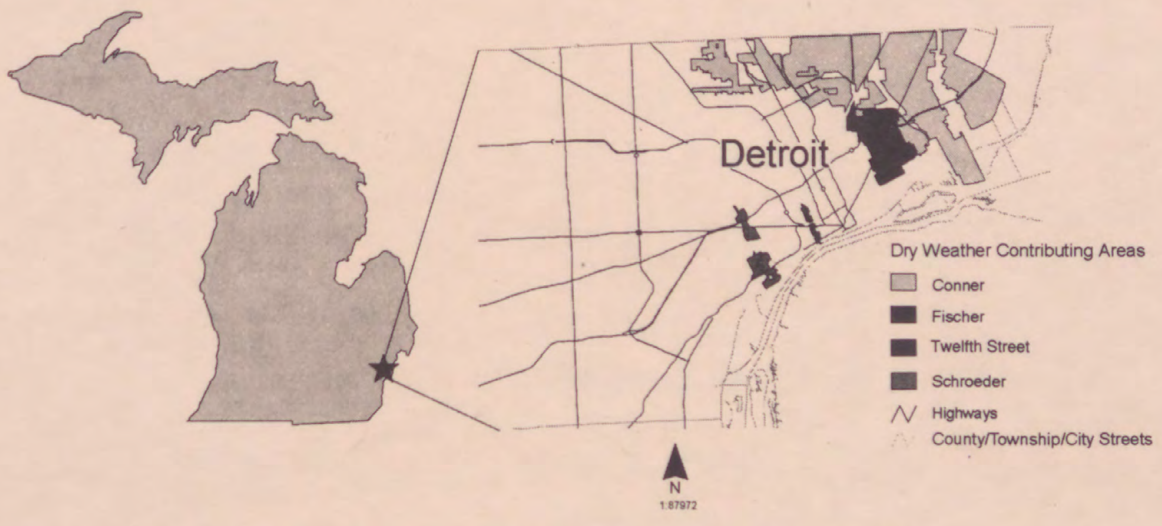


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U.S. GEOLOGICAL SURVEY
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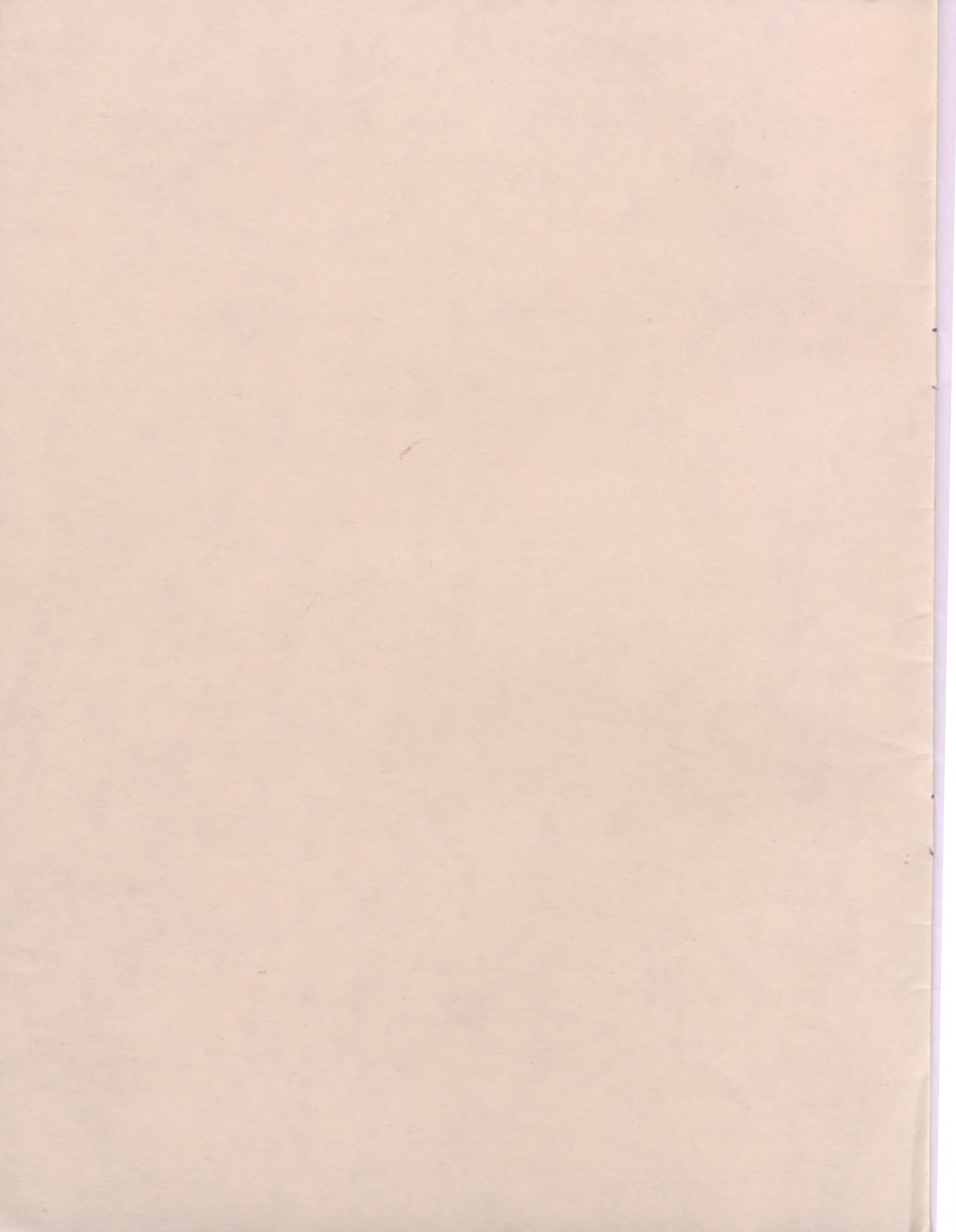


Southeast Michigan Council of Governments



Michigan Department of Environmental Quality





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Combined-Sewer Overflow Data and Methods of Sample Collection for Selected Sites, Detroit, Michigan

By M.J. Sweat and J.R. Wolf

Open-File Report 96-646

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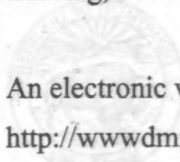
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CONVERSION FACTORS AND ABBREVIATED WATER QUALITY UNITS

Multiply	By	To Obtain
meter (m)	3.281	foot
centimeter (cm)	.3937	inch
meter per second (m/s)	3.281	feet per second
liter (L)	.2642	gallon
milliliters (ml)	.0002642	gallon

Abbreviated water-quality units used in this report: Chemical concentrations and water temperature are given in metric units. Chemical concentration is given in milligrams per liter (mg/L) and micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as a weight (milligrams) of solute per unit volume (liter) of water. Likewise, micrograms per liter is a unit expressing the concentration of chemical constituents in solution as a weight (micrograms) of solute per unit volume (liter) of water.

Combined-Sewer Overflow Data and Methods of Sample Collection for Selected Sites, Detroit, Michigan

By Michael J. Sweat and Jason R. Wolf

ABSTRACT

From October 1, 1994 through December 31, 1995, four combined sewers discharging to the Detroit River in Detroit, Michigan were monitored to characterize storm-related water quantity and quality. Water velocity, stage, and precipitation were measured continuously and recorded at 5-minute intervals. Water-quality samples were collected at discrete times during storms and analyzed for inorganic and organic pollutants. This report includes the sampling approach, field collection and processing techniques, and methods of chemical analysis, as well as a compilation of combined-sewer discharge volumes, chemical data, and quality control data. These data may be used by resource managers and scientists to (1) describe temporal variations for pollutant concentrations in combined-sewage from storm-to-storm; (2) describe spatial distribution of selected pollutants in four combined-sewer overflows discharging to the Detroit River; (3) calculate pollutant loads to the Detroit River from four combined-sewer overflows for monitored storm events; (4) estimate pollutant loadings from other combined-sewer overflow sites; and, (5) provide data and information which can be used to define appropriate management methods to reduce or eliminate untreated combined-sewer overflow discharges.

Discharge from selected combined-sewer overflows was sampled between 30 and 78 times for inorganic pollutants, and between 14 and 22 times for organic pollutants, depending on the site. These samples represented between 8 and 17 storms during which one or more of the four selected combined-sewer overflows discharged. The monitored pollutants included fecal coliform, fecal streptococci, and *Escherichia coli*; antimony, arsenic, beryllium, cadmium, hexavalent chromium, total chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, silver, thallium and zinc; and polychlorinated biphenyl con-

geners, volatile organic compounds, and polynuclear aromatic hydrocarbons. Metal and non-metal inorganic pollutants were detected at all sites. Many organic pollutants were not detected at all.

INTRODUCTION

The City of Detroit Water and Sewerage Department (DWSD) operates a combined sewer system with 78 discharge points. Forty-six sites are on the Detroit River and 32 sites are on the River Rouge. Combined sewers are designed, constructed, and operated to carry both sanitary sewage and storm-water runoff. Combined-sewer overflows (CSOs) are structural devices on combined sewer systems that divert sanitary sewage mixed with storm water to a river, stream, or lake. During dry weather all sanitary sewage is conveyed to the wastewater treatment plant. For small precipitation events the storm water is conveyed with the sanitary sewage to the wastewater treatment plant; however, during large precipitation events, those flows which exceed the capacity of the sewer system overflow to surface waters. Discharge from CSOs constitutes serious environmental and public health concerns because it is a direct discharge of both untreated sanitary sewage and storm water.

Untreated discharge from CSOs typically contains floatables, sediment, nutrients, organic material, oil and grease, metals, pathogens, and other pollutants. Floatables and oil and grease may cause aesthetic problems in some areas. Elevated bacteria levels have the potential for adverse impacts on bathing beaches. Long-term impacts of discharge from CSOs may also result in elevated pollutant loads to receiving waters. Adverse impacts may include reductions in dissolved oxygen, increases in sediment contamination, and increases in nutrients, suspended solids, and biodegradable organic matter, which can lead to eutrophication. Discharges of heavy metals and organic chemicals may contribute to chronic or acute toxicity impacts in receiving waters, such as loss of habitat, reproductive decline, and reductions in diversity.

The discharge of untreated sewage is illegal in Michigan unless permitted under Act 245 due to public health concerns. In October, 1992, the Michigan Department of Natural Resources (MDNR, now the Michigan Department of Environmental Quality) issued a discharge permit to Detroit authorizing dis-

charge from the City's 78 CSOs, and requiring that a long-term control plan be developed to achieve mandated water-quality standards in receiving waters. The U.S. Environmental Protection Agency (USEPA) issued a national CSO policy in April, 1994, which requires (1) operational improvements of existing systems to minimize discharges and prevent their occurrence in dry weather; (2) publicly operated treatment works (POTW) to characterize the frequency and volume of discharges; and (3) construction of CSO discharge control projects where necessary.

Stage 2 of the Detroit River Remedial Action Plan (RAP) (MDNR, 1994) identifies strategies to be undertaken to further identify and quantify pollutant loads, and to begin reducing discharges from CSOs. An accurate assessment of the variability in pollutant loads among CSOs is one step in being better able to predict pollutant effects on receiving waters. Once pollutant loads can be predicted, corrective measures necessary to minimize discharges and associated adverse impacts can be implemented. One prior study was conducted on similar sites in an attempt to document the number of CSOs that discharge in the City of Detroit, and the number of times that they discharged each year (Giffels, Black, and Veatch, 1980). In 1993, the Southeast Michigan Council of Governments (SEMCOG) requested assistance from the U.S. Geological Survey (USGS), in cooperation with DWSD and MDNR, Surface Water Quality Division, to address part of the technical data requirements for item 2 of Phase I, Stage 1 of the Detroit River RAP. The USGS scope of services for this investigation consisted of collection, compilation, and interpretation of the necessary hydrologic data, and documentation of results. USGS personnel maintained operational readiness of all instrumentation and managed field operations. In addition to USGS personnel, personnel from DWSD assisted with the field collection of samples and in alerting USGS personnel to CSO effluent discharges.

During the current study, four CSOs that discharge to the Detroit River were monitored to characterize water quantity and quality and to calculate pollutant loads from CSO discharges. To identify and quantify pollutant loads, automated, unattended gaging stations were designed and installed. Stage, velocity, and precipitation were continuously measured and recorded. Water-quality samples were collected during storms using automatic samplers.

The overall approach to this study involved data collection, interpretation, and documentation that formed a basic hydrologic description of each site, which was necessary to allow DWSD to document the quantity and chemistry of CSO water. In addition, information obtained from this study may be used to make decisions regarding improvement of CSO structures and remediation of CSO discharges.

USGS, with assistance from DWSD and SEMCOG, selected Conner Creek Sewer at Freud Avenue, Fischer Sewer at Burns Avenue, Twelfth Street Sewer at Rosa Parks Boulevard and Jefferson Avenue, and Schroeder Sewer at W. Jefferson Avenue for collection of CSO data. All overflows discharged to the Detroit River. Contributing sewage areas to the sampling sites vary, and were determined by SEMCOG and DWSD. Data for these CSOs have been entered into a computer database for use with the SEMCOG geographic information system (GIS).

PURPOSE AND SCOPE

This report includes documentation of discharge measurement methods, water-quality sampling approach, field water-quality sample collection and processing methods, and methods of chemical analysis used in this study. Tables listing the results of discharge measurements, water-chemistry data, and quality-assurance data are presented. These data may be used by resource managers and researchers to determine (1) frequency, duration, and magnitude of discharge; (2) pollutant loadings; and, (3) potential impacts of discharges from selected CSOs.

ACKNOWLEDGMENTS

This study was conducted as part of a cooperative agreement between the USGS, DWSD, Michigan Department of Environmental Quality (MDEQ), USEPA, Wayne State University (WSU), and SEMCOG. Successful completion of this project would not have been possible without the dedicated efforts of Ranu Meah, Ken Prybys, and John MacDonald of the DWSD Waste Water Collection Group (WWCG), who were typically the first to respond to storms. In addition, the support and assistance of Steve Perry and Ted Starbuck (SEMCOG) in scheduling and coordinating

meetings, and supplying the project team with illustrations, graphics, and presentation materials is acknowledged.

SITE DESCRIPTIONS

The equipment used at each site varied depending upon the type of land use present in the sewer-service area, the size of the sewer-service area, the design capacity of the sewer in question, and proximity to both the Detroit River Interceptor (DRI) sewer and the Detroit River. Locations are shown in figure 1, and site-specific descriptions of each sewer are presented below.

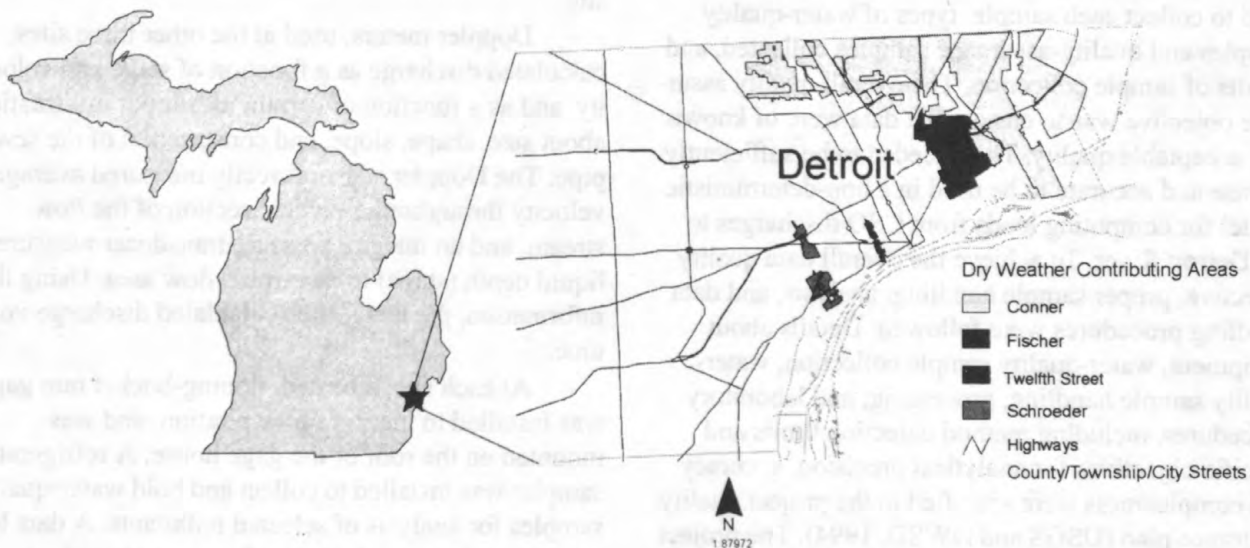


Figure 1. Location of Detroit, Michigan, and combined sewer sites monitored during this project.

Conner Sewer at Freud Avenue

Conner Sewer is a former creek channel that has been filled by a series of buried sewer pipes. Under dry weather conditions, sanitary sewage from the sewer enters a sump chamber where it is then diverted to the DRI. The CSO discharge point, located at the Freud Avenue bridge over the former creek channel, is at 42°21'51" north latitude, 82°57'29" east longitude and consists of three 5.64 meter (m) by 6.63 m box culverts that are open to the creek channel. The side-walls of the creek channel are vertical steel sheet-piles that follow the contours of the former Conner Creek channel.

Fischer Sewer at Burns Avenue

Fischer Sewer is a 4.19 m diameter buried sewer pipe that empties into a sump that allows flow of sanitary sewage into the DRI. Overflow can discharge to the Detroit River through three 3.89 m overflow pipes. The discharge point is located at 42°21'16" north latitude, 82°59'15" east longitude. Reverse flow of river water into the sewer system is controlled by a system of two backwater gates in each pipe that are kept closed by hydrostatic pressure of river water against the gate closest to the river. Hydraulic pressure caused by storm runoff is sufficient to overcome river water pressure and force the gates open.

Twelfth Street Sewer at Rosa Parks Boulevard and Jefferson Avenue

Twelfth Street Sewer is a 1.57 m diameter buried sewer pipe that empties into a sump that allows flow of sanitary sewage into the DRI. Overflow can discharge to the Detroit River through a 1.57 m buried pipe that splits into two 1.22 m pipes. The discharge point is located at 42°19'13" north latitude, 83°03'56" east longitude. Reverse flow of river water into the sewer system is controlled by a single backwater dam in the 1.57 m pipe.

Schroeder Sewer at West Jefferson Avenue

Schroeder Sewer consists of two buried sewer pipes, one 2.08 m diameter and the other 1.83 m diameter. The pipes enter a common sump chamber that allows flow of sanitary sewage into the DRI. Overflow discharges to the river by way of one 2.08 m pipe and one 1.83 m pipe. The discharge point is located at 42°17'32" north latitude, 83°06'00" east longitude. Reverse flow of river water into the sewer system is controlled by a single backwater dam in each barrel.

METHODS

The following sections describe the methods used to collect each sample, types of water-quality samples and quality-assurance samples collected, and results of sample collection. The overall quality assurance objective was to ensure that data were of known and acceptable quality. They needed to be sufficiently precise and accurate to be used in a non-deterministic model for computing loads from CSO discharges to the Detroit River. To achieve the overall data quality objective, proper sample handling, analysis, and data handling procedures were followed. Details about equipment, water-quality sample collection, water-quality sample handling, processing, and laboratory procedures, including method detection limits and specific objectives for analytical precision, accuracy and completeness were specified in the project quality assurance plan (USGS and DWSD, 1994). The project completeness objective was 90 percent, which represented the number of usable analytical results as a percentage of the number of samples submitted for analysis. To assess whether the overall quality assurance objectives were met, analyses of specific field quality-control samples were required. These quality-control samples included field blanks and field duplicates.

Velocity and Discharge Determination

Velocity of discharge was measured at each site with either a channel-mounted 4-transducer-array acoustic velocity meter (AVM) and a stilling well with a shaft encoder installed to measure stage (Conner Sewer), or with an upward-looking, bottom-mounted

Doppler flow meter that measured stage and velocity (Fischer Sewer, Twelfth Street Sewer, and Schroeder Sewer). Flow measuring stations were located as near as practicable to the outlet of each CSO.

In order to assess discharge in relation to the AVM velocity and stage data at Conner Sewer, it was necessary to make physical discharge measurements using standard USGS methods (Carter and Davidian, 1968, and Buchanan and Somers, 1969). However, in all but one instance, storm duration was not sufficient to allow completion of a discharge measurement. One measurement was made in November, 1995, near the end of a storm. This measurement was used to calculate preliminary discharge data for Conner Sewer. Additional discharge measurements were made in June 1996 to improve the velocity-area rating at this site.

Doppler meters, used at the other three sites, calculated discharge as a function of stage and velocity, and as a function of certain user input information about size, shape, slope, and construction of the sewer pipe. The Doppler sensor directly measured average velocity throughout a vertical section of the flow stream, and an integral pressure transducer measured liquid depth (stage) to determine flow area. Using this information, the meter then calculated discharge volume.

At each site, a heated, tipping-bucket rain gage was installed to measure precipitation, and was mounted on the roof of the gage house. A refrigerated sampler was installed to collect and hold water-quality samples for analysis of selected pollutants. A data logger was used to store all data from meters and rain gages, to analyze flow and precipitation data, and to initiate automatic sampling based on this analysis. A cellular phone was installed to allow two-way communication between gage instruments and field personnel. All equipment was operated by 12-volt storage batteries, which were kept charged by 110-volt alternating current (vac). The principal source of power to each gage was 110-vac.

Methods of Water-Quality Sample Collection

Water-quality samples were collected at each site with a refrigerated, automatic sampler capable of maintaining collected samples at 4 degrees Celsius

(°C). Each sampler contained four 10-liter (L) glass jars with Teflon[®] lids. Samples were drawn through 3.5 m of 0.95 centimeter (cm) Teflon[®] tubing at Conner Creek Sewer, through 8 m of 0.95 cm Teflon[®] tubing at Fischer Sewer, through 12 m of 0.95 cm Teflon[®] tubing at Twelfth Street Sewer, and through 2.75 m of 0.95 cm Teflon[®] tubing at Schroeder Sewer, to near the pump head. At the pump head, 15 cm of 0.95 cm polyethylene tubing was required to provide flexibility. The pump was operated at its lowest rate to prevent sample aeration.

Water-quality samples were collected by use of suction lift samplers employing a peristaltic pump, and as such are considered "automatic grabs" as defined in USEPA 833-B-92-001 (1992, p. 42). Pump samplers were used to collect samples at most sites due to the inaccessibility of, and hazards associated with, manual sample collection from sewer pipes. Field personnel typically arrived on site within one hour of the beginning of an event, and collected and processed samples as described below.

Sample bottles were acquired from the USGS National Water Quality Laboratory (NWQL) Ocala, Florida supply depot. Sample bottles were precleaned following the methods indicated in table 1. Sample bottles were not reused. All bottles obtained from the USGS were subjected to quality assurance/quality control practices, and were precleaned, baked or otherwise sterilized. Sample bottles were labelled in the sample preparation facility with information regarding the site name, unique site and sample numbers, and the analyses to be performed.

Since CSO effluent discharge was not subjected to chlorination, there was no expectation that residual chlorine would interfere with any samples. Tests were made for residual chlorine using potassium iodide-starch test paper and for hydrogen sulfide (H₂S) using lead acetate test paper during the first set of samples. These compounds were not found and subsequent samples were not treated to remove these substances.

Sample packaging and shipment were performed according to USEPA requirements as described in USEPA 833-B-92-001 (1992). Each sample container was enclosed in a clear plastic bag and placed in a cooler, which was then filled with ice. Coolers contained enough ice to maintain sample temperatures at ≤4°C. Each cooler was sealed and hand

delivered to the DWSD lab at the completion of each sampling event. Coolers delivered to the USGS NWQL were shipped once daily by overnight carrier.

A variety of types of samples were collected requiring different sampling techniques and handling procedures. Table 1 contains information on the types and quantities of sample containers required for each analysis, the sample preservation techniques, and holding times. All sample containers met the requirements outlined in USEPA 540/R-93/051 (1992).

Quality-assurance samples were submitted in numbers equal to about 10 percent of all sampled discharges from CSOs for which analyses were made. The selection of pollutants in water for analysis, and analytical protocols, including minimum detection levels, holding times, and quality assurance, were as required by USEPA final storm-water sampling regulations (USEPA, 1992).

Water-Quality Samples

Water-quality samples at all sites were collected at discrete times during storms, based upon the discharge hydrograph. In general, the routine for collecting water-quality samples at each site required the first sample to be collected at the beginning of discharge for each storm. The beginning of storm discharge was indicated either by the presence of water in an otherwise dry overflow channel, or by positive flow values, sustained for a predetermined length of time, in an ordinarily stagnant channel. When determined by positive flow values, the time required for sustained flow varied from 2 hours for velocities of 0.08 m/s to 15 minutes for velocities of 1.2 m/s. After the collection of the first sample, subsequent samples were collected based upon the performance of the discharge hydrograph at each site. In general, samples were desired at or near the peak of the hydrograph and during hydrograph recession. To obtain samples at the peak of the hydrograph, an algorithm was developed that 1) monitored velocity or flow values; 2) determined whether stage was rising or falling; and 3) determined whether velocity was increasing or decreasing. If a fall in stage or decrease in velocity was detected after a sustained period of rising stage or increasing velocity, sampling was initiated for the peak-of-the-hydrograph sample. Recession samples were generally manually triggered.

¹Use of trade names in this report is for identification purposes only and does not constitute an endorsement by the U.S. Geological Survey.

TABLE 1. Required sample containers, volumes, preservation techniques, and holding times [L, liters; ml, milliliters; °C, degrees Celsius]

Analyte	Container	Preservation ¹	Holding time ¹
PCB (Aroclors), Chlordane, α -BHC α -Endosulfan, Lindane	1 L glass bottle, baked at 450°C by laboratory.	Do not rinse bottle; Chill, maintain at 4°C.	7 days to extraction, 40 days to analysis
bisPhthalate, Chrysene, Fluoranthene, Hexachlorobenzene, Phenanthrene, Phenol, Pyrene	1 L glass bottle, baked at 450°C by laboratory.	Do not rinse bottle; Chill, maintain at 4°C.	7 days to extraction, 40 days to analysis
Acrylonitrile, Methylene chloride, Styrene	40 ml vial	Acidify to pH < 2 with 2 drops 1:1 HCl:H ₂ O; Chill, maintain at 4°C.	14 days
Carbonaceous Oxygen Demand (COD)	125 ml glass bottle, baked at 450°C by laboratory.	Do not rinse bottle. Add H ₂ SO ₄ to pH<2; Chill, maintain at 4°C.	28 days
Carbonaceous Biological Oxygen Demand (CBOD)	1 L glass bottle, baked at 450°C by laboratory.	Do not rinse bottle; Chill, maintain at 4°C.	48 hours
Total suspended solids, Total dissolved solids, Total volatile solids (TSS, TDS, TVS)	500 ml polyethylene bottle, field rinsed.	Use unfiltered sample to rinse bottles; Chill, maintain at 4°C.	7 days
Chloride (Cl)	250 ml polyethylene bottle, field rinsed.	Use unfiltered sample to rinse bottles; Chill, maintain at 4°C.	28 days
Alkalinity, pH	250 ml polyethylene bottle, field rinsed.	Use unfiltered sample to rinse bottles; Chill, maintain at 4°C.	14 days
Total phosphorus (P), In- organic P, Ammonium (NH ₃)	500 ml brown polyethylene bottle, field rinsed.	Use unfiltered sample to rinse bottles. Add 1 ampule H ₂ SO ₄ to pH < 2; Chill, maintain at 4°C.	28 days
Oil and grease	1 L oil and grease bottle, amber. Bottle baked at 450°C by laboratory.	Do not rinse bottle. Leave small air space. Add 2.0 ml H ₂ SO ₄ to pH 2; Chill, maintain at 4°C.	28 days

¹Source for all holding times and preservation methods is 40 CFR part 136.3 Table II.

TABLE 1. Required sample containers, volumes, preservation techniques, and holding times--Continued

Analyte	Container	Preservation ¹	Holding time ¹
METALS: [Antimony (Sb), Arsenic (As), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Manganese (Mn), Nickel (Ni), Silver (Ag), Thallium (Tl), and Zinc(Zn)]	500 ml polyethylene bottle, acid rinsed.	Use unfiltered sample to rinse bottles. Add HNO ₃ to pH < 2; Chill, maintain at 4°C.	6 months
Hexavalent chromium [Cr(VI)]	250 ml polyethylene bottle, acid rinsed.	Use unfiltered sample to rinse container; Chill, maintain at 4°C.	24 hours
Cyanide	500 ml polyethylene bottle, field rinsed.	Use unfiltered sample to rinse bottles. Add NaOH to pH>12; Chill, maintain at 4°C.	14 days
Mercury (Hg)	250 ml glass bottle, acid rinsed.	Use unfiltered sample to rinse bottles. Add 1 ampule HNO ₃ ; Chill, maintain at 4°C.	28 days
Total Kjeldahl Nitrogen (TKN)	500 ml brown polyethylene bottle, field rinsed.	Use unfiltered sample to rinse bottle. Add H ₂ SO ₄ to pH < 2; Chill, maintain at 4°C.	28 days
Fecal coliform, Fecal streptococci, and <i>E. Coli</i>	500 ml brown polyethylene bottle, field rinsed.	Do not rinse bottle; Chill, maintain at 4°C.	6 hours

¹ Source for all holding times and preservation methods is 40 CFR part 136.3 Table II.

In order to assure that samples were not missed, a timed sampling routine was also included in case personnel could not arrive at a site in time to manually trigger a sample.

Water-quality samples were stored in 10-L glass jars in the on-site refrigerated sampler until collected by field personnel. Each glass jar was prewashed, rinsed with deionized water (DIW), rinsed with 5% ultra-pure hydrochloric acid, rinsed with DIW, rinsed with ultra-pure methanol, and triple-rinsed with DIW before deployment in the refrigerated sampler. The glass jars were capped with Teflon[®] lined caps. Upon collection of a water-quality sample, field personnel removed the jars, stored them in coolers with ice, and transported them to a central sample-splitting site. Appendix A is a typical sample-splitting flow chart. Details of sample splitting are outlined below. The first samples to be split were those for VOCs. Samples were collected by holding the proper collection vial (table 1), containing the proper volume of preservative, over the outlet of the pump tubing in such a way that the end of the tubing is below the sample surface as the vial is filled. The vial was slightly overfilled so that a convex meniscus formed at the mouth of the vial; it was then capped in such a way that there were no air bubbles in the vial. The vial was gently inverted and examined for the presence of air bubbles. If air bubbles were observed, the sample was discarded and another was collected to replace it. Following VOC sample collection the end of the pump tubing was rinsed thoroughly with DIW to remove any traces of acid preservative contacted during the VOC sample collection.

The next samples to be collected were those for oil and grease and those for bacteria. These samples were collected by filling the proper types of containers (table 1) from the pump tubing. All remaining sample was poured into a churn splitter (Fishman and others, 1985) and subsamples were collected from the spigot of the churn while homogenization of the sample took place. The homogenization was carried out in such a way that excessive aeration of the sample did not occur.

Samples were collected in such a way as to avoid contamination with airborne volatiles or particulates from, for example, automobile exhaust or cigarette smoke, or from the handling of contaminating materials such as solvents, oils, greases, plastics, paints, painted surfaces, metal surfaces or objects

(keys, coins, tools). Collection and working surfaces in the field were covered with clear plastic sheeting, sample bottles and pump tubing were not allowed to touch surfaces other than those covered with plastic, and sampling personnel wore latex gloves and changed them as needed to prevent sample contamination. Whenever feasible, sample splitting was done in an enclosed, dedicated building after sample collection.

Blanks

Field blanks monitor contamination during all phases of sample collection, handling, storage, and analysis. Field blanks are distinct from method or laboratory blanks in that their intended purpose is to monitor contamination introduced in the field during sample collection and handling. Field-blank samples were collected at a frequency of one per group of twenty-to-thirty investigative samples per test parameter. The field blank was prepared from a certified organic and/or inorganic free blank water rinse of decontaminated sampling equipment, and was subjected to all aspects of sample collection, field processing, preservation, transportation, and laboratory handling as a water-quality sample. Field blank bottles were prepared and kept with the sample bottles used for each sampling trip. Field blanks were also analyzed in the same way as water-quality samples.

Trip blanks were analyzed for extractable-organic compounds. They monitored migration of extractable-organic compounds during sample shipment and storage. Trip blanks were collected at a frequency of one per every fifteen-to-twenty shipping coolers of extractable-organic-compounds samples sent to the lab.

Field duplicates were collected for selected sampling events and for selected analytes. At a minimum, duplicate analyses were conducted for two sampling events. Duplication focused on those pollutants of greatest concern, primarily metals and nutrients.

Spikes

Spikes are known concentrations of target pollutants added to water-quality samples, and are used to check a laboratory's ability to recover known concentrations of a given pollutant. Spikes were analyzed for extractable-organic compounds. Spikes were collected at a frequency of one per every 26 investigative sam-

ples. Spikes were prepared by adding pre-measured amounts of selected target pollutants to water-quality samples. The spike solutions were prepared by the NWQL and added to water-quality samples by field personnel.

Duplicates

Field duplicates were collected for 3 storms for selected pollutants. Duplicate samples, focusing on pollutants of greatest concern, were collected for the pollutants listed in table 1.

Methods of laboratory analysis

The Detroit Waste Water Treatment Plant (WWTP) lab provided analyses for conventional constituents and metals listed in table 2. Analyses for organic constituents shown in table 3 were done at the USGS NWQL in Denver, Colorado.

TABLE 2. Pollutants analyzed by DWSD Laboratory

Biologic, Nutrient, and Inorganic Pollutants					
CBOD	TDS	Inorganic P			
COD	TSS	Ammonium (NH ₃)			
Fecal Coliform	TVS	Cl			
Fecal Streptococci	TKN	Cyanide			
<i>E. Coli</i>	Total P	Alkalinity			
Oil and grease					

Metal pollutants					
Ag	As	Be	Cd	Co	Cr
Cr(VI)	Cu	Fe	Hg	Mn	Ni
Pb	Sb	Ti	Zn		

TABLE 3. Pollutants analyzed by NWQL

Organic pollutants	
Lindane	Phenol
Acrylonitrile	Hexachlorobenzene
Styrene	Chlordane
α-BHC	α-Endosulfan
bisPhthalate	Chrysene
Fluoranthene	Pyrene
Phenanthrene	Methylene chloride
PCBs (Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260)	

Analytical protocols, including minimum detection levels, holding times, and quality assurance, were as required by 40 CFR Part 136, and by the Standard Operating Procedures (SOPs) of the laboratory providing the analysis (USGS and DWSD, 1994). Methods of analytical determination are listed in table 4. SOPs for both laboratories are listed in the selected references section at the end of this report.

Methods of data analysis and storage

Water-quality samples were analyzed for the project's target pollutant list (table 1) by the appropriate analytical methods as described previously. The only matrix sampled for this project was combined-sewer water, a mixture of raw sanitary sewage and storm-water runoff. After completion of laboratory analyses, all results from the laboratories were returned in digital and paper copy to the principal investigators at both USGS and DWSD. Upon preliminary approval of the data by each agency, data was exchanged among the cooperating agencies involved in the project for use in data base creation, model calibration, and GIS analysis.

Statistical analysis was made of the water-chemistry analytical results to assure that each analysis was complete, accurate, within the reporting range requested, and properly assigned to each pollutant reported. Visual and statistical comparisons were made between the water-quality samples and the

Table 4. Methods of determination and detection limits for pollutants of interest

[GFAA, graphite-furnace atomic absorption; mg/L, milligrams per Liter; $\mu\text{g/L}$, micrograms per liter; CEAA, chelation-extraction atomic absorption; ROE, residue on evaporation; GR, gravimetric analysis; IEC, ion-exchange chromatography; ET, electrometric titration; CVAA, cold-vapor atomic absorption; MPN, Membrane filtration and most probable number; ml, milliliters; ASF, salicylate-hypochlorite automated-segmented flow colorimetric; EG, extraction gravimetric; GC/MS, purge and trap, gas chromatography and mass spectrometry]

Constituent	Method used	Detection limit	Units	Constituent	Method used	Detection limit	Units
Antimony	GFAA	1	mg/L	Cyanide	Barbituric acid, automated-segmented flow	0.5	mg/L
Arsenic	GFAA	1	$\mu\text{g/L}$	Carbonaceous biological oxygen demand	Winkler	10	mg/L
Beryllium	GFAA	10	$\mu\text{g/L}$	Fecal coliform	MPN	5	MPN/100ml
Cadmium	GFAA	1	$\mu\text{g/L}$	Fecal streptococci	MPN	5	MPN/100ml
Chromium	GFAA	1	$\mu\text{g/L}$	Escherichia coli	MPN	5	MPN/100ml
Hexavalent chromium	CEAA	1	mg/L	Methylene chloride	GC/MS	0.2	$\mu\text{g/L}$
Cobalt	GFAA	10	$\mu\text{g/L}$	Total phosphorus	ASF	0.01	mg/L
Copper	GFAA	1	$\mu\text{g/L}$	Inorganic phosphorus	ASF	0.01	mg/L
Iron	GFAA	10	$\mu\text{g/L}$	Ammonium	ASF	0.2	mg/L
Total Suspended solids	ROE,GR	1	mg/L	Total kjeldahl nitrogen	Distillation/Titration	1	mg/L
Total dissolved solids	ROE, GR	1	mg/L	Oil and grease	EG	5	mg/L
Total volatile solids	Volatiles on ignition, GR	1	mg/L	Fluoranthene	GC/MS	5	$\mu\text{g/L}$
Chloride	IEC	0.01	mg/L	Hexachlorobenzene	GC/MS	5	$\mu\text{g/L}$
Alkalinity	ET	0.5	mg/L	Phenanthrene	GC/MS	5	$\mu\text{g/L}$
pH	ET	0.01	units	Pyrene	GC/MS	5	$\mu\text{g/L}$
Lead	GFAA	1	$\mu\text{g/L}$	α -BHC	GC/MS	0.03	$\mu\text{g/L}$
Manganese	GFAA	0.2	mg/L	Chlordane	GC/MS	0.1	$\mu\text{g/L}$
Mercury	CVAA	0.1	$\mu\text{g/L}$	α -Endosulfan	GC/MS	0.1	$\mu\text{g/L}$
Nickel	GFAA	1	$\mu\text{g/L}$	Lindane	GC/MS	0.1	$\mu\text{g/L}$
Silver	GFAA	1	$\mu\text{g/L}$	Styrene	GC/MS	0.2	$\mu\text{g/L}$
Thallium	GFAA	0.5	$\mu\text{g/L}$				
Zinc	GFAA	0.5	$\mu\text{g/L}$				
Chemical oxygen demand	Closed reflux, colorimetric	10	mg/L				

Table 4. Methods of determination and detection limits for pollutants of interest--Continued

Constituent	Method used	Detection limit	Units
Acrylonitrile	GC/MS	20	µg/L
Phnol	GC/MS	5	µg/L
Crysene	GC/MS	10	µg/L
bs(2-Ethyl- Heyl) Phthalate	GC/MS	5	µg/L
Aroclor 1016	GC/MS	0.1	µg/L
Aroclor 1221	GC/MS	0.1	µg/L
Aroclor 1232	GC/MS	0.1	µg/L
Aroclor 1242	GC/MS	0.1	µg/L
Aroclor 1248	GC/MS	0.1	µg/L
Aroclor 1254	GC/MS	0.1	µg/L
Aroclor 1260	GC/MS	0.1	µg/L

quality-assurance samples to identify any results that may have been influenced by introduction of contaminants in processing of the raw sample, shipping of the sample, handling by the analytical laboratory, or other outside processes. Further analysis of the data is possible by other researchers to attempt to calculate pollutant loads to the Detroit River from each CSO sampled, to attempt to identify environmental processes active in the sewage system, and to attempt to determine other influences and processes that may be identified from the data set.

Data are stored in both the USGS water-quality data base and the City of Detroit water-quality data base. Final storage of all data is the responsibility of the USGS, and will be completed by the Lansing, Michigan District office. In addition, all original laboratory analyses completed by the DWSD laboratory will be stored by the Director, DWSD.

Results of Data Collection

Samples were first collected in August, 1994, at Conner Sewer, and were subsequently collected at all sites between December 1994 and December 1995.

Table 5 lists the number of storms sampled at each site, and the number and type of samples collected.

In general, each storm-caused CSO discharge during the study period was sampled. Sampling frequency varied from site to site, and was dependent upon a number of criteria, foremost of which was the amount of time since a previous event. To truly characterize water quality from CSO discharges, it was decided that events separated by less than 7 days would not be sampled, as a sufficient amount of time had not elapsed to allow for atmospheric deposition and surface accumulation of particulates.

In the early phases of the project, Conner Sewer at Freud Avenue and Fischer Sewer at Burns Avenue flowed during most significant precipitation events, and their flow could be somewhat anticipated. During the latter half of the project, however, both of these sites flowed less frequently and with less regularity. It is the opinion of City personnel involved in the project that changes made in the operation of the treatment plant and by operators controlling the flow in the sewer system, both intended to improve the efficiency of the treatment system, may have been responsible for this shift in the number of CSO discharges at both sites (personal communication, J. MacDonald, R. Meah, and K. Prybys, 1995, 1996).

Twelfth Street Sewer at Rosa Parks Boulevard and Jefferson Avenue was not sampled until June, 1995 because there were no measurable events at this site until that time; conversely, Schroeder Sewer at W. Jefferson Avenue was sampled more frequently than anticipated because of its proximity to the waste water treatment plant. When the plant was at capacity, and water was discharged through CSOs to the river, Schroeder Sewer was often the first site to be filled, and the last to be emptied when the treatment plant was operating at normal capacity.

Table 5. Number of storms and samples by sample type

Site	Number of storms sampled	Number of inorganic samples	Number of organic samples
Conner	10	30	21
Fischer	14	51	21
Twelfth	8	44	14
Schroeder	17	78	22

Discharge values for Conner Sewer are listed in table 7 on the enclosed diskettes. These values are in the "discharg" subdirectory. The files are in ascii, or text format, and have the extension "txt." The filenames follow the convention "sitename table-number period txt." For example, discharge values for Conner Sewer are in the file named "conner7.txt." Because of the character limitations for disk filenames "fisher" will be used for Fischer Sewer, "twelf" for Twelfth Street Sewer, and "schder" for Schroeder Sewer. Discharge values for Fischer Sewer are in table 8; discharge values for Twelfth Street Sewer are in table 9; discharge values for the east barrel of Schroeder Sewer are in table 10; and discharge values for the west barrel of Schroeder Sewer are in table 11. Because of their size fisher8, twelf9, schder10, and schder11 are compressed to fit on the data disks. They are given the extension ".gz" because of the compression process. These files will need to be decompressed by using the program gunzip.exe before they can be read. A copy of gunzip.exe is on diskette #1. A "readme" file is included on diskette #1 that explains how to use the program gunzip.exe.

Results of sample analyses for pollutants listed in table 1 are shown in tables 12, 13, 14, and 15. These tables are in the "results" subdirectory of the data disks included with this report. The files have the extension ".dif" for data interchange format. The filenames follow the format "sitename table-number period dif." For example, results of sample analyses for Conner Sewer are in the file named "conner12.dif."

Analyses for several organic pollutants other than those given in table 1 were completed by NWQL. A complete list of these results is on the data disks in tables 16, 17, 18 and 19 in the subdirectory "organic."

These files are in text format. The filenames follow the format previously described. For example, the organic pollutant results for Conner Sewer are in the file named "conner16.txt." These tables are more than 80 columns wide and therefore should be printed in landscape mode or displayed in a wide format.

DISCUSSION

In general, the equipment installed at each site worked as anticipated. In the early months of the project there were logistical difficulties with the AVM at Conner Sewer. A series of severe thunderstorms on August 18 and 19, 1994 caused discharge from the Conner Sewer CSO with velocities in excess of 1.43 m/s. This flow was great enough to physically move some of the equipment that was installed below the water level, and resulted in the loss of the sampler intake, misalignment of the stilling well, and movement and stretching of the AVM transducer cables more than 8 m downstream, causing internal breakage of wires in the transducer cables, and a malfunction of the AVM. Subsequently, the sampler intake was modified and reinforced to withstand velocities estimated as high as 1.5 m/s, the stilling well was remounted and reinforced, and the transducer wires were laid on the surface of the seawall and bridge at Conner Sewer. Following these modifications the gage operated as anticipated.

At Fischer Sewer, the flow meter was a bottom-mounted, upward-looking Doppler meter installed at the bottom of the sewer pipe. During a surcharged flow in this pipe, the doppler sensor was struck by an unknown object and dislodged from its mounting point. Numerous attempts were made to remount this sensor in a secure fashion to prevent it from becoming dislodged. The mechanism that finally resulted in success involved drilling 6 mounting holes along the leading (upstream) edge of the mounting bracket and installing 25-cm long mounting anchors in the sewer-pipe bottom.

Sampler triggering was accomplished by communication between the flow meter and the sampler or a water-level sensor and the sampler. The communication mechanism functioned as expected at all sites. All other equipment generally functioned as expected, including rain gages, stage sensors, data recorders, and cellular communications.

Data retrieval was accomplished by remote phone connection to a main-frame computer in the Madison, Wisconsin District office of the USGS. A program was written that called each gage at about 5:00 a.m. each day and retrieved the previous days data. This program functioned well, and the only difficulties encountered were occasional communication failures due to weather interference with the cellular communications installed in each gage.

As is shown in tables 20, 21, 22 and 23, in general, metal and inorganic pollutants were detected most frequently at all sites of interest. Percentage of detection of metals ranged from lows of 3.3%, 4.1%, and 0% of samples for hexavalent chromium at Conner, Fischer, and Twelfth Street Sewers respectively, and 0% and 9% of samples for antimony at Twelfth Street and Schroeder Sewers respectively, to highs of 100% of samples for iron, manganese and zinc at Conner Sewer, 100% of samples for copper, iron, manganese, and zinc at Fischer and Twelfth Street Sewers, and 100% of samples for iron and zinc at Schroeder Sewer.

Inorganic, non-metal pollutants were detected in as few as 32.5% to 65.5% of samples for cyanide at Schroeder and Conner Sewers, respectively, to as high as 100% of samples for chloride, total phosphorus, and inorganic phosphorus at Conner, Fischer, Twelfth Street, and Schroeder Sewers. Other non-metal pollutants which were detected in 100% of samples include total kjeldahl nitrogen at Conner and Schroeder sewers, fecal coliform and *E. Coli* at Twelfth Street and Schroeder sewers, and fecal streptococci at Conner, Twelfth Street, and Schroeder sewers.

Organic pollutants were found less frequently, and many organic pollutants of concern were not detected at all during this study. For example, 100% of samples for hexachlorobenzene, endosulfan, and Aroclors 1221, 1232, and 1248 were below the detection limit at all sites, whereas 31.6%, 42.9%, and 66.7% of samples for Aroclor 1242 at Conner, Twelfth Street, and Schroeder Sewers, respectively, were above the detection limit, and 75% of samples for phenanthrene and pyrene at Fischer Sewer, and 42.9% of samples for bis(2-ethyl-hexyl) phthalate and fluoranthene were above the detection limit at Twelfth Street Sewer.

SUMMARY AND CONCLUSIONS

The principal result expected of this investigation was the development of a data base of water chemistry, discharge volume, and storm frequency at each site studied. Results indicate that the instrumentation package designed for this

project, and the field approach used, were correctly implemented to establish this data base. This data base can be used to determine the relationship between discharge at CSOs and pollutant loads to receiving waters.

Differences in results between Schroeder Sewer, the most downstream CSO site studied, and the other three CSO sites which are upstream of Schroeder Sewer, indicate that processes may be active within the sewage transport system that have the potential to modify pollutant concentrations as combined storm sewage is moved through the system.

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Table 20. Summary table of number of samples collected, number of sample results below the detection limit, and maximum and minimum reported results for Conner Sewer

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Antimony	30	26	0.14	<0.05
Arsenic	30	12	8.11	<0.04
Beryllium	30	8	3	<0.1
Cadmium	29	8	19.1	<0.4
Chromium	30	6	288	<10
CRVI	30	29	0.08	<0.03
Cobalt	30	17	36	<10
Copper	30	2	212	<20
Iron	30	0	23,730	850
Lead	30	18	274	<10
Manganese	30	0	0.62	0.04
Mercury	30	27	0.6	<0.2
Nickel	30	13	56	<2
Silver	30	20	5.4	<0.2
Thallium	30	20	2.5	<0.2
Zinc	30	0	942	52
COD	29	0	431	22
TSS	30	0	765	20
TDS	30	0	462	90
TVS	30	0	185	15
Chloride	29	0	155	10
Alkalinity	29	0	135	34
pH	29	0	8.02	6.96
Total P	29	0	3.94	0.27
Inorg. P (PO4)	29	0	2.9	0.15

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Ammonia-N	29	7	5.3	<1.0
TKN	29	0	14.1	1.3
FOG	29	10	53	<5.0
Cyanide	29	19	0.011	<0.005
CBOD	29	12	106	10
Fecal coliform	21	2	9 x 10 ⁶	25,000
Fecal streptococci	21	0	12 x 10 ⁵	13,000
E. Coli	21	2	6 x 10 ⁶	25,000
Methylene chloride	21	6	4	<0.2
Styrene	21	16	1.5	<0.200
Acrylonitrile	4	4	<20.0	<20.0
Phenol	21	20	8	<5.0
Chrysene	21	21	<10.0	<10.0
bis(2-Ethyl-Hexyl) Phthalate	21	19	9	<5.00
Fluoranthene	21	21	<5.00	<5.00
Hexachlorobenzene	21	21	<5.00	<5.00
Phenanthrene	21	21	<5.00	<5.00
Pyrene	21	21	<5.00	<5.00
α-BHC	19	19	<0.030	<0.030
Chlordane	19	18	0.1	<0.100
α-Endosulfan	19	19	<0.100	<0.100

Table 20. Summary table of number of samples collected, number of sample results below the detection limit, and maximum and minimum reported results for Conner Sewer--Continued

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Aroclor 1016	19	18	0.2	<0.100
Aroclor 1221	19	19	<1.00	<1.00
Aroclor 1232	19	19	<0.100	<0.100
Aroclor 1242	19	13	0.3	<0.100
Aroclor 1248	19	19	<0.100	<0.100
Aroclor 1254	19	16	0.1	<0.100
Aroclor 1260	19	16	0.2	<0.100
Lindane	19	19	<0.030	<0.030

Table 21. Summary table of number of samples collected, number of sample results below the detection limit, and maximum and minimum reported results for Fischer Sewer

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Antimony	51	43	0.11	<0.06
Arsenic	51	14	20.8	0.76
Beryllium	51	9	4.2	0.04
Cadmium	51	23	30	0.36
Chromium	51	19	210	9.1
CRVI	49	47	0.08	<0.03
Cobalt	51	32	71	2.8
Copper	51	0	670	10
Iron	51	0	54300	1116
Lead	51	20	1013	<20
Manganese	51	0	1.28	0.05
Mercury	51	48	0.4	<0.2
Nickel	51	28	150	<10
Silver	50	40	6.3	0.2
Thallium	51	33	2.1	<0.1
Zinc	51	0	2,040	55
COD	51	1	786	25
TSS	51	0	1594	13
TDS	51	0	729	81
TVS	51	2	564	<10
Chloride	51	0	272.5	5
Alkalinity	51	0	215	7.11
pH	51	0	8.34	7
Total P	51	0	4.54	0.31
Inorg. P (PO4)	51	0	3.36	0.11

Table 21. Summary table of number of samples collected, number of sample results below the detection limit, and maximum and minimum reported results for Fischer Sewer--Continued

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Ammonia-N	51	27	3.8	0.3
TKN	51	2	13.2	1.1
FOG	51	16	126	<5.0
Cyanide	51	32	0.024	<0.005
CBOD	49	14	121	<10
Fecal Coliform	44	3	4 x 10 ⁷	1100
Fecal Streptococci	44	1	7 x 10 ⁶	6700
E. Coli	40	3	17 x 10 ⁵	10000
Methylene Chloride	21	10	0.6	<0.200
Styrene	21	18	0.3	<0.200
Acrylonitrile	4	4	<20.0	<20.0
Phenol	21	21	<5.00	<5.00
Chrysene	21	21	<10.0	<10.0
bis(2-Ethyl-Hexyl) Phthalate	21	10	330	<5.00
Fluoranthene	21	19	7	<5.00
Hexachlorobenzene	21	21	<5.00	<5.00
Phenanthrene	21	20	5	<5.00
Pyrene	21	20	5	<5.00
α-BHC	20	18	0.09	<0.030
Chlordane	20	19	0.1	<0.100
α-Endosulfan	20	20	<0.100	<0.100

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Aroclor 1016	20	20	<0.100	<0.100
Aroclor 1221	20	20	<1.00	<1.00
Aroclor 1232	20	20	<0.100	<0.100
Aroclor 1242	20	13	0.2	<0.100
Aroclor 1248	20	20	<0.100	<0.100
Aroclor 1254	20	17	0.1	<0.100
Aroclor 1260	20	18	0.4	<0.100
Lindane	20	20	<0.030	<0.030

Table 22. Summary table of number of samples collected, number of sample results below the detection limit, and maximum and minimum reported results for Twelfth Street Sewer

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value	Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Antimony	44	44	<0.06	<0.06	Ammonia-N	44	18	3.8	0.4
Arsenic	40	1	25.4	<0.04	TKN	44	1	23.7	<1
Beryllium	40	1	4	0.3	FOG	43	16	58	<5.0
Cadmium	44	32	9.8	<0.4	Cyanide	43	28	0.02	<0.005
Chromium	44	8	194	4	CBOD	43	20	308	<13
CRVI	41	41	<0.03	<0.03	Fecal Coliform	24	0	64 x 10 ⁵	13000
Cobalt	44	23	30	2	Fecal Streptococci	27	0	32 x 10 ⁴	5000
Copper	44	0	350	12	E. Coli	27	0	93 x 10 ⁴	5000
Iron	44	0	26100	980	Methylene Chloride	12	11	0.9	<0.200
Lead	44	5	390	<20	Styrene	12	12	<0.200	<0.200
Manganese	44	0	1.67	0.08	Phenol	14	14	<5.00	<5.00
Mercury	44	30	0.8	<0.2	Chrysene	14	13	21	<10.0
Nickel	44	23	98	<2	bis(2-Ethyl-Hexyl) Phthalate	14	8	36	<5.00
Silver	44	15	48	<0.1	Fluoranthene	14	8	48	<5.00
Thallium	44	31	2.1	<0.6	Hexachlorobenzene	14	14	<5.00	<5.00
Zinc	44	0	1071	49	Phenanthrene	14	13	32	<5.00
COD	44	0	1254	38	Pyrene	14	13	47	<5.00
TSS	44	0	934	58	α-BHC	14	14	<0.030	<0.030
TDS	44	0	287	60	Chlordane	14	12	0.2	<0.100
TVS	44	1	383	<10	α-Endosulfan	14	14	<0.100	<0.100
Chloride	44	0	55	5	Aroclor 1016	14	14	<0.100	<0.100
Alkalinity	44	0	148	31	Aroclor 1221	14	14	<0.100	<1.00
pH	44	0	7.82	6.48					
Total P	44	0	6.73	0.21					
Inorg. P (PO ₄)	44	0	2.31	0.09					

Table 22. Summary table of number of samples collected, number of sample results below the detection limit, and maximum and minimum reported results for Twelfth Street Sewer-- Continued

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Aroclor 1232	14	14	<0.100	<0.100
Aroclor 1242	14	8	0.3	<0.100
Aroclor 1248	14	14	<0.100	<0.100
Aroclor 1254	14	9	0.7	<0.100
Aroclor 1260	14	12	0.4	<0.100
Lindane	14	14	<0.030	<0.030

Table 23. Summary table of number of samples collected, number of sample results below the detection limit, and maximum and minimum reported results for Schroeder Sewer

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Antimony	78	71	0.18	<0.01
Arsenic	74	21	46.3	<0.04
Beryllium	74	13	1.8	<0.1
Cadmium	77	39	15	<0.4
Chromium	75	4	1071	<10
CRVI	74	54	0.47	<0.03
Cobalt	77	51	32	4
Copper	77	1	330	<10
Iron	77	0	20700	500
Lead	77	45	265	5
Manganese	78	2	1.63	<0.01
Mercury	76	65	0.4	<0.2
Nickel	77	49	82	<2
Silver	78	55	6.8	<0.1
Thallium	77	57	6	<0.2
Zinc	77	0	728	10
COD	76	0	678	35
TSS	78	1	472	<10
TDS	78	0	911	42
TVS	78	0	203	20
Chloride	77	0	287	2.5
Alkalinity	78	0	252	25
pH	78	0	72	6.89
Total P	78	0	138	0.28
Inorg. P (PO4)	78	0	8.04	0.11

Table 23. Summary table of number of samples collected, number of sample results below the detection limit, and maximum and minimum reported results for Schroeder Sewer--Continued

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Ammonia-N	78	24	6.5	<1.0
TKN	78	0	13.9	1.1
FOG	76	22	37.7	<5.0
Cyanide	77	25	0.05	<0.005
CBOD	77	18	145	<10
Fecal Coliform	55	0	17 x 10 ⁶	1000
Fecal Streptococci	67	0	10 x 10 ⁶	2700
E. Coli	65	0	93 x 10 ⁵	2000
Methylene Chloride	21	8	12	<0.200
Styrene	21	4	42	<0.200
Phenol	22	10	110	<5.00
Chrysene	22	22	<10.0	<10.0
bis(2-Ethyl-Hexyl) Phthalate	22	18	9	<5.00
Fluoranthene	22	22	<5.00	<5.00
Hexachlorobenzene	22	22	<5.00	<5.00
Phenanthrene	22	22	<5.00	<5.00
Pyrene	22	22	<5.00	<5.00
Alpha-BHC	21	21	<0.030	<0.030
Chlordane	20	19	0.1	<0.100
Endosulfan	21	21	<0.100	<0.100
Aroclor 1016	21	21	<0.100	<0.100

Pollutant	Number of samples taken	Number of samples below detection limit	Maximum reported value	Minimum reported value
Aroclor 1221	21	21	<1.00	<1.00
Aroclor 1232	21	21	<0.100	<0.100
Aroclor 1242	21	7	12	<0.100
Aroclor 1248	21	21	<0.100	<0.100
Aroclor 1254	21	11	4.5	<0.100
Aroclor 1260	21	17	0.2	<0.100
Lindane	21	20	0.03	<0.030

Appendix A

SAMPLING PROTOCOL

1. PREPARATION FOR SAMPLING

Put on gloves. Lay clear plastic sheeting over work surfaces (any place where sample bottles, churn or other working materials will be placed before, during or after sampling). Provide a protected environment for sample collection so that airborne particulates and volatiles will not enter sample bottles or touch pump tubing. Be prepared to put on new gloves any time you contact a surface other than that of a sample bottle or the pump tubing. Be especially mindful of contact with metals, including keys, coins, gage house walls, pump housing, etc. Do not permit automobile exhaust or cigarette smoke in the proximity of the sampling area. Be aware that paints, rubber surfaces and dyed plastics can contaminate metals samples. Once the clean pump tubing is installed in the pump head, one person should be responsible for holding it and directing flow into sample bottles held by a second person. The person holding the pump tubing should be responsible for seeing that it does not contact contaminating surfaces, preservative solutions, etc. during sample acquisition. Set up four storage and transport containers: one labelled FOR METALS, one labelled FOR NUTRIENTS one labelled FOR ORGANICS and one FOR MERCURY. Follow the steps below in the specified order to avoid contamination of samples and obtain samples of known quality.

2. COLLECTION OF FIELD BLANKS

Put on clean gloves. Insert a clean piece of... [type of] tubing into the pump head. Insert the intake end of the pump tubing into DIW which is contained in a sealed 1 liter bottle. Use a fresh, previously unopened bottle of DIW at each station. Draw the DIW through the pump tubing and fill the VOC field blank vial using the same procedure used to collect the VOC sample. When the VOC field blank sample has been collected, rinse the exterior surface of the outlet end of the pump tubing with DIW. Then draw additional DIW through the pump tubing and rinse the churn, allowing some DIW to pass through the spigot. Fill the churn par-

tially, then obtain the field blank for metals and the field blank for total P, inorganic P and NH_3 , by filling the appropriate bottles from the churn spigot. Place these samples aside to be preserved as appropriate. Attach the intake end of the pump tubing to the sewer intake line and flush with sample water for 1 minute.

3. TESTING FOR RESIDUAL CHLORINE AND/OR SULFIDES

Chlorine: From the outlet end of the pump tubing, allow a drop of CSO water to fall on the potassium iodide-starch paper previously moistened with acetate buffer. A blue color will indicate the need for special treatment of cyanide, organics and bacteria samples. See appendix for proper procedures if a blue color develops.

Sulfides: From the outlet end of the pump tubing allow a drop of CSO water to fall on the lead acetate test paper. Darkening of the lead acetate paper indicates the need for special treatment of the cyanide sample. See appendix for proper procedures if darkening occurs.

4. COLLECTION OF VOC SAMPLES

Put on clean gloves. DO NOT rinse bottle. Add acid preservative to a VOC sample vial, if this was not already done in the laboratory. Break the acid-containing ampule and carefully empty its contents into the VOC vial without touching your hands to the mouth of the vial. Place the empty vial in a disposal container. Change gloves. Place the mouth of the vial over the pump tubing outlet to collect a sample. The end of the pump tubing should remain below the surface of the sample being collected, and no bubbling should occur as the sample is collected. Carefully draw the sample vial down as the vial fills, until the surface of the sample is near the mouth of the vial. Fill the vial so that a meniscus (an outwardly rounded sample surface at the mouth of the vial) forms, but do not fill to overflowing since this will dilute the acid added as a preservative. Cap the vial with a smooth motion. Invert the vial and check for a captured air bubble. If a bubble is present, you must collect a new sample in a new vial. Place the vial at 4 °C in the FOR ORGANICS container.

5. COLLECTION OF OIL AND GREASE SAMPLES

DO NOT rinse bottle. Open a glass collection bottle and add acid preservative, if this was not already done in the laboratory. Fill the glass container to the appropriate level. Place at 4 °C in the FOR NUTRIENTS container. Dispose properly of ampule.

6. COLLECTION OF BACTERIA SAMPLES

Put on clean gloves. Rinse the sample bottle. Collect the bacteria sample by placing the bottle under the end of the pump tubing. Leave an air space at the top of the bottle.

7. FILLING OF THE CHURN

Rinse the churn with CSO water obtained from the outlet end of the pump tubing. Be sure some rinse water passes through the spigot. Be sure the churn is placed in a clean environment and that the spigot is protected from dirt or other sources of contamination. Fill the churn by placing the outlet end of the pump tubing over the opening in the churn cover. Do not insert the pump tubing into churn. Fill the churn to the desired volume at the designated rate. To obtain samples, one person will operate the churn handle while the second person will collect samples from the spigot. All additional samples will be obtained from the churn. Preservatives will be added once all sample bottles have been filled. The person collecting the samples will assure that the spigot remains uncontaminated during sample collection. DO NOT rinse sample bottles for PCBs, bisPhthalate/pyrene, COD, BOD. Rinse all other bottles.

8. ADDITION OF PRESERVATIVES

Since some of the preservatives can contaminate some of the samples, follow these steps in the exact order given. Store samples exactly as indicated. Under all circumstances be sure that the mercury sample, preserved with potassium dichromate, is not placed with either the metals sample or the hexavalent chromium sample, both of which will be analyzed for chromium. Also be sure that the mercury sample does not come in contact with the total P, inorganic P and NH₃ sample,

which will have mercuric chloride added as a preservative.

9. BOD, ALKALINITY, CHLORIDE, TSS/TDS/TVS, HEXAVALENT CHROMIUM

These samples require no added preservative. Place collected samples at 4 °C in the FOR NUTRIENTS container.

10. COD, TKN AND METALS

These samples require the addition of acid. Put on clean gloves. Add the appropriate ampules of acid (H₂SO₄, sulfuric acid, to the COD and TKN bottles; HNO₃, nitric acid, to the METALS bottle) to the collected samples. When you open the bottles, be sure not to allow contamination from airborne particles. You should add the acid to the samples in an enclosed area free from air currents or other sources of contamination (metal surfaces, etc.). Dispose of the acid ampules in the correct container. Remove acid-contaminated gloves before proceeding to the next samples. Place the preserved samples at 4 °C. Place the COD and TKN samples in the FOR NUTRIENTS container and the METALS sample in the FOR METALS container.

11. MERCURY

Put on clean gloves. Avoid contamination as described above. Add the ampule of HNO₃/K₂Cr₂O₇ (nitric acid/potassium dichromate) to the mercury sample. Dispose of the ampule and the contaminated gloves properly. Place the preserved sample at 4 °C in the FOR MERCURY container.

12. TOTAL P, INORGANIC P AND NH₃

Put on clean gloves, avoid contamination as described above, and add preservative to sample on a disposable piece of plastic or absorbent paper. Add the ampule of HgCl₂ (mercuric chloride) to the sample. Dispose of the ampule, plastic or paper and gloves properly. Place the sample at 4 °C in the FOR NUTRIENTS container.

13. CYANIDE

This sample may require special treatment if residual chlorine or sulfide is present. If so, see appendix. If not, add NaOH to pH > 12 and place at 4 °C in the FOR NUTRIENTS container.

14. PCB to LINDANE

This sample may require addition of sodium thiosulfate if chlorine is present. If so, see appendix. If not, place at 4 °C in the FOR ORGANICS container.

15. BISPHTHALATE to PYRENE

This sample may require addition of sodium thiosulfate if chlorine is present. If so, see appendix. If not, place at 4 °C in the FOR ORGANICS container.

(Disks kept in Desk file)

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