Final Report

Early Warning... Organics Detection System

a cooperative project of
Cincinnati Water Works
Evansville Water Works
Huntington Water Corporation
Louisville Water Company
Pittsburgh Department of Water
Portsmouth Water Works
Western Pennsylvania Water Company
West View Water Authority
Wheeling Water Department
and the U.S. Environmental Protection Agency

Ohio River Valley

Water Sanitation Commission

an interstate agency representing Illinois, Indiana, Kentucky, New York, Ohio, Pennsylvania, Virginia, and West Virginia

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*As of Sept. 1, 1981

FINAL REPORT

EARLY WARNING ORGANICS DETECTION SYSTEM

Ohio River Valley Water Sanitation Commission
414 Walnut Street
Cincinnati, Ohio
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EXECUTIVE SUMMARY

In 1977, a spill of carbon tetrachloride from the Kanawha River was inadvertently allowed to pass through Ohio River drinking water systems, and the Ohio River Valley became a focal point for public criticism that water pollution control agencies were not providing adequate protection against unforeseen spills and discharges. Out of such a negative climate, the Ohio River Valley Water Sanitation Commission (ORSANCO) conceived an innovative spill detection system, which was honed and refined through expert input from concerned water users along the Ohio River and from the US Environmental Protection Agency (US EPA). The two-year history of the Early Warning--Organics Detection System (EWODS) has substantiated the dedication, determination, and--most of all--the vision of all those involved in making it a reality.

HISTORY AND DEVELOPMENT

To plan the system, federal and state members of the commission consulted with the ORSANCO Water Users Committee, which represents public and private drinking water facilities using the Ohio and its major tributaries as sources. It was decided that daily analysis for organic compounds was needed to provide adequate detection of unusual spill and discharge events. The organics detection method preferred by the commission and its advisors was an 11-site system in which gas chromatographic equipment would be placed at operating water intakes to analyze daily for volatile organics. Analytical results could be immediately telecopied to ORSANCO headquarters, where they could be reviewed for unusual levels of organic materials. When unusual events occurred, immediate notification would be provided to state and federal agencies, as well as to downstream water users.

Armed with the clear support of valley water utilities, the commission sought funds from US EPA to purchase the equipment required for the detection network. US EPA expressed a willingness to support a limited demonstration of the system; a grant offer of $100,000 was received in September, 1977, to initiate a first-phase EWODS, which included seven stations and provided weekday, rather than daily, sampling. The US EPA grant was used to purchase analytical equipment--specifically, gas chromatographs (GC) for four sites and supplemental equipment for GC's already in use at three more locations. EWODS was officially launched in January, 1978, and all the first-phase stations were put into operation during that year.

In FY 1979, two additional US EPA grants were recieved: $135,000 for the detection system's four remaining stations and $140,000 for operational support, to allow expansion to the seven-day-per-week level. During 1979 and 1980 the additional stations were added and arrangements made for daily moni-

toring.

Objectives and Limitations

In initiating the project, the commission established a number of objectives for the system, based on the recognized needs and the potential of the method chosen: to provide a system for identifying increased levels of purgeable organic compounds and for notifying water users when unusual events were detected, to establish expected baseline levels of these compounds in the river to assess causes for fluctuations, and to establish a basis for regulatory control of organic effluents.

It was envisioned that the system, if successful, would provide an additional and essential safeguard for the three million people served by public drinking water facilities using the Ohio River and the major tributaries as sources. The timely detection of increased or unusual levels of volatile organic compounds in source waters and immediate notification of downstream water users would permit adjustment in water treatment practices to reduce levels of these materials in the finished water and thereby ensure a higher quality drinking water for the consumer. In addition, the location of the segment of the river(s) affected by a given incident would aid the regulatory agencies in identifying the source or sources and initiating appropriate corrective action. It was also theorized that the presence of an organics monitoring system, even a limited one, would serve as a deterrent to surreptitious spilling or discharging of organic wastes and would emphasize the need for vigilance by dischargers and at facilities located adjacent to the rivers monitored.

Though the hopes for the Early Warning--Organics Detection System were many, its limitations were also carefully documented. The analytical method chosen limited the number and types of organic compounds detectable to only those which are volatilized under specific GC conditions used. The selection of organic compounds that can be detected by this method is relatively narrow, though it includes compounds of special interest in the Ohio River system, such as carbon tetrachloride and chloroform. It was also recognized that even the minimum 11 stations left some sections of the river essentially uncovered. In addition, because of the innovative nature of the system, it was impossible to predict the optimum number of samples per day needed to accomplish project objectives, though it was clear that the number would vary with river flow and related travel time. Expectations were that only one sample could be analyzed each day, except during spill events, because of limited personnel and time resources.

IMPLEMENTATION

The EWODS sites were selected on the basis of several criteria. Of prime importance was location in relation to major sources of pollution and public water supply intakes. In addition, adequate laboratory facilities were required, as was 24-hour operation. The facility or company in question also needed to have adequate personnel to conduct the required analyses, and most of all, a willingness to dedicate time and effort to the project. The final sites chosen are as follows:

River	Water Intake	Mile Point Ohio	Mile Point Tributary
Allegheny (B)	Pittsburgh Dept. of Water	0.0	7.4
Monongahela (C)	Western Pennsylvania Water Company, Aldrich Plant	0.0	24.4
Ohio (C)	West View Water Authority	4.5	
Ohio (A)	Wheeling Water Department	86.6	
Ohio (C)	Industrial Intake, Parkersburg, WV	190.3	
Kanawha (A)	Industrial Intake, St. Albans, WV	256.6	38.3
Ohio (A)	Huntington Water Corp.	304.2	
Ohio (A)	Portsmouth Water Works	350.6	
Ohio (B)	Cincinnati Water Works	462.8	
Ohio (B)	Louisville Water Company	600.6	
Ohio (C)	Evansville Water Works	791.5	

A - First-phase installation, project GC
B - First-phase installation, utility-owned GC
C - Second-phase installation

Each participating facility has entered into an interagency agreement with ORSANCO detailing the responsibilities of each agency.

Analytical Equipment

Three broad categories of laboratory components are needed for the operating system: 1) a gas chromatograph unit, consisting of the purge device, gas chromatograph (GC) detectors, and the associated microprocessor controller; 2) an appropriate gas system, including high-pressure gas in cylinders, pressure regulators, traps and piping; and 3) expendable supplies, including columns and packing materials, syringes, chemical standards, microsyringes and micropipettes, and sample containers.

Because the equipment for the system has been purchased in two phases, instrumentation differs somewhat at several of the sites; however, there have been no identified differences in sensitivity or analytical results obtained from the various units.

Reference Laboratory

A reliable analytical reference laboratory is essential as backup support to the EWODS sampling stations. The initial project design called for a contract with a private consulting laboratory to:

a. confirm the identity and concentrations of substances found at unusual levels by the EWODS operators,

b. to furnish a complete analysis, using GC-MS techniques, of monthly EWODS samples, and

c. to assist in quality control by matching analyses of split samples with the EWODS sites.

Procedures

The same analytical procedure is followed at all of the sites. Daily raw water samples are collected from the water intake system prior to any treatment. Duplicate samples of organic-free water (blanks) are stored at the same time. A blank is spiked with a known amount of an internal standard and analyzed to test the gas chromatograph's (GC) quantitative accuracy. If no problems appear, the raw water sample is then analyzed. If high levels of one or more compounds or system problems are observed, the operator contacts the ORSANCO staff and/or transmits the chromatogram for staff evaluation. If it appears that a problem does indeed exist, the duplicate sample and the duplicate blank, along with a one gallon raw water sample, are shipped immediately to the reference laboratory for confirmatory analysis. If no problems are observed, all duplicates are discarded.

The levels of concern are any GC peak quantified as greater than 25 µg/l or greater than ten times the concentration of the same peak on the previous day. US EPA criteria for some organics, which became available in November, 1980, now are also used to assess results. The standard routine requires that the purge/GC calibration standard be run twice a week or whenever new GC columns are installed, to test the qualitative accuracy of the equipment. Training sessions in operating the equipment have been held for all GC operators.

Maintenance on the equipment is performed at four levels. The GC operator provides routine equipment housekeeping; two ORSANCO field personnel (surveillance specialists) perform regular equipment checks as part of their duties; the headquarters staff services the equipment when serious problems develop; and the equipment manufacturers may also provide field service.

Operational Modifications

During the course of the project a number of modifications have been made on the equipment and procedures used. Both the internal and calibration standards have been changed several times to improve the system's analytical capabilities. The current internal standard is 2-bromo-1-chloropropane. The calibration standard being used at this time contains 16 components and is producing concise, well-resolved chromatograms at all EWODS sites.

Adjustments have also been made in purge procedures used to assure more effective purging of compounds from the sample. A number of types of GC columns and packing have been tried, with variable results. The most successful columns have been: 1) 12-foot, 1/8-inch stainless steel packed with one foot of three percent carbowax 1500 on 60-80 mesh chromosorb-W and 11 feet of 0.2 percent carbowax 1500 on 60-80 mesh carbopack-C, 2) 12-foot, 3/16-inch stainless steel packed with n-octane of 100-120 mesh porosil-C; and 3) nine-foot, 1/8 inch nickel, packed with nine inches of three percent carbowax 1500 on 60-80 mesh chromosorb-W and eight feet, three inches of 0.2 percent carbowax in 60-80 carbopack-C.

Data Utilization

GC analytical results are presented as a printout of data after microprocessor interpretation; this printout is called a chromatogram. At any one site the raw water chromatograms have a background pattern of compound occurrence and concentration. Such patterns, however, are discernable only to skilled observers and become evident only after many months of daily inspection.

Comparison of a chromatogram with this general background allows the operator to identify significant deviations--abnormally high concentrations of compounds normally present or significant concentrations of compounds not normally observed at the site. If such a deviation occurs, the operator calls the headquarters staff and discusses the significance and appropriate follow-up of the deviation from normal.

Although initially the chromatograms were transmitted daily by telecopier, the present procedure is to transmit a weekly summary of analytical results and to mail the chromatograms. This change was based on the facts that few alert events had occurred, only a limited number of compounds were detected, concentrations of detected compounds were generally less than 1.0 µg/l, and immediate consultation and transmission of the chromatograms would provide all necessary information when unusually high concentrations of one or more compounds were observed.

Initially high concentrations were identified and verified by the project staff. With the revised reporting procedure, this identification is done by the GC operator, who evaluates each sample chromatogram and notifies ORSANCO staff if unusual concentrations are found.

When high concentrations are found, samples are sent to the reference laboratory for GC/MS confirmation. At the same time potentially affected water users and state and federal regulatory agencies are notified of an unconfirmed alert. Based on the results of the confirmatory analyses, if the high concentrations are not confirmed, the alert is called off; if confirmed, the alert is maintained.

QUALITY ASSURANCE PROGRAM

The EWODS program for monitoring the Ohio River and three tributaries for purgeable halocarbons at the microgram or submicrogram per liter concentration requires a detailed quality assurance program. The program has been developed using the US EPA 600 methods as published in the Federal Register (44FR No. 233) and EWODS system operating experience. Procedures have been formulated for glassware cleaning and handling, sample collection, sample analysis, and reference laboratory procedures for both purgeable and base-neutral extractable samples. These, together with the choice of adequate calibration and internal standards, operator training, equipment maintenance, analysis of check samples, and systematic review of chromatograms, constitute the assurance program.

Several factors complicate the quality assurance program. During the project the number of participating laboratories has increased from seven to eleven using five different GC assemblies. Purge absorption traps and GC columns lose efficiency with continued use, increasing the variation among laboratories. Each chromatogram of a raw water sample is, in fact, an analysis for 16 or 17 compounds, plus the internal standard, so that reported results on a sample may range from no detectable level of any compound to a complex of those not detected, those detected at low levels, and one or two compounds detected at 50, 100, or even 200 µg/l levels.

US EPA performance standards have been analyzed at the sites and by the reference laboratory at several points in the project period. In general, reported results compared to the true value have improved as operating experience is obtained at the individual laboratories and as operating and maintenance procedures are refined. To date the quality assurance program shows that the GC/halogen detector identification of purgeable halocarbons by the EWODS laboratories is very reliable. The precision of analysis will vary with the concentration of the sample. From the data collected the limits of precision have been established--less than 1.0 µg/l--concentrations are probably reliable within the ± 50 percent level. At concentrations higher than 10 µg/l--±30 to ± 20 percent levels are probably valid. These levels of accuracy are similar to those achieved in analysis of other trace materials (heavy metals, cyanide, phenolics) at comparable concentrations. Furthermore, the number of purge standards run--22 percent of the total number of analyses in 1979 and 1980, adds reinforcement to the reliability of the program.

DATA ASSESSMENT

The continuing record of levels of purgeable halocarbons provides the data to evaluate, on a limited basis, Ohio River quality. Each analysis of a river water sample for purgeable halocarbons identifies and quantifies 16 or 17 organic compounds and shows the presence of any additional compounds not included in the calibration standard.

With the exception of chloroform, criteria levels for the various compounds are not exceeded to any significant extent, considering that the criteria for possible carcinogenic compounds are based on steady-state life-time exposure. Even the percentage of samples above the criteria level for chloroform does not indicate significant health-effects potential. Moreover, it is important to remember that extreme precision is not a major concern when monitoring for spill events. What is important is that the compounds be correctly identified so that downstream water users can be notified speedily. In almost every case, when compounds from a spill event were identified by an EWODS site, this finding was later verified by the reference laboratory through GC/MS.

In addition to chloroform, the next most identified compounds are the highly chlorinated ethanes and ethylenes. Levels of these widely used solvents and degreasing agents do not approach criteria values, but their frequency of detection may justify consideration of source control.

Several distribution patterns for individual purgeable halocarbons can be identified using the percent of samples where the concentration is less than 1.0 µg/l. Chloroform shows the most widespread occurrence for a significant percent of the time at all EWODS sites. During both 1979 and 1980 chloroform levels were equal to or greater than 1.0 µg/l from 10 to 44 percent of the time at Portsmouth and all upstream stations. A similar pattern is observed for methylene chloride, which was reported more frequently at concontrations of 1.0 µg/l or more at Huntington and upstream locations.

The compound 1,1,1-trichloroethane was frequently reported at levels equal to or greater than 1.0 µg/l at Wheeling and Huntington during 1979 and at Wheeling, Huntington, and Portsmouth during 1980. Wheeling and Huntington also show a significant percentage of tetrachloroethylene identifications at the 1.0 µg/l or higher level.

Several compounds are associated with only one sampling location. Chlorobenzene was found at 1.0 µg/l or higher level in more than ten percent of the Huntington samples and in less than one percent of the samples at the other locations. Carbon tetrachloride, 1,2,-dichloroethane, and trichlorethylene were reported at the 1.0 µg/l or more concentration for the St. Albans station on the Kanawha River.

Carbon tetrachloride, the compound that energized the development of EWODS, continues to decline in frequency of detection. In 1979, it was found in more than ten percent of the samples collected and in 1980, it was found in only about seven percent of the samples. It has been replaced by 1,1,1-trichloroethane, a much less toxic organic compound; in fact, no criterion has been set for 1,1,1-trichloroethane by US EPA at this time, whereas criteria have been set for carbon tetrachloride at 4.0 µg/l and other compounds shown in Table 9.

Because of the low concentrations of these compounds and the fact that changes from season to season are small, definitive conclusions regarding seasonal variations cannot be made at this time.

UNUSUAL EVENTS

From 1978 through 1980 six significant spill events have been identified and/or tracked by the system. Four of them originated on the Kanawha River; the others, on the Ohio and the Allegheny. To each case the notification procedures functioned smoothly while GC/MS confirmation was being sought. No drinking water supplies were adversely affected. In most cases analyses by EWODS sites served to confirm the accuracy of the ORSANCO time-of-travel estimating procedures.

CONTINUING NEEDS

Operation of the Early Warning--Organics Detection System for two years has led to a recognition of additional areas for study and desirable expansions of the system's detection capabilities. Of prime importance is the need for a statistical analysis of the vast body of data collected by the system to assist in locating sources and provide a clearer picture of trends

in organic concentrations in the Ohio and the major tributaries. Additional detection capabilities are also desirable. A photoionization detector, which can trace purgeable aromatic hydrocarbons, has been demonstrated at two of the sites and plans are to provide similar equipment for all sites by FY 1983.

More extensive data on a wide range of organics would reinforce and strengthen the commission's entire organics detection program and add an important dimension to EWODS data. In FY 1982 the commission plans to restore its monthly organics sampling at each EWODS site. Samples taken will be analyzed by the reference laboratory for purgeable and solvent extractable organics to provide information about major bioaccumulative organics discharges and additional data to reconfirm EWODS sites' analytical reliability.

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Pittsburgh Department of Water
Western Pennsylvania Water Company
West View Water Authority
Wheeling Water Department
E. I. DuPont de Nemours, Inc.
Industrial Site at St. Albans, WV
Huntington Water Corporation
Portsmouth Water Works
Cincinnati Water Works
Louisville Water Company
Evansville Water Works

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SECTION 1

HISTORY AND DEVELOPMENT

In 1977, spills and accidental discharges of toxic substances into the Ohio River and its tributaries made the Ohio River Valley a focal point for public criticism that water pollution control agencies were not doing their job. When a carbon tetrachloride spill from the Kanawha River was inadvertently allowed to pass through some Ohio River drinking water systems, it became clear to all agencies and individuals dedicated to protecting water supplies that monitoring programs in the Ohio River system were not equipped to detect and respond to unreported spills and discharges of a great many organic chemicals.

Out of such a negative climate, an innovative spill detection system was born. Originally conceived by the Ohio River Valley Water Sanitation Commission (ORSANCO), the system was honed and refined through expert input from concerned water users along the Ohio River and from the US Environmental Protection Agency (US EPA). The two-year history of the Early Warning--Organics Detection System (EWODS) has supported the dedication, determination, and--most of all--the vision of all those involved in making it a reality.

BACKGROUND

In analyzing the causes for the carbon tetrachloride incident, the commission identified several lapses in systems operative at the time of the spill. Of prime consideration was the lack of monitoring on the Ohio and its tributaries for most organic compounds. Research efforts underway at the time were generating data on organics in the Ohio, but that information was neither immediately nor readily available; it was not useful for identifying unusual spill events on an emergency basis. The carbon tetrachloride incident had also dramatized the ineffectiveness of the operative notification scheme; public water suppliers and state water pollution control agencies had not been given timely notice of high carbon tetrachloride levels and were, therefore, unable to initiate effective response measures.

What kind of a monitoring system would fill these gaps? To find the answer to this question, federal and state members of the commission consulted with the ORSANCO Water Users Committee, which represents public and private drinking water facilities using the Ohio and its major tributaries as sources. It was decided that daily analysis for organic compounds was needed to provide adequate detection of unusual spill and discharge events. Prompt analysis of samples was also a requirement if the necessary notification to water users downstream was to be provided. Also essential was an adequate number of sam-

pling sites, strategically located below highly populated and industrialized areas.

One proposal considered was the use of field personnel to collect samples at selected sites; the samples would then be analyzed at several regional laboratories. Because at least five collection units staffed for seven-day-a-week sample collection would be necessary, with a minimum of four laboratories, this option was rejected as too expensive and too difficult to implement. Collection of samples by water utilities and industrial water users and subsequent analysis by reference laboratories were also eliminated because of the time lapse between sample collection and analysis. The organics detection method preferred by the commission and its advisors was a system whereby analytic equipment would be placed at operating water intakes to provide daily analysis for volatile organics. Analytical results could be immediately telecopied to ORSANCO headquarters, where they could be reviewed for unusual levels of organic materials. When unusual events occurred, immediate notification would be provided to states and federal agencies, as well as to downstream water users. Also, the water users could communicate effectively with each other. The commission also decided that a minimum of 11 sites was needed to provide adequate protection to Ohio River water users.

Members of the Water Users Committee expressed enthusiastic willingness to participate in such a system; however, while the commission had funds to initiate the planning of the system and provide some operational support, sufficient funds were not readily available to obtain the analytical and associated equipment needed. Armed with the clear support of valley water utilities, the commission sought funds from US EPA to purchase the required equipment. US EPA expressed a willingness to support a limited demonstration of the system; a grant offer of $100,000 was received in September, 1977. The commission was, however, determined that a full river demonstration of the system was needed. A compromise between the two positions allowed the initiation of a first-phase EWODS, which included seven stations and provided weekday, rather than daily, sampling. The US EPA grant was used to purchase analytical equipment--specifically, gas chromatographs (GC) for four sites and supplemental equipment for GC's already in use at three more locations. The commission based acceptance of the grant on assurance by US EPA that every attempt would be made to provide the additional funds needed to complete the system. EWODS was officially launched in January, 1978, and all the first-phase stations were put into operation during that year.

A grant proposal for the additional equipment needed to complete the network and for operating support was submitted to US EPA in December, 1977. No additional funding was provided in FY 1978, but Congress allocated in the US EPA FY 1979 budget $135,000 for the detection system's four additional stations and $140,000 for operational support to allow expansion to the seven-day-per-week level. The commission committed its support to obtaining state and local funds to continue operation beginning in FY 1981. (For details on the project's funding and budgetary allocation of these grants, see Appendix A).

ANALYTICAL APPROACH

The conceptualization of the Early Warning--Organics Detection System rested in large measure on the applicability of the analytical process chosen. The simple purge/GC analysis, it was theorized, could be practically implemented by laboratory technicians available at water user sites.

During the purge process an inert gas such as nitrogen or helium is used to remove organic compounds from the water by vaporization. The volatility, water solubility, and polar characteristics of the individual compounds, as well as the rate and duration of gas flow and purge temperature, determine which compounds will be removed from the water sample and absorbed on the column. These factors, the percentage of the compound removed by the purge operation, and the GC detector used determine which specific organic compounds will result in formation of a peak on the chromatogram, the line "read-out" of the analytical results. Under a controlled, standardized GC operation, the retention time after the start of the test is a reproducible characteristic of individual compounds and the peak area is a measure of the concentration of the compound. The purge/GC procedure provides quantification of a limited group of organic compounds generally designated as volatile organics.

OBJECTIVES AND BENEFITS

In initiating the project, the commission established a number of objectives for the system, based on the recognized needs and the potential of the method chosen:

1. To provide a system for identification of increased levels of purgeable organic compounds and for real-time notification of Ohio River public water supplies when unusual levels of these compounds are detected, with time-of-travel estimates and corresponding notification to the appropriate state and federal regulatory agencies;

2. To establish a baseline of the levels of these compounds at the sampling locations, identify the variability of these levels in relation to river flow, sampling location, and seasonal changes, and to identify river segments where variations in the type or concentrations of specific compounds are most significant;

3. To establish a basis for NPDES permit limitations or other effluent control programs and for stream quality criteria for one or more of these compounds which have potential health or aquatic life significance.

Subordinate objectives were:

1. To provide definitive information, within the limits of the purgeable GC analysis, on levels of organic chemicals in the Ohio River system;

2. To encourage development of organic analytical capability by state or reference laboratories in the Ohio River Basin;

3. To supplement the commission's ambient organics monitoring programs;

4. To provide information on the in-stream persistence or die-away of the identified compounds.

It was envisioned that the system, if successful, would have a number of real benefits in the basin. Most important, it would provide an additional and essential safeguard for the three million people served by public drinking water facilities using the Ohio River and the major tributaries as sources. The timely detection of increased or unusual levels of volatile organic compounds in source waters and immediate notification of downstream water users would permit adjustment in water treatment practices to reduce levels of these materials in the finished water and thereby ensure a higher quality drinking water for the consumer. In addition, the location of the segment of the river(s) affected by a given incident would aid the regulatory agencies in identifying the source or sources and initiating appropriate corrective action. It was also theorized that the presence of an organics monitoring system, even a limited one, would serve as a deterrent to surreptitious spilling or discharging of organic wastes and would emphasize the need for vigilance by dischargers and at facilities located adjacent to the rivers monitored.

Technical benefits were also envisioned for the system. The continuing record of daily and seasonal variations of the compounds measured and the relationship of concentration to river flow, weather conditions, and other water quality characteristics would provide a baseline of data which could aid in establishing regulatory programs. The project would also offer a practical demonstration of a protocol for water utilities to use in detecting organic substances. And last, the extensive data on organic materials in river water would serve as a cornerstone for building a comprehensive body of information about organic materials in water, sediment, and aquatic life.

LIMITATIONS

Though the hopes for the Early Warning--Organics Detection System were many, its limitations were also carefully documented. The analytical method chosen limited the number and types of organic compounds detectable to those which are volatilized under specific GC conditions used. The selection of organic compounds that can be detected by this method is relatively narrow, though it includes compounds of specific interest in the Ohio River system, such as carbon tetrachloride and chloroform. After two years of EWODS operation, expansion of its detection capabilities is now planned.

Even the minimum 11 stations eventually developed by EWODS leave some sections of the river essentially uncovered. When the system was set up, it was supposed that experience with the sites chosen might suggest the advisability of changes and/or additions. No changes have been made to this point, though some sites have proven to be more essential than others in protecting water users (Section 5).

Because of the innovative nature of the system, it was impossible to predict the optimum number of samples per day needed to accomplish project objectives, though it was clear that that number would vary with river flow and related travel time. In practice, the number of samples which can be analyzed at an installation is dependent on the GC cycle time and on personnel hours that can be committed to the program. Only in emergency or alert situations has more than one raw water sample been analyzed on a given day. When special samples have been necessary, however, utility cooperation in conducting analyses during overtime hours has been excellent.

Even with these expected limitations, the detection system envisioned by the commission is unique to the Ohio River Valley. The system has fulfilled most of the objectives in the original proposal; its potential for meeting all of its goals has been recognized.

SECTION 2

IMPLEMENTATION

SITE SELECTION

In selecting specific sites for the EWODS, the most important requirement was that the site be a water intake on the Ohio River or one of the major tributaries. Sites to consider, therefore, included all of the 25 water supplies and 100 industrial and power plants along the Ohio River, four public water supplies on the lower reaches of the Allegheny, two water utilities on the lower Monongahela and one on the Beaver River.

Several criteria were used in site selection. Adequate laboratory facilities were required as well as 24-hour operation. The water plant or industry selected also needed to provide personnel capable of learning and conducting the required analyses, and most of all, willing to devote time and effort to the project. Of prime importance also was the location in relation to potential sources of pollution and public water supply intakes. Although sampling sites which might provide more information about stream water quality existed, the major priority of the project to protect water supplies was the prime criterion in the selection of the final sites. A typical interagency agreement between ORSANCO and the cooperating utility is shown in Appendix C . The final sites chosen are shown in Table 1.

TABLE 1. EWODS SITES LOCATIONS

River	Water Intake	Mile Point Ohio	Mile Point Tributary
Allegheny (B)	Pittsburgh Dept. of Water, PA	0.0	7.4
Monongahela (C)	Western Pennsylvania Water Company	0.0	24.4
Ohio (C)	West View Water Authority, PA	4.5	
Ohio (A)	Wheeling Water Department, WV	86.6	
Ohio (C)	Parkersburg, West Virginia	190.3	
Kanawha (A)	St. Albans, West Virginia	265.6	38.3
Ohio (A)	Huntington Water Corp., WV	304.2	
Ohio (A)	Portsmouth Water Works, OH	350.6	
Ohio (B)	Cincinnati Water Works, OH	462.8	
Ohio (B)	Louisville Water Company, KY	600.6	
Ohio (C)	Evansville Water Works, IN	791.5	

A - First-phase installation, project GC
B - First-phase installation, utility-owned GC
C - Second-phase installation

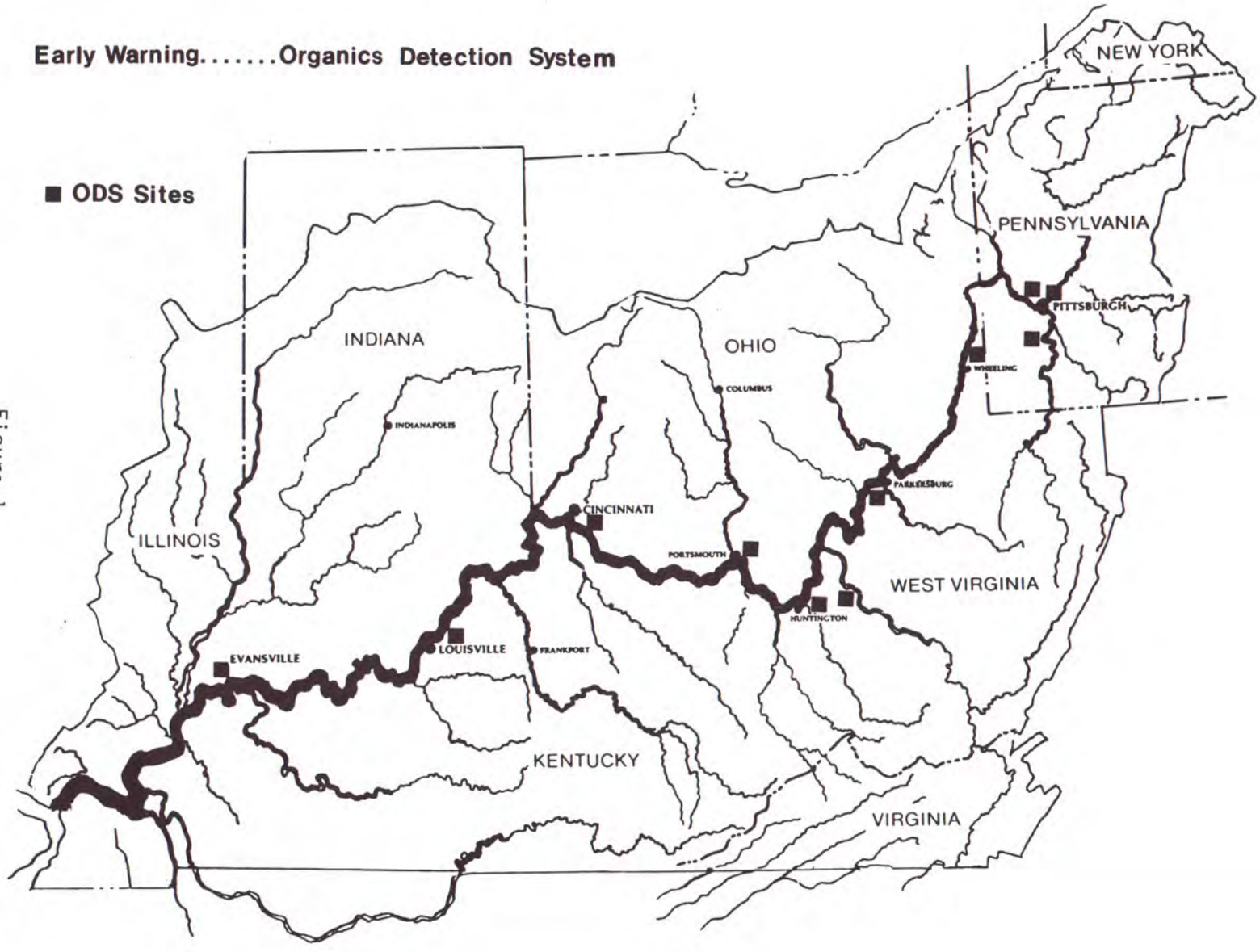

Early Warning.....Organics Detection System
■ ODS Sites
NEW YORK
PENNSYLVANIA
PITTSBURGH
WHEELING
INDIANA
OHIO
COLUMBUS
INDIANAPOLIS
PARKERSBURG
CINCINNATI
ILLINOIS
PORTSMOUTH
WEST VIRGINIA
HUNTINGTON
EVANSVILLE
LOUISVILLE
FRANKFORT
KENTUCKY
VIRGINIA

Figure 1

The proposed locations were selected to provide several typical monitoring situations. The utilities operated by the city of Pittsburgh on the Allegheny River and by the Western Pennsylvania Water Company on the Monongahela River represent initial points for the monitoring system which are impacted by upstream dischargers and provide information for downstream water users.

The West View Water Authority plant and the Wheeling water utility on the Ohio River are downstream from significant segments of the major municipal/industrial complex extending from Pittsburgh to below Wheeling. The industrial intake below Parkersburg is downstream from major municipal, industrial, and tributary discharges to the upper Ohio and provides information on volatile organics entering the next river segment. The sampling location on the Kanawha River identifies purgeable organics in the river below the Charleston chemical complex.

The Huntington, Portsmouth, Cincinnati, Louisville, and Evansville locations are larger water utilities where significant wastewater discharges are many miles upstream on the Ohio River and on major tributaries. They provide a gauge of the dilution rate of compounds detected upstream and serve as sentinels for their downstream colleagues, while collecting valuable information for their own treatment programs.

Two network locations are at different sites than initially proposed. On the Monongahela River the analytical equipment was installed further upstream at the Aldrich plant of the Western Pennsylvania Water Company because laboratory space was not available at the company's Hayes Mine Plant. It is planned to move the GC equipment to the Hayes Mine plant when its new laboratory is constructed.

The initial upstream Ohio River installation had been proposed to provide a sampling location between the confluence of the Beaver and Ohio Rivers at mile 25.4 and the Pennsylvania-Ohio-West Virginia state line at mile 40.0. When it was determined that none of the water users between mile 25.4 and 65.2 could provide suitable laboratory personnel and facilities, the West View Water Authority was chosen as the initial Ohio River site. The installation at this location will provide information on purgeable halocarbon compounds downstream from the Allegheny and Monongahela Rivers and the 200 MGD Allegheny County Sanitary Authority's regional sewage treatment plant.

Each participating facility has entered into an interagency agreement with ORSANCO detailing the responsibilities of each agency. To provide a basis for determining the value of the participant's service, each site periodically files a report of daily personnel hours allocated to the system and the appropriate hourly rate (see Appendices A & C).

ANALYTICAL EQUIPMENT AND SUPPLIES

Three broad categories of laboratory components are needed for the operating system: 1) a gas chromatograph unit, consisting of the purge device, gas chromatograph (GC) detectors, and the associated microprocessor controller;

2) an appropriate gas system, including high-pressure gas in cylinders, pressure regulators, traps and piping; and 3) expendable supplies, including columns and packing materials, syringes, chemical standards, microsyringes and micropipettes, sample containers, etc.

Gas Chromatograph and Associated Equipment

GC equipment was purchased under two separate grants. Specifications for the first group of GC's were prepared, bids received, and the purchase contract awarded in November and December, 1977. The basic unit was to consist of:

1. A GC designed to operate with two columns and two detectors;

2. A liquid sample concentrator of the Bellar purge type for measurement of volatile organic compounds;

3. A built-in microprocessor for control of such parameters as purge time, injection temperature, oven temperature, rate of gas flow, etc;

4. A printer/plotter controlled by the GC microprocessor and capable of producing a visible, transmittable trace of the gas chromatogram, along with a printed record of retention times of various peaks, peak areas, concentrations, sample identification and other pertinent information, all on a single output sheet.

In addition to four complete units, the supplier was to provide additional purge units, microprocessor, and detectors to bring the operating capability to the Varian Model 3700 GC at Cincinnati, the Hewlett-Packard Model 5830A GC at Pittsburgh, and 5840A GC at Louisville to the same analytical capability as the complete project units. The proposal also called for the supplier to provide a five-day hands-on training course for the potential operators from each participating site, one-day operator instruction after the unit was installed, and a service kit containing spare parts and components, tools, an operating manual, and a service manual. The proposal required that the successful bidder supply the total unit: the purge unit, GC and microprocessor, sensors, and the output device.

The contract eventually signed with Perkin-Elmer Corporation provided for units consisting of the SIGMA/1 Gas Chromatograph, including microprocessor and printer/plotter, the CDS 310-012 trapping concentrator manufactured by Chemical Data System; Model F1000-RG halogen-sensitive electrolytic conductivity detector manufactured by Western Scientific Associates; and the Perkin-Elmer Model 331-31000 FID detector.

Essentially the same specifications were used for the second set of equipment in a request for proposals sent out in April, 1979. The most significant difference was that separate proposals would be accepted for the purge unit, GC and microprocessor, and detectors. Separate bids were accepted for the Spectro-Physics microprocessor and Varian GC, the CDS purge unit, and

Western Scientific electrolytic conductivity detectors. Table 2 details the exact equipment in operation at each site. Participant-owned equipment from the first phase of the project has in some cases been replaced by equipment purchased with project funds. Flame ionization detectors and electron capture detectors are not currently being used. Photoionization detectors have been added at two sites and used experimentally, prior to purchase of similar units for other sites.

TABLE 2. EQUIPMENT AT EWODS SITES

EWODS Sampling Locations	Location	Purge & Trap System	GC System	GC Detector[2]
Pittsburgh, PA	Allegheny	CDS[1]	Varian[3]	CCD, FID
West Penn Water, PA	Monongahela	CDS	Varian[3]	CCD, FID
West View, PA	Ohio	CDS	PE SIGMA I	CCD, FID
Wheeling, WV	Ohio	CDS	PE SIGMA I	CCD, FID, PID
Parkersburg, WV	Ohio	CDS	Varian[3]	CCD, FID
St. Albans, WV	Kanawha	CDS	PE SIGMA I	CCD, FID
Huntington, WV	Ohio	CDS	PE SIGMA I	CCD, FID, PID
Portsmouth, OH	Ohio	CDS	PE SIGMA I	CCD, FID
Cincinnati, OH	Ohio	Tekmar	Varian 3700[4]	Tracor Hall 700, ECD
		CDS	Varian[3]	CCD, FID
Louisville, KY	Ohio	CDS	HP 5840[4]	CCD, FID, ECD
Evansville, IN	Ohio	CDS	Varian[3]	CCD, FID

[1]CDS 310-012 Sparging Concentrator
[2]CCD Coulson Electron Conductivity Detector
FID Flame Ionization Detector
ECD Electron Capture Detector
PID Photoionization Detector
[3]Spectro-Physics microprocessor and Varian GC
[4]GC system owned by participant

Although the purge-and-trap unit and GC detector are the same at most locations, the multiple sources of the GC and microprocessor output systems complicate service and repair and require separate operating instructions and programming. There are no identified differences in sensitivity or analytical results obtained from the various units when they are all in good working order. However, variations in design, ruggedness, availability of parts, accessability for repair, etc., all tend to complicate quality assurance procedures.

Compressed Gases and Related Equipment

The GC equipment requires compressed air to operate microprocessor-controlled hydraulic valves. Helium or nitrogen is used for the purge-desorb step and desorption from the GC column. Hydrogen is needed for combustion in the electrolytic conductivity detector. Since these high purity gases are obtained from high-pressure, 100-125 pound cylinder supplies, at the start of

the project price quotations were requested from the major suppliers of compressed gases. Linde was accepted as the supplier for the three gases. Contracts were signed with individual suppliers of Linde gases in the several metropolitan areas. The necessary stainless steel diaphragm, two-stage regulator, silica gel molecular sieve filter with a moisture indicator, and copper tubing and connectors were supplied by Linde.

To avoid downtime resulting from order or delivery delays, two cylinders of each gas are provided at each location. One cylinder is on line, while the second cylinder is available for replacement.

Expendable Supplies

The sampling and analytical procedure requires a variety of supplies, including such items as two-ounce and one-gallon sample bottles, microsyringes, purge and GC columns and packing material, resins for gas drying and purification, as well as the electrolytic conductivity detectors, gas system fittings, glass purge vessels, etc.

Since most of these materials are standard GC or regular laboratory supplies, they are purchased by ORSANCO from the various suppliers at catalog or list prices. As appropriate, stocks of individual items are maintained at project headquarters or by the surveillance specialists.

The capability of the purge-GC system to identify and quantify purgeable organic compounds is dependent on the compound used as the internal standard for all GC runs and the calibration standards used to provide standard retention times for the compounds to be identified. The chemical used as the internal standard is purchased from Chem Services, supplier of GC-grade chemicals. Pre-mixed, standardized calibration standards are purchased from Radian Corporation, Austin, Texas.

REFERENCE LABORATORY

In addition to the 11 sites, a contracted analytical laboratory is also essential to the implementation of the project. The initial project design called for the reference laboratory to perform the following functions:

1. Confirmation, on a priority basis, of the identity and concentration of compounds found at unusual levels at the EWODS sites and analysis of a larger sample by solvent extraction, solvent concentration, GC/detector or GC/MS for high levels of non-purgeable organic compounds;

2. Assistance in quality assurance through analysis of duplicate samples of raw water, to confirm the analysis at the site;

3. Analysis of monthly raw water samples from EWODS and other monitoring locations for purgeable and non-purgeable organic priority compounds.

During the start-up phase of the project a letter of inquiry regarding capability to provide reference laboratory services was sent to all identified commercial water laboratories in the Ohio Basin. Based on experience from an

earlier project, which involved analysis for trihalomethanes in raw and finished waters, a detailed request for proposal was formulated and sent to each interested laboratory.

After evaluation of the five proposals received, a contract was signed with PEDCo Environmental, Cincinnati, Ohio, on the basis of available facilities and personnel and comparative analytical costs. In addition to special priority analysis of samples, the contract provided for analysis of compounds in five analytical groups: purgeable organics by electrolytic conductivity and flame ionization detectors, and solvent extractable organics by electrolytic conductivity, flame ionization, and nitrogen-sensitive detectors. Very little useful data was obtained from the solvent extraction samples and such data does not appear in this report. Samples analyzed to verify and detail unusual levels of organics could include analysis for any one or more of these analytical groups, as determined by the project staff.

Results from analyses of the trihalomethane project samples showed that neither the flame ionization nor nitrogen compound detectors had the sensitivity to identify appropriate organic compounds in the Ohio River and tributary raw water samples. Based on these results PEDCo was not requested to implement procedures for these groups of compounds.

On quality assurance samples which were normally run two to three weeks after collection, PEDCo consistently showed lower concentrations or did not find compounds when results were compared to duplicate analyses at the EWODS sites. Replacement of the teflon septa with an aluminum septa on the two-ounce vial for the purgeable analysis improved the comparability of these duplicate analyses. PEDCo also analyzed the US EPA high and low concentration check samples used as part of the overall project quality assurance program (see Section 3).

Confirmation samples were analyzed on a priority basis--purgeable samples on receipt and solvent extractable samples within one to three days. These analyses generally confirmed and verified the EWODS data.

The request for proposals had included an estimate of the number of routine purgeable and solvent extractable samples which would be submitted for analysis. Because of costs and time extensions on the project, the number of samples actually run was only approximately one-third of the estimated program needs. Thus, limited project funding could not support the reference laboratory program necessary to initiate and maintain a satisfactory analytical and quality assurance effort over the entire time period of the project.

The one-year analytical contract with PEDCo was extended for a second year in June, 1979. In the spring of 1980, new contract proposals were requested and a contract signed with Environmental Consultants, Clarksville, Indiana. This contract was limited primarily to confirmation samples because of budget limitations.

PROCEDURES

Standardization of all sample and analytical procedures and a well-de-

fined quality assurance program are essential if the analytical results are to be valid and, with 11 different laboratories, comparable. Although details of the analytical procedure vary for the different GC units, the same general procedure is followed at all EWODS locations.

Sample Collection

Daily raw water samples are collected from the water intake system prior to chlorination or other treatment operations. A complete set of daily samples consists of: duplicate two-ounce raw water samples collected in vials without agitation but with complete filling and sealing; one one-gallon sample for possible solvent extraction and analysis; duplicate two-ounce vials of organic-free water.

GC Analysis

An organic-free water sample is spiked with the internal standard and analyzed. If GC peaks indicate extraneous organic compounds or if the retention time of the internal standard changes, corrective action is completed before the raw water sample is run. A 10ml sample of raw water is then injected with the internal standard and analyzed.

Initially the chromatogram and quantification printout was telecopied to ORSANCO for evaluation. If high levels of one or more compounds were observed the project staff would request copies of the output from the system blank (organic-free water) and last calibration runs. In 1980, limited funds required development of a less costly but acceptable procedure. Currently the GC operator evaluates the chromatogram. If high levels of one or more compounds or system problems are observed, the operator contacts headquarters staff and transmits the chromatogram for staff evaluation. The arbitrary levels of concern set by ORSANCO staff are any GC peak quantified as greater than 25 µl or greater than ten times the concentration of the same peak on the previous day. If the GC results are in the normal range, the operator discards the remaining samples, cleans the bottles and tallies the output on a weekly summary sheet which is telecopied each Friday and mails the week's GC output sheets to ORSANCO for review.

The standard routine also requires that the purge/GC calibration standard be run twice a week or whenever new GC columns are installed. The retention time and peak area of each standard compound relative to the internal standard are stored in and used by the microprocessor to interpret the detector output from sample runs.

When high levels of one or more compounds are reported, the staff assesses the data and may request additional analyses or declare an "alert." In either case the two-ounce raw water and organic-free samples and the one-gallon sample are packed in iced containers and shipped express to the reference laboratory for immediate analysis.

A detailed operating manual has been prepared. The manual provides step-by-step instruction tailored to the individual GC/microprocessor combination (See Appendix B).

Equipment Service and Maintenance

Although service personnel from the equipment supplier are necessary to the installation and testing of each GC system, the continuing cost of such service becomes significant; therefore, a multi-level service system has been developed utilizing utility and project personnel whenever possible. Four service and maintenance levels are provided.

1. The GC operator performs routine equipment housekeeping, changes gas cylinders, checks for and corrects gas leaks and other basic service operations. At some locations the operators repack and validate the purge trap and GC column. If the operator has problems, he contacts the project personnel for assistance. Telephone discussion and instructions for corrective action may be sufficient for the operator to correct the problem.

2. ORSANCO field personnel operating out of Pittsburgh, Cincinnati, and Evansville have been trained in GC operation and routine maintenance. these individuals visit the EWODS sites every other week to review operations with the laboratory personnel, check and service the GC unit, repack traps and columns, and verify proper operation of the equipment. Test equipment and tools permit limited field repairs and replacement of the electronic boards after consultation with staff. Since most of the EWODS locations are also ORSANCO manual sampling or electronic monitoring locations, the field personnel (surveillance specialists) combine EWODS visits with other duties.

3. A staff chemist is experienced in instrumental analyses and servicing of analytical equipment. When the surveillance person cannot correct a malfunction, the chemist may visit the site and take corrective action.

4. As appropriate, equipment such as the purge unit, detector, or GC components may be sent to the manufacturer for service. Field service by the manufacturer may also be requested.

This service and maintenance procedure minimizes equipment downtime and ensures that valid analytical results are obtained. It is an essential component of any successful monitoring network. In general, the most prevalent problems experienced have included gas leaks at the various connections, loose electrical connections, poor electrical contacts, and failure of electronic components.

Training

Requests for proposals and purchase contracts for the GC equipment included a seminar for potential operators and at least one day of on-site training when the equipment was installed. The seminar was to provide information on basic GC principles, the mechanical and electrical components of the system, and some hands-on operating experience. The first training session, conducted by Perkin-Elmer in 1978, was unsatisfactory for several reasons. Because the equipment transport was delayed, the trainees were not given training on func-

tioning equipment. Much of the information was too complex, and the following on-site training was not thorough enough. A subsequent session for the second phase of equipment installation was more successful. This session was held in cooperation with the US EPA's Briedenbach Environmental Research Center in Cincinnati, Ohio and involved detection equipment vendors who provided hands-on training to ODS operators. Furthermore, ORSANCO project personnel and surveillance specialists have gained considerable skill and expertise at instrument operation and are able to provide on-site training for current and new operating personnel.

Development of Analytical Standards

The calibration standard has been changed several times to minimize coelution problems and to accommodate compounds identified in raw water samples. Table 3 shows the composition of the calibration standards used. The first standard contained several coeluters. The compound 1,1,2,2-tetrachloroethane coeluted with both the internal standard, 1,4-dichlorobutane, and tetrachloroethylene. After use of the new internal standard began, coelution was still a problem between tetrachloroethylene and 1,1,2,2-tetrachloroethane. Also, it was discovered that the tetrachloroethane was an unstable compound, degrading to the two dichloroethanes and the two trichloroethanes contained in the purge standard.

A second purge standard was developed, with the addition of two early eluters discovered by PEDCo and the removal of 1,1,2,2-tetrachloroethane. This standard still contained coeluting compounds: dibromochloromethane, 1,1,2-trichloroethane and cis-1,3-dichloropropene. In an effort to eliminate this problem, 1,1,2-trichloroethane was removed, allowing the remaining two compounds to elute individually. Another early eluter, thought to be 1,1-dichloroethylene and detected in the upper Ohio River was added to this version of the purge standard, which went into use in March, 1980.

The current standard, developed and put in use in August, 1980, contains an additional compound, 1,4-dichlorobenzene, which is detected in 31 percent of the samples at Cincinnati. The trans and cis isomers of 1,3-dichloropropene have been eliminated from the current standard because they are rarely, if ever, detected in raw water samples and were causing coelution problems. The purgeable standard now contains 16 components and is producing concise, well-resolved chromatograms at all EWODS sites.

OPERATIONAL MODIFICATIONS

The difficulties encountered in putting the system into operation have led to a number of modifications to improve the analytical process and make the system more reliable. These modifications have extended to all major elements of the analytical unit.

Purge Unit

Early studies with the 16-component purgeable standard showed that the purge rate (40 ml/min helium flow) and purge period (11.0 $\pm$0.5 minutes) recommended by US EPA did not provide complete purging of the standard. Procedural modifications included:

1. Changing the design of the purge reservoir to ensure greater gas/li-

quid contact;

2. Decreasing total sample volume from 20 ml to 10 ml (At several stations where different equipment is used, the volume in the purge vessel is limited to 5 ml;*

3. Increasing the helium flow rate from 40 ml/min to 60 ml/min;

4. Increasing the purge time from 11 to 16 minutes.

The area of the purge standard's bromoform peak was considerably higher with the revised procedure, indicating more complete purging.

The CDS traps were initially packed with only Tenax GC; however, EPA, in using this packing with an eight-inch trap, found that some low boiling compounds, such as methylene chloride, were not retained. US EPA recommended using silica gel to retain the low boiling compounds. Though the CDS traps are 24 inches long and appeared to retain the low boiling compounds, they were changed at several locations to include silica gel, but the gel blocked the traps. Consequently, the original traps were returned, with no subsequent problems in retaining low boiling compounds.

Experience with CDS purge units indicated mechanical and electrical modifications which would increase the reliability of the unit. These modifications were incorporated in later production units and older system units were modified.

Column Packing

The GC column length and packing material determine the elution order, retention time, and separation from other compounds. Initially a nine-foot, 1/8-inch-ID glass column was used. It was packed for the first foot with 60-80 mesh chormosorb-W coated with three percent carbowax 1500 and the remaining eight feet with 60-80 mesh carbopack-C coated with 0.2 percent carbowax 1500. Initial experience showed that prepacked columns could not be shipped or transported, and materials were provided for packing at the sites.

During the course of the project, column length has varied from six to 12 feet and column material has been changed from glass to stainless steel and finally to nickel.** In late 1977, revised US EPA procedures recommended use of a six-foot, 0.1 inch-ID glass or stainless steel column packed with n-octane on 100-120 mesh porosil-C. This packing material was tested at the Pittsburgh site with a 12-foot, 0.147-inch ID stainless steel column. Tests showed that this column provided good separation of the calibration standard compounds, reduced coelution, and ease in packing.

* The Louisville site continues to use a 20 ml sample because of the low concentrations of organics at that part of the river.

** Since Louisville owns its own GC, it has continued to use a glass column, as specified in the original proposal.

TABLE 3. COMPOSITION OF CALIBRATION STANDARD

Compound	Date of First Use Initial	10/79	3/80	8/80	Lower Detection Level µg/l
Methylene chloride		X	X	X	0.1
Chloroform	X	X	X	X	0.1
Carbon tetrachloride	X	X	X	X	0.1
1,1,1 - trichloroethane	X	X	X	X	0.1
1,2 - dichloroethane	X	X	X	X	0.1
Dichlorobromomethane	X	X	X	X	0.1
Trichloroethylene	X	X	X	X	0.1
1,2 - dichloropropane	X	X	X	X	0.1
Trichlorofluoromethane		X	X	X	0.1
Chlorodibromomethane	X	X	X	X	0.1
1,1,2 - trichloroethane	X	X			0.1
1,1 - dichloroethylene			X	X	0.1
Tetrachloroethylene	X	X	X	X	0.1
Bromoform	X	X	X	X	0.1
Chlorobenzene	X	X	X	X	0.1
Trans-1,3 - dichloropropene	X	X	X		0.1
Cis - 1,3 - dichloropropene	X	X	X		0.1
1,1,2,2 - tetrachloroethane	X				0.1
1,4 - dichlorobenzene				X	0.1
1,1 - dichloroethane	X	X	X	X	0.1

Other column packings tested have included a six-foot column of n-octane on porosil-C, followed by a six-foot column of 0.2 percent carbowax 1500 on carbopack-C, a three-section column consisting of influent and effluent sections of four feet of 0.2 percent carbowax 1500 on carbopack-C and four-foot center section of 1 percent SP-1000 on carbopack-C and a Supelco prepacked column of SP-1000 shipped to Louisville for evaluation.

The most successful columns have been: 1) 12-foot, 1/8-inch stainless steel packed with one foot of three percent carbowax 1500 on 60-80 mesh chromosorb-W and 11 feet of 0.2 percent carbowax 1500 on 60-80 mesh carbopack-C; 2) 12-foot, 3/16-inch stainless steel packed with n-octane on 100-120 mesh porosil-C; and 3) nine-foot, 1/8-inch nickel, packed with nine inches of three percent carbowax 1500 on 60-80 mesh chromosorb-W and eight feet, three inches of 0.2 percent carbowax in 60-80 carbopack-C.

The 80-100 mesh carbopack-C has been found to be so fragile that it plugs the column and reduces the flow below acceptable levels. The one percent SP-1000 on carbopack-C has not been successfully applied, though it has been tried on four separate occasions. None of the columns gave acceptable flow. Supelco packed a 12-foot, 1/8-inch stainless steel column for the project. In tests it gave 43 ml of flow at 50 pounds per square inch (psi) helium. Once installed at the Louisville site, however, the column gave only 20 ml flow at 60 psi helium; acceptable flow is 40 ml at 60 psi.

The nickel column has many of the same advantages as glass, and it does not break so easily. It is especially effective in handling bromine compounds, which may "get lost" in stainless steel columns packed with carbowax on carbopack.

Electrolytic Conductivity Detector (CCD)

The halogen-sensitive detector's function is based on the reaction between the halocarbon and hydrogen to form a halogen acid which is then absorbed in deionized water. This solution passes through a flow cell, where the conductivity is measured. The change in conductivity is a direct measure of the halogen content and, therefore, the concentration of the halocarbon in the water sample. During the project the flow cell section of the detector was redesigned by the manufacturer to increase the sensitivity and efficiency of the unit. The redesigned flow cell increased the sensitivity at least two orders of magnitude over the older flow cell. All of the older detectors have been fitted with the new style of flow cells.

Resins utilized early in the project were found to be short-lived in that their coatings would deteriorate and cause resin failure. A proprietary mixed-bed resin was developed for Western Scientific Associates (the detector supplier) which has proven to be satisfactory. This resin provides deionized water for the flow cell for approximately three to four months.

Site Operation Performance

The many difficulties encountered in putting the system into operation resulted in numerous modifications. The modification noted in the sections

on purge unit, column packing and CCD detector allowed the sites to operate the equipment more reliably as the project developed. In early 1979, the operation had reached a better than sixty (60) percent operation and by the end of the project, about eighty (80) percent operation had been obtained. Table 4 - Summary of Operation Status gives a summary of the operation of the system in 1979 and 1980.

The above table also displays the amount of time that the samples were quantified. This is less than the operation performance because on some days the data could not be accepted because it did not meet the acceptable limits set by the quality control program.

This table also indicates the number of calibration standards performed by the sites. Examples of these are shown in Figures 2, 3, and 4.

DATA UTILIZATION

GC analytical results are presented as a printout of data after microprocessor interpretation. Figures 2, 3, and 4 show calibration standards run in Perkin-Elmer, Hewlett-Packard, and Varian GC's. Printouts from GC units differ somewhat but provide comparable data. The first part of each output is the chromatogram showing peak height and the retention time, which is printed near the end of the peak. These graphs are printed as the data are generated. The lower section of each figure shows the microprocessor interpretation of the data as the retention time, area under the peak, type of base line correction, relative retention time, response factor, concentration, and the identity of the compound. The number after each name is the identification number of the compound; the Hewlett-Packard printout provides only the identification number.

Use and handling of these data involve several steps, including operator assessment, transmission to ORSANCO, immediate review, storage, and long-term evaluation.

Operator Assessment

Each daily set of GC runs includes at least one system blank--organic free water plus the internal standard--and one or more water sample. Two or three times a week a run is also made using a multi-compound calibration standard, as shown in Figures 2, 3, and 4. With experience, the operator can determine whether the GC is operating properly from the output of the blank and calibration runs.

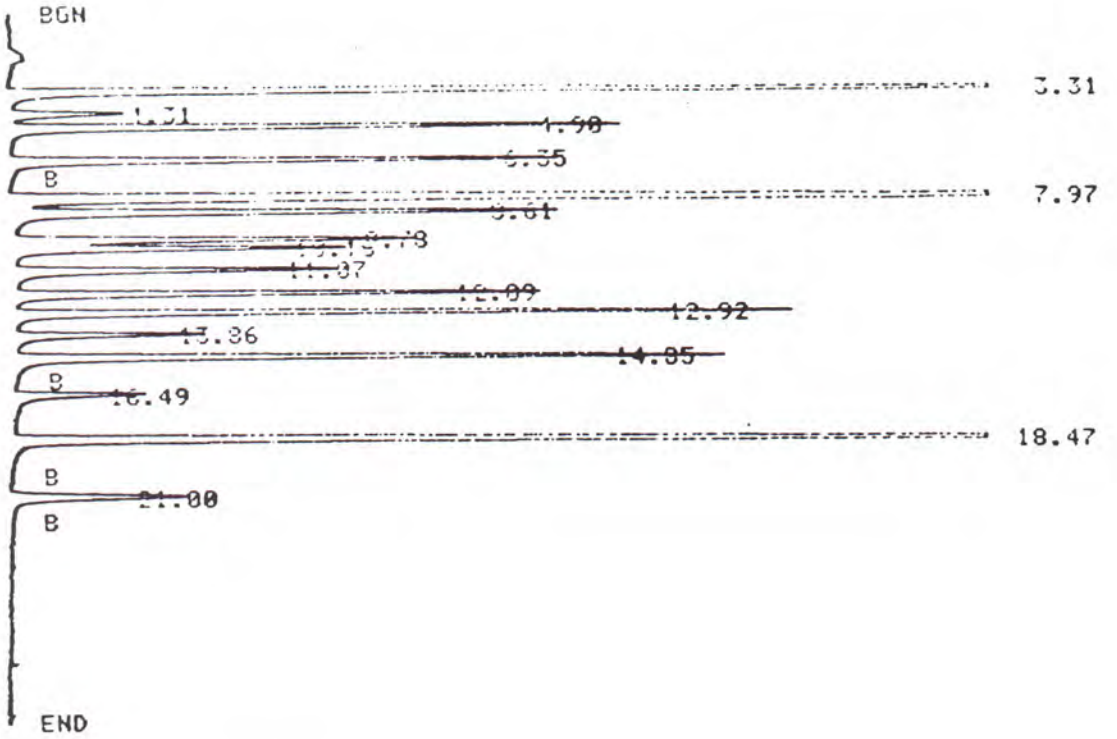
At any one site the raw water chromatograms have a pattern of compound occurrence and concentration, a background pattern. Comparison of a chromatogtam with this general background allows the operator to identify significant deviations--abnormally high concentrations of compounds normally present or significant concentrations of compounds not normally observed at the site. If such a deviation occurs, the operator calls the EWODS staff and discusses the significance and appropriate follow-up of the deviation from normal.

TABLE 4. Summary of the Operation Status

Period	Raw Water Samples*			Purge-Internal Standard	Scheduled Operating Days	% Operation	
	Anal'd	Quant'd	Special			Anal'd	Quant'd
Jan - March 1979	294	241		74	438	67.1	55.0
Apr - June 1979	314	298		59	516	60.9	57.8
July - Sept 1979	445	384		48	614	74.0	62.5
Oct - Dec 1979	568	506		112	698	81.0	72.5
Jan - March 1980	500	487		81	700	71.0	69.5
Apr - June 1980	561	537		113	730	77.0	73.6
July - Sept 1980	637	621		83	777	81.9	79.9
Oct - Dec 1980	674	625		110	821	82.0	76.1
TOTAL	3993	3699		680/17.0%	5294	74.4	69.9

* Anal'd - # of samples analyzed

Quant'd - # of samples quantified



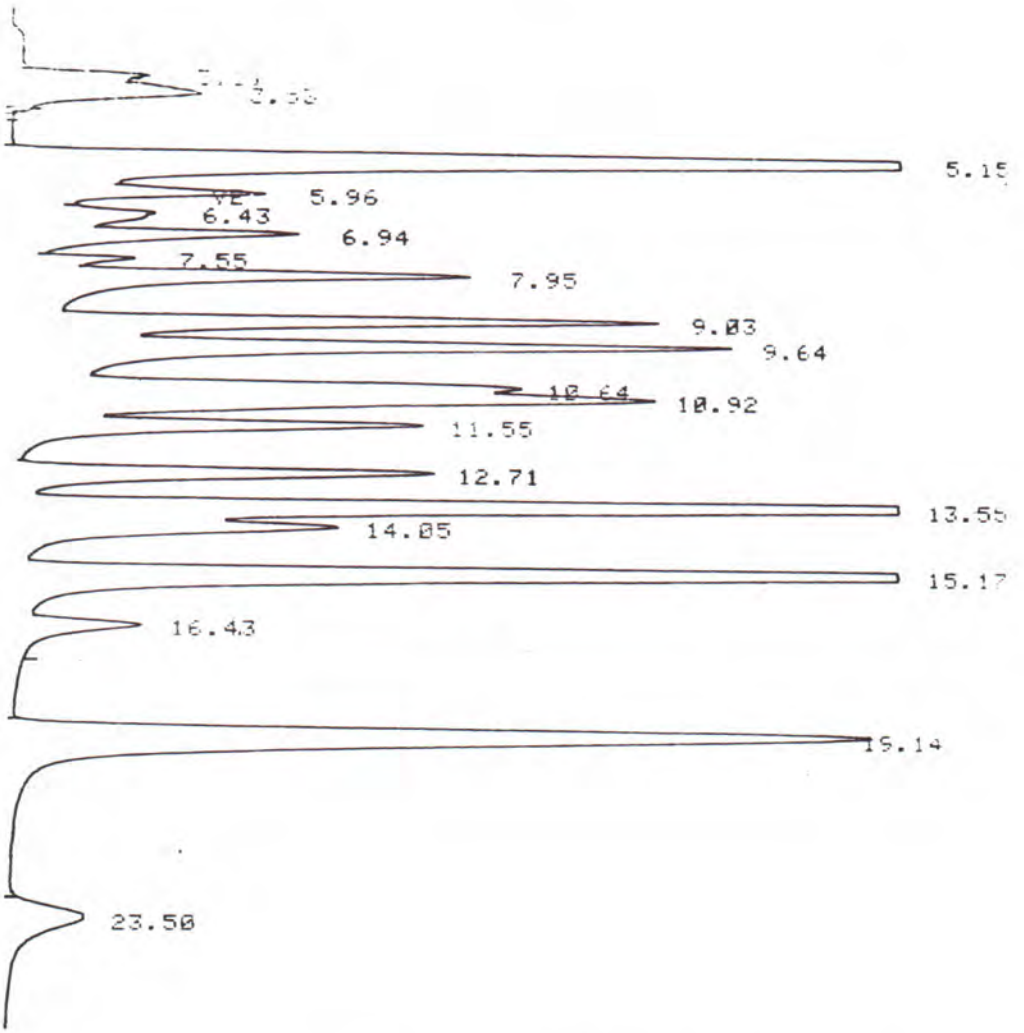
INST 1 METH 10 FILE 39

RUN 1 10 : 46.5 1 / 30 / 81

SENSITIVITIES 250 4

TIME	AREA	BC	RRT	RF	C	NAME
3.31	2.2968	T	2.228	1.030	3.4105	METHYLENE CHLORIDE-2:
4.31	0.2068	T	2.902	2.784	2.0474	TRI-CL-F-METHANE-3:
4.90	0.9788	V	3.299	0.617	2.1471	1,1DI-CL-ETHYLENE-21:
6.35	0.8981		4.276	0.650	2.0754	1,1DICHLOROETHANE-4:
7.97	3.3921	T	5.367	0.358	4.3174	CHLOROFORM-5:
8.61	0.9317	V	5.797	0.623	2.0636	1,2DICHLOROETHANE-6:
9.78	0.6335	T	6.585	0.901	2.0453	1,1,1TRICL-ETHANE-7:
10.16	0.5554	V	6.841	1.035	2.0437	CARBON TET-8:
11.07	0.5258	V	7.454	1.196	2.2360	BR-DICL-METHANE-9:
12.09	0.8088	V	8.141	0.688	1.9734	1,2DI-CL-PROPANE-10:
12.92	1.1498	V	8.700	0.530	2.1665	TRICHLOROETHYLENE-12:
13.86	0.3106	V	9.333	1.731	1.9116	DIBR-CL-METHANE-13:
14.85	1.1251		10.000	1.000	4.0000	2-BR-1-CL-PROPANE-IS:
16.49	0.2518	V	11.104	2.132	1.9039	BROMOFORM-16:
18.47	2.5316		12.437	0.680	6.1204	TET-CL-ETHYLENE-17:
21.00	0.3729		14.141	1.522	2.0179	CHLOROBENZENE-19:

Figure 2. Perkin-Elmer Calibration Standard Chromatogram

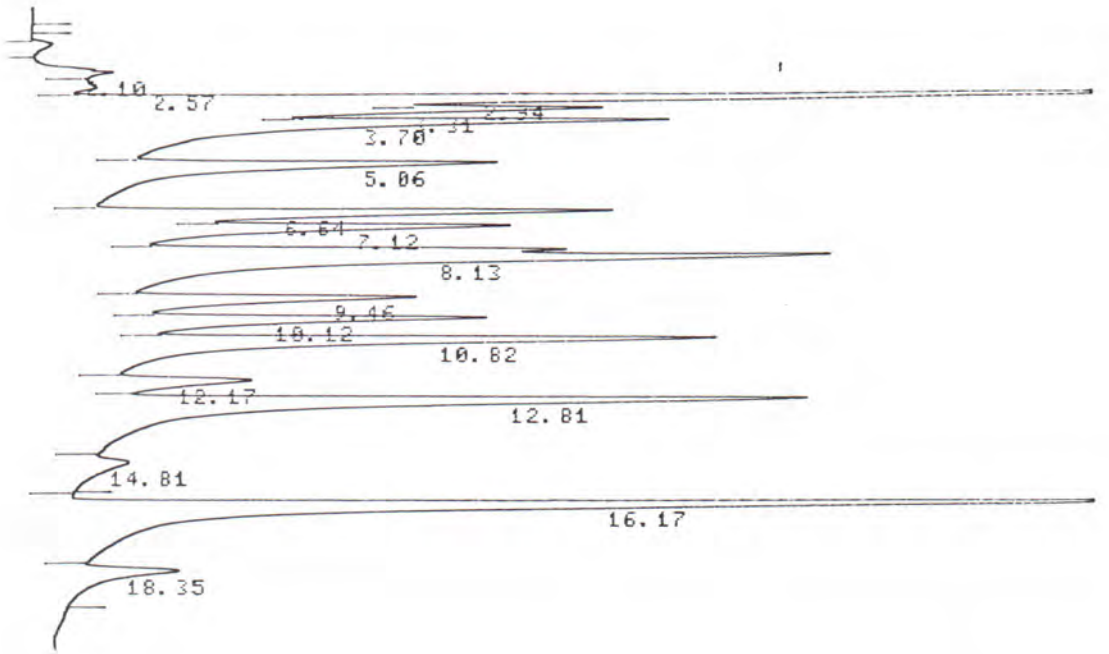


HP RUN # 348 JAN/12/81 TIME 12:49:43
ISTD

RT	EXP RT	AREA	CAL #	AMT
6.43	6.47	246300	3	2.759
6.94	6.99	397200	21	2.289
7.95	7.99	748800	4	2.199
9.03	9.07	823400	5	1.881
9.64	9.69	1137000	6	3.462
10.64	10.74	568900	7	2.165
10.92	11.04	1043000	8	2.495
11.55	11.64	572300	9	1.749
12.71	12.80	575200	10	1.752
13.55	13.52	1748000	12	5.513
14.05	14.10	507000	13	2.095
15.17	15.18	1839000	(R) 1	
16.43	16.46	191700	16	1.501
19.14	19.08	1862000	17	5.670
23.50	23.47	268400	19	2.540

DIL FACTOR: 1.0000 E+ 0 ISTD AMT: 8.0000 E+ 0

Figure 3. Hewlett-Packard Calibration Standard Chromatogram



ODS-CARBOWAX 19 09:53:59

FILE 3 METHOD 2. RUN 7 INDEX 1

ANALYST: EVANSVILLE

SAMPLE 1 RAW WATER

SA	IS	XF
1.	4.	1.

NAME	CONC	RT	AREA	BC	RF	RRT
METH CL	1.133	2.94	122300	02	0.38	0.23
TRICLFLMET	0.408	3.31	62381	02	0.269	0.258
DICLETHYLE	1.113	3.7	125774	02	0.363	0.289
1,1DICLETH	1.11	5.06	96794	02	0.471	0.395
CL-FORM	1.07	6.64	64914	02	0.676	0.518
1,2DICLETH	1.181	7.12	73065	02	0.664	0.556
CARBON-TET	1.079	8.13	190412	02	0.233	0.635
BRDICLMETH	1.193	9.46	56878	02	0.861	0.738
DICLPROPAN	1.097	10.12	63737	02	0.706	0.79
TRICLETHYL	1.18	10.82	136536	08	0.355	0.845
DIBRCLMETH	0.491	12.17	13729	06	1.467	0.95
INT STD	INTERNAL STD	12.81	164207	08	1.	1.
BR-FORM	2.559	14.81	6604	05	15.909	1.156
CL4ETHYLE	3.013	16.17	180387	08	0.686	1.262
CL-BENZENE	0.51	18.35	14742	05	1.42	1.432

Figure 4. Varian Calibration Standard Chromatogram

Data Transmission

When the project was organized, the ability to transmit copies of data to each participant was a basic requirement. This requirement was met by the installation of telecopier equipment. The lease costs of the telecopier units and the cost of separate project telephone service at each location have been paid by ORSANCO as a part of the project operating expense.

Initially, copies of all chromatograms (calibration, blank, and sample) were transmitted daily to ORSANCO headquarters for evaluation. Since each chromatogram requires six minutes for transmission, telephone line charges were a significant budget item. As operator proficiency increased, routine transmissions were limited to raw water sample chromatograms, unless the operator needed assistance in evaluating the GC system or troubleshooting operating problems.

The initial project proposal had included conversion of the chromatogram data for digital storage and transmission in second year equipment funding. Data transfer time for all three routine chromatograms would be reduced from 18-20 minutes per station per day to less than one minute. In 1979, a consultant was employed to evaluate alternative data transmission systems and associated costs. The consultant's report presented three alternatives:

1. Digitize, store, and transmit the complete chromatograms and numerical data at an estimated equipment cost of approximately $74,120.

2. Replace the existing facsimile equipment with new high speed equipment at an estimated purchase price of about $65,000. Significant reduction in telephone service costs would be realized.

3. Digitize and transmit only the numerical data sections of each chromatogram output sheet and complete purchase of the facsimile equipment at a cost of approximately $38,000.

Options 1 and 3 provided for the transfer of the data directly from the central receiver to ORSANCO's computer facility.

However, because of limited budget and based on the facts that few unusual events had occurred, only a limited number of compounds were detected, concentrations of detected compounds were generally less than 1.0 µg/l, and immediate consultation and transmission of the chromatograms would provide all necessary information when unusually high concentrations of one or more compounds were observed, another course of action was selected. This consisted of telecopier transmission of a weekly summary of daily analytical results and subsequent weekly mailing of the actual chromatograms. Facsimile equipment was purchased during the second quarter of 1980, at a cost of about $14,000. Figure 5 shows the weekly operating report transmitted to ORSANCO each Friday.

Immediate Data Evaluation

At project startup staff evaluated each chromatogram for data validity

Figure 5
OHIO RIVER ORGANICS DETECTION SYSTEM
WEEKLY OPERATION STATUS & QUALITY ASSURANCE

Station: _____ Period: _____ Name: _____

A. SAMPLING DATE		SAT	SUN	MON	TUES	WEDS	THURS	FRI
TIME								
B. VOLUME								
	Raw Water Sample (µL)							
	Internal Standard (µL)							
	Purgeable Standard (µL)							
C. CONCENTRATION (µg/L)								
2	Methylene chloride							
3	Trichlorofluoromethane							
21	1,1-Dichloroethylene							
22	Bromochloromethane							
4	1,1-Dichloroethane							
5	Chloroform							
6	1,2-Dichloroethane							
7	1,1,1-Trichloroethane							
8	Carbon tetrachloride							
9	Bromodichloromethane							
10	1,2-Dichloropropane							
12	Trichloroethylene							
13	Dibromochloromethane							
16	Bromoform							
17	Tetrachloroethylene							
19	Chlorobenzene							
20	1,4-Dichlorobenzene							
	Unknown							
TOTAL								
D. RETENTION TIME (Min.)								
	Internal Standard							
	Unknown							
E. AREA								
	Internal Standard							

GAS TANK PRESSURE (PSI): Helium_____ Hydrogen_____ Air_____

SPARES: (GAS TANK) Helium_____ Hydrogen_____ Air _____; Therm Paper_____

and to determine whether concentrations of one or more compounds justified confirmation and further action. With the revised data transmission schedule the staff reviews the routine data for validity. Normally after compound identification and concentration have been verified, the data are keypunched and entered into the computer for storage and summary.

Initially high concentrations were identified and verified by the project staff. With the revised reporting procedure, this identification is done by the GC operator, who evaluates each sample chromatogram and notifies ORSANCO staff if the concentration of any compound exceeds 25 µg/l or if the concentration of a compound is at least ten times higher than that of the same compound on the previous day. Criteria formulated by US EPA are also used to evaluate the findings. In either event, the operator transmits the chromatogram to ORSANCO for further action.

Response Action

Verification of unusually high levels of one or more of the purgeable halocarbons results in a series of actions by the project staff. Instructions to personnel at the EWODS site include requests for additional GC runs and for priority shipping of the two-ounce river water sample, two-ounce organic-free water (shipping blank), and one-gallon river water sample to the reference laboratory for GC/MS analysis. The reference laboratory is also notified of the sample shipment so analyses may be completed as soon as possible.

The notification process is an extension of ORSANCO's role in the Ohio Basin spill notification process, with one exception. Because the detection originates with the EWODS system, notification is a two-stage operation as shown in Figure 6 . The unconfirmed action level results in immediate notification of affected water users and state and federal response agencies, steps 1 through 5 in the chart. Based on the results of the confirmatory analyses, a non-confirmation is reported (step 6), or confirmed (steps 7 through 9). This two-stage process ensures that all concerned parties are notified as soon as possible. The process is similar to normal spill notification procedures, which are initiated before it is known whether the material will be contained or will affect water quality. The regional spill/bypass/abnormal discharge notification procedure has been developed over the last several years by joint agreement of the federal-state-local-ORSANCO personnel responsible for ensuring that all affected parties are informed of any significant event.

ORSANCO has several resources which are valuable in notification. The first is knowledge of the river and of the agencies concerned. For the latter, a directory of the agencies involved and their telephone numbers is maintained and distributed throughout the valley. Knowledge of the river first includes geographic knowledge--locations of waste discharges, water intakes, dams, and terminals. Lists of these are maintained in a looseleaf manual which is distributed to staff members and to state and federal spill response personnel. Also included is knowledge of the quantity of flow in the river at a given time. Each day a report of the current day's flow and estimates for the next three days at 20 mainstem locations and on 13 tribu-

ORSANCO EARLY WARNING--ORGANICS DETECTION SYSTEM

RESPONSE ACTION FOR

UNUSUAL LEVELS OF ORGANIC SUBSTANCES

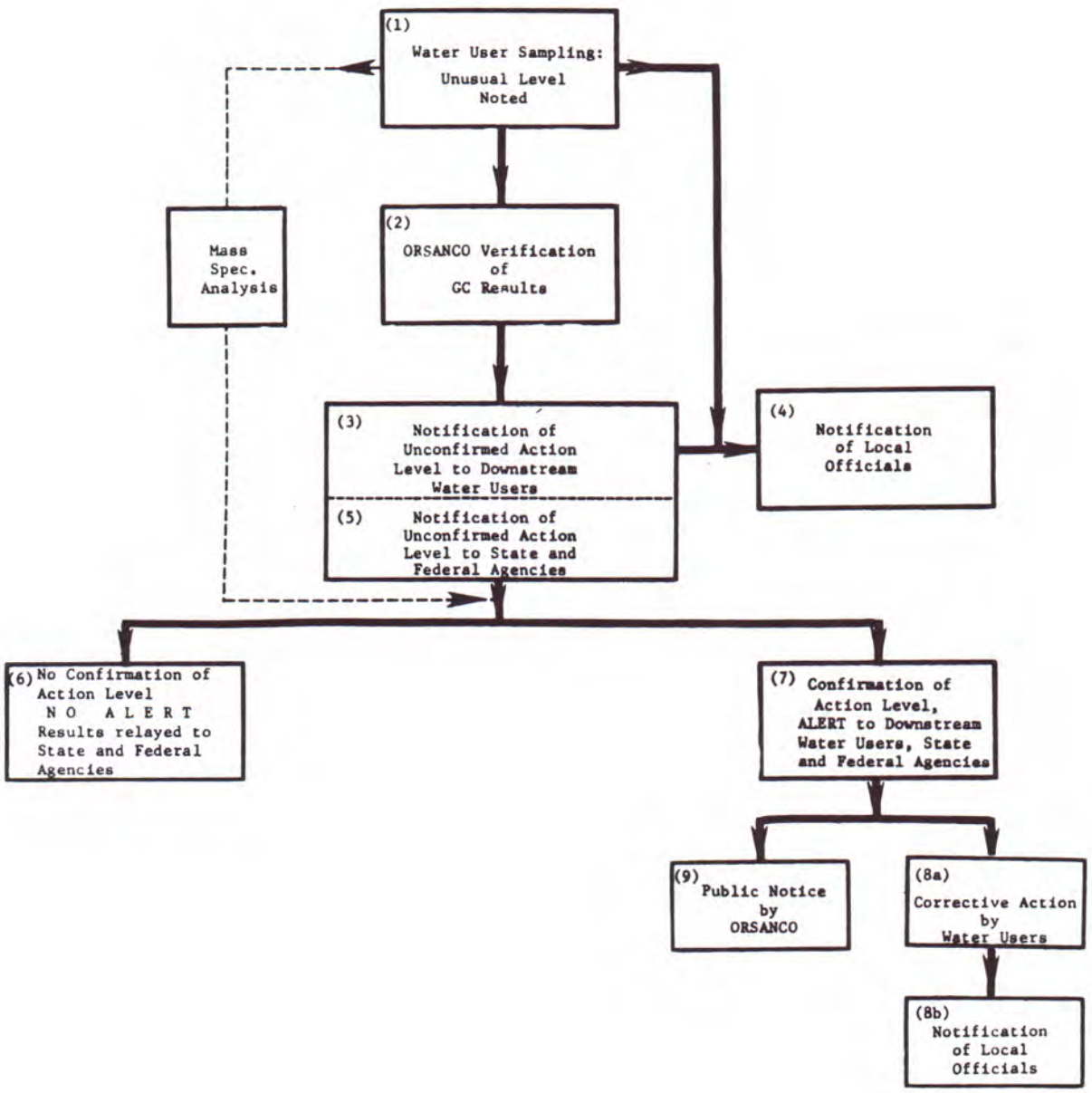


Figure 6. EWODS Notification Procedures

taries is received from the Cincinnati Flow Center of the National Oceanic and Atmospheric Administration. For general spill events a 24-hour answering service is contracted to receive calls during non-working hours. The service contacts a designated staff member upon receipt of a report and immediate follow-up is at the discretion of the staff person. The routine monitoring system provides up-to-date information on water quality conditions, including continuous monitoring of temperature, pH, specific conductance, and dissolved oxygen at 14 mainstem and eight tributary locations (pH and temperature can be of particular value in determining the toxicity of a substance spilled), and requested special sampling and analysis at affected EWODS sites.

A major available resource is a series of time-of-travel curves to assist the prediction of the movement of a spill downstream. The time-of-travel methodology derives from a mathematical model developed for the Ohio River entitled "STREAM." It is used together with the flow forecast reports to estimate the time of arrival at downstream locations. Graphs of time-of-travel versus river mile at various flows have been prepared and distributed to water users and spill response personnel. Acceptable results have been obtained on several occasions when substances arrived within hours of the estimate at locations as much as 300 miles downstream.

The entire notification procedure for all events is designed to ensure that appropriate agencies and utilities are notified of an event as soon as possible, including the identification of the chemicals, the impact on the receiving system, and predictive estimates of the time that the material will be near specified water intakes or other locations. Updates of travel-time are completed and reported daily as long as there is a cause for concern.

Data Storage

In anticipation of the vast amount of information to be generated by EWODS, computer programs were developed to store and arithmetically manipulate the data. For raw water analyses, the compound identifying numbers and concentrations of known compounds are stored if the concentration is 0.1 µg/l or greater. Data storage in files is arranged by sampling site and data. The data field includes the hour the sample was taken, so that several samples from the same day may be stored and retrieved without difficulty. Processing programs for the raw water analyses are designed to display and summarize concentrations of unidentified compounds under an assigned identifier. The concentrations of unidentified compounds are grouped and displayed under a range of retention times. All programs can be operated to process all sites and all parameters or to process selected lists of either. All programs also operate within a range of operator-specified dates.

The EWODS data are being entered into the STORET data system, with specific designation that the data are not MS/confirmed. Once the data are in the system, a wider range of arithmetic manipulations will be possible.

SECTION 3

QUALITY ASSURANCE PROGRAM

The monitoring of the Ohio River and its tributaries for organic chemicals at the microgram per liter level requires a stringent quality assurance program. The program has been developed based on the criteria for priority pollutants published in the Federal Register, Vol. 44, No. 233, Method 601, and from experience in operating the system. Procedures have been formulated for glassware cleaning and handling, sample collection, sample analysis, and reference laboratory analysis of both purgeable and base-neutral extractable samples. These, together with the choice of adequate calibration and internal standards, operator training, equipment maintenance, and systematic review of chromatograms outlined earlier (Section 2) constitute the assurance program.

PROCEDURES

Specific procedures for glassware cleaning and handling, sample collection and analysis, maintenance, and laboratory protocol are described in detail in ORSANCO Quality Control Assurance Program (1981). A summary of each of these elements of the program follows.

Glassware Cleaning and Handling

At the sampling sites, three different sizes of sample containers are used for organic sampling--two ounce, one liter, and one gallon. Initially, the reference laboratory supplies all the bottles in the sterile useable condition required by the water laboratory. After use the bottles, with seals and caps, are cleaned with organic-free water, air-dried, and sealed for subsequent use.

Each site is also supplied with a minimum of one 5-10 µl syringe, one 25-50 µl syringe, and one 20 ml syringe. Before use the syringes are flushed several times with acetone or methyl alcohol and air- or oven-dried.

To reduce the likelihood of cross-contamination between subsequently analyzed samples, the purging vessel is also 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 halocarbon levels, the purge vessel is washed with detergent, rinsed with distilled water, and oven-dried.

Sample Collection

The daily sample is drawn from the raw water intake tap. Two two-ounce

samples are taken, as well as a one-gallon sample. Duplicate organic-free water blanks are also collected and stored with the samples. If it is not necessary to ship any of the samples to the reference laboratory, the extra samples are discarded after analysis and the containers cleaned.

Sample Analysis

The daily procedure includes initial analysis of a 10-ml sample of organic-free water containing 2 µl of the internal standard solution. After the analysis of the organic-free water blank, the chromatogram is checked for extraneous peaks, internal standard retention time, and area response. If the system is found to be free of interference, the raw water sample is then analyzed.

A purgeable standard solution is analyzed a minimum of twice each week to ensure proper peak identification, identify problems such as column deterioration, and ensure analysis reproducibility. A 10-ml organic-free water sample is spiked with 2 µl of the internal standard and 20 µl of the purgeable standard.

Raw water analyses are terminated if interferences occur which cannot be explained and eliminated. This necessitates a service call from ORSANCO surveillance specialists, headquarters staff members, and/or chromatographic equipment service personnel.

If analysis of the raw water sample shows a higher than normal amount of purgeable organics, another raw water sample is drawn and analyzed to verify the initial findings. These chromatograms are then sent via facsimile telecopie to the ORSANCO office for staff inspection. An alert may be declared if a significant amount of organics in raw water is noted. During an alert situation, the remaining two-ounce samples of raw water and organic-free water, the one-liter organic-free water sample, and the one-gallon solvent-extractable sample are shipped by site personnel to the reference analytical laboratory for GC/MS confirmation. In an alert situation, the site personnel may be asked to analyze additional samples throughout the alert period. In non-alert situations, the extra samples are discarded and the bottles cleaned for the next day's sampling.

Check Samples

Once each month, surveillance specialists draw duplicate samples, in accordance with proper sampling techniques, to be analyzed on site and at the reference analytical laboratory. The site analyzes the two-ounce raw water sample, labels it as a quality control sample and sends the chromatogram to the ORSANCO staff. The surveillance specialist ships two (2) two-ounce raw water samples, a one-liter organic-free water sample, and the one-gallon solvent-extractable sample to the reference laboratory by 24-hour courier service. Reference laboratory results are compared with on-site analysis to assure the validity of the results. If results do not compare favorably, ORSANCO personnel may be dispatched to the site to correct discrepancies.

Round-robin performance evaluation analyses are conducted quarterly (or

when samples are available). The samples are provided by US EPA in sealed ampoules in two concentrations. Both the sites and the reference analytical laboratory analyze these samples to help identify any problems with equipment, personnel, or procedures. Results of these check samples are discussed later.

The precision of analysis will vary with the concentration of the sample. From the data collected, ORSANCO staff developed in 1979 the following limits of precision:

When Concentration is:	Mean Value ($\bar{X}$) should be:
0.1 to 1.0 µg/l	± 50% of true value
1.0 to 10 µg/l	± 30% of true value
10 to 100 µg/l	± 20% of true value
100 µg/l and greater	± 10% of true value

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

In 1980, the American Society for Testing and Materials' (ASTM) Annual Book of ASTM Standards for Water included an appendix to the Standard Test Method for Purgeable Organic Compounds Using Headspace Sampling (D 3871-79) which listed single-operator precision and accuracy values. This table is partially reproduced here:

Precision for the Purge and Trap Method for Organohalides

Concentration Range µg/l	0 to 0.99	1.0 to 9.9	10 to 19.9	20 to 99.9	100
Number of occurrences	16	28	13	10	12
Range of relative Standard Deviation, %	0 to 38	0 to 28	1 to 10	0 to 10	0 to 6

These values are compatible to the ORSANCO-developed table, particularly when it is recognized that the ORSANCO data was generated by 7 to 10 operators working at different locations along the Ohio River.

Surveillance Specialist Maintenance

The surveillance specialists visit each site at least twice per month. On each visit, these field people examine the equipment by following a check-list produced for that purpose (Figure 7). The surveillance specialist is responsible for: (1) assuring adequate pressure in the gas tanks; (b) regenerating molecular sieve and moisture filters; (c) assuring adequate supplies of fresh standards, microprocessor recording paper, organic-free water (if necessary), columns and column-packing material, and ion exchange resin; and (d) general troubleshooting.

ODS SERVICE REPORT FORM

Name:_____ Station:_____ Date:_____

GAS	Delivery Pressure(psi)	Tank Pressure(psi)	Spare Tank	Moisture Trap	Date Trap Change
Helium					
Hydrogen					
Air					

CDS (ORSANCO No.)	Flow Controller (cc/min)		Valve Temp.(°C)	Operation (✓ if OK)		
	Top	Bottom		Purge	Trap A	Rotation

GC (ORSANCO No.)	Injector Temp. (°C)	Oven Temp. (°C)		Column Flow (cc/min)		Memory Words	
		Initial	Final	Carbowax	n-Octane	Before	After
SIGMA							
HP*							
VARIAN (SP)							

GC	Spare Printer Paper	Observations (✓ if OK)				Remarks
		Printer Head	Door Opening	Fan		
SIGMA						
HP*						
VARIAN (SP)						

CCD (ORSANCO No.)	Temp. (°C)		Observations		Electrolyte Conductivity	Date Resin Replacement
	Valve	Furnace	Glass Trombone	Clips		

* None

Figure 7. ODS Service Report Form

Reference Laboratory Quality Control Procedures

The reference 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 are discontinued until the interference is identified and controlled.

QUALITY ASSESSMENT

Several factors complicate the quality assurance program. During the project the number of participating EWODS sites has increased from 7 to 11, using five different GC assemblies. Purge absorption traps and GC columns lose efficiency with continued use, increasing the variation. Each chromatogram of a raw water sample is, in fact, an analysis for 16 or 17 compounds, plus the internal standard. Thus, reported results on a sample may range from no detectable level of any compound to a complex of those not detected, those detected at low levels, and one or two compounds detected at 50, 100, or even 200 µg/l levels.

After feasible intra- and inter- laboratory quality assurance measures have been incorporated into a continuing program, the assessment of the program should be based on the analysis of one or more common unknown test solutions. US EPA performance standards are used by ORSANCO to check the ability of each EWODS site and the reference laboratory to identify and quantify purgeable halocarbons. The standard samples contain six or nine of the compounds in the current calibration standard sealed in ampoules containing high and low concentrations.

The initial performance evaluation standards were distributed during the fifth quarter of operation, October-December, 1978. Six of the sites and PEDCo analyzed the samples. The data are presented in Table 5 ; unacceptable values are shown. The unacceptable data occurred primarily in three laboratories. At St. Albans, the values were consistently below those reported by the other sites. The problem at that site was related to quantification by the microprocessor, compounded by poor resolution and coelution from the column. With the installation of a fresh column and recalibration of the microprocessor method, more acceptable data were obtained.

The problem at Wheeling was due, primarily, to improper storage of the sample. A similar problem occurred at Pittsburgh. Many of the difficulties associated with this study were also attributed to the internal standard coelution problem and to the difficulties with the column-packing material (see Section 2).

The second set of performance evaluation standards was distributed during the eighth quarter of the project, April-May, 1979. Most sites performed very well on identification and some very well on quantification, but others

TABLE 5. EPA PERFORMANCE VALUATION STANDARDS

FIFTH QUARTER

Compound	True Value	Outliers (by Q-Test)	Range	N	Average		Value outside 99% confidence level (including outliers)
(Sample #1)							
Chloroform	22.8	-	1.6 to 40.0	7	25.2		1.6 - 40.0
1,2-Dichloroethane	2.1	-	1.5 to 9.0	6	4.2		9.0
1,1,1-Trichloroethane	1.7	11.0	0.7 to 2.6	5	1.6		- (11.0)
Carbon Tetrachloride	4.2	23.0	2.7 to 5.4	5	4.3		- (23.0)
Bromodichloromethane	2.4	-	0.4 to 8.0	7	3.5		8.0
Trichloroethylene	1.9	18.0	0.5 to 3.3	6	1.7		- (18.0)
Dibromochloromethane	2.1	-	1.1 to 4.0	6	2.2		4.0
Bromoform	2.8	9.1	1.3 to 4.0	5	2.7		- (9.1)
Tetrachloroethylene	1.8	10.0	0.9 to 4.2	6	2.2		4.2 (10.0)
(Sample #2)							
Chloroform	91.2	4.2	78.7 to 145.0	6	112.8		114.1 - 145.0 (4.2)
1,2-Dichloroethane	17.3	89.0	14.6 to 32.3	5	22.4		32.3 (89.0)
Carbon Tetrachloride	16.8	-	2.4 to 117.4	7	38.0		78.0 - 117.4
Bromodichloromethane	23.8	-	2.6 to 110.0	7	33.5		70.0 - 110.0
Dibromodichloromethane	10.2	-	6.2 to 24.0	7	12.3		18.7 - 24.0
Bromoform	11.4	124.5	9.8 to 20.0	6	14.3		17.8 - 20.0 (124.5)

did not quantify within the expected range. The data, presented in Table 6 indicate that the EWODS laboratories have a satisfactory capability for detecting the commonly occurring purgeable halacarbons such as chloroform, carbon tetrachloride, and trichloroethane. Bromoform and other brominated compounds were also quantified with good accuracy in both samples.

Performance standards were again distributed during the ninth quarter, October-December, 1979. Sample 1 was a low concentration standard containing nine compounds between 1.7 and 22.8µg/l. Sample 2 was a higher level standard containing six compounds in a concentration range of 10.3 to 91.3µg/l. The results are summarized in Table 7. The overall performance of all the stations was encouraging.

During the eleventh quarter, April-June, 1980, the sites analyzed two performance standards of nine compounds each. With the exception of three incidents of coelution, all laboratories detected all of the compounds. Table 8 summarizes the measured values and shows values that are outside the 99 percent confidence limits of all reporting laboratories.

The Q-test is an alternate set of test statistics for testing outliers. It is only suitable for the detection of a single outlier either on the left or on the right. The ratio of the difference between a suspect outlier and its adjacent value divided by the range of the observations is compared to the critical values at 90 percent confidence limits.

Values outside 99 percent confidence limits are tested by "Substitute T-Ratios." The ratio of the difference between test-value and true value divided by the range of the observations is compared to the percentage point of the distribution at 99 percent confidence limits.

In general, reported results compared to the true value have improved as operating experience is increased at the individual laboratories and as operating and maintenance procedures are refined. To date the quality assurance program shows that the GC/halogen detector identification of purgeable halocarbons by the EWODS laboratories is very reliable. These levels of accuracy are similar to those achieved in analysis of other trace materials (heavy metals, cyanide, phenolics) at comparable concentrations.

The reliability of the procedures used in the EWODS system is further reinforced by the number of purgeable standards analyzed by each site. In Table 4 on page 21 , it was noted that a total of 3699 samples of raw river water were quanitified during 1979 and 1980. At Cincinnati, 659 of these samples were analyzed by the external method. In addition, the Cincinnati site ran a purge standard each day. At the other sites, a total of 680 purge standards were run by the internal method. Thus, at the sites other than Cincinnati, a purge standard was analyzed for every five (5) raw water samples run. At Cincinnati, the ratio was one to one. This means that approximately 22 percent of the anlyses done were purge standards.

TABLE 6. USEPA PERFORMANCE STANDARDS
EIGHTH QUARTER

Compound	True Value	Outliers (by Q-Test)	Range	N	Average		Values outside 99% confidence level (including outliers)
(Sample #1)							
Chloroform	9.1	27.9	2.0 to 14.8	7	9.6		2.0 - 14.8 (27.9)
1,2-Dichloroethane	1.4	6.9	1.0 to 2.5	7	1.9		2.5 (6.9)
Carbon Tetrachloride	1.7	-	1.3 to 2.9	8	1.9		2.8 - 2.9
Bromodichloromethane	1.2	10.5	1.1 to 2.9	6	1.8		2.4 - 2.9 (10.5)
Dibromochloromethane	2.7	-	1.4 to 3.0	8	1.9		1.4 - 1.6 1.7 - 1.8 - 1.9
Bromoform	2.8	1.2	2.2 to 3.9	7	2.8		3.9 (1.2)
(Sample #2)							
Chloroform	68.5	33.0	67.2 to 123.1	7	84.6		93.4 - 123.1 (33.0)
1,2-Dichloroethane	27.7	-	13.2 to 38.5	8	26.0		13.2 - 38.5
1,1,1-Trichloroethane	11 2	19.4	7.5 to 12.1	7	9.9		7.5 (19.4)
Carbon Tetrachloride	12.6	-	8.7 to 29.9	8	16.7		29.4 - 29.9
Bromodichloromethane	11.9	56.6	9.8 to 22.4	6	16.5		19.1-19.9-22.4 (56.6)
Trichloroethylene	19.0	-	5.9 to 30.8	7	16.3		5.9 - 30.8
Dibromochloromethane	17.2	-	1.9 to 21.2	8	11.5		1.9 - 6.7 9.1 - 9.7
Bromoform	14.2	-	5.8 to 21.7	8	13.3		5.8 - 21.7
Tetrachloroethylene	8.8	-	4.7 to 11.1	8	8.1		4.7

TABLE 7. USEPA PERFORMANCE STANDARDS

NINTH QUARTER

Compound	True Value	Outliers (by Q-Test)	Range	N	Average		Value outside 99% confidence outliers (including outliers)
(Sample #1)							
Chloroform	22.8	-	4.9 to 41.0	8	22.8		4.9 - 39.5 - 41.0
1,2-Dichloroethane	2.1	-	1.7 to 4.0	8	2.8		3.5 - 3.8 - 4.0
Carbon Tetrachloride	4.2	-	1.9 to 7.4	8	4.0		1.9 - 2.1 - 6.4 - 7.4
Bromodichloromethane	2.4	-	1.7 to 4.7	8	3.0		3.7 - 4.7
Dibromochloromethane	2.1	-	0.4 to 1.8	8	1.3		0.4 - 1.5
Bromoform	2.85	-	1.7 to 3.8	8	2.6		1.7 - 3.8
1,1,1-Trichloroethane	1.7	-	0.7 to 2.7	8	1.6		0.7 - 2.5 - 2.7
1,1,2-Trichloroethylene	1.9	-	0.6 to 3.9	8	1.7		3.9
Tetrachloroethylene	1.75	5.0	1.5 to 3.3	7	2.0		3.3 (5.0)
(Sample #2)							
1,2-Dichloroethane	91.3	18.0	78.7 to 178.7	7	114		178.7 (18.0)
Carbon Tetrachloride	17.3	-	15.6 to 40.5	8	25.0		27.7 - 32.4 - 40.5
Bromodichloromethane	16.8	-	9.2 to 25.6	8	16.2		9.2 - 25.6
Dibromochloromethane	23.8	-	20.4 to 74.7	8	36.7		48.0 - 74.7
Bromoform	10.3	-	1.8 to 9.4	8	5.6		1.8 - 3.9 - 6.9 -7.2
Tetrachloroethylene	11.4	-	10.8 to 16.9	8	12.8		14.3-15.0-15.6-16.9

TABLE 8. USEPA PERFORMANCE STANDARDS

ELEVENTH QUARTER

Compound	True Value	Outliers (by Q-Test)	Range	N	Average		Value outside 99% confidence level (including outliers)
(Sample #1)							
Chloroform	11.0	-	7.6 to 20.4	7	12.2		20.4
1,2-Dichloroethane	1.5	-	0.6 to 2.4	7	1.6		0.6 - 2.4
1,1,1-Trichloroethane	1.2	-	0.8 to 1.3	6	1.1		0.8 - 0.9
Carbon Tetrachloride	2.3	-	1.8 to 2.8	6	2.4		
Bromodichloromethane	1.7	-	1.0 to 3.7	8	2.0		3.3 - 3.7
1,1,2-Trichloroethylene	2.6	-	1.6 to 3.5	8	2.4		1.6 - 1.8 - 3.5
Dibromochloroethane	2.4	-	1.4 to 3.4	8	2.4		1.4 - 3.4
Bromoform	2.8	1.3	2.2 to 4.1	7	2.9		4.1 (1.3)
Tetrachloroethylene	1.1		0.6 to 1.2	8	1.0		
(Sample #2)							
Chloroform	45.6	-	27.3 to 67.0	7	43.2		27.3 - 67.0
1,2-Dichloroethane	20.0	62.7	15.7 to 26.7	6	20.3		- (62.7)
1,1,1-Trichloroethane	14.0	-	8.4 to 23.8	7	14.5		23.8
Carbon Tetrachoride	9.4	-	4.4 to 12.4	7	9.1		4.4
Bromodichloromethane	8.6	-	4.7 to 14.4	7	8.9		14.4
1,1,2-Trichloroethylene	13.0	-	6.5 to 14.8	7	10.8		6.5 - 8.3
Dibromochloroethane	12.0	-	10.3 to 16.5	7	12.4		16.5
Bromoform	10.4	24.4	6.7 to 15.9	6	12.3		15.9 (24.4)
Tetrachloroethylene	5.6		3.6 to 6.9	7	5.1		3.6 - 3.8

SECTION 4

DATA ASSESSMENT

The continuing record of levels of purgeable halocarbons provides the data to evaluate, on a limited basis, Ohio River quality. It is planned that a detailed summary of the data will be available through STORET. However, it is important to remember that extreme precision is not the primary concern when monitoring for spill events--which is the major purpose of the EWODS system.

What is most important is that the specific compounds be correctly identified. This ability has been demonstrated through the US EPA's check sample analyses. Furthermore, in almost every case in which a site identified a specific compound during a spill event, samples sent to the reference laboratory have verified this finding by GC/MS.

Another fulfilled goal of the EWODS system is the protection of water supply intakes from spill events by providing early detection and speedy notification. The generation of data describing the levels of halocarbons at the EWODS sites is another benefit of the system, and it has been found that 75 to 80 percent of the concentration values in 1979 and 1980 fell at 1.0 µg/l or below. This data is evaluated below by three approaches: by compound and year, by compound and location, and by seasonal variations.

SUMMARIES BY COMPOUND

Each analysis of a river water sample for purgeable halocarbons identifies and quantifies 16 or 17 organic compounds and shows the presence of any additional compounds not included in the calibration standard. For each halocarbon Table 9 shows the percent of samples in which the compound was identified, the maximum value measured, and the percent of samples in which the concentration exceeded the US EPA water quality criteria as published in the Federal Register. The last column gives the criteria value and, by footnote, the basis for the criteria.

With the exception of chloroform, criteria levels for the various compounds are not exceeded to any significant extent. Considering that the criteria for possible carcinogenic compounds are based on steady-state life-time exposure, even the percentage of samples above the criteria level for chloroform does not indicate significant health-effects potential.

In addition to chloroform, the next most identified compounds are the highly chlorinated ethanes and ethylenes. Levels of these widely used sol-

TABLE 9. SUMMARY OF PURGEABLE HALOCARBON DATA: 1979 and 1980

COMPOUND	Percent of samples with values equal to or greater than 0.1 ug/l		Maximum value ug/l		Percent of samples exceeding criteria		Criteria Level (1)
	1979	1980	1979	1980	1979	1980	ug/l
Chloroform	78.3	73.0	80.0	220.0	10.7	8.0	1.9 (2,8)
1,1,1-trichloroethane	37.4	38.3	19.0	43.0			NC
Tetrachloroethylene	36.5	37.8	20.0	23.0	0.3	0.3	8 (2)
Trichloroethylene	29.0	26.7	4.6	9.0			27 (2)
Methylene chloride (5) (7)	13.4	16.2	8.1	28.0	0.8	1.5	1.9 (2)
Dichlorobromomethane	11.5	12.0	7.8	9.0	0.6	0.5	1.9 (3,8)
Carbon tetrachloride	10.3	7.4	15.0	9.1	1.0	0.3	4.0 (2)
1,4-dichlorobenzene (7)	6.6	3.1	0.7	7.1			400.0 (4)
1,2-dichloroethane	5.4	4.6	4.2	3.3			9.4 (2)
1,1-dichloroethylene (7)	-	4.9	-	2.5	-	4.0	0.33 (2)
Chlorobenzene	4.0	4.9	54.0	20.0	0.1	0.0	22.0 (5)
1,2-dichloropropane	3.9	5.8	3.7	11.0			8,180 (6)
Dibromochloromethane	3.2	4.2	2.1	9.4	0.1	0.2	1.9 (3,8)
1,1,2-trichloroethane (7)	2.4	-	4.4	-			6.0 (2)
Trans-1,3-dichloropropene (7)	1.3	0.9	2.2	3.7			87.0 (4)
1,1-dichloroethane	1.1	1.4	2.5	2.7			NC
Cis-1,3-dichloropropene (7)	-	0.6	-	2.0			87.0 (4)
Bromoform	0.5	1.3	2.9	4.0	0.1	0.3	1.9 (3,8)
Trichloroflouromethane (7)	0.3	2.0	0.5	31.0			NC
1,1,2,2-tetrachloroethane (7)	0.1	0.1	0.1	0.7			1.7 (2)

NC--No criteria value

1. Water Quality Criteria, USEPA, Federal Register, Nov. 28, 1980, Part V
2. 10^{-5} lifetime risk as a carcinogen
3. 10^{-5} lifetime risk extrapolated from chloroform data
4. Human health criteria
5. Based on taste and odor considerations
6. Aquatic life
7. Calibration standard did not include compound for entire two-year period.
8. Compounds belonging in the family of Trihalomethanes (THMs). Federal criteria for THMs in drinking water is 100µg/l (Federal Register, Nov. 29, 1979).

vents and degreasing agents do not approach criteria values but their frequency of detection may justify consideration of source control.

Comparison of even maximum concentrations with criteria levels suggests that consideration of applicable stream quality criteria will require limiting concentrations based on some value related to the frequency distribution of the individual analytical values. This need is shown in Table 10 , where between 17 and 20 percent of the chloroform and slightly more than five percent of the 1,1,1-trichloroethane samples had concentrations of 1.0 µg/l or more. In more than 95 percent of the samples of all other purgeable halocarbons, the concentration was less than 1.0 µg/l.

Carbon tetrachloride, the compound that caused the EWODS to be developed, continues to be detected less frequently. During 1979 it was found in about ten (10) percent of the samples collected and in 1980, it was found in only about seven (7) percent of the samples. It has been replaced by 1,1,1-trichloroethane, a much less toxic organic compound; in fact, no criteria has been set for it to date. Carbon tetrachloride has a 4.0 µg/l criteria level set for 10^{-5} lifetime risk as a carcinogen by US EPA. These values are shown in Table 9 . The higher values shown in Table 9 occurred during unusual events. (See Section 5).

SUMMARIES BY LOCATION

Several distribution patterns for individual purgeable halocarbons can be identified using the percent of samples where the concentration is less than 1.0 µg/l. Chloroform, Table 11 , shows the most widespread occurrence for a significant percent of the time at all EWODS sites. During both 1979 and 1980 chloroform levels were equal to or greater than 1.0 µg/l from 10 to 44 percent of the time at Portsmouth and upstream stations. A similar pattern is observed for methylene chloride, Table 12 ; it was reported more frequently at concentrations of 1.0 µg/l or more at Huntington and upstream locations.

Table 13 shows that 1,1,1-trichloroethane was frequently reported at levels equal to or greater than 1.0 µg/l at Wheeling and Huntington during 1979 and at Wheeling, Huntington, and Portsmouth during 1980. About five percent of the samples from Parkersburg and Louisville contained levels of 1.0 µg/l or more during 1980. Wheeling and Huntington also show a significant percentage of tetrachloroethylene identifications at the 1.0 µg/l or higher level,(Table 14).

Several compounds are associated with only one sampling location. For example, Table 15 shows that chlorobenzene was found at the 1.0 µg/l or higher level in more than ten percent of the Huntington samples and in less than one percent of the samples at the other locations. The influence of the Kanawha River on the Ohio River is indicated by the frequency of identification of carbon tetrachloride, 1,2 dichloroethane and trichloroethylene at Huntington, the first downstream Ohio River location. (Tables 16, 17, and 18).

Similar observations cannot be made for the other purgeable halocarbons because the number of samples with concentrations at or above 1.0 µg/l is too small. If the above observation is verified in subsequent EWODS data, a pro-

TABLE 10. FREQUENCY DISTRIBUTION OF CONCENTRATION OF SEVERAL PURGEABLE HALOCARBONS: 1979 and 1980

		Cumulative % of Samples Less Than									
	Not Detected	0.5 µg/l	1.0 µg/l	2.0 µg/l	3.0 µg/l	4.0 µg/l	5.0 µg/l	10.0 µg/l	25.0 µg/l	50.0 µg/l	>50 µg/l
Chloroform 1979	21.7	63.6	80.0	89.4	93.0	95.1	96.5	99.1	99.8	99.9	100.0
1980	27.0	71.8	83.5	92.0	94.8	96.4	97.3	98.6	99.4	99.9	100.0
1,1,1-trichloroethane 1979	62.6	86.8	94.3	98.0	99.1	99.4	99.6	99.8	100.0		
1980	61.7	88.0	94.3	97.4	98.4	99.0	99.4	99.7	99.9	100.0	
Tetrachloroethylene 1979	63.5	87.4	96.2	98.5	99.0	99.2	99.3	99.7	100.0		
1980	62.7	91.3	96.0	98.6	99.2	99.5	99.6	99.7	100.0		
Trichloroethylene 1979	71.0	94.0	97.9	99.3	99.6	99.8	100.0				
1980	73.3	96.0	98.6	99.4	99.7	99.8	99.9	100.0			
Methylene chloride 1979	86.6	96.1	97.9	99.2	99.4	99.5	99.5	100.0			
1980	83.8	94.1	97.3	98.5	98.9	99.1	99.2	99.6	99.9	100.0	
Dichlorobromomethane 1979	88.5	96.9	98.4	99.4	99.6	99.8	99.9	100.0			
1980	88.0	96.2	98.6	99.5	99.6	99.8	99.8	100.0			
Carbon tetrachloride 1979	89.7	93.6	95.4	96.9	98.2	99.0	99.2	99.9	100.0		
1980	92.6	95.6	96.7	98.9	99.5	99.7	99.8	100.0			
1,2-dichloroethane 1979	94.6	98.5	99.4	99.6	99.9	99.9	100.0				
1980	95.4	98.0	98.9	99.8	99.0	100.0					
Chlorobenzene 1979	96.0	98.7	99.0	99.4	99.8	99.8	99.9	99.9	99.9	99.9	100.0
1980	95.1	97.9	98.8	99.3	99.6	99.7	99.8	99.9	100.0		
1,2-dichloropropane 1979	96.1	98.6	99.6	99.9	99.9	100.0					
1980	94.2	97.4	99.3	99.9	99.9	99.9	99.9	99.9	100.0		

TABLE 11. FREQUENCY DISTRIBUTION BY LOCATION: 1979 and 1980

CHLOROFORM Values in µg/l

1979	Not Detected	Cumulative % of Samples Less Than 0.5 µg/l	1.0 µg/l	2.0 µg/l	3.0 µg/l	4.0 µg/l	5.0 µg/l	10.0 µg/l	25.0 µg/l	50.0 µg/l	250.0 µg/l
Elrama - Monongahela											
Pittsburgh - Allegheny	19.5	41.4	69.5	82.1	89.0	92.8	95.7	98.1	100.0		
Wheeling - Ohio	0.9	33.9	55.7	73.7	83.5	87.6	91.4	98.1	99.0	99.7	100.0
Parkersburg - Ohio											
St. Albans - Kanawha	7.6	23.9	60.9	85.7	87.0	90.2	97.4	97.8	100.0		
Huntington - Ohio	10.0	45.7	64.3	88.6	90.0	97.1	97.1	100.0			
Portsmouth - Ohio	33.8	71.6	89.2	95.9	97.3	98.6	98.6	100.0			
Cincinnati - Ohio	3.3	91.3	98.0	99.0	99.0	99.0	99.0	99.7	100.0		
Louisville - Ohio	49.1	87.8	97.8	98.6	99.6	99.6	99.6	100.0			
Evansville - Ohio	86.6	100.0									
Total	21.7	63.6	80.0	89.4	93.0	95.1	96.5	99.1	98.8	99.9	100.0
1980											
Elrama - Monongahela	20.0	57.1	71.4	94.3	100.0						
Pittsburgh - Allegheny	36.6	67.2	84.0	92.7	94.4	95.2	97.4	99.6	100.0		
Wheeling - Ohio	2.3	43.6	61.4	76.9	84.8	90.4	93.0	96.6	98.8	100.0	
Parkersburg - Ohio	41.0	55.2	78.1	99.0	100.0						
St. Albans - Kanawha	19.4	25.8	33.9	59.7	74.2	83.9	87.9	95.2	97.8	99.2	100.0
Huntington - Ohio	23.8	61.4	80.2	87.8	90.9	92.4	93.4	95.4	96.4	99.0	100.0
Portsmouth - Ohio	48.2	78.8	89.1	99.0	100.0						
Cincinnati - Ohio	2.5	90.6	96.7	98.3	98.6	99.2	100.0				
Louisville - Ohio	45.8	98.6	100.0								
Evansville - Ohio	40.0	80.4	93.6	99.4	100.0						
Total	27.0	71.8	83.5	92.0	94.8	96.4	97.3	98.6	99.4	99.9	100.0

TABLE 12. FREQUENCY DISTRIBUTION BY LOCATION: 1979 and 1980

METHYLENE CHLORIDE Values in µg/l

		Cumulative % of Samples Less Than									
1979	Not Detected	0.5 µg/l	1.0 µg/l	2.0 µg/l	3.0 µg/l	4.0 µg/l	5.0 µg/l	10.0 µg/l	25.0 µg/l	50.0 µg/l	250.0 µg/l
Elrama - Monongahela											
Pittsburgh - Allegheny	86.2	90.1	94.3	97.6	98.1	98.1	98.1	100.0			
Wheeling - Ohio	78.2	96.2	98.4	99.7	100.0						
Parkersburg - Ohio											
St. Albans - Kanawha	65.2	82.6	90.2	96.7	97.8	97.8	97.8	100.0			
Huntington - Ohio	90.0	94.3	97.1	97.1	97.1	98.0	98.6	100.0			
Portsmouth - Ohio	98.6	100.0									
Cincinnati - Ohio	83.6	99.0	100.0								
Louisville - Ohio	98.5	99.3	99.3	100.0							
Evansville - Ohio	100.0										
Total	86.5	96.1	97.9	99.2	99.4	99.5	99.5	100.0			
1980											
Elrama - Monongahela	88.6	88.6	91.4	91.4	94.3	97.1	97.1	100.0			
Pittsburgh - Allegheny	71.1	86.2	94.4	97.4	97.4	97.8	97.8	99.6	100.0		
Wheeling - Ohio	59.4	83.9	93.0	95.6	97.1	97.4	97.7	98.5	99.7	100.0	
Parkersburg - Ohio	64.8	79.0	89.5	97.1	97.1	98.1	99.0	100.0			
St. Albans - Kanawha	88.7	96.0	96.8	97.6	98.4	99.2	99.2	100.0			
Huntington - Ohio	88.8	97.0	97.5	97.5	100.0						
Portsmouth - Ohio	93.8	97.4	99.5	99.5	100.0						
Cincinnati - Ohio	84.7	99.7	100.0								
Louisville - Ohio	99.2	99.7	100.0								
Evansville - Ohio	94.4	98.6	99.7	100.0							
Total	83.8	94.1	97.3	98.5	98.9	99.1	99.2	99.6	99.9	100.0	

TABLE 13. FREQUENCY DISTRIBUTION BY LOCATION: 1979 and 1980
1,1,1-TRICHLOROETHANE Values in µg/l

1979	Not Detected	Cumulative % of Samples Less Than 0.5 µg/l	1.0 µg/l	2.0 µg/l	3.0 µg/l	4.0 µg/l	5.0 µg/l	10.0 µg/l	25.0 µg/l	50.0 µg/l	250.0 µg/l
Elrama - Monongahela											
Pittsburgh - Allegheny	59.5	90.0	95.2	98.6	99.0	99.0	100.0				
Wheeling - Ohio	29.4	69.0	86.4	96.2	98.1	99.4	99.9	100.0			
Parkersburg - Ohio											
St. Albans - Kanawha	77.2	92.4	97.8	98.9	100.0						
Huntington - Ohio	38.6	60.0	77.1	81.4	92.8	94.3	95.7	95.7	100.0		
Portsmouth - Ohio	94.6	95.9	98.6	100.0							
Cincinnati - Ohio	75.2	98.0	99.7	100.0							
Louisville - Ohio	69.0	90.8	97.0	100.0							
Evansville - Ohio	100.0										
Total	62.6	86.8	94.3	98.6	99.1	99.4	99.6	99.8	100.0		
1980											
Elrama - Monongahela	97.1	100.0									
Pittsburgh - Allegheny	74.1	90.5	96.6	99.6	99.6	100.0					
Wheeling - Ohio	17.0	78.4	85.4	92.6	97.7	98.2	99.4	100.0			
Parkersburg - Ohio	89.5	94.3	95.2	97.1	98.1	99.0	100.0				
St. Albans - Kanawha	94.4	96.8	98.4	99.2	100.0						
Huntington - Ohio	46.2	65.0	84.3	91.4	93.9	98.0	99.0	99.5	100.0		
Portsmouth - Ohio	62.7	86.5	90.7	93.8	93.8	94.8	95.3	96.9	99.0	100.0	
Cincinnati - Ohio	82.2	99.4	100.0								
Louisville - Ohio	29.2	80.9	95.2	99.2	99.7	99.7	99.7				
Evansville - Ohio	93.3	98.9	99.7	100.0							
Total	61.7	88.0	94.3	97.4	98.4	99.0	99.4	99.7	99.9	100.0	

TABLE 14. FREQUENCY DISTRIBUTION BY LOCATION: 1979 and 1980

TETRACHLOROETHYLENE Values in µg/l

1979	Not Detected	Cumulative % of Samples Less Than 0.5 µg/l	1.0 µg/l	2.0 µg/l	3.0 µg/l	4.0 µg/l	5.0 µg/l	10.0 µg/l	25.0 µg/l	50.0 µg/l	250.0 µg/l
Elrama - Monongahela											
Pittsburgh - Allegheny	81.9	89.5	92.8	94.8	95.7	96.2	96.7	98.1	100.0		
Wheeling - Ohio	3.2	55.4	90.8	98.4	99.4	99.7	99.7	100.0			
Parkersburg - Ohio											
St. Albans - Kanawha	95.6	98.9	98.9	100.0							
Huntington - Ohio	52.8	81.4	88.6	91.4	94.3	95.7	97.1	100.0			
Portsmouth - Ohio	100.0										
Cincinnati - Ohio	68.6	99.7	100.0								
Louisville - Ohio	83.0	99.3	99.6	100.0							
Evansville - Ohio	100.0										
Total	63.5	87.4	96.2	98.5	99.0	99.2	99.3	99.7	100.0		
1980											
Elrama - Monongahela	100.0										
Pittsburgh - Allegheny	78.9	95.7	98.3	98.7	99.6	100.0					
Wheeling - Ohio	9.9	65.5	81.9	94.2	96.2	97.1	98.0	98.2	100.0		
Parkersburg - Ohio	97.1	97.1	98.1	98.1	99.0	99.0	100.0				
St. Albans - Kanawha	57.2	87.9	96.0	100.0							
Huntington - Ohio	39.6	83.8	93.4	98.5	99.0	99.5		100.0			
Portsmouth - Ohio	51.8	91.7	97.4	99.0	99.5	100.0					
Cincinnati - Ohio	75.0	100.0									
Louisville - Ohio	70.8	99.2	100.0								
Evansville - Ohio	89.1	99.2	99.7	99.7	100.0						
Total	62.7	91.3	96.0	98.6	99.2	99.5	99.6	99.7	100.0		

TABLE 15. FREQUENCY DISTRIBUTION BY LOCATION: 1979 and 1980

CHLOROBENZENE Values in µg/l

1979	Not Detected	Cumulative % of Samples Less Than 0.5 µg/l	1.0 µg/l	2.0 µg/l	3.0 µg/l	4.0 µg/l	5.0 µg/l	10.0 µg/l	25.0 µg/l	50.0 µg/l	250.0 µg/l
Elrama - Monongahela											
Pittsburgh - Allegheny	100.0										
Wheeling - Ohio	99.0	99.7	99.7	100.0							
Parkersburg - Ohio											
St. Albans - Kanawha	100.0										
Huntington - Ohio	72.8	81.4	82.8	87.1	95.7	95.7	97.1	98.6	98.6	98.6	100.0
Portsmouth - Ohio	100.0										
Cincinnati - Ohio	88.3	98.3	99.3	100.0							
Louisville - Ohio	100.0										
Evansville - Ohio	100.0										
Total	96.0	98.7	99.0	99.4	99.8	99.8	99.9	99.9	99.9	99.9	100.0
1980											
Elrama - Monongahela	100.0										
Pittsburgh - Allegheny	96.1	97.0	99.1	99.6	99.6	100.0					
Wheeling - Ohio	97.7	99.5	99.7	99.7	100.0						
Parkersburg - Ohio	98.1	99.0	99.0	99.0	100.0						
St. Albans - Kanawha	96.8	98.4	100.0								
Huntington - Ohio	66.5	84.3	88.8	93.9	95.9	95.9	98.5	99.0	100.0		
Portsmouth - Ohio	93.8	97.4	99.5	100.0							
Cincinnati - Ohio	97.2	100.0									
Louisville - Ohio	99.7	100.0									
Evansville - Ohio	100.0										
Total	95.1	97.9	98.8	99.3	99.6	99.7	99.8	99.9	100.0		

TABLE 16. FREQUENCY DISTRIBUTION BY LOCATION: 1979 and 1980

CARBON TETRACHLORIDE

Values in µg/l

1979	Not Detected	Cumulative % of Samples Less Than 0.5 µg/l	1.0 µg/l	2.0 µg/l	3.0 µg/l	4.0 µg/l	5.0 µg/l	10.0 µg/l	25.0 µg/l	50.0 µg/l	250.0 µg/l
Elrama - Monongahela											
Pittsburgh - Allegheny	90.5	97.1	99.0	99.5	100.0						
Wheeling - Ohio	98.1	99.0	100.0								
Parkersburg - Ohio											
St. Albans - Kanawha	6.5	14.1	32.6	53.5	72.8	84.8	88.0	97.8	100.0		
Huntington - Ohio	87.1	98.6	98.6	98.6	100.0						
Portsmouth - Ohio	93.2	98.6	98.6	100.0							
Cincinnati - Ohio	94.0	99.7	100.0								
Louisville - Ohio	98.9	100.0									
Evansville - Ohio	100.0										
Total	89.7	93.6	95.4	96.8	98.2	99.0	99.2	99.9	100.0		
1980											
Elrama - Monongahela	97.1	100.0									
Pittsburgh - Allegheny	92.2	98.3	99.1	99.1	100.0						
Wheeling - Ohio	100.0										
Parkersburg - Ohio	96.2	99.0	99.0	99.0	99.0	100.0					
St. Albans - Kanawha	16.1	29.8	46.8	83.9	92.7	96.0	98.4	100.0			
Huntington - Ohio	93.9	97.0	98.5	99.5	99.5	99.5	99.5	100.0			
Portsmouth - Ohio	94.8	98.4	98.4	99.5	99.5	99.5	99.5	100.0			
Cincinnati - Ohio	96.4	100.0									
Louisville - Ohio	97.8	100.0									
Evansville - Ohio	99.7	99.7	100.0								
Total	92.6	95.6	96.7	98.9	99.5	99.7	99.8	100.0			

TABLE 17. FREQUENCY DISTRIBUTION BY LOCATION: 1979 and 1980

1,2-DICHLOROETHANE Values in µg/l

1979	Not Detected	Cumulative % of Samples Less Than									
		0.5 µg/l	1.0 µg/l	2.0 µg/l	3.0 µg/l	4.0 µg/l	5.0 µg/l	10.0 µg/l	25.0 µg/l	50.0 µg/l	250.0 µg/l
Elrama - Monongahela											
Pittsburgh - Allegheny	86.7	99.5	100.0								
Wheeling - Ohio	99.7	100.0									
Parkersburg - Ohio											
St. Albans - Kanawha	62.0	80.4	92.4	94.6	98.9	100.0					
Huntington - Ohio	100.0										
Portsmouth - Ohio	100.0										
Cincinnati - Ohio	98.0	100.0									
Louisville - Ohio	97.4	98.9	99.6	99.6	99.6	99.6	100.0				
Evansville - Ohio	100.0										
Total	94.6	98.5	99.4	99.6	99.9	99.9	100.0				
1980											
Elrama - Monongahela	100.0										
Pittsburgh - Allegheny	90.5	97.0	98.7	99.6	100.0						
Wheeling - Ohio	99.1	100.0									
Parkersburg - Ohio	81.0	97.1	99.0	100.0							
St. Albans - Kanawha	66.1	71.8	84.7	98.4	99.2	100.0					
Huntington - Ohio	95.4	99.0	99.0	99.5	100.0						
Portsmouth - Ohio	100.0										
Cincinnati - Ohio	99.7	100.0									
Louisville - Ohio	98.0	100.0									
Evansville - Ohio	99.7	100.0									
Total	95.4	98.0	98.0	99.8	99.9	100.0					

TABLE 18. FREQUENCY DISTRIBUTION BY LOCATION: 1979 and 1980

TRICHLOROETHYLENE

Values in µg/l

1979	Not Detected	Cumulative % of Samples Less Than 0.5 µg/l	1.0 µg/l	2.0 µg/l	3.0 µg/l	4.0 µg/l	5.0 µg/l	10.0 µg/l	25.0 µg/l	50.0 µg/l	250.0 µg/l
Elrama - Monongahela											
Pittsburgh - Allegheny	93.3	96.2	98.1	100.0							
Wheeling - Ohio	18.4	82.6	94.0	98.1	99.4	100.0					
Parkersburg - Ohio											
St. Albans - Kanawha	75.0	89.1	95.6	96.7	96.7	97.8	100.0				
Huntington - Ohio	70.0	97.1	100.0								
Portsmouth - Ohio	100.0										
Cincinnati - Ohio	85.6	99.7	100.0								
Louisville - Ohio	81.9	98.2	99.6	100.0							
Evansville - Ohio	92.8	95.9	97.9	99.0	100.0						
Total	71.0	94.0	97.9	99.3	99.6	99.8	100.0				
1980											
Elrama - Monongahela	100.0										
Pittsburgh - Allegheny	98.3	98.4	100.0								
Wheeling - Ohio	27.8	93.8	99.7	99.7	100.0						
Parkersburg - Ohio	100.0										
St. Albans - Kanawha	62.1	86.3	88.7	93.5	96.7	99.2	99.2	100.0			
Huntington - Ohio	62.9	87.8	95.4	98.5	99.0	99.0	99.5	100.0			
Portsmouth - Ohio	79.8	93.9	97.9	99.5	99.5	99.5	99.5	100.0			
Cincinnati - Ohio	86.7	100.0									
Louisville - Ohio	66.0	98.0	99.4	100.0							
Evansville - Ohio	89.9	97.5	99.7	100.0							
Total	73.3	96.0	98.6	99.4	99.7	99.8	99.9	100.0			

gram for source identification and evaluation of the feasibility of implementing controls is advisable.

SEASONAL VARIATIONS

Seasonal variations in the concentration of a constituent result from river flow fluctuations, temperature, rate of biological activity, and other factors. Because most of the purgeable halocarbons are resistant to biological breakdown and do not bioaccumulate, the primary mechanism for removal of these compounds from the environment is transfer from the water to air by volatilization and photolysis in the stratosphere and probably by absorption on clays and other particulate material.

The 1979 and 1980 data for chloroform and 1,1,1-trichloroethane were tallied by calendar quarters and frequency distributions prepared (Table 19. Seasonal variations at one or more concentrations would be indicated by lower cumulative percentages during the low temperature, high flow periods, and higher percentages during other periods.

As shown in Table 20 the percentage of values less than 1.0 µg/l, 2.0 µg/l, and 3.0 µg/l follows a pattern generally related to temperature during 1979. Most values equal to or greater than the specific concentration, indicated by the lower percentage figure, occur in the first and fourth quarters of 1979. For both compounds, concentrations decrease from the first quarter to minimums in the third quarter and increase in the fourth quarter. There was a similar seasonal pattern for the first three quarters of 1980; however, concentrations decreased further during the fourth quarter. One possible explanation is that flows were extremely low and the temperatures below normal for both November and December.

Because of the low concentrations of these compounds and the fact that changes from season to season are small, definitive conclusions regarding seasonal variations were not made. It is postulated that as additional information is obtained, reanalysis may confirm the appearance of an inverse relation to temperature--the higher the temperature of the river water, the lower the concentration of purgeable halocarbons.

ADDITIONAL ASSESSMENT

More concentrated evaluation of the EWODS data is clearly needed. A major question which remains essentially unanswered is whether any substantial organic load to the river is constituted by these compounds. Such an evaluation would, of necessity, take into account changes in stream flow and might explain some of the anomalies noted in evaluation by concentration alone. It would also help to determine if seasonal variations in load do in fact exist, if biological activity in breaking down these compounds is effectively nil, and if the major removal of these materials is by transfer to the air through volatilization and photolysis in the atmosphere.

TABLE 19. QUARTERLY FREQUENCY DISTRIBUTIONS: 1979 and 1980

Chloroform		Not Detected	Cumulative % of Samples Less Than									
			0.5 µg/l	1.0 µg/l	2.0 µg/l	3.0 µg/l	4.0 µg/l	5.0 µg/l	10.0 µg/l	25.0 µg/l	50.0 µg/l	250.0 µg/l
January - March	1979	32.8	65.1	76.3	86.3	89.6	92.1	94.2	98.3	99.6	99.6	100.0
April - June	1979	19.5	64.4	80.5	90.6	95.3	95.6	97.0	99.3	99.7	100.0	
July - September	1979	14.1	71.9	91.1	95.0	96.6	96.9	97.6	99.2	99.7	100.0	
October - December	1979	23.5	56.1	73.3	85.8	90.5	94.9	96.4	99.2	100.0		
January - March	1980	26.7	68.4	77.0	86.4	90.8	93.4	95.1	97.1	99.2	100.0	
April - June	1980	33.4	78.0	87.0	93.1	94.9	96.5	97.9	99.3	99.6	100.0	
July - September	1980	25.9	75.8	85.5	93.1	95.5	96.8	97.3	97.9	98.7	99.5	100.0
October - December	1980	22.6	64.8	83.5	94.4	97.1	98.4	98.7	100.0			
1,1,1-trichloroethane												
January - March	1979	73.8	85.5	93.4	97.5	98.8	99.2	99.6	100.0			
April - June	1979	62.4	90.3	96.3	99.3	99.3	100.0					
July - September	1979	57.8	91.7	97.4	99.0	99.7	99.7	99.7	100.0			
October- December	1979	61.1	81.8	91.3	96.6	98.6	98.8	99.4	99.4	100.0		
January - March	1980	50.7	83.8	91.2	97.1	99.2	99.4	99.8	100.0			
April - June	1980	59.5	87.8	93.3	96.6	97.7	98.8	99.1	99.8	100.0		
July - September	1980	65.5	89.0	94.5	97.3	98.1	98.9	99.5	99.7	99.8	100.0	
October - December	1980	68.5	90.6	97.3	98.6	98.9	99.2	99.2	99.4	99.8	100.0	

TABLE 20. SEASONAL VARIATION OF CHLOROFORM AND 1,1,1-TRICHLOROETHANE

	Cumulative Percent of Values less than					
	1.0 µg/l		2.0 µg/l		3.0 µg/l	
	1979	1980	1979	1980	1979	1980
Chloroform						
January - March	76.3	77.0	86.3	86.4	89.6	90.8
April - June	80.5	87.0	90.6	93.1	95.3	94.9
July - September	91.1	85.5	95.0	93.1	96.6	95.5
October - December	73.3	83.5	85.8	94.4	90.5	97.1
1,1,1-trichloroethane						
January - March	93.4	91.2	97.5	97.1	98.8	99.2
April - June	96.3	93.3	99.3	96.6	99.3	97.7
July - September	97.4	94.5	99.0	97.3	99.7	98.1
October - December	91.3	97.3	96.6	98.6	98.6	98.9

SECTION 5

UNUSUAL EVENTS

The major objective of the project is to identify abnormal concentrations of organic compounds, indicating a spill, by-pass, or excessive discharge upstream, and to notify downstream water users that might be affected. As indicated in Section 2, a concentration is judged unusual if it exceeds 25 µg/l or if it is at least ten times higher than that of the same compound on the previous day. During the May, 1978-June, 1980, project period there have been several incidents of unusual levels of one or more purgeable halocarbons observed at EWODS stations.

WHEELING, WV, MAY 23, 1978 - *OHIO RIVER*

The analysis of the May 23, 1978, raw water sample at Wheeling presumptively identified 1,1,1-trichloroethane, trichloroethylene, or 1,1,2,2-tetrachloroethane at about 10-12 µg/l. A sample shipment to the reference laboratory was requested and downstream water treatment plants and state and federal spill response agencies informed. Because of the low concentration, GC/MS analysis did not confirm the presumptive identifications.

ST. ALBANS, WV, MAY, 1978 - *KANAWHA RIVER*

During May, 1978, concentrations of chloroform and carbon tetrachloride were observed in Kanawha River samples at St. Albans for three successive midweek periods. The pattern of occurrence is shown in Figure 8 .

State and federal agencies and Ohio River water utilities were notified of each incident. The West Virginia Division of Water Resources initiated source investigations after the first report and corrective action was completed after the third week. As shown in the composite chromatogram in Figure 9 ., chloroform was the major purgeable halocarbon; therefore, downstream water utilities did not initiate special corrective action.

PITTSBURGH, PA, JUNE 9, 1978 - *ALLEGHENY RIVER*

On the morning of June 9, 1978, Pittsburgh water plant personnel notified the EWODS staff that an explosion at the PPG Industries on June 8 had resulted in the discharge of organic compounds at about Allegheny River mile 20. No purgeable halocarbons were identified in the Pittsburgh raw water or in samples sent to the reference laboratory. GC/MS analysis of the base-neutral solvent extract of a large sample was completed by the reference laboratory. Diotylphthalate, bis-(2-ethylhexyl)phthalate, diethylphthalate, phenyl phosphate, and a fluorinated (CF_3) group were identified. These

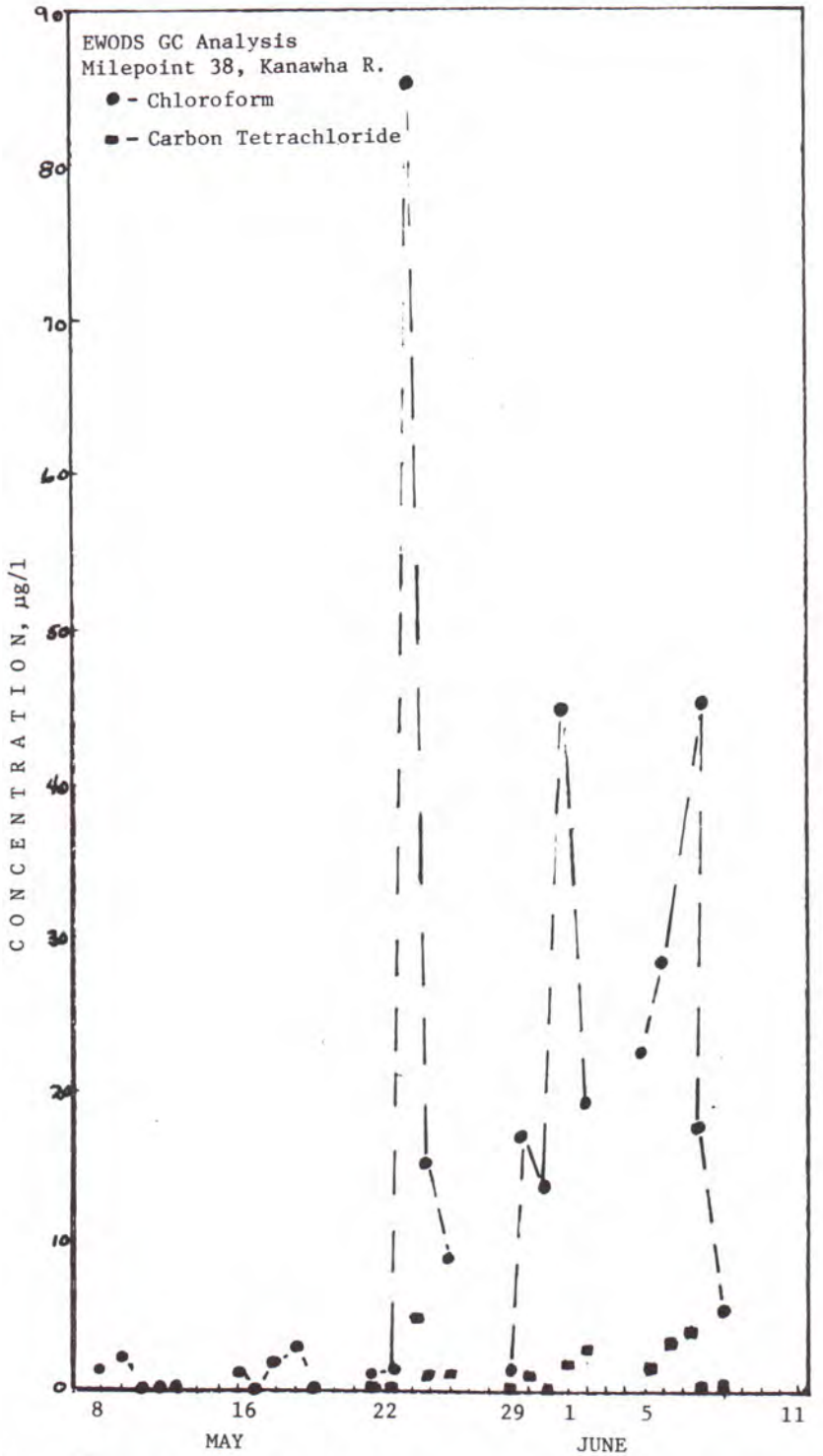


Figure 8. Occurrence of Chloroform and Carbon Tetrachloride at Kanawha River Site

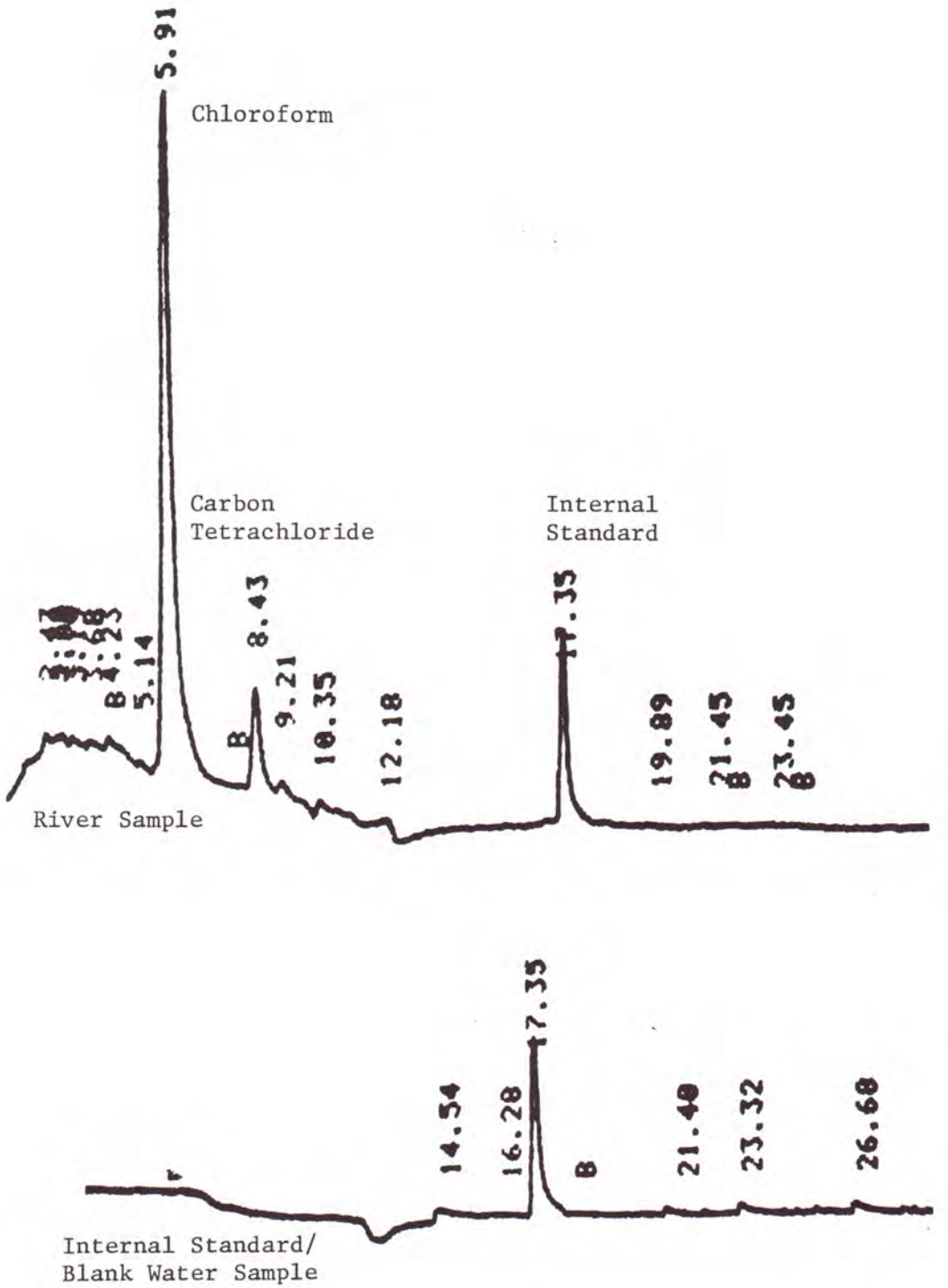


Figure 9. Composite Chromatograph, May 10, 1978, Kanawha River Site

results were reported to the Allegheny County Health Department, Pennsylvania Department of Environmental Resources, and US EPA Region III.

Downstream water utilities, Ohio and West Virginia spill response centers, and US EPA Region V were notified of the incident and probable travel time to affected locations. Because the phthalate esters are not considered to be toxic, downstream water plants did not institute special treatment practices.

ST. ALBANS, WV, NOVEMBER 27-28, 1978 - *KANAWHA RIVER*

On November 27 and 28, 1978, Kanawha River samples showed the presence of unusual concentrations of chloroform, carbon tetrachloride, 1,1-dichloroethane and/or 1,1,1-trichloroethane. GC/MS analysis of duplicate samples by the reference laboratory confirmed the identification of chloroform and 1,1,1-trichloroethane. Reference laboratory GC/MS analysis of Ohio River samples collected at the Huntington water plant showed 2 µg/l of 1,1,1-trichloroethane, 12-20 µg/l of 1,1,2-trichloroethane, and 10 µg/l of chloroform.

A notification was issued and confirmed to response centers at US EPA Regions III, IV, and V, and West Virginia, Ohio, and Kentucky, and Ohio River water utilities downstream from the Kanawha River. Based on travel-time estimates, evidence of the spill was observed in chromatograms of river samples at the Portsmouth and Cincinnati EWODS stations. Because of relatively low concentrations of these compounds, water plant operating practices were not modified.

ST. ALBANS, WV, FEBRUARY 12, 1979 - *KANAWHA RIVER*

Concentrations of 1,1-dichloroethane as high as 205 µg/l were presumptively identified in Kanawha River samples on February 12 and 13. The chromatograms also showed slightly elevated levels of chloroform and other purgeable halocarbons. The presumptive identifications were confirmed by the reference laboratory. An alert was issued to affected water utilities and to state and federal response agencies.

With daily travel-time estimates from ORSANCO, the spill was tracked for 38 miles on the Kanawha River by US EPA Region III and for some 340 miles on the Ohio River by the EWODS stations at Huntington, Portsmouth, Cincinnati, and Louisville. Although concentrations of less than 10 µg/l were estimated for the Ohio River downstream from the Kanawha, the same concentration ratio of 1,1-dichloroethane/chloroform/carbon tetrachloride was found in Kanawha and Ohio River samples. Due to the low concentrations, water treatment practices were not modified.

PITTSBURGH, PA, FEBRUARY 20-24, 1979 - *ALLEGHENY RIVER*

Several chlorinated compounds were detected during February 20-24, 1979, by the Pittsburgh plant personnel. The data are listed in Table 21 and Figure 10. The data indicate that tetrachloroethylene was the dominant chlorinated compound. Lower concentrations of 1,1,1-trichlorethane, 1,1,2-trichloroethane, trichloroethylene, and tetrachloroethylene also occurred.

TABLE 21. OCCURRENCE OF CHLORINATED COMPOUNDS AT PITTSBURGH, PA. DURING 2/20-24/79

Sample Time	Retention Time	Presumed Identification	Concentration (µg/l)	(nm/l) (1)
2/20/79	15.89	Carbon tetrachloride	0.2511	1.63
	16.68	Chloroform or 1,1-Dichloroethane	0.214	
	17.57	1,1,1-Trichloroethane	1.057	7.92
	18.11	Trichloroethylene	0.922	7.01
	20.49	Tetrachloroethylene	1.404	8.45
		Chlorinated Ethane Compounds		23.38
2/21/79	15.87	Carbon tetrachloride	0.198	1.29
	16.66	Chloroform or 1,1-Dichloroethane	0.252	
	17.52	1,1,1-Trichloroethane	1.580	11.84
	18.09	Trichloroethylene	1.252	9.52
	20.47	Tetrachloroethylene	12.882	77.60
	24.85	1,1,2-Trichloroethane	0.462	3.46
		Chlorinated Ethane Compounds		102.42
2/22/79	15.85	Carbon tetrachloride	0.268	1.740
	16.85	Chloroform or 1,1-Dichloroethane	0.260	
	17.53	1,1,1-Trichloroethane	2.851	21.36
	18.09	Trichloroethylene	1.547	11.76
	20.48	Tetrachloroethylene	9.597	57.81
	24.84	1,1,2-Trichloroethane	0.197	1.48
		Chlorinated Ethane Compounds		92.41
2/23/79	15.87	Carbon tetrachloride	0.335	2.18
	16.67	Chloroform or 1,1-Dichloroethane	0.214	
	17.55	1,1,1-Trichloroethane	1.452	10.88
	18.11	Trichloroethylene	1.010	7.68
	20.48	Tetrachloroethylene	20.05	120.80
	24.85	1,1,2-Trichloroethane	0.212	1.59
		Chlorinated Ethane Compounds		140.95
2/24/79	16.71	Chloroform or 1,1-Di chloroethane	1.56	
	17.59	1,1,1-Trichloroethane	0.04	0.30
	18.16	Trichloroethylene	0.30	2.28
	20.47	Tetrachloroethylene	0.11	0.67
		Chlorinated Ethane Compounds		3.25

(1) nanomoles/liter (nm/l)= $\frac{\text{nanogram (ng) chlorinated ethene compound/L}}{\text{molecular weight chlorinated ethane compound (ng)}}$

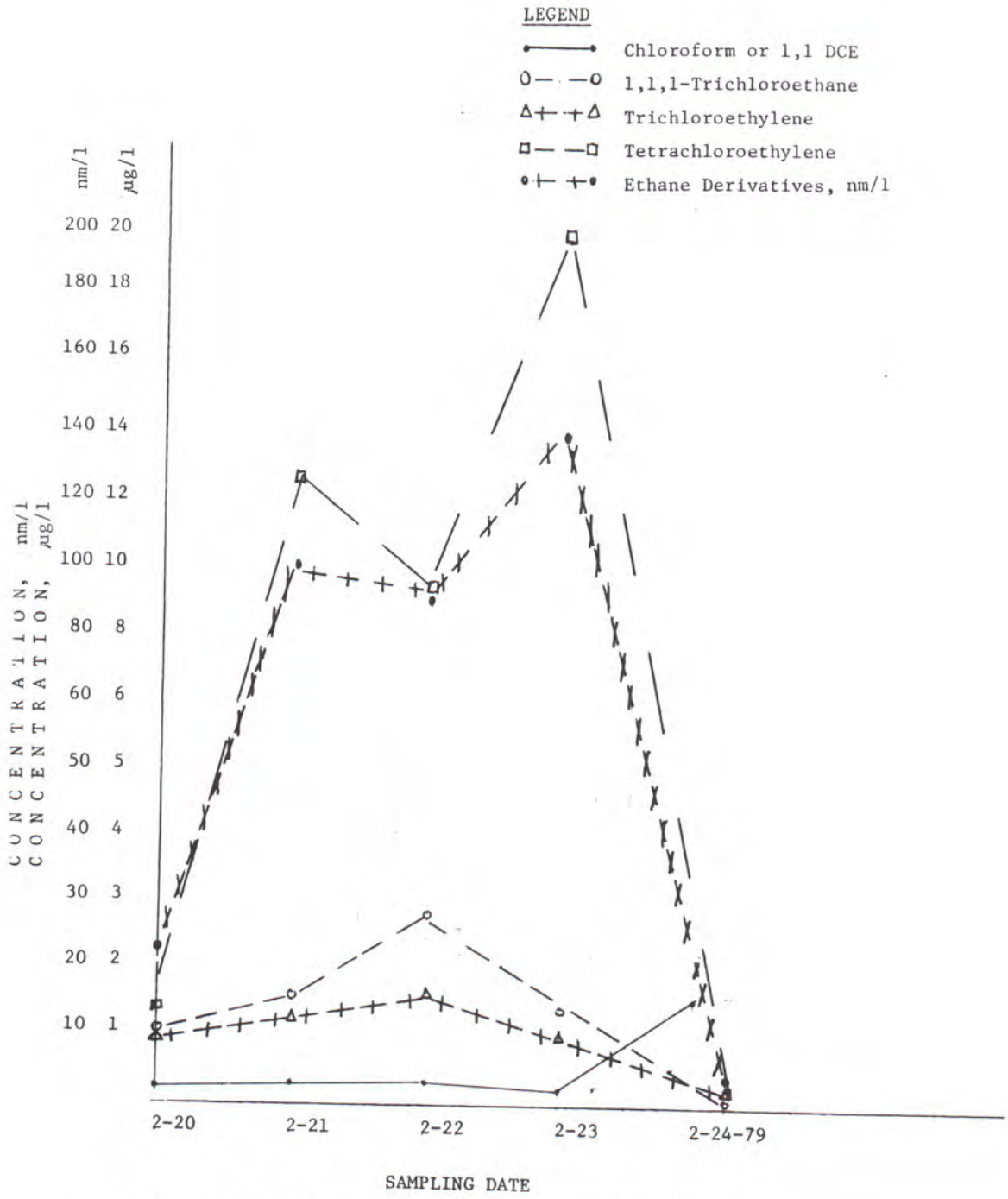


Figure 10. Chlorinated Compounds at Pittsburgh Site

Observation during February 21-22 indicates the following:

1. The tetrachloroethylene concentration decreased, while the remainder of the chlorinated compounds increased in concentration.

2. This trend is understandable because the inverse relation between the chlorinated compounds may have been due to a chemical mass balance being maintained during the synthesis of a chlorinated compound. This is assumed because the linear graph of the compound in namomoles/liter (nm/l) indicates the same region tends to plateau.

3. The rise in the plateaued chloroform while the other chlorinated compounds are decreasing could be the result of flushing reactors, tanks, and other equipment with the process solvent.

These data appear to indicate that the source of chlorinated compounds could be a chemical process waste effluent.

The information shown in Table 21 was provided by the personnel at the Pittsburgh Water Plant. There was no confirmation of this by the reference laboratory.

WHEELING, WV, FEBRUARY, 1980 - *OHIO RIVER*

During February, 1980, Wheeling reported elevated levels of tetrachloroethylene and chloroform. As shown in Figure 11 , tetrachlororoethylene concentrations on February 15 ranged from 10 to 23 µg/l, while chloroform levels as high as 45 and 38 µg/l were reported on February 16 and February 20 respectively. No cause for this event was identified. Downstream water utilities and state and federal agencies were notified. A sample was sent to the reference laboratory but the values were not confirmed.

ST. ALBANS, WV, JUNE 11-12, 1980 - *KANAWHA RIVER*

Analysis of the 8:00 AM, June 11, 1980, sample at the St. Albans site showed 24 µg/l chloroform. Analyses of the 10:30 AM and 2:00 PM samples showed 36 µg/l and 25 µg/l respectively. The reference laboratory confirmed 22 µg/l chloroform in a duplicate of the 2:00 PM sample. June 12 samples showed lower, near normal chloroform levels. Increased chloroform levels were not observed at Huntington because of dilution by the Ohio River and volatilization. Regulatory agencies in West Virginia, Kentucky and Ohio were notified.

ST. ALBANS, WV, AUGUST 11, 1980 - *KANAWHA RIVER*

On August 11, 1980, the West Virginia Department of Natural Resources reported an unknown spill accidentally lost from an industrial plant at Institute, West Virginia. On August 13, the St. Albans site measured 220 µg/l chloroform in a sample taken at 8:15 AM. The EWODS staff was subsequently notified by the West Virginia Department of Natural Resources that the spill had been 3800 pounds of chloroform. Time-of-travel estimates indicated arrival at the Huntington Site on August 18; a peak of 30 µg/l chloroform was

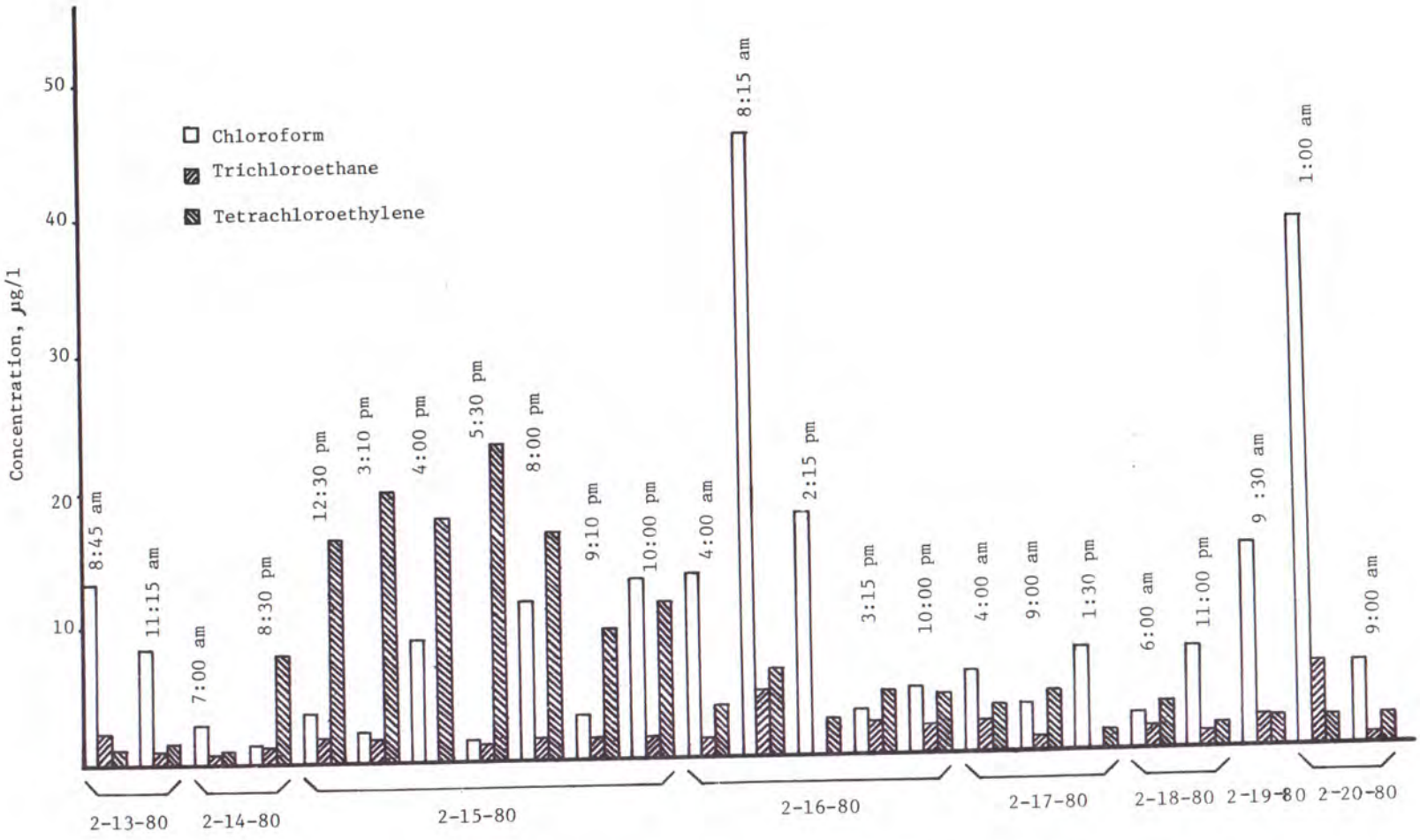


Figure 11. Presumptively Identified Purgeable Organics at Wheeling Site, February 13-20, 1980

detected on August 18 at 3:00 PM. Downstream states and water utilities were notified of the spill; samples at Portsmouth on August 20, the predicted arrival time, showed no unusual levels of chloroform.

SECTION 6

CONTINUING NEEDS

Operation of the Early Warning--Organics Detection System for two years has led to a recognition of additional areas for study and desirable expansions of the system's detection capabilities. As indicated in Section 4, a statistical analysis of the vast body of data collected by the system would provide a clearer picture of trends in organics concentrations in the Ohio and the major tributaries. Such an analysis would be a valuable aid to source location.

The initially installed EWODS equipment was limited to detection of purgeable halogenated organic compounds. The purgeable halogenated organic compounds represent only a limited number of the possible organic pollutants that might affect stream water quality. While there are techniques available to increase the number of organic compounds that can be detected, all methods require considerably more time to perform the test. Also, the evaluation of the resulting data becomes more difficult at the low levels present in the river.

The ORSANCO Water Users Advisory Committee recommended a long-range Organics Detection System plan that provided for expanded analytical capability only after adequate experience had been gained at a few stations. Another important group of organics substances produced in the Ohio Valley are the benzene-related compounds, purgeable aromatic hydrocarbons. The investigation of this group of organics began in 1980 with the installation of photoionization detectors (PID) at Wheeling and Huntington.

The PID is a nondestructive detector which detects purgeable aromatic hydrocarbons at the µg/l range and some inorganic species in the effluent of a gas chromatograph. The PID is equipped with a sealed ultraviolet (UV) light source that emits photons which pass through a UV transmitting window into an ionization chamber, where the photons are absorbed by the eluted compound. These compounds with an ionization potential less than the UV source energy are ionized. A positively biased high voltage electrode accelerates the resulting ions to a collection electrode. The current produced by the ion flow is measured by the electrometer and is proportional to the concentration.

With these detectors, bromobenzene is used as an internal standard. The initial purgeable calibration standard contains the following aromatics:

Benzene
Chlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Ethylbenzene
Toluene

An expanded program of daily monitoring for this group of trace organics was authorized in May, 1981. Installation of PID's is planned for five additional sites in FY 1982 and for the remaining four sites in the present system in FY 1983.

Another identified need is a continuing broadly based organic sampling program. Additional data are needed on all of the organic compounds that are bioaccumulative or have a known health effect. Additional state funds in FY 1982 provide for reinstituting monthly collection of samples for analysis for base neutral extracts by the reference laboratory.

The Water Users Advisory Committee in the long-range plan previously mentioned discussed the expansion of the present eleven (11) stations from two aspects: 1) protection of the water users along the river and, 2) capital cost for equipment and ongoing maintenance. The committee felt that a number of areas along the Ohio River are not being adequately monitored so that downstream users can be alerted of unusual conditions in a timely manner.

The committee recommended that means be explored to:

1. assist the commission in meeting maintenance needs;

2. assist the water utilities in meeting operation costs;

3. obtain and install equipment that will expand the number of compounds that can be detected;

4. provide for better availability of spare parts; and

5. expand the number of stations to cover the voids now present in the system.

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APPENDIX A

PROJECT BUDGET AND FUNDING SOURCES

A detailed proposal for establishment of the Early Warning--Organics Detection System was submitted to US EPA in August, 1977. A sharp difference of opinion developed between that agency and the commission as to the extent of the proposed project. An agreement was reached with US EPA on a two-phase approach, and a considerably reduced special grant offer of $100,000 for the project, "Demonstration of an Early Warning Organics Detection System for the Ohio River," (R00425723) was accepted by the commission in October, 1977. This grant provided funds for the purchase of gas chromatographic equipment for installation of four sites and additional equipment for GC instruments owned by three other participants. The commission funded general operating costs for the system--ORSANCO analytical personnel, data transmission, the reference laboratory, and other general expenses--by shifting funds from other ongoing programs. Because of the limited grant, only weekday operation was achievable.

In February, 1979, and September, 1979, US EPA special grants of $140,000 and $135,000 were received to fund daily operation and equipment for the second phase of the system. The commission was committed to continue operation of the system in 1981 using state funds and US EPA administered ongoing program grant funds provided under Section 106 of the Clean Water Act.

The funds used to purchase equipment and to operate and maintain the system from October, 1977, through June, 1980, are shown below:

PARTICIPATING SITES

Cost to install and operate GC's at utilities:

FY 1978, seven (7) units for 5 days/wk	$ 37,794	
FY 1979, seven (7) units for 5 days/wk	67,506	
FY 1980, eight (8) units for 7 days/wk and two (2) units for 5 days/wk	119,600	
		$224,900

US EPA SPECIAL GRANT FUNDS

Phase I		$100,000	
Four (4) GC units and accessories at three (3) additional sites			
Phase II			
Operation		140,000	
Equipment		135,000	
			$375,000

Four (4) GC units and accessories at two (2) additional sites and eleven (11) telecopiers at sites and one (1) at office

ORSANCO

Cost to provide project direction and equipment maintenance:

FY 1978			
State funds	$45,653		
US EPA 106 funds	35,149		
		$ 80,802	
FY 1979			
State funds	$57,473		
US EPA 106 funds	43,534		
		101,007	
FY 1980			
State funds	$44,345		
US EPA 106 funds	31,785		
		76,130	
			$257,939

SUMMARY

Participating Sites		$224,900	
US EPA Special Grants		375,000	
ORSANCO			
State funds	$147,471		
US EPA 106 funds	110,468		
		257,939	
			$857,839

The cost for laboratory GC/MS confirmation of site analyses of samples with unusual concentrations was included in operation costs absorbed by the commission from October, 1977, through March, 1979. The US EPA special grant of $140,000 for operational costs received in February, 1979, covered the reference laboratory costs from April, 1979, through June, 1980. Among these

costs were monthly broad analyses for all priority pollutant organics for one year, including solvent extractable analyses and duplicate purgeable analyses of samples from each of the system's sites.

Based on the cost of the system for FY 1980, an average annual cost per station for operation on a seven (7) day a week basis and maintenance of the system would be:

Participating Sites		$14,352
ORSANCO		8,130
	TOTAL	$22,482

This figure is for 1980 cost; no inflation has been considered. This figure does not include the equipment cost. If future sites are established, the cost of equipment could be considerably less because of technological advances in this analytical area.

A P P E N D I X B

PROTOCOL

PROTOCOL FOR PURGEABLE ORGANICS IN RAW WATER BY THE PURGE-AND-TRAP METHOD

414 Walnut Street
Cincinnati, Ohio 45202

October, 1978

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FOREWORD

The narrative which follows reflects the current state-of-the-art in purge-and-trap analysis of raw water, as used by the ORSANCO Early Warning--Organics Detection System (EWODS). The detection system incorporates the staff's original plan, as well as advice and suggestions from various qualified EPA personnel and from the equipment supplier's representatives. The system is designed to detect and measure volatile organics (as defined by the Bellar method[1]) at the part per billion level in a treatment plant's raw water supply.

Currently, GC analytical equipment for the EWODS is installed at five locations along the Ohio River and one each on the Allegheny and the Kanawha Rivers. The equipment consists of Perkin-Elmer Co. SIGMA I GC's at all sites, with the exception of Pittsburgh and Louisville, which have a Hewlett-Packard 5830 GC and Hewlett-Packard 5840 GC, respectively. All of the GC systems have demonstrated their effectiveness in detecting purgeable organics at the 1 µg/1 level. Station locations are shown in Figure 1 and the equipment at these locations are listed in Table I:

TABLE I

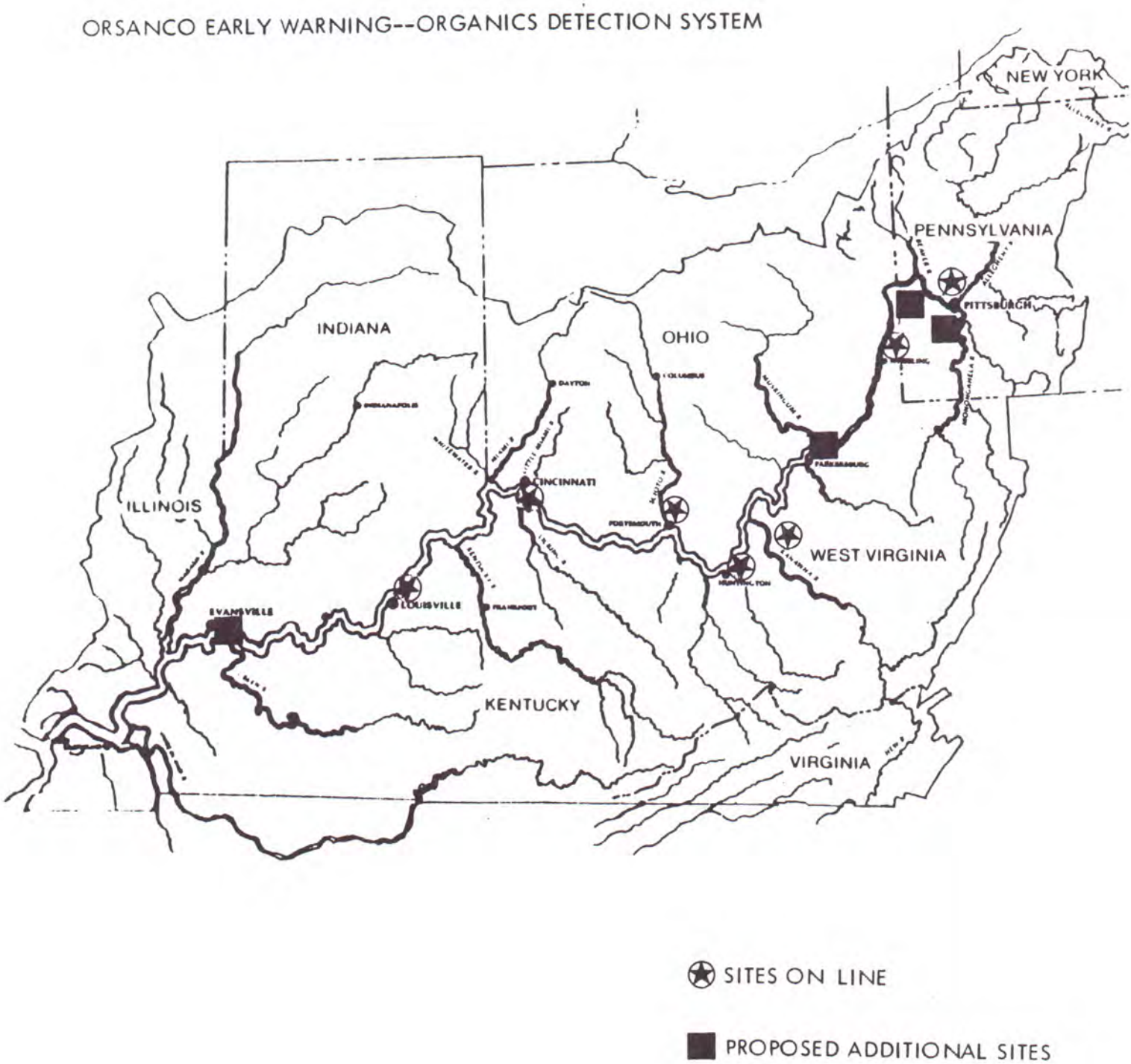
Location and Type of Equipment at EWODS Sites

EWODS Sampling Locations	Location	Purge & Trap System	GC System	GC Detector
Pittsburgh, Pa.	Allegheny	CDS*	HP 5830	CCD, FID, ECD**
Wheeling, W.Va.	Ohio	CDS	PE SIGMA I	CCD, FID
St.Albans, W.Va.	Kanawha	CDS	PE SIGMA	CCD, FID
Huntington, W.Va.	Ohio	CDS	PE SIGMA	CCD, FID
Portsmouth, Oh.	Ohio	CDS	PE SIGMA I	CCD, FID
Cincinnati, Oh.	Ohio	CDS	PE SIGMA I	CCD, FID
Louisville, Ky.	Ohio	CDS	HP 5840	CCD, FID, ECD

* CDS 310-012 Sparging concentrator - CDS

** CCD - Coulson Electroconductivity Detector
FID - Flame Ionization Detector
ECD - Electron Capture Detector

Figure 1


ORSANCO EARLY WARNING--ORGANICS DETECTION SYSTEM
NEW YORK
PENNSYLVANIA
PITTSBURGH
INDIANA
OHIO
DAYTON
COLUMBUS
CINCINNATI
ILLINOIS
EVANSVILLE
LOUISVILLE
WEST VIRGINIA
KENTUCKY
VIRGINIA
SITES ON LINE
PROPOSED ADDITIONAL SITES

The daily routine of the EWODS is as follows: Each day the plant chemist at each station takes duplicate two-ounce non chlorinated raw water samples which are headspace free. Simultaneously, he collects a one-gallon solvent-extractable sample for possible alert situations. One of the two-ounce samples is run through the purgeable GC analytical protocol by the plant operator, in accordance with quality control procedures. An internal standard, 1,4-dichlorobutane, is spiked into organic-free water and run before the daily raw water sample 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.

The resulting raw water GC plot and printout is telecopied to ORSANCO headquarters in Cincinnati. At the ORSANCO headquarters the incoming telecopy materials are examined by the EWODS staff members. If a significant concentration of one or more organics is noted, an alert may be declared, after consultation between ORSANCO staff and the plant operator. During an alert situation the remaining two-ounce sample and one-gallon solvent-extractable samples are shipped by plant personnel to the Cincinnati-based contract analytical laboratory for GC-MS confirmation. During non-alerts the samples are discarded the next day and the bottles are cleaned for subsequent usage.

The standard routine also involves running a 16-component purgeable organic standard purchased from Radian Corporation. These purgeable standards are run on alternate weekdays and quantitation of raw water standards is based on the response factors obtained from the last purgeable standard run.

The 16 halogenated compounds contained in the standard and their elution order are given below:

1,1-Dichloroethane
Chloroform
1,2-Dichloroethane
1,1,1-Trichloromethane
Carbon tetrachloride
Bromodichloromethane
1,2-Dichloropropane
Trans-1,3-Dichloropropene
Trichloroethylene
* Cis-1,3-Dichloropropene
* 1,1,2-Trichloroethane
* Dibromochloromethane
Bromoform
* 1,1,2,2-Tetrachloroethane
* Tetrachloroethylene
Chlorobenzene

Certain of these compounds (indicated by an asterisk) are co-eluters. As a result, the typical chromatogram produced by this standard contains only 13-14 distinct peaks instead of 16.

The purgeable standards data from each EWODS site--i.e. retention time, relative retention time, response factors--are tabluated, along with the statistically evaluated mean, standard deviation, and range for each significant GC peak. Observation of these data enables the EWODS staff to define areas where they may be of assistance to the site operators. Eventually, the hand-tabluated data from purgeable standard-internal standard runs and raw water-internal standard runs will be key-punched and processed by the Commission's IBM 1130 computer.

A more complete description of the system is given below. The material is presented using the accepted EPA-EMSL format for analytical procedures[2]. While there is considerable detail included in this writeup, the very fine details of instrument operation required for the procedure are omitted. Instead, the minutiae of the procedure, including step-by-step instructions for operation of the purge-and-trap units, the detector and the microprocessor, are contained in another document intended specifically for the station operators and other interested parties.

1. Scope

1.1 This method is applicable to the determination of purgeable organics in raw river and drinking waters. Some of the purgeable organics, but not all, are as follows:

1,1-Dichloroethane	trans-1,3-Dichloropropene
Chloroform	Trichloroethylene
1,2-Dichloroethane	Cis-1,3-Dichloropropene or
1,1,1-Trichloroethane	1,1,2-Trichloroethane or
Carbon tetrachloride	Dibromochloromethane
Bromodichloromethane	Bromoform
1,2-Dichloropropane	1,1,2,2-Tetrachloroethane or
Chlorobenzene	Tetrachloroethylene
	1,4-Dichlorobutane (Int. Std.)

1.2 The method is reported by USEPA to be sensitive to purgeable organics over a concentration range of 0.1 to 1500 µg/l. The actual detection limits are dependent upon various instrumental factors and operator's skills.

2. Summary of Method

2.1 Trihalomethanes and certain other volatile organic compounds which exhibit low water solubility and a vapor pressure greater than water are extracted by an inert gas, i.e., helium or nitrogen, and trapped on a column containing Tenax GC polymeric sorbent. After a predetermined purge time the trapped compounds are thermally desorbed and backflushed onto the head of a gas chromatographic column and separated under programmed conditions. Measurement is accomplished with an electrolytic conductivity detector that is halogen-specific. The quantitation is based on the internal standard mode of calculation.

2.2 Organic standards and an internal standard are analyzed under identical conditions in order to compensate for operational differences and to establish relative retention times (RRT), response factors (RF), and quantitative values.

2.3 The sample analysis time, based on the temperature program, is approximately 30 minutes. The daily routine includes an internal standard run followed by a raw water run. Purgeable standards containing an internal standard are run on alternate weekdays. No analyses are performed on Saturday or Sunday.

3. Interferences

3.1 Purge gas impurities and organic compounds out-gasing from the plumbing ahead of the trap may cause a contamination problem. Observation of the daily internal standard chromatogram for extraneous organics and changing response factors may indicate whether out-gasing is occurring. (See Appendix 1)

3.2 Bent, nicked, or deformed Teflon ferrules in the purge gas transfer lines may permit a vapor leak at a fitting, resulting in a decrease in peak areas. This difficulty is most easily detected by comparing peaks of purgeable standard runs.

3.3 Severe contamination of samples and purge units may occur if the syringes are not properly cleaned. Between uses the syringes should be flushed with reagent grade methyl alcohol or acetone and baked out in a 70°C oven. (See Appendix 2)

Note: The syringe should not be dried in an oven at temperatures higher than 70°C; the uneven glass-metal expansion will crack it!

3.4 Special care should be taken to minimize the storage and use of volatile organics in the analysis area. Sample contamination may occur through the septum seal into the sample. The sample blank is used to monitor for this problem.

3.5 Cross-contamination may occur when raw water samples and purgeable standards are sequentially analyzed. To reduce the likelihood of this, purge reservoir and sample syringe should be rinsed out twice between samples run, raw water sample, and purgeable standard run. A bake-out of the GC separation column at 170°C and 40 ml/min. carrier flow for one hour should be initiated after each purgeable standard run. The CDS 310-012 Tenax GC traps should also be baked out under manual control at 200°C at a helium rate of 40 ml/min. for a period of one hour after each purgeable standard run. All extraneous organic materials should be absent from the succeeding internal standard run before attempting another raw water analysis. (See Appendix 3)

3.6 Excessive base line noise during the GC-CCD runs is an indication of the exhaustion of the mixed-bed demineralizer attached to the CCD detector. When this occurs the resin should be replaced. (See Appendix 4)

3.7 Qualitative identifications are sometimes a problem in GC analysis because of co-eluting organics compounds. In order to minimize the possibility of incorrect identification during alert situations, GC/MS analysis will be conducted by the consulting analytical laboratory to provide confirmatory qualitative identification.

4. Apparatus

4.1 The purge-trap equipment at each site is a Chemical Data System (CDS), sparging concentrator-model 310-012, consisting of a purging reservoir, trap and desorber. This is an automated instrument that operates in the manual, prompter, and automated mode, as selected. The automated mode of operation is used routinely. The volatile organics are removed by the purging gas and concentrated on a trap which consists of a 1/8 inch OD by 24-inch long tube packed with Tenax GC. The concentrated organics are pulse heated from the trap onto the head of the GC column. Since the CDS system has two traps, a second sample may be purged while the first sample is being desorbed. Each EWODS site is supplied with an operation manual which discusses the installation of the CDS unit with descriptions of the manual, prompter, and automatic operation modes.

4.2 The gas chromatographs used at each site are listed in Table I. The Perkin-Elmer SIGMA I units are equipped to contain a packed column and a capillary column. The Hewlett-Packard units are equipped to contain two packed columns.

The SIGMA I's keyboard is used to set analytical parameters, including carrier gas flow rates, automatic switching of analog to digital interface outputs, and external event timing. A printer-plotter attached to the SIGMA I microprocessor supplies a data printout, a detector chromatogram, and specific method control data.

The Perkin-Elmer gas chromatographs are equipped with 12 foot x 2 mm I.D. stainless steel columns. The packing used is 0.2% Carbowax 1500 on Carbopack-C, 60/80 mesh.

4.3 Each GC in EWODS is equipped with a Coulson electrolytic conductivity detector (CCD) capable of detecting nanogram quantities of halides. The specific details of construction and operation are given in the operator's manual.

4.4 Micro syringes, 10 µl, 50 µl, 100 µl, 500 µl (2 each).
Syringe needles, 20 cm x 20 gauge with female Leur end.
Syringe, 20/30 ml, gas tight with male Leurlock tip (2 each).
Valve, 2 way, with male and female Leur ends (2 each).

4.5 Gas pressure regulators, 2-stage stainless steel diaphragm, with check valve for helium, hydrogen and air (one each).

4.6 Gas drying tube with 1/4 or 1/8 Swagelock connection packed with molecular sieve 5A and moisture color indicator for drying helium, hydrogen, and air.

5. Reagents and Materials

5.1 Tenax GC, 2,6-diphenyloxide, porous polymer packing, 60/80 mesh, chromatographic grade for purge traps.

5.2 0.2% Carbowax 1500 on Carbopack-C, 60/80 mesh (NOTE: EPA protocol recommends Batch # R-1579 for GC separation columns).

5.3 Organics-free water. A Millipore-Super Q system or its equivalent may be used to generate organic-free water. Alternatively, organic-free water may be generated by passing distilled water through a column of granulated activated carbon at a flow rate to allow a retention time of about 15 minutes. The following carbons are adequate: Filtrasorb 400, pore size 50 A or Filtrasorb C, pore size 5 A, designed for low molecular weight compounds, both available from Calgon Corporation.

5.4 Molecular Sieve 5 A or 4 A, 8/12 mesh, with moisture color indicator for packing moisture removal traps on gas lines.

5.5 Helium gas, high purity - 99.95% purging and carrier gas.
Hydrogen gas, high purity - 99.95% detector fuel.
Dry air, maximum moisture 3 ppm, FID air source; or if necessary, use for mechanical pneumatics, i.e., CDS axial valve and SIGMA I oven door lift.
NOTE: Compressed air for operation of pneumatic valves; may be house supply source regulated to 40 ± 10 PSI. Moisture and compressor contaminants should be removed with a trap containing a

suitable sorbent such as molecular sieve 5A, 4A (Cf 5.4). The trap should be placed close to the air supply line junction toward the CDS pneumatic valve and the GC oven lid lift.

5.6 Methanol, ACS reagent grade, distilled in glass.

5.7 1,4-Dichlorobutane, ACS reagent grade.

5.8 Purgeable standards, halogenated (containing 16 halogenated compounds).

The 16 halogenated compounds contained in the standard and their elution order are given below:

1,1-Dichloroethane	
Chloroform	Trichloroethylene
1,2-Dichloroethane	*Cis-1,3-Dichloropropene
1,1,1-Trichloroethane	*1,1,2-Trichloroethane
Carbon tetrachloride	*Dibromochloromethane
Bromodichloromethane	Bromoform
1,2-Dichloropropane	*1,1,2,2-Tetrachloroethane
Trans-1,3-Dichloropropene	*Tetrachloroethylene
	Chlorobenzene

Certain of these compounds (indicated by an asterisk) are co-eluters. as a result the typical chromatogram produced by this standard contains only 13-14 distinct peaks instead of 16.

6. Sample Containers

6.1 Two-ounce screw cap vials sealed with Teflon-faced silicone septa for head-space free purgeable organic samples. The vials are supplied clean by the contract analytical laboratory.

6.2 One-gallon bottles, sealed with Teflon-faced silicone septa for solvent-extract samples. These bottles are supplied clean by the contract analytical laboratory.

6.3 The two-ounce screw cap vials and one-gallon bottles in use at each station may be washed for reuse following the procedure described in 8.3.

7. Preparation of Standards

7.1 Clean all glassware before use by rinsing first with organic-free water, and then with reagent grade methanol or acetone, followed by oven drying at 105°C.

7.2 Internal standard, stock solution. Place about 9.8 ml of reagent grade methanol in a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand unstoppered about 10 minutes or until all methanol-wetted surfaces have dried. Stopper the flask and weigh to the nearest 0.1 mg. Using the 25 ul syringe, fill the syringe barrel with ACS reagent grade 1,4-dichlorobutane until bubbling in the syringe subsides. Adjust the syringe contents to approximately 17.6 ul of 1,4-dichlorobutane. Immediately add the contents of the syringe to the methanol in the tared 10 ml. volumetric flask. Stopper the flask, then reweigh. Be sure the 1,4-dichlorobutane is released into the methanol without contacting the neck of the flask. Dilute the stock to volume with methanol, stopper, then invert to facilitate mixing.
NOTE: Prepare standard dilutions in a well-ventilated hood.
Calculate the concentration in milligrams per liter from the net gain in weight (mg/l).
Store the 1,4-dichlorobutane stock solution at $4^{o}C$.

7.3 Internal standard, working solution. Add sufficient quantity (approximately 100 μl) of the stock 1,4-dichlorobutane to 10 ml. of methanol in a glass-stoppered volumetric flask to produce a 20 mg/1 working solution. Store the working solution at $4^{o}C$.
NOTE: Methanol solutions are stable up to about four weeks when stored under these conditions. They should be discarded if a GC-CCD run indicates contamination or loss of concentration.

8. Sampling Containers and Sampling

8.1 The contract analytical laboratory initially supplies narrow-mouthed two-ounce bottles which have been detergent washed, rinsed and dried at $400^{o}C$. A Teflon-faced silicone septa is sealed in place with an open-top cap.

8.2 The contract analytical laboratory also supplies clean narrow-mouthed one-gallon bottles to each EWODS site. A Teflon-faced silicone septa is sealed in place with a plastic cap.

8.3 When it is necessary for an EWODS operator to prepare containers for sample collection, the bottles and caps should be washed with a detergent, rinsed with tap water and finally very thoroughly with

organic-free water. Allow the bottles, seals, and caps to air dry at ambient temperatures, place in a 105°C oven for one hour, then allow to cool in an area free of organic vapors.

NOTE: Do not heat the Teflon seals for longer than one hour because the silicone layer degrades at 105°C. When cool; seal the bottles using the Teflon seals that will be used for capping the samples.

8.4 Secure a sample from a water tap as follows: Turn on the water and allow the system to flush. When the temperature of the water has stabilized, adjust the flow to minimize bubbling in the sample bottle and collect duplicate samples from the flowing stream. When a two-ounce sample is being collected place the completely filled bottle on a level surface, position the Teflon side of the seal on the convex sample meniscus and seal the bottle by screwing the cap on tightly. Invert the bottle and lightly tap the cap on a solid surface. The absence of entrapped air indicates a successful seal. If a small bubble, larger than an upper case "O" is present, add a few additional drops of sample and reseal the bottle as above.

8.5 Collect blanks in duplicate at the laboratory by filling and sealing sample bottles with organic-free water at the same time the regular samples are secured. Store the blanks and samples collected at the same time in the same place. (Label samples, Appendix 5)

8.6 When samples are to be shipped from the sampling point to the analysis site, the blank sample should be transported similarly. Any contaminating impurities picked up by the sample during shipping should also show up in the blank.

8.7 The EWODS routine sampling protocol should include duplicate two-ounce tap water samples, a one-gallon tap water sample and appropriate blanks. Bottles not shipped to Cincinnati may be washed for reuse, following the procedure described in 8.3.

9. Analytical Procedure

9.1 The various components of the analytical system are set prior to use according to the manufacturer's directions for the trap:

Trap temperature	-	Purge — Ambient Desorb — 180°C.
Trap flows	-	Purge — 60 ml/min. for 16 min. Desorb — 40 ml/min. for 4 min.

9.2 For routine analysis of organic-free waters, internal standards, purgeable standards, and raw water samples the following settings are used for the gas chromatograph:

Injection temperature	250°C.
Carrier gas to column	40 ml/min.
Effluent valve temperature	200°C.
Initial oven temperature for 4 minutes	60°C.
Temperature program	8°/min. to 170°C for 13 min.

9.3 Using the 20 or 30 ml syringe, place 10 ml of organic-free water in the syringe chamber. Add 2.0 µl of internal standard working solution through the 2-way valve into the organic-free water, attach the syringe needle to the 2-way valve. Inject the contents into the purge reservoir. Commence purge and proceed through analytical sequence according to the SIGMA I microprocessor controls. Examine the resulting printout and chromatograph for stable baseline and absence of extraneous peaks. If the chromatogram is satisfactory, proceed with raw water analysis.

9.4 If the organics-free-internal standard chromatogram shows an unsteady baseline, extraneous peaks, or other unusual behavior, discuss the difficulty with the ORSANCO staff for corrective measures.

9.5 Using the 20 ml or 30 ml syringe, place 10 ml of non-chlorinated raw river water into the syringe chamber and spike in a 2.0 µl of internal standard working solution. Proceed through the analytical sequence using precisely the same microprocessor controls as for the blank-internal standard run. Examine the resulting printout and chromatograph for evidence of unusual organic materials or for unusual concentrations of compounds known to be present normally.

9.6 On alternate days prepare, in the 20 or 30 ml syringe, a purgeable standard from the purgeable standard stock solution, spike it with 2.0 µl of 1,4-dichlorobutane working standard, place it in the CDS purge unit, run in the same manner as the internal standard and raw water samples. Develop response factors from purgeable standard file by use of microprocessor controlled calibration directive. These developed response factors will be recalled for raw water sample quanitation by a report directive.

9.7 Transmit copies of all printouts and chromatograms, along with proper identification of source, time, etc., and any pertinent observations, via telecopier to ORSANCO headquarters.

10. Alert Situations

10.1 When the daily raw water is taken for the purge analysis, prepare a duplicate sample at the same time. Also at the same time secure a one-gallon sample in a clean jar; also prepare the necessary blank samples and hold or ship as required (Cf 8.5, 8.6 and 8.7).

10.2 If an alert situation is declared the duplicate sample and blanks are shipped immediately to the contract analytical laboratory by quick delivery service previously chosen. When it is certain that the duplicate samples are not required, they should be discarded.

11. Calculations

11.1 Most of the 16 purgeable halogenated compounds in the stock standard solution provided by Radian Corporation are present at concentrations of 20 mg/l. When diluted to 2 µg/l and GC-analyzed, these standard components have different area responses or response factors (RF). The RF's are calculated by comparison of peak areas and known concentrations for each component, using the microprocessor controlled calibration directive. The RF values are then recalled to calculate concentrations of halogenated compounds that may appear in the raw water sample by using a microprocessor controlled report directive.

11.2 The retention times (RT), relative retention time (RRT), and response factors (RF) from purgeable internal standards samples are tabulated, and mean and standard deviations are computed. Review of this data facilitates GC peak identifications and possible detections of column deterioration by observation of changes in RRT and RF.

11.3 The RT's and RRT's and concentrations of components in raw water samples are tabulated, and mean and standard deviations values are calculated. Review of this data permits observation of trends in occurrence and concentration of purgeable compounds in the raw water.

B I B L I O G R A P H Y

1. Bellar, T. A., Lichtenberg, J. J., Determining Volatile Organics at the Microgram per Litre Levels by Gas Chromatography, Journal AWWA., 66, 739 (December, 1974).

2. The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method, EPA, EMSL, Sept., 1977.

A P P E N D I C E S

1. Linde, high purity helium gas, 99.995% purity. cylinder content is discharged through a stainless steel diaphragm, two-stage regulator and then filtered through molecular sieve 5A,with moisture color indicator, prior to being split for use as a purging gas and GC carrier gas.

2. The device shown in the accompanying sketch may be used for cleaning and drying the hypodermic syringes.

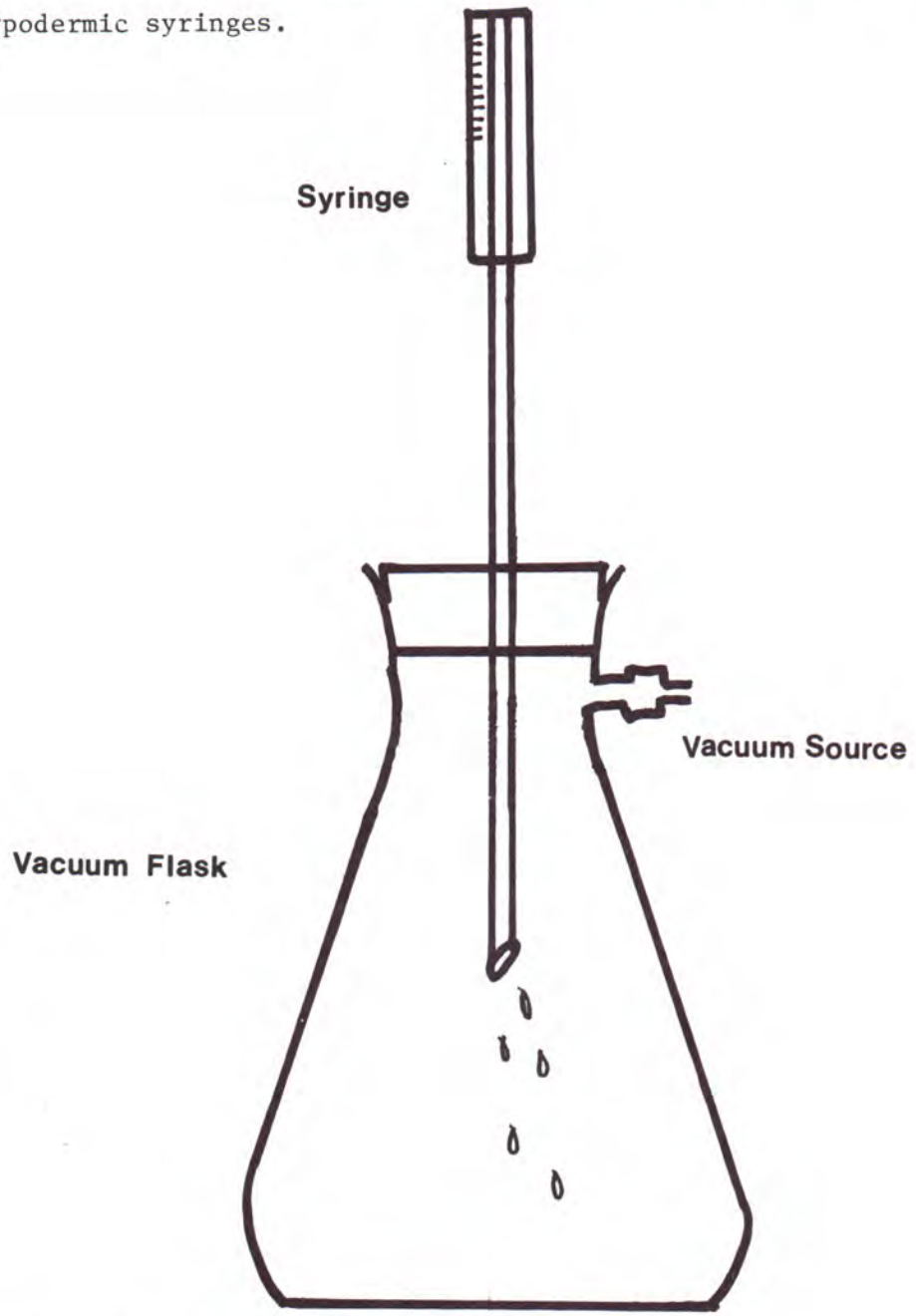


Figure 1 Syringe Evacuator

3. Certain heavier molecular weight compounds may not be completely recovered. The efficiency of recovery may be related to sample volume, purge time, purge flow rate, purge temperature, etc. It is important, therefore, that samples and standards be analyzed using identical procedures.

4. A fresh supply of mixed-bed resin may be obtained from ORSANCO-EWODS. The resin used is Bio-Rad, AG 501-X8D.

5. Label samples - The samples and blanks are to be labeled and should contain the following information, i.e., site location, sampling time and date, sampler's initials, analyzer's initials, and source of sample.

APPENDIX C

Prototype Interagency Agreement and Letter of Understanding entered into between ORSANCO and each EWODS site.

COOPERATIVE AGREEMENT

FOR

DEMONSTRATION OF EARLY WARNING
ORGANICS DETECTION SYSTEM
IN THE OHIO RIVER BASIN

THIS AGREEMENT, by and between the Ohio River Valley Water Sanitation Commission, hereinafter referred to as "ORSANCO," and the _____ _____, hereinafter referred to as "_____ _____."

W I T N E S S E T H:

WHEREAS, in accordance with an understanding reached at the ORSANCO Water Users Committee meeting on September 29, 1977 and reaffirmed at a meeting of the participants in the Early Warning-Organics Detection System on February 2, 1979, ORSANCO requests the _____ to participate in a cooperative project to demonstrate an Early Warning Organics Detection System as set forth herein; and

WHEREAS, participation in the demonstration project will require the _____ and ORSANCO to assume certain responsibilities relating to operation of various aspects of the system which are enumerated herein, and the _____ is desirous of cooperation with ORSANCO in order to continue, improve and expand an early warning Detection System in order to improve _____water supply system; and

WHEREAS, ORSANCO has received federal assistance in implementing the project, a copy of which is annexed hereto and identified as Appendix A, and the _____ responsibilities involve the taking of samples, furnishing of laboratory space, and the furnishing of personnel, but do not involve the direct expenditure of money as a contribution to the

project; and

WHEREAS, the services provided by ORSANCO are not competitive in nature and are urgently required by the _____ as a means of improving its drinking water supply system through the early detection of organic contaminants;

NOW, THEREFORE, in consideration of the mutual promises, terms and conditions contained herein, the parties hereto do hereby agree as follows:

1. ORSANCO will pay for the following expenses incurred in the operation of the project:

   a. Purchase, install and maintain a gas chromatograph and accessories needed to meet established project standards.

   b. Furnish a transceiving device and assume associated telephone charges for transmitting and receiving information needed by the project.

   c. Contract laboratory fees for confirming of gas chromatograph presumptive analyses of raw water samples through mass spectrometer identification, including cost of bottles, shipping containers, and transport expenses.

   d. Supply standards for identification of organic substances.

2. The _____ shall provide the following:

   a. Suitable laboratory facilities for performing the presumptive tests and transmitting presumptive results.

   b. Technical personnel on a seven-day-a-week basis to collect daily river samples, perform presumptive test(s), including preparation of standards, transmit results to ORSANCO, including the forwarding of such remaining or additional samples as may be required for confirmation by mass spectroscopy during an unusual situation, and for such other assistance as may be required in coordination with the ORSANCO staff to properly maintain the instrument.

3. Dissemination of data resulting from the project shall be in accordance with procedures agreed upon by the ORSANCO Water Users Committee, a copy of which is attached to this letter as Appendix B.

4. All areas to be included in the project will be determined by mutual agreement between the _____ and ORSANCO. Laboratory methods employed shall demonstrate the recommended protocol developed in coordination with the U. S. EPA through the National Screening Program for Organics in Drinking Water. Agreed project standards shall be maintained by the _____ to assure accuracy and to permit comparison with data from other project locations.

5. The _____ shall maintain adequate accounting records of its "in-kind services" in a manner mutually agreed upon by the _____ and ORSANCO. These records shall be used in computing the matching share requirements under this project, which is funded, in part, by the U. S. EPA.

6. If the services to be provided by the _____ are not being carried on in a mutually satisfactory manner, either ORSANCO or the _____ may terminate this agreement upon 60 days written notice to the other party. If the understanding is renewed beyond the performance period identified in paragraph 7 below, the understanding may be thereafter terminated for the convenience of either party upon 60 days written notice to the other party.

7. The service to be provided is effective for the period _____ through _____ and shall automatically renew for an

additional one year period, unless the understanding is terminated pursuant to paragraph 6 above.

8. Upon completion or termination of the understanding, any non-expendable property acquired with Federal funds and/or any equipment, accessories, and supplies furnished by ORSANCO shall be disposed of in such a manner as may be prescribed in writing by ORSANCO and shall be in accordance with 40CFR30.810 EPA grant regulations.

9. Records resulting from this project shall be deposited in the ORSANCO office and shall become part of the records of that office. Copies shall be furnished to the _____ upon request.

IN WITNESS WHEREOF, the parties have hereunto subscribed their names, the _____ by and through _____, on the _____ day of _____, 1979, and the Ohio River Valley Water Sanitation Commission (ORSANCO) by Leo Weaver, its Executive Director and Chief Engineer, on the _____ day of _____, 19 .

OHIO RIVER VALLY WATER
SANITATION COMMISSION

By_____

Date _____

If you find these conditions acceptable, please indicate your acceptance below:

The responsibilities described above are acceptable to:

The Huntington Water Corporation	Ohio River Valley Water Sanitation Commission
by_____	by_____
Date_____	Date_____