Watershed Assessment



The Watersheds Associated with Lowndes County, Georgia

Submitted to Lowndes County

And The Georgia Environmental Protection Division of the Department of Natural Resources

by The University of Georgia Biological and Agricultural Engineering Department's Watershed Group

and Carter & Sloope, Inc. May 2001

Table of Contents



Table of Contents

Report

Appendix I – Background Information

Planning for Domestic Wastewater Systems Attachment 2	1-1
NPDES Permitted Facilities	1-8
Hazardous Waste (generators, transporters, treaters, storers and disposers)	1-8
Impaired Streams from 303(d)	1-9
Population Information.	1-11
Average Monthly Precipitation	1-13

Appendix II – Maps

Fig 1. Lowndes County Relative to Major Watersheds	2-1
Fig 2. Stream and Street Network Map	2-2
Sampling Sites	
Bioassessment Sites	
Information About Figure 3	2-3
Fig 3. Water Service Areas	
Fig 4. Existing Groundwater Wells	2-5
Fig 5. Wastewater Service Areas	
South Lowndes Wastewater Treatment Facility	
Fig 6. Location	2-7
Fig 7. Site Plan	2-8
Fig 8. General Soils	2-9
Fig 9. Basins Modeled	2-10
Fig 10. Sub-Watersheds and Growth Corridor	

Appendix III – Biological and Habitat Assessment

Bioassessment of Streams Associated with Lowndes County, GA	-1
Interpretative Graphs of Bioassessment Results	32

Appendix IV – Sample Collection and Transport

SOP's for Collection and Transport4-1	
Equipment Specifications4-7	

Appendix V – Sample Testing

SOP's for the Evaluation of Water Quality Criteria		
BOD	5-1	
COD	5-8	
Fecal Coliform	5-12	
Fecal Streptococci	5-18	

Table of Contents

TSS	5-24
Nitrate-Nitrite	5-28
Ammonia	5-32
Phosphate	5-36
Total Nitrogen	
Metals	5-47

Appendix VI – Water Quality

In-situ and Laboratory Analyzed Data	.6-1
Pesticide Testing	5-20
Existing Data (from NPDES)	j -21

Appendix VII – Model Information and Results

Model Information	7-1
Modeling Overview	
Appendices Table of Contents	
Appendix A	
Appendix B	
Appendix C	

Appendix VIII – Watershed Management Recommendations

Management and Monitoring Plan

Appendix IX – News Articles and Press Releases

Press Releases/News Articles	
Web Site Information9-7	

Appendix X - References

*Hazardous Waste Permits include generators, transporters, treaters, storers, and disposers of hazardous waste.

Table of Contents

Report



Introduction and Background

Lowndes County covers 511 square miles (327,040 acres) in south-central Georgia. It is bordered by Florida to the South, Brooks County to the West, Echols and Clinch Counties to the East and Cook and Berrien Counties to the North. The Little River makes up the northwestern boundary of Lowndes County then joins with the Withlacoochee River, which flows from the northeast through the center of Lowndes County, to form the southwestern boundary of the county. The Alapaha River forms part of Lowndes County's eastern boundary. The Withlacoochee River and Little River as well as two smaller streams, Bevel Creek and Franks Creek, are included in the Lowndes County Watershed Assessment Project. Franks Creek discharges into Little River and Bevel Creek discharges into the Withlacoochee River in north-central Florida. Lowndes County spans three major watersheds, the center portion of the Withlacoochee River watershed (1510.74 mi²), the southwest portion of the Alapaha River watershed (1815.56 mi^2) and the southeast portion of the Little River watershed (881 mi^2) (See Appendix II, Figure 2-1). The watersheds modeled for the Lowndes County Watershed Assessment are sub-watersheds of the Withlacoochee and Little River watersheds. (See Appendix II, Figures 2-2 & 2-3). Figures 2-4 through 2-7 in Appendix II show water and wastewater service areas as well as general soils for the Lowndes County Area.

Lowndes County, Georgia operates one wastewater treatment facility (WWTF), the South Lowndes Regional Wastewater Treatment Facility located in Southern Lowndes County near Big Grassy Pond (See Appendix II, Figure 2-8). The facility incorporates a facultative lagoon (a lagoon or treatment pond with an aerobic upper section and an

anaerobic bottom section so that both aerobic and anaerobic biological processes can occur simultaneously) for wastewater treatment and a land application system. The wastewater is applied in two spray fields adjacent to the facultative lagoon (See Appendix II, Figure 2-9). Currently, the South Lowndes Regional Wastewater Treatment Facility holds an NPDES (National Pollutant Discharge Elimination System) Permit for 0.5 million gallons per day (mgd) discharge. The county is seeking to increase the discharge of the South Lowndes Regional Wastewater Treatment Facility to 2.0 mgd, which will require a new NPDES Permit. The State of Georgia's Environmental Protection Division (GAEPD) requires a comprehensive watershed assessment for the Lowndes County area in order to obtain the permits necessary to begin the expansion of the WWTF and land application site. Lowndes County chose The University of Georgia's Watershed Group and Carter & Sloope, Inc. to conduct the watershed assessment. The watershed assessment will determine the current health of Lowndes County's waterways and will help predict health of streams and rivers after expansion of the County's wastewater treatment facilities. Based on the findings of the watershed assessment, the GAEPD will be able to make a decision on whether or not the county will receive permits for the expansion of their wastewater treatment facility and land application system. See Appendix I for the GAEPD's watershed assessment criteria and background information for Lowndes County.

Watershed assessment, simply defined, is the use of chemical, physical, and biological indicators to assess the current health of a watershed. Also included in watershed assessment are predicting future watershed conditions and suggesting management

practices that will maintain and improve the health of the watershed. While this definition may seem straightforward, the actual process of assessing a watershed is very complex. Lowndes County's watershed assessment required the collaboration of the State of Georgia Environmental Protection Division, Lowndes County, several State and Federal Agencies (Farm Services Agency, Natural Resource Conservation Service, Cooperative Extension Service), the USGS Patuxent Wildlife Research Center, Carter & Sloope, Inc. and the University of Georgia's Watershed Group. Each organization involved in the Lowndes County watershed assessment had a key role in the completion of the project. Mark Gatlin, of Carter & Sloope, Inc. consulted on the project and provided management for the watershed assessment in Lowndes County, GA. The USGS Patuxent Wildlife Research Center in Athens, GA played an important role in the beginning of the watershed assessment conducted in Lowndes County by performing biological and habitat assessments on all streams associated with watersheds in the Lowndes County area. The NRCS, FSA and the Cooperative Extension Service in Lowndes County were helpful in obtaining information on crops, tillage, and pesticide application throughout the county and the County Manager, Mr. Brad Arnold, served as an administrative contact for the Watershed Group. The University of Georgia's Watershed Group had the most involved role in Lowndes County's watershed assessment. The group was charged with water quality monitoring, data collection, watershed modeling, public education, interpretation of test and model results, and developing a management plan to ensure the streams of Lowndes County will not be adversely affected by development.

Characterization and Monitoring

The first step in accurately characterizing the streams in Lowndes County was to choose sites for biological and habitat assessment as well as water quality sampling. Sites were determined based on their location to significant stream confluences, wastewater treatment facilities, and other key stream junctions.

Refer to Appendix II, Figure 2-10 and Table 2-1 for Lowndes County sampling site details.

- Withlacoochee River 1 bioassessment and water quality downstream Sheriff's Boys Ranch Sewage Disposal Pond NPDES permitted discharge
- Withlacoochee River 2 bioassessment and water quality downstream Moody Air Force Base NPDES permitted discharge
- Withlacoochee River 3 bioassessment and water quality upstream of the limestone sinks and the confluence with Cherry Creek
- Withlacoochee River 4 bioassessment and water quality downstream of the limestone sinks and the confluence with Cherry Creek
- Bevel Creek 1– bioassessment and water quality downstream from Browns Pond and Paradise Fish Camp
- Bevel Creek 2 bioassessment and water quality upstream of Cypress Lake, wooded area with some pasture and residential areas
- Bevel Creek 3 water quality downstream of Cypress Lake and upstream of Tenneco's NPDES permitted discharge
- Franks Creek 1 water quality downstream of Hahira LAS NPDES permitted discharge
- Franks Creek 2 water quality above confluence with Little River
- Little River 1 bioassessment and water quality reference site

After the representative sites were selected, investigators began examining the streams associated with the Lowndes County watershed assessment. Characterization began with the biological and habitat assessments. As mentioned in the introduction, a team from the USGS Patuxent Wildlife Research Center in Athens, GA performed these assessments using the USEPA's Rapid Bioassessment Protocols as a guide. Dr. Parley Winger, Dr. Peter Lasier, and Kurt Bogenrieder began extensive examination of the selected biological and habitat assessment sampling sites in October 1999. They evaluated physical and chemical parameters at each site and identified fish and benthic macroinvertebrate (aquatic insect) populations. According to the results of the biological and habitat assessments, "the sites evaluated in this bioassessment of Lowndes County streams were categorized as nonimpaired" (Winger, P, et.al). The term "nonimpaired" was determined by a ratio between the total RBP score for each site (habitat score + benthos score + fish score) and the total RBP score for the Little River reference site. If the ratio was above 70%, the stream site was determined to be nonimpaired. The biological and habitat assessment also stated that, "differences among sites were minimal and the variability probably represented more of a reflection of flows and basic habitat type (glide/pool – riffle/run) than biological differences. The overall biological integrity of the aquatic systems included in these assessments may have been negatively impacted by the below normal flows" due to drought conditions throughout the State of Georgia (Winger, P, et.al). A complete version of the Lowndes County biological and habitat assessment can be found in Appendix III of this document.

After completion of the biological and habitat assessments, a team from the UGA Watershed Group began the collection of water quality samples. The stream sites were sampled every three to five weeks to get representative samples from each stream. Regular sampling events began on January 27, 2000 and ended on June 8, 2000. This time span allowed for six different sampling events. Unfortunately, due to drought conditions, a storm event was not sampled for Lowndes County. This impacted the modeling process by making it necessary to estimate which pollutants would contribute to storm event runoff.

The team from UGA measured several in-situ water quality parameters (dissolved oxygen, conductivity, turbidity, water temperature, and pH) using a multi-parameter meter. All in-situ data, other pertinent information about the sampling site, weather, and possible equipment inaccuracies were recorded in a field notebook. The team also collected samples for laboratory analysis. For each sampling event, a one-liter bottle and two sterile whirl packs were used for accurate sample testing. The sampling team used protocol outlined in <u>Standard Methods for the Examination of Water and Wastewater</u> for collecting and transporting stream samples. See Appendix IV for detailed techniques and protocol for water quality sampling as well as specifications on sampling equipment.

The University of Georgia's Department of Biological and Agricultural Engineering Environmental Water Quality Laboratory performed the majority of water quality testing for the Lowndes County watershed assessment. The lab tested for BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand), TSS (Total Suspended Solids),

ammonia, phosphorus, nitrate-nitrite and fecal coliform in keeping with standard testing procedures (Appendix V). According to the document "List of Waters 2000" edition which lists impaired waters, Lowndes County has two waterways, Franks Creek and sections of the Withlacoochee River, partially supporting their designated uses, fishing (GAEPD, 2000). The nine-mile reach of Franks Creek within the Lowndes County study area violates dissolved oxygen and fecal coliform criteria due to nonpoint source pollution. The upper and lower reaches of the Withlacoochee River (from Cook and Berrien Counties to Bay Branch) violate fish consumption guidelines due to naturally occurring mercury. The middle reach, from Bay Branch to the confluence with Little River, violates fecal coliform (due to nonpoint sources) and fish consumption guidelines criteria. Because of these violations, close attention was paid to the findings of the laboratory testing for dissolved oxygen (Franks Creek) and fecal coliform (Franks Creek and the Withlacoochee River). The fish consumption guidelines violations in Franks Creek and the Withlacoochee River are caused by naturally occurring mercury and do not violate any standard criteria. In August of 1999 streams in the Withlacoochee River were tested for pesticides since several derivatives of DDT were listed as contaminants in the Withlacoochee River in the 1996-1997 "Water Quality in Georgia". The Agricultural and Environmental Services Laboratories Pesticide and Hazardous Waste Laboratory in Athens, GA performed the tests and, according to the results of the pesticide analysis, pesticides in the Withlacoochee River and the other streams were not detectable. Please see Appendix VI for detailed results of the pesticide testing. The College of Agricultural and Environmental Sciences Soil, Plant, and Water Laboratory in Athens, GA performed metals analysis on the stream samples. Representative samples were

taken from study sites and analyzed for lead, zinc, cadmium, and copper. Levels of zinc and copper were negligible and, for the most part, were below the acute criteria limit (Bevel Creek 3 had slightly high copper for one sampling event). Levels of lead were well below the EPA's maximum level of 15 ppb. The only metal that caused some concern was Cadmium. At the parts per million sensitivity level, Cadmium was slightly high in all streams, about 0.0003 ppm above allowable levels. The Cadmium samples were reevaluated at a more sensitive level (parts per billion) to determine if Cadmium levels were actually too high. Test results showed the levels of Cadmium to be well below the allowable level established by the GAEPD. Laboratory test results and detailed metals analysis results as well as in-situ water quality measurements and previous (existing) water quality data can be found in Appendix VI of this document.

Modeling

Lowndes County was modeled to predict the effects of growth and development on receiving water quality in the county. The model selected for the Lowndes County Project, Soil and Water Assessment Tool (SWAT), was developed for the USDA-ARS (United States Department of Agriculture - Agricultural Research Service) at the Blacklands Research Center in Temple, Texas. SWAT is a continuous-simulation model capable of predicting the influence of land management practices on water, sediment, and agricultural chemical yields in large watersheds with various soils, land uses, and management conditions. The model requires information about soils, weather, vegetation, topography, and land management practices within a watershed. With these inputs, SWAT can model physical processes associated with water movement, sediment

movement, nutrient cycling, etc. SWAT incorporates in-stream nutrient water quality equations from QUAL2E (Enhanced Stream Water Quality Model) as well as urban build up/wash off (runoff) equations from SWMM (Storm Water Management Model). See Appendix VII for more detail on SWAT.

Once the model was selected, the Watershed Group began extensive data collection. Lowndes County provided the UGA Watershed Assessment Team with several data sets, including soils information, land use, and water use, which are required for SWAT to accurately model the watersheds. The Watershed Group obtained Digital Orthophoto Quarter Quadrangles (aerial photography in digital form), Digital Elevation Models, and Digital Raster Graphics (digital topographic maps of the DOQQ's), which gave a good idea of the land use and the general topography. Weather and climate data were obtained from CIRRUS (Climate Interactive Rapid Retrieval Users System), which is maintained by the Southeast Regional Climate Center, based at the South Carolina Department of Natural Resources and from USGS gauging stations in the Valdosta area. Land management, including pesticide application, irrigation, and best management practice information was gathered from the Farm Service Agency and the Natural Resources Conservation Service in Lowndes County. Hydrography data was obtained from the South Georgia Regional Development Center (SGRDC) and soils data came from the USDA-NRCS soil survey for Lowndes County. Existing water quality data (from point source pollution) were acquired from the Water Discharge Permits Query Form on the U.S. Environmental Protection Agency's website, which affords water quality data from NPDES permitted facilities and through various water quality studies of the Lowndes

County area. All other data required by the SWAT model were collected in the field and analyzed in the laboratories mentioned in the Characterization and Monitoring section.

The Withlacoochee River and Little River basins were modeled in order to predict the effects of growth in Lowndes County. Each large basin was divided into smaller subwatersheds, which allowed for even more accurate modeling. The growth area was determined based on creating a 1000m buffer around the proposed and existing sewer service lines. Each large basin located within the growth area was modeled for three scenarios. The first scenario was based on current conditions of the watersheds. The second and third scenarios were based on development from a low to medium density residential and from light to medium industrial/commercial. The period between 1995 and 2000 was used to compare the three scenarios using the SWAT model. The results, from the large basins, showed relatively little change in pollutant loading between the baseline scenario and the development scenarios at the watershed level. See Tables 1 & 2 in Appendix VII for a description and results for each modeling scenario. To more accurately predict potential pollutant loadings, data from selected sub-watersheds were compared. These sub-watersheds were also part of the growth corridor shown on page 7-10 of Appendix VII. More information on the land use of these sub-watersheds and their output loadings are outlined in Appendix VII. Potential pollutants and parameters that were modeled included flow, sediment, soluble phosphorus, organic phosphorus, nitrate, ammonium, organic nitrogen, bacteria, metals, carbonaceous biochemical oxygen demand, and dissolved oxygen. These outputs are in average daily cubic meter per second (flow), count/hectare (bacteria), and kilogram/hectare for all other parameters.

The output data generated by SWAT (in concentration format) showed that because flow rates increased as loads increased, the effects of the pollutant loads on the streams was dampened. A complete summary of the results for each sub-watershed as well as the entire SWAT modeling report can be found in Appendix VII.

During the time of this project, the makers of the SWAT model developed an updated, more robust version, SWAT 2000. The SWAT 2000 model made many improvements to the existing model including debugging code, correcting errors in equations, and solving problems with the QUAL2E (water quality) interface. The Lowndes County simulations can be run in the future using SWAT 2000 for even more accurate and reliable results.

Interpretation and Management

From the results of the characterization and modeling studies, and discussions with county officials, the Watershed Team was able to suggest a management plan to protect Lowndes County's watersheds. There are three main goals to a Watershed Assessment Management Plan: 1. Maintain the current conditions and ensure future watershed health by implementing a comprehensive storm water management plan, 2. Set up a long term monitoring program to assess the success of the management practices and identify areas where additional efforts might be needed, 3. Incorporate public education and involvement. Initially, the Watershed Team provided Lowndes County with general guidelines that were designed to help the County develop a management plan suitable for their needs. Please see Appendix VIII for general management recommendations. From

these recommendations and additional support from the Watershed Group, Lowndes County should be able to successfully manage their watersheds.

Public Education and Involvement

Public education and involvement in the Lowndes County watershed assessment is very important to Carter & Sloope, Inc and The University of Georgia Watershed Group. To increase public awareness, Carter & Sloope, Inc and The University of Georgia conducted a public meeting on February 1, 2000 at 7:00 pm in Nevins Hall on the VSU Campus. The primary objective of the meeting was to give the public a working definition of watershed assessment, to give them an idea of what will be going on regarding the Lowndes County watershed assessment in the months to come, and to field any questions the public might have. The meeting was advertised in the local newspaper, The Valdosta Daily News, for two weeks prior to the meeting. The meeting was well attended by many different groups including representatives from Lowndes County Utility and Solid Waste Management, Lowndes County Board of Commissioners, Keep Lowndes/Valdosta Beautiful, Adopt-A-Stream, Valdosta State University student environmental groups as well as concerned citizens. After the initial public meeting, a series of one on one meetings occurred between members of the Watershed Assessment Team and the Lowndes County Manager, Brad Arnold. These meetings were opportunities for the Watershed Assessment Team to update the County on the status of the watershed assessment and to hear any concerns raised by any of Lowndes County's citizens. In late January 2001, the Watershed Team presented final water quality and biological assessment results as well as preliminary modeling results and a general

management plan to the Lowndes County Planning Commission. A website was developed to keep the public updated on the progress of the watershed assessment. The website addresses basic watershed assessment concepts, including background information, model information, interpretation of results and best management practices that will help protect the watersheds associated with Lowndes County, Georgia. The implementation of the management plan will call for increased public education and involvement. Citizens will be encouraged to participate in a number of watershed related activities. Among these activities are volunteering for river and stream clean up projects conducting water quality and biological sampling, and gathering information for future watershed modeling.

Appendix I



Background Information



ATTACHMENT #2

Guidelines for Watershed Assessments for Domestic Water Systems

A Watershed Assessment includes the gathering of existing information about a watershed and its point and nonpoint pollution sources, as well as the collection of new chemical, physical and biological monitoring data. This information is then used to evaluate current and predicted future water quality problems and to recommend short and long term solutions. The local government can use these recommendations to develop a Watershed Protection Plan, parts of which will be incorporated into an NPDES discharge permit or other enforceable watershed or water resources protection program. The guidelines outlined here may be supplemented by additional requirements from EPD.

General Information

Name and address of local government, group of governments, watershed protection group or other responsible entity.

Name, address, telephone number, fax number and E-mail address of contact person(s).

Defining the Watershed

The purpose of this section is to describe or identify the watershed, responsibilities and resources for watershed management, and to collect information needed to assess and project the future impacts of management scenarios on water quality. Identify, describe, or cite: 1) the political jurisdictions, pertinent authorities and organizations within the watershed(s); 2) the physical characteristics, land use, and population information; 3) facilities and activities which can affect or are affected by water quality or quantity; 4) service areas and areas which warrant special water quality protection measures in the watershed(s). It is recommended that watershed information be compiled in a Geographic Information System (GIS) format.

Topographic map (USGS 7.5 Minute or equivalent with scale between 1:10,000 and 1:24,000) which includes the following information:

Delineation of the watershed(s) to be assessed and the surrounding areas for at least one mile outside these watershed limits. At a minimum, the watershed assessment area must include all streams and other water bodies in the current and proposed service area of the water pollution control plant being built or expanded. This service area may encompass entire watersheds, portions of watersheds, or both. To the extent possible watershed delineations should coincide with those established by the USGS under contract with the EPD. The local government should check with the EPD to determine if the watersheds delineated by the USGS are available for the study area.

Land use activities (current and projected for the next 10-25 years).

Current zoning designations.

Soil types within the watershed.

Population densities (current and projected for the next 10-25 years).

Areas in the watershed which are served by municipal or private wastewater treatment facilities versus areas served by individual septic systems.

Drinking water sources (surface water intakes and community wells).

Stormwater treatment facilities such as detention and retention basins, constructed and natural wetlands, inground treatment systems and other structural controls. Particular attention should be paid to regional ponds and other large-scale stormwater control facilities in the watershed.

Areas in the watershed which are affected by EPD's Rules for Environmental Planning Criteria, including water supply watersheds, groundwater recharge areas, wetlands, river corridor and mountain protection areas. State stream buffer protection requirements and any existing local buffer requirements should also be noted.

Previous watershed protection and management efforts should also be referenced in the assessment.

Note: Local governments are required by the Georgia Planning Act of 1989 to prepare comprehensive plans and update them on a regular basis. These plans are submitted to the Georgia Department of Community Affairs and must address certain Environmental Planning Criteria requirements. The plans can provide valuable information on current and projected future conditions and activities in the watershed, and should be reviewed as part of the watershed assessment procedure. Any other planned or ongoing environmental assessments or protection efforts should be noted and coordination of all such efforts is strongly encouraged. For example, EPD or the local government(s) may be conducting assessments for the Safe Drinking Water Act Source Water Assessment Program. Local governments may also be implementing stormwater management programs to comply with their NPDES municipal separate storm sewer system discharge permits.

Legal Authority Evaluation

Identify all local governments who have authority over the zoning and development activities of any of the delineated areas of the watershed.

Evaluate each local government's codes and other regulations to determine if adequate authority exists to perform a watershed assessment, develop a watershed plan and implement a plan for each entity.

Identify weaknesses in each local government's authority and areas where additional requirements need to be included.

Source Identification (Point and Nonpoint)

Date 2/24/00

Location and description of the following facilities, which should be also be indicated on appropriate maps:

NPDES-permitted discharges, including municipal and industrial wastewater facilities, and areas/facilities covered by municipal and industrial stormwater permits.

Other permitted wastewater treatment facilities, such as land application systems and water reuse facilities.

Waste treatment systems greater than 10,000 GPD which are under Department of Human Resources (DHR) control, including inground disposal systems such as drip irrigation and drain fields. These systems do not receive permits from EPD, but must be approved by EPD before a construction permit can be issued by DHR.

Locations covered by Land Disturbance Activity permits and the NPDES General Permit for Stormwater Discharges from Construction Activities (once this permit becomes effective). Mapping of these locations can help to identify areas of high growth, as well as potential erosion and sedimentation problems in the watershed(s).

Operating and closed municipal landfills and hazardous waste sites.

Note: Visual surveys and local knowledge may be needed to identify some pollutant sources. Adopt-A-Stream surveys and citizen complaints to the local government can provide valuable information about problem areas, while land use and zoning information is also useful for identifying potential sources of certain pollutants.

Watershed Assessment

Select and describe the assessment procedure or model(s) which will be used to assess and project the relative effects of major sources of background, point and nonpoint source impacts under current and various future management scenarios. Identify stream segments and lakes in the watershed(s) and describe the condition of those water bodies as described in the latest report on "Water Quality in Georgia (Section 305 (b) report) and other applicable sources of data and information. Describe and quantify to the extent possible, estimated significant background, point and nonpoint sources of pollution, and the source or cause of those effects by stream segment or water body. Describe additional data or information needed to evaluate conditions and support the assessment procedures or model(s) employed.

Existing Water Quality Information

Monthly mean rainfall estimates for the most current past five years, at a minimum.

Estimated runoff coefficients (ratio of runoff to rainfall) for each land use type.

List of all water bodies within the watershed(s).

List of all impaired water bodies (i.e., rivers, streams, lakes, reservoirs and estuarine waters partially meeting or not meeting their designated uses), as listed in the most current edition of the "Water

Quality in Georgia" Report. All available information on each water body should be given, including 305(b) and 303(d) status, criterion violated, potential cause, etc.

Existing dry weather (base flow) and wet weather stream flow data (from USGS gaging stations, etc.).

Existing dry and wet weather water quality data. This information may include local, State and Federal stream and watershed monitoring information, Adopt-A-Stream monitoring and streamwalk reports and a variety of other information.

Existing aquatic biomonitoring (fish and benthic macroinvertebrate) and habitat information.

Discharge monitoring reports (DMRs) from permitted wastewater facilities and stormwater discharge information collected for stormwater permit compliance.

Note: The USEPA "Surf Your Watershed" internet site (http://www.epa.gov.surf) also provides information on many indices of water quality, as well as links to numerous existing databases with useful information for watershed assessments.

Watershed Monitoring

An initial proposal or scope of work for the watershed monitoring activities must be submitted to EPD for review and approval. The proposed plan should identify the nature and extent of additional data collection necessary to adequately assess the condition of water bodies in the watershed.

Sampling locations, including an explanation of why each site was selected. The number of sites will vary according to the size of the watershed, variety of land uses, hydrology, known or suspected pollutant sources and other factors.

Sampling schedule for wet and dry weather sample collection. The monitoring program must include both types of sampling in order to provide representative data. The sampling schedule should provide realistic time frames which reflect the uncertainties of wet weather sampling, but there must be an estimated completion date for all work.

Dry and wet weather sampling criteria. Suggested dry weather criteria is a period of at least 72 hours since the last rainfall; suggested wet weather criteria is at least 0.1 inches of rainfall with an interevent period of at least 72 hours. An interevent period is the time elapsed since the previous rainfall event.

Standard operating procedures and a description of the equipment to be used, including automated sampling devices, if applicable. Monitoring must be conducted according to approved test procedures set forth in 40 CFR Part 136, unless other approved test procedures have been specified. Clean sampling techniques are strongly recommended for metals analyses.

Analytical parameters. The following parameters should be included: BOD, COD, TSS, TP, NO2+NO3-N, NH3-N, TKN, total lead, total copper, total zinc, total

cadmium, fecal coliform, pH, dissolved oxygen, hardness, turbidity, specific conductance, water temperature and air temperature. Any pollutant which is listed as a "criterion violated" on the 305(b)/303(d) list or is suspected as a source of impairment for a particular water body <u>must</u> be included as a monitoring parameter in that area.

Biological evaluation should include habitat assessment, fish and aquatic macroinvertebrate community assessments and reference stations. Impacts on biological communities must be evaluated for the pollutant or stressor causing the impact.

Evaluation and Discussion

Describe water quality goals. Evaluate, identify, and describe water bodies within the watershed(s) which are or may be impaired or fail to support designated uses, the reason, and the actions necessary to protect the beneficial use of each water body.

This portion of the assessment should provide a detailed discussion of the watershed assessment information and identify the current and predicted point and nonpoint source pollution problems in the watershed. The discussion should integrate this information with the water quality problems identified in the 305(b)/303(d) listings and any ongoing actions to alleviate these problems. Predictive tools (water quality models) should be used to demonstrate how water quality standards can and will be met in the watershed. Such predictions should include forecasted trends toward changing activities and land uses, as well as the predicted effects of various controls and BMPs recommended in the assessment.

Recommended Corrective Actions

Identify potential corrective actions and responsibilities which may feasibly be employed to restore or protect existing or potentially impaired or nonsupporting water bodies in the watershed(s). Establish a schedule for evaluating, selecting, and implementing corrective actions within the watersheds assessed.

The **Watershed Assessment** must include a list of recommended corrective actions to address the specific problems identified in the assessment and to improve and ultimately meet water quality standards. This list of corrective actions should be comprehensive and may include structural and non-structural controls, best management practices, suggested changes to the local government's existing legal authority, ideas for additional future activities, funding needs, cooperative projects and other activities in the watershed.

The local government can then use this list to choose actions for its **Watershed Protection Plan** which are appropriate for its size and resources. The Plan must include specific actions and detailed schedules for implementation.

Appendices and References

As appropriate

NPDES Permitted Facilities

Facility Name	Address
1 Moody Air Force Base	347th CES/CC Moody Air Force Base 31699-1707
2 Hahira LAS	102 S. Church Street Hahira, GA 31632
3 Lowndes County South	Near Big Grassy Pond
4 Georgia Sheriff's Boy's Ranch	Boys Ranch Road Hahira, GA 31632
5 Hamilton Pointe	2400 Bemiss Road Valdosta, GA 31603
6 Tennenco Packaging	Near Clyattville, GA

Hazardous Waste Sites (Includes generators, transporters, treaters, storers and disposers of hazardous waste)

	Facility Name	Address
1	Hahira Service Center	I-75 Hahira Exit Hahira, GA 31632
2	Carlton Company	2966 Highway 84 West Valdosta, GA 31601
3	John T Friis Company	110 S. East Street Lake Park, GA 31636
4	Roadway Express	6470 Bellville Road Lake Park, GA 31636
5	Tomlinson Paint & Body	516 S. Church Street Hahira, GA 31632
6	Griffin Corporation	2509 Rocky Ford Road Valdosta, GA 31603

	LOCATION	WATER USE CLASSIFICATION	CRITERION VIOLATED	EVALUATED	ACTIONS TO ALLEVIATE	MILES	305(b)	303(d)	Priority
			ST. MAR	ST. MARYS RIVER BASIN					
N. Prong St. Marys River (1)	Headwaters to Cedar Cr. (Charlton Co.)	Fishing	FCG,DO	NAT,NP	Fish consumption guidelines due to natural source of mereury, no standard violation. EPD will address nonpoint sources through a watershed protection strategy.	19	×	N/A,X	NA.2
N. Prong St. Marys River	Codar Cr. to S. Prong St. Marys River (Charlton Co.)	Fishing	FCG	NAT	Fish consumption guidelines due to natural source of mercury, no standard violation.	6	×	N/A	N/A
	Lotig Branch to St. Marys River (Charlton Co.)	Fishing	FC	UR	EPD will address nonpoint source (urban runoff) through a watershed protection strategy.	4	×	×	3
	S. Prong St. Marys River to St. Marys Cut (Charlton/Canden Co.)	Fishing	FCG	NAT	Fish consumption guiddines due to natural sources of mercury, no standard violation.	55	×	N/A	N/A
	Upstream Cabbage Bend to Catfish Cr. (Camden Co.)	Fishing	Q	ďN	EPD will address nonpoint sources through a watershed protection strategy.	15	×	×	2
			SUWANN	SUWANNEE RIVER BASIN					
	Sand Crock to U.S. Hwy. 129/Ga. Hwy. 11 (Irwin/Tift/Berrien Co.)	Fishing	DO,FCG	NP,NAT	EPD will address nonpoint sources through a watershold protection strategy for the basin. Fisk consumption guidelines due to natural source of mercury, no standard violation.	16	×	X,N/A	2,N/A
	U.S. Hwy. 129/Ga. Hwy. 11 to Statcline (Berrich/Atkinson/Lanier/Lowndes/Echols Co.)	Fishing	FCG	NAT	Fish consumption guidelines due to natural source of mercury, no standard violation.	102	×	N/A	N/A
Alapahoochee River (1)	Confluence of Mud and Grand Bay Cr. to Stateline (Echols Co.)	Fishing	FCG	NAT	Fish consumption guidelines due to natural source of mercury, no standard violation.	=	×	N/A	N/A
	City of Adel Lake to Withlacoochee River (Cook Co.)	Fishing	DO,FC	W	WPCP is a LAS with a hydrograph controlled release. Engineers are working on replacement sprinklens due to high water table in the LAS area including Bear Creek.	4	×	×	2
	SR107 to Alapaha River near Irwinville (Irwin Co.)	Fishing	DO	ďX	EPD will address nonpoint sources through a watershed protection strategy.	6	×	×	2
	Headwaters to Alapaha River (Clinch/Lanier/Echols Co.)	Fishing	DO	đž	EPD will address nonpoint sources through a watershed protection strategy.	4	×	×	2
	W. Fork Deep Cr. to Lake Cr., E. of Ashbum (Turner Co.)	Fishing	DO	đa	EPD will address nonpoint sources through a watershed protection strategy.	6	×	×	2
	St. Rt. S1780 to Little River near Hahira (Lowndes Co.)	Fishing	DO,FC	л	EPD will address nonpoint source (urban runoff) through a watershed protection strategy.	6	×	×	2
	U/S U.S. Hwy. 41/SR 7 to Bear Cr., Addl (Cook Co.)	Fishing	Q	R	EPD will address nonpoint source (urban runoff) through a watershed protection strategy.	-	×	×	2
	U.S. Hwy. 319, S. of Tifton to Withlaccochec River (Tift/Berrien Co.)	Fishing	DQ	Ê	EPD will address nonpoint sources through a watershed protection strategy.	17	×	×	2
	Headwaters near Sylvester to Warrior Cr. (Worth Co.)	Fishing	DO	đN	EPD will address nonpoint sources through a watershed protection strategy.	13	×	×	2
	Stump Cr. to Reedy Cr. S. of Ocilla (Irwin Co.)	Fishing	DO	đN	EPD will address nonpoint sources through a watershed protection strategy.	4	×	×	2
	Ashburn Branch, W. of Sycamore to Warrior Cr.	Fishing	DO	đ	EPD will address nonpoint sources through a watershed protection	41	×	×	2

A-50

RIVERS/STREAMS PARTIALLY SUPPORTING DESIGNATED USES

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BASIN/STREAM (Data Source)	LOCATION	WATER USE CLASSIFICATION	CRITERION VIOLATED	EVALUATED CAUSE(S)	ACTIONS TO ALLEVIATE	MILES	305(b)	303(d)	Priority
Negro Branch (1)	Headwaters to Piscola Cr., Quitman (Brooks Co.)	Fishing	DQ	đN	EPD will address nonpoint sources through a watershed protection strategy.	6	x	×	2
New River (1)	Reedy Cr. to Gum Branch near Lenox (Cook Co.)	Fishing	DO,FC	ЧИ	EPD will address nonpoint sources through a watershed protection strategy.	7	x	х	2
New River (1)	Brushy Cr. to Withlacoochec River, E. of Sparks (Bernen/Cook Co.)	Fishing	DO	đN	EPD will address nonpoint sources through a watershed protection strategy.	4	x	х	2
Okapiteo Creck (1)	Upstream SR S1540 to U.S. Hwy. 319, Moultrie (Colquit Co.)	Fishing	DO	đN	EPD will address nonpoint sources through a watershed protection strategy.	10	х	х	2
Okapileo Creek (1)	SR 37 to Hog Cr., S. of Moultric (Colquit Co.)	Fishing	DO	UR	EPD will address nonpoint source (urban runoff) through a watershed protection strategy.	10	x	х	2
Okapileo Creck (1)	SR 76, Quitman to Withlacoochec River (Brooks Co.)	Fishing	DO	dN	EPD will address nonpoint sources through a watershed protection strategy.	S	x	х	2
Reedy Creek (1)	Little Creek (upstream U.S. Hwy. 319/SR 35) to Little Brushy Cr., S. of Ocilla (Irwin Co.)	Fishing	DO	ЧР	EPD will address nonpoint sources through a watershed protection strategy.	10	x	х	2
Sand Crock (1)	Headwaters E. of Sycamore to Alapaha River (Tumer/Twin Co.)	Fishing	DO	dN	EPD will address nonpoint sources through a watershed protection strategy.	14	x	х	2
Southside Branch (2)	Tributary to New River, Tifton (Tift Co.)	Fishing	FC	UR	EPD will address nonpoint source (urban runoff) through a watershed protection strategy.	-	х	3	3
Suwarmce Canal (1)	Okenfenokee Swamp (Charlton/Ware Co.)	Fishing	FCG	NAT	Fish consumption guidelines due to natural source of mercury, no standard violation.	27	x	N/A	N/A
Suwannee River (1,10)	Mainstem-Suwannee Canal to Stateline (Charlton/Ware/Clinch/Echols Co.)	Fishing	FCG	NAT	Fish consumption guidelines due to natural source of mercury, no standard violation.	40	х	N/A	N/A
Town Creek (10	Headwaters to Warrior Cr. near Sylvester (Worth Co.)	Fishing	DO	UR	EPD will address nonpoint source (urban runoff) through a watershed protection strategy.	6	x	х	2
Tributary to Withlacoochec River (1)	Upstream Morris Pond, Nashvillo (Berrien Co.)	Fishing	DO	NP	EPD will address nonpoint sources through a watershed protection strategy.	2	x	x	2
Ty Ty Crock (1)	Little Cr. near Ty Ty to Tucker Cr. near Omoga (Worth/Tift Co.)	Fishing	DO	NP	EPD will address nonpoint sources through a watershed protection strategy.	10	x	х	2
Warrior Crock (1)	Horso Cr. to Rock Cr. near Norman Park (Worth/Colquitt Co.)	Fishing	DO	NP	EPD will address nonpoint sources through a watershed protection strategy.	10	х	х	2
Willacoochee River (1)	Turkey Branch, upstream SP90/U.S. Hwy. 319 N. of Ocilia to SR 90, S.E. of Ocilia (Irwin Co.)	Fishing	DO	NP	EPD will address nonpoint sources through a watershed protection strategy.	13	х	х	2
Willacoochee River (1)	SR 158 to Alapaha River (Berrien Co.)	Fishing	DO	AP	EPD will address nonpoint sources through a watershed protection strategy.	н	x	х	2
Withlacoochec River (1)	New River to Bay Branch (Cook/Berrien/Lowndes Co.)	Fishing	FCG	NAT	Fish consumption guidelines due to natural source of mercury, no standard violation.	23	x	N/A	N/A
Withlacoochec River (1)	Bay Branch to Little River (Lowndos Co.)	Fishing	FCFCG	NP,NAT	EPD will address nonpoint sources through a watershed protection standay. Fish consumption guidelines due to natural source of mercury, no standard violation.	6	×	X,N/A	3,N/A
Withlacoochee River (1)	Little River to Stateline (Lowndes/Brooks Co.)	Fishing	FCG	NAT	Fish consumption guidelines due to natural source of mercury, no standard violation.	33	×	N/A	N/A

1-10

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Get Tract Whole County	
[Georgia Home Page] [Search for City, Town, CDP] [Search for County] [Down	load Data]
1990 Census of Population and Housing Lowndes County, Georgia	Page 1
Total population	75,981
SEX Male	37,201
Female	38,780
AGE	1 005
Under 1 year	1,085 2,607
3 and 4 years	2,508
5 years	1,263
6 years	1,217
7 to 9 years	3,500
10 and 11 years	2,354
12 and 13 years	2,248
14 years 15 years	1,102 1,118
16 years	1,085
17 years	1,154
18 years	1,486
19 years	1,856
20 years	1,695
21 years	1,771
22 to 24 years	4,444
25 to 29 years	7,098
30 to 34 years	6,341 5,751
40 to 44 years	4,922
45 to 49 years	3,783
50 to 54 years	3,073
55 to 59 years	2,787
60 and 61 years	988
62 to 64 years	1,504
65 to 69 years	2,365
70 to 74 years	1,893 1,429
80 to 84 years	920
85 years and over	634
Median age	28.9
Under 18 years	21,241
Descent of total nervilation	28.0
Percent of total population	7,241

General Profile for Lowndes County, Georgia

Summary	
. Housing	
<u>. Income</u>	
<u>. Labor</u>	
. Social	
Georgia Home Page] [Search for City, Town, CDP] [Search for County] [Downl pack to Search List]	oad Data J [Go
1990 Census of Population and Housing	Page 1
Valdosta city, Georgia	Page 1
Total population	39,806
3EX	
Male	18,462
Female	21,344
AGE	622
Under 1 year	632
3 and 4 years	1,406 1,374
5 years	672
6 years	630
7 to 9 years	1,832
10 and 11 years	1,226
12 and 13 years	1,115
14 years	562
15 years	574
16 years	573
17 years	581
18 years	931 1,216
20 years	1,054
21 years	1,041
22 to 24 years	2,426
25 to 29 years	3,421
30 to 34 years	3,028
35 to 39 years	2,807
40 to 44 years	2,379
45 to 49 years	1,825
50 to 54 years	1,441
55 to 59 years	1,405 552
62 to 64 years	789
65 to 69 years	1,320
70 to 74 years	1,101
75 to 79 years	864
80 to 84 years	584
85 years and over	445
Median age	28.0
Jnder 18 years	11,177
Percent of total population	28.1
	4,314 10.8
Percent of total population	

1 of 3

12/7/00 8:49 AM

Month		-	-			Year	-				
	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998
January	4.0300	0.4935	2.7226	13.9260	8.7167	7.8097	6.6333	6.7452	2.3355	6.4042	3.3065
February	6.5800	2.4679	4.0750	1.5786	4.4103	2.2143	3.1552	3.3640	1.0793	4.0964	6.6964
March	4.2839	3.8355	2.3774	6.2613	3.9138	5.7935	8.0935	2.3548	13.7840	0.6645	4.4258
April	no data	2.5400	0.7900	2.6700	0.9733	0.0000	2.4967	3.2267	2.5967	4.6467	7.8767
May	1.8258	1.4452	2.2097	4.2613	3.3774	0.7065	0.6903	2.1065	1.0806	4.2323	2.0700
June	1.2833	6.9367	0.8233	5.5633	5.4867	5.4800	10.7400	2.7167	0.8967	7.6767	2.7267
July	2.8368	4.0097	3.5290	7.4645	6.0323	5.2903	5.1097	4.4742	4.3613	1.1516	2.9390
August	10.1390	3.6258	2.0903	4.9581	4.9323	2.6032	6.7321	4.8375	6.5231	3.3516	
September	7.6833	2.6767	0.8333	2.2033	0.5433	2.6433	3.2333	1.7100	3.8633	2.4200	
October	1.3613	1.3452	3.4323	0.8516	3.4419	5.2129	11.9130	4.0645	4.5226	7.7903	
November	2.6000	0.7967	0.7700	0.0000	4.8933	2.5800	1.2267	1.1933	0.3300	6.6733	
December	0.8710	4.3903	2.4194	2.5467	1.3900	2.4935	4.6387	1.8710	1.8613	1.5000	

Average Monthly Precipitation - Lowndes County, GA (1988-1998)

From:

CIRRUS (Climate Interactive Rapid Retrieval Users System) from the Southeast

Regional Climate Center based at the South Carolina Department of Natural Resources

Appendix II







Lowndes County Relative to Major Watersheds Figure 2-1



Figure 2-2. Basins Simulated


Figure 2-3. Subbasins Simulated



Figure 2-4



Figure 2-5



Figure 2-6



Figure 2-7. General Soils



Figure 2-8



Figure 2-9



Figure 2-10 Lowndes County, Georgia Water Quality, Bioassessment,

Water Quality and Bioassessment Sites	
Withlacoochee 1	GA Hwy 122, E of intersection with Skipper Bridge Road
Withlacoochee 2	McMillan/Skipper Bridge Road
Withlacoochee 3	River Chase Road, cul-de-sac
Withlacoochee 4	Langdale Park
Bevel Creek 1	Loch Laurel Road / Paradise Fish Camp
Bevel Creek 2	Lake Park Road, W of intersection with Loch Laurel Road
Bevel Creek 3	Cypress Lake Trail
Franks Creek 1	Old Valdosta Road
Franks Creek 2	Shiloh Road
Little River 1 - ref.	GA Hwy 122

Table 2-1. Water Quality and Bioassessment Sites

Appendix III



Biological and Habitat Assessment

BIOASSESSMENT OF STREAMS IN LOWNDES COUNTY, GEORGIA

Submitted To:

Matt Smith and David Gattie Department of Agricultural Engineering University of Georgia Athens, GA

Prepared By:

Parley V. Winger, Peter J. Lasier, Kurt J. Bogenrieder

USGS-Patuxent Wildlife Research Center Warnell School of Forest Resources University of Georgia Athens, GA 30602

> Telephone: 706-546-2146 FAX: 706-546-2109 Email: parley_winger@usgs.gov

> > June 2000

Abstract

Using the Rapid Bioassessment Protocols (RBP), bioassessments were conducted at a reference site on Little River and 6 stations on the Withlacoochee River and a tributary stream in Lowndes County, GA during October 1999. The assessments included an evaluation of habitat at each site, as well as benthic macroinvertebrate populations and fish populations. The streams and rivers were considered soft-water systems (specific conductance <200 microsiemens per centimeter (μ S/cm) and hardness < 40 milligrams per liter (mg/L) as CaCO₃) with little buffering capacity (alkalinity < 50 milligrams per liter (mg/L) as CaCO₃). Stream temperatures were higher in Bevel Creek (~25 °Celcius (C)) than those in the Withlacoochee and Little Rivers (15 -17 °C). Discharge was highest at Station 4 on the Withlachoochee River. Discharge at the lower stations on the Withlacoochee River was influenced by the loss of water into sinkholes. Bottom substrates were dominated primarily by sand. Streambanks showed little erosion and were generally heavily vegetated. Habitat integrity based on Total RBP scores was similar among sites and generally exceeded that of the reference station. About 110 benthic taxa were identified in the samples collected during the bioassessment of the streams. Most were collectors and intermediate to moderate in their tolerance to pollution. The benthic assemblages were dominated by Odonata and Diptera (Chironomidae). Only one site, Station 6 (Withlacoochee River at Langdale Park), was rated as slightly impaired; the other stations were nonimpaired. Thirty-eight fish species were collected. The highest number of species was from the Centrarchidae family. Most fish species were categorized as intermediate in tolerance to pollution. Based on Total RBP scores, fish populations were impaired at all sites except Station 3; Station 1 was moderately impaired and the others were slightly impaired. The overall rating of the biological integrity based on the combined RBP scores from the three matrices categorized all sites as nonimpaired. Although rated as unimpaired, Station 6 had the lowest overall rating (74). This was attributed to the lack of flow and stagnant conditions caused by the complete loss (sink holes) of water from the river. Overall, streams/river evaluated in Lowndes County were of good quality, although negatively influenced by low flow conditions.

Introduction

The quality of stream habitat is dependent upon the integrity of the physical, chemical and biological components of the system. Degradation in any one of these results in degraded stream quality. Physical features, such as substrate stability, suitable stream flow and sedimentation, can have a profound effect on the habitat quality. Similarly, chemical characteristics are also integral to the basic quality of the habitat; lack of dissolved oxygen, elevated stream temperatures, or presence of agricultural and industrial chemicals can significantly reduce habitat quality. Although biological assemblages generally reflect the suitability of the physical and chemical components, adverse biological conditions, such as exotic species, infections and out of balance populations, can also influence biological communities. Field evaluations used to establish the biological integrity of streams should incorporate assessments of the biological, chemical and physical components.

Using an integrated approach, the Rapid Bioassessment Protocol (RBP) incorporates the biological, chemical and physical components in a systematic field evaluation of stream integrity (Plafkin et al. 1989; Barbour et al. 1999). This holistic evaluation provides information on each of the components, which can be combined to express an overall assessment. This "weight of evidence" approach provides a more robust assessment than would be possible using only one of the environmental components.

Methods and Materials

Study Sites

Seven sites in Lowndes County, GA were included in this evaluation: 2 on Bevel Creek, 4 on the Withlacoochee River and 1 reference site on Little River. <u>Station 1</u> was Bevel Creek 1 (upstream) located at the crossing on Loch Laurel Road, downstream from the Brown's Pond outlet. The stream in this area was pond like (mostly pool with no stable substratum) with emergent vegetation (e.g., pickerelweed, *Pontederia lanceolata* and spatterdock, *Nuphar luteum*) and heavily vegetated stream banks (cattail, *Typha* sp. and elephant-ear, *Colocasia esculentum*).

Station 2 on Bevel Creek 2 (downstream) was at the road crossing on Lakes Boulevard (west) off of I-75 at Exit 5. This site was more stream like than the upstream station and it had a sandy bottom and a small amount of gravel. There were rocks in the channel associated with the bridge.

Station 3 was the most upstream site on the Withlacoochee River (1) and was located at the road crossing of Highway 122. This was a very scenic area. The river channel had numerous log snags, sandy substratum and a diverse channel morphology (bends and alternating shallow/deep areas).

<u>Station 4</u> was on the Withlacoochee River (2) at the crossing with McMillan Road. This site had high, steep banks with little vegetation. However, the over-bank areas were heavily vegetated. The substratum was primarily sand.

<u>Station 5</u> on the Withlacoochee River (3) was accessed through the River Chase Subdivision off Val Del Road at the Lefife residence (3561 River Chase). This was a very picturesque area with high, fairly steep banks, large trees (many large cypress) lining the banks and pooled, slow-moving water. The sampling area was upstream of a karst formation that caused pooling for a long distance upstream. The sinkholes (where all the river water disappeared into the ground at several locations) were located approximately 500 meters downstream from this karst formation. Station 6 was on the Withlacoochee River (4) at the boat ramp at Langdale Park off North Valdosta Road. The water was pooled at this site and there was essentially no flow. This very pretty area had numerous large trees, especially on the far (west) bank (the side not used by the park visitors).

<u>Station 7</u> was the reference site on Little River located upstream of the Highway 122 road crossing. This attractive area had a large number of logs and snags in the river channel. The substratum was mostly sand and the depth varied from shallow to deep, giving the appearance of riffles in a couple areas. The banks were high and steep and may be erodible during high flows.

Field and Laboratory Procedures

The sampling area at each site was generally 100 meters (m) in length. At each site, a 500-milliliter (mL) water sample was collected for measurement in the laboratory of alkalinity and hardness by titration. Temperature, pH, dissolved oxygen, and specific conductance were measured in the field using the appropriate meters and electrodes. The physical characteristics associated with the stream and stream bank were tabulated on site, as well as a general description of adjacent land usage. Measurements in the stream included average width, depth and velocity, which were used to calculate discharge. Metrics used to categorize the habitat quality at each site were rated and used to calculate the Rapid Bioassessment Protocol (RBP) score and included substratum type and stability, channel morphology, and stream bank stability.

Benthic macroinvertebrate populations were sampled from all available habitats using an aquatic kick net. Kick samples were transferred into white plastic trays and sorted in the field. Three samples were collected at each site; each consisted of about 100 individuals that represented a cross section of the animals present. These samples were preserved and taken to

- 5 -

the laboratory for identification and enumeration. In the laboratory, each sample was randomly distributed in a white plastic tray by shaking and swirling, and a Sequential Comparison Index (SCI) was tabulated following the procedures described by Cairns et al. (1968) and Cairns and Dickson (1971). The animals were identified to genera using the following taxonomic keys: Sinclair (1964), Brigham et al. (1982), Pennak (1978), Parrish (1975), Edmunds et al. (1976), Wiggins (1977), Wiederholm (1983), Klemm (1995), Epler (1995, 1996). The numbers for each organism from the three samples were combined to form one sample that was used to calculate percent abundance and the Shannon-Weaver diversity index (Poole 1974) and other metrics for the RBP scores. Tolerance to pollution and feeding habitats were determined using Merritt and Cummins (1978), Klemm et al. (1990) and Barbour et al. (1999). The metrics used to compare benthic assemblages among sites and to calculate the RBP score included: number of taxa, Sequential Comparison Index, Shannon-Weaver diversity index, equitability, total number of taxa represented by Ephemeroptera, Plecoptera and Trichoptera (EPT), the total abundance of Ephemeroptera, Plecoptera and Trichoptera/ the number of Chironomidae (EPT/C ratio), Hilsenhoff Biotic Index (HBI), percent contribution of the three dominant taxa, and the Community Similarity Index (Plafkin et al. 1989).

Fish were collected at each site using either a backpack or boat Smith-Root electrofisher. The backpack unit was used if the stream/river was wadeable, but if the water was too deep to wade, the boat electrofisher was used. Fish were identified to species, counted, weighed and returned to the stream/river unless laboratory verification was needed. Identification in the laboratory was aided by Eddy (1957) and Rohde et al. (1994). Approximately 100 m of stream/river were electrofished, but this varied with stream reach. At stations where the full 100m section could not be electrofished, numbers of fish collected per unit distance were extrapolated to a 100-m stream length for comparative purposes. Fish data were evaluated similarly to those of benthos. Metrics used for comparisons and RBP scores were: number of taxa, number collected, weight of fish collected, Shannon-Weaver diversity index, equitability, number of Centrarchidae, number of Cyprinidae, number of insectivores, number of piscivores, percent contribution of the three dominant taxa and Community Similarity Index. Pollution tolerance and feeding guild were assigned based on Barbour et al. (1999).

Metrics for habitat, benthos and fish from each site were compared (normalized) to the reference site by dividing the metric value from the study area by that metric from the reference station (Station 7) on Little River. The percentages derived from these comparisons were rated on a scale from 0 to 6, and the sum of these scores represented the RBP score for that station for the respective matrix (habitat, benthos, fish).

Results and Discussion

Although Bevel Creek (Stations 1 and 2) was substantially smaller than the sites on the Withlacoochee and Little Rivers, discharge was higher, except for Station 4 on the Withlacoochee River. The flow-pattern characteristics at each site were primarily the glide/pool type and consisted of pooled, slow moving water. The overall low-flow conditions were a reflection not only of the season of the year that the assessments were conducted, but also the severity of the drought. Lower than normal flow probably had an over-riding negative influence on the integrity of the rivers and streams included in this assessment.

The streams and rivers were characterized as soft-water systems with low hardness and ionic strength. Hardness of the water at all sites was less than 40 mg/L as CaCO3 and specific conductance ranged from a low of around 40 μ S/cm in Bevel Creek to 100 - 200 μ S/cm at the river sites (Tables 1 and 2). The pH at all sites was within acceptable limits and ranged from 5 to

6 in Bevel Creek and averaged about 7 for the river stations. The buffering capacity (alkalinity) of these systems was on the low end with concentrations around 16 mg/L as CaCO3 in Bevel Creek and around 40 mg/L in the Withlachoochee and Little Rivers. Water at all the sites had the characteristic tannic color of black-water systems that is generally indicative of elevated concentrations of dissolved organic carbon. Dissolved oxygen was noticeably low at Station 1 on Bevel Creek downstream of the lake and in the Withlachoochee River at Langdale Park (Station 6). The amount of aquatic vegetation in the lake and in the outfall from the lake and the associated organic matter probably contributed to the low dissolved oxygen (DO) at Station 1. The stagnant conditions at Station 6 reflected the absence of flow (downstream of where the river water went underground), which may be responsible for the low D.O.

The stream banks at each site were generally stable and lined with woody vegetation that provided considerable shading and cover to the channel. Sand was the predominant substratum at all sites, with the exception of the upstream site (Station 1) on Bevel Creek. Bottom substratum at this site was primarily mud and silt, which probably originated from the upstream lake. Woody debris (snags, roots, logs) was common at the river sites, but was absent from the Bevel Creek sites. Conversely, aquatic vegetation was common at the Bevel Creek sites and generally sparse at the river sites.

The overall Total Habitat Scores were fairly uniform across all sites with values ranging from a low of 171 at Station 5 (Withlachoochee River at River Chase) to a high of 205 at Station 7, the reference site on Little River (Tables 1 and 2). The scarcity of riffles was the main factor causing the somewhat lower habitat scores at most of the sites.

Over 110 benthic macroinvertebrate taxa were collected at the 7 study sites in the streams/rivers included in the Lowndes County assessment (Table 3). The majority of the taxa occurring in these systems were classified as intermediate in their tolerance to pollution (Barbour

- 8 -

et al. 1999), which may be typical for the benthic organisms that would inhabit these type of sandy, warm-water stream systems. The majority of the benthic organisms collected at each site were classified as some type of collector. Benthic animals in this category generally rely on allochthonous detritus (organic matter, such as leaves, produced outside of the stream/river). There were also a number of predators such as Heteroptera and Odonata. About a third (35) of the taxa collected were found at only one station. Four taxa (Oligochaeta, *Caenis, Ischnura, Polypedilum*) were collected at all sites, and an additional 6 taxa (*Ferrisa*, Hydracarina, *Palaemonetes, Procambarus, Stenelemis, Tanytarsus*) were found at 6 of the 7 stations. *Caenis* (mayfly) and *Ischnura* (damselfly) were generally one of the more dominant taxa at each site. Both of these taxa are fairly tolerant of pollution and are commonly found in sand/silt dominated habitats.

Metrics for the benthic macroinvertebrates are shown in Table 4. The highest numbers of taxa were found at Stations 4 and 5 (55 and 51, respectively) on the Withlacoochee River. These stations also had the highest diversities for both the SCI (33 and 32) and the Shannon-Weaver Index (5.4 and 5.7). Diversities generally decrease with increasing pollution. However, the Hilsenhoff Biotic Index (HBI), which measures tolerance of the benthic macroinvertebrates, was also highest at these stations; this metric generally increases with disturbance/pollution. The station with the highest percentage for the three dominant taxa was Station 7, the reference site on Little River. This was surprising, because this metric generally increases with increasing disturbance/pollution. Benthic communities at Stations 3, 4, and 5 (upper stations on the Withlacoochee River) were most similar to those of the reference site on Little River.

Comparisons of the benthic metrics from each station with those of the reference site are shown in Table 5. Comparison with the reference site essentially normalizes the information from each station to the reference site for comparative purposes. For each metric, sites that are

-9-

most similar to the reference site will have the highest values (percent comparison with the reference) and those that are less similar will have lower values (comparisons are shown in the upper portion of Table 5). The scoring criteria for each metric are shown in Table 6 and these values reflect the biological condition, with 6 representing the highest or best conditions and 0 representing the worst case condition. The summation of the biological condition of the benthic population based on the metric scores is shown in the lower portion of Table 5. The Total RBP Scores were quite similar across stations, but Station 6 (Withlachoochee River at Langdale Park) had a somewhat lower Total RBP Score than the other stations. Based on the scoring criteria in Table 7, the overall comparison of the RBP Scores at each station with that of RBP Score for the reference indicated that benthic assemblages were moderately impaired at Station 1, slightly impaired at Station 6 and nonimpaired at the other sites.

There were 38 species of fish collected from the 7 study sites in Lowndes County (Table 8). The majority of these species were classified as insectivores, but there were 8 piscivores and 1 omnivore. Most of the fish species collected in these systems were classified as being intermediate in tolerance to pollution, but there were 4 classified as tolerant and 1 as intolerant. Two species (pirate perch and largemouth bass) were collected at all sites, and 9 species were collected at only one site (Tables 9 and 10). The Centrarchidae family was represented with the greatest number of species (13), and the redbreast sunfish was generally one of the most abundant species at each site.

The metrics for the fish assemblages are shown in Table 11. Fifteen species of fish were collected at the reference site and 8 species were collected at Stations 1 and 6. The highest number of fish (224) collected was at the reference site (Station 7) and the lowest number (26) was collected at Station 2 on lower Bevel Creek. The greatest weight (2,353 g) of fish was collected at Station 3 (upper Withlacoochee River) and was comprised mostly of largemouth

- 10 -

bass, crappie and chain pickerel. The lowest biomass of fish (197 g) was collected at Station 1. Station 3 had the highest diversity and equitability and Station 4 had the lowest values for these two metrics. The three dominant taxa had the highest percentage at Station 4 and the lowest at Station 3. Fish assemblages at Station 4 and 5 were most similar to that at the reference site and least similar at Station 1. Comparisons of fish metrics from each site with those at the reference site are summarized in the top half of Table 12. As with the benthos, this comparison normalizes the data for the fish from each site with the reference site for comparative purposes. Using the Scoring Criteria in Table 13, the biological condition of each site based on the specific metrics is shown in the bottom half of Table 12. Station 1 had the lowest Total RBP Score (26) and Station 3 had the highest (excluding the reference site). Using the Scoring Criteria in Table 14, the level of impairment was obtained by comparing the RBP Score from each site to the RBP Score for the reference site. Based on the fish assemblages, all sites, except Station 3, showed some level of impairment. Station 3 was categorized as nonimpaired, Station 1 as moderately impaired and the rest were slightly impaired.

Combining the RBP evaluations for all three matrices (habitat, benthos and fish) together provides an overall evaluation of the biological integrity of each of the study sites (Table 15). The total RBP Scores were lowest for Stations 1, 5 and 6, but by contrasting these scores with that of the reference site and following the Scoring Criteria in Table 14, the sites evaluated in this bioassessment of Lowndes County streams were categorized as nonimpaired. The values exceeded 70% at all sites. Differences among sites were minimal and the variability probably represented more of a reflection of flows and basic habitat type (glide/pool - riffle/run) than biological differences. The overall biological integrity of the aquatic systems included in these assessments may have been negatively impacted by the below normal flows.

- 11 -

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Lowndes County Habitat Score



Benthic RBP Score Compared to Reference Station



Fish RBP Score Compared to Reference Station



Total RBP Score Compared to Reference Station



Parameter	Stations					
	1	2	3	4	5	6
Land Use	lake-agricultural	residenital	forest-residential	forest-agricultural	forest-residential	forest-residential
Erosion	absent	minor	minor	moderate	minor	minor
Channel stability	stable	stable	stable	some erosion	stable	some erosion
Predominant substrate	mud/silt	sand	sand	sand/muck	sand	sand
Woody debris	sparse	sparse	common	common	common	common
Leaf Packs	sparse	sparse	common	common	common	sparse
Undercut banks	common	common	common	common	common	common
Aquatic vegetation	common	common	sparse	sparse	sparse	common
Gravel/rubble	absent	sparse	absent	absent	absent	absent
Sand	absent	common	common	common	common	common
Mud/Muck/Silt	common	sparse	sparse	common	common	sparse
Hardpan/bedrock	absent	absent	absent	absent	absent	absent
Sediment bars	absent	absent	absent	sparse	absent	absent
Pool deposits	mud/silt	sand/silt	sand/silt	sand/muck	sand/silt	sand/silt
Observable impact	no, dam	no	none	sedimentation	none	yes, campground
Pollution source	-	-	-	-	-	-
Odors	normal	normal	normal	normal	normal	normal
Canopy cover (%)	80	75	25	60	70	40
Stream type	glide/pool	riffle/run	glide/pool	glide/pool	glide/pool	glide/pool
Number of riffles/100 m	0	2	1 (run)	0	0	0
Number of bends/100 m	1	1	2	2	3	1
Channel width (m)	8	6	20	20	20	10
Average width (m)	6.6	5	6.5	12	16	0.74
Average depth (m)	0.45	0.52	0.18	0.62	0.34	0.05
Velocity (m/sec)	0.25	0.38	0.29	0.18	0.12	0.125
Discharge (m3/sec)	0.7	0.9	0.34	1.33	0.65	0.01
Land Use	lake-agricultural	residenital	forest-residential	forest-agricultural	forest-residential	forest-residential
Color	tannic	tannic	tannic	tannic	tannic	tannic
Stream temperature (C)	25	24	15	16	15	17
Dissolved oxygen (mg/L)	3.4	6	7.2	7.8	7	4.1
рН	5.1	5.9	7.1	7.2	7.1	6.9
Conductivity (S/cm)	37	41	215	152	160	112
Alkalinity (mg/L CaCO3)	16	16	48	36	46	40
Hardness (mg/L CaCO3)	-	-	40	40	40	36
Instream cover*	17	19	18	18	16	18
Benthic substrate*	13	18	15	17	17	16

Table 1 & 2 Physical and chemical characteristics of study sites in the Withlacoochee River Watershed--Lowndes Co, GA in October, 1999.

Pool substrate*	9	14	10	10	12	10	
Pool variability*	11	14	11	16	11	16	
Parameter	Stations						
	1	2	3	4	5	6	
Channel alteration*	18	16	16	16	18	16	
Sediment deposition*	19	17	18	14	11	11	
Frequency of riffles*	4	15	18	4	4	4	
Sinuosity*	11	10	19	19	19	17	
Channel flow status*	18	18	15	16	11	16	
Bank vegetation* left							
right	9	9	2	9	9	7	
	9	9	8	9	9	9	
Bank stability* left							
right	9	9	6	6	8	6	
	9	9	6	6	8	4	
Riparian vegetation* left							
right	9	9	3	9	9	6	
-	9	7	8	9	9	9	
Total Habitat Score	174	193	173	178	171	165	

*Values included in Total Habitat Score for habitat assessment

ſ	7
ſ	forest
I	minor
I	stable
ſ	sand
ľ	common
ľ	sparse
ſ	common
ſ	sparse
ſ	sparse
ſ	common
ſ	sparse
ſ	absent
I	absent
ſ	sand
ſ	no
	-
ſ	normal
I	50
ſ	glide/pool
ſ	1
	2
	20
L	8
	0.13
L	0.4
	0.4
ļ	forest
ļ	tannic
ļ	17
ļ	5.8
l	7
ļ	116
	36
ļ	36
l	19
L	19

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Appendix IV



Sample Collection and Transport

5010 INTRODUCTION

5010 A. General Discussion

Analyses for organic matter in water and wastewater can be classified into two general types of measurements: those that quantify an aggregate amount of organic matter comprising organic constituents with a common characteristic and those that quantify individual organic compounds. The latter can be found in Part 6000. The former, described here in Part 5000, have been grouped into four categories: oxygen-demanding substances, organically bound elements, classes of compounds, and formation potentials.

Methods for total organic carbon and chemical oxygen demand are used to assess the total amount of organics present. Gross fractions of the organic matter can be identified analytically, as in the measurement of BOD, which is an index of the biodegradable organics present, oil and grease, which represents material extractable from a sample by a nonpolar solvent, or total organic halide (TOX), which measures organically bound halogens. Trihalomethane formation potential is an aggregate measure of the total concentration of trihalomethanes formed upon ehlorination of a water sample.

Analyses of organics are made to assess the concentration and general composition of organic matter in raw water supplies, wastewaters, treated effluents, and receiving waters; and to determine the efficiency of treatment processes.

5010 B. Sample Collection and Preservation

The sampling, field treatment, preservation, and storage of samples taken for organic matter analysis are covered in detail in the individual introductions to the methods. If possible, analyze samples immediately because preservatives often interfere with the tests. Otherwise, store at a low temperature (4°C) immediately after collection to preserve most samples. Use chemical preservatives only when they are shown not to interfere with the examinations to be made (see Section 1060). Never use preservatives for samples to be analyzed for BOD. When preservatives are used, add them to the sample bottle initially so that all portions are preserved as soon as collected. No single method of preservation is entirely satisfactory: choose the preservative with due regard to the determinations that are to be made. All methods of preservation may be inadequate when applied to samples containing significant amounts of suspended matter.

5020 QUALITY CONTROL

Part 1000 contains important information relevant to analyses included in Part 5000. Give particular attention to Sections 1020B (Quality Control). 1060 (Collection and Preservation of Samples), 1080 (Reagent-Grade Water), and 1090 (Safety), all of which are critical for many of the Part 5000 methods.

Take special precautions when analyses are performed by independent laboratories. Reliable use of independent laboratories deserves the same quality assurance procedures observed for inhouse analyses: replicate samples, samples with known additions, and blanks.

Preparation of samples with known additions may not be fea-

sible for certain analyses. In such cases, consider using a mixture, in varying ratios, of several samples. Use the reported concentrations in the samples and the proportions in which they were mixed to calculate the expected concentration in the mixture. Examine laboratory performance using externally prepared standards and check samples (see Section 1020B).

Type I reagent water (Section 1080) should give satisfactory results for most of the analyses in Part 5000, but additional purification steps may be needed for certain methods, such as total organic halide (TOX) and trihalomethane formation potential (THMFP).

5210 BIOCHEMICAL OXYGEN DEMAND (BOD)*

5210 A. Introduction

1. General Discussion

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test has its widest application in measuring waste loadings to treatment plants and in evaluating the BOD-removal efficiency of such treatment systems. The test measures the oxygen utilized during a specified incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It also may

^{*} Approved by Standard Methods Committee, 1988.

5-2

Although only the 5-d BOD (BOD_s) is described here, many variations of oxygen demand measurements exist. These include using shorter and longer incubation periods, tests to determine rates of oxygen uptake, and continuous oxygen-uptake measurements by respirometric techniques. Alternative seeding, dilution, and incubation conditions can be chosen to mimic receiving-water conditions, thereby providing an estimate of the environmental effects of wastewaters and effluents.

2. Carbonaceous Versus Nitrogenous BOD

Oxidation of reduced forms of nitrogen, mediated by microorganisms, exerts nitrogenous demand. Nitrogenous demand historically has been considered an interference in the determination of BOD, as clearly evidenced by the inclusion of ammonia in the dilution water. The interference from nitrogenous demand can now be prevented by an inhibitory chemical.¹ If an inhibiting chemical is not used, the oxygen demand measured is the sum of carbonaceous and nitrogenous demands.

Measurements that include nitrogenous demand generally are not useful for assessing the oxygen demand associated with organic material. Nitrogenous demand can be estimated directly from ammonia nitrogen (Section 4500-NH₃): and carbonaceous demand can be estimated by subtracting the theoretical equivalent of the reduced nitrogen oxidation from uninhibited test results. However, this method is cumbersome and is subject to considerable error. Chemical inhibition of nitrogenous demand provides a more direct and more reliable measure of carbonaceous demand.

The extent of oxidation of nitrogenous compounds during the 5-d incubation period depends on the presence of microorganisms capable of carrying out this oxidation. Such organisms usually are not present in raw sewage or primary effluent in sufficient rumbers to oxidize significant quantities of reduced nitrogen forms in the 5-d BOD test. Many biological treatment plant effluents contain significant numbers of nitrifying organisms. Because oxidation of nitrogenous compounds can occur in such samples, inhibition of nitrification as directed in ¶ B.4e6) is recommended for samples of secondary effluent, for samples seeded with secondary effluent, and for samples of polluted waters.

Report results as CBOD₅ when inhibiting the nitrogenous oxygen demand. When nitrification is not inhibited. report results as BOD₅.

AGGREGATE ORGANIC CONSTITUENTS (5000)

3. Dilution Requirements

The BOD concentration in most wastewaters exceeds the concentration of dissolved oxygen (DO) available in an air-saturated sample. Therefore, it is necessary to dilute the sample before incubation to bring the oxygen demand and supply into appropriate balance. Because bacterial growth requires nutrients such as nitrogen, phosphorus, and trace metals, these are added to the dilution water, which is buffered to ensure that the pH of the incubated sample remains in a range suitable for bacterial growth. Complete stabilization of a sample may require a period of incubation too long for practical purposes; therefore, 5 d has been accepted as the standard incubation period.

If the dilution water is of poor quality, effectively, dilution water will appear as sample BOD. This effect will be amplified by the dilution factor. A positive bias will result. The method included below contains both a dilution-water check and a dilution-water blank. Seeded dilution waters are checked further for acceptable quality by measuring their consumption of oxygen from a known organic mixture, usually glucose and glutamic acid.

The source of dilution water is not restricted and may be distilled, tap, or receiving-stream water free of biodegradable organics and bioinhibitory substances such as chlorine or heavy metals. Distilled water may contain ammonia or volatile organics: deionized waters often are contaminated with soluble organics leached from the resin bed. Use of copper-lined stills or copper fittings attached to distilled water lines may produce water containing excessive amounts of copper (see Section 3500-Cu).

4. Reference

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5210 B. 5-Day BOD Test

1. General Discussion

a. *Principle:* The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 d. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the

initial DO is determined immediately after the dilution is made. all oxygen uptake, including that occurring during the first 15 min, is included in the BOD measurement.

b. Sampling and storage: Samples for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analyzing sample promptly or by cooling it to near-freezing BIOCHEMICAL OXYGEN DEMAND (5210)/5-Day BOD Test

temperature during storage. However, even at low temperature, keep holding time to a minimum. Warm chilled samples to 20°C before analysis.

1) Grab samples—If analysis is begun within 2 h of collection. cold storage is unnecessary. If analysis is not started within 2 h of sample collection, keep sample at or below 4°C from the time of collection. Begin analysis within 6 h of collection: when this is not possible because the sampling site is distant from the laboratory, store at or below 4°C and report length and temperature of storage with the results. In no case start analysis more than 24 h after grab sample collection. When samples are to be used for regulatory purposes make every effort to deliver samples for analysis within 6 h of collection. *

2) Composite samples—Keep samples at or below 4°C during compositing. Limit compositing period to 24 h. Use the same criteria as for storage of grab samples, starting the measurement of holding time from end of compositing period. State storage time and conditions as part of the results.

2. Apparatus

a. Incubation bottles, 250- to 300-mL capacity. Clean bottles with a detergent, rinse thoroughly, and drain before use. As a precaution against drawing air into the dilution bottle during incubation, use a water-seal. Obtain satisfactory water seals by inverting bottles in a water bath or by adding water to the flared mouth of special BOD bottles. Place a paper or plastic cup or foil cap over flared mouth of bottle to reduce evaporation of the water seal during incubation.

b. Air incubator or water bath, thermostatically controlled at $20 \pm 1^{\circ}$ C. Exclude all light to prevent possibility of photosynthetic production of DO.

3. Reagents

a. Phosphate buffer solution: Dissolve 8.5 g KH₂PO₄, 21.75 g K₂HPO₄, 33.4 g Na₂HPO₄, 7H₂O, and 1.7 g NH₄Cl in about 500 mL distilled water and dilute to 1 L. The pH should be 7.2 without further adjustment. Discard reagent (or any of the following reagents) if there is any sign of biological growth in the stock bottle.

b. Magnesium sulfate solution: Dissolve 22.5 g MgSO₄·7H₂O in distilled water and dilute to 1 L.

c. Calcium chloride solution: Dissolve 27.5 g $CaCl_2$ in distilled water and dilute to 1 L.

d. Ferric chloride solution: Dissolve 0.25 g FeCl₃·6H₂O in distilled water and dilute to 1 L.

e. Acid and alkali solutions, 1N, for neutralization of caustic or acidic waste samples.

1) Acid—Slowly and while stirring, add 28 mL conc sulfuric acid to distilled water. Dilute to 1 L.

 Alkali—Dissolve 40 g sodium hydroxide in distilled water. Dilute to 1 L.

f. Sodium sulfite solution: Dissolve 1.575 g Na₂SO₃ in 1000 mL distilled water. This solution is not stable; prepare daily.

g. Nitrification inhibitor, 2-chloro-6-(trichloro methyl) pyridine.*

h. Glucose-glutamic acid solution: Dry reagent-grade glucose and reagent-grade glutamic acid at 103°C for 1 h. Add 150 mg

glucose and 150 mg glutamic acid to distilled water and dilute to 1 L. Prepare fresh immediately before use.

i. Ammonium chloride solution: Dissolve 1.15 g NH₄Cl in about 500 mL distilled water, adjust pH to 7.2 with NaOH solution, and dilute to 1 L. Solution contains 0.3 mg N/mL.

4. Procedure

a. Preparation of dilution water: Place desired volume of water in a suitable bottle and add 1 mL each of phosphate buffer. MgSO₄, CaCl₂, and FeCl₃ solutions/L of water. Seed dilution water, if desired, as described in \P 4*d*. Test and store dilution water as described in \P s 4*b* and *c* so that water of assured quality always is on hand.

Before use bring dilution water temperature to 20°C. Saturate with DO by shaking in a partially filled bottle or by aerating with organic-free filtered air. Alternatively, store in cotton-plugged bottles long enough for water to become saturated with DO. Protect water quality by using clean glassware, tubing, and bottles.

b. Dilution water check: Use this procedure as a rough check on quality of dilution water.

If the oxygen depletion of a candidate water exceeds 0.2 mg/L obtain a satisfactory water by improving purification or from another source. Alternatively, if nitrification inhibition is used. store the dilution water, seeded as prescribed below, in a darkened room at room temperature until the oxygen uptake is sufficiently reduced to meet the dilution-water check criteria. Check quality of stored dilution water on use, but do not add seed to dilution water stored for quality improvement. Storage is not recommended when BODs are to be determined without nitrification inhibition because nitrifying organisms may develop during storage. Check stored dilution water to determine whether sufficient ammonia remains after storage. If not, add ammonium chloride solution to provide a total of 0.45 mg ammonia/L as nitrogen. If dilution water has not been stored for quality improvement, add sufficient seeding material to produce a DO uptake of 0.05 to 0.1 mg/L in 5 d at 20°C. Incubate a BOD bottle full of dilution water for 5 d at 20°C. Determine initial and final DO as in \$s 4g and j. The DO uptake in 5 d at 20°C should not be more than 0.2 mg/L and preferably not more than 0.1 mg/L.

c. Glucose-glutamic acid check: Because the BOD test is a bioassay its results can be influenced greatly by the presence of toxicants or by use of a poor seeding material. Distilled waters frequently are contaminated with copper: some sewage seeds are relatively inactive. Low results always are obtained with such seeds and waters. Periodically check dilution water quality, seed effectiveness, and analytical technique by making BOD measurements on pure organic compounds and samples with known additions. In general, for BOD determinations not requiring an adapted seed, use a mixture of 150 mg glucose/L and 150 mg glutamic acid/L as a "standard" check solution. Glucose has an exceptionally high and variable oxidation rate but when it is used with glutamic acid, the oxidation rate is stabilized and is similar to that obtained with many municipal wastes. Alternatively, if a particular wastewater contains an identifiable major constituent that contributes to the BOD, use this compound in place of the glucose-glutamic acid.

Determine the 5-d 20°C BOD of a 2% dilution of the glucoseglutamic acid standard check solution using the techniques outlined in ¶s 4*d-j*. Evaluate data as described in ¶ 6. Precision and Bias.

^{*} Nitrification Inhibitor 2579-24 (2.2% TCMP), Hach Co., or equivalent.

CHEMICAL OXYGEN DEMAND (5220)/Open Reflux Method

Reduced inorganic species such as ferrous iron. sulfide. manganous manganese. etc., are oxidized quantitatively under the test conditions. For samples containing significant levels of these species, stoichiometric oxidation can be assumed from known initial concentration of the interfering species and corrections can be made to the COD value obtained.

3. Sampling and Storage

Preferably collect samples in glass bottles. Test unstable samples without delay. If delay before analysis is unavoidable, preserve sample by acidification to $pH \le 2$ using conc H₂SO₄. Preferably acidify any sample that cannot be analyzed the same day

5-7

it is collected. Blend samples containing settleable solids with a homogenizer to permit representative sampling. Make preliminary dilutions for wastes containing a high COD to reduce the error inherent in measuring small sample volumes.

4. References

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5220 B. Open Reflux Method

1. General Discussion

a. Principle: Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent. Keep ratios of reagent weights, volumes, and strengths constant when sample volumes other than 50 mL are used. The standard 2-h reflux time may be reduced if it has been shown that a shorter period yields the same results.

2. Apparatus

Reflux apparatus, consisting of 500- or 250-mL erlenmeyer flasks with ground-glass 24/40 neck⁹ and 300-mm jacket Liebig. West, or equivalent condenser⁺ with 24/40 ground-glass joint, and a hot plate having sufficient power to produce at least 1.4 W/cm² of heating surface, or equivalent.

3. Reagents

a. Standard potassium dichromate solution, 0.0417M; Dissolve 12.259 g K₂Cr₂O₇, primary standard grade, previously dried at 103°C for 2 h, in distilled water and dilute to 1000 mL.

b. Sulfuric acid reagent: Add Ag_2SO_4 , reagent or technical grade, crystals or powder, to conc H_2SO_4 at the rate of 5.5 g $Ag_2SO_4/kg H_2SO_4$. Let stand 1 to 2 d to dissolve Ag_2SO_4 .

c. Ferroin indicator solution: Dissolve 1.485 g 1.10-phenanthroline monohydrate and 695 mg FeSO₄·7H₂O in distilled water and dilute to 100 mL. This indicator solution may be purchased already prepared. \ddagger

d. Standard ferrous ammonium sulfate (FAS) titrant, approximately 0.25M: Dissolve 98 g Fe(NH₄)₂(SO₄)₂-6H₂O in distilled water. Add 20 mL conc H₂SO₄, cool, and dilute to 1000 mL. Standardize this solution daily against standard $K_2Cr_2O_7$ solution as follows:

Dilute 10.0 mL standard $K_2Cr_2O_7$ to about 100 mL. Add 30 mL conc H_2SO_4 and cool. Titrate with FAS titrant using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator.

Molarity of FAS solution

 $= \frac{Volume \ 0.0417 M \ K_2 Cr_2 O_7}{Volume \ FAS \ used \ in \ titration, \ mL} \times \ 0.25$

e. Mercuric sulfate. HgSO4, crystals or powder.

f. Sulfamic acid: Required only if the interference of nitrites is to be eliminated (see 5220A.2 above).

g. Potassium hydrogen phthalate(KHP) standard: Lightly crush and then dry potassium hydrogen phthalate (HOOCC₀H₄COOK) to constant weight at 120°C. Dissolve 425 mg in distilled water and dilute to 1000 mL. KHP has a theoretical COD¹ of 1.176 mg O₂/mg and this solution has a theoretical COD of 500 µg O₂/ mL. This solution is stable when refrigerated for up to 3 months in the absence of visible biological growth.

4. Procedure

a. Treatment of samples with COD of >50 mg O₂/L: Place 50.0 mL sample (for samples with COD of >900 mg O₂/L, use smaller sample portion diluted to 50.0 mL) in a 500-mL refluxing flask. Add 1 g HgSO₄, several glass beads, and very slowly add 5.0 mL sulfuric acid reagent, with mixing to dissolve HgSO₄. Cool while mixing to avoid possible loss of volatile materials. Add 25.0 mL 0.0417*M* K₂Cr₂O₇ solution and mix. Attach flask to condenser and turn on cooling water. Add remaining sulfuric acid reagent (70 mL) through open end of condenser. Continue swirling and mixing while adding the sulfuric acid reagent. CAU-TION: Mix reflux mixture thoroughly before applying heat to prevent local heating of flask bottom and a possible blowout of flask contents.

Cover open end of condenser with a small beaker to prevent foreign material from entering refluxing mixture and reflux for 2 h. Cool and wash down condenser with distilled water. Disconnect reflux condenser and dilute mixture to about twice its volume with distilled water. Cool to room temperature and titrate

^{*} Corning 5000 or equivalent.

^{*} Corning 2360, 91548, or equivalent.

[‡] GFS Chemical Co., Columbus, Ohio,
2540 A. Introduction

The terms "solids," "suspended," and "dissolved," as used herein, replace the terms "residue," "nonfiltrable," and "filtrable" of editions previous to the 16th. Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. For these reasons, a limit of 500 mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

1. Definitions

"Total solids" is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids includes "total suspended solids," the portion of total solids retained by a filter, and "total dissolved solids," the portion that passes through the filter.

The type of filter holder, the pore size, porosity, area, and thickness of the filter and the physical nature, particle size, and amount of material deposited on the filter are the principal factors affecting separation of suspended from dissolved solids. "Dissolved solids" is the portion of solids that passes through a filter of 2.0 μ m (or smaller) nominal pore size under specified conditions. "Suspended solids" is the portion retained on the filter.

"Fixed solids" is the term applied to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature. The weight loss on ignition is called "volatile solids." Determinations of fixed and volatile solids do not distinguish precisely between inorganic and organic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts. Better characterization of organic matter can be made by such tests as total organic carbon (Section 5310). BOD (Section 5210), and COD (Section 5220).

"Settleable solids" is the term applied to the material settling out of suspension within a defined period. It may include floating material, depending on the technique (2540F.3b).

2. Sources of Error and Variability

Sampling, subsampling, and pipeting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling. Mix small samples with a magnetic stirrer. If suspended solids are present, pipet with widebore pipets. If part of a sample adheres to the sample container, consider this in evaluating and reporting results. Some samples dry with the formation of a crust that prevents water evaporation; special handling is required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

The temperature at which the residue is dried has an important bearing on results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating. Each sample requires close attention to desiccation after drying. Minimize opening desiccator because moist air enters. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

Residues dried at 103 to 105°C may retain not only water of crystallization but also some mechanically occluded water. Loss of CO_2 will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization usually will be very slight. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

Residues dried at $180 \pm 2^{\circ}$ C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of CO₂ results from conversion of bicarbonates to carbonates and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost. In general, evaporating and drying water samples at 180°C yields values for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

To rinse filters and filtered solids and to clean labware use Type III water. Special samples may require a higher quality water; see Section 1080.

Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

To aid in quality assurance, analyze samples in duplicate. Dry samples to constant weight if possible. This means multiple dryingcooling-weighing cycles for each determination.

Analyses performed for some special purposes may demand deviation from the stated procedures to include an unusual constituent with the measured solids. Whenever such variations of technique are introduced, record and present them with the results.

3. Sample Handling and Preservation

Use resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls. Begin analysis as soon as possible because of the impracticality of preserving

^{*} Approved by Standard Methods Committee, 1991.

4. Selection of Method

Methods B through F are suitable for the determination of solids in potable, surface, and saline waters, as well as domestic and industrial wastewaters in the range up to 20 000 mg/L. Method G is suitable for the determination of solids in sediments, as well as solid and semisolid materials produced during water and wastewater treatment.

5. Bibliography

- THERIAULT, E.J. & H.H. WAGENHALS. 1923. Studies of representative sewage plants. *Pub. Health Bull.* No. 132.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Methods for Chemical Analysis of Water and Wastes. Publ. 600/4-79-020, rev. Mar. 1983. Environmental Monitoring and Support Lab., U.S. Environmental Protection Agency, Cincinnati, Ohio.

2540 B. Total Solids Dried at 103-105°C

1. General Discussion

a. Principle: A well-mixed sample is evaporated in a weighed dish and dried to constant weight in an oven at 103 to 105°C. The increase in weight over that of the empty dish represents the total solids. The results may not represent the weight of actual dissolved and suspended solids in wastewater samples (see above).

b. Interferences: Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Exclude large, floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue (see 2540A.2).

2. Apparatus

 Evaporating dishes: Dishes of 100-mL capacity made of one of the following materials:

1) Porcelain, 90-mm diam.

2) Platinum-Generally satisfactory for all purposes.

3) High-silica glass.*

b. Muffle furnace for operation at 500 \pm 50°C.

c. Steam bath.

d: Desiccator, provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator.

e. Drying oven, for operation at 103 to 105°C.

f. Analytical balance, capable of weighing to 0.1 mg.

g. Magnetic stirrer with TFE stirring bar.

h. Wide-bore pipets. †

3. Procedure

a. Preparation of evaporating dish: If volatile solids are to be measured ignite clean evaporating dish at $500 \pm 50^{\circ}$ C for 1 h in a muffle furnace. If only total solids are to be measured, heat

* Vycor, product of Corning Glass Works, Corning, N.Y., or equivalent, * Kimble Nos, 37005 or 37034B, or equivalent. clean dish to 103 to 105°C for 1 h. Store and cool dish in desiccator until needed. Weigh immediately before use.

b. Sample analysis: Choose a sample volume that will yield a residue between 10 and 200 mg. When very low total suspended solids are encountered (less than 10 mg/L), less residue may be collected; compensate by using a high-sensitivity balance (0.002 mg). Pipet a measured volume of well-mixed sample to a preweighed dish and evaporate to dryness on a steam bath or in a drying oven. Stir sample with a magnetic stirrer during transfer. If necessary, add successive sample portions to the same dish after evaporation. When evaporating in a drving oven, lower temperature to approximately 2°C below boiling to prevent splattering. Dry evaporated sample for at least 1 h in an oven at 103 to 105°C, cool dish in desiccator to balance temperature, and weigh. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained. or until weight change is less than 4% of previous weight or 0.5 mg. whichever is less. When weighing dried sample, be alert to change in weight due to air exposure and/or sample degradation. Duplicate determinations should agree within 5% of their average.

4. Calculation

mg total solids/L =
$$\frac{(A - B) \times 1000}{\text{sample volume. mL}}$$

where:

A = weight of dried residue + dish, mg, and B = weight of dish, mg.

5. Precision

Single-laboratory duplicate analyses of 41 samples of water and wastewater were made with a standard deviation of differences of 6.0 mg/L.

6. Bibliography

SYMONS, G.E. & B. MOREY. 1941. The effect of drying time on the determination of solids in sewage and sewage sludges. Sewage Works J. 13:936.

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MEASURING PROCEDURE 1) Select the "Power Off/On/Hold Switch " (3–2, Fig. 1) to	 Determine temperature unit to °C or °F by slide the "°C/ °F Switch " (3-4, Fig. 1). Remark : Remark : * If select to " °C " position, LCD will show the unit of " °C " on the upper right * If select to " °F " position, LCD will not show any unit, just blank. Determine the display resolution to 0.1° or 0.01° by select "0.1°/0.01° Switch " (3-3, Fig. 1) Connect the " Probe Plug" (3-8, Fig. 1) into the " Input 	 Socket " (3 – 6, Fig. 1). Display will show the temperature value that sensing from the end position of probe. 5) Data Hold : 5) During the measurement, slide the " Power Off/On/Hold Switch " (3 – 2, Fig. 1) will freeze the display value & LCD will show the " D.H." marker. Slide the " Power Off/On/Hold Switch " will release the data hold function. 5. REPLACEMENT OF BATTERY 	 When LCD display show the "marker," it indicate a normal battery output of less than 6.5 V - 7.5 V. It is necessary to replace the battery. However, in -spec measurement may still be made for several hours after low battery indicator appears before the instrument become inaccurate. 	
1				
FRONT PANEL DESCRIPTION	3-2 - 2-2 - 2-2 - - - -	Fig. 1	 3-1 Display 3-2 Power On/Off/Hold Switch 3-3 0.1°/0.01° Switch 3-4 C°/F° Switch 3-5 Battery Cover/Compartment 3-6 Input Socket 3-7 PT 100 ohm Temp. Probe (optional) 3-8 Probe Plug 	

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ns for Probe	Cooperate with an 0.00385 alpha coefficient, meet DIN IEC 751. 100 ohm. -50 ° C to 400 ° C. -58 ° F to 752 ° F. DIN plug, 4 pins/4 wires. Class A. ± (0.15 + (0.002 × T))° C. T : measuring temperature. For example : Accuracy is ± 0.15 °C for 0 °C reading. Accuracy is ± 0.15 °C for 100 °C reading. Accuracy is ± 0.15 °C for 100 °C reading. Probe length - 245 mm.	
2-2 Specifications for Probe	Features O °C resistance Measuring Range Plug Class Accuracy Plug Terminal Layout	
	ц у 1	
2) Slide the " Battery Cover " (3-5, Fig. 1) away from the	 instrument by the coin and remove the battery. 3) Replace with 9V battery (heavy duty type) and reinstate the cover. 4) Make sure the battery cover is secured after change the battery. 	

 Introduction Introduction International content of the system is a joint development by Grant The 3800 Water Chandidge List of the United Kingglog System is a joint development by Grant performance (Cambridge) List of the United Kingglog List of the United Kingglog List of the United Kingglog System is a solut development by Grant water quality Demander (Cambridge) List of the United Kingglog System is a solut development by Grant water quality Demander Cambridge) and the United Kingglog System is a solution used with the probes contains probes for massuring several water developments of the system is a solution used with the probes contains probes for massuring several water developments of the system is a several water development by Chant High Mark High Distribution of Maintenance for developments of the system is ease to use lightweight. A full Sistemation of Maintenance for developments and efflorents. The Sistematic and Size Lift and Siz	The 3800 Water Quality Logging System consists of the parts listed below. Optional probes, software, and accessories are listed in section 1.3,	Accessories. The east numbering system for VCI and Grant is the same with the	In part numeering system for 10 and Oranu is negative, who use exception of the prefix letters. When ordering parts from YSI, use the prefix letters "YSI" (for example, YSI 3815 Sonde). When ordering parts from Grant, use the prefix letters "WQL" (for example, WQL 3815 Sonde). Part	Number Description 3812 Water Quality Logger 3818 Field Carrier or 3824 or 3839 Backpack Field Carrier		 3873 3800 Water Quality Logger to IBM-AT cable and 9 to 25 pin adapter 3828 3800 Water Quality Logger to printer cable 5731 D.O. membrane can bit (6 acch) 		The 3812 Water Quality Logger is housed in a waterproof case. The logger can measure up to 13 channels. Channels are displayed in pairs with the sample's temperature. See section 3.1, Overview - groups, channels, inputs, and probes.	There are two internal switches. One applies power to the logger and the other selects a power supply rejection frequency. The switches are described in section 5.1, <i>Internal Switches</i> .	Probes may be calibrated and the logger configured to display and store the readings as desired by use of the logger's front panel buttons. Calibration settings and logger configuration information are stored in nonvolatile memory in the logger. This information will not be lost if the logger loses power or is reset.	Up to 100 sites may be identified with a number and a 10 character site identity, see section 4.6, <i>Site Indentity</i> . Measured data from these sites may be logged and stored in the logger's volatile memory. A unique run number is assigned to each set of recorded readings can	be reviewed on the display of printed on a printer, the restange and also be downloaded to a computer using Grant Instruments' Filewise software, included in the back of this manual. A spreadsheet program such as Lotus 123 or SuperCale can then be used for further analysis.
	Introduction		The 3800 Water Quality Logging System is a joint development by Grant Instruments (Cambridge) Ltd. of the United Kingdom, and YSI Incorpo- rated of the United States of America. Major components of the system are the logger and a sonde which contains probes for measuring several water quality parameters.	WARNING: Solutions used with the probes contain chemicals which are harmful to humans if not handled carefully. See section 1.4, <i>HEALTH and SAFETT INFORMATION</i> , for more details.	WARNING: BEFORE SUBMERGING THE SONDE ENSURE THAT A FULL SET OF PROBES AND PLUGS ARE FITTED AND THAT THEY ARE SECURELY LOCATED IN THE SONDE PLATE. See section 6 Maintenance for details of pressure relief mechanisms.	The battery-powered system is easy to use, lightweight, weatherproof, and suitable for use in a range of aquatic environments and effluents. The 3800 Water Quality Logging System has been designed for ease of calibration and maintenance.	The system is capable of measuring and recording the following standard parameters: Conductivity	Dissolved oxygen mV/mA pH Count of pulse or frequency Salinity	Temperature The system is also capable of measuring and recording the following ontional parameters:	Ammonia/Ammonium Depth ISE ORP Nitrate	Inrotative The displays of ammonia (NH ₄ ⁺ -N), and nitrate (NO ₄ ⁺ -N) are not their absolute concentrations, but are the concentrations of nitrogen due to the presence of ammonium, and nitrate.	1671 Japp Lev. 1000 D. Casen 1911 fr. From D. Casen Georgia Co. YSZ/

1.3 ACCESSORIES	Miscellaneous parts	Part Number Number 3001 Description 311 110-120Y 50/06Hz Power supply - UK 13A plug 3002 3011 220-240Y 50/06Hz Power supply - UK 13A plug 3003 3021 220-240Y 50/06Hz Power supply - UK 13A plug 3003 3021 220-240Y 50/06Hz Power supply - UK 13A plug 3003 3021 220-240Y 50/06Hz Power supply - UK 13A plug 3003 3021 220-240Y 50/06Hz Power supply - UK 13A Nove: Power supply - EVOT waterpool and are intended for indoor are only 50 in 15m (25 ft) soude to logger cable 3863 3022 3001 (100 ft) soude to logger cable 3863 5001 (100 ft) soude to logger cable 3863 3038 Screw-on sonde transport cup 6044 Soude sologger cable 3863 3041 Soude sologger cable 3863 5001 (100 ft) soude to logger cable 3863 3053 Screw-on sonde transport cup 6044 Soude solution 3383 3064 Into 00 fth soude cologger cable 3863 5000 (100 fth) soude cologger cable 3863 3075 Into 100 fth soude cologger cable 3863 5000 (100 fth) soude cologger cable 3864 5000 (100 fth) soude cologger cable 3865 3085 Into 100 fth soude cologger cable 3864 5000 (100 fth) soude cologger cable 3865 5000 (100 fth) soude cologger cable 3866 3086	1-4 Introduction
	3812 Water Quality Logger	Communications assa computer Cache assa retries	Issue 2.0, 6/94 1-3

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8595 Grovemont Circle Gaithersburg, Maryland (301) 869-4700 1-800-388-2723

Appendix V



Sample Testing

Environmental Water Quality Laboratory Department of Biological and Agricultural Engineering University of Georgia, Athens, GA 30602

STANDARD OPERATING PROCEDURES

SOP # 610-BAE:	Procedure to determine Chemical Oxygen Demand of Stream Water using the Reactor Digestion Method w Spectrophotometer.		
WRITTEN BY: UPDATED BY:	Krista Peterson Emily Cantonwine Vicki Collins	July 27, 1993 July 06, 2000 September 14, 2001	
PURPOSE:	To describe the procedures used to determine the COD of stream water samples by means of the Micro COD digestion Procedure.		

BACKGROUND INFORMATION

The Chemical Oxygen Demand (COD) test is used as a measurement of the oxygen equivalent of the organic matter content in a sample that is susceptible to oxidation by a strong chemical oxidant. (Standard Methods, 5220)

PROCEDURES:

- A. Apparatus
 - 1. Pipet (5ml disposable glass)
 - 2. Hach COD reactor, Model 45600
 - 3. 100ml volumetric flask (5)
 - 4. 1L volumetric flask
 - 5. 401 Spectrophotometer
 - 6. Test tube rack
 - 7. Kimwipes
- B. Reagents
 - 1. Deionized water
 - 2. Potassium Hydrogen Phthalate, oven dried, 425mg

- 3. Hach low range, 0-150 mg/L COD digestion reagent vials.
- C. Sample collection and preservation COD page 2/3
 - 1. Collect sample in 1L Nalgene bottle and composite sampler. Keep on ice or in refrigerator. Test should be done within 48 hours of sample collection.
- D. Prepare Potassium Hydrogen Phthalate (KHP) standards
 - 1. Weigh out 106.25mg of oven dried KHP and add to 250mL of super DI water to yield a 500mg/L COD solution. (Each mg of KHP requires 1.175 mg Oxygen for complete oxidation). Mix well.
 - 2. Prepare 5 working standards and a blank by adding the volume of 500mg/L KHP solution designated in the table to a 100ml volumetric flask. Fill flasks to 100ml mark with super DI water.

* Use Kimax pipets to prepare standards

1							
	COD concentration (mg/L)	ml of 500mg/L COD solution					
	0.0	0 (100% super DI water)					
	5.0	1					
	25.0	5					
	50.0	10					
	100.0	20					
	150.0	30					

- 3. Cap and mix.
- 4. You will need a clean vial filled with only super DI water to zero the spec when reading at 420 nm. This vial can be saved and reused.
- E. Micro COD digestion procedure
 - 1. Turn on COD reactor and preheat to 150°C.
 - 2. Label Low range COD vials with Sharpie on marking spot or top of cap.
 - 3. Add samples and standards to individual COD vials.
 - a. Pipet 2ml of sample using pipet aid and 5ml disposable glass pipet.
 - b. Remove cap of COD reagent vial and tilt vial to a 45° angle to minimize splashing and additional oxygenation. Tilt open end away from you.
 - c. Carefully dispense the 2ml of sample into vial and replace cap tightly.
 - d. Hold the vial tight and gently invert vial several times to mix the contents well. Vial will get hot!

- e. Repeat a-d for all samples and all standards including a blank (2ml DI water).
- 4. Place all vials in the COD reactor and heat for 2 hours (set timer on reactor) at 150°C. If the front left switch on the reactor is set to the infinity mark then that means that when the timer goes off it will ring and you will have to manually switch off the heat. If the switch is set to TIMER then when the timer goes off the reactor will turn off the heat but the timer does not ring.
- 5. After 2 hours, take vials out of reactor and gently invert each vial to mix contents well. Place in test tube holder and put under a box to let vials cool to 120°C or less in the dark (20-30 minutes).
- 6. Turn on Spectrophotometer to warm up.
- F. Colorimetric Measurement with Spectrophotometer
 - 1. Turn on and allow machine to warm up for 30 minutes.
 - 2. Set wavelength to 420nm (press 4, 2, 0, go to λ)
 - 3. Set detector to absorbance (will see an A on the display)
 - 4. Clean the outside of the DI water vial with a Kimwipe and insert into the adapter slot. Place the black tube cover over the adapter. Allow the reading to stabilize and press AUTO ZERO. Reading should be 0.000A at 420nm.
 - 5. Remove DI vial from adapter
 - 6. Clean the outside of the lowest standard vial and place into the adapter and cover. Record reading as % absorbance.
 - 7. Repeat step 8 with the remaining standards and sample vials
 - * NOTE: Check DI vial occasionally to insure accurate readings.
 - ** FOR SPRINGFIELD DAIRY SAMPLES, ALSO MEASURE AT 600nm, <u>ZEROING WITH THE BLANK</u>.
- G. Clean up
 - 1. Turn off spectrophotometer and return dust cover.
 - 2. Make sure COD digestion reactor is turned off.
 - 3. COD vials contain hazardous materials and must be disposed of through HAZMAT pick up. Therefore, keep used COD vials in a location designated for hazardous materials and request for HAZMAT pick up when enough vials are accumulated. They will take vials as is...you do not have to dump contents into a separate container, although if you would like to reuse the COD vials this is an option.

H. Calculation of COD

- 1. Calculate standard curve equation using the % absorbance reading from the standards.
- 2. Use standard curve equation to determine sample COD in mg/L.
- 3. See data management procedure for more information.

Environmental Water Quality Laboratory Department of Biological and Agricultural Engineering University of Georgia, Athens, GA 30602

STANDARD OPERATING PROCEDURES

SOP # 612-BAE:	Procedure for the Enumeration of Fecal Streptococci in Stre Water Using the Membrane Filtration Method.		
WRITTEN BY: UPDATED BY:	Krista Peterson Emily Cantonwine	July 27, 1993 July 06, 2000	
PURPOSE:	To describe the procedures used to determine the presence and number of fecal streptococci in stream water samples by membrane filtration method.		

PROCEDURES:

A. Apparatus

- 1. 250ml erlenmeyer flask
- 2. Hot Plate
- 3. Stir Bar
- 4. 50mm sterile petri dishes
- 5. 150ml autoclavable dilution water bottles
- 6. Autoclavable squirt bottles
- 7. Sterile whirl-pak bags
- 8. Cooler with ice for transportation
- 9. 10ml sterile transfer pipets
- 10. 47mm-diameter, 0.45µm sterile membrane filters
- 11. Autoclavabale filtration funnel
- 12. Vacuum filtration system (1liter vacuum flask and vacuum bar)
- 13. Forceps
- 14. Incubator (35°C)
- 15. Inoculating loop, sterile
- 16. Microscope slides
- 17. Screw-top test tubes, 10ml

- B. Reagents
 - 4. KF Streptococcus Agar
 - 5. 1% 2, 3, 5-Triphenyltetrazolium Chloride (TTC) Solution
 - 6. Peptone powder pillow, Hach Co.
 - 7. 10% Sodium Carbonate solution, sterilized
 - 8. Brain Heart Infusion agar Slants, Hach Co.
 - 9. Brain Heart Infusion dehydrated
 - 10. Oxgall
 - 11. 3% Hydrogen Peroxide
 - 12. 10% ethanol
- C. Sample Collection and Storage
 - 1. Grab samples with sterile whirl-paks. Keep on Ice and test within 24 hours.
- D. Preparing growth media



- 1. Add 7.64g of KF Streptococcis Agar to 100ml of DI water in a 250ml erlenmeyer flask.
- 2. Heat on hot plate and use a stir bar to dissolve medium. After completely dissolved (when it begins to boil), heat an additional 5 minutes being careful not to let it boil over.
- 3. Cool to 50-60°C and add 1ml of sterile 1% 2, 3, 5-Triphenyltetrazolium chloride solution.
- 4. Remove stir bar with magnetic rod from the outside (try to not contaminate medium with non-sterile magnetic rod).
- 5. In Biological hood, pour medium into 50mm sterile petri dishes. One batch of agar makes 10-16 plates. Try to just cover the bottom of the dish and reduce chunks of agar and air bubbles.
- 6. Let cool in hood for 5 minutes and then on counter for 30 minutes. Store in 4°C refrigerator for no more than 2 weeks.
- E. Preparation of Sterile Dilution Water

Day Before

- Add contents of 1 peptone powder pillow to 1 liter of DI water. Mix well. Transfer 100ml of the dilution water into autoclavable dilution bottles and squeeze bottles. Keep bottle tops loose for autoclaving. Sterilize in an autoclave on wet cycle for 15 minutes per liter (10 100mls = 1 liter) up to 60 minutes.
- 2. Let cool and tighten bottle tops. Sterile fecal dilution water is good for up to 3 weeks.

F. Sterilization of Filters

Day 1. Wash filters and cover all open areas with aluminum foil. Before 2. Autoclave on dry cycle for 15 minutes, or add to dilution water autoclave run.

- G. **Determining Dilution Concentrations**
 - 1. The ideal dilution for fecal streptococci testing yields between 20-100 colonies.
 - 2. To insure at least one dilution falls within the range, three different dilutions should be filtered for samples where the streptococci number is uncertain
 - 3. Begin by filtering volumes of 100, 50 and 10ml. If the number of colonies per filter is too numerous, then increase the dilutions. Comn

mon	dilution	com	binat	ions

a.	50, 10, 1ml
b.	10, 1, 0.1ml
c.	1, 0.1, 0.01ml
d.	0.1, 0.01, 0.001

For Springfield Dairy we use dilutions 10, 1 and 0.1ml sample. For Watershed samples we typically use 100, 10, 1ml

- H. Dilution technique
 - 1. Wash hands, put on gloves and wipe off counters with 10% ethanol.
 - 2. Shake sterile sample (whirl-pak) vigorously at least 25 times.
 - 3. Organize dilution bottles and loosen caps, but do not take caps off.
 - 4. With a sterile transfer pipet, pipet desired quantity of sample to a sterile dilution water bottle.
 - 5. Recap dilution bottle and shake vigorously.
 - 6. If more dilutions are needed repeat steps 4-5 using clean sterile pipets (the same one can be used if it is the same sample and has not touched anything) and additional bottles of sterile dilution water.
 - 7. Examples of dilution series 10,1.0 and 0.1ml are as follows
 - a. Pipet 11ml of sample from sterile whirl-pak and add to sterile dilution bottle.
 - b. Recap dilution bottle and shake vigorously.
 - c. To create a 1ml dilution, transfer 11ml of 10ml dilution to new sterile dilution bottle. Shake vigorously.
 - d. 0.1ml dilution is created by transferring 11ml of 1ml dilution to new sterile dilution bottle. Shake vigorously and then remove 11ml from 0.1ml dilution to return the volume to 100ml.
 - ** Discard final 11ml or continue with dilutions.

- I. Fecal Strep Test
 - 1. Filter sample dilution bottles and at least 1 blank (dilution water with no sample added).
 - a. Place sterile filter on vacuum bar and turn on main vacuum line.
 - b. Sterilize forceps by dipping forcep tips in 10% ethanol and then heating with a flame from a bunsen burner until ethanol is completely evaporated.
 - c. Use forceps to transfer a sterile membrane to filter.
 - d. Make sure filter is in place and empty the lowest concentration of sample dilution water (ec. 0.01) into filter. You can turn filter vacuum on either before, after or during pouring the sample in.
 - e. Rinse with sterile dilution water using squeeze bottle and turn vacuum off.
 - f. Use sterile forceps to transfer membrane from filter to KF agar plate. Minimize air bubbles between membrane and agar.
 - 2. Repeat b-f with same filter for all dilutions of the same sample. Change to a new sterile filter when sample site changes.
 - 3. Place agar plate upside down in 35°C incubator for 48 hours.
- J. Read Strep Test
 - 1. After 48 hours, count typical colonies (dark red to pink). They can be very small to fairly large.
 - 2. Choose the dilution that had between 20-100 colonies and use the equation to determine colonies per 100ml

colonies per 100ml = colonies counted * (100/dilution concentration)

- 3. Average results if more than one dilution fell within the range.
- 4. Adjust value as needed according to verification results (see K7)

Environmental Water Quality Laboratory Department of Biological and Agricultural Engineering University of Georgia, Athens, GA 30602

STANDARD OPERATING PROCEDURES

SOP # 613-BAE:	Procedure for the Enumeration of Fecal Coliforms in Stream Water Using the Membrane Filtration Method.		
WRITTEN BY: UPDATED BY:	Krista Peterson Emily Cantonwine	July 27, 1993 July 06, 2000	
PURPOSE:	To describe the procedures used to determine the presence and number of fecal coliforms in stream water samples by membrane filtration method.		

PROCEDURES:

A. Apparatus

- 18. 50mm sterile petri dishes
- 19. 50mm gelman sterile absorbent pads
- 20. 150ml autoclavable dilution water bottles
- 21. Autoclavable squirt bottles
- 22. Sterile whirl-pak bags
- 23. Cooler with ice for transportation
- 24. 10ml sterile transfer pipets
- 25. 47mm-diameter, 0.45µm sterile membrane filters
- 26. Autoclavabale filtration funnel
- 27. Vacuum filtration system (1liter vacuum flask and vacuum bar)
- 28. Forceps
- 29. Hot Bath (44.5°C)
- 30. Inoculating loop, sterile
- 31. Screw-top test tubes, 10ml
- B. Reagents
 - 13. m-FC/Rosolic Acid Broth Ampules
 - 14. Lauryl tryptose broth tubes
 - 15. Peptone powder pillow, Hach Co.
 - 16. EC medium broth
 - 17. 10% ethanol

- C. Sample Collection and Storage
 - 8. Grab samples with sterile whirl-paks. Keep on Ice and test within 24 hours.
- D. Preparing Fecal Coliform Plates
 - 1. Prepare right before use.
 - 2. In Biological hood, transfer 1 sterile absorbent pad into each 50mm sterile petri dishes.
 - 3. Pop open m-FC/Rosolic Acid broth ampules and empty contents onto pad in petri dishes. 1 ampule per dish.
- E. Preparation of Sterile Dilution Water

Day Before

- Add contents of 1 peptone powder pillow to 1 liter of DI water. Mix well. Transfer 100ml of the dilution water into autoclavable dilution bottles and squeeze rinse bottles. Keep bottle tops loose for autoclaving. Sterilize in an autoclave on wet cycle for 15 minutes per liter (10 100mls = 1 liter) up to 60 minutes.
- 2. Let cool and tighten bottle tops. Sterile fecal dilution water is good for up to 3 weeks.

F. Sterilization of Filters.



- Wash filters and cover all open areas with aluminum foil.
 Autoclave on dry cycle for 15 minutes, or add to dilution water autoclave run.
- G. Determining Dilution Concentrations
 - 1. The ideal dilution for fecal streptococci testing yields between 20-100 colonies.
 - 2. To insure at least one dilution falls within the range, three different dilutions should be filtered for samples where the streptococci number is uncertain.
 - Begin by filtering volumes of 100, 50 and 10ml. If the number of colonies per filter is too numerous, then increase the dilutions. Common dilution combinations a. 50, 10, 1ml

a.	50, 10, 1ml
b.	10, 1, 0.1ml
c.	1, 0.1, 0.01ml
d.	0.1, 0.01, 0.001

For Springfield Dairy we use dilutions 10, 1 and 0.1ml sample. For Watershed samples we typically use 100, 10, 1ml H. Dilution technique

- 1. Wash hands, put on gloves and wipe off counters with 10% ethanol.
- 9. Shake sterile sample (whirl-pak) vigorously at least 25 times.
- 10. Organize dilution bottles and loosen caps, but do not take caps off.
- 11. With a sterile transfer pipet, pipet desired quantity of sample to a sterile dilution water bottle.
- 12. Recap dilution bottle and shake vigorously.
- 13. If more dilutions are needed repeat steps 4-5 using clean sterile pipets (the same one can be used if it is the same sample and has not touched anything) and additional bottles of sterile dilution water.
- 14. Examples of dilution series 10,1.0 and 0.1ml are as follows
 - a. Pipet <u>11ml</u> of sample from sterile whirl-pak and add to sterile dilution bottle.
 - b. Recap dilution bottle and shake vigorously.
 - c. To create a 1ml dilution, transfer <u>11ml</u> of 10ml dilution to new sterile dilution bottle. Shake vigorously.
 - d. 0.1ml dilution is created by transferring <u>11ml</u> of 1ml dilution to new sterile dilution bottle. Shake vigorously and then remove 11ml from 0.1ml dilution to return the volume to 100ml.
 - ** Discard final 11ml or continue with dilutions.
- I. Fecal Coliform Test
 - 2. Filter sample dilution bottles and at least 1 blank (dilution water with no sample added).
 - a. Place sterile filter on vacuum bar and turn on main vacuum line.
 - b. Sterilize forceps by dipping forcep tips in 10% ethanol and then heating with a flame from a bunsen burner until ethanol is completely evaporated.
 - c. Use forceps to transfer a sterile membrane to filter.
 - d. Make sure filter is in place and empty the lowest concentration of sample dilution water (ec. 0.01) into filter. You can turn filter vacuum on either before, after or during pouring the sample in.
 - e. Rinse with sterile dilution water squeeze bottle and turn vacuum off.
 - f. Use sterile forceps to transfer membrane from filter to coliform plate.
 - 2. Repeat b-f with same filter for all dilutions of the same sample. Change to a new sterile filter when sample site changes.
 - 3. Put plates in a tightly sealed zip lock bag and place in 44.5°C water bath for 24 hours.

- J. Read Coliform Test
 - 1. After 24 hours, count typical colonies (blue to dark blue). They can be very small to fairly large.
 - 2. Choose the dilution that had between 20-100 colonies and use the equation to determine colonies per 100ml

colonies per 100ml = colonies counted * (100/dilution)

- 3. Average results if more than one dilution fell within the range.
- 4. Adjust value as needed according to verification results (see K5)
- K. Coliform verification
 - 1. Pick 10 typical colonies from a membrane and inoculate a Lauryl Tryptose Broth tube with a sterile inoculating needle or loop.
 - 2. Invert the tube to eliminate air trapped inside the inner glass tube.
 - 3. Incubate the inoculated tubes and a control tube for 48 hours in a 35C incubator.
 - 4. If gas is not produced in 48 hours, the colony was not fecal coliform. If gas is produced, use a sterile loop to inoculate an EC medium broth tube. Incubate EC medium tubes at 44.5C for 24 hours. Gas production in EC medium confirms the presence of fecal coliform.
 - 5. Multiply the % of verified colonies (ec. 10 verified of 10 tested = 1; 8 of 10 tested = 0.8) to numbers counted during plate counts. Use this number to report number of colonies.

- K. Strep verification
 - 1. Pick 10 typical colonies from a membrane and inoculate a brain heart infusion agar slant with a sterile inoculating needle.
 - 2. Incubate the inoculated slants and a control slant for 24-48 hours in a 35°C incubator.
 - 3. If growth is detected, transfer a loopful of growth using a sterile inoculating loop to a clean slide and add a few drops of 3% hydrogen peroxide to the smear. The absence of bubbles indicates a negative catalase test (probably a streptococcal culture). If there are no bubbles, discontinue test.
 - 4. If growth <u>did not</u> bubble, transfer a loopful of growth from the brain heart infusion slant to a 20X150mm tube of sterile brain heart infusion broth using a sterile inoculating loop. Incubate at 45°C for 48 hours. (see next section for preparation of brain heart infusion broth)
 - 5. Transfer another loopful of growth from the slant into a 20X150mm tube of sterile bile broth medium. Incubate at 35°C for 3 days. (see next section for bile broth recipe)
 - 6. Growth (turbidity) in the brain heart infusion broth means the colony is of the fecal streptococcus group. Growth in the bile broth indicates that the colony belongs to the enterococcus group.
 - Multiply the % of verified colonies (ec. 10 verified of 10 tested = 1; 8 of 10 tested = 0.8) to numbers counted during plate counts. Use this number to report number of colonies.
- L. Preparation of verification broths.
 - 1. Brain Heart Infusion Agar Slants are pre-prepared and purchased from VWR or Hach Co.
 - Brain Heart Infusion Broth add 9.25g of dehydrated brain heart infusion to 250ml of distilled water. Add 5ml solution to autoclavable test tubes with screw caps and place caps on loosely. Autoclave for 20 minutes. Tighten caps when solution is cool.
 - 3. Bile Broth Medium Add 3ml of sterile Brain Heart Infusion Broth to an autoclavable test tube and autoclave. Before use, add 2ml of 10% oxgall solution to 3ml BHI broth.

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STANDARD OPERATING PROCEDURES

SOP # 614-BAE:		ining Biochemical Oxygen Demand er Using 5 day BOD Test.	
WRITTEN BY: UPDATED BY:	Krista Peterson Emily Cantonwine	July 27, 1993 July 06, 2000	
PURPOSE:	To describe the procedures used in measuring BOD of strewater samples using 5 day BOD test.		

BACKGROUND INFORMATION:

The biological oxygen demand (BOD) test is used to determine the relative oxygen requirements of waters. The 5 day BOD test measures the molecular oxygen utilized during a 5 day incubation period for the biochemical degradation of organic material and the oxidation of some inorganic material such as sulfides and ferrous iron. (Standard Methods, 5210)

PROCEDURES:

- A. Apparatus
 - 1. Low temperature (20°C) incubator
 - 2. 1 gallon carboy and 10 liter carboy
 - 3. 300ml BOD bottles
 - 4. 1 liter Nalgene bottles
 - 5. Stir plate
 - 6. Air pump and stone
 - 7. Pipet Aid
 - 8. 5ml disposable glass pipet
 - 9. 100ml graduated cylinder
 - 10. 400ml beaker
 - 11. Plastic BOD bottle caps and glass bottle stoppers
 - 12. pH meter
 - 13. Dissolved oxygen probe with stirrer and meter

B. Reagents

- 1. BOD nutrient buffer pillows (Hach Co.)
- 2. Sodium Hydroxide, 1N (if necessary)
- 3. Polyseed-NX®
- 4. Glucose and glutamic acid
- 5. Deionized (DI) water, reagent grade
- C. Sample Collection and Storage
 - 1. Collect grab sample of stream water in 1L Nalgene bottle. Store on ice from field to the lab.
- D. Preparation of BOD Dilution Water
 - 1. When preparing BOD dilution water, the DI water must be at 20°C and saturated with oxygen. To obtain this
 - a. Fill a 1 gallon carboy with 3liters DI water, or a 10 liter carboy with 6 liters or 9 liters DI water, depending on how much BOD dilution water is needed.
 - b. Let water sit for at least 24 hours in 20°C incubator to saturate water with oxygen. Quick oxygen saturation method is to oxygenate DI water with air stone. Quick technique is not recommended and should be used only in emergency situations.
 - 2. Add the appropriate amount of BOD nutrient buffer pillows to oxygenated DI water. (ex. 3L pillow in 3L water).
 - a. Shake pillow(s) well, cut open, and add contents to carboy.
 - b. Cap carboy and shake vigorously for 1 minute to mix.
 - c. Be sure to label carboy appropriately so you know BOD pillows have been added.
 - 3. Check to make sure the pH of the BOD dilution water is between 7.0 and 7.2. Adjust with 1N sodium hydroxide if necessary.
- E. Preparation of Seed Solution
 - 1. Place the contents of one Polyseed-NX capsule in 250ml of prepared BOD dilution water in 400ml beaker.
 - 2. Stir the seeded water with stir-bar and stir-plate and aerate with air pump for at least 1 hour. Continue to stir and aerate throughout the preparation of the test. Use seeded water within 6 hours of rehydrating the Polyseed-NX capsule.

F. Preparing DO meter for readings

- 1. Turn on DO meter and let machine warm up for at least 30 minutes.
- 2. Check DO probe membrane for air bubbles.
 - a. If there are no air bubbles, dry membrane with kimwipe and return to BOD storage bottle. Storage bottle should be filled with 1" water to provide 100% relative humidity.
 - b. If there are air bubbles, or if membrane has not been changed in awhile, change membrane with YSI 5906 membrane cap kit. Screw off old membrane. Fill new membrane with O2 probe solution and screw membrane in place. Make sure there are no bubbles underneath the membrane. Let probe stand at least 30 minutes with meter on after changing a membrane.
- 3. Calibrate meter
 - a. Press CALIBRATE soft-key
 - b. When display readings are stable, press DO CAL
 - c. Adjust % humidity using UP, DOWN and DIGIT until the DO (mg/L) reading and the meter temperature fit the DO and Temperature equation: DO = [(temp 71.26) / -5.76]
 - d. Press ENTER and then MODE.
- G. Check pH of samples
 - 1. Turn on pH meter and let warm up for 30 minutes.
 - 2. Calibrate meter.
 - 3. Samples should have a pH between 6.5 and 7.5 at 25°C. If they do not, adjust sample pH using 1N NaOH or 10% H2SO4.
- H. BOD test preparation
 - 1. Prepare Standards
 - a. 2 Blank bottles (100% BOD dilution water)
 - b. 2 Glucose and Glutamic Acid (GGA) standards (6ml GGA, 3ml
 - seeded water (seed), rest BOD dilution water)...see GGA section.
 - c. 3 Seed standards

5ml seed	(5ml seed, rest BOD water)
10ml seed	(10ml seed, rest BOD water)
15ml seed	(15ml seed, rest BOD water)

- 2. Prepare Samples
 - a. 3 dilutions for each sample.
 For stream water use a graduated cylinder to put 50ml, 150ml and 300ml of sample into 3 separate BOD bottles.
 - For other types of water, see Dilution Volume Chart.
 - b. Add 3ml seed to all samples right before Initial DO reading.
 - c. Fill the rest of each bottle with BOD water just below the lip to insure a tight air seal.

I. Measuring DO

- 1. Insert DO probe into BOD bottle
- 2. Turn stir bar ON with red switch located on the probe.
- 3. Check for air bubbles and an airtight seal. If there are air bubbles, stop stir bar, lift up probe and allow air to float to suface. If there is not an airtight seal, add more BOD water.
- 4. Water temperature must be between 19°C and 21°C to take reading. If not, then let samples sit on countertop to warm up or place in 4°C refrigerator to cool down.
- 5. When temperature is within range, allow DO reading to stablize and report reading in Initial DO reading slot.
- J. Final DO readings
 - 1. After samples have been stored in 20°C incubator for 5 days, recalibrate meter and take a final DO reading.
- K. Calculating Results
 - 1. Use the following equation to calculate BOD:

$$BOD = \frac{(D1-D2) - ((B1-B2)*f)}{p}$$

BOD = biochemical oxygen demand of sample (mg/L)

D1 = initial DO reading of sample (mg/L)

D2 = final DO reading of sample (mg/L)

B1 = initial DO of seed standard that depleted 40%-70% DO (mg/L)

B2 = final DO of same seed standard

f = ratio of seed in sample to seed in chosen seed standard used in B1&B2.

- p = volume of sample (50, 150, 300) divided by total volume (300ml).
- 2. Reportable BOD
 - a. BOD reading are reportable if Test BLANKS depleted < 0.2 mg/L.
 - b. Average all BOD readings that fulfill the 2 requirements.
 - 1) Depletion minus seed correction factor (BOD * p) is >2.0.
 - 2) Reading variation is not too large (use GGA variation to determine limits.)
 - c. If no BOD readings have a depletion minus seed correction factor >2.0, then report BOD as <2.0.

- L. Preparation of Glucose and Glutamic Acid Standard
 - 1. Dry reagent-grade glucose and glutamic acid at 103°C for one hour.
 - 2. Add 150mg glucose and 150mg glutamic acid to DI water and dilute to 1 liter. Prepare fresh immediately before use.
 - 3. Determine the 5 day 20°C BOD of a 2% dilution of the GGA standard. Add 6ml GGA standard, 3ml seed and fill the rest of the BOD bottle up with BOD dilution water.
 - 4. The calculated BOD of the GGA standard should be in the range of 198 mg/L \pm 30.5 mg/L.
 - Use the GGA BOD readings to create a coefficient of variation (CV) (relative standard variation). CV can be used to determine which sample BOD readings should be included in the average. See ADVMAN/Rev:08/01-01-97 pg 32 for more details.

M.	Determining Sample Volume
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A. Minimum Sample Size		B. Maximum Sample Size				
Sample	Est. BOD	Sample	Estimated I	Estimated BOD (mg/L) at Elevation:		
Туре	(mg/L)	1	Sea Level	305 m	1524 m	Sample Size (ml)
Strong trade waste	600	1	2460	2380	2032	1
Raw and Settled Sewage	300	2	1230	1189	1016	2
	200	3	820	793	677	3
	150	4	615	595	508	4
	120	5	492	476	406	5
	100	6	410	397	339	6
	75	7	304	294	251	8
	60	8	246	238	203	10
Oxidized Effluents	50	12	205	198	169	12
	40	15	164	158	135	15
	30	20	123	119	101	20
	20	30	82	79	68	30
	10	60	41	40	34	60
Polluted River Waters	6	100	25	24	21	100
	4	200	12	12	10	200
	2	300	8	8	7	300

ml of sample taken and diluted to 300ml in standard BOD bottle with BOD dilution water.

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STANDARD OPERATING PROCEDURES

SOP # 615-BAE:	Procedure for Measuring Total Suspended Solids (TSS) in Stream Water Using the Gravimetric Method.		
WRITTEN BY: UPDATED BY:	Krista Peterson Emily Cantonwine	July 27, 1993 July 06, 2000	
PURPOSE:	To describe the procedure that is used when measuring the amount of TSS in stream water samples by use of the gravimetric method.		

PRINCIPLE:

A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103°C. The increase in weight of the filter represents the total suspended solids. (Standard Methods 2540 D)

PROCEDURES:

- A. Apparatus
 - 8. Drying oven set at 103°C.
 - 9. 2µm, 47mm-diameter glass fiber filter disks
 - 10. Aluminum weigh pans
 - 11. Filtration apparatus consisting of reservoir and coarse fritted disk as filter support. Gelman No. 4201 or equivalent.
 - 12. Filter clamp
 - 13. Vacuum filtration system (1liter vacuum flask and vacuum bar)

B. Reagents

18. Deionized water

- C. Sample collection and preservation
 - 2. Collect sample in 1L Nalgene bottle.
- D. Gravimetric Method for determining TSS.
 - 1. Set up vacuum filtration system and turn on vacuum.
 - 2. Set drying oven to 103°C.
 - 3. Pre-rinse glass fiber disks.
 - a. Use forceps to place a glass fiber filter disk in the filter holder with the wrinkled surface upward.
 - b. Clamp the top of the filter in place.
 - c. Add 200ml DI water to filter and turn on vacuum.
 - d. Remove the disk from the filter and place in aluminum weigh pan.
 - e. Do this for all samples and a blank.
 - f. Place aluminum weigh dished with filters in 103C oven and let dry for 1 hour.
 - 4. Take initial weights of disks.
 - a. After 1 hour of drying, cool disks in a desiccator for 5 minutes.
 - b. With forceps weigh each disk to the nearest 0.1 mg.
 - 5. Filter samples and Blank
 - a. Again place disk in the filter (wrinkled side up) and clamp filter top in place.
 - b. Filter 200ml (less is solids are high) of well-mixed sample through filter. (200ml DI water for blank)
 - c. Rinse filter and apparatus with DI water.
 - 6. Return filters to aluminum weigh pans and dry in oven for 1 hour.
 - 7. After 1 hour, allow filters to cool in desiccator and take final weight to nearest 0.1 mg.
- E. Calculation of TSS

Use the equation below to determine TSS

TSS (mg/L) = [(A-B)*1000]/ sample volume (ml)

Where A = final weight (mg)B = initial weight (mg)

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STANDARD OPERATING PROCEDURES

SOP no #:	Procedure for Measuring Total Solids (TS), including Total Volatile Solids (TVS) and Total Non-Volatile Solids (TNVS) in Stream Water Using Evaporation Method.		
WRITTEN BY:	Emily Cantonwine July 06, 2000		
PURPOSE:	To describe the procedure that is used when measuring the amount of TS, TVS and TNVS in stream water samples by use of the evaporation method.		

BACKGROUND INFORMATION:

PRINCIPLE:

A well-mixed sample is added to an evaporation plate and the water is allowed to evaporate off, leaving all solids in the plate. TVS are determined by heating the plate and solids at extremely high temperatures for 1.5 hours thus volitalizing all solids volatile in nature.

PROCEDURES:

A. Apparatus

- 14. Drying oven set at 98°C and 103°C.
- 15. Ceramic evaporation plates
- 16. 550°C muffle oven
- 17. Pipet aid and 25ml pipet &/OR 100ml graduated cylinder
- 18. Tongs
- B. Reagents
 - 19. Deionized water

- C. Sample collection and preservation
 - 3. Collect sample in 1L Nalgene bottle.
- D. Evaporation Method for determining TS.
 - 1. Pre-fire evaporating plates (EP) for all samples and a blank at 550°C for 1 hour. When muffle oven temperature is between 250°C 100°C take EP out of oven using tongs and allow them to cool to room temperature in a desiccator.
 - 2. Weigh EP and place in 98°C drying oven. Throughout entire process only touch EP with tongs. Do not set EP plates anywhere where they may pick up extra solids or oils.
 - 3. Add a well-mixed sample to a designated EP using either a clean graduated cylinder or a pipet. EP can hold 75ml-100ml at a time. If more sample is needed for the test then repeat this step after evaporation until appropriate amount has been added. Be sure to record amount added.
 - 4. After total amount has been added and all EP are dry, raise the temperature to 103°C and for at least 1 hour.
 - 5. Let EP cool to room temperature in desiccators and take a second weight.
 - 6. Fire EP at 550°C in muffle oven for 1.5 hours. (2 hours from time muffle oven is turned on).
 - 7. Allow EP to cool to room temperature in desiccator.
 - 8. Take final (3^{rd}) weight of EP.
- E. Calculation of TS, TVS and TNVS

TS (mg) = 2^{nd} weight (mg) -1^{st} weight (mg) TS (mg/L) = [TS (mg)*1000] / sample volume (ml)

TVS (mg) = 2^{nd} weight (mg) -3^{rd} weight (mg) TVS (mg/L) = [TVS (mg)*1000] / sample volume (ml)

TNVS (mg) = TS (mg) – TVS (mg) TNVS (mg/L) = TS (mg/L) – TVS (mg/L) From The Stable Isotope/Soil Biology Laboratory of the University of Georgia Institute of Ecology

NITROGEN, NITRATE-NITRITE

Method 353.2 (Colorimetric, Automated, Cadmium Reduction)

STORET NO .: Total 00630

1. Scope and Application

1.1 This method pertains to the determination of nitrite singly, or nitrite and nitrate combined in surface and saline waters, and domestic and industrial wastes. The applicable range of this method is 0.05 to 10.0 mg/l nitrate-nitrite nitrogen. The range may be extended with sample dilution.

2. Summary of Method

2.1 A filtered sample is passed through a column containing granulated coppercadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.

3. Sample Handling and Preservation

3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4 degrees C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml conc. H2SO4 per liter) and refrigeration.

Caution: Samples for reduction column must not be preserved with mercuric chloride.

4. Interferences

4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered.

4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.

4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

5. Apparatus

5.1 Technicon AutoAnalyzer (AAI or AAII) consisting of the following components: **5.1.1** Sampler.

5.1.2 Manifold (AAI) or analytical cartridge (AAII).

5.1.3 Proportioning Pump

5.1.4 Colorimeter equipped with a 15 mm or 50 mm tubular flow cell and 540 nm filters.

5.1.5 Recorder.

5.1.6 Digital printer for AAII (Optional).

6. Reagents

6.1 Granulated cadmium: 40-60 mesh (E M Laboratories, Inc., 500 Exec. Blvd., Elmsford, NY 10523, Cat. 2001 Cadmium, Coarse Powder).

6.2 Copper-cadmium: The cadmium granules (new or used) are cleaned with dilute HCI (6.7) and copperized with 2% solution of copper sulfate (6.8) in the following manner:

6.2.1 Wash the cadmium with HCI (6.7) and rinse with distilled water. The color of the cadmium so treated should be silver.

6.2.2 Swirl 10 g cadmium in 100 ml portions of 2% solution of copper sulfate (6.8) for five minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the cadmium-copper with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.

6.3 Preparation of reduction column AAI: The reduction column is an 8 by 50 mm glass tube with the ends reduced in diameter to permit insertion into the system. Copper-cadmium granules (6.2) are placed in the column between glass wool plugs. The packed reduction column is placed in an up-flow 20 degree incline to minimize channeling. See Figure 1.

6.4 Preparation of reduction column AAII: The reduction column is a U-shaped, 35 cm length, 2 mm I.D. glass tube (Note 1). Fill the reduction column with distilled water to prevent entrapment of air bubbles during the filling operations. Transfer the copper- cadmium granules (6.2) to the reduction column and place a glass wool plug in each end. To prevent entrapment of air bubbles in the reduction column be sure that all pump tubes are filled with reagents before putting the column into the analytical system. NOTE 1: A 0.081 I.D. pump tube (purple) can be used in place of the 2 mm glass tube.

6.5 Distilled water: Because of possible contamination, this should be prepared by passage through an ion exchange column comprised of a mixture of both strongly acidic-cation and strongly basic-anion exchange resins. The regeneration of the ion exchange column should be carried out according to the manufacturer's instructions.

6.6 Color reagent: To approximately 800 ml of distilled water, add, while stirring, 100 ml conc. phosphoric acid, 40 g sulfanilamide, and 2 g N-(1-naphthyl)-ethylenediamine dihydrochloride. Stir until dissolved and dilute to 1 liter. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.

6.7 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCI to 100 ml with distilled water.

6.8 Copper sulfate solution, 2%: Dissolve 20 g of CuSO4 x 5H20 in 500 ml of distilled water and dilute to 1 liter.

6.9 Wash solution: Use distilled water for unpreserved samples. For samples preserved with H2SO4, use 2 ml H2SO4 per liter of wash water.

6.10 Ammonium chloride-EDTA solution: Dissolve 85 g of reagent grade ammonium chloride and 0.1 g of disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide and dilute to 1 liter. Add 1/2 ml Brij-35 (available from Technicon Corporation).

6.11 Stock nitrate solution: Dissolve 7.218 g KNO3 and dilute to 1 liter in a volumetric flask with distilled water. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months. 1 ml = 1.0 mg NO3-N.

6.12 Stock nitrite solution: Dissolve 6.072 g KNO2 in 500 ml of distilled water and dilute to 1 liter in a volumetric flask. Preserve with 2 ml of chloroform and keep under refrigeration. 1.0 ml = 1.0 mg NO2-N.

6.13 Standard nitrate solution: Dilute 10.0 ml of stock nitrate solution (6.11) to 1000 ml. 1.0 ml = 0.01 mg NO3-N. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months.

6.14 Standard nitrite solution: Dilute 10.0 ml of stock nitrite (6.12) solution to 1000 ml. 1.0 ml = 0.01 mg NO2-N. Solution is unstable; prepare as required.

6.15 Using standard nitrate solution (6.13), prepare the following standards in 100.0 ml volumetric flasks. At least one nitrite standard should be compared to a nitrate standard at the same concentration to verify the efficiency of the reduction column.

Concentration, mg NO2-N or NO3-N/l	ml Standard Solution/100 ml
0.0	0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0
2.00	20.0
4.00	40.0
6.00	60.0

NOTE 2: When the samples to be analyzed are saline waters, Substitute Ocean Water (SOW) should be used for preparing the standards; otherwise, distilled water is used. A tabulation of SOW composition follows:

NaCl - 24.53 g/l	MgCl2 - 5.20 g/l	Na2SO4 - 4.09 g/l
CaCl2 - 1.16 g/l	KCl - 0.70 g/l	NaHCO3 - 0.20 g/l
KBr - 0.10 g/l	H3BO3 - 0.03 g/l	SrC12 - 0.03 g/l
NaF - 0.003 g/l		

7. Procedure

7.1 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH40H.

7.2 Set up the manifold as shown in Figure 2 (AAI) or Figure 3 (AAII). Note that reductant column should be in 20 degree incline position (AAI). Care should be taken not to introduce air into reduction column on the AAII.

7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line. NOTE 3: Condition column by running 1 mg/l standard for 10 minutes if a new reduction column is being used. Subsequently wash the column with reagents for 20 minutes.

7.4 Place appropriate nitrate and/or nitrite standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.5 For the AAI system, sample at a rate of 30/hr, 1:1. For the AAII, use a 40/hr, 4:1 cam and a common wash.

7.6 Switch sample line to sampler and start analysis.

8. Calculations

8.1 Prepare appropriate standard curve or curves derived from processing NO2 and/or NO3 standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 Three laboratories participating in an EPA Method Study, analyzed four natural water samples containing exact increments of inorganic nitrate, with the following results:

	Accuracy as		
Precision as			
		Bias,	
mg N/liter	00	mg N/liter	
0.012	+ 5.75	+0.017	
0.092	+18.10	+0.063	
0.318	+ 4.47	+0.103	
0.176	- 2.69	-0.067	
	Standard Deviation mg N/liter 0.012 0.092 0.318	Precision as Standard Deviation Bias, mg N/liter % 0.012 + 5.75 0.092 +18.10 0.318 + 4.47	

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From The Stable Isotope/Soil Biology Laboratory of the University of Georgia Institute of Ecology

NITROGEN, AMMONIA

Method 350.1 (Colorimetric, Automated Phenate)

STORET NO .:

Total 00610 Dissolved 00608

1. Scope and Application

1.1 This method covers the determination of ammonia in drinking, surface, and saline waters, domestic and industrial wastes in the range of 0.01 to 2.0 mg/l NH3 as N. This range is for photometric measurements made at 630-660 nm in a 15 mm or 50 mm tubular flow cell. Higher concentrations can be determined by sample dilution. Approximately 20 to 60 samples per hour can be analyzed.

2. Summary of Method

2.1 Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside.

3. Sample Handling and Preservation

3.1 Preservation by addition of 2 ml conc. H2SO4 per liter and refrigeration at 4 degrees C.

4. Interferences

4.1 Calcium and magnesium ions may be present in concentration sufficient to cause precipitation problems during analysis. A 5% EDTA solution is used to prevent the precipitation of calcium and magnesium ions from river water and industrial waste. For sea water a sodium potassium tartrate solution is used.

4.2 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used will also interfere.

5. Apparatus

5.1 Technicon AutoAnalyzer Unit (AAI or AAII) consisting of:

5.1.1 Sampler.

5.1.2 Manifold (AAI) or Analytical Cartridge (AAII).

5.1.3 Proportioning pump.

5.1.4 Heating bath with double delay coil (AAI).

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 630-660 nm filters.

5.1.6 Recorder.

5.1.7 Digital printer for AAII (optional).

6. Reagents

6.1 Distilled water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer.

NOTE 1: All solutions must be made using ammonia-free water.

6.2 Sulfuric acid 5N: Air scrubber solution. Carefully add 139 ml of conc. sulfuric acid to approximately 500 ml of ammonia-free distilled water. Cool to room temperature and dilute to 1 liter with ammonia-free distilled water.

6.3 Sodium phenolate: Using a 1 liter Erlenmeyer flask, dissolve 83 g phenol in 500 ml of distilled water. In small increments, cautiously add with agitation, 32 g of NaOH. Periodically cool flask under water faucet. When cool, dilute to 1 liter with distilled water.

6.4 Sodium hypochlorite solution: Dilute 250 ml of a bleach solution containing
5.25% NaOCl (such as "Clorox") to 500 ml with distilled water. Available chlorine level should approximate 2 to 3%. Since "Clorox" is a proprietary product, its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of this product, storage over an extended period should be avoided.
6.5 Disodium ethylenediamine-tetraacetate (EDTA) (5%): Dissolve 50 g of EDTA

(disodium salt) and approximately six pellets of NaOH in 1 liter of distilled water.

NOTE 2: On salt water samples where EDTA solution does not prevent precipitation of cations, sodium potassium tartrate solution may be used to advantage. It is prepared as follows:

6.5.1 Sodium potassium tartrate solution: 10% NaKC4H4O6 x 4H2O. To 900 ml of distilled water add 100 g sodium potassium tartrate. Add 2 pellets of NaOH and a few boiling chips, boil gently for 45 minutes. Cover, cool, and dilute to 1 liter with ammonia-free distilled water. Adjust pH to 5.2 +/-.05 with H2SO4. After allowing to settle overnight in a cool place, filter to remove precipitate. Then add 1/2 ml Brij-35 (note 4) (available from Technicon Corporation) solution and store in stoppered bottle.

6.6 Sodium nitroprusside (0.05%): Dissolve 0.5 g of sodium nitroprusside in 1 liter of distilled water.

6.7 Stock solution: Dissolve 3.819 g of anhydrous ammonium chloride, NH4CI, dried at 105 degrees C, in distilled water, and dilute to 1000 ml. 1.0 ml = 1.0 mg NH3-N. **6.8** Standard Solution A: Dilute 10.0 ml of stock solution (6.7) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NH3-N.

6.9 Standard solution B: Dilute 10.0 ml of standard solution A (6.8) to 100.0 ml with distilled water. 1.0 ml = 0.001 mg NH3-N.

6.10 Using standard solutions A and B. prepare the following standards in 100 ml volumetric flasks (prepare fresh daily):

Standard Solution/100 ml	NH3-N, mg/l
Solution B	
1.0	0.01
2.0	0.02
5.0	0.05
10.0	0.10
Solution A	
2.0	0.20

ml

0.50
0.80
1.00
1.50
2.00

NOTE 3: When saline water samples are arnlyzed, Substitute Ocean Water (SOW) should be used for preparing the above standards used for the calibration curve; otherwise, distilled water is used. If SOW is used, subtract its blank background response from the standards before preparing the standard curve.

 Substitute Ocean Water (SOW)

 NaCl
 24.53 g/l
 NaHCO3
 0.20 g/l

 MgCl2
 5.20 g/l
 KBr
 0.10 g/l

 Na2SO4
 4.09 g/l
 H3BO3
 0.03 g/l

 CaCl2
 1.16 g/l
 SrCl2
 0.03 g/l

 KCl
 0.70 g/l
 NaF
 0.003 g/l

7. Procedure

7.1 Since the intensity of the color used to quantify the concentration is pH dependent, the acid concentration of the wash water and the standard ammonia solutions should approximate that of the samples. For example, if the samples have been preserved with 2 ml conc. H2SO4/liter, the wash water and standards should also contain 2 ml conc. H2SO4/liter.

7.2 For a working range of 0.01 to 2.00 mg NH3-N/l (AAI), set up the manifold as shown in Figure 1. For a working range of .01 to 1.0 mg NH3-N/l (AAII), set up the manifold as shown in Figure 2. Higher concentrations may be accommodated by sample dilution.

7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through sample line.

7.4 For the AAI system, sample at a rate of 20/hr, 1:1. For the AAII use a 60/hr 6:1 cam with a common wash.

7.5 Arrange ammonia standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.6 Switch sample line from distilled water to sampler and begin analysis.

8. Calculations

8.1 Prepare appropriate standard curve derived from processing ammonia standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.41, 0.77, 0.59 and 0.43 mg NH3-N/l, the standard deviation was +/-0.005.

9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.16 and 1.44 mg NH3-N/l, recoveries were 107% and 99%, respectively.

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From The Stable Isotope/Soil Biology Laboratory of the University of Georgia Institute of Ecology

PHOSPHORUS, ALL FORMS

Method 365.1 (Colorimetric, Automated, Ascorbic Acid)

STORET NO .:

Total 00665 Total Orthophosphate (P-ortho) 70507 Total Hydrolyzable Phosphorus (P-hydro) 00669 Total Organic Phosphorus (P-org) 00670 Dissolved Phosphorus (P-D) 00666 Dissolved Orthophosphate (P-D, ortho) 00671 Dissolved Hydrolyzable Phosphorus (P-D, hydro) 00672 Dissolved Organic Phosphorus (P-D, org) 00673 Insoluble Phosphorus 00667 Insoluble orthophosphate00674 Insoluble Hydrolyzable Phosphorus 00675 Insoluble Organic Phosphorus 00676

1. Scope and Application

1.1These methods cover the determination of specified forms of phosphorus in drinking, surface and saline waters, domestic and industrial wastes.



1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pretreatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are defined in Section 4.

1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples. Insoluble forms of phosphorus are determined by calculation.
1.3 The methods are usable in the 0.001 to 1.0 mg P/l range. Approximately 20-30 samples per hour can be analyzed.

2. Summary of Method

2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by manual sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by manual persulfate digestion(2). The developed color is measured automatically on the AutoAnalyzer.

3. Sample Handling and Preservation

3.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

3.2 Sample containers may be of plastic material; such as cubitainers, or of Pyrex glass.

3.3 If the analysis cannot be performed the same day of collection, the sample should be preserved by the addition of 2 ml conc. H2SO4 per liter and refrigeration at 4 degrees C.

4. Definitions and Storet Numbers

4.1 Total Phosphorus (P) - all of the phosphorus present in the sample regardless of form, as measured by the persulfate digestion procedure. (Storet #00665)

4.1.1 Total Orthophosphate (P-ortho) - inorganic phosphorus [(PO4)-3] in the sample as measured by the direct colorimetric analysis procedure. (70507)

4.1.2 Total Hydrolyzable Phosphorus (P-hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus predetermined orthophosphates. This hydrolyzable phosphorus includes polyphosphates [(P207)-4, (P3O10)-5, etc.] plus some organic phosphorus. (00669)

4.1.3 Total Organic Phosphorus (P-org) - phosphorus (inorganic plus oxidizable organic) in the sample as measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)

4.2 Dissolved Phosphorus (P-D) - all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)

4.2.1 Dissolved Orthophosphate (P-D, ortho) - as measured by the direct calorimetric analysis procedure. (00671)

4.2.2 Dissolved Hydrolyzable Phosphorus (P-D, hydro) - as measured by the sulfuric acid hydrolysis procedure and minus predetermined dissolved orthophosphates. (00672)

4.2.3 Dissolved Organic Phosphorus (P-D, org) - as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)

4.3 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

4.3.1 Insoluble Phosphorus

(P-I) = (P) - (P-D) (00667)

4.3.1.1 Insoluble orthophosphate

(P-I, ortho) = (P, ortho) - (P-D, ortho) (00674)

4.3.1.2 Insoluble Hydrolyzable Phosphorus

(P-I, hydro) = (P.hydro) - (P- D, hydro) (00675)

4.3.1.3 Insoluble Organic Phosphorus

(P-I, org) = (P. org) - (P-D, org) (00676)

4.4 All phosphorus forms shall be reported as P. mg/l, to the third place.

5. Interferences

5.1 No interference is caused by copper, iron, or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron

concentrations can cause precipitation of and subsequent loss of phosphorus.

5.2 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

5.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus. However, at concentrations found in sea water, it does not interfere.

5.4 Sample turbidity must be removed by filtration prior to analysis for orthophosphate. Samples for total or total hydrolyzable phosphorus should be filtered only after digestion. Sample color that absorbs in the photometric range used for analysis will also interfere.

6. Apparatus

6.1Technicon AutoAnalyzer consisting of:

6.1.1 Sampler.

6.1.2 Manifold (AAI) or Analytical Cartridge (AAII).

6.1.3 Proportioning pump.

6.1.4 Heating bath, 50 degrees C.

6.1.5 Colorimeter equipped with 15 or 50 mm tubular flow cell.

6.1.6 650-660 or 880 nm filter.

6.1.7 Recorder.

6.1.8 Digital printer for AAII (optional).

6.2 Hot plate or autoclave.

6.3 Acid-washed glassware: All glassware used in the determination should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is

done, the treatment with 1:1 HCI and reagents is only required occasionally. Commercial detergent should never be used.

7. Reagents

7.1 Sulfuric acid solution, 5N: Slowly add 70 ml of conc. H2SO4 to approximately 400 ml of distilled water. Cool to room temperature and dilute to 500 ml with distilled water.

7.2 Antimony potassium tartrate solution: Weigh 0.3 g K(SbO)C4H4O6 x 1/2H20, dissolve in 50 ml distilled water in 100 ml volumetric flask, dilute to volume. Store at 4 degrees C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 4 g (NH4)6Mo7O24 x 4H2O in 100 ml distilled water. Store in a plastic bottle at 4 degrees C.

7.4 Ascorbic acid, 0.1M: Dissolve 1.8 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if prepared with water containing no more than trace amounts of heavy metals and stored at 4 degrees C.

7.5 Combined reagent (AAI): Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H2SO4 (7.1), 5 ml of antimony potassium tartrate solution (7.2), 15 ml of ammonium molybdate solution (7.3), and 30 ml of ascorbic acid solution (7.4). Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until the turbidity disappears before processing. This volume is sufficient for 4 hours operation. Since the stability of this solution is limited, it must be freshly prepared for each run.

NOTE 1: A stable solution can be prepared by not including the ascorbic acid in the combined reagent. If this is done, the mixed reagent (molybdate, tartrate, and acid) is pumped through the distilled water line and the ascorbic acid solution (30 ml of 7.4 diluted to 100 ml with distilled water) through the original mixed reagent line.

7.6 Sulfuric acid solution, 11 N: Slowly add 310 ml conc. H2S04 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Acid wash water: Add 40 ml of sulfuric acid solution (7.6) to 1 liter of distilled water and dilute to 2 liters. (Not to be used when only orthophosphate is being determined).

7.9 Phenolphthalein indicator solution (5 gal): Dissolve 0.5 g of phenolphthalein in a solution of 50 ml of ethyl or isopropyl alcohol and 50 ml of distilled water.

7.10 Stock phosphorus solution: Dissolve 0.4393 g of pre-dried (105 degrees C for 1 hour) KH2PO4 in distilled water and dilute to 1000 ml. 1.0 ml = 0.1 mg P.

7.11 Standard phosphorus solution: Dilute 100.0 ml of stock solution (7.10) to 1000 ml with distilled water. 1.0 ml = 0.01 mg P.

7.12 Standard phosphorus solution: Dilute 100.0 ml of standard solution (7.11) to 1000 ml with distilled water. 1.0 ml = 0.001 mg P.

7.13 Prepare a series of standards by diluting suitable volumes of standard solutions (7.11) and (7.12) to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Standard	Conc,
Phosphorus Solution (7.12)	mg P/l

0.0	0.00
2.0	0.02
5.0	0.05
10.0	0.10
ml of Standard Phosphorus Solution (7.1.1)	mg P/l
2.0	0.20
5.0	0.50
8.0	0.80
10.0	1.00

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of sulfuric acid solution (7.6) to a 50 ml sample and/or standard in a 125 ml Erlenmeyer flask.

8.1.2 Add 0.4 g of ammonium persulfate.

8.1.3 Boil gently on a preheated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternately, heat for 30 minutes in an autoclave at 121 degrees C (15-20 psi).

8.1.4 Cool and dilute the sample to 50 ml. If sample is not clear at this point, filter. **8.1.5** Determine phosphorus as outlined in (8.3.2) with acid wash water (7.8) in wash tubes.

8.2 Hydrolyzable Phosphorus

8.2.1 Add l ml of sulfuric acid solution (7.6) to a 50 ml sample and/or standard in a 125 ml Erlenmeyer flask.

8.2.2 Boil gently on a preheated hot plate for 30 10 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121 degrees C (15-20 psi).

8.2.3 Cool and dilute the sample to 50 ml. If sample is not clear at this point, filter. **8.2.4** Determine phosphorus as outlined in (8.3.2) with acid wash water (7.8) in wash tubes.

8.3 Orthophosphate

8.3.1 Add l drop of phenolphthalein indicator solution (7.9) to approximately 50 ml of sample. If a red color develops, add sulfuric acid solution (7.6) drop-wise to just discharge the color. Acid samples must be neutralized with 1 N sodium hydroxide (40 g NaOH/l).

8.3.2 Set up manifold as shown in Figure 2, AAI or Figure 3. AAII.

8.3.3 Allow both calorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.

8.3.4 For the AAI system, sample at a rate of 20/hr, I minute sample, 2 minute wash. For the AAII system, use a 30/hr, 2:1 cam, and a common wash.

8.3.5 Place standards in Sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

8.3.6 Switch sample line from distilled water to Sampler and begin analysis.

9. Calculation

9.1 Prepare a standard curve by plotting peak heights of processed standards against known concentrations. Compute concentrations of samples by comparing sample peak heights with standard curve. Any sample whose computed value is less than 5% of its immediate predecessor must be rerun.

10. Precision and Accuracy (AAI system)

10.1 Six laboratories participating in an EPA Method Study, analyzed four natural water samples containing exact increments of orthophosphate, with the following results:

		Accu	racy as
Increment as	Precision as		
Orthophosphate	Standard Deviation	Bias,	Bias,
mg P/liter	mg P/liter	00	mg P/liter
0.04	0.019	+16.7	+0.007
0.04	0.014	- 8.3	-0.003
0.29	0.087	-15.5	-0.05
0.30	0.066	-12.8	-0.04

10.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.04, 0.19, 0.35, and 0.84 mg P/l, standard deviations were ± -0.005 , ± -0.000 , ± -0.000 , and ± -0.000 , respectively.

10.3 In a single laboratory (EMSL), using surface water samples at concentrations of 0.07 and 0.76 mg p/l, recoveries were 99% and 100%, respectively.

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3120 METALS BY PLASMA EMISSION SPECTROSCOPY*

3120 A. Introduction

1. General Discussion

Emission spectroscopy using inductively coupled plasma (ICP) was developed in the mid-1960's^{1,2} as a rapid, sensitive, and convenient method for the determination of metals in water and wastewater samples.³⁻⁶ Dissolved metals are determined in filtered and acidified samples. Total metals are determined after appropriate digestion. Care must be taken to ensure that potential interferences are dealt with, especially when dissolved solids exceed 1500 mg/L.

2. References

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3120 B. Inductively Coupled Plasma (ICP) Method

1. General Discussion

a. Principle: An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field typically oscillating at 27.1 MHz. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding a quartz "torch" that supports and confines the plasma. A sample aerosol is generated in an appropriate nebulizer and spray chamber and is carried into the plasma through an injector tube located within the torch. The sample aerosol is injected directly into the ICP, subjecting the constituent atoms to temperatures of about 6000 to 8000°K.1 Because this results in almost complete dissociation of molecules, significant reduction in chemical interferences is achieved. The high temperature of the plasma excites atomic emission efficiently. Ionization of a high percentage of atoms produces ionic emission spectra. The ICP provides an optically "thin" source that is not subject to self-absorption except at very high concentrations. Thus linear dynamic ranges of four to six orders of magnitude are observed for many elements.2

The efficient excitation provided by the ICP results in low detection limits for many elements. This, coupled with the extended dynamic range, permits effective multielement determination of metals.³ The light emitted from the ICP is focused onto the entrance slit of either a monochromator or a polychromator that effects dispersion. A precisely aligned exit slit is used to isolate a portion of the emission spectrum for intensity measurement using a photomultiplier tube. The monochromator uses a single exit slit/photomultiplier and may use a computer-controlled scanning mechanism to examine emission wavelengths sequentially. The polychromator uses multiple fixed exit slits and corresponding photomultiplier tubes; it simultaneously monitors

all configured wavelengths using a computer-controlled readout system. The sequential approach provides greater wavelength selection while the simultaneous approach can provide greater sample throughput.

b. Applicable metals and analytical limits: Table 3120:I lists elements for which this method applies, recommended analytical wavelengths, and typical estimated instrument detection limits using conventional pneumatic nebulization. Actual working detection limits are sample-dependent. Typical upper limits for linear calibration also are included in Table 3120:I.

c. Interferences: Interferences may be categorized as follows:

1) Spectral interferences-Light emission from spectral sources other than the element of interest may contribute to apparent net signal intensity. Sources of spectral interference include direct spectral line overlaps, broadened wings of intense spectral lines, ion-atom recombination continuum emission, molecular band emission, and stray (scattered) light from the emission of elements at high concentrations.4 Avoid line overlaps by selecting alternate analytical wavelengths. Avoid or minimize other spectral interference by judicious choice of background correction positions. A wavelength scan of the element line region is useful for detecting potential spectral interferences and for selecting positions for background correction. Make corrections for residual spectral interference using empirically determined correction factors in conjunction with the computer software supplied by the spectrometer manufacturer or with the calculation detailed below. The empirical correction method cannot be used with scanning spectrometer systems if the analytical and interfering lines cannot be precisely and reproducibly located. In addition, if using a polychromator, verify absence of spectral interference from an element that could occur in a sample but for which there

^{*} Approved by Standard Methods Committee, 1989.

PLASMA EMISSION SPECTROSCOPY (3120)/Inductively Coupled Plasma Method

Element	Suggested Wavelength nm	Estimated Detection Limit $\mu g/L$	Alternate Wavelength* nm	Calibration Concentration mg/L	Upper Limit Concentratior <i>mg/L</i>
Aluminum	308.22	40	237.32	10.0	100
Antimony	206.83	30	217.58	10.0	100
Arsenic	193.70	50	189.04†	10.0	100
Barium	455.40	2	493.41	1.0	. 100
Beryllium	313.04	0.3	234.86	1.0	10
Boron	249.77	5	249.68	1.0	50
Cadmium	226.50	4	214.44	2.0	50
Calcium	317.93	10	315.89	10.0	100
Chromium	267.72	7	206.15	5.0	50
Cobalt	228.62	7	230.79	2.0	50
Copper	324.75	6	219.96	1.0	50
Iron	259.94	7	238.20	10.0	100
Lead	220.35	40	217.00	10.0	100
Lithium	670.78	4‡		5.0	100
Magnesium	279.08	30	279.55	10.0	100
Manganese	257.61	2	294.92	2.0	50
Molybdenum	202.03	8	203.84	10.0	100
Nickel	231.60	15	221.65	2.0	50
Potassium	766.49	100‡	769.90	10.0	100
Selenium	196.03	75	203.99	5.0	100
Silica (SiO ₂)	212.41	20	251.61	21.4	100
Silver	328.07	7	338.29	2.0	50
Sodium	589.00	30‡	589.59	10.0	100
Strontium	407.77	0.5	421.55	1.0	50
Thallium	190.86†	40	377.57	10.0	100
Vanadium	292.40	8		1.0	50
Zinc	213.86	2	206.20	5.0	100

TABLE 3120:1. SUGGESTED WAVELENGTHS, ESTIMATED DETECTION LIMITS, ALTERNATE WAVELENGTHS, CALIBRATION CONCENTRATIONS, AND UPPER LIMITS

* Other wavelengths may be substituted if they provide the needed sensitivity and are corrected for spectral interference.

† Available with vacuum or inert gas purged optical path.

Sensitive to operating conditions.

is no channel in the detector array. Do this by analyzing singleelement solutions of 100 mg/L concentration and noting for each element channel the apparent concentration from the interfering substance that is greater than the element's instrument detection limit.

2) Nonspectral interferences

a) Physical interferences are effects associated with sample nebulization and transport processes. Changes in the physical properties of samples, such as viscosity and surface tension, can cause significant error. This usually occurs when samples containing more than 10% (by volume) acid or more than 1500 mg dissolved solids/L are analyzed using calibration standards containing $\leq 5\%$ acid. Whenever a new or unusual sample matrix is encountered, use the test described in ¶ 4g. If physical interference is present, compensate for it by sample dilution, by using matrix-matched calibration standards, or by applying the method of standard addition (see ¶ 5d below).

High dissolved solids content also can contribute to instrumental drift by causing salt buildup at the tip of the nebulizer gas orifice. Using prehumidified argon for sample nebulization lessens this problem. Better control of the argon flow rate to the nebulizer using a mass flow controller improves instrument performance. b) Chemical interferences are caused by molecular compound formation, ionization effects, and thermochemical effects associated with sample vaporization and atomization in the plasma. Normally these effects are not pronounced and can be minimized by careful selection of operating conditions (incident power, plasma observation position, etc.). Chemical interferences are highly dependent on sample matrix and element of interest. As with physical interferences, compensate for them by using matrix matched standards or by standard addition (\P 5*d*). To determine the presence of chemical interference, follow instructions in \P 4*g*.

2. Apparatus

a. *ICP source:* The ICP source consists of a radio frequency (RF) generator capable of generating at least 1.1 KW of power, torch, tesla coil, load coil, impedance matching network, nebulizer, spray chamber, and drain. High-quality flow regulators are required for both the nebulizer argon and the plasma support gas flow. A peristaltic pump is recommended to regulate sample flow to the nebulizer. The type of nebulizer and spray chamber used may depend on the samples to be analyzed as well as on the equipment manufacturer. In general, pneumatic nebulizers

of the concentric or cross-flow design are used. Viscous samples and samples containing particulates or high dissolved solids content (>5000 mg/L) may require nebulizers of the Babington type.⁵

b. Spectrometer: The spectrometer may be of the simultaneous (polychromator) or sequential (monochromator) type with airpath, inert gas purged, or vacuum optics. A spectral bandpass of 0.05 nm or less is required. The instrument should permit examination of the spectral background surrounding the emission lines used for metals determination. It is necessary to be able to measure and correct for spectral background at one or more positions on either side of the analytical lines.

3. Reagents and Standards

Use reagents that are of ultra-high-purity grade or equivalent. Redistilled acids are acceptable. Except as noted, dry all salts at 105°C for 1 h and store in a desiccator before weighing. Use deionized water prepared by passing water through at least two stages of deionization with mixed bed cation/anion exchange resins.⁶ Use deionized water for preparing all calibration standards, reagents, and for dilution.

- a. Hydrochloric acid, HCl, conc and 1+1.
- b. Nitric acid, HNO3, conc.

c. Nitric acid, HNO_3 , 1+1: Add 500 mL conc HNO_3 to 400 mL water and dilute to 1 L.

d. Standard stock solutions: See 3111B, 3111D, and 3114B. CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

1) Aluminum: See 3111D.3k1).

2) Antimony: See 3111B.3j1).

3) Arsenic: See 3114B.3k1).

4) Barium: See 3111D.3k2).

5) Beryllium: See 3111D.3k3).

6) Boron: Do not dry but keep bottle tightly stoppered and store in a desiccator. Dissolve 0.5716 g anhydrous H_3BO_3 in water and dilute to 1000 mL; $1 \text{ mL} = 100 \text{ }\mu\text{g}$ B.

7) Cadmium: See 3111B.3j3).

8) Calcium: See 3111B.3j4).

9) Chromium: See 3111B.3j6).

10) Cobalt: See 3111B.3j7).

11) Copper: See 3111B.3j8).

12) Iron: See 3111B.3j11).

13) Lead: See 3111B.3j12).

14) Lithium: See 3111B.3j13).

15) Magnesium: See 3111B.3j14).

16) Manganese: See 3111B.3j15).

17) Molybdenum: See 3111D.3k4).

18) Nickel: See 3111B.3j16).

19) Potassium: See 3111B.3j19).20) Selenium: See 3114B.3n1).

21) *Silica:* See 3111D.3*k*7).

21) Suica: See S111D.3k7).

22) Silver: See 3111B.3j22).

23) Sodium: See 3111B.3j23).24) Strontium: See 3111B.3j24).

25) Thallium: See 3111B.3j25).

26) Vanadium: See 3111D.3k10).

27) Zinc: See 3111B.3j27).

e. Calibration standards: Prepare mixed calibration standards containing the concentrations shown in Table 3120:1 by combining appropriate volumes of the stock solutions in 100-mL volumetric flasks. Add 2 mL 1 + 1 HNO₃ and 10 mL 1 + 1 HCl and dilute to 100 mL with water. Before preparing mixed standards, analyze each stock solution separately to determine possible spectral interference or the presence of impurities. When preparing mixed standards take care that the elements are compatible and stable. Store mixed standard solutions in an FEP fluorocarbon or unused polyethylene bottle. Verify calibration standards initially using the quality control standard; monitor weekly for stability. The following are recommended combinations using the suggested analytical lines in Table 3120:I. Alternative combinations are acceptable.

1) Mixed standard solution I: Manganese, beryllium, cadmium, lead, selenium, and zinc.

2) Mixed standard solution II: Barium, copper, iron, vanadium, and cobalt.

3) Mixed standard solution III: Molybdenum, silica, arsenic, strontium, and lithium.

4) Mixed standard solution IV: Calcium, sodium, potassium, aluminum, chromium, and nickel.

5) Mixed standard solution V: Antimony, boron, magnesium, silver, and thallium. If addition of silver results in an initial precipitation, add 15 mL water and warm flask until solution clears. Cool and dilute to 100 mL with water. For this acid combination limit the silver concentration to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 d. Higher concentrations of silver require additional HCl.

f. Calibration blank: Dilute $2 \text{ mL } 1 + 1 \text{ HNO}_3$ and 10 mL 1 + 1 HOI to 100 mL with water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

g. Method blank: Carry a reagent blank through entire sample preparation procedure. Prepare method blank to contain the same acid types and concentrations as the sample solutions.

h. Instrument check standard: Prepare instrument check standards by combining compatible elements at a concentration of 2 mg/L.

i. Instrument quality control sample: Obtain a certified aqueous reference standard from an outside source and prepare according to instructions provided by the supplier. Use the same acid matrix as the calibration standards.

j. Method quality control sample: Carry the instrument quality control sample (¶ 3*i*) through the entire sample preparation procedure.

k. Argon: Use technical or welder's grade. If gas appears to be a source of problems, use prepurified grade.

4. Procedure

a. Sample preparation: See Section 3030F.

b. Operating conditions: Because of differences among makes and models of satisfactory instruments, no detailed operating instructions can be provided. Follow manufacturer's instructions. Establish instrumental detection limit, precision, optimum background correction positions, linear dynamic range, and interferences for each analytical line. Verify that the instrument configuration and operating conditions satisfy the analytical requirements

PLASMA EMISSION SPECTROSCOPY (3120)/Inductively Coupled Plasma Method

and that they can be reproduced on a day-to-day basis. An atomto-ion emission intensity ratio [Cu(I) 324.75 nm/Mn(II) 257.61 nm] can be used to reproduce optimum conditions for multielement analysis precisely. The Cu/Mn intensity ratio may be incorporated into the calibration procedure, including specifications for sensitivity and for precision.⁷ Keep daily or weekly records of the Cu and Mn intensities and/or the intensities of critical element lines. Also record settings for optical alignment of the polychromator, sample uptake rate, power readings (incident, reflected), photomultiplier tube attenuation, mass flow controller settings, and system maintenance.

c. Instrument calibration: Set up instrument as directed (¶ b). Warm up for 30 min. For polychromators, perform an optical alignment using the profile lamp or solution. Check alignment of plasma torch and spectrometer entrance slit, particularly if maintenance of the sample introduction system was performed. Make Cu/Mn or similar intensity ratio adjustment.

Calibrate instrument according to manufacturer's recommended procedure using calibration standards and blank. Aspirate each standard or blank for a minimum of 15 s after reaching the plasma before beginning signal integration. Rinse with calibration blank or similar solution for at least 60 s between each standard to eliminate any carryover from the previous standard. Use average intensity of multiple integrations of standards or samples to reduce random error.

Before analyzing samples, analyze instrument check standard. Concentration values obtained should not deviate from the actual values by more than $\pm 5\%$ (or the established control limits, whichever is lower).

d. Analysis of samples: Begin each sample run with an analysis of the calibration blank, then analyze the method blank. This permits a check of the sample preparation reagents and procedures for contamination. Analyze samples, alternating them with analyses of calibration blank. Rinse for at least 60 s with dilute acid between samples and blanks. After introducing each sample or blank let system equilibrate before starting signal integration. Examine each analysis of the calibration blank to verify that no carry-over memory effect has occurred. If carry-over is observed, repeat rinsing until proper blank values are obtained. Make appropriate dilutions and acidifications of the sample to determine concentrations beyond the linear calibration range.

e. Instrumental quality control: Analyze instrument check standard once per 10 samples to determine if significant instrument drift has occurred. If agreement is not within \pm 5% of the expected values (or within the established control limits, whichever is lower), terminate analysis of samples, correct problem, and recalibrate instrument. If the intensity ratio reference is used, resetting this ratio may restore calibration without the need for reanalyzing calibration standards. Analyze instrument check standard to confirm proper recalibration. Reanalyze one or more samples analyzed just before termination of the analytical run. Results should agree to within \pm 5%, otherwise all samples analyzed after the last acceptable instrument check standard analysis must be reanalyzed.

Analyze instrument quality control sample within every run. Use this analysis to verify accuracy and stability of the calibration standards. If any result is not within \pm 5% of the certified value, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock solution and a new calibration standard and repeat calibration.

f. Method quality control: Analyze the method quality control sample within every run. Results should agree to within \pm 5% of the certified values. Greater discrepancies may reflect losses or contamination during sample preparation.

g. Test for matrix interference: When analyzing a new or unusual sample matrix verify that neither a positive nor negative nonlinear interference effect is operative. If the element is present at a concentration above 1 mg/L, use serial dilution with calibration blank. Results from the analyses of a dilution should be within \pm 5% of the original result. Alternately, or if the concentration is either below 1 mg/L or not detected, use a post-digestion addition equal to 1 mg/L. Recovery of the addition should be either between 95% and 105% or within established control limits of \pm 2 standard deviations around the mean. If a matrix effect causes test results to fall outside the critical limits, complete the analysis after either diluting the sample to eliminate the matrix effect while maintaining a detectable concentration of at least twice the detection limit or applying the method of standard additions.

5. Calculations and Corrections

a. Blank correction: Subtract result of an adjacent calibration blank from each sample result to make a baseline drift correction. (Concentrations printed out should include negative and positive values to compensate for positive and negative baseline drift. Make certain that the calibration blank used for blank correction has not been contaminated by carry-over.) Use the result of the method blank analysis to correct for reagent contamination. Alternatively, intersperse method blanks with appropriate samples. Reagent blank and baseline drift correction are accomplished in one subtraction.

b. Dilution correction: If the sample was diluted or concentrated in preparation, multiply results by a dilution factor (*DF*) calculated as follows:

$DF = \frac{\text{Final weight or volume}}{\text{Initial weight or volume}}$

c. Correction for spectral interference: Correct for spectral interference by using computer software supplied by the instrument manufacturer or by using the manual method based on interference correction factors. Determine interference correction factors by analyzing single-element stock solutions of appropriate concentrations under conditions matching as closely as possible those used for sample analysis. Unless analysis conditions can be reproduced accurately from day to day, or for longer periods, redetermine interference correction factors found to affect the results significantly each time samples are analyzed.^{7, 8} Calculate interference correction factors (K_{ij}) from apparent concentrations observed in the analysis of the high-purity stock solutions:

$$K_{ii} = \frac{\text{Apparent concentration of element } i}{\text{Actual concentration of interfering element } i}$$

where the apparent concentration of element i is the difference between the observed concentration in the stock solution and the observed concentration in the blank. Correct sample concentrations observed for element i (already corrected for baseline drift), for spectral interferences from elements j, k, and l; for example:

Concentration of element i corrected for spectral interference

 $\begin{array}{l} \label{eq:concentration} \begin{array}{l} \mbox{Observed} & \mbox{Observed} \\ \mbox{concentration} & - & (K_{ii}) \begin{array}{c} \mbox{concentration} \\ \mbox{of interfering} \\ \mbox{element } j \end{array} = \begin{array}{c} \mbox{Concentration} \\ \mbox{of interfering} \\ \mbox{element } k \end{array} \\ \begin{array}{c} \mbox{Observed} \\ \mbox{Observed} \\ \mbox{Observed} \\ \mbox{Observed} \\ \mbox{oncentration} \\ \mbox{of interfering} \\ \mbox{element } l \end{array}$

Interference correction factors may be negative if background correction is used for element *i*. A negative K_{ii} can result where an interfering line is encountered at the background correction wavelength rather than at the peak wavelength. Determine concentrations of interfering elements *j*, *k*, and *l* within their respective linear ranges. Mutual interferences (*i* interferes with *j* and *j* interferes with *i*) require iterative or matrix methods for calculation.

d. Correction for nonspectral interference: If nonspectral interference correction is necessary, use the method of standard additions. It is applicable when the chemical and physical form of the element in the standard addition is the same as in the sample, *or* the ICP converts the metal in both sample and addition to the same form; the interference effect is independent of metal concentration over the concentration range of standard additions; and the analytical calibration curve is linear over the concentration range of standard additions.

Use an addition not less than 50% nor more than 100% of the element concentration in the sample so that measurement precision will not be degraded and interferences that depend on element/interferent ratios will not cause erroneous results. Apply the method to all elements in the sample set using background correction at carefully chosen off-line positions. Multielement standard addition can be used if it has been determined that added elements are not interferents.

e. Reporting data: Report analytical data in concentration units of milligrams per liter using up to three significant figures. Report results below the determined detection limit as not detected less than the stated detection limit corrected for sample dilution.

6. Precision and Bias

As a guide to the generally expected precision and bias, see the linear regression equations in Table 3120:II.⁹ Additional interlaboratory information is available.¹⁰

Element	Concentration Range µg/L	Total Digestion* $\mu g/L$	Recoverable Digestion* $\mu g/L$
Aluminum	69-4792	$\begin{array}{rcl} X &=& 0.9273C + 3.6 \\ S &=& 0.0559X + 18.6 \\ SR &=& 0.0507X + 3.5 \end{array}$	$\begin{array}{rcl} X &=& 0.9380C + 22.1\\ S &=& 0.0873X + 31.7\\ SR &=& 0.0481X + 18.8 \end{array}$
Antimony	77-1406	$\begin{array}{rcl} X &=& 0.7940C - 17.0 \\ S &=& 0.1556X - 0.6 \\ SR &=& 0.1081X + 3.9 \end{array}$	$\begin{array}{rcl} X &=& 0.8908C + 0.9 \\ S &=& 0.0982X + 8.3 \\ SR &=& 0.0682X + 2.5 \end{array}$
Arsenic	69-1887	$\begin{array}{rcl} X &=& 1.0437C - 12.2\\ S &=& 0.1239X + 2.4\\ SR &=& 0.0874X + 6.4 \end{array}$	$\begin{array}{rcl} X &=& 1.0175C + 3.9 \\ S &=& 0.1288X + 6.1 \\ SR &=& 0.0643X + 10.3 \end{array}$
Barium	9-377	$\begin{array}{rcl} X &=& 0.7683C + 0.47 \\ S &=& 0.1819X + 2.78 \\ SR &=& 0.1285X + 2.55 \end{array}$	$\begin{array}{rcl} X &=& 0.8380C + 1.68\\ S &=& 0.2540X + 0.30\\ SR &=& 0.0826X + 3.54 \end{array}$
Beryllium	3-1906	$\begin{array}{rcl} X &=& 0.9629C + 0.05\\ S &=& 0.0136X + 0.95\\ SR &=& 0.0203X - 0.07 \end{array}$	$\begin{array}{rcl} X &=& 1.0177C - 0.55\\ S &=& 0.0359X + 0.90\\ SR &=& 0.0445X - 0.10 \end{array}$
Boron	19-5189	$\begin{array}{rcl} X &=& 0.8807C + 9.0 \\ S &=& 0.1150X + 14.1 \\ SR &=& 0.0742X + 23.2 \end{array}$	$\begin{array}{rcl} X &=& 0.9676C + 18.7\\ S &=& 0.1320X + 16.0\\ SR &=& 0.0743X + 21.1 \end{array}$
Cadmium	9-1943	$\begin{array}{rcl} \mathcal{X} &=& 0.9874C - 0.18 \\ \mathcal{S} &=& 0.0557X + 2.02 \\ \mathcal{S} \mathcal{R} &=& 0.0300X + 0.94 \end{array}$	$\begin{array}{rcl} X &=& 1.0137C - 0.65\\ S &=& 0.0585X + 1.15\\ SR &=& 0.0332X + 0.90 \end{array}$
Calcium	17-47 170	$\begin{array}{rcl} X &=& 0.9182C - 2.6\\ S &=& 0.1228X + 10.1\\ SR &=& 0.0189X + 3.7 \end{array}$	$\begin{array}{rcl} X &=& 0.9658C \ + \ 0.8\\ S &=& 0.0917X \ + \ 6.9\\ SR &=& 0.0327X \ + \ 10.1 \end{array}$
Chromium	13-1406	$\begin{array}{rcl} X &=& 0.9544C + 3.1 \\ S &=& 0.0499X + 4.4 \\ SR &=& 0.0009X + 7.9 \end{array}$	$\begin{array}{rcl} X &=& 1.0049C - 1.2\\ S &=& 0.0698X + 2.8\\ SR &=& 0.0571X + 1.0 \end{array}$

TABLE 3120:II. ICP PRECISION AND BIAS DATA

PLASMA EMISSION SPECTROSCOPY	(3120)/Inductively Coupled Plasma Method
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Element	Concentration Range $\mu g/L$	Total Digestion* $\mu g/L$	Recoverable Digestion* $\mu g/L$
Cobalt	17-2340	$\begin{array}{rcl} X &=& 0.9209C \;-\; 4.5\\ S &=& 0.0436X \;+\; 3.8\\ SR &=& 0.0428X \;+\; 0.5 \end{array}$	$\begin{array}{rcl} X &=& 0.9278C \; - \; 1.5 \\ S &=& 0.0498X \; + \; 2.6 \\ SR &=& 0.0407X \; + \; 0.4 \end{array}$
Copper	8-1887	$\begin{array}{rcl} X &=& 0.9297C - 0.30 \\ S &=& 0.0442X + 2.85 \\ SR &=& 0.0128X + 2.53 \end{array}$	$\begin{array}{rcl} X &=& 0.9647C - 3.64 \\ S &=& 0.0497X + 2.28 \\ SR &=& 0.0406X + 0.96 \end{array}$
ron	13-9359	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{rcl} X &=& 0.9830C + 5.7 \\ S &=& 0.1024X + 13.0 \\ SR &=& 0.0790X + 11.5 \end{array}$
Lead	42-4717	$\begin{array}{rcl} X &=& 0.9699C \;-\; 2.2\\ S &=& 0.0558X \;+\; 7.0\\ SR &=& 0.0353X \;+\; 3.6 \end{array}$	$\begin{array}{rcl} X &=& 1.0056C + 4.1 \\ S &=& 0.0799X + 4.6 \\ SR &=& 0.0448X + 3.5 \end{array}$
Magnesium	34-13 868	$\begin{array}{rcl} X &=& 0.9881C \;-\; 1.1 \\ S &=& 0.0607X \;+\; 11.6 \\ SR &=& 0.0298X \;+\; 0.6 \end{array}$	$\begin{array}{rcl} X &=& 0.9879C + 2.2\\ S &=& 0.0564X + 13.2\\ SR &=& 0.0268X + 8.1 \end{array}$
Manganese	4-1887	$\begin{array}{rcl} X &=& 0.9417C \ + \ 0.13 \\ S &=& 0.0324X \ + \ 0.88 \\ SR &=& 0.0153X \ + \ 0.91 \end{array}$	$\begin{array}{rcl} X &=& 0.9725C+0.07\\ S &=& 0.0557X+0.76\\ SR &=& 0.0400X+0.82 \end{array}$
Molybdenum	17-1830	$\begin{array}{rcl} X &=& 0.9682C \ + \ 0.1 \\ S &=& 0.0618X \ + \ 1.6 \\ SR &=& 0.0371X \ + \ 2.2 \end{array}$	$\begin{array}{rcl} X &=& 0.9707C-2.3\\ S &=& 0.0811X+3.8\\ SR &=& 0.0529X+2.1 \end{array}$
Nickel	17-47 170	$\begin{array}{rcl} X &=& 0.9508C + 0.4 \\ S &=& 0.0604X + 4.4 \\ SR &=& 0.0425X + 3.6 \end{array}$	$\begin{array}{rcl} X &=& 0.9869C + 1.5 \\ S &=& 0.0526X + 5.5 \\ SR &=& 0.0393X + 2.2 \end{array}$
Potassium	347-14 151	$\begin{array}{rcl} X &=& 0.8669C \;-\; 36.4 \\ S &=& 0.0934X \;+\; 77.8 \\ SR &=& -0.0099X \;+\; 144.2 \end{array}$	$\begin{array}{rcl} X &=& 0.9355C - 183.1\\ S &=& 0.0481X + 177.2\\ SR &=& 0.0329X + 60.9 \end{array}$
Selenium	69-1415	$\begin{array}{rcl} X &=& 0.9363C - 2.5\\ S &=& 0.0855X + 17.8\\ SR &=& 0.0284X + 9.3 \end{array}$	$\begin{array}{rcl} X &=& 0.9737C \; - \; 1.0 \\ S &=& 0.1523X \; + \; 7.8 \\ SR &=& 0.0443X \; + \; 6.6 \end{array}$
Silicon	189-9434	$\begin{array}{rcl} X &=& 0.5742C \;-\; 35.6\\ S &=& 0.4160X \;+\; 37.8\\ SR &=& 0.1987X \;+\; 8.4 \end{array}$	$\begin{array}{rcl} X &=& 0.9737C - \ 60.8\\ S &=& 0.3288X + \ 46.0\\ SR &=& 0.2133X + \ 22.6 \end{array}$
Silver	8-189	$\begin{array}{rcl} X &=& 0.4466C + 5.07 \\ S &=& 0.5055X - 3.05 \\ SR &=& 0.2086X - 1.74 \end{array}$	$\begin{array}{rcl} X &=& 0.3987C + 8.25\\ S &=& 0.5478X - 3.93\\ SR &=& 0.1836X - 0.27 \end{array}$
Sodium	35-47 170	$\begin{array}{rcl} X &=& 0.9581C + 39.6 \\ S &=& 0.2097X + 33.0 \\ SR &=& 0.0280X + 105.8 \end{array}$	$\begin{array}{rcl} X &=& 1.0526C + 26.7\\ S &=& 0.1473X + 27.4\\ SR &=& 0.0884X + 50.5 \end{array}$
Thallium	79-1434	$\begin{array}{rcl} X &=& 0.9020C \;-\; 7.3\\ S &=& 0.1004X \;+\; 18.3\\ SR &=& 0.0364X \;+\; 11.5 \end{array}$	$\begin{array}{rcl} X &=& 0.9238C + 5.5 \\ S &=& 0.2156X + 5.7 \\ SR &=& -0.0106X + 48.0 \end{array}$
Vanadium	13-4698	$\begin{array}{rcl} X &=& 0.9615C - 2.0 \\ S &=& 0.0618X + 1.7 \\ SR &=& 0.0220X + 0.7 \end{array}$	$\begin{array}{rcl} X &=& 0.9551C + 0.4 \\ S &=& 0.0927X + 1.5 \\ SR &=& 0.0472X + 0.5 \end{array}$
Zinc	7-7076	$\begin{array}{rcl} X &=& 0.9356C - 0.30 \\ S &=& 0.0914X + 3.75 \\ SR &=& -0.0130X + 10.07 \end{array}$	$\begin{array}{rcl} X &=& 0.9500C + 1.22\\ S &=& 0.0597X + 6.50\\ SR &=& 0.0153X + 7.78 \end{array}$

TABLE 3120:11, CONT.

*X = mean recovery, $\mu g/L$, C = true value, $\mu g/L$, S = multi-laboratory standard deviation, $\mu g/L$, SR = single-analyst standard deviation, $\mu g/L$.

Appendix VI



Water Quality

Biochemical Oxygen Demand



Cadmium



Chemical Oxygen Demand



Conductivity



Copper



Dissolved Oxygen



Fecal Coliform



Hardness



Ammonia



Nitrate-Nitrite









рΗ



Water Temperature

Total Kjeldahl Nitrogen



Total Phosphorus



Total Suspended Solids



Turbidity



1.4 1.2 1.0 Velo. (ft/s) 0.8 0.6 0.4 0.2 Withecooches^A 0.0 with acoothee 3 With Beoochee 2 Bevelcreat Benel Cleek? with acoochee1 Bevel Creek? Franks Creek? Franks Creek? Sampling Site **27-Jan-00 17-Feb-00** 23-Mar-00 **6**-Apr-00 28-Apr-00 **9**-Jun-00

Velocity



Zinc
Appendix VII



Model Information and Results



SWAT is the acronym for Soil and Water Assessment Tool, a river basin, or watershed, scale model developed by Dr. Jeff Arnold for the USDA Agricultural Research Service (ARS). SWAT was developed to predict the impact of land management practices on water, sediment and agricultural chemical yields in large complex watersheds with varying soils, land use and management conditions over long periods of time. To satisfy this objective, the model

 is physically based. Rather than incorporating regression equations to describe the relationship between input and output variables, SWAT requires specific information about weather, soil properties, topography, vegetation, and land management practices occurring in the watershed. The physical processes associated with water movement, sediment movement, crop growth, nutrient cycling, etc. are directly modeled by SWAT using this input data.

Benefits of this approach are

- watersheds with no monitoring data (e.g. stream gage data) can be modeled
- the relative impact of alternative input data (e.g. changes in management practices, climate, vegetation, etc.) on water quality or other variables of interest can be quantified
- uses readily available inputs. While SWAT can be used to study more specialized processes such as bacteria transport, the minimum data required to make a run are commonly available from government agencies.
- is computationally efficient. Simulation of very large basins or a variety of management strategies can be performed without excessive investment of time or money.
- enables users to study long-term impacts. Many of the problems currently addressed by users involve the gradual buildup of pollutants and the impact on downstream water bodies. To study these types of problems, results are needed from runs with output spanning several decades.

SWAT is a continuous time model, i.e. a long-term yield model. The model is not designed to simulate detailed, single-event flood routing.

http://www.brc.tamus.edu/swat/newmanual/intro/intro.html

DEVELOPMENT OF SWAT

SWAT incorporates features of several ARS models and is a direct outgrowth of the SWRRB model (Simulator for Water Resources in Rural Basins) (Williams et al., 1985; Arnold et al., 1990). Specific models that contributed significantly to the development of SWAT were CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) (Knisel, 1980), GLEAMS (Groundwater Loading Effects on Agricultural Management Systems) (Leonard et al., 1987), and EPIC (Erosion-Productivity Impact Calculator) (Williams et al., 1984).

Development of SWRRB began with modification of the daily rainfall hydrology model from CREAMS. The major changes made to the CREAMS hydrology model were: a) the model was expanded to allow simultaneous computations on several subbasins to predict basin water yield; b) a groundwater or return flow component was added; c) a reservoir storage component was added to calculate the effect of farm ponds and reservoirs on water and sediment yield; d) a weather simulation model incorporating data for rainfall, solar radiation, and temperature was added to facilitate long-term simulations and provide temporally and spatially representative weather; e) the method for predicting the peak runoff rates was improved; f) the EPIC crop growth model was added to account for annual variation in growth; g) a simple flood routing component was added; h) sediment transport components were added to simulate sediment movement through ponds, reservoirs, streams and valleys; and i) calculations of transmission losses were incorporated.

The primary focus of model use in the late 1980s was water quality assessment and development of SWRRB reflected this emphasis. Notable modifications of SWRRB at this time included: a) incorporation of the GLEAMS pesticide fate component; b) optional SCS technology for estimating peak runoff rates; and c) newly developed sediment yield equations. These modifications extended the model's capability to deal with a wide variety of watershed management problems.

In the late 1980s, the Bureau of Indian Affairs needed a model to estimate the downstream impact of water management within Indian reservation lands in Arizona and New Mexico. While SWRRB was easily utilized for watersheds up to a few hundred square kilometers in size, the Bureau also wanted to simulate stream flow for basins extending over several thousand square kilometers. For an area this extensive, the watershed under study needed to be divided into several hundred subbasins. Watershed division in SWRRB was limited to ten subbasins and the model routed water and sediment transported out of the subbasins directly to the watershed outlet. These limitations led to the development of a model called ROTO (Routing Outputs to Outlet) (Arnold et al., 1995), which took output from multiple SWRRB runs and routed the flows through channels and reservoirs. ROTO provided a reach routing approach and overcame the SWRRB subbasin limitation by "linking" multiple SWRRB runs together. Although this approach was effective, the input and output of multiple SWRRB files was cumbersome and required considerable computer storage. In addition, all SWRRB runs had to be made independently and then input to ROTO for the channel and reservoir routing. To overcome the awkwardness of this arrangement, SWRRB and ROTO were merged into a single model, SWAT. While allowing simulations of very extensive areas, SWAT retained all the features which made SWRRB such a valuable simulation model.

Since SWAT was created in the early 90s, it has undergone continued review and expansion of http://www.brc.tamus.edu/swat/newmanual/intro/intro.html 12/8/00

- 2 -

capabilities. The most significant improvements of the model between releases include:

- SWAT94.2: Multiple hydrologic response units (HRUs) incorporated.
- SWAT96.2: Auto-fertilization and auto-irrigation added as management options; canopy storage of water incorporated; a CO₂ component added to crop growth model for climatic change studies; Penman-Monteith potential evapotranspiration equation added; lateral flow of water in the soil based on kinematic storage model incorporated; in-stream nutrient water quality equations from QUAL2E added; in-stream pesticide routing.
- SWAT98.1: Begin FORTRAN90 recode; snow melt routines improved; in-stream water quality improved; nutrient cycling routines expanded; grazing, manure applications, and tile flow drainage added as management options; model modified for use in Southern Hemisphere; urban build up/wash off equations from SWMM added along with regression equations from USGS.
- SWAT99.1: Bacteria transport routines added; rice/wetland routines improved; Green & Ampt infiltration added; weather generator improved. —*To be released Fall 1999.*

In addition to the changes listed above, interfaces for the model have been developed in Windows (Visual Basic), GRASS, and ArcView. SWAT has also undergone extensive validation.

http://www.brc.tamus.edu/swat/newmanual/intro/intro.html



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Measured Point Source |

Daily records (recday da Monthly records (recmo Yearly records (recyear

Average annual records

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Home	Software	Documentation	Publications	Education	Applications	
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incorporate a searchable database so that users can locate input variables related to a particular process more easily. The database will be on-line sometime in 2001.

Reservoir/Lake Data Reservoir Input File (.res) Lake Water Quality Input File (.lwq)

Last Updated: 21-April-2000, SLN

http://www.brc.tamus.edu/swat/swatinp.html



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Home	Software	Documentation	Publications	Education	Applications
SWAT:	Inputs	Outputs	Theor	y Da	tahases
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Last Updated: 21-April-2000, SLN

http://www.brc.tamus.edu/swat/swatout.html

Lowndes County Management Plan Modeling Overview Wes Byne 5 Oct 2000

RESOURCES

The data required to model Lowndes County included soils, elevation, hydrography, and landuse. All of this information was available in a geographic information system (GIS), which is a database attached to spatial data. The soils information was obtained from the South Georgia Regional Development Center (SGRDC), and is an electronic version of the USDA NRCS soil survey for Lowndes County. The elevation information was obtained from the Georgia GIS Clearinghouse in the form of 30m resolution USGS digital elevation models (DEMs). The hydrography information was obtained from the SGRDC (for Lowndes County) and Georgia Clearinghouse (for upstream counties), and was used to verify that flow calculations based on the DEMs were appropriate. The landuse information was obtained by digitizing 1993 digital orthophoto quarter quadrangles (DOQQs) from the National Aerial Photography Program (NAPP) and was verified by comparison to aerial photography flown for the county's tax assessor office. The 16 landuses used in modeling are included in Table 8-1. Because counties above Lowndes were only modeled to correctly account for flow in the study watersheds, generalized information was used to model upstream areas. STATSGO (STATe Soil GeOgraphic) soils data and the state DNR landuse data from 1988 were used to simulate conditions in upstream areas.

Table 8-1: Landuses Used in Lowndes County Simulation

1 117
1. Water
2. Forest
3. Roads
4. Crops
5. Urban (Heavy)
6. Urban (Light)
7. Industrial
8. Pasture
9. Airport
10. Wetland
11. Residential (Low-Density)
12. Planted Pines
13. Forest (Sparse)
14. Pecan Orchard
15. Unknown
16. Commercial

MODEL

Lowndes County was modeling using the SWAT (Soil and Water Assessment Tool) model available from USDA Agricultural Research Service (ARS) at the Blacklands Research Center, Texas A&M. It is a process-based, basin-scale model, originally designed to simulate the long-term effects of management practices on agricultural watersheds. In recent years, an urban component has been added, and therefore the model is applicable to mixed land-use watersheds. The model incorporates the QUAL2E receiving water model, and model inputs are managed by an ArcView interface. The SWAT model will be incorporated into the BASINS package of modeling tools in BASINS 3.0.

The Lowndes County simulation was divided into two major basins, with the outlet of the first being Highway 84 at the Withlacoochee River and the outlet of the second being the third sampling site in the Twin Lakes Area. Both are shown in Figure 8-1. The first basin was further divided into 5 smaller watersheds, representing sampling points in the Little River and the Withlacoochee River basins. The second basin was simulated as a single watershed. All watersheds were further subdivided into subwatersheds using ArcView, assuming a minimum watershed area of 2471 acres (1000 ha). Landuse and soils for each subwatershed was calculated using the Arcview tool, assuming that the dominant soil and landuse combination would control runoff and loading from each subwatershed.

PARAMETERS

Parameters modeled for Lowndes county include flow rate, nitrogen, phosphorus, dissolved oxygen (DO), carbonaceous biochemical oxygen demand (CBOD), sediment, fecal bacteria, chromium, zinc, aluminum, and pesticides where applicable. The SWAT model has internal routines capable of generating nutrient and sediment loads, and routing these to determine their effects on water quality. Fecal loads may be input as point sources or as distributed sources through manure application, however there is no provision for non-point source (NPS) generation. Metals may be input as point sources (e.g.-municipal WWTP or industry discharges), however there is not an upland load generation component to the model. For this reason, urban point loads for fecal bacteria and metals were calculated for each subwatershed based on PLUARG (Marsalek, 1978) studies and input into the model as direct point loads to streams. The loads were

calculated based on yearly averages, and only assumed to be input to the model when rainfall exceeded one inch per day. The model then routes these constituents through the basin. Pesticide loadings are calculated based on application rate, and any number may be simulated at the subwatershed level, however due to the complexity of the simulation, only one may be routed through the basin at a time. Several parameters were calibrated, including flow rate, nitrification rates, and algal settling rates, and are describe in more detail below.

SCENARIOS

Three scenarios were modeled for Lowndes County. The first was a baseline condition, designed to represent current conditions. The second was a growth scenario calculated by assuming medium or low-density residential growth within a 3280 ft (1000 m) buffer of the proposed Lowndes County sanitary sewer service line. The third scenario utilized the same buffer, but assumed growth would be commercial. The different landuses affected flow and pollution load in the model. Figure 8-2 shows the 3280 ft (1000 m) buffer representing potential growth areas in the county.

BASELINE

The current scenario was modeled for a period of 38 years to allow the water balance to come to equilibrium in the model. The period of record was also chosen to allow flow calibration on the entire basin. Several USGS gaging stations have been in place along the Withlacoochee or Little Rivers in the past, and have historical records. The period of time allowed calibration and validation of model flow at four points in the basin, one below Lenox, one below Adel, one at Skipper Bridge Road in Lowndes County, and one at Highway 84 in Lowndes County. No flow data were available for calibration of the Twin Lakes basin, however the calibrated parameters from the first basin were used as best estimates of inputs. The calibrated model was found to fit measured flow data adequately.

Measured pollutant loads were compared to modeled data to determine quality of model predictions. The baseline simulation of both scenarios was calibrated by manipulation of soil organic carbon and algal settling rates which controlled CBOD and subsequently DO. Also, rate constants that affected nitrification were adjusted to improve model fit. The nutrient predictions fit the measured data adequately, while CBOD and DO predictions fit measured data well. There was no validation period due to the limited number of sampling points, all of which were baseflow measurements due to the lack of rainfall in the basin in the previous twelve months.

SCENARIO 1

The first scenario utilized the same time period as the baseline simulation, however landuse differed from the baseline simulation. The 3280 ft (1000 m) buffer generated around the proposed sanitary service area was superimposed on the subwatersheds used in the simulation to determine the areas that would be affected. Each affected area was then converted to the appropriate landuse and routed with its parent subwatershed. The landuse change for scenario1 was urban-residential, medium to low density.

SCENARIO 2

The second scenario was prepared in the same manner as Scenario 1, however the landuse was assumed to change from baseline conditions to commercial development.

RESULTS

The period of 1995 to 2000 was used for comparison of model results between the different scenarios. Five-year monthly averages and maximum values were compared, and the results are included in Table 8-2 and Table 8-3. Calculations are shown in mg/L to three decimal places or four decimal places where appropriate because the concentrations were calculated from predicted loads and therefore do not exhibit significant variation.

DISCUSSION

Comparison of Prediction Scenarios

Basin 1, Withlacoochee River at Highway 84

Modeling results from basin 1 indicated increased average and peak flow rates, as would be expected from urbanization. Predicted average sediment concentration decreased between baseline and residential landuse, and increased between residential and commercial landuse, while overall average sediment concentration decreased. Maximum sediment concentration increased from baseline to residential to commercial, corresponding to increased peak flow rate. Average and maximum phosphorus concentrations decreased as increased flow rates caused dilution. Average and maximum nitrogen concentrations increased due to predicted increased loadings from the urbanizing landuses. Nitrate values decreased on average, while peak concentration decreased from baseline to residential and increased from residential to commercial landuse. Again this is due to the variation of loading assumed with the urbanizing landuses. Algae concentration remained constant while CBOD decreased in both average and maximum concentrations from baseline conditions to residential conditions, and slightly increased in average concentration from residential to commercial landuse. Maximum concentration increased slightly greater than 1 mg/L as landuse changed from residential to commercial. Dissolved oxygen, which is driven by CBOD and reaeration rate, followed the opposite trend of CBOD. Average and maximum predicted fecal bacteria increased from baseline conditions to residential, and decreased from residential to commercial. The low baseline fecal concentration was due to lack of unit-load information for the mixed conditions as they currently exist, and therefore baseline loads were assumed to only originate from point WWTP sources. For this reason, the relative loading of fecal coliforms indicated overall increase of bacteria as landuse changed from baseline to residential, and then decreased as landuse changed from residential to commercial. The simulated residential landuse would probably not differ from the baseline condition as greatly as the numbers indicate. Average and maximum chromium values did not vary with landuse, while average and maximum zinc concentrations increased as landuse changed from baseline conditions to residential and then to commercial. Average and maximum predicted aluminum concentrations increased from baseline to residential conditions while average concentration decreased from residential to commercial and the maximum concentration remained unchanged. All predicted pesticide concentrations were small enough that they were well under detection limits, and are not included here for comparison.

Basin 2, Bevel Creek Sampling Site #3

Modeling results from basin 2 indicated unchanged average flow rate from baseline to residential conditions, while peak flow rate decreased. Predicted average and peak commercial landuse flow rates were greater than residential landuse and baseline landuse. Sediment concentration predictions decreased from baseline to residential for both average and peak, and increased from residential to commercial landuse. Overall, average and peak sediment concentrations decreased. Total average phosphorus concentration decreased from baseline conditions to residential, while peak concentration increased. Total average phosphorus concentration increased from residential to commercial, and peak concentration increased. Average TKN increased average and peak concentrations as landuse changed from baseline to residential to commercial. Peak and average nitrate values increased from current to residential conditions, while average and peak values decreased from residential to commercial. Average algae concentration decreased from baseline to residential landuse, while peak concentration decreased by one-half. Average and peak concentrations of algae increased from residential to commercial landuse. Average and peak CBOD concentrations decreased from baseline to residential and then to commercial scenarios. Average and peak dissolved oxygen showed the opposite trend, except that peak DO levels did not increase from residential to

commercial landuse. Fecal bacteria once again show relative increased contribution due to the lack of available data for estimating unit fecal loads. The predictions indicate increased average and peak concentration from baseline to residential to commercial landuse. Once again, the proposed residential landuse would probably not differ from the baseline conditions as greatly as the numbers indicate. Average and peak chromium concentrations increased from baseline to residential landuse, while decreasing from residential to commercial landuse. Zinc concentrations followed the same trend.



Study Watersheds – Lowndes County, GA Figure 8-1



Study Watersheds and Predicted Build Out Lowndes County, GA Figure 8-2

Table 8-2

Scenario	Value	Flow	Sed. Conc.	P (Org+Sol)	N (Org+NH4)	NO3	Algae	CBOD ⁴	DO 5	Fecal Bacteria 6	Chromium 6	Zinc 6	Aluminum ⁶
		(cms)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(ct/100 mL)	(mg/L)	(mg/L)	(mg/L)
Scenario 1 ¹	average	41.30	35.92	0.256	0.446	1.081	0.011	2.53	5.90	0.03	0.0002	0.0001	0.0007
	max	195.50	111.20	0.609	1.200	6.509	0.054	17.26	7.27	0.17	0.0008	0.0003	0.0032
Scenario 2 ²	average	41.46	35.19	0.252	0.472	1.077	0.011	2.34	5.96	14.50	0.0002	0.0003	0.0010
	max	195.70	113.00	0.598	1.198	6.450	0.053	14.44	7.27	73.32	0.0008	0.0015	0.0041
Scenario 3 ³	average	41.75	35.72	0.250	0.474	1.072	0.011	2.35	5.97	7.42	0.0002	0.0004	0.0009
	max	196.20	113.50	0.589	1.205	6.471	0.053	15.55	7.26	37.16	0.0008	0.0017	0.0041

Withlacoochee River - Basin 1

1. Baseline simulation of current conditions in the watershed

- 2. Baseline simulation assuming 5 years with medium to low density residential buildout in the 1000 meter buffer
- 3. Baseline simulation assuming 5 years with commercial density buildout in the 1000 meter buffer
- 4. CBOD calculated based on soil organic carbon and shows reduction due to decreased soil exposure
- 5. DO calcuated as a direct function of CBOD and flow
- 6. Bacteria and metals calculated based on unit loads measured in PLUARG studies. (Marsalek, 1978)

Marsalek, J (1978). Pollution Due to Urban Runoff: Unit Loads and Abatement Measures, Pollution from Land Use Activities Reference Group, International Joint Commission, Windsor, Ontario. (reference and info taken from Novotny & Olem's Water Quality, Prevention, Identification, and Management of Diffuse Pollution, 1994, Van Nontrand Reinhold)

Table 8-3

Bevel Creek - Basin 2

Scenario	Value	Flow	Sed. Conc.	P (Org+Sol)	N (Org+NH4)	NO3	Algae	CBOD ⁴	DO ⁵	Fecal Bacteria ⁶	Chromium ⁶	Zinc ⁶
		(cms)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(ct/100 mL)	(mg/L)	(mg/L)
Scenario 1 ¹	average	0.80	66.80	0.19	0.28	0.90	0.005	3.70	4.00	0.00	0.0000	0.0000
	max	4.90	213.70	0.78	0.62	3.80	0.018	8.90	6.70	0.00	0.0000	0.0000
Scenario 2 ²	average	0.80	35.90	0.17	0.36	1.00	0.001	1.10	6.20	93.70	0.0004	0.0088
	max	4.70	104.50	1.03	1.99	6.50	0.009	5.30	9.70	1018.00	0.0039	0.0844
Scenario 3 ³	average	1.10	50.40	0.19	0.36	0.60	0.003	0.80	7.30	111.00	0.0002	0.0047
	max	5.40	113.40	1.96	3.75	5.60	0.010	3.80	9.70	613.40	0.0012	0.0260

1. Baseline simulation of current conditions in the watershed

- 2. Baseline simulation assuming 5 years with medium to low density residential buildout in the 1000 meter buffer
- 3. Baseline simulation assuming 5 years with commercial density buildout in the 1000 meter buffer
- 4. CBOD calculated based on soil organic carbon and shows reduction due to decreased soil exposure
- 5. DO calcuated as a direct function of CBOD and flow
- 6. Bacteria and metals calculated based on unit loads measured in PLUARG studies. (Marsalek, 1978)

Marsalek, J (1978). Pollution Due to Urban Runoff: Unit Loads and Abatement Measures, Pollution from Land Use Activities Reference Group, International Joint Commission,
 Windsor, Ontario. (reference and info taken from Novotny & Olem's *Water Quality, Prevention, Identification, and Management of Diffuse Pollution*, 1994, Van Nontrand Reinhold)

Appendix VIII



Watershed Management Recommendations

Lowndes County Watershed Assessment

Management and Monitoring Plan

May 2001

Prepared by: Watershed Assessment Team Department of Biological and Agricultural Engineering The University of Georgia Athens, Georgia

And

Carter & Sloope, Inc. Consulting Engineers Macon, Valdosta, Athens & Savannah

Background

Storm water runoff is the water from rain and snow melt that flows across land. Pollutants that have been deposited on land are carried by runoff into nearby rivers, streams, lakes, ponds, wetlands, marine waters, and ground water. This contaminated runoff significantly degrades water quality and aquatic habitat. Storm water runoff also may increase flooding and erosion. Development increases storm water runoff, which alters natural drainage features, increases flooding, and may reduce the ground water recharge to support wetlands and maintain base flows in streams. Development also increases the concentration and types of pollutants that can be carried by runoff, including nutrients, solids, metals, salt, pathogens, pesticides, and hydrocarbons. Storm water runoff and discharges from storm water drainpipes are often the largest contributors to water quality problems in rivers, streams, and marine waters. The state's surface water quality standards, which identify and protect water uses such as water supplies and fish and wildlife habitat, are not being met in many locations.

In 1999, Lowndes County, Georgia commissioned Carter & Sloope, Inc and the University of Georgia's Watershed Team to conduct a comprehensive watershed assessment. The watershed assessment was mandated by new rules issued by the Georgia DNR, Environmental Protection Division (EPD) associated with permits for the discharge of wastewater. The purpose of the project was to assess the current health of the watersheds in Lowndes County, to predict future watershed health and to develop a management plan for the purpose of maintaining the high quality of Lowndes County's streams.

A watershed assessment project is typically composed of four steps: characterization of the local watersheds, streams, potential pollutant sources, etc.; modeling to help explain the current conditions and predict impacts of future land use changes; development of a management plan, which becomes part of the wastewater discharge permit, to correct current deficiencies and prevent future problems; and ongoing monitoring to demonstrate improvement in stream health if the streams are currently impaired or to demonstrate that the management plan is effectively protecting the streams as land uses change due to growth. If ongoing monitoring shows that the current management plan is not meeting the expressed goals, then the plan should be modified in order to meet the expressed stream health objectives. Thus the management plan should be viewed as a work in progress. It would be impossible for city/county/regional planners to foresee precise growth patterns and economic development trends. As conditions vary from those upon which the management plan was developed, the plan should be revisited and modified such that the ultimate goal of maintaining healthy streams is achieved.

Summary of Characterization Study

Bioassessment

To begin the characterization phase of the watershed assessment, investigators from the Watershed Team conducted preliminary site visits to meet with county officials and regional planners to discuss current and projected future growth patterns. Based on these discussions that focused on the future expansion of sewerage service areas along certain corridors, the Team selected sites for water quality sampling and biological and habitat assessments along the Little River, Withlacoochee River, Bevel Creek and Franks Creek. The sites were selected to represent

current land uses and development in the county as well as to characterize areas that might be impacted by future development. These preliminary visits also gave the team a chance to establish a working relationship with key stakeholders in the County.

In October 1999, a team of investigators from the USGS Patuxent Wildlife Research Center in Athens, GA performed biological and habitat assessments at seven study sites (two on Bevel Creek – Stations 1 & 2, four on Withlacoochee River – Stations 3-6, and one on the Little River – see bioassessment section of the complete watershed assessment report for location map). Franks Creek was not included in the bioassessments due to zero flow conditions. The team used indicator species of benthic macroinvertebrates (aquatic insects) and fish to determine biological health and assessed physical and chemical characteristics to determine habitat health for representative 325-foot long sections of the streams. These physical, chemical, and biological assessments were based on methods that, taken together, comprise what is known as the Rapid Bioassessment Protocol (RBP).

The study streams were all characterized as soft-water systems with acceptable pH levels (between 5 and 7), and elevated concentrations of dissolved organic carbon (tannin) due to the decay of aquatic vegetation and tree leaves from the heavily vegetated streams common in this area. Stream banks were, for the most part, stable with enough vegetation to provide substantial shade and cover to the channel. Taking into account the water quality and the general habitat description, the investigators concluded that all study stream sites fell into the "optimal" RBP Habitat Condition Category.

Biological assessments were conducted at all the study sites. Over 100 different benthic macroinvertebrates were identified at the study sites with the majority of them classified as having intermediate tolerance to pollution. Using several indices that measure tolerance and diversity, investigators found that benthic macroinvertebrate assemblages were slightly impaired at station 6 (Withlacoochee River at Langdale Park) and nonimpaired at all the rest of the stations.

Fish were also sampled at all study sites. Thirty-eight species were collected at the study sites; most were classified as having intermediate tolerance to pollution. There were four species classified as tolerant to pollution and one species was classified as intolerant. Based on species of fish collected, all sites were classified as slightly impaired, except site 3 (Withlacoochee River at Highway 122) was nonimpaired and site 1 (Bevel Creek at Loch Laurel Road) was moderately impaired.

Combining the evaluations for habitat, benthic macroinvertebrates, and fish gives an overall assessment of each study site. Investigators determined that while some of the sites had lower RBP Scores, all the streams associated with the Lowndes County watersheds are nonimpaired. It was also noted that severe drought conditions resulting in extremely low flow most likely had a negative influence on the overall integrity of the study streams. See Biological and Habitat Assessment Interpretive Graphs at the end of this document.

Water Quality Monitoring

Water Quality sampling began in January 2000 on ten study sites (1 on the Little River, 2 on Franks Creek, 3 on Bevel Creek, and 4 on the Withlacoochee River). Several parameters were measured in-situ including dissolved oxygen (DO) concentration, electrical conductivity (EC), temperature, pH and depth. Laboratories on the University of Georgia campus measured other parameters. The Environmental Water Quality Laboratory tested for fecal coliform, biochemical oxygen demand, chemical oxygen demand, total suspended solids, turbidity, total phosphorus, ammonia, total Kjeldahl nitrogen, and nitrate-nitrite. The Soil, Plant, and Water Laboratory measured lead, copper, cadmium, zinc and hardness, and the UGA Cooperative Extension Service Laboratory tested for pesticides. Measuring pesticide levels in the streams of Lowndes County was very important initially because the mainstem of the Withlacoochee River was listed on the 303(d) List of Impaired Waters (part of the Clean Water Act) for several derivatives of the pesticide DDT. The UGA Cooperative Extension Service Laboratory found no traces of the DDT derivatives in the streams of Lowndes County. The measured data and the laboratory data results were compared to the limits for water quality parameters as outlined in the State of Georgia's Rules and Regulations for Water Quality Control. All of the water quality parameters were within limits with the exception of cadmium, which was slightly high at all of the study sites. This was likely due to the measurement range used during the testing. The streams of Lowndes County will be sampled for cadmium and re-tested at a more sensitive level, parts per billion instead of parts per million. If the levels of cadmium are still too high, the streams of Lowndes County will be monitored for water quality and a specific component of the management plan will be developed to reduce cadmium levels if the problem persists.

Using data collected for the biological and habitat assessments and the data from water quality testing, Watershed Team investigators concluded that the current health of the watersheds associated with Lowndes County is, for the most part, excellent. Thus, there is no need for a component of the overall management plan to address improving the current health of Lowndes County streams. The Management Plan outlined in this document will address ways to maintain the health of the watersheds as Lowndes County develops and land uses change.

Modeling Impacts of Growth

In order to suggest ways to prevent pollution, future pollutant loadings must be predicted. To do this, the Watershed Team used a computer model called the Soil and Water Assessment Tool (SWAT). SWAT makes use of data sets (soils, weather, vegetation, topography, etc.) to predict the impact of land management practices (development and watershed protection measures) on watersheds.

The County was divided into two major basins, the Withlacoochee River (with the outlet near Highway 84) and Bevel Creek (with the outlet in the Twin Lakes area). The two large basins were subdivided into smaller watersheds. The Withlacoochee River basin was divided into five sub-watersheds and the Bevel Creek basin was divided into three sub-watersheds. Three scenarios were modeled, using SWAT, for the Withlacoochee River and the Bevel Creek basin. The first was a baseline condition, designed to represent current conditions. The second was a growth scenario calculated by assuming medium or low-density residential growth along the proposed Lowndes County sewer service line. The third scenario also used the proposed sewer

service line as a guide and assumed medium or low-density commercial growth. Details of the modeling procedures and results are present in the full watershed assessment report

Modeling results from both the Withlacoochee River and Bevel Creek basins indicated increased average and peak flow rates, corresponding to decreases in vegetative cover and increases in impervious cover. The predicted average sediment concentrations decreased between baseline and residential development conditions representing decreased agricultural impacts, and increased between residential and commercial conditions, while overall average sediment concentrations decreased with increased development. Maximum sediment concentrations increased with increasing development, corresponding to increased peak flow rates and corresponding increases in stream channel scour. Sediments are the leading cause of stream impairment in Georgia. Interactions between rainfall, runoff, land use, and channel hydraulics are very complex. Decreased inputs of sediments to a stream channel might not result in decreased sediment concentrations within the channel if there is a corresponding increase in flow rates. The increased velocities within the channel can scour the banks and bottoms of channels and entrain new sediments into the water or resuspend existing sediment deposits within the channel. Many of the other potential pollutants in water are associated with sediment concentrations and are usually transported into the water body with the sediments. Thus, decreasing sediment transport from the land surface to the stream can often significantly reduce many other pollutants. The other water quality parameters that are of interest did not change significantly as land use changed from current conditions to increased residential and increased commercial development.

Modeling development scenarios generally requires assumptions of steady state conditions. That is we model a baseline scenario with, say, 10% residential land use and we model an increased residential scenario with, say, 50% residential land use. It is generally not possible to accurately represent the varied conditions as the development occurs. That is, it is difficult to model widely dispersed areas as the land is being disturbed to build houses or commercial developments. Many of the expected water quality problems, such as increased sedimentation, arising from development occur during these transition periods and are reduced as the new land uses are stabilized and mature.

From the results of the characterization and modeling studies and discussions with county officials, the Watershed Team was able to suggest a management plan to protect Lowndes County's watersheds. The plan that follows is presented for discussion and comment by county officials and stakeholders. It is anticipated that these discussions will lead to modifications in the suggested plan prior to being finalized for submission to the EPD.

The Management Plan

The Management Plan for the watersheds associated with Lowndes County has three primary objectives: 1) maintain the current conditions and ensure future watershed health by implementing a comprehensive storm water management plan, 2) set up a long term monitoring program to assess the success of the management practices and identify areas where additional efforts might be needed, and 3) public education and involvement. Achievement of the

objectives will require clearly established responsibilities and time lines for the associated activities.

Storm Water Management Activities

The goal of storm water management activities is to protect and maintain the current high quality of the streams and rivers in Lowndes County. Since it is almost always more expensive to correct environmental problems than it is to prevent them, the focus of activities should be to prevent deterioration of stream health as the county grows and develops. The primary causes of stream deterioration associated with changes in land use are changes in the hydrology of the watershed (increased peak flows, often decreased base flows) and transport of pollutants from the land surface into the streams by storm water. Based on these considerations, storm water management activities should focus on efforts to:

- 1. Reduce generation of runoff from storm events
- 2. Retain runoff on the land surface for as long as is practicable
- 3. Minimize generation of potential water pollutants from land use activities
- 4. Provide opportunities to remove pollutants prior to the water entering the receiving stream.

These general goals can be achieved in many different ways. Ideally selected practices will help meet more than one of these goals. It is not the intention of this plan to provide proscriptive methods of achieving this goal. These approaches are best left to local planning agencies and citizens to determine based upon specific site conditions and their acceptability to those who would be impacted. In general, however, these approaches should take the form of local zoning and ordinances that limit the overall degree of impervious surfaces that are constructed and to create opportunities to increase the infiltration of storm water runoff. It is recommended that these ordinances themselves not be too proscriptive, but instead to identify targets for storm water and pollutant reduction and leave flexibility for developers and engineers to be innovative and economical in selection of practices necessary to meet the targets.

It is suggested that current land-use and zoning ordinances be modified, or a comprehensive Storm Water Management Plan (SWMP) developed, that incorporate specific targets for storm water management such as:

- 1. No new storm water conveyances (e.g., outfalls) may discharge untreated storm water directly to or cause erosion in wetlands or waters of the State.
- 2. Storm water management systems must be designed so that post-development peak discharge rates do not exceed pre-development peak discharge rates.
- 3. Loss of annual recharge to groundwater should be minimized through the use of infiltration measures to the maximum extent practicable. The annual recharge from the post-development site should approximate the annual recharge from the pre-development or existing site conditions, based on soil types.
- 4. For new development, storm water management systems should be designed to remove 80% of the average annual load (post-development conditions) of Total Suspended Solids

(TSS). Due to difficulties in quantifying such compliance, it could be presumed that this standard is met when:

(a) Suitable nonstructural practices for source control and pollution prevention are implemented,

(b) Storm water management best management practices (BMPs) are sized to capture the prescribed runoff volume; and

(c) Storm water management BMPs are maintained as designed.

The new State NPDES General Permit for storm water discharges have essentially the same presumptive attainment guidelines and may result in satisfactory compliance with this suggested guideline.

- 5. Storm water discharges from areas with higher potential pollutant loads require the use of specific storm water management BMPs. The use of infiltration practices in these areas without pretreatment should be prohibited.
- 6. Storm water discharges to critical areas must utilize certain storm water management BMPs approved for critical areas. Critical areas in Lowndes County should include recharge areas for public water supplies and public swimming areas.
- 7. Redevelopment of previously developed sites must meet the storm water management standards to the maximum extent practicable. However, if it is not practicable to meet all the standards, new (retrofitted or expanded) storm water management systems must be designed to improve existing conditions.
- 8. Erosion and sediment controls must be implemented to prevent impacts during construction or land disturbance activities (careful review of land disturbing activity permit requests for proper BMP design, local enforcement of LDA BMP installation and maintenance).
- 9. All storm water management systems must have an operation and maintenance plan to ensure that systems function as designed.

The County should develop a technical guidance document to help developers and engineers select BMPs that are effective, economical and appropriate to the local conditions. Unfortunately, the State does not have a comprehensive technical guidance document for storm water BMPs. Many of the BMPs contained in the Manual for Erosion and Sediment Control in Georgia (the Green Book) are appropriate for some storm water management activities. However, they were developed primarily for minimization of erosion on construction sites and, therefore, are not sufficient in themselves to satisfy the need for additional technical guidance. Gwinnett County has developed a technical guidance document for storm water management and it presumed that other counties are doing likewise. Some of these documents could be modified, based on local conditions, for use in the Lowndes County Storm Water Management Plan.

In developing or revising local ordinances, Lowndes County must first address a fundamental question: should storm water be treated and controlled on a localized or more regional scale. Localized management essentially places the burdens of compliance on developers, project owners, and individuals with enforcement by the County. Larger scale management of storm water essentially becomes a County service that is provided to the citizens of the County, just like waste water services, and is funded through some type of tax or utility fee.

The localized approaches to SWMP represents the traditional, and probably still the most common planning approach to runoff control. Under this approach local problems are addressed without evaluating the potential of the control measure to adversely impact downstream areas. This type of approach is preferred when the program is:

- Single-goal oriented, especially flood control;
- Aimed at managing runoff from new development;
- Oriented primarily towards structural controls;
- Targeted at technically preventable problems caused by new development; and
- Limited by financial funding.

Under the localized approach, runoff control responsibilities are usually delegated through ordinances and various regulations to local land developers. With this approach, each developer is responsible for constructing control facilities to maintain site post-development peak discharge rates, volume, and pollutant loads at pre-development levels. Little thought is given to cumulative effects of the individual developments and their control facilities on downstream lands and waters.

Potential disadvantages of the localized approach include:

- Greater risk of negative effects.
- Insignificant flood protection results from emphasis on reducing minor localized flooding.
- Ineffective regional runoff control results from the failure to evaluate locational differences in the effectiveness of control facilities.
- High local costs for facility maintenance usually result as the outcome of small-scale structural solutions rather than large-scale non-structural solutions.
- Flooding problems may be solved upstream but are often increased downstream.

In contrast to the traditional piecemeal approach, the regional, or watershed, approach entails the development of a comprehensive watershed plan. The watershed approach is increasingly becoming more common. This approach is preferred when a program is:

- Multiple-goal oriented;
- Targeted at existing runoff problems;
- Incorporates non-structural controls; and
- Adequately funded (usually from dedicated sources).

Focused at the regional or basin level, the watershed SWMP identifies appropriate structural and also nonstructural BMPs and optimal locations for control facilities. The watershed approach requires a long-term commitment of time, energy and money. However, it is thought that the long-term benefits and cost savings make the effort and investment worthwhile. The following components are typical for a watershed-based SWMP.

- An inventory of watershed characteristics.
- The use of a single control system to address the regional problem of post-development runoff.
- The use of storm water conveyance improvements upstream from the regional facility.
- The use of nonstructural management practices through the watershed. Examples are: acquisition of floodplains, wetlands, natural storm water depressional storage areas; control of land use development; limited amounts of impervious cover; use of innovative structural facilities (i.e.: grassed swales and redirection of runoff).

Advantages of the watershed approach include the following.

- Reductions in capital and operation and maintenance costs.
- Reductions in risks of downstream flooding.
- Ability to better manage storm water problems.
- Increased opportunities for recreational uses of water bodies.
- Contributions to local land use planning.
- Increased opportunities for storm water reuse.
- Is popular among land developers.
- Management goals can be resource oriented and aimed at protection rather than the more costly goal of restoration.

The following disadvantages are identified.

- Requires extensive studies of the watershed prior to locating and designing facilities.
- A future land use plan must be available and implemented so that the facility will be designed properly for loads resulting from upstream development and impervious surfaces.
- Smaller streams above the regional facility may be inadequately protected
- Facilities must be planned, designed, financed and built prior to local development.
- Water quality oriented maintenance activities may be extreme if the public perceives the facility as primarily a recreational facility.

Long Term Monitoring

Water Quality:

• Local groups interested in maintaining and improving stream health in Lowndes County should coordinate monitoring and conduct the sampling.

- The Watershed Assessment Team will be available as a resource for managers and monitors.
- The Watershed Assessment Team will provide local coordinators with standard operating procedures (SOP's) for the collection and transport of water quality samples. The Watershed Team will also compile a list of sampling equipment (sampling bottles, sterile whirl-packs, etc) that will be necessary to conduct water quality sampling. Standard data recording formats should be used. Good examples are forms used by Georgia Adopt-A-Stream.
- Water quality sampling should be conducted on a seasonal basis; once each spring, summer, fall, and winter. Samples should also be collected during (or immediately after) significant storm events (those events with at least one (1) inch of rain per hour) or as prescribed by law.
- Water quality samples should be collected for the following streams and rivers: Bevel Creek, Franks Creek, Withlacoochee River and Little River. Local monitoring coordinators will be supplied with maps and descriptions indicating the locations of sampling sites used in this study.
- The water samples should be tested for the following parameters: water temperature (at the site), pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), fecal coliform, turbidity, dissolved oxygen (DO), electrical conductivity (EC), total lead, total cadmium, total zinc, total copper, ammonia, total Kjeldahl nitrogen (TKN), nitrate-nitrite, and total phosphorus.
- The UGA Environmental Water Quality Laboratory and other laboratories on the UGA Campus can complete sample analysis. However, local alternatives, such as commercial or governmental (water treatment plants) are recommended, as some tests have to be run within hours of collection. The University of Georgia's Tifton Campus is capable of running many of the water quality tests, as is the USDA in Tifton

Biological and Habitat Assessment:

- Local public service groups interested in biological and habitat assessments will be encouraged to perform the majority of the monitoring for biological and habitat assessments. The Watershed Team will be available to assist with the biological and habitat assessments or will advise Lowndes County should they choose to explore other avenues for biological and habitat assessment such as private consultants.
- Standard data recording forms and methods should be used for biological and habitat assessments. Good examples are forms and methods used by Georgia Adopt-A-Stream.
- Biological and habitat assessments should be conducted at each of the monitoring sites utilized in this study, and others if local conditions warrant it, at least once every two (2) years. If local groups are conducting the monitoring, it is suggested that they monitor

four sites per year (3 sites plus the reference site) in order to develop and maintain their proficiency in bioassessment. In this way, every site will be assessed at least once every two years.

• Follow-up biological and habitat assessments should include the collection of habitat and water chemistry data as well as benthic macroinvertebrate and fish data. Local groups might not have the resources available to conduct fish surveys. If this is the case, then this portion of the ongoing biological monitoring program should be contracted to qualified consultants.

Public Education and Participation

A key component of any watershed management plan is a public education/participation program. Lowndes County can organize and implement a public education and awareness program on its own, or it can support the development of a program by local public interest groups. It is likely that some components of the overall program will reside within the County government (such as education of staff, developers, etc.) and public interest groups could best handle other components.

First, the goals of the education program need to be determined. Program goals should promote clear identification and understanding of the problem and the solutions, identify responsible parties and efforts to date, promote community ownership of the problems and the solutions, and integrate public feedback into program implementation.

In order to effectively achieve desired goals, the target audience must be identified. Educational programs should be targeted not only at the general public and the regulated community, but also to the officials, agencies, and county employees who will be involved in the SWMP implementation. The target audience may potentially include:

- Political elected officials, Chambers of Commerce, and heads of departments, agencies and commissions
- Technical (internal) county department and agency staffs
- Technical (external) state agencies and neighboring governments
- Business commercial and industrial, including trade associations
- Community groups fraternal, ethnic, hobby, horticultural, senior citizen, and service
- Environmental groups
- General public/residential
- Schools/Youth groups
- Media print and electronic
- Pollutant-defined groups of individual defined by the specific pollutant(s) they discharge (e.g., used motor oil, pesticides).

To increase the acceptance and success of a SWMP, the public must be taught and encouraged to appreciate the importance of a SWMP and understand how everyday activities contribute to runoff problems. A goal of most education programs is to help the community understand the regulations so that compliance with the regulations is enhanced. As part of the education

program, small businesses that may not be regulated by state, federal, or local regulations need to be informed of how their operations may affect urban runoff.

Additional technical training may be necessary for county employees who will be required to perform new tasks related to the SWMP as well as county employees whose department may not be directly related to storm water but whose actions may affect it. As needed, special training and/or certification are recommended for plan reviewers, inspectors, designers, and contractors. Continuity among local officials and agencies is very important in the permitting and regulatory processes of a SWMP and these individuals/entities should be well informed on all aspects of the SWMP.

The typical components of a public relations program include:

- Identify audience(s)
- Identify communication medium(s)
- Measure results (qualitative and quantitative)

The first component of any public information program is the identification of your audience(s). An audience is the group or groups with whom you would like to communicate. For the purpose of educating persons about nonpoint source pollution, audiences are likely to include manufacturers, developers, builders, commercial interests, media, homeowners or even your own county employee base.

The medium you choose for communicating your message depends on who your audience is. For example, a builder's group can be communicated with through its trade magazines and local builders' association. City staff can be informed through intranet, informational meetings or staff newsletters, and so on.

The effectiveness of a public information education program should be measured on a regular basis to:

- Validate any activities;
- Determine if the messages are clear and concise enough to be accepted;
- Prioritize activities for future funding; and
- Establish the impact and successes of the program.

To ensure responsiveness and to identify successful activities as well as those that need adjustment, public education programs should be tracked to ensure that the techniques being utilized are effective. Establishing a baseline from information collected through surveys at the beginning of a program's implementation is an excellent tool for evaluating success. Surveys may be used to gather information such as the use of toxic materials, perceptions of health risk, disposal practices, support and willingness to pay for new programs, and overall environmental awareness. Over time the survey results can be compared to evaluate changes in public awareness, perception, and support. Conducted on a regular basis, surveys can be used to rate the effectiveness of the education program.

Summary

A watershed assessment was undertaken as a component of an application for a modified wastewater treatment permit for Lowndes County. This assessment, to date, has consisted of characterization of the current health of streams in Lowndes County and suggestions for measures necessary to prevent deterioration of the health of the local streams as land uses in Lowndes County change with growth and development.

The current health of the streams in Lowndes County is very good. These resources are a uniquely beautiful asset to the county and are certainly one of the reasons behind the growth and development in this area. It is in the best interests of everyone in the county therefore to work together to protect these resources from degradation through uncontrolled growth and development.

These resources can, and will, be protected though a comprehensive Storm Water Management Program (SWMP). The primary goals of the SWMP will be to: 1) maintain the current conditions and ensure future watershed health, 2) set up a long term monitoring program to assess the success of the management practices and identify areas where additional efforts might be needed, and 3) public education and involvement. The first goal will be achieved through changes in local ordinances and zoning designed with the objective of water resources protection. The second goal can be achieved through contractual sampling by commercial entities, but the far preferable method will be by soliciting the involvement of local environmentally oriented groups. Having these groups conduct the monitoring provides a sense of ownership in the results and also helps meet the third goal of public education and involvement. The third goal should be achieved through a combination of governmental and public serve groups. The county can seek to educate its own staff, developers, and those immediately impacted by the regulations on their intent, provisions, and enforcement. Local civic groups should undertake a continuing program of education for the county as a whole concerning water resources, storm water management, their impacts on water quality and other issues as well as providing and promoting opportunities for direct participation through act ivies such as steam monitoring and clean up.

Suggested Time Table:

Development of the Comprehensive Storm Water Management Plan is to begin immediately. Data from ongoing monitoring activities and observed compliance with the regulations will be utilized to modify the plan on a regular basis. At a minimum, the success of the plan will be formally evaluated at least every two years.

Pre	iminary Act	tions	Year One	Year Two	Year Three	Year Four	Year Five
Lowndes County Approval of Watershed Assessment	GAEPD Approval of Lowndes County Watershed Assessment	NPDES Permit Approved for Lowndes County LAS by GAEPD	Seasonal Water Quality Sampling, Storm Event Sampling, Data Collection for Future Modeling	Biological and Habitat Assessment, Seasonal Water Quality Sampling, Storm Event Sampling, Data Collection for Future Modeling	Sampling, Storm Event Sampling, Data Collection for Future	Biological and Habitat Assessment, Seasonal Water Quality Sampling, Storm Event Sampling, Data Collection for Future Modeling	Watershed Modeling for NPDES Permit Renewal, Seasonal Water Quality Sampling, Data Collection for Future Modeling

Repeat Five Year Process

Category	Parameters	Possible Sources	Effects
Sediments	Organic and inorganic - Total suspended solids (TSS) - Turbidity - Dissolved solids	Construction sites Urban/agricultural runoff CSOs Landfills, septic fields	Turbidity Habitat alteration Recreational and aesthetic loss Contaminant transport Navigation Bank erosion
Nutrients	Nitrate Nitrite Ammonia Organic nitrogen Phosphate Total phosphorous	Urban/agricultural runoff Landfills, septic fields Atmospheric deposition Erosion Fertilizers	Surface waters - Algal blooms - Ammonia toxicity Groundwater - Nitrate toxicity
Pathogens	Total coliforms Fecal coliforms Fecal streptococci Viruses <i>E. Coil</i> Enterococcus	Urban/agricultural runoff Septic systems Illicit sanitary connections Sanitary sewer overflows Boat discharges Domestic/wild animals	Ear/intestinal infections Recreational/aesthetic loss
Organic enrichment	Biochemical oxygen demand (BOD) Chemical oxygen demand (COD) Total organic carbon (TOC) Dissolved oxygen	Urban/agricultural runoff Sanitary sewer overflows Landfills Septic systems	Dissolved oxygen depletion Odors Fish kills
Toxic pollutants	Toxic metals Toxic organics Oil and grease	Urban/agricultural runoff Pesticides/herbicides Underground storage tanks Hazardous waste sites Landfills Illegal oil disposal Industrial discharges	Bioaccumulation in food chain organisms and potential toxicity to humans and other organisms
Salts	Sodium chloride	Urban runoff Roadway deicing	Vehicular corrosion Contamination of drinking water Harmful to salt-intolerant plants

Adapted from: U.S. EPA, Urban Runoff Pollution Prevention and Control Planning Handbook, 1993.

Total RBP Score Compared to Reference Station



Categories of BMPs	Pollution Prevention Practices	Source Controls	Treatment Controls
Pollution Prevention Practices Source Controls Treatment Controls	 Land Use Planning Public Education Materials Management Illegal Dumping Controls Illicit Connection Controls Street and Parking Lot Maintenance Erosion Control 	 Minimize Impervious Area Filter Strips and Swales Infiltration Devices Oil Water Separators 	 Extended Detention Retention or Wet Ponds Wetlands Filters

Management Practice Descriptions

Description	BMP Description/ Design Notes
Bioretention	Bioretention BMPs replace the traditional "parking lot islands" with a system designed to treat storm water runoff. Similar designs are also used in residential settings, acting as a landscaped area. Runoff is directed onto the facility, and filtered through the sand and organic material in a planted bed. In addition, the storm water provides supplemental irrigation for the plants. Planting with native vegetation is encouraged in bioretention facilities.
Deep Wet Pond	Deep wet ponds are designed with a permanent wet pool to provide water quality treatment. The pond will be designed with an "average" and "minimum" wet pool elevation, based on a water balance analysis. It is possible to use this system as a water reuse pond, where storm water is used as supplemental irrigation, such as for a golf course.
Detention Pond	Pond designed primarily for flood control. These facilities are generally "dry", and do not provide water quality treatment. They can, however provide downstream channel protection if designed properly.
Dry Swale	Dry swales are modifications of the traditional drainage channel. Dry swales are designed with an underdrain system, and a soil bed of sand, designed to filter storm water runoff. Dry swales are often designed with check dams to ensure detention of storm water for a sufficient time period to treat storm water runoff. These systems may need irrigation in semi-arid areas.
Dry Well	Dry wells infiltrate storm water into the ground. Traditionally, dry wells have been used in the Southwest as a storm water disposal method. Dry wells are recommended only for the treatment of residential rooftop runoff, if sufficient pretreatment can be provided. This practice is not allowed by TNRCC in the Edwards Aquifer recharge zone.
ED Shallow Wetland	ED Shallow wetlands have a shallow pool with some wetland plants, such as rushes or cattails, during wet seasons. Although the wetland plants may provide some pollutant uptake and settling, the primary removal mechanism is extended detention provided with an orifice at the outlet of the wetland.
Filter Strip	Filter strips treat runoff as it flows over grassed vegetation, through filtration and some infiltration. These systems can become "short circuited" if runoff becomes concentrated, or if uniform vegetation is not maintained. Like grassed channels, filter strips are best used as pretreatment to or in combination with another BMP.
Grassed Channel	Grassed channels are very similar to traditional drainage ditches, with some modifications. They are designed with flat bottoms, and shallow slopes to promote some infiltration in the channel. Although these BMPs cannot provide full water quality treatment, they can be effective as pretreatment to another BMP, or as supplemental treatment.

Illicit Connection Controls	These practices insure that wastes intended for the sanitary collection system are not connected to the storm drainage system. These practices also require the removal of any improper connections.
Infiltration Basin	Infiltration basins work on the same principle as infiltration trenches, but are designed to treat larger drainage areas, and infiltrate storm water through a flat basin bottom rather than a trench. In small drainage areas, infiltration basins can be designed as combination evaporation/infiltration basins, where standing water in the basin is treated through evaporation. These BMPs are also not recommended in the Edwards Aquifer recharge zone, and should be carefully selected based on soil infiltration rates.
Infiltration Trench	Infiltration trenches (trenches filled with rock) treat runoff as it filters through the soil. They also modify the water balance to be more similar to the pre-development hydrograph by reducing total surface runoff. Infiltration trenches are not recommended in the Edwards Aquifer recharge zone because of the potential for groundwater contamination.
Infrastructure Maintenance	These practices require pollution prevention approaches when drainage infrastructure is being maintained. This includes vegetation controls, storm drain flushing, detention/infiltration device maintenance, and drainage channel/creek maintenance.
Material Controls	These include practices governing the management of materials that can cause storm water pollution. These include advocating safer alternative products, better management of pesticide/fertilizer use, material storage control and reduction in vehicle use.
Material Disposal / Recycling and Illegal Dumping	These practices encourage the proper disposal of materials that can cause storm water pollution and include such practices as storm drain system signs, household hazardous waste collection, used oil recycling, and other illegal dumping controls.

Organic Sand Filter	Organic sand filters have a layer of organic material, such as peat, to increase the ability of sand filters to remove pollutants, such as metals.
Perimeter Sand Filter	Perimeter sand filters are designed for very small and completely impervious parking lots. They operate on the same principle of other sand filters, but the entrance to these filters is the curb grating at the edge of a parking lot.
Planning Management	These practices include those designed to prevent storm water pollution through modification to land use planning/management procedures and through requirements for impervious area reductions.
Spill Prevention and Cleanup	These practices focus on spill prevention, containment, and cleanup.
Submerged Gravel Wetland	Submerged gravel wetlands treat runoff as it flows through a bed of gravel. Wetland plants, usually rushes, provide some treatment through uptake and filtering. This system shows promise, but little research has been conducted to validate its effectiveness, especially long term.
Surface Sand Filter	Surface sand filters treat surface runoff first by settling in a pretreatment chamber and then filtering through a bed of sand. These filters are widely used in the Austin and San Antonio regions.
Underground Detention Chamber	These underground chambers provide the same function as detention ponds. They are extremely expensive to construct, and consequently are only recommended in situations where land is at a premium, such as at highly impervious sites.
Underground Sand Filter	Underground sand filters are similar to surface sand filters, but the entire system is underground.
Water Quality Extended Detention Pond	In Water Quality ED Ponds, the design is slightly modified to provide modest water quality treatment. The outlet orifices of these ponds are designed to provide detention for water quality in addition to providing flood control. The pond has a pretreatment and outlet protection to prevent scouring of the pond bottom

Appendix IX



News Articles and Press Releases

Website Information

Watershed Assessment Website URL: http://watershed.bae.uga.edu

Lowndes County Watershed Assessment Website URL: http://watershed.bae.uga.edu/lowndes

Appendix X



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