38 (top front center on the chassis deck).

Preventive Maintenance

Wipe the flow-cell-drawer slides with a clean dry cloth to remove dirt and dirty lubricant. Lubricate with light oil applied in moderation to all segments of the slide assembly.

There are obvious benefits to keeping the insides of the cubicles clean and dry. Dust left in the cubicle will circulate and moisture can be harmful. The advantages of keeping the outside of the cabinet clean are largely aesthetic; but it is recommended that it be given enough attention to present an orderly appearance. A sloppy exterior appearance of instrumentation is often closely related to carelessness in other phases of its operation and maintenance.

There may be other service needs which will be noticed during work with the electronic monitor. An effort should be made to take care of these as they arise.

Checkout

1. Perform checkout procedure. This procedure is subject to streamlining and some rearrangement may be made based on experience; however, any short cuts devised must still accomplish the end results intended for the above routines, all of which are considered essential to assuring good performance.



CHAPTER V

QUALITY ASSURANCE PROGRAM FOR THE ORGANICS DETECTION SYSTEM

The monitoring of the Ohio River and its tributaries for priority pollutants at the microgram per liter level also requires a stringent quality assurance program. This program has been developed from the Federal Register, Vol. 44, No. 233, Method 601, and from experience in operating the system. Additions based on operational experience with the Organics Detection System (ODS) have been incorporated into the US EPA method to improve the quality of data produced. The resulting quality assurance program includes glassware cleaning and handling, sample collection, sample analysis, and contract laboratory procedures for purgeable, base-neutral extractable and Polynuclear Aromatic Hydrocarbon samples.

Glassware Cleaning and Handling

At the sampling sites, three different sizes of sample containers are used for organics sampling. Initially, the contract laboratory supplies all the bottles in the sterile usable condition required by the water laboratory.

The three sizes of bottles are 2-ounce, 1-liter and 1-gallon. All bottles are equipped with Teflon-lined plastic screw caps.

A shipping container is supplied to each ODS station. This heavy duty insulated plastic container with a tight fitting lid is used to ship samples to the contract laboratory. Artificial "blue" ice packs are placed in the container with sample bottles and polyurethane shock insulation.

The sample containers must be carefully cleaned following prescribed protocol, as follows:

1. Wash all sample bottles and caps in detergent and rinse thoroughly with finished tap water.
2. Rinse again with organic-free blank water and allow to air dry in an area free of organic

vapors. The 2-ounce bottles may be dried in a 150°C oven for one hour, then allowed to cool in air free of organic vapors.

3. When cool, seal the bottles with the Teflon-lined caps. The 1-gallon and 1-liter containers will crack if placed in the oven; merely drain, air dry and seal them.

Each site is supplied with a minimum of one 5-10 ul syringe, one 25-50 ul syringe and one 5-10 ml syringe. These must be kept scrupulously clean to avoid contamination of the standards and samples. Before using the standard ul syringes, flush them several times with acetone or methyl alcohol. The remaining traces of solvent may be removed by pulling clean air through the syringe using a vacuum flask and a small-holed rubber stopper. The syringe may also be dried in an oven at 70°C. Higher temperatures will crack the syringe because of the glass-metal expansion coefficient difference. The sample syringe should also be cleaned before and between sample analyses. Rinse the syringe twice with organic-free water, then with methanol. Heat in a 70°C oven for several minutes to drive off the methanol. Again, do not use higher temperatures or the syringe will crack.

To reduce the likelihood of cross-contamination between subsequently analyzed samples, the purging vessel should also be rinsed twice with organic-free water. In the event of samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high halocarbons levels, it may be necessary to wash the purge vessel with detergent, rinse it with distilled water and dry it in a 105°C oven between analyses. If solids accumulate on the frit of the vessel and cannot be removed by the above methods, the vessel may be soaked in a dilute chromic acid solution.

Sample Collection

The daily sample is drawn from the raw water intake tap. Turn on the water and allow the system to flush. When the temperature of the water has stabilized, adjust the flow to minimize bubbling and collect duplicate samples in the 2-ounce bottles. Immediately place the samples on a solid level surface and seal the bottle by tightening the cap. Invert the bottle to check for entrapped air. If there is no air or only a small bubble, the seal is successful. If a bubble larger than an upper case "O" is present, add a few additional drops of sample and reseal. At the same time the 2-ounce samples are collected, fill the 1-gallon container with raw water and seal the bottle with the Teflon-lined cap.

It is not necessary that this container be headspace free. If analysis of the sample does not occur immediately after collection, store all samples together. Stored samples should be refrigerated at 10°C or lower. Identify the sample by labeling with site code, date, time and sampler's name.

If it is necessary to send samples to the contract laboratory, duplicate organic-free water blanks are collected in 2-ounce bottles and also in a 1-liter bottle by the same procedure as stated above. Samples and blanks are packed in the shipping container and sent via the fastest method available to the contract laboratory.

Usually, it is not necessary to ship any of the samples to the contract laboratory. In this case, the operator should empty the sample containers and clean them according to the procedure described under "Glassware Cleaning and Handling".

Analysis of the Sample

Daily Analyses

The daily analysis procedure includes initial analysis of a 5-10 ml sample of organic-free water containing 2 ul of the internal standard solution. The chromatogram obtained is checked for extraneous peaks and internal standard retention time and area response. If the system is found to be free of interference, then the raw water sample is analyzed. The following procedure is used in running an organic-free water sample:

1. Using a 5-10 ml gas-tight syringe, obtain 5 ml of organic-free water, close the two-way valve, and detach the 6 1/2 inch needle.
2. Using a 5 or 10 ul syringe, withdraw 2 ul of the internal standard (2 Bromo - 1 Chloropropane).
3. Open the two-way valve on the 5-10 ml gas-tight syringe and inject the 2 ul of internal standard into the 5 ml of organic-free water.
4. Withdraw the needle and close the two-way valve.
5. Attach the 5-10 ml gas-tight syringe to the 3-way valve on the Tekmar LSC-3 concentrator.
6. Inject the sample into the 5 ul purge vessel*, close the valve, and remove the syringe. The blank sample is now ready for analysis.

*ODS stations are currently using a 5 ml purge vessel. If needed or preferred, 25 ml purge vessels are available.

Bi-weekly Analyses

A purgeable standard solution should be analyzed at least twice each week to ensure proper peak identification, identify problems such as column deterioration and ensure analysis reproducibility. The following procedure is used in running the purgeable standard:

1. Using a 5-10 ml gas-tight syringe, obtain 5 ml of organic-free water, close the two-way valve, and detach the 6 1/2 inch needle.
2. Using a 5 or 10 ul syringe, withdraw 2 ul of the internal standard.
3. Open the two-way valve on the 5-10 ml gas-tight syringe and inject the 2 ul of internal standard into the 5 ml of organic-free water.
4. Withdraw the needle and close the two-way valve.
5. Using a 25 ul syringe, withdraw 10 ul of 16 component purgeable standard.
6. Open the two-way valve on the 5-10 ml syringe and inject the 10 ul of purgeable standard into the organic-free water.
7. Withdraw the needle and close the two-way valve.
8. Attach the 5-10 ml gas-tight syringe to the 3-way valve on the Tekmar LSC-3 concentrator.
9. Inject the sample into the 5 ml purge vessel, close the valve, and remove the syringe. The purgeable standard sample is now ready for analysis.

To avoid cross-contamination of subsequently analyzed samples, follow proper cleaning procedures and analyze in this order:

1. Organic-free water blank plus 2 ul internal standard.
2. Raw water plus 2 ul internal standard.
3. Organic-free water plus 10 ul purge standard and 2 ul internal standard.

Raw water analyses are terminated if interferences occur which cannot be explained and eliminated. This will necessitate a service call from Commission field personnel, other Commission staff and/or chromatographic equipment service personnel.

If analysis of the raw water sample shows a significant amount of purgeable organics, another raw

water sample should be drawn and analyzed to verify the initial findings.** These chromatograms are then sent via telecopier to the Commission offices in Cincinnati, Ohio for inspection by staff. An alert may then be declared. During an alert situation, the remaining 2-ounce samples of raw water and organic-free water, the 1-liter organic-free water sample and the 1-gallon solvent-extractable sample are shipped by site personnel to the contract analytical laboratory for GC-MS confirmation. The site personnel may also be asked to analyze additional samples throughout the alert period. However, under normal circumstances, the extra samples are discarded and the bottles cleaned for the next day's sampling.

Quarterly Analyses

Each of the 13 stations in the ODS collects samples for analysis for base neutral extractable and polynuclear aromatic hydrocarbon (PAH) compounds quarterly. Each ODS station receives a 1/2-gallon bottle and an amber 1-liter bottle for base neutral sampling. The 1/2-gallon bottle is filled with raw water and the amber 1-liter bottle is filled with organic-free water for use as a shipping blank. For PAH sampling, each ODS station receives four 1-liter amber bottles. Three are filled with raw water and one is filled with organic-free water. All bottles are labeled with content, sampler's name, date and time of sampling. The samples are then sent to their respective contract laboratories by ground delivery via a commercial carrier service for analysis. The contract laboratories send the results to the Commission for evaluation.

Semi-annual analysis

Round-robin US EPA performance evaluation analyses are conducted semi-annually. The samples, which are provided by US EPA, are sealed ampules in two concentrations. All ODS sites and the contract laboratories analyze these samples to help identify problems with equipment or quality control.

Maintenance of Equipment

Commission staff visits each station at least once each month. They are responsible for assuring adequate pressure in the gas cylinders; regenerating molecular sieve and moisture filters; assuring adequate supplies of fresh standards, microprocessor recording paper,

**A significant concentration has been defined by the Commission to be more than 25 ug/l or 10 times the previous day's detection.

organic-free water, columns, and column packing material and ion-exchange resin; and general trouble-shooting. A preventive maintenance program for the ODS has been formally established. The frequency of service and a maintenance schedule has been set and forms have been developed for use with the program. (See Figures 3A-C)

Contract Laboratory Quality Control Procedures

At submicrogram and microgram per liter (ug/l) levels of analysis for organic compounds, a stringent quality assurance program is necessary to ensure the validity of the data. The program is necessary for two reasons: (a) reports of an organic compound should be the result of its presence in the water at the time it was sampled and (b) the significance of the data must be known before interpretation.

The contract laboratory must follow extensive laboratory quality control practices to ensure that interferences are at a definable and acceptably low level. These practices should include the following: (a) cleaning, preparation and handling of sample bottles and laboratory glassware; (b) preparation and storage of organic-free water for blank analyses and glassware rinses; (c) identification and control of interferences from such materials as gases and solvents; and (d) storage of samples to maintain integrity prior to analysis. When system blanks are shown to contain unacceptable interferences, analyses should be discontinued until the interference is identified and controlled.

Daily Quality Assurance for Purgeable Organics

The daily quality control routine should follow this sequence:

1. Blank water analysis.
2. Analysis of calibration standard.
3. Analysis of US EPA reference standard.
4. Analysis of current field samples.
5. Analysis of an aliquot of a previously analyzed field sample.
6. Blank water analysis.
7. Analysis of a duplicate sample from a randomly chosen field site.
8. Analysis of calibration standard.

The precision of analysis will vary with the concentration of the sample. From the data collected by the ODS using the Coulson Conductivity Detector, the following limits of precision have been established:

Figure 3A
 ODS Maintenance Scheduling Work Sheet

ODS Station	MAS NO.	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC
Elrama, PA	1001	M	M	Q	M	M	A	M	M	Q	M	M	SA
Pittsburgh, PA	1001	M	M	Q	M	M	A	M	M	Q	M	M	SA
West View, PA	2001	M	M	Q	M	M	A	M	M	Q	M	M	SA
East Liverpool, OH	2001	M	M	Q	M	M	A	M	M	Q	M	M	SA
Wheeling, WV	2001	M	M	Q	M	M	A	M	M	Q	M	M	SA
Parkersburg, WV	1001	M	M	Q	M	M	A	M	M	Q	M	M	SA
St. Albans, WV	2001	M	M	Q	M	M	A	M	M	Q	M	M	SA
Huntington, WV	2001	M	M	Q	M	M	A	M	M	Q	M	M	SA
Portsmouth, OH	2001	M	M	Q	M	M	A	M	M	Q	M	M	SA
Louisville, KY	1001	M	M	Q	M	M	A	M	M	Q	M	M	SA
Evansville, IN	1001	M	M	Q	M	M	A	M	M	Q	M	M	SA

Figure 3B
ODS Maintenance Action Sheet (MAS)

MAS NO: 1001

Page 1 of 2

No.	Maintenance Action	Freq.	Remarks
1	Gas Cylinders - He, H ₂ and Air		
	1.1 Check pressure gauge readings	M	Regulator: He-60 to 75 psi H ₂ -40 to 50 psi Air - 50 to 60 psi
	1.2 Check Gas purifier indicator	M	Blue-good; pink-bad.
	1.3 Check gas link leak if suspected	M	SNOOP leak detector
2	Tekmar LSC-3 Concentrator		
	2.1 Check indicator lamps	M	
	2.2 Check heated transfer line	M	Should feel hot.
	2.3 Check desorb temperature	M	180°C
	2.4 Check trap bake temperature	M	225°C
	2.5 Check purge flow	M	40 ml/min.
3	GC - Varian 3700		
	3.1 Check heat zones	M	Set vs. actual temperature
	3.2 Check oven door opening	M	
	3.3 Check column head pressure	M	
	3.4 Inspect oven fans	M	Notice any vibration or noise
	3.5 Check system leak if suspected	M	'Plug' method.
4	Spectra-Physic 4100 Integrator		
	4.1 Check PT & PW	M	
	4.2 Check TIME	M	
	4.3 Check file printout	M	
	4.4 Check integrator status	M	
5	Coulson Conductivity Detector (CCD)		
	5.1 Check indicator lamps	M	
	5.2 Check oven block & furnace temp	M	220°C & 820°C
	5.3 Check H ₂ floating ball movement	M	
	5.4 Check water reservoir level	M	
	5.5 Inspect detector cell	M	Remove air bubble if present

Figure 3B

ODS Maintenance Action Sheet (MAS)MAS NO: 1001Page 2 of 2

No.	Maintenance Action	Freq.	Remarks
6	Inspect purge vessel teflon ferrules	Q	1/8" & 1/4" teflon ferrules.
7	GC - Varian 3700 + SP4100		
	7.1 Adjust zero on SP4100	Q	
	7.2 Clean air filter on SP4100	Q	
	7.3 Clean printer head and guide rods	Q	
8	Replace resin and dist. water	Q	
9	Replace gas purifier refill	SA	
10	Check 8-port valve shaft assembly in GC	SA	Replace if plugged or worn.
11	GC - Varian 3700 + SP4100		
	11.1 Measure \pm 15V power supply	SA	On "Readout" & ALTP boards.
	11.2 Clean static dirt	SA	
	11.3 Inspect cooling fans	SA	
12	Replace gas drying tube refill	A	Supelco
13	Replace column packing material	A	SP-1000
14	Varian 3700 GC		
	14.1 Calibrate oven temperature	A	at 150°C.
	14.2 Calibrate flow controller	A	He flow rate - 40 cc/min.
15	Inspect water pump motor	A	

Figure 3C

ODS Maintenance Action Sheet (MAS)MAS NO. 2001Page 1 of 2

No.	Maintenance Action	Freq	Remarks
1	Gas Cylinders - He, H ₂ and Air		
	1.1 Check pressure gauge readings	M	Regulator: He-60 to 75 psi H ₂ -40 to 50 psi Air - 50 to 60 psi
	1.2 Check gas purifier indicator	M	Blue-good; pink-bad.
	1.3 Check gas link leak if suspected	M	SNOOP leak detector.
2	Tekmar LSC-3 Concentrator		
	2.1 Check indicator lamps	M	
	2.2 Check heated transfer line	M	Should feel hot.
	2.3 Check desorb temperature	M	180°C
	2.4 Check trap bake temperature	M	225°C
	2.5 Check purge flow	M	40 ml/min.
3	GC - HNU 401		
	3.1 Check heated zones	M	Set vs. actual temperature
	3.2 Check oven cool down	M	
	3.3 Inspect oven fans	M	Notice any vibration or noise
	3.4 Check system leak if suspected	M	
4	Spectra-Physics 4270 integrator		
	4.1 Check PT & PW	M	
	4.2 Check TIME	M	
	4.3 Check file printout	M	
	4.4 Check integrator status	M	
5	Coulson Conductivity Detector (CCD)		
	5.1 Check indicator lamps	M	
	5.2 Check oven block & furnace temp	M	220°C & 820°C.
	5.3 Check heated transfer line	M	180°C
	5.4 Check H ₂ floating ball movement	M	
	5.5 Check water reservoir level	M	
	5.6 Inspect detector cell	M	Remove air bubble if present.

Figure 3C

ODS Maintenance Action Sheet (MAS)MAS NO. 2001Page 2 of 2

No.	Maintenance Action	Freq	Remarks
6	Inspect purge vessel teflon ferrules	Q	1/8" & 1/4" teflon ferrules
7	GC - HNU 401		
	7.1 Check He flow through system	Q	
	7.2 Clean printer head & guide rods	Q	
	7.3 Clean air filters	Q	
8	Replace resin and dist. water	Q	
9	Replace gas purifier refill	SA	
10	HNU 401 GC		
	10.1 Measure \pm 5V power supply	SA	Within \pm 0.05V
	10.2 Clean static dirt	SA	
	10.3 Inspect cooling fans	SA	
11	Replace gas drying tube refill	A	Supelco
12	Replace column packing material	A	SP-1000
13	Inspect water pump motor	A	

<u>When Concentration is:</u>	<u>Mean Value (\bar{X}) should be:</u>
0.1 to 1.0 ug/l	\pm 50% of true value
1.0 to 10 ug/l	\pm 30% of true value
10 to 100 ug/l	\pm 20% of true value
100 ug/l and greater	\pm 10% of true value

Photoionization Detectors are used at four of the ODS stations. The limits of precision are determined to be the same as those for the Coulson Detector. Flame Ionization Detectors are used at two of the ODS stations. Precision limits for this detector have yet to be determined due to the higher detection limits.

When analyses of the US EPA standard do not fall within these limits, analyses should be terminated until the cause is identified and eliminated.

Periodic Equipment Controls

Because the integrator assumes linearity of the detector (Hall or Coulson) response when quantifying, the linear relationship between amount purged and amount detected must be checked periodically. By using concentrations of the compounds in all expected ranges, a standard curve can be plotted. Studies have shown that the above detectors can be expected to detect the compounds in a linear fashion between the concentrations of 0.1 ug/l and 200 ug/l.

Daily Quality Assurance for Base-Neutral Extractable Organics

The daily quality control routine for base-neutral extractables is based on a group analysis concept. One bottle of methylene chloride contains sufficient volume for six extractions -- four samples and two control blanks per bottle of solvent. Samples are extracted, concentrated, stored and analyzed in groups with the associated solvent blanks. Daily analysis includes the following components per group: four field samples, direct injection calibration standards, two solvent blanks, and a previously analyzed field extract. In addition, one of the monthly samples should be randomly chosen and analyzed in duplicate.

The quality control procedure should be in the following sequence:

1. Analysis of calibration standard.
2. Solvent blank analysis.

3. Field sample analysis.
4. Field sample analysis.
5. Standard sample analysis.
6. Field sample analysis.
7. Solvent blank analysis.
8. Reanalysis of sample from previous day.
9. Field sample analysis
10. Analysis of calibration standard as an unknown to determine stability of the system.

After it has been firmly established that all problems relating to quality control are eliminated and veracity of the data is assured, the laboratory may then consider elimination of steps 5, 7 and 9 in the above sequence.

Periodically, extraction recoveries of the base-neutral extractable compounds at several concentrations should be determined by spiking the calibration standard compounds into organic-free water. Extraction can then be evaluated by averaging the recoveries to triplicate extraction and concentration tests.

Daily Quality Assurance for Polynuclear Aromatic Hydrocarbons (PAH's)

The daily quality control routine for PAH's is based on analytical controls set up for group analyses. Typical controls are:

1. One instrument standard per run.
2. One laboratory control per run.
3. One reagent blank per run.
4. Some samples can be selected and coded by the Quality Assurance Unit for re-entry by the Sample Entry Department and repeated as blind controls.

Spiked controls may be specified by the method procedures and may also be added by the analyst.

ODS samples are analyzed in sets of 12 following the analytical protocol outlined in the US EPA Method #610. With each set there will be a blank, a duplicate, and a spiked sample included for quality control. Each sample is extracted with Methylene Chloride to a final volume of 0.2 ml. Each sample is spiked with deuterated polynuclear aromatics, depending upon their availability. This is done to monitor recovery for each sample. Instrumental analysis will involve capillary GC/MS similar to the procedure described in US EPA Method #625.

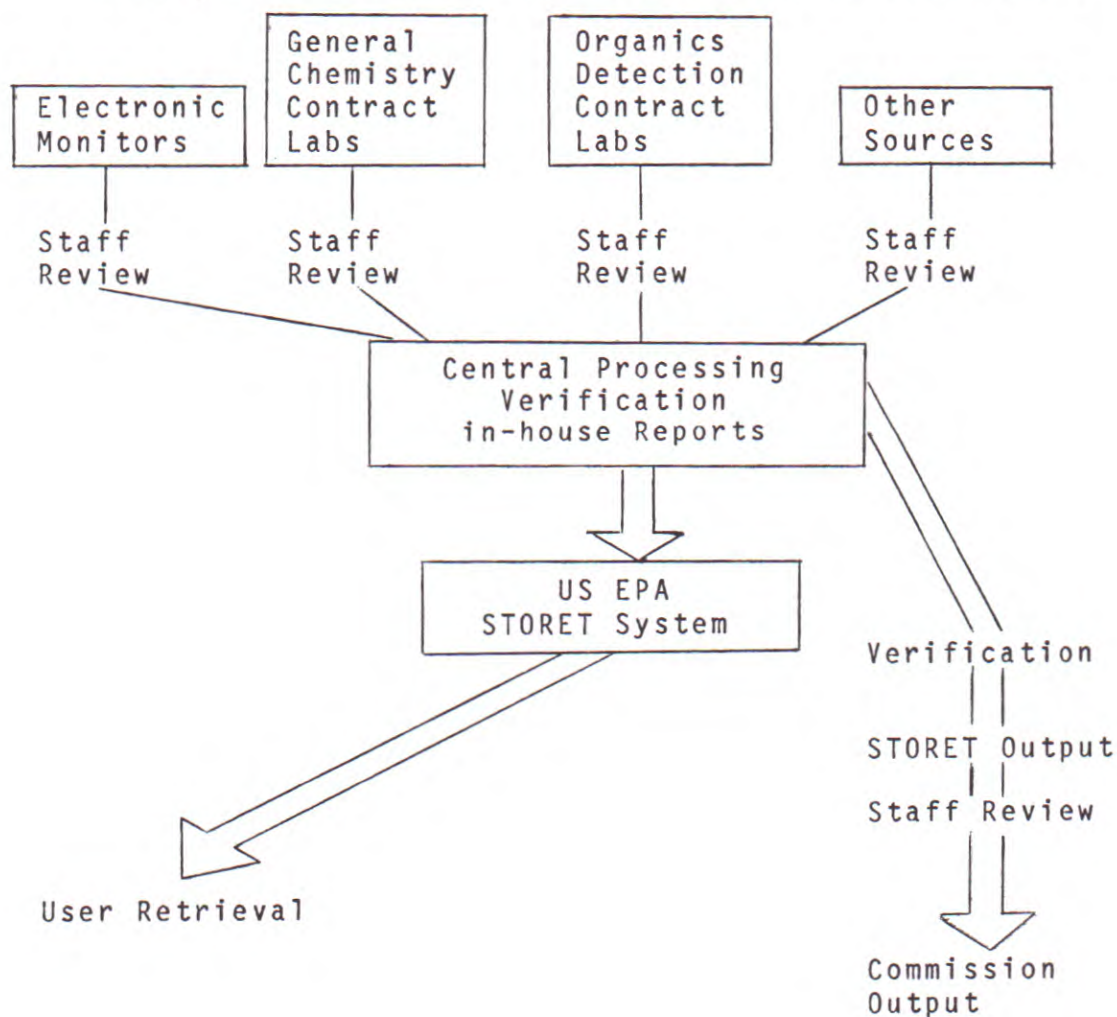


VI

DATA HANDLING AND PROCESSING

The quality of the output from monitoring, field and laboratory testing, the data and the reports is what quality assurance activity is about. Adhering to good standard practices as outlined in other sections of this Procedures Manual will assure that the results are valid and scientifically defensible. Integrity of the results is preserved by following standard practices of data verification in data-handling and by close scrutiny of data values recorded and stored.

The chart below diagrams the flow of data as gathered in Commission water quality monitoring network and indicates data quality assurance measures taken through staff review and verification at each level.





APPENDIX A
MONITORING SITES
AND
STATION DESCRIPTION



A.1
MASTER LIST ORSANCO HISTORIC MONITORING NETWORK

STORET PRIMARY STATION NO.	SECONDARY STATION NO.	DESCRIPTION	STATE/ COUNTY CODE	LAT.-LONG.NO.	TYPE
AR1973R	29	Allegheny R. @ Kinzua Dam, PA	42123	415038007908580	E
AR30.4R	30	Allegheny R. @ Lock & Dam #5, PA	42005	404100007940080	E
KI10.9R	31	Kiskiminetas R. @ Vandergrift, PA	42129	403620007933150	E
AR.13.3R	10	Allegheny R. @ Oakmont, PA	42003	403151007950120	E
AR12.3	233*	Allegheny R. @ Oakmont, PA	42003	403150007950140	W
AR13.3M	1233	Allegheny R. @ Oakmont, PA	42003	403151007950120	M
AR-8.9	231	Allegheny R. @ Wilkensburg, PA	42003	402855007952380	W
AR7.40	020DS	Allegheny R. @ Pittsburgh, PA	42003	402940007949300	O
MR42.6R	09*	Monongahela R. @ Charleroi, PA	42125	400830007953350	E
MR42.5	239*	Monongahela R. @ Charleroi, PA	42125	400757007953250	W
MR24.5	010DS	Monongahela R. @ Western Pa. Water Co.	42125	401500007949300	O
YR15.5	*	Youghiogheny R. @ McKeesport, PA	42003	402115507951460	W
MR15.5	241	Monongahela R. @ McKeesport, PA	42003	402115507951460	W
MR-4.5R	32	Monongahela R. @ So. Pittsburgh, PA	42003	402436007957150	E
MR-4.5M	1237	Monongahela R. @ So. Pittsburgh, PA	42003	402436007957150	M
MR-4.0	237	Monongahela R. @ So. Pittsburgh, PA	42003	402438007957150	W
OR9789	206*	Ohio River @ Reed Power, PA	42003	402753008002230	W
OR976.50	030DS	Ohio R. @ West View, PA	42003	402934008004180	O
OR9658R	08	Ohio R. @ So. Heights, PA	42003	403412008013470	E
OR9658M	1201	Ohio R. @ So. Heights, PA	42003	403412008013470	M
OR9652	201*	Ohio R. @ So. Heights, PA	42003	403414008013480	W
BR-5.3R	06	Beaver R. @ Beaver Falls, PA	42007	404548008018550	E
BR-5.3M	1242	Beaver R. @ Beaver Falls, PA	42007	404548008018550	M

A.1
MASTER LIST ORSANCO HISTORIC MONITORING NETWORK

STORET PRIMARY STATION NO.	SECONDARY STATION NO.	DESCRIPTION	STATE/ COUNTY CODE	LAT.-LONG.NO.	TYPE
BR-5.3	242	Beaver R. @ Beaver Falls, PA	42007	404548008018550	W
OR9408R	33	Ohio R. @ East Liverpool, OH	39029	403820008031150	E
OR9408M	1500	Ohio R. @ East Liverpool, OH	39029	403820008031150	M
OR9408	120DS	Ohio R. @ East Liverpool, OH	39027	403820008031150	O
OR9272R	05*	Ohio R. @ Stratton, OH	39081	403100008037220	E
OR9267	500*	Ohio R. @ Stratton, OH	39081	403119008037345	W
OR9219	507*	Ohio R. @ Toronto, OH	39081	402758508035525	W
OR9194	403	Ohio R. @ Weirton Steel, WV	54029	402454008036195	W
OR9192	402*	Ohio R. @ Weirton, WV	54029	402458508036195	W
OR9157	505	Ohio R. @ Steubenville, OH	39081	402130008036330	W
OR9017	404*	Ohio R. @ Power, WV	54009	401234508039465	W
OR8975	502	Ohio R. @ Yorkville, OH	39081	400936008042045	W
OR8968M	1405	Ohio R. @ Pike Island, WV	54069	400859008042060	M
OR8945	405	Ohio R. @ Wheeling, WV	54069	400418008043345	W
OR894.2	040DS	Ohio R. @ Wheeling, WV	54069	400418008043345	O
OR8818	406	Ohio R. @ Moundsville, WV	54051	395509008045060	W
OR8786R	34	Ohio R. @ Shadyside, OH	39013	395431008045350	E
OR8786M	1521	Ohio R. @ Shadyside, OH	39013	395431008045350	M
OR8616	407	Ohio R. @ Natrium, WV	54051	394443508050405	W
OR8546M	1423	Ohio R. @ Hannibal Lock, OH	39111	393810008052310	M
OR8205	408*	Ohio R. @ Willow Island, WV	54073	3921360080118495	W
OR8204R	16*	Ohio R. @ Willow Island, WV	54073	3915000080115000	E
OR8192M	1408	Ohio R. @ Willow Island Lock, OH	39167	3921280080119090	M

A.1
MASTER LIST ORSANCO HISTORIC MONITORING NETWORK

STORET PRIMARY STATION NO.	SECONDARY STATION NO.	DESCRIPTION	STATE/ COUNTY CODE	LAT.-LONG.NO.	TYPE
MU66.8	534*	Muskingum R. @ Philo, OH	39119	395137508154555	W
MU28.0R	04*	Muskingum R. @ Beverly, OH	39039	393327008138000	R
MU28.0	532	Muskingum R. @ Beverly, OH	39039	393327008138465	W
MU-5.8M	1531	Muskingum R. Near Marietta, OH	39167	392813008129280	M
OR7965	409	Ohio R. @ Parkersburg, WV	54107	391613508133570	W
OR790.7	050DS	Ohio R. @ Parkersburg, WV	54107	391546008140040	O
OR7771M	1421	Ohio R. @ Belleville Lock, OH	39105	390707008144320	M
OR7394R	14*	Ohio R. @ New Haven, WV	54053	385745008145300	E
OR7394	411	Ohio R. @ New Haven, WV	54053	385921008158165	W
OR7210R	37	Ohio R. @ Addison, OH	39053	3854490082077390	E
OR7210M	1510	Ohio R. @ Addison, OH	39053	3854490082077390	M
OR7196	510	Ohio R. @ Addison (Kyger Creek), OH	39053	385313508208450	W
NR1939R	28*	New River @ Glen Lyn, VA	51071	365200008952000	E
NR93.9	366*	New River @ Glen Lyn, VA	51071	372215008051390	W
KR72.0	454*	Kanawha R. @ Cabin Creek, WV	54039	381158008128430	W
KR38.3	060DS	Kanawha R. @ St. Albans, WV	54039	382330008149560	O
KR31.1R	03	Kanawha R. @ Winfield, WV	54053	383132008154400	E
KR31.1M	1450	Kanawha R. @ Winfield, WV	54053	383132008154400	M
OR7018R	39	Ohio R. @ Gallipolis Dam, WV	54053	384054008211170	E
OR7018M	1422	Ohio R. @ Gallipolis Dam, WV	54053	384054008211170	M
OR6741R	02	Ohio R. @ Huntington, WV	54011	382557008225570	E
OR6741M	1412	Ohio R. @ Huntington, WV	54011	382557008225570	M
OR674.1	070DS	Ohio R. @ Huntington, WV	54011	382557008225570	O

A.1
MASTER LIST ORSANCO HISTORIC MONITORING NETWORK

STORET PRIMARY STATION NO.	SECONDARY STATION NO.	DESCRIPTION	STATE/ COUNTY CODE	LAT.-LONG.NO.	TYPE
OR674Ø	412	Ohio R. @ Huntington, WV	54Ø11	382524ØØ8225Ø3Ø	W
OR6652M	1523	Ohio R. @ Kenova, WV	54Ø99	382421ØØ823424Ø	M
OR663Ø	5Ø6*	Ohio R. @ South Point, OH	39Ø87	3825ØØØØ823524Ø	W
SR2Ø.3R	17	Big Sandy R. @ Louisa, KY	21127	381Ø16ØØ8238Ø5Ø	E
SR2Ø.3M	163Ø	Big Sandy R. @ Louisa, KY	21127	381Ø16ØØ8238Ø5Ø	M
SR2Ø.3	63Ø*	Big Sandy R. @ Louisa, KY	21127	38Ø633ØØ823557Ø	W
OR64ØØM	1621	Ohio R. @ Greenup Dam, KY	21Ø89	383848ØØ825138Ø	M
SC15.ØM	1538	Scioto R. @ Lucasville, OH	39145	385252ØØ83Ø1Ø3Ø	M
OR63Ø3	5Ø3*	Ohio R. @ Portsmouth, OH	39145	384345ØØ8259495	W
OR63Ø.9	Ø80DS	Ohio R. @ Portsmouth, OH	39145	384345ØØ8259495	O
OR5448R	24*	Ohio R. @ Meldahl Dam, OH	39Ø25	38475ØØØ841ØØØØ	E
OR5448M	1511	Ohio R. @ Meldahl Dam, OH	39Ø25	38475ØØØ841ØØØØ	M
OR5292R	18*	Ohio R. @ Beckjord (New Richmond), OH	39Ø25	3854ØØØØ8315ØØØ	E
OR5182R	Ø1	Ohio R. @ Cincinnati, OH	39Ø61	39Ø411ØØ842557Ø	E
OR5182M	15Ø4	Ohio R. @ Cincinnati, OH	39Ø61	39Ø411ØØ842557Ø	M
OR518.2	Ø90DS	Ohio R. @ Cincinnati, OH	39Ø61	39Ø411ØØ842557Ø	O
OR5182	5Ø4	Ohio R. @ Cincinnati, OH	39Ø61	39Ø411ØØ842557Ø	W
LM-7.5M	1571	Little Miami R. @ Cincinnati, OH	39Ø61	39Ø633ØØ8424Ø6Ø	M
LM-3.4R	23*	Little Miami R. @ Cincinnati, OH	39Ø25	391Ø17ØØ841753Ø	E
LR-4.5R	21	Licking R. @ Kenton County, KY	21117	39Ø3Ø5ØØ842942Ø	E
LR-4.5M	1634	Licking R. @ Kenton County, KY	21117	39Ø3Ø5ØØ842942Ø	M
OR5Ø97R	19*	Ohio R. @ West End (Cincinnati), OH	39Ø61	39Ø4Ø2ØØ84323ØØ	E
OR5Ø35	5Ø9*	Ohio R. @ Anderson Ferry (Cinti), OH	39Ø61	39Ø4285Ø843712Ø	W

A.1
MASTER LIST ORSANCO HISTORIC MONITORING NETWORK

STORET PRIMARY STATION NO.	SECONDARY STATION NO.	DESCRIPTION	STATE/ COUNTY CODE	LAT.-LONG.NO.	TYPE
OR5019R	26*	Ohio R. @ Anderson Ferry (Cinti), OH	39061	390730008432300	E
OR4910R	07*	Ohio R. @ North Bend, OH	39061	390630008448315	E
OR4910M	1508	Ohio R. @ North Bend, OH	39061	390630008448315	M
OR4907	508	Ohio R. @ Miami Fort, OH	39061	390630008448315	W
GM-5.5R	25*	Great Miami R. @ Lost Bridge, OH	39061	390911008447380	E
GM-5.5M	1551	Great Miami R. @ Lost Bridge, OH	39061	390911008447380	M
OR4843R	27*	Ohio R. @ Aurora, IN	18029	390707008445000	E
OR4495M	1600	Ohio R. @ Markland Dam, KY	21077	394629008457520	M
OR4495R	22	Ohio R. @ Markland Dam, IN	18155	384500008507000	E
OR4215R	20*	Ohio R. @ Clifty Creek (Madison), IN	18077	384409008522150	E
OR4215	702	Ohio R. @ Madison, IN	18077	384409008522015	W
OR3804R	11	Ohio R. @ Louisville, KY	21111	381652008542080	E
OR3804M	1601	Ohio R. @ Louisville, KY	21111	381652008542080	M
OR380.4	100DS	Ohio R. @ Louisville, KY	21111	381652008542080	O
OR3804	601	Ohio R. @ Louisville, KY	21111	381649508542105	W
OR3642R	12*	Ohio R. @ Cane Run (Louisville), KY	21111	382200008550000	E
OR3551R	35	Ohio R. @ West Point, KY	21111	380205008554510	E
OR3551M	1622	Ohio R. @ West Point, KY	21111	380205008554510	M
OR2603R	41	Ohio R. @ Cannellton Dam, IN	18123	375358008642200	E
OR2603M	1721	Ohio R. @ Cannellton Dam, IN	18123	375358008642200	M
GR41.3M	1656	Green R. @ Seebree, KY	21101	375530008718150	M
OR1895R	15	Ohio R. @ Evansville, IN	18163	375820008734350	E
OR1895M	1703	Ohio R. @ Evansville, IN	18163	375820008734350	M

A.1
MASTER LIST ORSANCO HISTORIC MONITORING NETWORK

STORET PRIMARY STATION NO.	SECONDARY STATION NO.	DESCRIPTION	STATE/ COUNTY CODE	LAT.-LONG.NO.	TYPE
OR189.5	110DS	Ohio R. @ Evansville, IN	18163	3758200008734350	O
OR1895	703	Ohio R. @ Evansville, IN	18163	3758200008734350	W
OR1350M	1722	Ohio R. @ Uniontown, KY	21225	3748000008759000	M
WA9295R	43	Wabash R. @ New Harmony, IN	18129	3807550008756250	E
WA9295M	1741	Wabash R. @ New Harmony, IN	18129	3807550008756250	M
WA1740R	13*	Wabash R. @ Hutsonville, IL	17033	3907000008740000	E
OR62.5R	48	Ohio R. @ Smithland Dam, IL	17151	3708450008824250	E
OR62.5M	1820	Ohio R. @ Smithland Dam, IL	17151	3708450008824250	M
CR30.6M	1645	Cumberland R. near Grand Rivers, KY	21129	3701180008813160	M
TR-6.0M	1650	Tennessee R. near Paducah, KY	21145	3702160008831460	M
OR45.5R	49	Ohio R. @ Paducah, KY	21145	3706000008836300	E
OR45.5M	1625	Ohio R. @ Paducah, KY	21145	3706000008836300	M
OR45.5	130DS	Ohio R. @ Paducah, KY	21145	3706000008836300	O
OR28.7R	46	Ohio R. @ Joppa, IL	17127	3712000008851000	E
OR28.7M	1821	Ohio R. @ Joppa, IL	17127	3712000008851000	M

W - Water Users
E - Electronic
M - Manual
O - ODS
* - Inactive

A.2
MANUAL AND ELECTRONIC MONITORING
STATION CODES AND DESCRIPTIONS
M = MANUAL R = ELECTRONIC

STORET PRIMARY STATION NO.	STATION NAME	STATION DESCRIPTION LOCATION
AR13.3M AR13.3R	Allegheny R. @ Oakmont, PA Allegheny R. @ Oakmont, PA	Intake to Borough of Oakmont Water-works, Oakmont, PA, M.P. 13.3 (tap on raw water line from pumping station to treatment plant).
MR-4.5M MR-4.5R	Monongahela R. @ So. Pitts- burgh, PA Monongahela R. @ So. Pitts- burgh, PA	Intake to Western Pennsylvania Water Co., Division of American Waterworks Co. M.P. 4.5 (tap on raw water line in pumping station of water works).
OR9658M OR9658R	Ohio R. @ So. Heights, PA Ohio R. @ So. Heights, PA	Intake to South Heights, PA, Duquesne Power Generating Plant (Phillips Stations) M.P. 15.2 (tap on raw water line in pump house).
BR-5.3M BR-5.3R	Beaver River @ Beaver Falls, PA Beaver River @ Beaver Falls, PA	Intake to Beaver Falls, PA, Water-works located in Beaver Falls, PA, M.P. 5.3 (tap on intake line in pumping stations).
OR9408M OR9408R	Ohio R. @ East Liverpool, OH Ohio R. @ East Liverpool, OH	Intake to City of East Liverpool, OH, Waterworks M.P. 40.2 (tap in raw water line from pumping station to treatment plant).
OR8968M	Ohio R. @ Pike Island Lock, WV	Pike Island Lock and Dam near Wheeling, WV, M.P. 84.2 (sample collected from upstream end of guidewall to lock).
OR8786M OR8786R	Ohio R. @ Shadyside, OH Ohio R. @ Shadyside, OH	Intake to Burger Power Generating Plant of Ohio Edison Company near Shadyside, OH, M.P. 102.4 (tap in raw water line near pumps).
OR8546M	Ohio R. @ Hannibal Lock, OH	Hannibal Lock and Dam M.P. 126.4 (sample collected at upstream end to lock).
OR8192M	Ohio R. @ Willow Island Lock, OH	Willow Island Lock and Dam M.P. 161.8 (sample collected from upstream end of lock wall).

STORET PRIMARY STATION NO.	STATION NAME	STATION DESCRIPTION LOCATION
MU-5.8M	Muskingum R. near Marietta, OH	Lock and Dam No. 2 of USCE near Marietta, OH, M.P. 5.8 (sample collected from lock wall on up-stream side of dam).
OR7771M	Ohio R. @ Belleville Lock, OH	Belleville Lock and Dam near Reedsville, OH, M.P. 203.9 (sample collected at upstream end of guide-wall to lock).
OR7210M OR7210R	Ohio R. @ Addison, OH Ohio R. @ Addison, OH	Intake to Kyger Creek Power Generating Plant of Ohio Valley Electric Corp. near Addison, OH, M.P. 260.0 (tap in raw water line next to pumps).
OR7018M OR7018R	Ohio R. @ Gallipolis Dam, WV Ohio R. @ Gallipolis Dam, WV	Gallipolis Lock and Dam near Gallipolis, OH, M.P. 279.2 (submersible pump mounted on lock wall pumps to monitor in control building).
KR31.1M KR31.1R	Kanawha R. @ Winfield, WV Kanawha R. @ Winfield, WV	Winfield Lock and Dam - hydro generating facility of Kanawha Power Company near Winfield, WV, M.P. 31.1 (tap in turbine channel).
OR6741M OR6741R	Ohio R. @ Huntington, WV Ohio R. @ Huntington, WV	Huntington, WV, Waterworks at 24th Street pump station M.P. 306.9 (tap in raw water line in pumping house).
OR6652M	Ohio R. @ Kenova, WV	Near N. Kenova, OH, M.P. 315.8 (sample collected from barge at South Point Barge Salvage docks).
SR20.3M SR20.3R	Big Sandy R. @ Louisa, KY Big Sandy R. @ Louisa, KY	Intake of Kentucky Power Company near Louisa, KY, M.P. 20.3 (tap in raw water line in pumping house).
OR6400M	Ohio R. @ Greenup Dam, KY	Greenup Lock and Dam, M.P. 341.0 (sample collected upstream end of guidewall to lock).
SC15.0M	Scioto R. @ Lucasville, OH	State Highway bridge, Ohio State Route No. 348 near Lucasville, OH, M.P. 15.0 (sample collected from bridge over mid-channel).

STORET
PRIMARY
STATION
NO.

STATION
NAME

STATION
DESCRIPTION
LOCATION

OR5448M	Ohio R. @ Meldahl Dam, OH	Meldahl Lock and Dam, M.P. 436.2 (sample collected at upstream end of guidewall to lock).
OR5182M	Ohio R. @ Cincinnati, OH	Intake to City of Cincinnati, OH,
OR5182R	Ohio R. @ Cincinnati, OH	Waterworks M.P. 462.8 (tap in raw water line in pump house).
LM-7.5M	Little Miami R. @ Cincinnati, OH	Newtown Road bridge over the Little Miami River M.P. 7.5 (sample collected over mid-channel).
LR-4.5M	Licking R. @ Kenton County, KY	Intake to Kenton County Waterworks,
LR-4.5R	Licking R. @ Kenton County, KY	Covington, KY, M.P. 4.5 (tap on raw water line in water treatment plant).
OR4910M	Ohio R. @ North Bend, OH	Near intake of Miami Fort Power Generating Station of Cincinnati Gas and Electric Company near North Bend, OH, M.P. 490.0.
GM-5.5M	Great Miami R. @ Lost Bridge, OH	Lost Bridge over Miami River located at junction of Lawrenceburg and Miami View Roads, M.P. 5.5 (bridge closed to vehicular traffic).
OR4495M	Ohio R. @ Markland Dam, KY	Markland Dam, KY, M.P. 531.5 (sample collected at upstream end of guidewall to lock).
OR4495R	Ohio R. @ Markland Dam, IN	Intake to Public Service of Indiana Hydro Electric Plant (tap on intake to turbines).
OR3804M	Ohio R. @ Louisville, KY	Louisville Water Company, River
OR3804R	Ohio R. @ Louisville, KY	Road, Louisville, KY, M.P. 600.6 (tap in raw water line in pumping station).
OR3551M	Ohio R. @ West Point, KY	Mill Creek Power Generating Plant of
OR3551R	Ohio R. @ West Point, KY	Louisville Gas and Electric Company near West Point, KY, M.P. 625.9 (tap in raw water line at cooling pumps).
OR2603M	Ohio R. @ Cannelton Dam, IN	Cannelton Lock and Dam near
OR2603R	Ohio R. @ Cannelton Dam, IN	Cannelton, IN, M.P. 720.7 (submersible pump located near upstream end of guidewall to lock).

STORET PRIMARY STATION NO.	STATION NAME	STATION DESCRIPTION LOCATION
GR41.3M	Green R. @ Seebree, KY	Big Rivers RECC intake near Seebree, KY, M.P. 41.3 (sample collected from the platform over river intake structure to plant).
OR1895M	Ohio R. @ Evansville, IN	City of Evansville, IN, Waterworks intake M.P. 791.5 (tap in raw water line in pumping station).
OR1895R	Ohio R. @ Evansville, IN	
OR1350M	Ohio R. @ Uniontown Dam, IN	Uniontown Lock and Dam near Uniontown, KY, M.P. 846.0 (sample collected at upstream end of guide-wall to lock).
WA9295M	Wabash R. @ New Harmony, IN	Highway toll bridge of White County Bridge Commission, U.S. Route 460 in New Harmony, IN, M.P. 51.5 (submersible pump located on upstream side of center bridge pier. Sample pumped to monitor located on bridge pier beneath bridge. Access by ladder on downstream side of structure).
WA9295R	Wabash R. @ New Harmony, IN	
OR62.5M	Ohio R. @ Smithland Dam, IL	Smithland Lock and Dam near Hamlettsburg, IL, M.P. 918.5 (submersible pump located on lock wall).
OR62.5R	Ohio R. @ Smithland Dam, IL	
CR30.6M	Cumberland R. near Grand Rivers, KY	Hydroelectric power generating plant at Barkely Dam near Lake City, KY, M.P. 30.6 (sample collected from tap on service water intake line to power station adjacent to turbines).
TR-6.0M	Tennessee R. near Paducah, KY	Ashland Oil Company Terminal docks, M.P. 6.0 (sample collected from terminal pier at upstream end).
OR28.7M	Ohio R. @ Joppa, IL	Intake to Electric Energy Corp. Generating Plant near Joppa, IL, M.P. 952.3 (tap in raw water line in pump station adjacent to river).
OR28.7R	Ohio R. @ Joppa, IL	
OR45.5M	Ohio R. @ Paducah, KY	City of Paducah, KY, Waterworks Intake. M.P. 935.5 (tap in raw water line)
OR45.5R	Ohio R. @ Paducah, KY	

A.3

MONITORING STRATEGY

Manual Sampling Schedule

Station	Station ID	Monthly Parameters	Quarterly Parameter (Jan, Apr, Jul, Oct)	
Oakmont	1233	Cyanide	Ammonia-Nitrogen (N)	Arsenic
South Pitts.	1237	Hardness	Nitrite-Nitrate-N	Chromium
Beaver Falls	1242	Phenolics	Total Kjeldahl-N	Nickel
		Suspended Solids	Total Phosphorus-P	Selenium
		Sulfate	COD	Silver
		Cadmium	BOD	
		Copper	Fecal Coliform	
		Iron	Manganese	
		Lead	Magnesium	
		Mercury		
		Zinc		
		Alkalinity		
South Heights	1201	Cyanide	Ammonia-Nitrogen (N)	Sodium
East Liverpool	1500	Hardness	Nitrite-Nitrate-N	Barium
		Phenolics	Total Kjeldahl-N	Arsenic
		Suspended Solids	Total Phosphorus-P	Chromium
		Sulfate	COD	Nickel
		Cadmium	BOD	Selenium
		Cooper	Fecal Coliform	Silver
		Iron	Manganese	
		Lead	Magnesium	
		Mercury		
		Zinc		
		Alkalinity		
Shadyside	1521	Cyanide		Sodium
Kenova	1523	Hardness	<u>MAY thru OCT / ONLY</u>	Barium
Meldahl	1511	Phenolics	Ammonia-Nitrogen (N)	Arsenic
Cincinnati	1504	Suspended Solids	Nitrite-Nitrate-N	Chromium
North Bend	1508	Sulfate	Total Kjeldahl-N	Nickel
Markland	1600	Cadmium	Total Phosphorus-P	Selenium
Cannelton	1721	Copper	BOD	Silver
Uniontown	1722	Iron	Fecal Coliform	
Smithland	1820	Lead		
Paducah	1625	Mercury		
		Zinc		
		Manganese		
		Magnesium		

Station	Station ID	Monthly Parameters	Quarterly Parameter (Jan, Apr, Jul, Oct)	
Pike Island	1405	Cyanide	Ammonia-Nitrogen (N)	Sodium
Hannibal	1423	Hardness	Nitrite-Nitrate-N	Barium
Willow Island	1408	Phenolics	Total Kjeldahl-N	Arsenic
Belleville	1421	Suspended Solids	Total Phosphorus-P	Chromium
Addison	1510	Sulfate	COD	Nickel
Gallipolis	1422	Cadmium	BOD	Selenium
Huntington	1412	Copper	Fecal Coliform	Silver
Greenup	1621	Iron	Manganese	
Louisville	1601	Lead	Magnesium	
West Point	1622	Mercury		
Evansville	1703	Zinc		
Joppa	1821			
L-2 Muskingum	1531	Cyanide		Arsenic
Winfield	1450	Hardness	<u>MAY thru OCT / ONLY</u>	Chromium
Scioto	1538	Phenolics	Ammonia-Nitrogen (N)	Nickel
Little Miami	1571	Suspended Solids	Nitrite-Nitrate-N	Selenium
Great Miami	1551	Sulfate	Total Kjeldahl-N	Silver
New Harmony	1741	Cadmium	Total Phosphorus-P	
Cumberland R.	1645	Copper	BOD	
		Iron	<u>Fecal Coliform</u>	
		Lead		
		Mercury		
		Zinc		
		Manganese		
		Magnesium		
Louisa	1630	Cyanide	Ammonia-Nitrogen (N)	Arsenic
Licking R.	1634	Hardness	Nitrite-Nitrate-N	Chromium
Greenup R.	1656	Phenolics	Total Kjeldahl-N	Nickel
Tennessee R.	1650	Suspended Solids	Total Phosphorus-P	Selenium
		Sulfate	COD	Silver
		Cadmium	BOD	
		Copper	Fecal Coliform	
		Iron	Manganese	
		Lead	Magnesium	
		Mercury		
		Zinc		

A.4

ORGANICS DETECTION SYSTEM MONITORING STATION CODES AND DESCRIPTIONS

<u>STORET PRIMARY NO.</u>	<u>STATION NAME</u>	<u>STATION DESCRIPTION</u>
AR7.40	City of Pittsburgh Water Treatment Plant	Allegheny River at Pittsburgh, PA
MR24.5	Western Penn Water Company	Monongahela River at Elrama, PA
OR976.50	West View Water Authority	Ohio River at West View, PA
OR9408	City of East Liverpool Water Works	Ohio River at East Liverpool, OH
OR894.2	Wheeling Water Treatment Plant	Ohio River at Wheeling, WV
OR790.7	E.I. duPont deNemours & Co.	Ohio River at Parkersburg, WV
KR38.3	Appalachian Power Company	Kanawha River at St. Albans, WV
OR674.1	Huntington Water Corporation	Ohio River at Huntington, WV
OR630.9	City of Portsmouth Water Treatment Plant	Ohio River at Portsmouth, OH
OR518.2	City of Cincinnati Water Works	Ohio River at Cincinnati, OH
OR380.4	Louisville Water Company	Ohio River at Louisville, KY
OR189.5	Evansville Water Works	Ohio River at Evansville, IN
OR45.5	Paducah Water Works	Ohio River at Paducah, KY



REGULATORY AGENCIES OF THE SIGNATORY STATES

ILLINOIS

Division of Water Pollution Control
Environmental Protection Agency
State of Illinois
2200 Churchill Road
Springfield, IL 62706
217/782-1654

INDIANA

Stream Pollution Control Board
State Board of Health
P.O. Box 1964
Indianapolis, IN 46206
317/633-0700

KENTUCKY

Division of Water
Natural Resources and Environmental
Protection Cabinet
18 Reilly Road
Frankfort, KY 40601
502/564-3410

NEW YORK

Division of Water
Dept. of Environmental Conservation
50 Wolf Road
Albany, NY 12233
518/457-6674

OHIO

Ohio Environmental Protection
Agency
P.O. Box 1049
Columbus, OH 43216
614/466-7427

PENNSYLVANIA

Bureau of Water Quality Management
Dept. of Environmental Resources
P.O. Box 2063
Harrisburg, PA 17120
717/787-2666

VIRGINIA

State Water Control Board
P.O. Box 11143
Richmond, VA 23230
804/257-0056

WEST VIRGINIA

Division of Water Resources
Dept. of Natural Resources
1201 Greenbrier Street
Charleston, WV 25311
304/348-2107

**Ohio River Valley
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414 Walnut St.
Cincinnati, Ohio 45202**