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Impact of Organic Matter Composition from Urban Streams and Storm Water on Oxygen Consumption in the Jordan River

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IMPACT OF ORGANIC MATTER COMPOSITION FROM URBAN STREAMS AND
STORM WATER ON OXYGEN CONSUMPTION IN THE JORDAN RIVER

by

Jacob Matt Richardson

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER of SCIENCE

in

Civil and Environmental Engineering

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2014

ABSTRACT

Impact of Organic Matter Composition from Urban Streams and Storm Water on Oxygen
Consumption Rates in Receiving Waters

by

Jacob M. Richardson, Master of Science

Utah State University, 2014

Major Professor: Dr. R. Ryan Dupont
Department: Civil and Environmental Engineering

Coarse particulate organic matter (CPOM) is an essential part of the food chain in aquatic ecosystems because it represents a readily available carbon and energy source. The process by which it decomposes in rivers has been well studied and documented. However, the rate and extent of biodegradability of various CPOM components (i.e., twigs, leaves, grass, etc.) in storm drains is not well understood. The Jordan River TMDL study identified storm water generated CPOM as a likely cause of low dissolved oxygen levels in the lower Jordan River, but recent investigations have suggested that dissolved organic matter generated from this CPOM in storm drains and culverts entering into the Jordan River, rather than the CPOM itself, is the main driver of oxygen impairment. The degradability of CPOM components transported and stored in the storm drain system was studied to understand its relative impact on dissolved oxygen and nutrient status in the Jordan River. Results indicate the generation of highly degradable organic material is a

function of the starting CPOM, and oxygen consumption is associated with the dissolved portion of organic material leached from CPOM in water. Leaves and grass produced the highest levels of all parameters studied. Between 93% to 95% of total oxygen demand is generated within the first 1 to 3 hours of the 24 hour test. Chemical oxygen demand and dissolved organic carbon proved to be the best indicator of biochemical oxygen demand. By using the results of the leaching study an estimate of water quality indicator levels in the Jordan River was made, and was compared to levels in samples collected from the Jordan River. The estimate proved accurate for dissolved organic carbon but not for total or volatile suspended solids. Results of this study were used to discuss possible solutions to reduce oxygen demand in the Jordan River.

(106 pages)

PUBLIC ABSTRACT

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The water quality of the Jordan River has been the subject of a Total Maximum Daily Load study conducted under the direction of the Utah Department of Environmental Quality's Water Quality Division (DWQ). They have determined the oxygen impairment issues in the river are most likely tied to the amount of organic material entering the river from various sources.

The focus of the study conducted by Jacob Richardson was organic material that enters the Salt Lake City storm drain system, and is eventually released into the Jordan River. He found that leaves, grass, and wood particles that enter the storm drain can have a significant negative impact on the levels of biodegradable material in the storm water. Current practices include capturing these leaves, referred to as coarse particulate organic matter or CPOM, at the outlet of the storm drain to the river. Results indicate that it should be removed within 1 hour to limit its impact on water quality in the Jordan River.

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Jacob Matt Richardson

CONTENTS

	Page
ABSTRACT.....	ii
PUBLIC ABSTRACT	iv
ACKNOWLEDGMENTS	v
LIST OF TABLES.....	viii
LIST OF FIGURES	ix
INTRODUCTION	1
The Jordan River.....	2
Research Objectives.....	2
LITERATURE REVIEW	5
CPOM, The River Continuum Concept, and The Urban Continuum Concept	5
DOC in Streams	7
OM in Jordan River Studies.....	8
Jordan River TMDL.....	8
MATERIALS AND METHODS.....	10
Sample Collection and Analysis (Objective 1 and 3)	10
Sample Characterization (Objective 1).....	12
Leaching Test (Objective 2).....	12
Biochemical Oxygen Demand (Objective 3).....	14
Statistical Methods.....	15
Objective 1: Determination of Chemical Characteristics of CPOM Types.....	17
Carbon and Nitrogen Content of CPOM Samples	17
Chemical Oxygen Demand of CPOM Samples	17
Objective 2: Determination of Generation Rate of Leachate Parameters.....	18
Total and Volatile Suspended Solids.....	21
Dissolved Organic Carbon	21
Total Dissolved Nitrogen	23
Objective 3: Compare Laboratory Results to Jordan River Water Samples, and Determine the Biochemical and Chemical Oxygen Demands of the Leachate from the CPOM Samples.....	24

River Water and Leaching Test Comparison	24
Chemical and Biochemical Oxygen Demands of Leachate from CPOM	26
Chemical Oxygen Demand	27
Biochemical Oxygen Demand.....	29
BOD Decay Rate Constants.....	32
Analysis of CPOM Composition	34
Comparison Plots and Regression Equations	34
Carbon to Nitrogen Ratio in Leachate.....	34
SUMMARY OF RESULTS AND DISCUSSION	37
Engineering Significance	38
Non-Structural Solutions	38
Structural Solutions	39
QUAL2kw Water Quality Model.....	40
CONCLUSIONS.....	42
Objective 2: Determination of generation rate of various water quality parameters in CPOM leachate.....	42
Objective 3: Compare laboratory results to Jordan River water samples, and determine the biochemical and chemical oxygen demands of the leachate from the CPOM samples.	43
Future Studies	44
REFERENCES	45
APPENDICES	47
Appendix A – Map of sampling locations	48
Appendix B - The Amplified Long Term BOD Test.....	50
Appendix C – Selected results of preliminary studies	89
Appendix D – Raw data from leaching test and subsequent analyses.....	91
Appendix E – First order versus second order plots for parameters analyzed in the leaching test.....	99
Appendix F – Summary data from Thomas Method determination of BOD rate constants	103
Appendix G – Photos and summary of Chesapeake Bay water wheel trash collector	105

LIST OF TABLES

Table		Page
1	Summary of water sampling containers, preservatives, and holding times ..	11
2	Samples generated from leaching test	14
3	Summary of experiments, data generation and significance to study	16
4	Carbon and nitrogen content of CPOM samples	17
5	Chemical oxygen demand of CPOM solids	18
6	Generation of DOC during leaching test	22
7	DOC generation second-order rate constants	22
8	Generation of TDN during leaching test	23
9	TDN generation second-order rate constants	24
10	Mass estimation calculation summary	26
11	Comparison of water sample and leaching test sample analyses	26
12	Generation of COD in unfiltered leachate from leaching test	28
13	Generation of COD in filtered leachate from leaching test	28
14	COD generation second-order rate constants	28
15	Ultimate total BOD generated during leaching test	30
16	Ultimate carbonaceous BOD generated during leaching test	30
17	Ultimate nitrogenous BOD generated during leaching test	30
18	BOD decay rate constants	33
19	C:N ratio of the CPOM solids and leachates	36
20	Overall generation rate constant for each parameter	38
21	Summary of potential solutions for CPOM impact to the Jordan River	41

LIST OF FIGURES

Figure		Page
1	Jordan River tributaries and canals	3
2	The River Continuum Concept	5
3	The Urban Continuum Concept	6
4	Diagram of experimental analysis of samples	12
5	Sample flow during the leaching test.....	14
6	Typical result of the leaching test	19
7	Generation of DOC during leaching test	22
8	Generation of TDN during the leaching test.....	24
9	Generation of total COD in leachate.....	28
10	Generation of soluble COD in leachate	29
11	Soluble total BODu generated during leaching test.....	31
12	cBODu generated during leaching test	31
13	nBODu generated during leaching test	31
14	Example of a Thomas Method plot.....	33
15	cBODu decay rate constants	33
16	Comparison of DOC to total BODu.....	35
17	Comparison of COD to soluble total BODu	35
18	Ratio of total BODu to DOC versus leaching time.....	35

INTRODUCTION

Coarse particulate organic matter (CPOM) is described in general as the portion of organic particulates that are larger than 1 mm in diameter (Vannote et al. 1980). In stream ecology, CPOM's role in an ecosystem is to provide an energy source for riverine biology. Bacteria metabolize the CPOM as well as soluble portions of organic matter (OM) that have dissolved into the water column. As these bacteria consume the biodegradable portions of the OM, dissolved oxygen (DO), when present in the water column or sediments, is consumed as it is used as an electron acceptor. The rate of this metabolism and its associated oxygen consumption is the major focus of this study.

Sources of CPOM are typically low-order mountain streams that have high amounts of allochthonous inputs of leaves and woody debris as it falls from trees and shrubs that line the stream's banks (Vannote et al. 1980). Different stream ecosystems will produce different types of CPOM depending on the plant types and species found in the contributing watershed. An extensive number of studies have been conducted on the differences in consumption rates of dissolved organic matter (DOM, diameter $<0.45\mu\text{m}$) (for example see Dahm (1981) and cited references). Results from these studies show significant DOM consumption within the first 1 to 4 hours of study depending on CPOM species (Dahm 1981; McArthur and Richardson 2002; Sun et al. 1997).

The processes involved in the utilization of DOM across ecosystems are reasonably well known (Cleveland et al. 2004), but the oxygen consumption associated with these processes is not as well studied, nor have these studies been widely applied to

the field of civil engineering in the design of storm water runoff collection and conveyance systems.

The Jordan River

Located in northern Utah, the Jordan River runs south to north bisecting the Salt Lake Valley. Several creeks and streams originate in the mountains to the east and pass through the urbanized areas of Salt Lake City and its suburbs, eventually reaching the Jordan River (Figure 1). Currently, several of these streams are conveyed to the Jordan River via a system of pipes and box culverts that also collect storm runoff during rain events. Associated with these storm water flows are loads of organic and inorganic material accumulated from the contributing natural and urbanized watersheds. These stream and storm water conveyance systems have recently become part of a larger study of the Jordan River and water quality issues related to DO, that is below state and federal standards for its designated uses (Cirrus 2012). The current understanding of CPOM metabolism and its associated oxygen consumption was applied to the types of organic material collected in the storm drain system which discharges into the Jordan River to determine if CPOM loading from storm water runoff in this system has significant impacts on the depletion of DO in the river.

Research Objectives

The hypothesis of this study is that CPOM stored in the storm drain systems that discharge into the Jordan River results in significant input of biochemical oxygen demand (BOD) during storm events in the form of biodegradable dissolved organic carbon (DOC) and biodegradable OM. To test this hypothesis, four objectives were established.

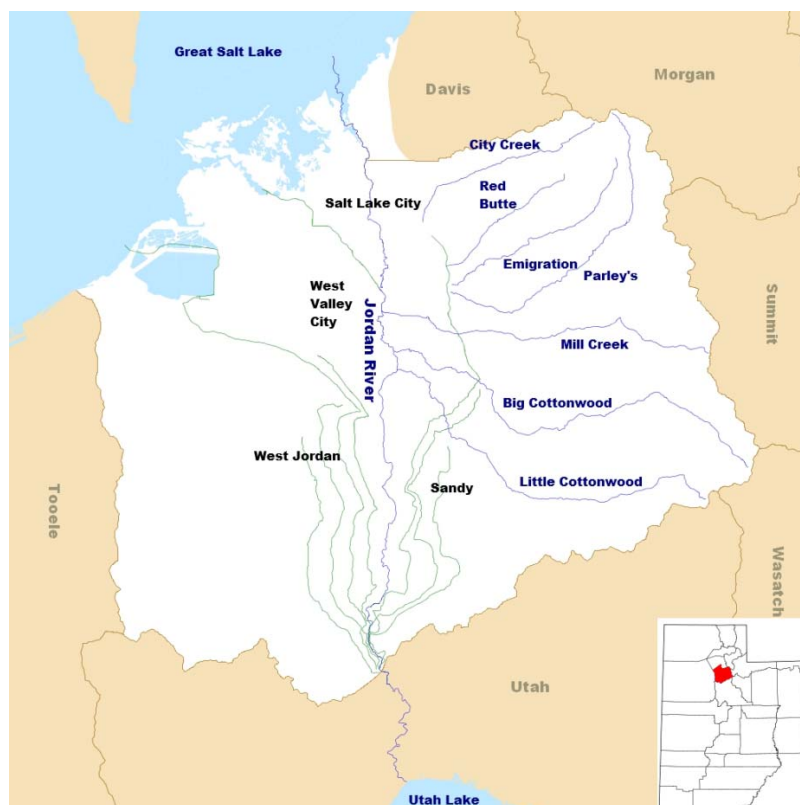


Figure 1: Jordan River tributaries and canals (Wikipedia.org 2010)

Objective 1 was to determine the chemical characteristics of the various CPOM sample types originating from the drainage area. Three groups of CPOM samples were identified; wood (twigs and branches), leaves (fresh and green), and grass (lawn clippings). Subsamples from each group were dried, ground, and analyzed for chemical oxygen demand (COD) and carbon and nitrogen content. Oxygen consumption was compared to the chemical characteristics (COD and C, N content) of each group to determine which characteristic best predicted the group's associated oxygen consumption.

Objective 2 was to quantify the rate of decomposition of those groups of CPOM that are found in the stream and storm water that enters the lower reaches of the Jordan River. The rate of decomposition was measured by the rate at which the CPOM breaks

down into finer sized particles ($0.45\mu\text{m} < \text{diameter} < 1\text{mm}$, referred to as fine particulate organic matter (FPOM) in the aquatic ecology literature, and VSS in the environmental engineering literature), dissolved organic carbon (DOC), and ammonia, organic nitrogen, nitrate and nitrite (measured as total dissolved nitrogen, TDN). These parameters were also compared to oxygen consumption to see which one best predicted the observed oxygen consumption.

Objective 3 was to establish the biochemical oxygen demand (BOD) for the CPOM groups. Included in this objective was determining the portions of the total BOD that are carbonaceous (cBOD) and nitrogenous (nBOD). The BOD values were then compared to the results of the test conducted as part of Objectives 1 and 2 to determine which chemical characteristic or parameter best predicted BOD. The BOD values were then also used to determine a rate constant “k.” The purpose for this was to make the results of this study useful in the application to water quality modeling for the Jordan River, as well as for water bodies receiving similar types of CPOM. Part of this objective also included determining if the method outlined in this study could be used in estimating BOD loading to the Jordan River. This was done by estimating flow and mass loading rates to determine concentrations of each of the parameters, and comparing them to the results of the analysis of the water samples taken at a location in the Jordan River downstream of the Salt Lake City storm drain discharge point.

Based on results from the study, recommendations were made on how to proceed in terms of management and control of storm water pollutants. Future work was also suggested to better understand the full impact of CPOM on the Jordan River.

LITERATURE REVIEW

CPOM, The River Continuum Concept, and The Urban Continuum Concept

During the late 1970s large amounts of research was focused on understanding the physical variables that govern the aquatic ecology of streams from their headwaters to their mouths. These efforts were compiled and summarized into what is called The River Continuum Concept (Figure 2). According to this concept, sources of CPOM are low order, headwater streams where organic material from riparian vegetation is abundant and relative channel width is small. Autotrophic activity is limited by shading, and allochthonous detritus contributions are large. As the CPOM moves downstream, it is reduced to FPOM (Volatile Suspended Solids, VSS) by physical abrasion, and chemical and biological decomposition. This concept has served as a background for stream ecology for several decades, but in cases where urban growth and infrastructure has changed the way low order streams are conveyed, this concept is no longer applicable.

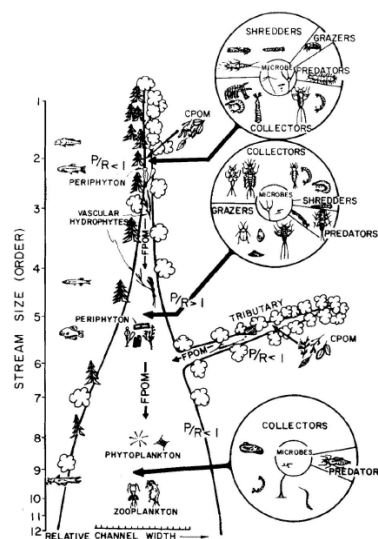


Figure 2: The River Continuum Concept (Vannote et al. 1980)

Recently Kaushal and Belt (2012) proposed the Urban Watershed Continuum that provides a framework for understanding how changes to the natural landscape and hydrology in urban areas has affected the ecological function of natural waterways. Their research, which has been focused on the Baltimore Maryland area, considers how urbanization typically includes the burial of low order streams which can cause increases in organic matter from engineered storm drains, swales, leaky sewers, and ditches. Figure 3 illustrates these modifications and their effects. Modifications associated with urban systems have also been found to alter the transport and retention of nutrients from headwaters to outlets. Kaushal and Belt's (2012) results indicate a reduction in nitrate along streams. One possible explanation for this is that increased carbon inputs enhance uptake and denitrification. Further study of the effects of urbanization is needed to clearly define modifications to organic carbon and nutrient transport and retention in the urban water systems.

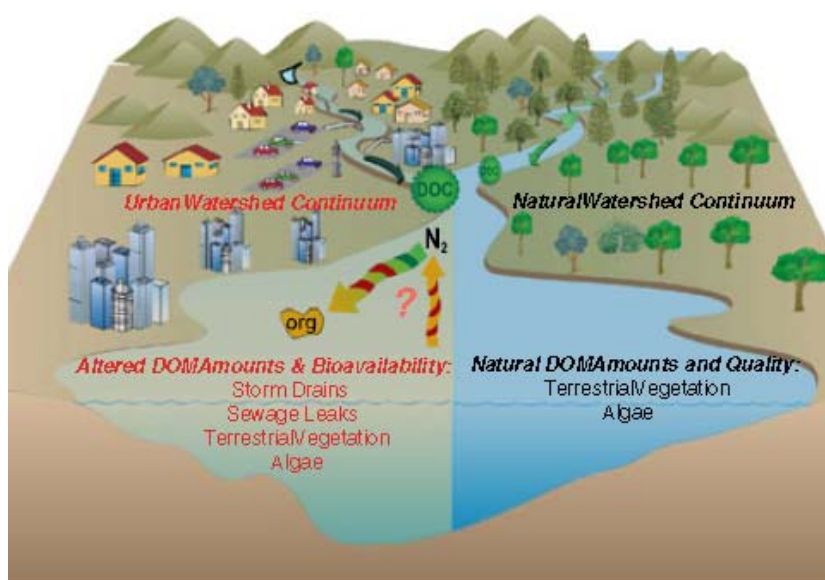


Figure 3: The Urban Continuum Concept (Kaushal and Belt 2012)

DOC in Streams

The role of DOC in stream ecology has been extensively studied. It is well understood that significant sources of DOC include leaf litterfall from the watershed. In a study conducted by Meyer et al. (1998) in the Coweeta Hydrologic Laboratory in Macon County North Carolina, a stream was deprived of litterfall for 3 years. The impact on DOC levels in the stream was measured and showed that approximately 30% of daily DOC exports in this stream were from leaf litter stored in the stream. McArthur and Richardson (2002) studied the utilization rates of DOC derived from five species of leaves common to a research watershed in British Columbia, Canada. Bacterial growth was measured using [^3H] leucine incorporated into protein. They found that there are significant differences in the DOC leaching and utilization rates from different leaf species, and that the carbon to nitrogen ratio was the best predictor of bacterial growth during the study.

Several studies have looked at the effect of different sources of DOC found in streams. Mulholland (1997) showed by a comparative analysis of DOC concentration versus organic matter input and storage that watershed processes were more important than in-stream processes in controlling DOC in stream water. The importance of terrestrial sources during seasonal and weather variations has also been shown (Hornberger et al. 1994). In contrast, Aiken et al. (1996) found that DOC comes from autochthonous organic material stored in the channel in well-lit streams draining watersheds where there are few terrestrial DOC sources.

OM in Jordan River Studies

Several other researchers are studying the OM content in the Jordan River. Baker et al. (personal communication Aug. 7, 2013) are looking into how the surface and benthic OM loading and composition change throughout the length of the river. Results from their study are not yet published but initial observations indicate that the CPOM concentrations in the river do not vary with time. Also, extremely high levels of DOM were measured in winter samples. In addition to the data being collected and analyzed by Baker et al., there are data available for VSS and BOD₅ for synoptic survey events of the Jordan River collected by representatives of wastewater treatment plants that discharge into the Jordan River (samples were collected from 1998-2008) (Cirrus 2010). These data have been used in past studies of the Jordan River and may prove useful in comparing current loading to past conditions.

Jordan River TMDL

The Jordan River was listed as impaired on the State of Utah's 303(d) list of impaired water bodies. According to the Federal Clean Water Act, the State of Utah is required to determine the maximum amount of pollutants the Jordan River can receive and still meet the designated water quality requirements (Cirrus 2010). The current TMDL is focused on determining the processes that are affecting the DO levels in the lower Jordan River. Below is a summary of the four processes that have been identified as possible contributors to low DO (Cirrus 2010):

1. Physical factors, including water temperature and channel characteristics that influence reaeration from the atmosphere.

2. Aerobic decomposition of OM and inorganic nitrification of NH_4 in the water column (measureable as biochemical oxygen demand, BOD)
3. Aerobic decomposition of OM and inorganic oxidation at the interface between the water column and bottom sediments (measureable as sediment oxygen demand, SOD).
4. Algal growth generating a net increase in DO during daylight hours and net consumption of DO associated with respiration during the night (Cirrus 2010).

It is important to point out these four processes in order to understand that the results of this study are not intended to be the entire solution to the low DO problem in the lower Jordan River. Instead they are intended to provide input to a portion of the overall solution. With that said, the results of this study will hopefully provide insight into the second process listed, aerobic decomposition of OM and inorganic NH_4 in the water column.

MATERIALS AND METHODS

Sample Collection and Analysis (Objective 1 and 3)

Site description - Water samples used for this study were collected from a location downstream of the outlet of one of the Salt Lake City storm drain discharge points (Objective 3) (see Appendix A). CPOM samples were collected from Liberty Park, and more specifically the area surrounding the lake (Objective 1). This park was used as a representative sample for the contributing watershed for the storm drain system that runs below the 900 South and 1300 South roadways in Salt Lake City, and discharge into the Jordan River.

Water samples were collected as grab samples using a 1 L plastic bottle attached to a pole with the sample being retrieved from approximately 1 foot below the water surface when possible. The water was then distributed into containers as explained in Table 1. As each of the sample containers were filled, a label was attached to the container indicating location, date, time, sampler name, preservation method, and bottle type. Sample containers were kept cool while they were transported. Samples were analyzed at the Utah Water Research Laboratory Water Quality Lab in Logan, Utah that is located approximately 1.5 hours away from the sampling sites. Once at the testing laboratory, a laboratory log number and log-in date were added to the sample label, and the samples were placed in cold storage at 4°C until they were analyzed. The holding time for each of the samples is also indicated in Table 1 (Objective 3).

Water samples were analyzed for total suspended solids (TSS), volatile suspended solids (VSS), total dissolved nitrogen (TDN), and DOC. The VSS of the

sample indicates the amount of particulate organic material present in the sample, and was used to compare the portion of OM that is particulate versus dissolved (Objective 3).

Table 1: Summary of water sampling containers, preservatives, and holding times

Analyte	Container Type	Volume	Preservation	# of Replicates	Holding Time (days)
DOC	Amber Glass Vial	40 mL	Phosphoric Acid - H_3PO_4	3	28
TSS/VSS	Plastic Bottle	100 mL	Store at 4°C	3	2
TDN	Plastic Bottle	100 mL	Sulfuric Acid - H_2SO_4	3	28

CPOM samples for the DOC/TDN leaching and BOD tests were collected fresh so that a more complete view of the decomposition process could be obtained than if samples were collected from the storm drain or river. This is due to the fact that significant leaching from dried (Nykqvist 1962; Saunders 1976) and fresh (Gessner 1991) leaves has been reported to occur within 24 hours. CPOM samples were collected in 1-gallon plastic bags and stored at 4°C until testing was conducted. Approximately 20 to 40 grams each of wood, leaves, and grass were collected. All of these samples were collected manually in early Spring of 2014. Samples were taken to the Utah State University Intermountain Herbarium, but species identification was not successfully completed. Figure 4 illustrates the experiments and measurements that were conducted with the samples (Objective 1-3).

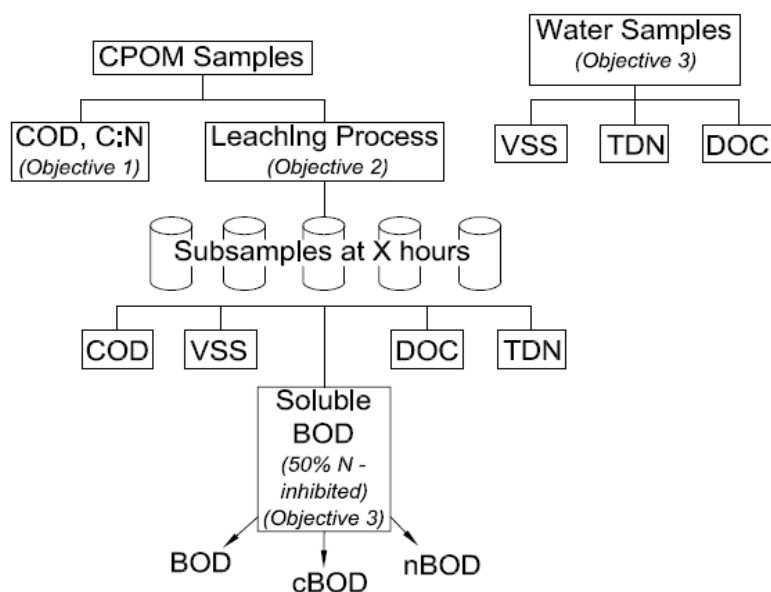


Figure 4: Diagram of experimental analysis of samples

Sample Characterization (Objective 1)

The samples were analyzed to determine their COD and carbon to nitrogen ratio. The COD test was conducted according to the Hach Reactor Digestion Method (Method 8000). Total carbon and nitrogen were determined by combustion followed by IR and thermal conductivity detection, respectively, at the Utah State University Analytical Laboratory (Leco TruSec C/N Analyzer).

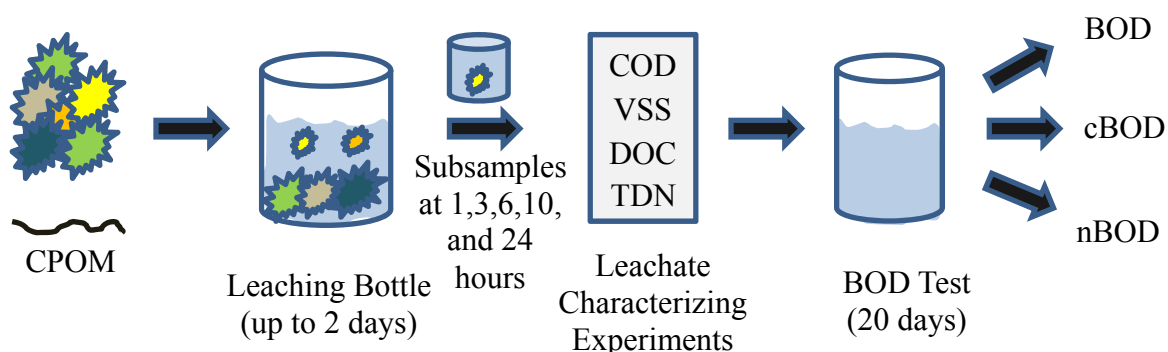
Leaching Test (Objective 2)

Known masses (1-3 g) of solids from the fresh plant and wood samples were dried at 60°C overnight. The solids were then added to 900-mL of deionized water in 1 L bottles and were kept at 25°C on a mixing platform for 24 hours. At times 1 hour, 3 hours, 6 hours, and 10 hours, and 24 hours, the entire 900 mL volume of water was retrieved from each bottle. Nine hundred milliliters of fresh deionized water was re-added

to the 1 L bottles and the bottles were placed back on the mixing platform. The collected water was filtered through a 1 mm mesh field sample net filter to capture any suspended CPOM particles. The captured material was rinsed from the filter back into the 1 L bottle with approximately 5 -10 mL deionized water. A 60 mL volume of subsample filtered through the 1mm filter, and 120 mL of subsample filtered through a 0.45 μ m Whatman Glass Fiber filter (Cat No. 1827 047) were separated out from each sample for BOD testing. A standard TSS test was conducted using 100 mL of subsample. A standard VSS test was conducted using the filters from the TSS test. Ten mL each of both filtered and unfiltered sample were preserved with sulfuric acid and stored at 4°C for COD analysis. Approximately 40 mL of the subsample was filtered and placed in three amber vials for DOC analysis, and were preserved with phosphoric acid and stored at 4°C until analyzed. Approximately 50 mL of the subsample was filtered and placed in a 125 mL plastic bottle for TDN analysis, and was preserved with sulfuric acid and stored at 4°C until analyzed. DOC analysis was completed using a Teledyne Tekmar Apollo 9000 Combustion TOC Analyzer. Analysis of TDN was done using a Seal Analytical AQ2 Automated Discrete Analyzer (Serial # 090749). The TDN samples were digested per the EPA Standard Method 365.1 prior to analysis. Table 2 summarizes the samples generated during the leaching test, and Figure 5 illustrates the process of the leaching test.

Table 2: Samples generated from leaching test

Analyte	Volume (mL)	Filtered/Unfiltered
TSS/VSS	100	Unfiltered
DOC	120	Filtered
TDN	50	Filtered
COD	10	Unfiltered
COD	10	Filtered
BOD	60	Unfiltered
BOD	120	Filtered

**Figure 5:** Sample flow during the leaching test

Biochemical Oxygen Demand (Objective 3)

The biochemical oxygen demand (BOD) analyses were conducted in general accordance with the procedures found in Standard Methods for Examination of Water and Wastewater: 5210 Biological Oxygen Demand (BOD) #1 (APHA 2012), and in The Amplified Long-Term BOD Test published by the Georgia Environmental Protection Division (GEPD 1989; Appendix B). The Standard Method BOD test (BOD₅) provides specific laboratory procedures for determining the 5-day BOD for a sample. The GEPD method (BODLT) provides laboratory procedures and test specifications for analyzing samples for longer periods. A summary of the procedures used in this study is included here. For further detail, the full procedures of the BODLT test are included in Appendix

B. The BOD₅ test is a standardized test and can be found in Standard Methods for the Examination of Water and Wastewater (APHA 2012).

The 60 mL unfiltered subsample obtained from the leaching test was placed in a 300-mL bottle, and diluted to a 1 to 5 ratio of subsample to dilution water. The 120 mL filtered subsample was divided into two 60 mL samples. Both 60 mL volumes were placed in 300 mL BOD bottles and diluted to a 1 to 5 ratio, but one of the bottles also had a nitrification inhibitor added in accordance with Section 4.e.6 of APHA (2012). Dilution water was obtained from the Logan River which is located adjacent to the Utah Water Research Laboratory where the BOD test was conducted. Dilution water was prepared in accordance with Section 4.a of APHA (2012). Bottles were placed in an incubator at 20°C in the dark, and DO measurements were taken in each bottle every 2-3 days and recorded until the change in DO was less than 0.1 mg/L/day or to Day 20, whichever occurred first. If the change in DO was less than 0.1mg/L/day, the bottle was placed in the incubator and no longer analyzed for DO. On the 20th day of the experiment, the DO was measured for all bottles. In the event that the DO levels in the sample dropped below 3.0 mg/L during the test, reaeration was performed in accordance with Section 2.5.5 of BODLT (GEPD 1989).

Statistical Methods

Data analyses, including linear regression, and standard statistical values (mean, confidence intervals, standard of deviation, analysis of variance (ANOVA), etc.) were used to determine statistical significance of the results. Triplicate tests were used to

determine laboratory procedure variance, and triplicate samples were taken to measure sampling procedure variance.

Table 3 contains a summary of the experiments that were conducted as part of this study, the data they each generated, and the significance of the data.

Table 3: Summary of experiments, data generation and significance to study

Experiment	Samples Tested	Data Generated	Significance
Carbon/Nitrogen Content (Objective 1)	CPOM	% Carbon % Nitrogen	- C:N ratio used in solids classifications and regression building
DOC/TDN Leaching (Objective 2)	Leachate	DOC generated – mg DOC/L TDN generated - mgN-NO ₃ /L	- Leaching rate used in development of DOC/TDN mitigation strategies - Leachate used in BOD testing of soluble organic carbon and nitrogen
BOD <i>50% of tests run with nitrifying inhibitors</i> (Objective 3)	Leachate	BODu - mg O ₂ /L cBODu - mg O ₂ /L nBODu - mgO ₂ /L	- Determines biodegradable fraction of DOC and TDN - Used in identifying actions to be taken to mitigate impacts - Used in calculating rate constants “k” for cBODu and nBODu.
Total (TSS) and Volatile Suspended Solids (VSS) Total Dissolved Nitrogen (TDN) (Objectives 2 & 3)	Water Samples and Leachate	TSS - mg/L VSS - mg/L TDN - mg/L	- Quantified amount of organic material in particulate form; includes all forms of volatile organic materials - Indicated background levels of TDN in system
Chemical Oxygen Demand (COD) (Objectives 1,2 & 3)	Water Samples and Leachate	COD - mg/L	- Results compared to the BOD of the sample; possible way to estimate BOD

RESULTS AND DISCUSSION

Objective 1: Determination of Chemical Characteristics of CPOM Types

Carbon and Nitrogen Content of CPOM Samples

The CPOM samples used in this study were collected from Liberty Park in Salt Lake City, UT in the Spring of 2014. They were analyzed for carbon and nitrogen content at the Utah State University Analytical Laboratory in Logan, UT after they were dried and ground to a powder. The samples showed varying percentages of both nitrogen and carbon, with wood having the highest carbon to nitrogen ratio (81.8:1), and grass having the lowest (13.3:1). These results are summarized in Table 4, and are consistent with the understanding that woody organic materials are higher in lignin and cellulose content than green leafy organic materials. Also, these results were used in comparison to results presented in later sections of this study.

Table 4: Carbon and nitrogen content of CPOM samples

Sample Type	% Total Nitrogen	% Total Carbon	C/N Ratio
Wood	0.55	45.0	81.8
Leaves	3.47	46.3	13.3
Grass	3.93	44.5	11.3

Chemical Oxygen Demand of CPOM Samples

The CPOM samples were analyzed for chemical oxygen demand (COD) of the dried and ground samples at the Utah Water Research Laboratory. The COD of the CPOM solids (Table 5) shows a high amount of variability among the triplicate samples for each type of CPOM, and therefore statistically they are not significantly different

from each other. The high amount of variability in the leaf samples could be due to the variations in the structure of the leaf. Even though the samples were ground and homogenized per standard procedures it is possible that the samples contained varying amounts of leaf lamina (potentially more labile) and leafstalk (potentially more recalcitrant).

Table 5: Chemical oxygen demand of CPOM solids

Sample Type	COD (mg/L/g solid)
Wood	529 ± 80
Leaves	1,090 ± 778
Grass	655 ± 281

Objective 2: Determination of Generation Rate of Leachate Parameters

The CPOM samples were used in a leaching test to determine the generation rate of certain parameters that could be used to predict oxygen demand associated with the CPOM particles in water. The parameters measured were total and volatile suspended solids (TSS and VSS), dissolved organic carbon (DOC), and total dissolved nitrogen (TDN). Samples were obtained from the leaching test by removing the entire volume of water from the reactor at 1, 3, 6, 10, and 24 hours from the time the solids were placed in the reactor. Analyses were conducted on the water removed and not the solids placed in the reactor. After the leachate water was removed fresh water was placed in the reactor and the leaching test continued until the next sampling time. Figure 6 shows a typical result of the leaching test.

The leaching test and subsequent analyses were performed three times. The first two tests were considered preliminary for the purposes of determining proper dilution

ratios, and to refine laboratory methods during the analysis. The results of the third and final leaching test and analyses are presented here with a few references to the preliminary tests for comparison. (Selected results from preliminary testing are located in Appendix C.)

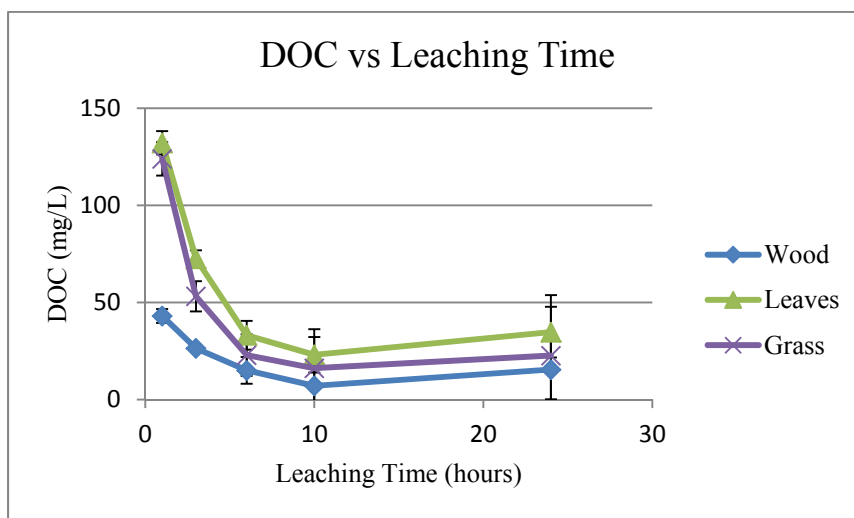


Figure 6: Typical result of the leaching test (DOC concentration versus leaching time is shown in this graph as a function of CPOM type)

The results presented in the remainder of this section are shown in units of milligram of analyte per gram of dry solid in the leaching reactor per hour(s) of leaching. This is obtained from taking the results of the analyses and dividing them by the mass of dry solids placed in the leaching reactor at the start of the test. This result is then divided by the number of hours since the prior sampling event. For example, a sample taken at the 6th hour would be divided by 3 since it had been 3 hours since the prior $t = 3$ hour sampling event.

The generation of each parameter was evaluated to determine if it would be more accurately modeled by a first or second-order model. Accuracy was based on the linearity

of the data after the first or second order transformation. Once it was determined which model more accurately described the data, the rate constant for the parameter was estimated.

First-order approximation models take the form of an exponential model, Equation 1, where L = concentration at time t , mg/L, L_0 = initial concentration, mg/L; and k = first order rate constant, 1/hr.

$$L = L_0 e^{-kt} \quad (1)$$

This expression can be rearranged and natural log-transformed to allow the determination of the rate constant as shown in Equation 2.

$$\ln\left(\frac{L}{L_0}\right) = -kt \quad (2)$$

The natural log of the quotient of the parameter at time i over the initial parameter reading were plotted against the leaching time. The slope of this plot is the first-order rate constant in units of 1/hour. The 95% confidence intervals on the slope were also calculated to determine its level of significance ($P < 0.05$). For first-order approximations, a smaller value for k indicates a slower rate of transformation.

The integrated form of second-order approximation models take the form shown in Equation 3.

$$\frac{1}{L} - \frac{1}{L_0} = kt \quad (3)$$

Once the data were in this form they were plotted against time and the slope of the regression line was the second-order rate constant “ k ,” with typical units of 1/(mg/L-day). Again, the 95% confidence intervals on the slope were calculated to determine its level of significance ($P < 0.05$). For second-order approximations a higher rate constants indicate a

smaller change between concentrations for each time step, and thus a slower rate of transformation.

Total and Volatile Suspended Solids

Production rates for total and volatile suspended solids (TSS and VSS) were found by analyzing the leachate samples from each of the subsamples taken at 1, 3, 6, 10, 24 hours from the start of the leaching experiment. Due to many of the results being below the detection limit for the method used, and the high amounts of variability in the data, these results are not presented here, but the raw data can be found in Appendix D.

Dissolved Organic Carbon

Generation of dissolved organic carbon (DOC) during the leaching test was analyzed and the results are shown in Table 6 and Figure 7. DOC generation from each of the CPOM types followed a similar pattern during the test, but the leaf and grass samples produced nine to 10 times more DOC than the wood samples. These results also indicate there is a significant difference between the amounts of DOC leached from each of the materials from 1-6 hours from the start of the test. After 6 hours the different materials begin to have similar DOC generation rates. Also, within 1-3 hours 87% - 92% of the total DOC measured during the analysis is leached from the materials.

Rate constants of DOC generation were also calculated for each CPOM type using a second-order approximation (Table 7, and Appendix E). The 95% confidence interval indicates that each rate constant is statistically significant since the confidence region does not include zero, and that all rates are statistically the different. An ANOVA analysis of the three rates compared to each other confirmed this ($P = 0.02$). These results

also indicate that DOC is being generated from wood at a significantly slower rate than from leaves and grass.

Table 6: Generation of DOC during leaching test

CPOM Type	DOC (mg/g/hour)				
	Leaching Time (hours)				
	1	3	6	10	24
Wood	6.5 ± 0.63	1.5 ± 0.12	0.64 ± 0.4	0.35 ± 0.57	0.21 ± 0.19
Leaves	64.3 ± 3.15	16.4 ± 1.1	4.7 ± 1.3	2.5 ± 1.2	1.2 ± 0.49
Grass	52.0 ± 3.9	11.7 ± 1.8	3.5 ± 1.6	1.7 ± 2.3	0.66 ± 1.0

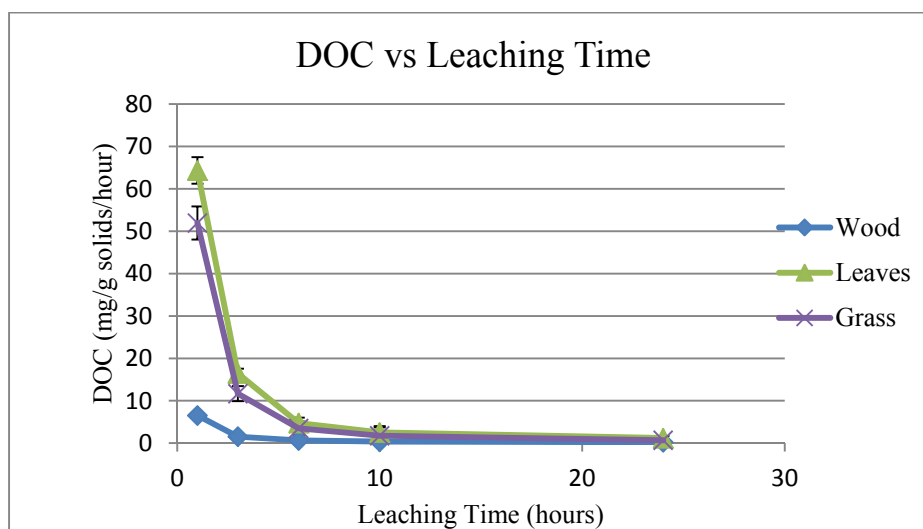


Figure 7: Generation of DOC during leaching test (95% conf. interval shown)

Table 7: DOC generation second-order rate constants (95% conf. interval shown)

CPOM Type	Rate Constant k (1/(mg/g-hour))	R^2
Wood	0.204 ± 0.074	0.93
Leaves	0.037 ± 0.002	0.99
Grass	0.068 ± 0.013	0.99

Total Dissolved Nitrogen

Generation of total dissolved nitrogen (TDN) during the leaching test was analyzed and the results are shown in Table 8 and Figure 8. The results of this analysis indicate that grass generates the highest levels of TDN during the first 1-10 hours of the test. Also, during the first hour of the test the materials are significantly different in the amount of TDN they produce. After that they are no longer significantly different. During the first 1-3 hours of the test 83% -87% of the total TDN measured during this analysis was leached from the materials.

TDN generation rates were calculated for this dataset using a second-order approximation, and are shown in Table 9. The 95% confidence intervals do not overlap and do not include zero so each of the three constants are statistically different. An ANOVA analysis of the three rates compared to each other confirmed this ($P=0.007$). The higher rate constants for wood indicate that TDN is being generated from wood at a slower rate than from grass and leaves.

Table 8: Generation of TDN during leaching test

CPOM Type	TDN (mg/g/hour)				
	Leaching Time (hours)				
	1	3	6	10	24
Wood	0.33 ± 0.06	0.06 ± 0.01	0.04 ± 0.02	0.03 ± 0.01	0.01 ± 0.0
Leaves	1.9 ± 0.15	0.63 ± 0.03	0.18 ± 0.18	0.14 ± 0.03	0.06 ± 0.0
Grass	2.9 ± 0.45	0.66 ± 0.67	0.45 ± 0.31	0.14 ± 0.03	0.05 ± 0.02

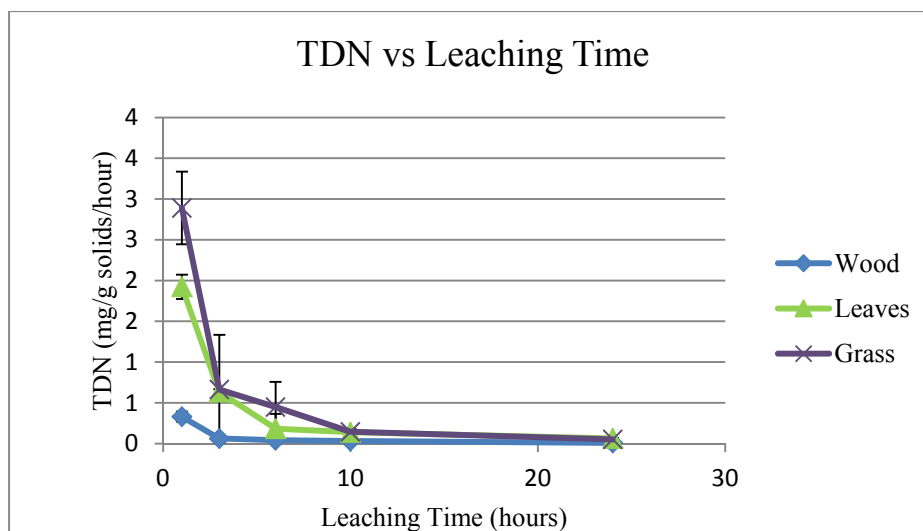


Figure 8: Generation of TDN during the leaching test (95% conf. interval shown)

Table 9: TDN generation second-order rate constants

CPOM Type	Rate Constant k (1/(mg/g-hour))	R^2
Wood	5.38 ± 1.25	0.96
Leaves	0.68 ± 0.02	0.99
Grass	0.91 ± 0.31	0.99

Objective 3: Compare Laboratory Results to Jordan River Water Samples, and Determine the Biochemical and Chemical Oxygen Demands of the Leachate from the CPOM Samples.

River Water and Leaching Test Comparison

The results of the leaching test were compared to the results of water samples collected from the Jordan River at 9th South. Water samples were collected on three different days with no rain and were analyzed for DOC.

In order to compare the leaching test results to the water sample results it was necessary to estimate concentrations based on visual observations in the 13th South storm drain pipe using results from the leaching test and an organic matter dilution factor for

each of the CPOM types (W_{dil} , L_{dil} , G_{dil}). The dilution factor was used to more closely describe the mass of wood, leaves, and grass observed in the Jordan River since this was not considered when conducting the leaching test. The mass of organic material in the storm drain pipe (MP_{wood} , MP_{leaves} , MP_{grass} ,) was estimated by multiplying the mass of organic material (M_{wood} , M_{leaves} , M_{grass}) by its dilution factor and the ratio of the pipe volume (Vol_{pipe}) and the reactor volume ($Vol_{reactor}$). Vol_{pipe} is known from the dimensions of the circular pipe. The storm drain pipe concentration estimate ($Conc_{pipe}$) was found by multiplying the leaching test DOC (Table 9) results for wood ($W_{test\ i}$), leaves ($L_{test\ i}$), and grass ($G_{test\ i}$) by the mass estimated in the pipe and the leaching time for each of the five subsamples (Δt_i) all divided by Vol_{pipe} . “i” is the index for each of the time at which a subsample was taken. The values used in this estimation and the results are shown in Table 10 and 11, respectively.

$$MP_{wood} = M_{wood} * W_{dil} * \frac{Vol_{pipe}}{Vol_{reactor}} \quad (4)$$

$$MP_{leaves} = M_{leaves} * L_{dil} * \frac{Vol_{pipe}}{Vol_{reactor}} \quad (5)$$

$$MP_{grass} = M_{grass} * G_{dil} * \frac{Vol_{pipe}}{Vol_{reactor}} \quad (6)$$

$$Conc_{pipe} = \frac{\sum_{i=1}^5 ((W_{test\ i} * MP_{wood}) + (L_{test\ i} * MP_{leaves}) + (G_{test\ i} * MP_{grass}) * \Delta t_i)}{Vol_{pipe}} \quad (7)$$

Flow data obtained from a USGS stream gauge site at 1700 South in Salt Lake City was used to find Q_{JR} . Q_{JR} was then divided by a visually estimated velocity (V_{JR}) to get a flow area (A_{JR}) for the river reach where the samples were collected. The A_{JR} was converted to a flow volume (Vol_{JR}) by multiplying it by a 1 foot cross section of river.

$$A_{JR} = \frac{Q_{JR}}{V_{JR}} \quad (8)$$

$$\text{Conc}_{JR} = \text{Conc}_{\text{pipe}} \frac{\text{Vol}_{\text{pipe}}}{\text{Vol}_{JR}} \quad (9)$$

Table 10: Mass estimation calculation summary

Volume Estimation				Mass Estimation				
Q_{JR}	180	CFS	Leaching Test		Dilution		Mass in	
V_{JR}	2	FPS	M_{wood}	Mass (g)	W_{dil}	0.05	MP_{wood}	Vol_{pipe}
A_{JR}	90	SF	M_{leaves}	1.84	L_{dil}	0.10	MP_{leaves}	124 g
Vol_{JR}	2,548	L	M_{grass}	2.60	G_{dil}	0.05	MP_{grass}	57 g
Vol_{pipe}	556	L						80 g
$\text{Vol}_{\text{reactor}}$	0.9	L						

The results of this comparison indicate that the leaching can accurately estimate DOC loading (Table 11).

Table 11: Comparison of water sample and leaching test sample analyses

	TSS	VSS	DOC
	Concentration	Concentration	Concentrations
	(mg/L)	(mg/L)	(mg/L)
Estimated	0.56	0.86	10.1
Measured	48 ± 20	11.0 ± 5.0	10.3 ± 2.0

Chemical and Biochemical Oxygen Demands of Leachate from CPOM

The leachate from the leaching test was analyzed for chemical and biochemical oxygen demand (COD and BOD) to determine the oxygen demands associated with the CPOM-derived particulate and dissolved materials. The analyses were conducted at the

Utah Water Research Laboratory, and followed the methods outlined in earlier sections of this study.

Chemical Oxygen Demand

Production rates of chemical oxygen demand (COD) were analyzed as both filtered and unfiltered leachate from the leaching test. The rate of production of COD was highest for both the filtered and unfiltered samples during the first 1 hour of the test, then decreased throughout the remainder of the study (see Tables 12 and 13; Figures 9 and 10). The results of this analysis also indicate that there is not a significant difference between the unfiltered and filtered COD results (with exception of the 10-hour samples, see Figure 11). From this it is inferred that the COD of this study can be attributed to the dissolved material in the sample. This small amount of particulate COD is consistent with the low solids concentrations in these leachate samples reported above. The rate constants of COD generation were also calculated and are presented in Table 14 as a mean value for the combination of unfiltered and filtered since the two datasets are not significantly different. The three rates are significant because their 95% confidence intervals do not overlap zero. An ANOVA analysis of the rates produced a P-value equal to 0.056 which conflicts with the confidence interval results. According to the ANOVA analysis the rate constants are uniquely significant at $P < 0.1$ or at a 90% confidence interval.

Table 12: Generation of COD in unfiltered leachate from leaching test (95% conf. interval shown)

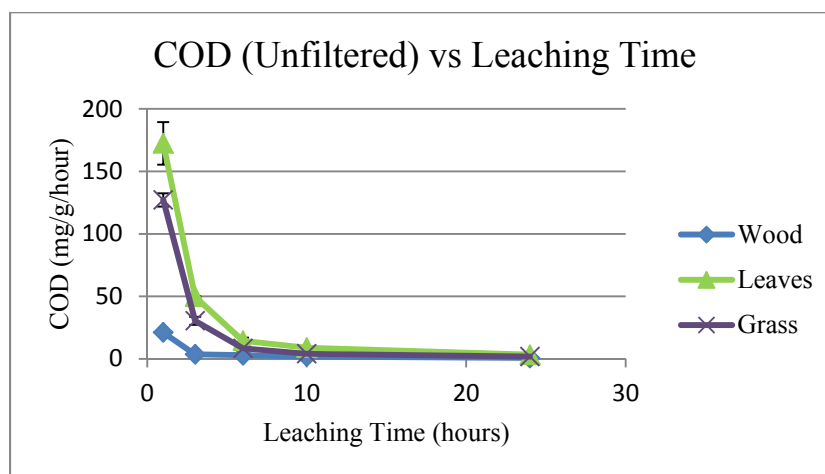
COD (Unfiltered) (mg/g/hour)					
CPOM Type	Leaching Time (hours)				
	1	3	6	10	24
Wood	21.1 ± 1.9	3.6 ± 0.36	2.92 ± 1.7	1.8 ± 0.37	0.74 ± 0.23
Leaves	172 ± 17.0	49.7 ± 0.39	14.5 ± 2.5	9.0 ± 0.81	3.3 ± 0.12
Grass	127 ± 5.3	30.5 ± 3.2	8.4 ± 1.6	4.1 ± 1.4	1.8 ± 0.37

Table 13: Generation of COD in filtered leachate from leaching test (95% conf. interval shown)

COD (Filtered) (mg/g/hour)					
CPOM Type	Leaching Time (hours)				
	1	3	6	10	24
Wood	10.1 ± 2.6	4.3 ± 1.7	2.1 ± 0.62	1.5 ± 0.71	0.73 ± 0.23
Leaves	169 ± 7.2	49.7 ± 1.4	14.0 ± 2.7	6.5 ± 0.36	2.6 ± 0.07
Grass	122 ± 5.9	31.0 ± 3.0	9.2 ± 1.8	5.9 ± 1.7	1.5 ± 0.22

Table 14: COD generation second-order rate constants (95% conf. interval shown)

CPOM Type	Rate Constant k (1/(mg/g-hour))	R²
Wood	0.057 ± 0.012	0.91
Leaves	0.015 ± 0.002	0.99
Grass	0.028 ± 0.003	0.98

**Figure 9:** Generation of total COD in leachate (95% conf. interval shown)

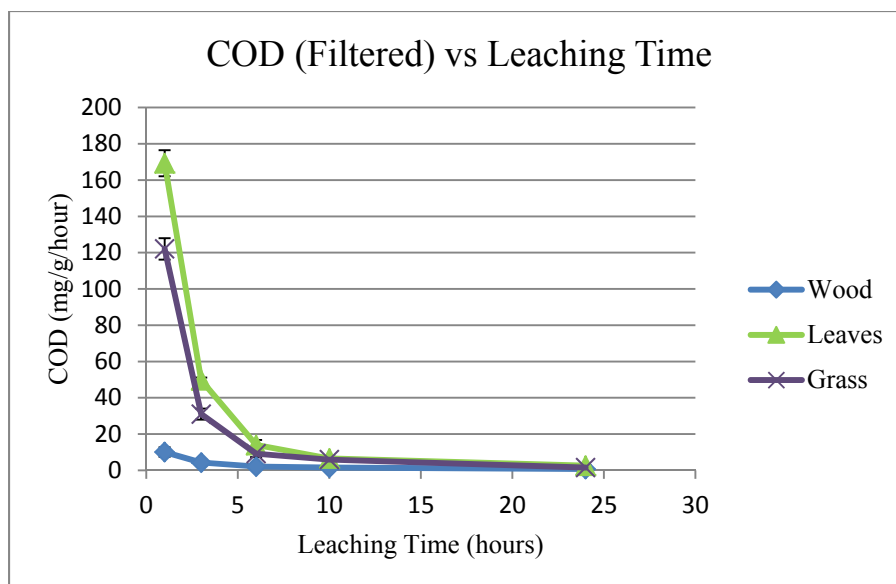


Figure 10: Generation of soluble COD in leachate (95% conf. interval shown)

Biochemical Oxygen Demand

Rates of production of ultimate total, carbonaceous, and nitrogenous biochemical oxygen demand (BODu, cBODu, and nBODu) were analyzed and the results are summarized in Tables 15, 16, and 17 and Figures 11, 12, and 13. The results of these analyses indicate that the generation rates follow a similar pattern as the other parameters. Results show that the percentage of total BODu that is carbonaceous is between 83% and 100%, and that during the first 1-3 hours 93% - 95% of the total BODu and 93%-94% of the total cBODu generated during the test were leached. The results of the nBODu were not consistent with expected results. This is likely due to the fact that dissolved oxygen (DO) levels for the 1 and 3 hour leaf and grass samples dropped below 0.50 mg/L several times during the 20-day test period. When the DO levels get that low the aerobic nitrification process is halted and no longer produces nitrate. The DO levels were able to drop to that level because the oxygen depletion rates were so rapid that the laboratory procedure for reaeration could not be performed sufficiently often enough to maintain a

more desirable DO level in the test bottle. Results that were below the detection level have been omitted.

Table 15: Ultimate total BOD generated during leaching test

Total BODu (mg/g/hour)					
CPOM Type	Leaching Time (hours)				
	1	3	6	10	24
Wood	9.3 ± 2.7	1.5 ± 0.07	0.33 ± 0.20	0.32 ± 0.04	0.16 ± 0.03
Leaves	96.4 ± 10.2	24.9 ± 2.5	3.3 ± 1.6	2.2 ± 0.47	1.1 ± 0.18
Grass	65.0 ± 3.1	18.2 ± 1.7	3.2 ± 0.31	1.9 ± 0.37	0.71 ± 0.10

Table 16: Ultimate carbonaceous BOD generated during leaching test

cBODu (mg/g/hour)					
CPOM Type	Leaching Time (hours)				
	1	3	6	10	24
Wood	7.0 ± 2.3	1.5 ± 0.19	0.14 ± 0.13	0.37 ± 0.08	0.2 ± 0.06
Leaves	99.9 ± 6.6	21.3 ± 2.8	6.2 ± 1.8	2.2 ± 0.57	1.2 ± 0.28
Grass	64.9 ± 2.9	16.0 ± 2.6	3.6 ± 0.84	1.6 ± 0.65	0.76 ± 0.06

Table 17: Ultimate nitrogenous BOD generated during leaching test

nBODu (mg/g/hour)					
CPOM Type	Leaching Time (hours)				
	1	3	6	10	24
Wood	2.2 ± 0.76	0.05 ± 0.13	0.20 ± 0.32		
Leaves		3.5 ± 4.8			
Grass	0.14 ± 3.7	2.2 ± 1.3		0.25 ± 0.37	

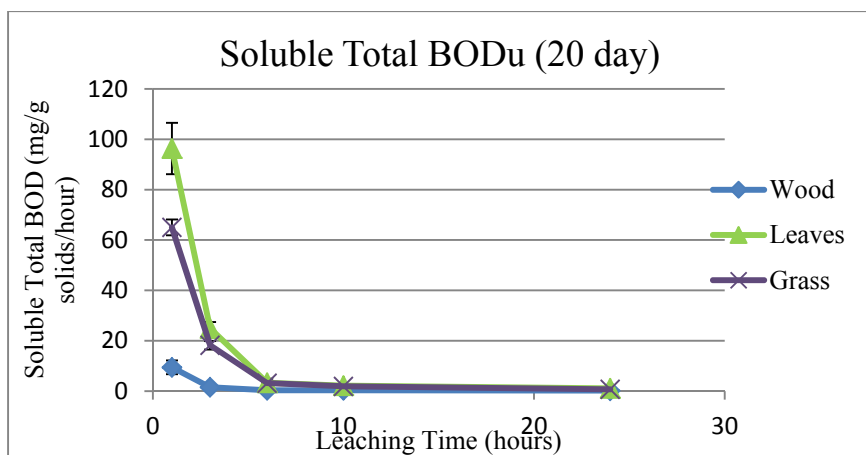


Figure 11: Soluble total BODu generated during leaching test (95% conf. interval shown)

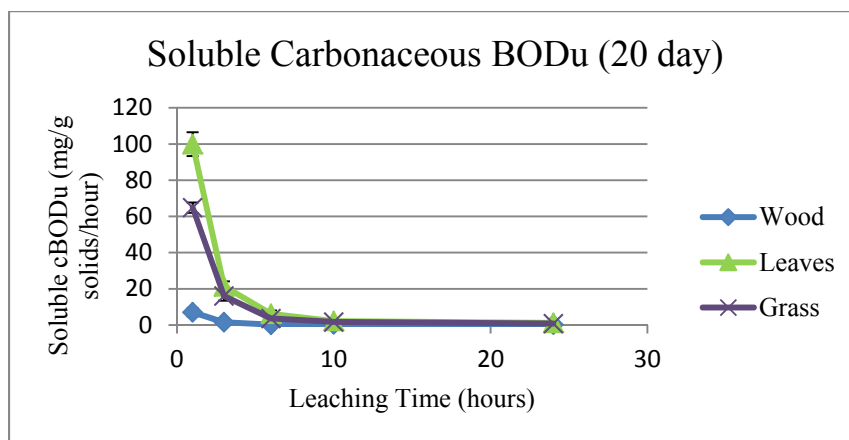


Figure 12: cBODu generated during leaching test (95% conf. interval shown)

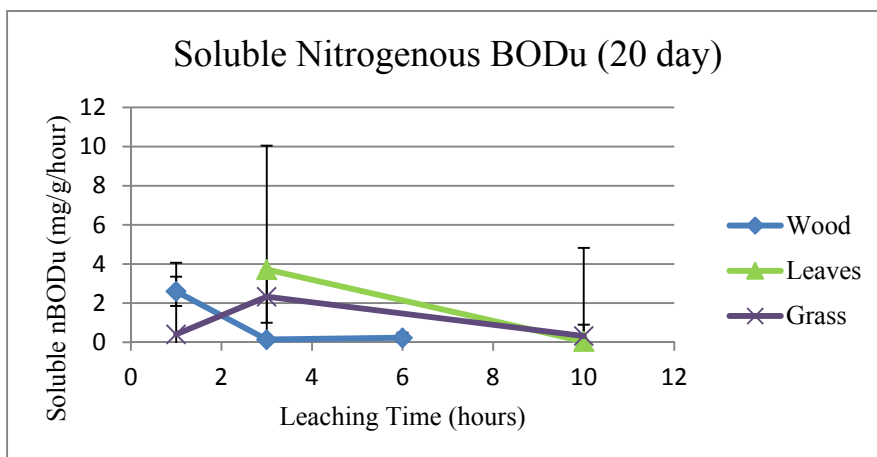


Figure 13: nBODu generated during leaching test (95% conf. interval shown)

BOD Decay Rate Constants

The decay rate constants for each of the BOD tests were calculated using the Thomas Method (Metcalf and Eddy 1979). This method uses a series expansion of the BOD equation (Equation 10), which is then rearranged to linearize the results (Equation 11). The raw BOD data are time adjusted (t_{adj}) for a lag phase (0 – 5 days), and BOD associated with nitrification is disregarded.

$$Y = L_0(1 - e^{-k_1 t}) \quad (10)$$

$$\left(\frac{t}{Y}\right)^{\frac{1}{3}} = \frac{k_1^{\frac{2}{3}}}{6L_0^{\frac{1}{3}}}t + (k_1 L_0)^{-\frac{1}{3}} \quad (11)$$

A plot of the adjusted data is produced with adjusted time on the x-axis and adjusted time over BOD all to the one-third power on the y-axis (see Figure 14). The slope and intercept of the linear regression line provide two equations that can be used to determine the values of the ultimate BOD and the decay rate constant (base e) for the data set. This method is only valid for the cBOD_u measurements. The results of these calculations are shown in Table 18, and indicate that the BOD decay rates for leaves and grass were at a maximum in the 1-hour samples, and a minimum in the 3-hour samples. The 6-, 10-, and 24-hour samples are statistically the same. This suggests that the material in the 3-hour samples is less biodegradable than at 1 hour. It also suggests that the materials in the 6-, 10-, and 24-hour samples are similar to each other in biodegradability. The 1-hour wood decay rate constant was the highest rate produced, and is consistent with that of treated wastewater effluent (Masters and Ela 2008). The 3-, 10-, and 24-hour samples are statistically the same. Again, this suggests that there is a portion of soluble material that leaches from the wood and is highly biodegradable. Due to the high levels of variability

the rates for wood in the 6-hour samples have been excluded from Table 18 and Figure 15. Also, for summary tables of the Thomas Method calculations please refer to Appendix F.

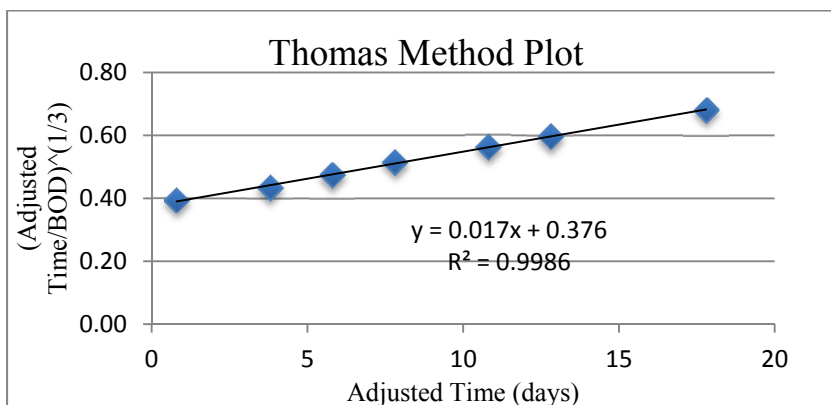


Figure 14: Example of a Thomas Method plot

Table 18: BOD decay rate constants

Decay Rate Constant “k” (1/day)					
CPOM Type	Leaching Time (hours)				
	1	3	6	10	24
Wood	0.29 ± 0.06	0.04 ± 0.01		0.04 ± 0.02	0.03 ± 0.01
Leaves	0.08 ± 0.01	0.01 ± 0.00	0.02 ± 0.00	0.02 ± 0.01	0.02 ± 0.00
Grass	0.09 ± 0.00	0.01 ± 0.00	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.00

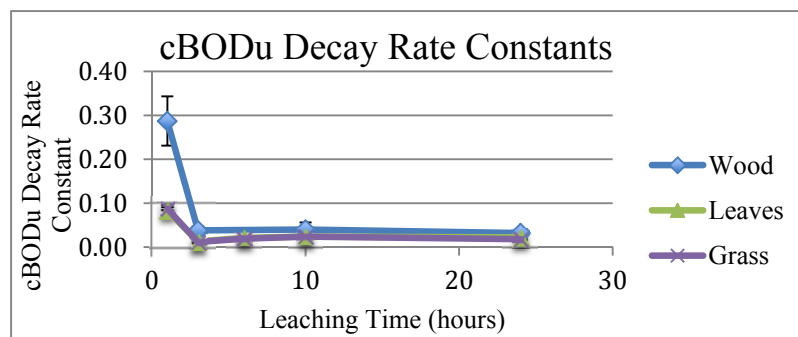


Figure 15: cBODu decay rate constants

Analysis of CPOM Composition

Comparison Plots and Regression Equations

The results of the DOC, TDN, and COD analyses were plotted in comparison to soluble BOD and regression equations were determined to evaluate which of these parameters was the best indicator(s) for BOD (see Figures 16 and 17). This understanding would be useful in determining the BOD associated with a parameter that is more easily or quickly measured. The DOC and COD analyses produced the highest correlation coefficients (0.9893 and 0.9956, respectively) that suggest that DOC and COD would be good parameters for use in predicting BOD.

There are a few exceptions to this pattern such as for the BOD to DOC ratio for wood, which has a sharp increase from 6 to 10 hours then a gradual decrease to 24 hours. Figure 18 shows the graph of the ratio of BOD to DOC vs time. The graphs of BOD to COD and BOD to TDN are located in Appendix D. This suggests that the substances leaching from the CPOM samples during the first 1-3 hours are the most labile, but with continuing contact with water there continues to be somewhat less biodegradable organic material leaching at a steady rate.

Carbon to Nitrogen Ratio in Leachate

The ratio of carbon to nitrogen in the leachate was determined using the DOC and TDN results. Comparing the C:N ratio in the leachate to the C:N ratio in the solids gives an indication of the nature of the material leaching out of the solids. Table 19 contains the C:N ratio of the solids and the leachate.

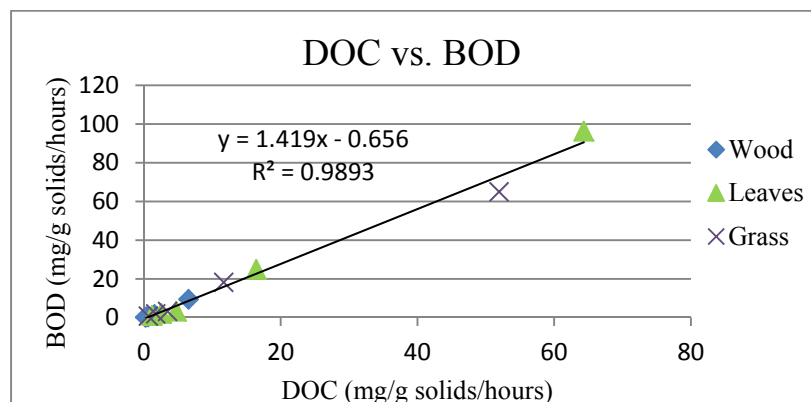


Figure 16: Comparison of DOC to total BODu

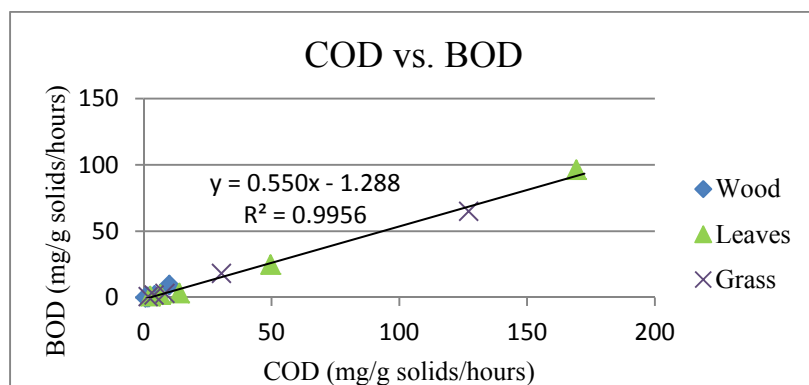


Figure 17: Comparison of COD to soluble total BODu

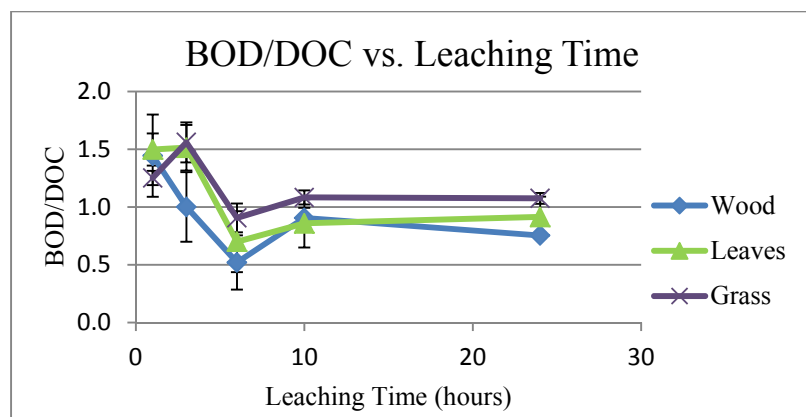


Figure 18: Ratio of total BODu to DOC versus leaching time

Table 19: C:N ratio of the CPOM solids and leachates

C:N Ratios		
CPOM Type	Solids	Leachate
Wood	81.8	20.6 ± 5.6
Leaves	13.3	23.0 ± 5.9
Grass	11.3	12.9 ± 2.8

The wood samples show a decrease in the C:N ratio from the solids to the leachate which suggests that the carbon compounds in the wood are less soluble than the small amounts of nitrogen compounds contained in the wood. Conversely the ratio increases for leaves which suggests the carbon compounds are more soluble than the nitrogen compounds. The ratio for grass is statistically the same for both the solids and the leachate which suggests the carbon and nitrogen compounds are equally soluble.

The ideal C:N ratio for biological breakdown of organic material has been determined to be 30 to 35 (Washington State University-Whatcom County Extension 2014), so the results of this study indicate that CPOM comprised of wood, leaves, and grass produce conditions that are nitrogen rich in the leachate. These results indicate that the biological processes involved in the decomposition of organic matter are dependent on the amount and type of carbon present, and not the amount of nitrogen.

SUMMARY OF RESULTS AND DISCUSSION

The impact of the CPOM collected and stored in storm drains and outlets into the Jordan River has been partially quantified in this study by comparing the rate of decomposition of CPOM in water into particulate and dissolved materials to its associated oxygen consumption. Also shown was that 87% to 92% of the total dissolved material generation and 93% - 95% of the total oxygen demanding materials leaches from the CPOM within the first 1 to 3 hours after the CPOM enters the water.

By comparing the results of DOC, COD, and BOD analyses, it was determined that DOC and COD are good parameters for use in predicting the BOD of a CPOM-derived dissolved organic material. It was also determined that the nature of the material leaching from CPOM in water varies with time with the most labile materials being generated within the first 1 to 3 hours after entering the water. Also, the ratio of carbon to nitrogen in the leachate suggests that the processes are regulated by the levels of biodegradable carbon. Therefore using DOC to estimate BOD would be justified.

Generation rate constants for DOC, TDN and COD were calculated and presented for each CPOM type. DOC and TDN rate constants were estimated with a second-order approximation, and were analyzed separately for each CPOM type. This produced three rate constants which were averaged and a confidence interval was determined. Table 20 shows the overall generation rate for each parameter in the leaching test.

Table 20: Overall generation rate constant for each parameter

Parameter	Rate Constant (1/mg/g-hour)
DOC	0.10 ± 0.05
TDN	2.32 ± 1.54
COD	0.035 ± 0.014

Engineering Significance

Based on the results of this study, it can be said that CPOM captured in storm drain systems can have a significant impact on the dissolved oxygen levels in the storm and river water into which the CPOM is discharged within just a few hours after entering the waterway. However, the true magnitude of the impact of CPOM on the Jordan River has not been determined in this study because only estimations were made of flow and mass loading rates to the river. Further study of stream and storm drain flow rates and CPOM loading rates in the watershed is necessary to determine the extent of mitigation efforts necessary to improve water quality in the Jordan River.

This study does provide an understanding of what type of mitigation efforts should be implemented if it is confirmed that they are necessary. While the final selection of mitigation efforts is dependent on the loading and flow rates to be mitigated, a few possible structural and non-structural solutions are discussed below.

Non-Structural Solutions

A non-structural solution is one that does not involve construction of a structure such as a best management practice (BMP) or an existing storm drain. These solutions would involve changes to or implementation of management practices that are intended to reduce CPOM loading or prevent CPOM from entering storm drains or waterways in the first place. An example of this would be Salt Lake City's Curbside Compost program

that is already in place (<http://www.slcgov.com/slccgreen/curbsidecompost>). While the purpose of this program is to reduce loading on the city's landfill, it could also be used to encourage Salt Lake City residents to more closely manage the amount of yard waste that escapes their yards and ends up in a storm drain or gutter.

Salt Lake City also conducts routine street-sweeping operations throughout the city. On average the City sweeps the entire city every 40 days (<http://www.slcgov.com/streets/streets-traffic-operations>). These efforts could be modified to plan their sweepings in areas that produce the highest CPOM loadings 1-2 days prior to an anticipated storm event. Limitations with this solution include the fact that with rain often comes wind and freshly swept curbs can quickly fill with wind-blown debris and leaves.

Structural Solutions

A structural solution is one that would involve installation and maintenance of a structure such as a bio-swale, storm drain, or mechanical CPOM removal system. As with non-structural solutions, the selected solution is dependent on results of future studies of CPOM loading and stream and storm drain flow rates. Based on the understanding from this study that the majority of the BOD is generated within the first 1 to 3 hours after the CPOM enters the water, the selected solution should be located in the watershed where it can remove any CPOM in the water within a matter of minutes after it entered. Also, the selected solution must be able to completely remove the CPOM from the water in order to prevent further leaching of CPOM to generate soluble BOD in the stormwater. The current practice of capturing the CPOM at storm drain outlets to the Jordan River does

not accomplish either of these selection criteria. Table 21 summarizes the benefits and drawbacks of different potential solutions that could be implemented.

QUAL2kw Water Quality Model

The results of this study can also be applied to water quality modeling efforts using models like QUAL2Kw or similar programs. This study has developed a better understanding of the cBODu rate constants that can be applied to the Jordan River QUAL2Kw model. This model considers the initial cBOD loading rates from point and non-point sources, as well as a “fast” and “slow” decay rate for cBOD. During the first phase of the Jordan River TMDL study, the QUAL2kw model had no values inputted for cBODu loading, and the “fast” and “slow” decay rate constants was left at the default value of 0.06. Results presented in previous sections from this study suggest a more appropriate value would be in the range of 0.08/day to 0.09/day for “fast” and 0.01/day to 0.02/day for “slow”. This indicates that the QUAL2Kw model underestimates the “fast” cBOD decay while overestimating the “slow” cBOD decay. The ultimate effect of these incorrect estimations is dependent on the estimates of initial cBOD both in the headwaters as well as the river reaches.

Table 21: Summary of potential solutions for CPOM impact to the Jordan River

Solution	Benefit	Drawback
Modify Green Waste Collection Program (Non-Structural)	<ul style="list-style-type: none"> - Already implemented - No construction required 	<ul style="list-style-type: none"> - Program must be managed continually for the foreseeable future - May require additional city/county staff
Modify Street Sweeping Program (Non-Structural)	<ul style="list-style-type: none"> - Already implemented - Manages other pollutants as well 	<ul style="list-style-type: none"> - Requires anticipation of rain events - Storms can cause additional CPOM to fall and enter storm drains
Bio-swale (Structural)	<ul style="list-style-type: none"> - Utilizes natural processes for pollutant removal - Removes other pollutants as well - Can retain CPOM until removed by routine maintenance - Pollutant removal efficiencies well studied 	<ul style="list-style-type: none"> - Requires routine maintenance of CPOM removal and landscaping - Can only treat portion of flows; would require significant reconfiguring of storm drain system
Self - Cleaning Trash Screen (Structural)	<ul style="list-style-type: none"> - Continuous removal of trash and CPOM in waterway - Can be self-powered to eliminate motors etc. (Example photos located in Appendix E) 	<ul style="list-style-type: none"> - Only treats trash and CPOM problems - Requires routine maintenance - May not be appropriate for flows and loading at 13th and 9th South locations

CONCLUSIONS

The hypothesis of this study was that CPOM stored in the storm drain systems that discharge into the Jordan River results in significant input of biochemical oxygen demand (BOD) during storm events in the form of biodegradable dissolved organic carbon (DOC) and biodegradable OM was studied using three objectives. The three study objectives are restated below as well as conclusions associated with each objective:

Objective 1: Determination of chemical characteristics of CPOM types.

The conclusions drawn as part of Objective 1 are:

- The organic materials used in this study exhibited difference in carbon and nitrogen content and chemical oxygen demand. The carbon to nitrogen ratio of the wood was approximately 6 to 7 times higher than those of leaves and grass.
- The chemical oxygen demand of the various CPOM exhibited high levels of variability among the triplicate samples of each CPOM type, and therefore could not be considered statistically different from each other.

Objective 2: Determination of generation rate of various water quality parameters in CPOM leachate.

The conclusions drawn as part of Objective 2 are:

- The CPOM solids in the leaching test exhibited similar patterns for each of the parameters analyzed. The maximum normalized amount of each parameter was measured in the first hour samples and the minimum normalized amount was measured in the last sample.

- An estimation of TSS, VSS and DOC in the Jordan River using the results of the leaching test produced DOC levels that were consistent with those measured in water samples taken from the Jordan River. This suggests that based on loading and flow rates the Salt Lake City storm drain system could be a significant source of CPOM-derived BOD in the Jordan River.
- DOC production in relation to the C:N ratio of the CPOM types was found to be consistent with the patterns discussed in McArthur and Richardson (2002), namely that the green leafy materials produced 1.5 to 8 times more DOC than woody materials. The results of this experiment were in the range of 8 to 10 as more from the green materials over the wood materials.
- The change in C:N ratio from the solid to the leachate indicate that there are significant differences in the materials leaching from each CPOM type, and that the system is limited by the amount and types of carbon present rather than nitrogen.

Objective 3: Compare laboratory results to Jordan River water samples, and determine the biochemical and chemical oxygen demands of the leachate from the CPOM samples.

The conclusions drawn as part of Objective 3 are:

- There was a correlation between the DOC from the leaching test and the BOD test, which means DOC could be used as a surrogate measurement for BOD when conducting water sampling in the Jordan River.
- BOD decay rate constants were between 0.08/day and 0.09/day for the 1-hour samples, and 0.01/day to 0.04/day for the 3-, 6-, 10-, and 24-hour samples. The rate used in the Jordan River QUAL2Kw model was 0.06/day.

Future Studies

This study was conducted to determine the impact of CPOM decomposition in storm drains on surface water quality by investigating the rate of decomposition of CPOM and the production of oxygen demanding materials once CPOM enters a waterway. Future studies that could be conducted to compliment this study might include a measurement of CPOM loading to the Salt Lake City storm drain system, as well as an evaluation of CPOM sources in the contributing watershed. Also, a study to evaluate the effectiveness of structural and non-structural BMPs in the Salt Lake City area could use the results from this study to establish initial loading conditions to determine their technical and economic viability as a control measure for water quality improvement in the Jordan River.

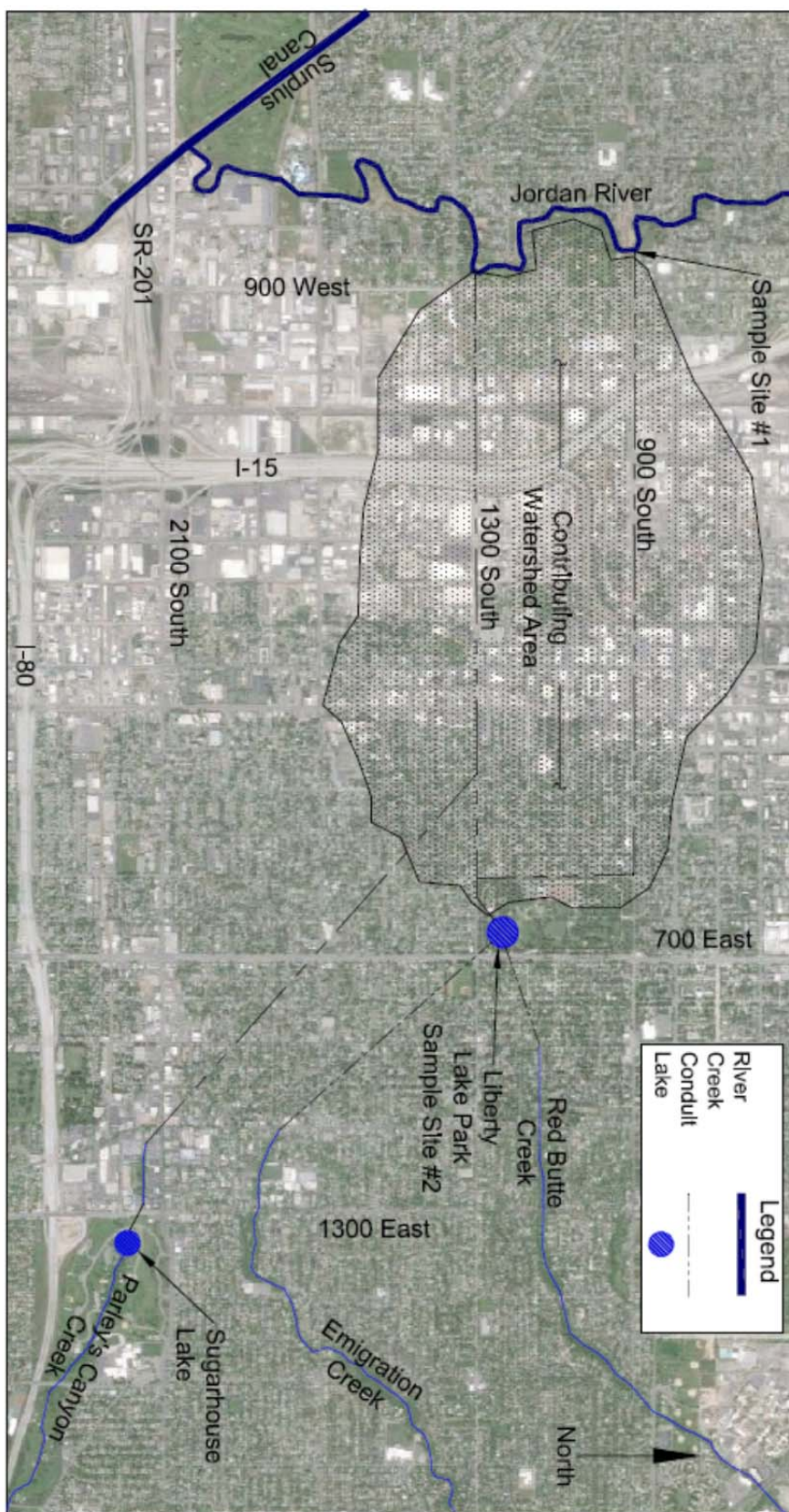
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APPENDICES

Appendix A
Map of Sampling Locations



Appendix B

The Amplified Long Term BOD Test
Georgia Environmental Protection Division,
1989

THE AMPLIFIED LONG-TERM BOD TEST
Protocol/Procedure and Test Specifications

ENVIRONMENTAL PROTECTION DIVISION
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November 15, 1989

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PREFACE

Uses for the "Amplified" Test

The "Long-Term BOD Test" is important. The Test provides the main foundation for defensible wasteload allocations (WLA) and NPDES Permits — especially those derived from mathematical water quality models. There are four key uses for Long-Term BOD Test results:

First: Point source NPDES Permits typically contain BOD limitations expressed as a 5-day BOD (BOD_5). However, math models calculate BOD concentrations as an ultimate BOD (BOD_U). The conversion factor between the two is called the f-ratio, where $f = BOD_U/BOD_5$. Hence, to introduce a BOD_5 Permit limit correctly into a water quality model, BOD_5 must be multiplied by an f-ratio for that particular point source discharge. The appropriate f-ratio comes from a Long-Term BOD Test.

Second: (a) River water (receiving water) for point source discharges contains BOD—a mixture of BOD naturally occurring plus BOD added by point sources along the way. A properly calibrated water quality model requires prior field measurement of the total river BOD, expressed as ultimate BOD. (b) In addition, a calibrated model requires estimates of the rate at which river BOD decays over time. This rate-of-reaction, called k_1 , specifies the fraction of BOD (present at the beginning of a day) lost by biochemical oxidation over the course of a day. (c) Both of these, k_1 and ultimate river BOD, are derived from a Long-Term BOD Test.

Third: BOD can be exerted in two distinct ways— carbonaceous BOD (CBOD) and nitrogenous BOD (NBOD). Successful water quality models require measurements for each component, hence, a correct separation of two different biochemical reactions. The Long-Term BOD Test provides a means for separating CBOD and NBOD for a given water sample.

Fourth: Water quality models provide wasteload allocations expressed as an allowable (point source) concentration of ultimate BOD. Since NPDES Permits require BOD limitations expressed as BOD_5 model results (BOD_U) must be converted back to BOD_5 by dividing by an appropriate f-ratio for that particular discharge. As before, the appropriate f-ratio is derived from a Long-Term BOD Test.

Needs for "Amplified" Test Precision

Amplified precision in the measurement of long-term BOD is important. Precision helps to provide defensibility for wasteload allocations and NPDES Permits. Furthermore, the need for greater test precision has grown in recent years. There are four key reasons for greater Long-Term BOD Test precision:

First: As the number of NPDES Permits increase at a given river location, the assimilative capacity remaining for new Permits shrinks accordingly. Thus, as time passes, defining "remaining" assimilative capacity can require more exacting calculations of ultimate BOD in the river. This circumstance requires more exacting laboratory measurements of BOD, which requires greater precision and quality control during the Long-Term BOD Test.

Second: NPDES Permits can grow more stringent over successive Permit renewal periods. Secondary treatment Permits can tighten to advanced secondary; advanced secondary Permits can tighten further to advanced tertiary treatment levels. With each successive tightening, the quality of discharged BOD changes from a more-enriched faster-acting BOD, to "leaner" slower-acting BOD. Measuring leaner, slower-acting BOD requires greater precision and quality control during the Long-Term BOD Test.

Third: As levels of waste treatment improve in a given river system, river BOD levels usually drop—approaching natural "background" concentrations. Measuring lower, background concentrations of river BOD (for water quality modeling) requires greater precision and quality control during the Long-Term BOD Test.

Fourth: Regulatory decisions evolve over time; simpler more straightforward wasteload allocations are generally developed first. More complex, more strongly contested NPDES Permits take more time and, thus, remain to be developed after the simpler permits have been resolved. More complex, more strongly contested wasteload allocations need to be supported by more defensible BOD measurements which, therefore, require greater precision and quality control during the Long-Term BOD Test.

Changing Long-Term BOD Test Requirements

To provide adequately for the defensibility of contemporary water quality models, the Division has promoted four key changes in Long-Term BOD Test requirements:

First: The Division now requires more tests than ever before for important projects. A recent modeling effort required 106 tests. By comparison, a successful study 10-15 years ago might have used a dozen tests at most. Since each test occupies a fixed amount of laboratory incubator space, the need for incubator space alone has increased ten-fold. Moreover, for a given project, all tests must be performed under strictly identical conditions with consistent temperature control. Identical conditions are relatively easy to achieve for 12 concurrent tests. Uniform conditions are much more difficult to attain for 106 concurrent tests. Problems for records keeping and proper data management likewise increase, in similar proportions, as the number of concurrent tests increase.

Second: The Division now requests tests of longer duration than ever before. Gone are the days of the 15-day or 21-day test. Samples now must be incubated for at least 40 days, and often for 60 days, 90 days, or longer. Since each test, day-by-day, must be consistently

controlled and measured, a 40-day test creates more demanding laboratory expectations than a 21-day test. Even a change in laboratory personnel in the middle of a 40-day test can adversely affect defensibility of test results.

Third: Calculations applied to long-term data now make finer distinctions between various test results than ever before. In the past, rates-of-reaction (k_1) were commonly found to be around 0.3 to 0.6. Then, even rough calculations and graphical approximations could detect a difference between sample rates at this level. Now, however, rates-of-reaction are generally lower. Calculations must distinguish between rates-of-reaction as low as 0.04 to 0.06. Similarly, in the past, ultimate BOD's could run as high as 20 or 30 mg/L in the laboratory bottle. Rough calculations of these ultimate BOD values were acceptable then. Now, important BOD samples may contain an ultimate BOD as low as 2 or 3 mg/L. This fact requires more exacting calculations and more precise laboratory measurements.

Fourth: In the past, BOD test results could be processed easily by hand by inexperienced technicians. However, tests of longer duration mean more-and-more data points for a single sample. Furthermore, more exacting sample results demand more sophisticated calculations. To this, add statistical calculations of mean square error and other statistical measures of precision and confidence. Thus, hand calculations now are not only impractical, they are impossible. The processing of Long-Term BOD Test data now requires repetitive non-linear curve-fitting by numerical methods. This means (1) calculations must be performed by computer, (2) laboratory tests must be designed to produce results suitable for sophisticated data processing, and (3) experienced analysts are required.

An "Amplified" Long-Term BOD Capability

To keep pace with these developments, the Division has taken two major steps to improve our long-term capability:

Step 1: We have sponsored user-friendly computer software for non-linear, multiple-component analysis of long-term BOD data. This program (LT/BOD), designed for our HP9845A computer, provides for repetitive first-order or logistics curve fitting to time-series BOD data, and produces statistical measures and useful graphics for each curve fitting attempt.

Step 2: We have sponsored this laboratory protocol to standardize the fine techniques of long-term BOD measurement. This protocol provides the systematic quality assurance/quality control (QA/QC), to be applied during the Long-Term BOD Test, necessary for the ever growing demands on the use of long-term BOD data.

Protocol User Groups

This protocol has been designed for three user groups. Group 1: The Division will use this procedure in our laboratory. Group 2: The Division will attach this document to contracts for long-term BOD laboratory services, thereby requiring that commercial laboratories conform to these procedures by contract. Group 3: The Division will provide this document to reviewers who wish to examine the quality control measures supporting the Division's long-term BOD work.

NOTE:

This document does not substitute for procedures published in Standard Methods and/or EPA's Methods for Chemical Analysis of Water and Wastes. Instead, this document assumes these two procedural references as a starting point.

TABLE OF CONTENTS

	Page
PART 1 - A BRIEF INTRODUCTION TO BIOCHEMICAL OXYGEN DEMAND	58
1.1 Carbonaceous BOD	58
1.2 Nitrogenous BOD	62
1.3 The Need for Exact QA/QC	62
 PART 2 - PROTOCOL/PROCEDURE FOR THE "AMPLIFIED"	
LONG-TERM BOD TEST	64
2.1 Planning, Test Design, and Coordination with the Division	65
2.1.1 Test duration	65
2.1.2 Dilution water (dilution water)	65
2.1.3 Bacterial seed	66
2.1.4 Special test requirements	66
2.1.4.1 Nitrification inhibition	66
2.1.4.2 Filtering	66
2.1.4.3 Concurrent chemical testing	67
2.1.5 Labware and laboratory equipment	67
2.1.6 Systematic sample identification convention	67
2.2 Laboratory and Labware Preparation	68
2.3 Handling and Preparation of Dilution and Sample Waters	68
2.3.1 Sample receipt and initial handling	68
2.3.2 Dilution water handling and preparation	68
2.3.3 Sample water handling, preparation, and special treatments	69
2.3.3.1 Untreated ("Straight") BOD test samples	70
2.3.3.2 Treatment for inhibited samples	70
2.3.3.3 Treatment for filtered samples	70
2.3.4 Test continuity	70
2.4 Instrument Calibration	71
2.4.1 Conductivity meter calibration	71
2.4.1.1 Selection of conductivity standards	71
2.4.1.2 Development of probe calibrations	
2.4.2 DO meter preparation and calibration	72
2.4.2.1 Probe and membrane care	72

TABLE OF CONTENTS (CONT.)

2.4.2.2 Probe and sample bottle adapter assembly	73
2.4.2.3 DO meter calibration	73
2.5 Sample Set-up and Measurement	73
2.5.1 Set-up time	73
2.5.2 Sample set-up	73
2.5.3 Test sample measurement	74
2.5.3.1 Measurement frequency	74
2.5.3.2 Measurement procedure	75
2.5.3.3 Sample replacement and measurement closure	75
2.5.4 Measurement trouble-shooting	76
2.5.5 Sample Reaeration	76
2.5.5.1 Reasons for sample reaeration	76
2.5.5.2 Reaeration procedure	77
2.6 Test Management, Records, and Results	77
2.6.1 Test management	77
2.6.2 Test records	78
2.6.2.1 Instrument calibration data	78
2.6.2.2 Test measurement data	81
2.6.3 Test results	81
2.6.4 Final project laboratory results	81

PART 3 - LIST OF EQUIPMENT	86
-----------------------------------	-----------

LIST OF FIGURES

	Page
FIGURE 1 Typical BOD and DO Remaining Curve	59
FIGURE 2 Typical Two-Stage BOD Curve	60
FIGURE 3 Typical Relationship between Carbonaceous BOD and Bacteria Population	61
FIGURE 4 Typical Relationship between Nitrogenous BOD and Bacteria Population	63
FIGURE 5 Conductivity Meter Calibration Record	79
FIGURE 6 Dissolved Oxygen Meter Calibration Record	80
FIGURE 7 Dissolved Oxygen Measurement Record	82
FIGURE 8 Representative Long-Term BOD Test Plot	83
FIGURE 9 Sample Graph Paper	84

PART 1: A BRIEF INTRODUCTION TO BIOCHEMICAL OXYGEN DEMAND

The Biochemical Oxygen Demand (BOD) Test measures the oxygen required by bacteria to stabilize decomposable organic matter in an aerobic water sample. BOD will also include the oxygen required to oxidize certain inorganic substances (e.g., ferrous iron and sulfides) and reduced forms of nitrogen, namely NH_3 and NO_2^- . The laboratory procedure to measure BOD includes the following general steps: (1) aerate the original water sample; (2) measure the dissolved oxygen in the aerated sample; (3) place the sample in an air tight container; (4) incubate the sample in complete darkness at constant temperature (20°C); then (5) measure dissolved oxygen (DO) regularly over a period of time. As shown in Figure 1, laboratory test results should be plotted as the "DO remaining" curve. By definition, BOD is the mirror image of the DO remaining curve.

The long-term BOD reaction often contains two stages. Carbonaceous BOD (CBOD), or 1st stage BOD, represents the oxygen required by saprophytic bacteria to consume the sample's carbonaceous organic matter. Nitrogenous BOD (NBOD), or 2nd stage BOD, represents the oxygen required by nitrifying bacteria to convert NH_3 to NO_2^- , then NO_2^- to NO_3^- . These two "stages" combined can produce a typical two-stage BOD reaction as shown in Figure 2.

Theoretically, a complete CBOD reaction yields CO_2 and water. A complete stepwise NBOD reaction converts organic nitrogen, ammonia (NH_3), and nitrite (NO_2^-) into nitrate (NO_3^-) as the end product. Therefore, the analysis of BOD laboratory data can often be enhanced by measuring CO_2 and nitrogen species at the beginning and end of each test, and at selected intervals within a given test.

1.1 Carbonaceous BOD

Kinetics (rates) of the carbonaceous BOD reaction depend on the availability of bacteria, availability of organic matter (food), and the nature of the organic matter. Each of these factors can effect the biochemical rate-of-reaction and, therefore, the curvature of the BOD graph. Moreover, any limitations on food and/or bacteria can also change the pattern of BOD reactions over time.

For example, immediately following BOD discharge to a receiving water, the BOD reaction is typically bacteria limited. There is more food (BOD) initially present than the available bacteria can consume. Subsequently, the bacterial population will increase until food becomes the limiting factor. As shown in Figure 3, the bacterial population will increase for a time, then decrease as available food is consumed.

The food-limited portion of this reaction can be usefully approximated by the following first-order equation:

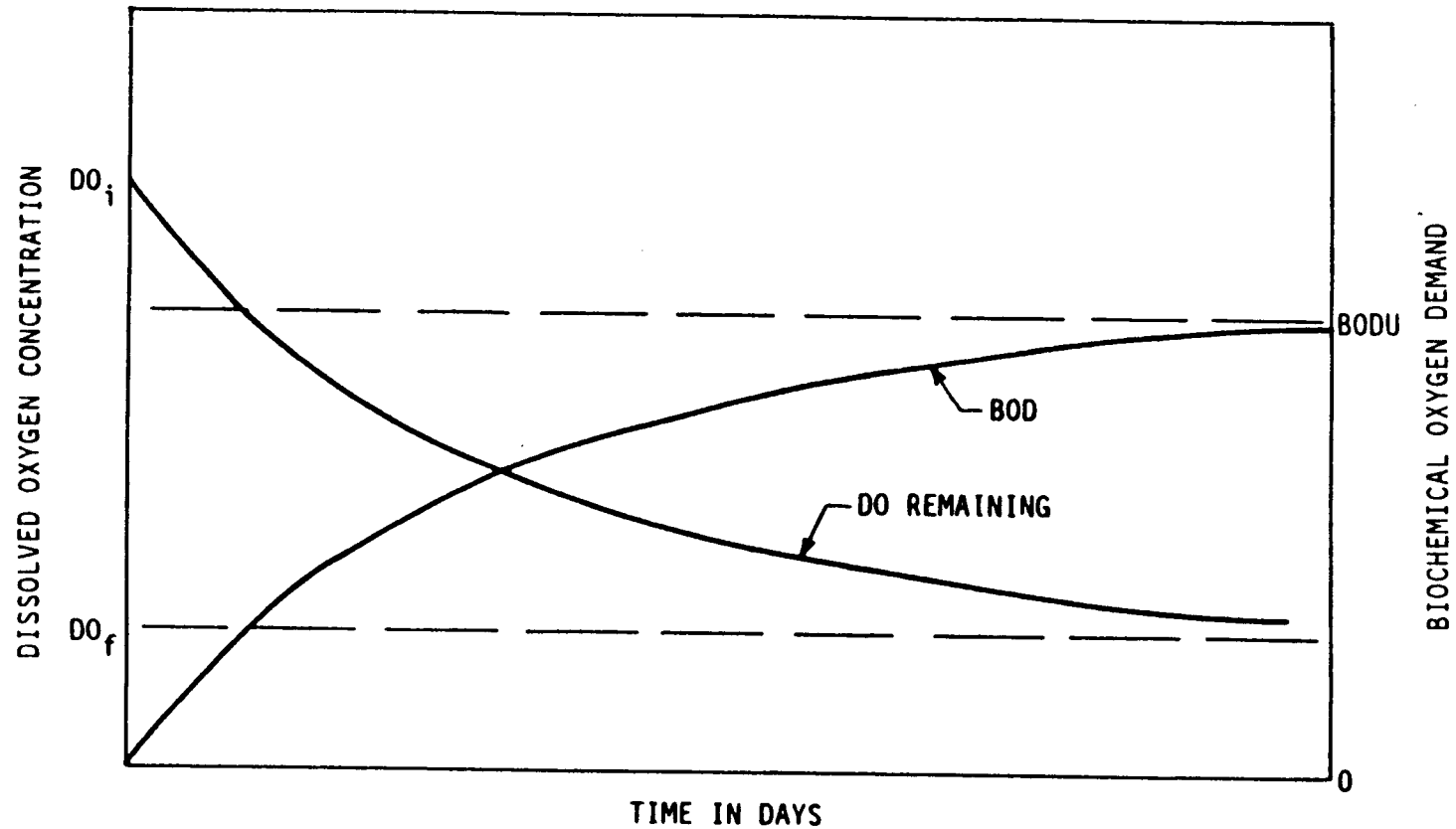
$$\text{BOD}_t = \text{BOD}_u (1 - e^{-k_1 t})$$

where: BOD_t - Biochemical Oxygen Demand after time (t)

BOD_u - Ultimate Biochemical Oxygen Demand

k_1 - Carbonaceous deoxygenation rate

t - Time since beginning of the test



LEGEND

DO_i - INITIAL DO

DO_f - FINAL DO

BODU - ULTIMATE BOD

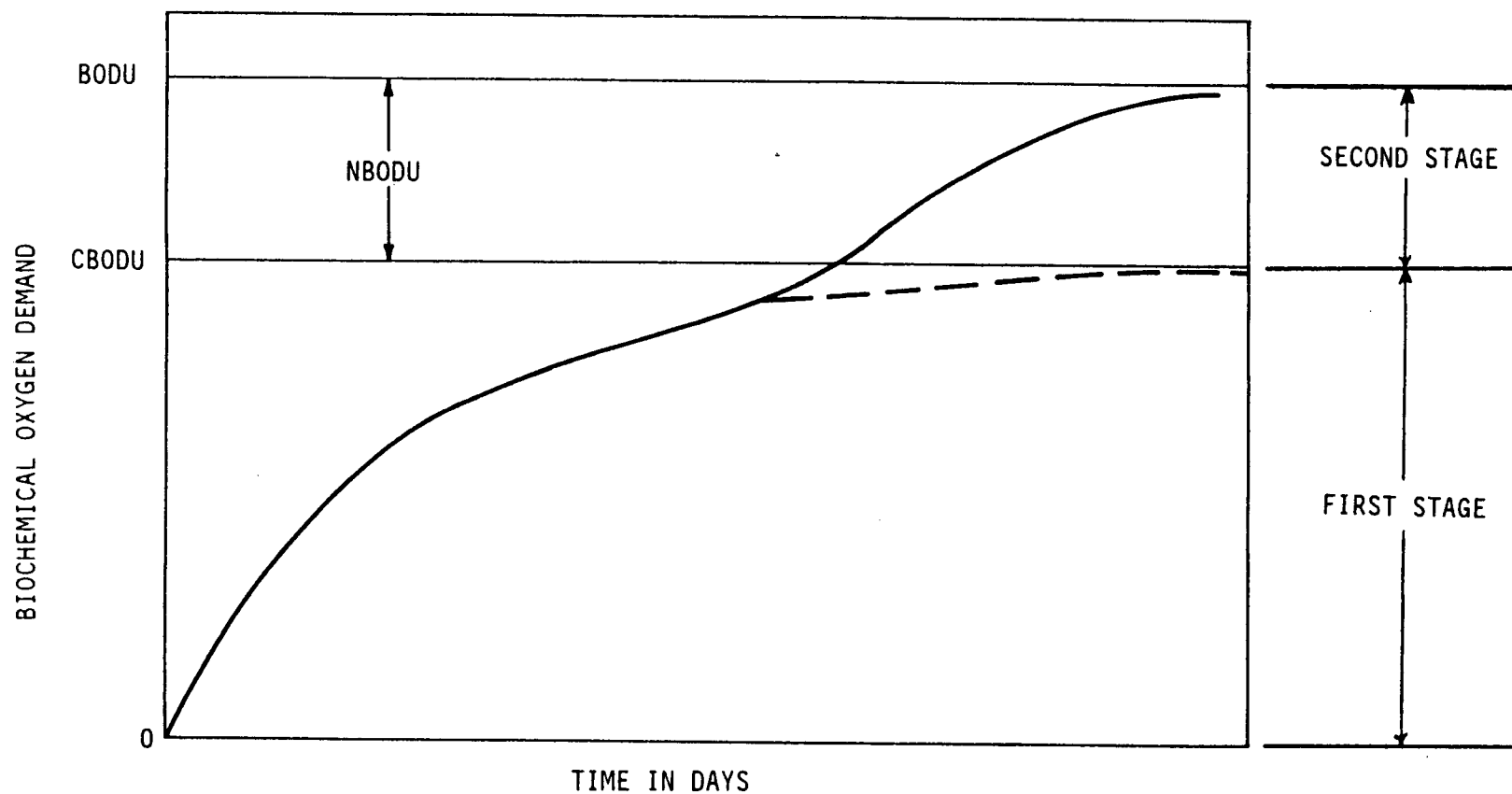
THE AMPLIFIED LONG-TERM
BOD TEST



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TYPICAL BOD AND DO
REMAINING CURVE

FIGURE 1



LEGEND

BODU - ULTIMATE BOD

CBODU - ULTIMATE CARBONACEOUS BOD

NBODU - ULTIMATE NITROGENOUS BOD

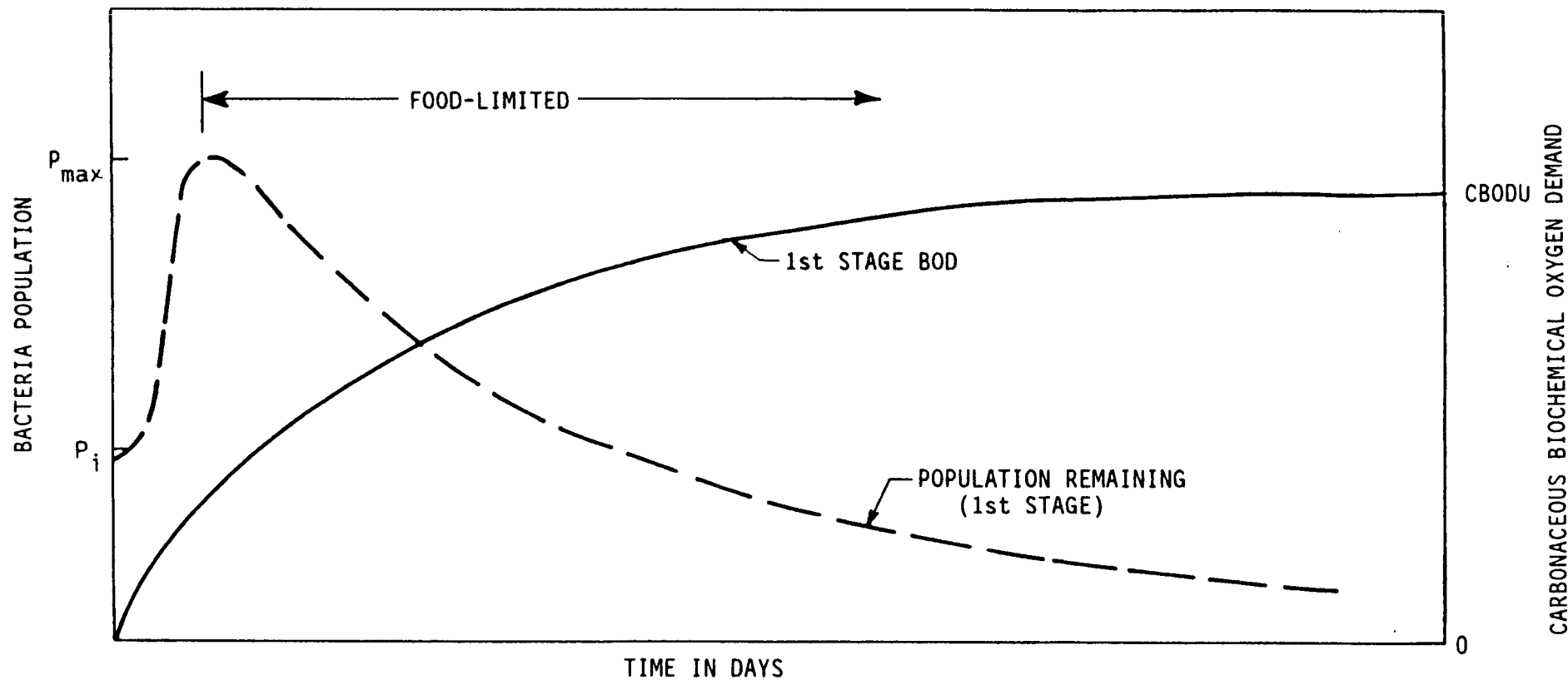
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TYPICAL TWO STAGE
BOD CURVE

FIGURE 2



LEGEND

P_i - INITIAL BACTERIA POPULATION
 P_{max} - MAXIMUM BACTERIA POPULATION
 CBODU - ULTIMATE CARBONACEOUS BOD

THE AMPLIFIED LONG-TERM
 BOD TEST



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TYPICAL RELATIONSHIP BETWEEN
 CARBONACEOUS BOD AND
 BACTERIA POPULATION

FIGURE 3

1.2 Nitrogenous BOD

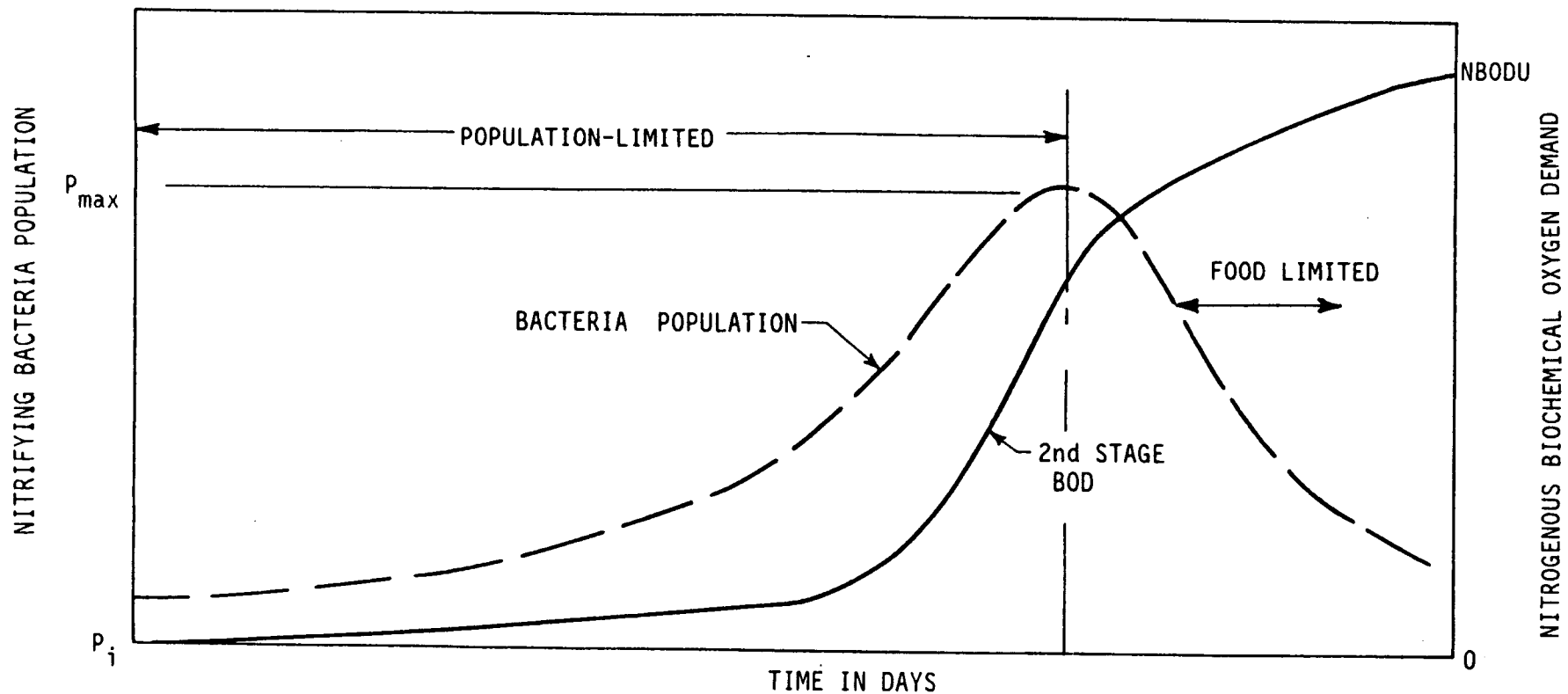
Nitrogenous reactions typically delay onset until after a portion of the carbonaceous demand has been exerted. This time lag represents a natural lag in the population growth of nitrifying bacteria. (It has been theorized that nitrifying bacteria prefer an environment with low concentrations of oxidizable carbon.) Accordingly, depending on the nature of the organic matter (slow or fast reacting) and the concentrations of organic matter, this lag period can vary considerably.

Similar to carbonaceous BOD, this "second stage" reaction (nitrification) is population limited until the maximum nitrifying bacteria population is realized. Then the reaction becomes food limited as shown in Figure 4. The food limited portion can also be usefully approximated by a first-order reaction similar to carbonaceous BOD.

1.3 The Need for Exacting QA/QC

This brief discussion of CBOD and NBOD reactions emphasizes that useful test results depend on the exacting control of living conditions in the laboratory test bottle for carbonaceous and nitrifying bacteria. Exacting control may be relatively easy in the standard 5-day BOD test. However, for 40-day tests (and longer) maintenance of correct and consistent long-term conditions requires careful planning, preparation, setup, incubation, sample handling, DO measurement, removal of subsamples, reaeration, protection from contamination, watchful monitoring, records keeping, and regular documentation of test history. Quality control slippage on any element of the test procedure can change bacterial living conditions, rates of bacterial activity, and thus, rates of oxygen utilization. These changes, when projected over a 40-day, 60-day, or 90-day test, can substantially affect the results for (1) ultimate BOD, (2) $CBOD_u$ versus $NBOD_u$, (3) rates-of-reaction for both CBOD and NBOD, and (4) BOD_u to BOD_5 ratios.

Long-term BOD Tests are thereby expensive and demanding. Yet, high quality, defensible long-term results are crucial to WLA's and NPDES Permits. Low quality long-term BODs will mean low defensibility for technical results. Thus, the Division cannot afford to invest in long-term BODs without concurrent assurance of vigorous quality control throughout the entire duration of each test. As a consequence, the following protocol spells out the Division's QA/QC requirements for each separate test activity from planning through measurements to record keeping and presentation of raw data.



LEGEND

P_i - INITIAL BACTERIA POPULATION
 P_{max} - MAXIMUM BACTERIA POPULATION
 NBODU - ULTIMATE NITROGENOUS BOD

THE AMPLIFIED LONG-TERM
 BOD TEST



GEORGIA ENVIRONMENTAL
 PROTECTION DIVISION

TYPICAL RELATIONSHIP BETWEEN
 NITROGENOUS BOD AND
 BACTERIA POPULATION

FIGURE 4

PART 2: PROTOCOL/PROCEDURE FOR THE AMPLIFIED LONG-TERM BOD TEST

Traditionally, Long-Term BOD Tests used the "multiple bottle" procedure which required, for each test, a series of paired 300 ml BOD bottles. Initially, all bottles were filled with correctly diluted sample, then incubated in total darkness at constant temperature. As the test progressed, DO was measured in a pair of bottles, after which bottle contents were discarded. Depending on test duration, the multiple-bottle technique could consume huge numbers of bottles and occupy vast quantities of incubator space. The growing demand for more Long-Term BOD Tests of longer duration requires a cost-effective alternative.

The "single-bottle" test converted by the Division into the "Amplified" Test represents a modification of the technique developed by the National Council of the Paper Industry for Air and Stream Improvement (NCASI). The single-bottle Long-Term BOD Test measures the decrease in dissolved oxygen (DO) over time in a single (0.5 to 1.0 gallon) "monitored" glass bottle. A second bottle (0.5 to 1.0 quart) serves as a sample make-up "reservoir" to refill the monitored bottle following: (1) DO readings; (2) sample withdrawal for chemical analyses; and/or (3) sample losses for any reason from the monitored bottle. Together the monitored and reservoir bottles contain the same test sample; thus, both bottles must experience identical conditions for the duration of the test. The remainder of this protocol describes in detail the Division's requirements and specifications for this amplified single-bottle test. The Division's specifications are not limited to laboratory bench techniques. Instead, they cover: (1) essential aspects of adequate planning, especially for projects requiring large numbers of tests of long duration; (2) necessary laboratory and labware preparation; (3) proper receipt, handling, and preparation of delivered samples for both dilution water and test water; (4) clear requirements for instrument calibrations for dissolved oxygen and conductivity; (5) correct test set-up measures, and procedures for sample measurement; (6) appropriate safeguards for continuous maintenance of QA/QC; and (7) complete test record keeping including formatting of results.

We place special emphasis on complete record-keeping throughout all phases of the project. It should be possible, from adequate records, to reconstruct the complete test history for each sample. Proper records should also contain a complete history for each instrument used, including all calibration data. Records should contain descriptions of any relevant laboratory conditions encountered during the test that could affect test results or the interpretation of test results. (This will require a diary by the laboratory supervisor, who is also responsible for reviewing test results each day as they become available). Complete records should contain an identification of the laboratory personnel performing each step in the test. Ideally, the same person should perform all DO measurements to eliminate potential bias. Finally, the laboratory results should be recorded and transmitted in a format specified by the Division designed to fit our data-processing needs.

2.1 Planning, Test Design, and Coordination With the Division

The Division's engineer responsible for the water quality modeling project will pre-specify (1) the number of tests required, (2) the duration of each test, (3) appropriate sample dilutions, (4) the chemical sub-samples required during each test, and (4) the distribution of inhibited and filtered BOD's among the test samples. Other test design considerations will include selection of dilution water and duration of dilution water "aging", and the design and use of bacterial seeds. The importance of these planning issues requires very close coordination, and clear communication between the water quality modeling engineer and the laboratory supervisor. This is especially true for large projects with large numbers of samples and long test durations.

2.1.1 Test duration

The duration of each test depends on the nature and amount of BOD in each sample, the intended use of the data, and laboratory costs. For example, if BOD is expected to be slow acting, the test needs to be longer; if nitrification is anticipated, the test should span the completion of nitrifying reactions. Hence, each long-term BOD sample could require a unique, pre-specified duration. Because of the constraints imposed by laboratory costs, the overall design of any testing program involves trade-offs and balancing between laboratory costs and project data requirements. This balancing activity requires close coordination between the engineer and laboratory manager to ensure cost-effectiveness, and to minimize mis-communication.

2.1.2 Dilution water

Dilution of raw samples will be required whenever the total oxygen demand of an undiluted (100%) sample would exceed the original oxygen content of monitored and reservoir test bottles. During a test, oxygen should never drop below 3.0 mg/L in any test bottle; and reaerations should not exceed 1 in every 10 days (on the average). Because of these restrictions, "strong" samples must be diluted; however, while meeting the two DO criteria above, the percent dilution water in any test sample should still be kept to a minimum.

A variety of "waters" historically have been used for sample dilution. Often, a solution of distilled water, nutrients, and bacterial seed will be used when measuring the BOD of wastewater. Such solutions are intended to eliminate any limiting factor (e.g., nutrients, bacteria) in the raw BOD sample that could affect final results. However, when wastewater BOD measurements are to be used for wasteload allocations, and when estimates of in-stream reaction rates are also needed, experience prefers (instead of distilled water) an "aged" receiving water. By using receiving water for dilution, test results will be more relevant to the actual BOD reaction occurring in the receiving water in question. Regardless of the dilution water selected, the basic provisions and safeguards spelled out in Standard Methods for dilution water should be met.

In the event that "aged" receiving water is selected, close coordination will be required between the Division's project engineer and the laboratory manager. Dilution water, properly collected in the field, will be delivered to the laboratory at least 3 weeks prior to the delivery of test samples. A given sample to be diluted can require as much as 1 to 2 gallons of aged dilution water. The dilution water must then be "aged" in total darkness to allow its BOD to decay to low, stable levels. When actual testing begins, residual BOD_u in the dilution water should never exceed about 10 percent of the total BOD_u in the laboratory bottle for the diluted test sample. Typically, the ultimate BOD

of "aged" dilution water should be less than 1 mg/L. In all cases, the complete test history for the dilution water in any long-term BOD project should be carefully documented as a part of a permanent project record.

2.1.3 Bacterial seed

A bacterial seed is sometimes necessary for a test sample initially deficient in bacteria. Also, aged receiving water or distilled water solutions may require a bacterial seed. Seeding must be performed with caution, when performing BOD tests for waste load allocation studies, because seed can effect the rate at which BOD is consumed. Seeding should conform to the specifications and requirements described in Standard Methods and requires close coordination between the project engineer and laboratory manager.

2.1.4 Special test requirements

Special test procedures are usually included in a long-term BOD project to enhance the usefulness of laboratory data, and/or to obtain more meaningful results in certain situations. These special procedures include nitrification inhibition, filtering, and concurrent chemical testing.

2.1.4.1 Nitrification inhibition

The analysis of BOD test results usually requires the separation of carbonaceous and nitrogenous oxygen demands. Separation can be achieved by adding a chemical reagent to the test sample which inhibits the action of nitrifying bacteria but does not inhibit CBOD reactions. Consequently, this approach requires a second, parallel long-term test that is not inhibited. The difference between the two tests represents the nitrogenous BOD fraction. Though chemical inhibition is generally accepted for suppressing nitrogenous BOD, experience indicates that nitrification inhibition can also inhibit the carbonaceous reaction, as well. Therefore, inhibitors should be used with caution; and, when used, the test should be supplemented with nitrogen species measurements, as described later.

During the planning stage, the Division's engineer, in coordination with the laboratory manager, will (1) adopt the specific chemical inhibitor to be used for nitrification suppression, and will (2) identify the specific test samples to be inhibited. The Division currently recommends 2-chloro-6-(trichloromethyl) pyridine as the preferred inhibitor. Other inhibitors may be adopted with concurrence of the Division.

2.1.4.2 Filtering

During the analysis of BOD test results it may become necessary to separate the BOD associated with dissolved organic carbon (DOC) from the oxygen demand created by suspended, particulate organic carbon (POC).

A "standard method" for filtering BOD samples to address these questions has not been developed. Depending on project needs, specific filtering routines will require the adoption of (1) standard filtering procedures, (2) specific filter types, and (3) the ratio of filtered sample to total sample volume. These details must be agreed upon during the project planning as a result of consultation between the Division's project engineer and the laboratory manager.

2.1.4.3 Concurrent chemical testing

The CBOD reaction produces CO_2 and water; while the NBOD reaction converts organic nitrogen to NH_3 , NH_3 to NO_2 , and NO_2 to NO_3 . Thus, the analysis and interpretation of BOD data can be improved by measuring CO_2 and nitrogen species at the beginning and end of each test period and at selected intervals during the test.

Concurrent chemical testing thereby requires (1) the removal (and subsequent loss) of chemical subsamples from the monitored test bottle, and (2) the reaeration of monitored and reservoir bottle contents after subsample removal. Consequently, proper planning requires close coordination between the project engineer and the laboratory manager to establish: (1) the concurrent chemical tests for each BOD sample, and (2) the number and timing of each concurrent test.

2.1.5 Labware and laboratory equipment

Labware needed to perform a "typical" single bottle BOD test includes a 0.5 to 1.0 gallon glass bottle with special air tight seals, a 0.5 to 1.0 quart plastic or glass reservoir bottle, and a self stirring DO meter with a matching bottle mouth adapter. The size of the reservoir bottle will be dictated by (1) the size of the monitored bottle, (2) the length of the test, and (3) the frequency and extent of the intermediate chemical testing. A specification of essential labware and equipment can be found in Part 3 of this protocol. However, as a part of the planning process, the project engineer and laboratory manager should consult and clarify all issues concerning laboratory materials, labware, and equipment.

2.1.6 Systematic sample identification convention

For large projects, with many long-term BOD tests, systematic sample identification will be essential. Sample identifiers should be designed and assigned early before field samples are delivered to the laboratory. The labeling/identification system must facilitate an error-free tracking of each sample during the laboratory phase, and should conform to data processing requirements of the Division's long-term BOD data management system.

The sample labeling convention should incorporate the field sampling station identification scheme developed by the project engineer for the field study. In addition, the convention should identify the types of analyses to be performed on each sample. For example, a long-term BOD sample to be filtered could have an F suffix or prefix, while an inhibited BOD sample could have an I suffix or prefix. A successful labeling system will not only uniquely identify each sample, but will also provide a laboratory red-flag by indicating anticipated results (i.e., nitrogen series chemical results should not change over time in an inhibited sample labeled with an "I").

Sample labeling conventions should be completely established prior to sample delivery by consultation between the project engineer and laboratory manager. This coordination must include: (1) labeling materials and laboratory labeling methods, (2) laboratory management safeguards to fully protect sample identity and autonomy, and (3) laboratory records keeping designed to accommodate the sample labeling convention.

2.2 Laboratory and Labware Preparation

"New" glassware and plasticware should be used for the Amplified Long-Term BOD Test. This will minimize contamination and eliminate troublesome questions that can arise during model defensibility. The cost of new glassware and plasticware is immaterial when compared (1) to the costs needed to collect and analyze the samples, and (2) to the potential costs associated with resultant engineering decisions. (Part 3 contains a more complete specification of acceptable glassware and plasticware.)

If old glassware and plasticware must be used, they should be scrupulously scrubbed with hot water and non-phosphate laboratory grade soap until clean. This should be followed by copious rinsing with tap water to remove all traces of soap. Finally, perform at least three rinses of the labware with deionized water to remove the tap water. Heat dry all glassware and drain dry all plasticware before use. Do not use acid to rinse any labware which may contact the test sample.

2.3 Handling and Preparation of Dilution and Sample Waters

The receipt, handling and preparation of dilution and sample waters is critical in any long-term BOD project. This task will effect all subsequent measurements and can potentially invalidate an entire test. Detailed records must be kept (1) to document all procedures used in sample handling and preparation, and (2) to initiate the complete laboratory history of each test sample. All clock times should be expressed in the 24-hour military convention.

2.3.1 Sample receipt and initial handling

Following sample collection, dilution and sample waters will be immediately iced and preserved in the field, and then quickly transported directly to the laboratory for preparation and storage. Each sample will have been labeled in the field with the date, time, and location of collection, consistent with the Division's labeling convention. After sample delivery, laboratory personnel should immediately transfer this labeling information to laboratory records and labware.

2.3.2 Dilution water handling and preparation

The same dilution water should be used for all BOD samples in a given project. If different dilution water samples are collected, complete laboratory records should be kept on each. The specific dilution water used in each test should be carefully recorded in each sample's laboratory history. Different dilution waters should not be combined into a single composite dilution water. The procedures used to store and age each dilution water should be clearly documented in the laboratory record for future reference.

Prior to aging, dilution water should be aerated until DO concentrations approach saturation. It will be necessary to check the DO concentration of the dilution water periodically during the storage period. If DO falls to 3.0 mg/L, again reaerate the dilution water. The frequencies of checks and reaerations will depend on the behavior of the dilution water during the course of storage.

For high BOD dilution water samples it may be necessary to supplement nutrients in the dilution water that have been consumed during "aging". Too much aging may also produce a die-off of dilution water bacteria, and may thus require bacterial seeding in the test bottle prior to use. Since the addition of new bacteria and/or nutrients to the test sample will effect BOD reaction rates, this should be avoided where possible. Therefore, select dilution water with low initial BOD, and then age the dilution water for approximately three (3) weeks. The duration of aging will be specified by the Division.

In the laboratory, dilution water should be stored in a cool (approximately 20°C) dark area in either glass or nalgene containers. The dilution water should be tightly covered and the container double black-bagged in order to totally prevent exposure to light.

After completion of the specified aging process, combine the contents of all aged dilution water containers (for a given dilution water sample) into one large dilution water storage container (e.g., a 30-gallon stainless steel drum with a lid or a 13-gallon nalgene carboy). This container should be thoroughly cleaned prior to use, using the cleaning procedures discussed in Section 2.2 for glassware. After transfer, thoroughly mix the dilution water batch.

Allow solids in the aged dilution water batch to settle (in total darkness) for one to two days prior to the set-up of long-term BOD tests. After settling, carefully pour or siphon off the clear supernatant for test use and discard the settled solids. Thoroughly mix this dilution water supernatant immediately prior to the dilution of each test sample.

If additional long-term BOD tests are to be set-up (using the same dilution water) on later days, store the dilution water under original storage conditions (approximately 20°C, in total darkness).

An uninhibited long-term BOD test should be performed on a sample of 100% dilution water to measure that portion of the total BOD in any diluted test attributable to the dilution water. An inhibited test on the dilution water is also desirable.

2.3.3 Sample water handling, preparation, and special treatments

Laboratory records should document the date, time and procedures used in preparing sample waters for each BOD test. If a given sample is delivered to the laboratory in more than one container, immediately combine the sub-samples into a single clean container to insure a homogeneous mixture from the outset. Otherwise, immediately upon delivery perform the preliminary sample treatments described below. **Do not store samples or delay set-up activities once samples have been delivered to the laboratory.**

Following special treatments, each sample should be aerated until the DO approaches 9.0 mg/L or its saturation concentration at 20°C. If the temperature of the sample is below 20°C, caution should be exercised when aerating. Below 20°C DO concentrations can be easily raised above 9.0 mg/L. If concentrations rise above 9.0 mg/L at temperatures lower than 20°C, air bubbles can easily form when the sample temperature equilibrates at 20°C. Since entrained bubbles will bias test results, these overly saturated samples should sit still prior to test initiation to remove all entrained bubbles.

2.3.3.1 Untreated ("Straight") BOD test samples

Measure with a graduated cylinder the amount of raw sample calculated to give a drop in DO of not more than 30 mg/L over 40 days. This would require about 4 reaerations in 40 days consistent with reaeration criteria specified earlier. Pour the measured sample into a clean eight-liter plastic carboy. Add the correct volume of prepared (conditioned) dilution water from a graduated cylinder to the raw test sample to make a final combined test volume. Gently shake or stir the sample/dilution water mixture until the two portions are fully mixed. Prevent the entrainment of air bubbles. Record the volumes of dilution water and raw sample in the test record.

2.3.3.2 Treatment for inhibited samples

If the sample is to be inhibited, then the pre-specified inhibiting reagent should be added immediately after the test sample has been diluted. Follow inhibitor instructions. Gently shake or stir the test mixture until the inhibitor has completely dissolved. Again, avoid any entrainment of air bubbles. Stir slowly or gently rock the test mixture. Make necessary entries in the appropriate laboratory record.

2.3.3.3 Treatment for filtered samples

Filtering effluent samples. Procedures for filtering effluent samples remove those solids that may settle in the receiving water. One procedure allows the sample to stand quietly for about one (1) day, and then decants the sample supernatant into the BOD test container. Another procedure requires filtering the sample through a new Gelman (No. 61,631) glass fiber filter with a vacuum filtration apparatus.

Filtering for algae. Removing algae from test sample requires a slightly different technique since algae do not readily settle. This technique requires filtering 90% of the test sample through a new 15-cm (diameter) Whatman 4 Filter Paper with a MILLIPORE pressure filtration device. Using a graduated cylinder, add the 90% filtered portion to an eight-liter plastic carboy. Add to the carboy unfiltered sample as the remaining 10 percent of the total sample volume. The 10% unfiltered portion replenishes the microorganisms removed in the filtering process and thereby, serves as a seed for the filtered test.

If the filtered sample is also to be inhibited and/or diluted, then begin these treatments with the 90-10 (new) mixture and proceed to set-up the test sample as described above. When special treatments have been completed, make all necessary entries in the laboratory record. Especially note any unusual aspects of this procedure that may later assist the interpretation of test results.

2.3.4 Test continuity

The continuity of each test should not be interrupted. After field samples have been delivered to the laboratory each subsequent step--sample handling, preparation, special treatment, test set-up, and sample measurement--should comprise a single unbroken process with conditions controlled and documented throughout. In the event that multiple field samples are delivered (which is usually the case), all samples must be moved through the process in parallel. Handling, preparation, treatment, and set-up times should be approximately the same for all samples in a given delivery.

2.4 Instrument Calibrations

Each Long-Term BOD Test requires the use of a conductivity meter, DO meter, and a temperature-controlled darkened incubator. If chemical sub-samples are specified a number of other laboratory instruments will also be used. For the duration of a long-term project each instrument must be regularly and carefully calibrated. Complete documentation of all calibration activities become a part of the permanent project laboratory record. Calibration procedures should conform to those spelled out in Standard Methods and other methods manuals for each instrument.

Conductivity and dissolved oxygen measurements are critically essential to BOD test results and subsequent analyses. For this reason, the Division requires that calibrations of conductivity and DO meters follow the steps, and conform to the criteria, described in this section. All clock times should be expressed in the 24-hour military convention.

2.4.1 Conductivity meter calibration

DO probe readings in waters with appreciable salinity must be adjusted for the effect of salinity on probe response. This should be accomplished by multiplying the DO probe reading by a salinity correction factor (SCF) which is calculated from: (1) the measured conductivity of the sample expressed at 25°C, and (2) the temperature of the sample at the time the DO probe reading was taken. Hence, an accurate DO value requires an accurate SCF; an accurate SCF requires accurate conductivity and temperature readings; and accurate conductivity readings require accurate conductivity meter calibration.

All conductivity meter calibrations become a part of the permanent project laboratory record (discussed later). Meter calibration data must accompany the long-term BOD test data. This is not simply for casual reference. Instead, conductivity meter calibration data are used in the calculation of salinity correction factors and, in this manner, must be included in submitted laboratory "results".

CAUTION: Some DO meters can measure sample "salinity" directly, and then internally correct probe readings when the meter's salinity knob is turned to the measured salinity value. This approach is not used by the Division, and cannot be used for salinity correction during a Long-Term BOD Test. Thus, if DO measurements are taken with meters that have a "salinity knob", all measurements must be taken with the salinity knob set to zero. The zero setting should be checked frequently to ensure that it has not been inadvertently moved from zero during other use of the instrument.

2.4.1.1 Selection of conductivity standards

Conductivity meters should be calibrated against (1) reference grade KCl solutions as listed in the 16th Edition Standard Methods, or (2) analytical grade conductivity standards from chemical supply companies. A useful range of KCl concentrations and corresponding conductivities as shown below are taken from Standard Methods.

KCl Normality	Conductivity (at 25°C) umhos/cm
0.01	1413
0.02	2767
0.05	6668
0.10	12900
0.20	24820
0.50	58640

Other analytical grade primary reference conductivity standards purchased from chemical supply catalogs, may be used as a substitute for KCl solutions.

First: Roughly determine the conductivity of a test sample (or group of test samples when conductivities are similar). **Second:** Identify the two KCl reference standards whose conductivities best bracket the test sample value.

2.4.1.2 Development of probe calibrations

Perform a trial measurement on the higher conductivity standard. If the trial measurement (at 25°C) differs from the standard's conductivity by more than 10%, assume the meter needs to be checked or the cell needs to be refurbished.

After the meter reads the conductivity standard to within 10%, develop cell calibration data by the following procedure:

1. Rinse the conductivity probe thoroughly with distilled water;
2. Measure conductivity (at T°C) and temperature of the first standard;
3. Rinse the probe thoroughly with distilled water; and
4. Measure conductivity (at T°C) and temperature of the second standard.

After this, measure test sample and dilution conductivities and temperatures.

A given long-term BOD project will be considered incomplete without (1) conductivity meter calibration data, and (2) conductivity and temperature measurements on the dilution water and each test sample.

2.4.2 DO meter preparation and calibration

Measure dissolved oxygen concentrations with a YSI Model 57 DO meter and Model 5720A DO probe, or their equivalent. This combination has a self-contained stirring device that is essential to the test. DO probes used in the Long-Term BOD Test must have an operational stirring attachment.

2.4.2.1 Probe and membrane care

If the DO probe is handled carefully, a new membrane can endure several days of measurements in waters with salinities as high as 5 to 10 ppt. Immediately after DO readings begin to drift or appear erratic, consider replacement of the membrane and probe solution. Follow the manufacturer's instructions for membrane replacement. Some safeguards to follow include:

- o Rinse the interior of the DO probe with filling solution at least once before finally filling the probe and sealing with a new membrane.
- o Do not stretch the membrane during installation.
- o Do not touch the working surface of the membrane.
- o After sealing the new membrane, with the black rubber O-ring, invert the probe and tap it to confirm that no air bubble has been trapped. If any bubbles or any other foreign matter appear under the membrane, remove and replace the membrane.
- o Leave only a very small amount of membrane overlap at the black O-ring seal, never enough to reach the cathode (gold ring).
- o Thoroughly trim the excess membrane and store the assembled probe in water-saturated air.

2.4.2.2 Probe and sample bottle adapter assembly

Since the probe by itself will not provide the correct air-tight seal with mouth of the test bottle, an adapter must be rigged to eliminate inadvertent introduction of oxygen into the test sample. As an example, prepare this adapter by cutting a correctly-sized hole in a plastic cap (Laboratory Products P301 Series). Fit the cap onto the DO probe so that the probe can wedge snugly and securely into the mouth of the sample jug during DO measurement.

2.4.2.3 DO meter calibration

The DO meter should be calibrated using the following steps:

1. From a single reservoir of aerated deionized water, fill two 300-mL BOD bottles. The filling procedure should conform to the inverted-siphon technique, with at least two-volumes of turnover, to ensure that the DO in both BOD bottles are equal, and equal to the DO in the reservoir.
2. Immediately "fix" the DO in one bottle using steps 1 and 2 of the Winkler Procedure as described in Standard Methods.
3. As quickly as possible, measure the DO in the second BOD bottle with the DO probe and bottle adapter assembly.

If the DO probe reading equals the DO as measured by the completed Winkler test, the DO meter is calibrated. If the two measurements differ by more than 0.05 mg/L, the DO meter is out of calibration and must be adjusted.

If the DO meter needs adjustment, assume the Winkler measurement is correct. Subtract the DO probe reading from the Winkler result. If the probe reading is lower than the Winkler, the adjustment is positive (+) and equals the "difference" between the two readings. If the probe reading is higher than the Winkler, the opposite is true.

Adjust the DO meter. Then, draw two more samples from the reservoir of aerated deionized water. Immediately "fix" one bottle for a Winkler test, as before. Quickly measure DO in the second bottle. Compare the adjusted DO reading to the new Winkler result.

If the new Winkler and the new DO reading agree to within 0.05 mg/L, the instrument is calibrated. If the two readings do not agree, then repeat the process until DO meter adjustment is not required. At that point, the meter is calibrated.

The following criteria should be met during the calibration process:

- o Carefully protect the sample bottle from inadvertent introduction of oxygen during the probe insertion step;
- o Step 3 of the Winkler test should be performed immediately after the probe reading is recorded;
- o The temperature of all DO samples must be exactly the same;
- o Clock times and sample temperatures should be recorded in the laboratory test records along with each DO reading, after each step in the process. Document each step as each step is taken. **Do not work from memory;**
- o During a long-term BOD test calibration should be checked at least once every two hours, or more frequently if any questions arise over proper meter functioning;
- o Whenever DO meter drift is noticed, or whenever calibration is required (for any reason), the calibration steps described above should be performed; and
- o A permanent documentation of all calibration checks, calibrations, and meter adjustments must be incorporated into the project laboratory record.

2.5 Sample "Set-Up" and Measurement

2.5.1 Set-up time

Once sample handling, preparation, and special treatment have been completed, as described in Section 2.3, the next step in the uninterrupted procedure is sample "set-up." The set-up time, the official reference time for all calculations and analyses performed on laboratory results, must be uniquely determined for, and clearly recorded in the laboratory record for each test. All clock times in the Long-Term BOD Test should be recorded in the 24-hour military convention.

2.5.2 Sample set-up

After handling, preparation, and special treatment, each test sample will be contained in an eight-liter carboy. The sample must be free of entrained air bubbles, and its DO must lie between 8.0 and 9.0 mg/L (at 20°C).

If the test sample is cool (<15°C), any mixing should be accomplished by gently inverting the carboy. This minimizes excessive aeration and prevents bubble formation when the sample adjusts to 20°C.

If the test sample is warm ($>25^{\circ}\text{C}$), mixing can be accomplished by shaking the carboy vigorously for at least 30 seconds. In either case, ensure that initial DO lies between 8.0 and 9.0 mg/L at 20°C , and ensure that gas bubbles do not form.

Next, pour the properly aerated test sample into each of these four containers:

1. Monitored Bottle. Fill the 0.5 gallon glass jug (example, CMS 147-850) completely, to the top;
2. Reservoir bottle. Fill the 1.0 quart glass jug (example, CMS 031-146) completely, to the top;
3. Nutrient Bottle. Correctly fill a 500 mL nalgene bottle already prepared with H_2SO_4 to "fix" nitrogen species for subsequent testing. (Consult with the Division for correct preparation steps for the nutrient bottle and for alternative sample sizes for later chemical subsample.)
4. Salinity Bottle. Fill a 500 mL nalgene bottle and refrigerate. When time permits, allow this bottle to return to room temperature. Then measure conductivity and temperature in accordance with the criteria contained in Section 2.4.1. These data will be used to calculate the salinity correction factor for that test.

Remove any air bubbles stuck to the side of the one-half-gallon monitored bottle by tapping. If the sample is cool ($<15^{\circ}\text{C}$), wait one-half to one hour after tapping away the bubbles to be sure no fresh bubbles form as the sample warms.

Perform the initial DO measurement and close the monitored and reservoir bottles as described in Section 2.5.3 below. If the initial DO exceeds 9.0 mg/L, lower the DO either (1) by waiting and tapping, or (2) by pouring the sample from the monitored and reservoir bottle back into the eight-liter carboy and agitating. (It may be necessary to raise the sample temperature to near 20°C to lower the DO to 9.0 mg/L).

After these initial conditions have been met: (1) measure initial DO and temperature in the monitored bottle; (2) immediately close and seal the monitored and reservoir bottles; (3) record the date and exact clock time in the laboratory test record along with initial DO and temperature; these entries become a part of the official set-up conditions for the entire test; then, (4) place the monitored and test samples side-by-side in the laboratory incubator, in total darkness, at $20^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$.

2.5.3 Test sample measurement

2.5.3.1 Measurement frequency

Test measurement frequency should be established during the project planning phase by consultation between the Division project engineer and the laboratory manager. Usually, the samples will be measured at least once a day for the first seven (7) days, every other day for the next fourteen (14) days, then every third day for the remainder of the test.

However, measurement frequency will be established ultimately by the need (1) to properly define the shape changes (kinetics) of the "DO remaining" curve (Figure 1), and (2) to detect problems in the test that required immediate attention.

The next Section 2.6 contains specifications for interim review of results, by the laboratory manager, to detect problems and/or the need for changes in measurement frequency. During each of the first 5 days of the testing period, twenty (20) percent of the test samples selected at random should be measured every 12 hours to catch any problems of sample acclimation as they occur.

2.5.3.2 Measurement procedure

Remove a sample from the incubator not more than ten (10) minutes before starting the DO measurement. Remove the water seal from the monitored bottle. Protect the sample cap so that its surface contacting the sample does not become contaminated. If the cap does potentially become contaminated, rinse it thoroughly with deionized water or replace with a new cap.

Carefully insert the DO probe with adapter into the monitored bottle, turn on the DO probe stirrer and observe the sample temperature. Record the sample temperature after it has stabilized (this usually takes one to two minutes).

After recording the sample temperature switch the meter function to "DO". Ensure that the meter salinity knob has been set to zero. Allow about 45 seconds to elapse before noting the DO reading. Wait an additional 30 seconds to verify that the DO reading has not drifted. If the DO reading appears stable, record the DO and the clock time. If the DO reading changes or does not appear stable, repeat the waiting period and re-read. If the meter continues to change or drift repeat the calibration procedure of Section 2.4.2 and/or examine the meter itself.

When the measurement has been completed, turn off the DO probe stirrer and remove the DO probe. Check the salinity knob. Rinse the probe, including the monitor bottle cap, with deionized water. Place the probe in the next monitored bottle or in a holding station of water-saturated air. Be careful not to touch the membrane against any solid surfaces.

A sample should not be out of the incubator for more than 20 minutes. Any deviations from this limit must be recorded in the test record. Check the salinity knob frequently.

2.5.3.3 Sample replacement and measurement closure

During incubation the monitored bottle must be water sealed air tight and be completely full without air-space at the top. However, sample handling and measurement generally produces a small loss of sample volume which must be fully replaced prior to re-incubation.

The reservoir bottle for each test provides sample replacement volume. Hence, after DO measurement gently mix the reservoir by swirling (or inverting) and prevent the introduction of air bubbles. Gently pour or siphon sample from the reservoir to re-fill the monitored bottle. Do not introduce bubbles into the monitored bottle.

Replace both the monitored and reservoir bottles side-by-side, in the incubator. The measurement is "closed" when the clock time for re-incubation has been entered in the laboratory record.

2.5.4 Measurement trouble-shooting

In the Long-Term BOD Test, DO should decrease with each successive measurement. If DO increases with a subsequent measurement something is wrong; corrective action must be taken. Common sources of DO increase include: (1) inadvertent reaeration of the sample--laboratory technique is faulty; (2) temperatures not constant at 20°C--laboratory temperature control is faulty; (3) algae growth in the sample bottle has caused oxygen production--samples have not been kept in total darkness; (4) DO meter malfunction or faulty DO calibration--laboratory technique is faulty; and (5) test continuity has been interrupted for some unfortunate reason.

Conversely, even though DO should decrease, the decrease should not be drastic. A problem exists if DO drops more than 1 mg/L in any 24-hour period during the first 7 days, or more than 1 mg/L in 3-5 days during the remainder of the test. Causes for drastic drops in DO include faulty laboratory techniques, improper temperature control, meter malfunction, or interruption of test continuity. Another, more revealing cause might be a miscalculation in dilution water volume; hence, the raw sample is stronger than expected and has not been diluted enough.

Thus, both DO increase and sharp DO decrease point to problems with the test that must be investigated and solved as quickly as possible. Accordingly, each DO measurement, as soon as its recorded, should be compared to the previous value for that test. Corrective action should be initiated whenever a potential problem has been detected in the DO profile. Corrective action is the laboratory manager's responsibility.

2.5.5 Sample Reaeration

2.5.5.1 Reasons for sample reaeration

Test samples should be reaerated: (1) whenever DO is expected to drop below 3.0 mg/L in the monitored bottle (2) whenever chemical sub-samples are removed from the monitored bottle, and (3) whenever test continuity has been interrupted, say by an accidental crack in or spillage of the monitored bottle. In all cases, reaeration represents an "effective re-start" and thus, should be performed carefully.

- (a) If dilutions are improperly calculated or if the raw sample strength is high in BOD, then DO in the monitored bottle can suddenly drop below 3 mg/L. When DO falls that low in the monitored bottle, the kinetics of oxygen-demanding bacteria can be suppressed or changed in ways that adversely affect the validity of test results. BOD should be measured in an oxygen-rich environment, one in which the availability of oxygen does not become a limiting factor in BOD kinetics. Accordingly, reaeration (replenishing the oxygen supply in the test sample) occasionally becomes necessary. There are draw-backs, however. Reaeration, by definition, disrupts test continuity, opens the test to inadvertent errors, and introduces a sudden slug of oxygen which can pulse BOD kinetics. Drawbacks aside, after each DO measurement the laboratory technician should examine the existing DO profile. If DO is expected to fall below 3 mg/L before the next measurement, the test sample should be reaerated before replacement in the incubator.

- (b) When chemical sub-samples are removed from the monitored bottle, sample volume must be replaced from the reservoir. Usually, DO in the monitored and reservoir bottles will be different. For this reason, without reaeration, the addition of make-up sample will disrupt test continuity and adversely affect test results. Thus, when chemical sub-samples must be removed, DO should be measured first in the monitored bottle. Sub-samples can then be removed carefully. The monitored bottle should be refilled from the reservoir. Next, the test sample should be reaerated before replacement in the incubator.
- (c) Occasionally it becomes necessary to re-start a test after major disruption of test continuity. Sample bottles can be cracked or broken; samples can be inadvertently left out of the incubator; laboratories can experience power failures; any number of things can happen. Major test disruptions cause major losses in test validity. However, useful information can be salvaged by re-starting the test immediately after a major disruption has been detected. Test re-starting requires that the entire test sample be reaerated, and that initial DO and temperature be taken before sample replacement in the incubator.

2.5.5.2 Reaeration procedure

After recording the pre-aeration temperature, DO, time, and date as described in the typical DO measurement Section (2.5.3), mix the entire contents of the monitored and reservoir bottles in a clean eight-liter plastic carboy. Shake the carboy at least 30 seconds. Allow any bubbles to surface. Fill the monitored bottle to the top with reaerated sample. Pour the rest of the sample back into the reservoir bottle. Confirm that there are no bubbles remaining in the monitored bottle. If bubbles are present, remove them. Measure and record the post-reaeration temperature, DO, time and date. Finally, "close" the monitored and reservoir bottles and continue incubation.

During the entire reaeration process, the steps and safeguards described in the sections on sample handling and set-up should be adhered to.

2.6 Test Management, Records, and Results

In water quality modeling for wasteload allocation and NPDES Permit development, the values used for ultimate BOD can "drive" the ultimate decisions. That is, NPDES Permit limits are strongly influenced by long-term BOD test results, and wastewater treatment costs can be very high. Therefore, since BOD results can play a crucial role in expensive engineering solutions, the laboratory results must be able to pass strict tests for defensibility. Successful defensibility requires constant test management, careful laboratory techniques, complete and unambiguous test records, and intermediate scrutiny of test results.

2.6.1 Test management

Each long-term BOD test has a life history--a beginning, middle, and end. During these phases, each test experiences different technicians, multiple procedures and handlings, and a variety of environmental conditions. Hence, the test sample cannot be left to fend for itself. Instead, continuity and defensibility require consistent attentive management designed to ensure that each test survives to its end with meaningful results intact.

Prior to the beginning of the laboratory phase, i.e., during the planning process, the project engineer and laboratory supervisor should meet and agree upon the project management plan. This plan should include provisions for regular communications between the engineer and laboratory supervisor, and between the laboratory supervisor and his laboratory personnel. The plan should also include: specifications for regular test monitoring, requirements for records keeping, identification of responsibilities and those responsible, contingencies for handling problems, and procedures in the case of emergencies. The project engineer and laboratory supervisor should also meet at intervals throughout the test period to exchange data, discuss test progress, and solve intermediate problems as they occur. Records of these meetings become a part of the permanent project record. **There is too much at stake with long-term BOD tests to leave essential items to chance.**

2.6.2 Test records

From project test records, one should be able to reconstruct the entire life history of each test sample. This means knowing who, what, when, where, why, and how; who handled the samples and performed the measurements; what procedures were carried out, when and under what conditions were they carried out; where was the sample at all times; why were certain activities carried out; and how were special measures implemented. The project record also includes the laboratory supervisor's diary of project events from sample receipt through handling, preparation, set-up, calibration, measurement, monitoring, review and presentation of final results. In addition to the supervisor's diary, two specific types of data sheets should be maintained: (1) those for instrument calibration, and (2) those for test measurements.

2.6.2.1 Instrument calibration data

All conductivity and dissolved oxygen meter calibrations should be recorded on data sheets for each instrument designed specifically for that purpose. Proper notations should also be made in the record for each test sample to show, without ambiguity, which instruments and calibrations apply to that test and when they were performed. (Calibrations for other chemical tests and instruments become a part of the permanent project record but do not have their own specifically designed data sheets.)

- (a) Conductivity meter calibration. Figure 5 contains the data sheet for conductivity meter calibrations. Calibrations should be performed according to the procedures and criteria presented in Section 2.4.1.
- (b) Dissolved Oxygen Meter Calibration. Figure 6 contains the data sheet for DO meter calibrations. As shown, the date, time, meter number (if applicable), temperature, DO readings with Winkler measurements, and the resulting meter adjustment should be recorded for each calibration. In addition, comments should include the reasons for the calibration and a description of the corrective actions taken. Also, the data sheets for each test should show when during the test DO calibration were performed.

[illegible]

LABORATORY QA MANAGER

DATE: _____

* CORRECTION = 1.91% PER DEG.

FIGURE 5

2.6.2.2 Test measurement data

Figure 7 contains the form that should be used to record the DO measurements for each sample. The date, times, temperature, DO readings, calibration adjustment, reaeration reading, and remarks concerning adjusted DO readings, chemical subsample removal, and perceived problems should be recorded. **NOTE: This form has been designed for a specific data processing facility and should not be modified without prior approval by the Division.**

2.6.3 Test results

BOD kinetics in the laboratory bottle can depend on many variables like bacterial food, available nutrients, temperature, light, and sample handling techniques. Also, in addition to the assumed first-order behavior of BOD kinetics, actual bottle reactions may reflect 2nd and higher order kinetics and may comprise multiple BOD reactions that lag and overlap. Thus, a BOD curve plotted from actual laboratory data may depart, in shape, from the smooth curves predicted by first-order theory.

Accordingly, one cannot always judge the behavior of a given test simply by looking at a "column" of DO measurements on the laboratory data sheet. For instance, a DO change of 0.1 mg/L from point-to-point in one sample can have a meaning different than a 0.1 mg/L change in the next sample. For these reasons, BOD graphs of each test should be plotted measurement-by-measurement as tests progress. Seeing the growth of BOD in real time will provide valuable checks on and insights about test progress. Close observation of test results can identify problems and suggest corrective measures and procedural changes. For example: the "rate" of BOD growth can help schedule subsequent reaerations; unexpected surges in BOD could encourage an examination of meters and laboratory controls; an "outlier" should trigger an immediate DO re-measurement and/or meter calibration to adjust the "outlier" or resolve an undetected problem.

Figure 8 contains a representative plot of typical readings from a long term BOD test. As shown, projection of the first 8 points would result in a low estimate of the value expected on the 9th reading. Even though the 9th reading may be valid, it should be checked after recalibration of the meter.

Figure 9 contains a sample sheet of graph paper which can be copied to provide separate graphs for each test sample. However, any equivalent laboratory-precision graph paper may be substituted.

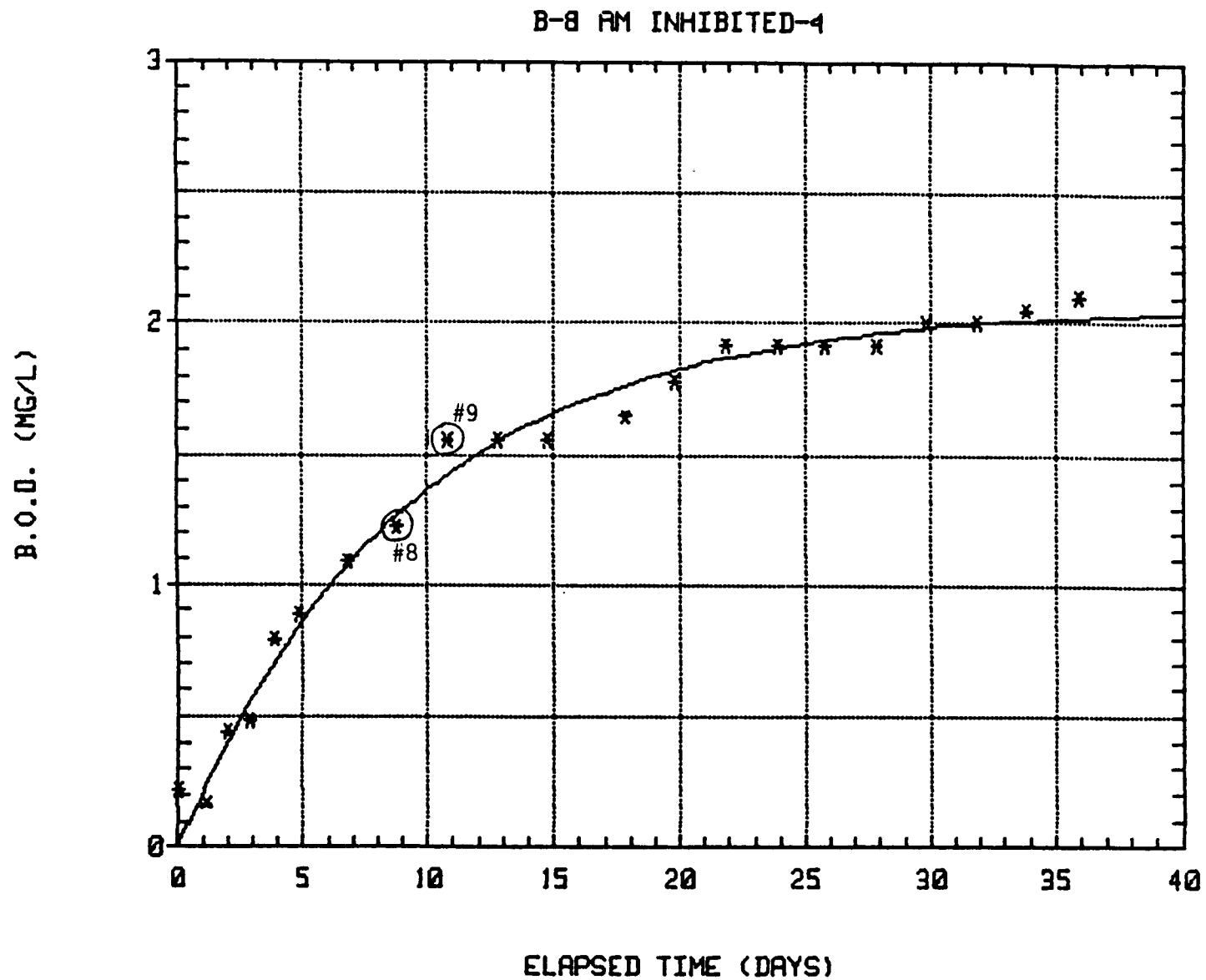
2.6.4 Final project laboratory results

Complete project results from the amplified Long-Term BOD test include the following:

1. The laboratory supervisor's diary and working graphs for each test;
2. Calibration data sheets for conductivity meters and dissolved oxygen meters;
3. Complete and unambiguous data sheets for each long-term BOD test; and
4. Access to calibration files for other tests and instruments used in the project;

DATE: _____

FIGURE 7



THE AMPLIFIED LONG-TERM
BOD TEST



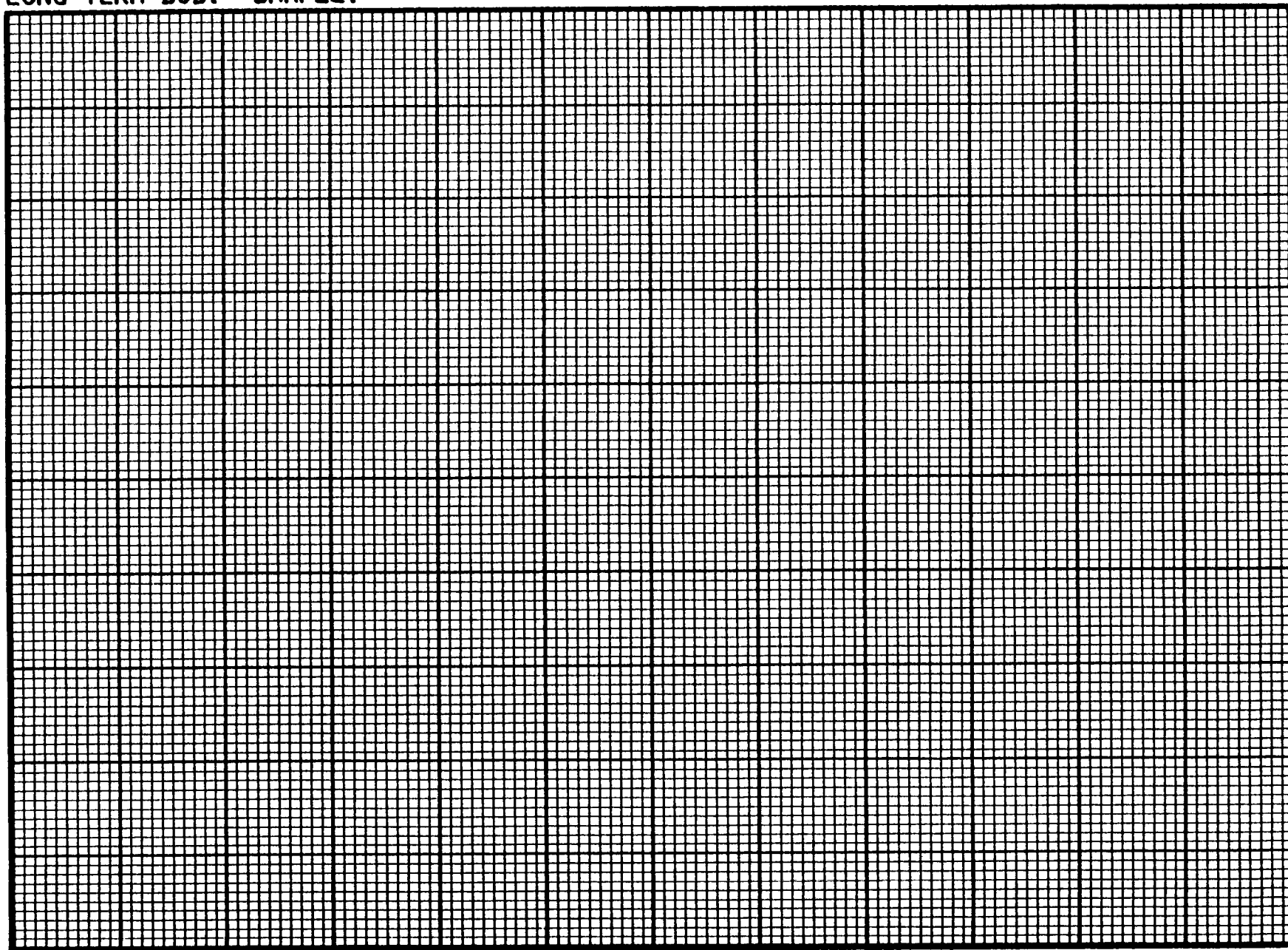
GEORGIA ENVIRONMENTAL
PROTECTION DIVISION

REPRESENTATIVE LONG-TERM
BOD TEST PLOT

FIGURE 8

LONG-TERM BOD. SAMPLE:

DISSOLVED OXYGEN (mg/l)



ELAPSED TIME (days)

Environmental Protection Division

SAMPLE GRAPH PAPER

FIGURE 9

Each data sheet should be examined and checked by the responsible laboratory manager, then signed and dated to authenticate the results. All data sheets should be arranged, sorted, and enclosed in a note book or binder to enhance convenient retrieval of any portion of the project record. The data volume should be transmitted to the Division under a brief letter report describing (1) the nature of work performed, (2) problems encountered and corrective actions taken, (3) and items of special note that can affect data analysis and interpretation.

PART 3: LIST OF EQUIPMENT

<u>ITEM</u>	<u>SUPPLIER*</u>
I. Glass and Plasticware	
0.5 gal glass bottles	Smith Container
0.5 to 1 L reservoir bottles	Smith Container
1 gal glass or plastic bottles	Smith Container
Sample collection device (Beta Bottle)	Wildco
10 or 15 L nalgene carboy	Scientific Products
8 L plastic carboy	Scientific Products
for reaeration & composite samples	
500 mL nalgene bottles	Curtin Matheson Scientific
for nutrient & salinity samples	
300 mL BOD bottles	Curtin Matheson Scientific
graduated cylinders	Curtin Matheson Scientific
burettes for Winkler	Curtin Matheson Scientific
volumetric pipettes	Curtin Matheson Scientific
plastic stoppers	Curtin Matheson Scientific
26 by 32 mm polyethylene hollow stoppers	
erlenmeyer flasks	Curtin Matheson Scientific
beakers	Curtin Matheson Scientific
volumetric flasks	Curtin Matheson Scientific
II. Equipment	
DO meter (YSI model 57)	Curtin Matheson Scientific
self stirring DO probe (5720)	Curtin Matheson Scientific
extra membranes & O-rings	
conductivity meter	Curtin Matheson Scientific
BOD incubator	Curtin Matheson Scientific
burette stand and holder	Curtin Matheson Scientific
hypodermic needles and syringes	Curtin Matheson Scientific
vacuum filter apparatus	Curtin Matheson Scientific
Millipore pressure filtration device	Curtin Matheson Scientific
No 61631 Gelman glass fiber filters	Curtin Matheson Scientific
15 cm Whatman filter paper	Curtin Matheson Scientific
refrigerator	Curtin Matheson Scientific
water deionizer	
bottled air	Curtin Matheson Scientific
tygon tubing	Curtin Matheson Scientific
snapper hose clamps	Curtin Matheson Scientific

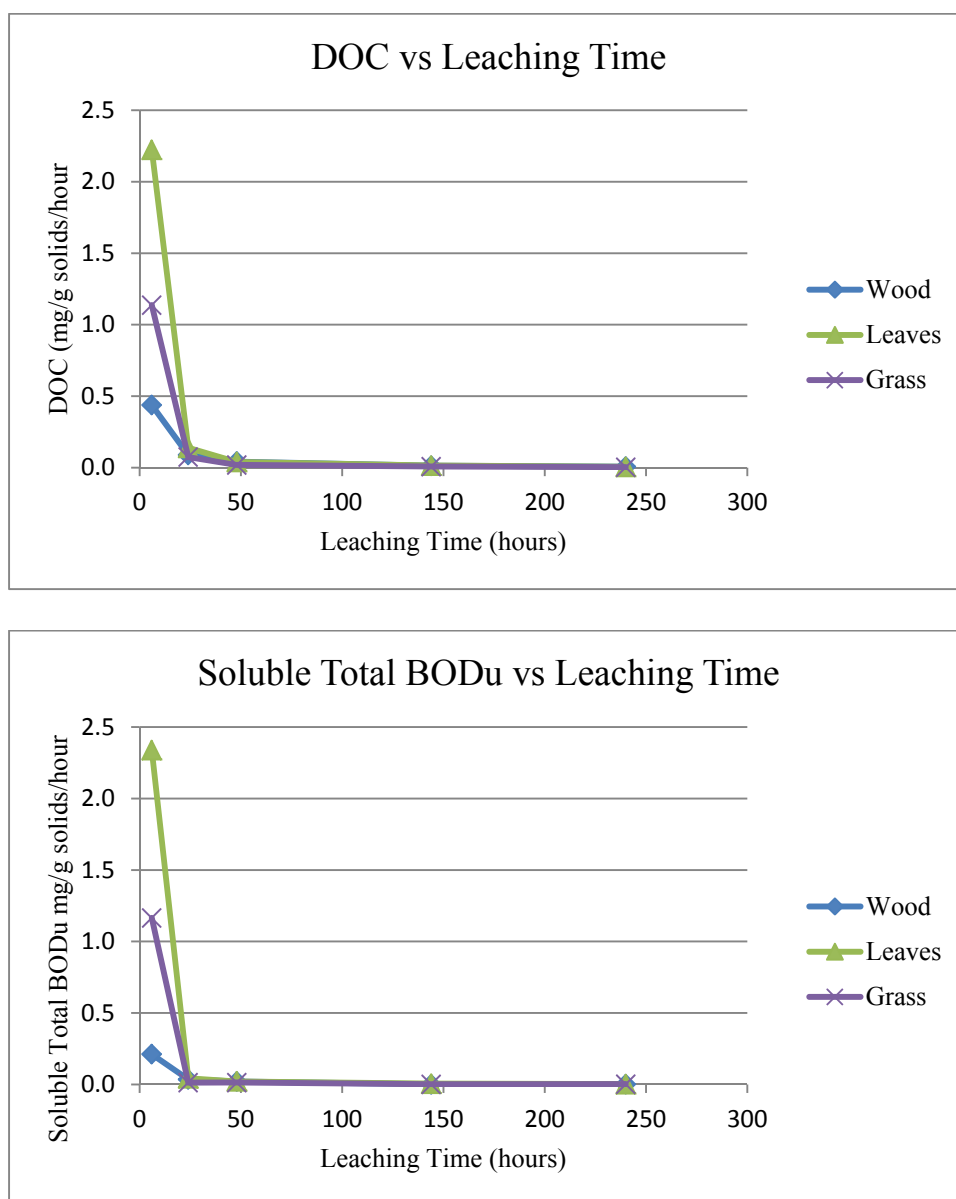
ITEM**III. Chemicals****H₂SO₄****NaOH****KCl reference grade****2 chloro-6(trichloromethyl)pyridine****Na₂SO₃****Mn SO₄****NaN₃****NaI****laboratory-grade starch****salicylic acid****Na₂S₂O₃·5H₂O for tritant****KH(IO₃)₂ for back titration****KI for standardization****Dilution Water****KH₂PO₄****K₂HPO₄****Na₂PO₄·7H₂O****NH₄Cl****MgSO₄·7H₂O****CaCl₂****FeCl₃·6H₂O****IV. Miscellaneous****manicure scissors****aquarium pumps****tubing for air pumps****clock****ice chest****labels****labeling pens****lab notebooks****black garbage bags****nonphosphate detergent****plastic bags****rubber bands**

* Listing of supplies does not constitute an endorsement by either the Georgia EPD or Law Environmental, Inc.

Appendix C

Selected results of preliminary studies

The following graphs were generated from data obtained in preliminary tests conducted over a 240 hour period rather than 48 hours. The magnitudes of the results are less than those presented in the final test but the patterns show that beyond 48 hours the decreasing pattern continues for both DOC and BOD,



Remove the bolded header and show 1 decimal place on the y-axis for both figures and all numbers.

Appendix D

Raw data from leaching test and subsequent analyses

COD Solids (mg/L)						
CPOM Type		Boat (g)	Sample (g)	Boat + Unused Sample (g)	COD (mg/L)	COD (mg/L/mg)
Wood	1	0.5312	0.003	0.5313	1340	462.07
Wood	2	0.52	0.0017	0.52	954	561.18
Wood	3	0.5395	0.0021	0.5397	1136	597.89
Leaves	1	0.5507	0.002	0.5507	1056	528.00
Leaves	2	0.5271	0.0017	0.5276	485	404.17
Leaves	3	0.5065	0.0014	0.5072	1156	1651.43
Grass	1	0.5575	0.0023	0.5576	1437	653.18
Grass	2	0.5944	0.0026	0.5945	1018	407.20
Grass	3	0.5422	0.002	0.5431	994	903.64

Raw TSS Data (mg/L)								
CPOM Type		Mass of Sample (air dried) (g)	Leaching Time (hours)					
			1	3	6	10	24	
Wood	1	5.6979	0	1	7	5	2	
Wood	2	3.0369	6	0	0	2	3	
Wood	3	3.2691	0	3	1	3	5	
Leaves	1	1.9145	8	2	0	2	4	
Leaves	2	1.9656	3	7	2	2	2	
Leaves	3	1.6407	2	2	4	4	0	
Grass	1	2.2018	2	0	2	4	6	
Grass	2	2.8786	0	3	1	4	3	
Grass	3	2.7278	5	3	0	0	2	

Raw VSS Data (mg/L)								
CPOM Type		Mass of Sample (air dried) (g)	Leaching Time (hours)					
			1	3	6	10	24	
Wood	1	5.6979	3	6	6	5	1	
Wood	2	3.0369	6	4	5	7	3	
Wood	3	3.2691	1	3	3	6	5	
Leaves	1	1.9145	7	2	2	3	3	
Leaves	2	1.9656	5	7	2	5	1	
Leaves	3	1.6407	5	2	3	4	3	
Grass	1	2.2018	5	5	4	4	6	
Grass	2	2.8786	0	5	3	10	3	

Grass	3	2.7278	5	3	2	0	1
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Raw DOC Data (mg/L)							
CPOM Type		Mass of Sample (air dried) (g)	Leaching Time (hours)				
			1	3	6	10	24
Wood	1	5.6979	43.06	26.38	15.05	7.10	15.49
Wood	2	3.0369	21.80	7.71	6.86	4.92	9.89
Wood	3	3.2691	22.99	10.05	4.95	5.95	12.58
Leaves	1	1.9145	132.23	72.54	33.14	23.10	34.76
Leaves	2	1.9656	141.11	70.12	32.02	22.25	37.62
Leaves	3	1.6407	120.77	59.15	22.59	16.90	28.42
Grass	1	2.2018	123.95	53.18	22.91	16.14	22.63
Grass	2	2.8786	154.88	84.45	39.45	27.31	34.65
Grass	3	2.7278	172.02	66.31	29.10	17.56	23.47

Raw TDN Data (mg/L)							
CPOM Type		Mass of Sample (air dried) (g)	Leaching Time (hours)				
			1	3	6	10	24
Wood	1	5.6979	2.1909	0.6911	0.4644	0.6885	0.7549
Wood	2	3.0369	1.2674	0.4564	0.4677	0.5112	0.4171
Wood	3	3.2691	0.9754	0.4587	0.5938	0.4307	0.3277
Leaves	1	1.9145	4.0393	2.7031	1.6201	1.4078	1.8399
Leaves	2	1.9656	3.9440	2.6220	1.9353	1.1124	1.9905
Leaves	3	1.6407	3.7653	2.4116		0.8854	1.5807
Grass	1	2.2018	8.1647	4.1740	1.8149	1.1136	1.3033
Grass	2	2.8786	8.3016		3.2660	2.2271	3.1146
Grass	3	2.7278	8.2940	6.8945	6.8945	1.7609	1.9936

Raw COD Data (Unfiltered) (mg/L)								
CPOM Type			Mass of Sample (air dried) (g)	Leaching Time (hours)				
				1	3	6	10	24
Wood	1		5.6979	146	41	24	47	48
Wood	2		3.0369	68	25	34	20	35
Wood	3		3.2691	73	28	45	31	48
Leaves	1		1.9145	357	213	104	83	95
Leaves	2		1.9656	350	217	99	73	101
Leaves	3		1.6407	345	180	66	64	87
Grass	1		2.2018	312	141	56	37	65
Grass	2		2.8786	391	216	96	70	93
Grass	3		2.7278	399	175	68	38	61

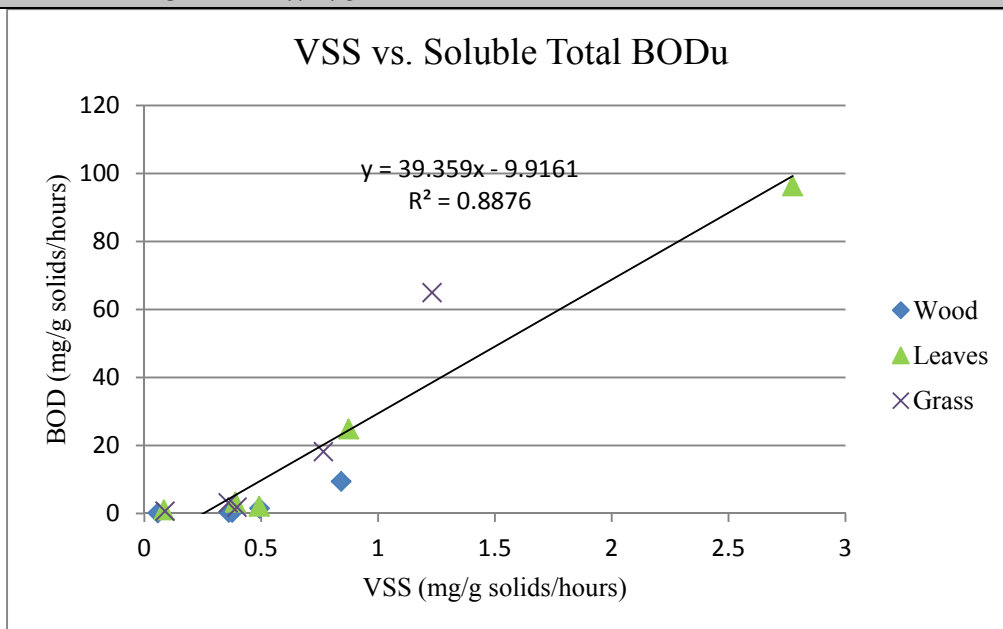
Raw COD Data (Filtered)								
CPOM Type			Mass of Sample (air dried) (g)	Leaching Time (Hours)				
				1	3	6	10	24
Wood	1		5.6979	55	37	30	35	44
Wood	2		3.0369	43	27	20	12	40
Wood	3		3.2691	32	43	29	31	43
Leaves	1		1.9145	352	213	104	53	79
Leaves	2		1.9656	362	211	93	57	78
Leaves	3		1.6407	322	185	63	50	65
Grass	1		2.2018	286	155	68	45	48
Grass	2		2.8786	390	213	103	96	78
Grass	3		2.7278	386	170	68	68	60

Raw BODu Data (Filtered) (mg/L)							
		Mass of Sample (air dried) (g)	Leaching Time				
			1	3	6	10	24
CPOM Type							
Wood	1	5.6979	75.38	19.88	6.68	6.87	11.02
Wood	2	3.0369	30.83	9.63	4.73	4.22	7.42
Wood	3	3.2691	25.68	11.08	1.33	4.82	9.32
Leaves	1	1.9145	202.43	99.03	31.43	15.12	36.72
Leaves	2	1.9656	191.78	119.58	17.43	22.62	28.07
Leaves	3	1.6407	192.73	86.78	12.23	15.02	26.37
Grass	1	2.2018	154.83	80.48	20.58	18.27	24.07
Grass	2	2.8786	202.63	121.83	31.63	28.17	35.87
Grass	3	2.7278	206.43	115.08	29.68	18.67	26.17

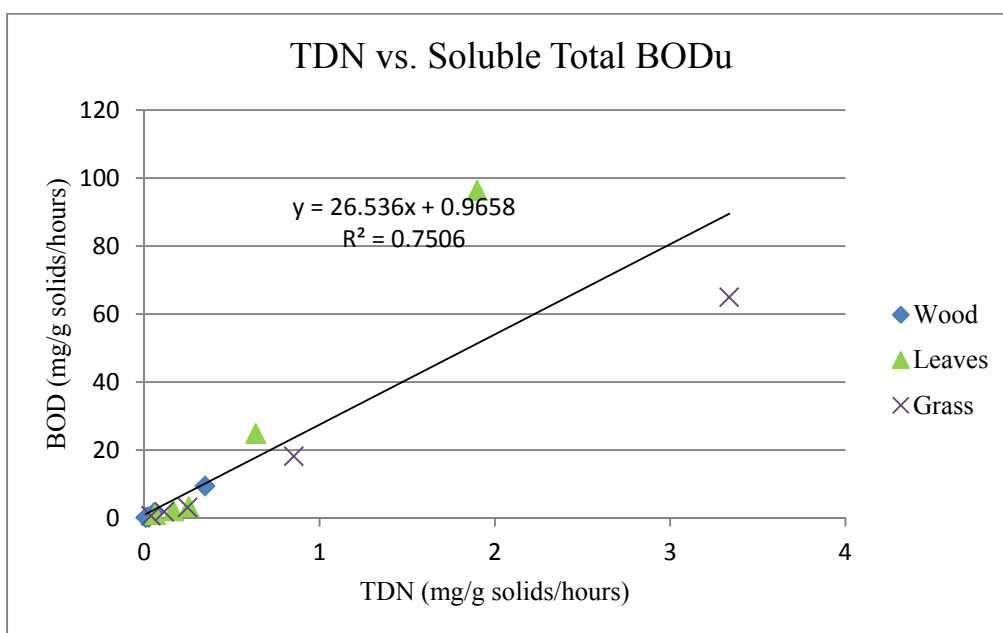
Raw BODu Data (Nitrification inhibited) (mg/L)							
		Mass of Sample (air dried) (g)	Leaching Time (hours)				
			1	3	6	10	24
CPOM Type							
Wood	1	5.6979	57.70	18.50	2.45	6.85	13.05
Wood	2	3.0369	20.20	7.80	0.45	3.75	7.00
Wood	3	3.2691	18.90	10.85	1.40	5.55	12.10
Leaves	1	1.9145	201.80	101.90	42.90	14.65	25.05
Leaves	2	1.9656	212.85	85.70	47.00	23.45	40.15
Leaves	3	1.6407	193.15	71.95	22.75	13.85	30.45
Grass	1	2.2018	162.80	65.75	19.50	11.95	25.50
Grass	2	2.8786	197.40	115.65	34.80	28.50	35.10
Grass	3	2.7278	197.80	96.85	37.65	14.60	28.95

Raw BODu Data (Unfiltered) (mg/L)							
		Mass of Sample (air dried) (g)	Leaching Time (hours)				
			1	3	6	10	24
CPOM Type							
Wood	1	5.6979	67.18	22.73	0.33	4.37	9.77
Wood	2	3.0369	26.38	6.48	6.23	1.17	11.92
Wood	3	3.2691	31.33	11.68	6.13	4.32	19.97
Leaves	1	1.9145	192.18	111.13	39.53	19.22	45.12
Leaves	2	1.9656	212.48	111.48	31.33	24.27	39.62
Leaves	3	1.6407	188.63	92.68	21.43	16.87	35.17
Grass	1	2.2018	133.88	71.88	16.78	11.87	12.32

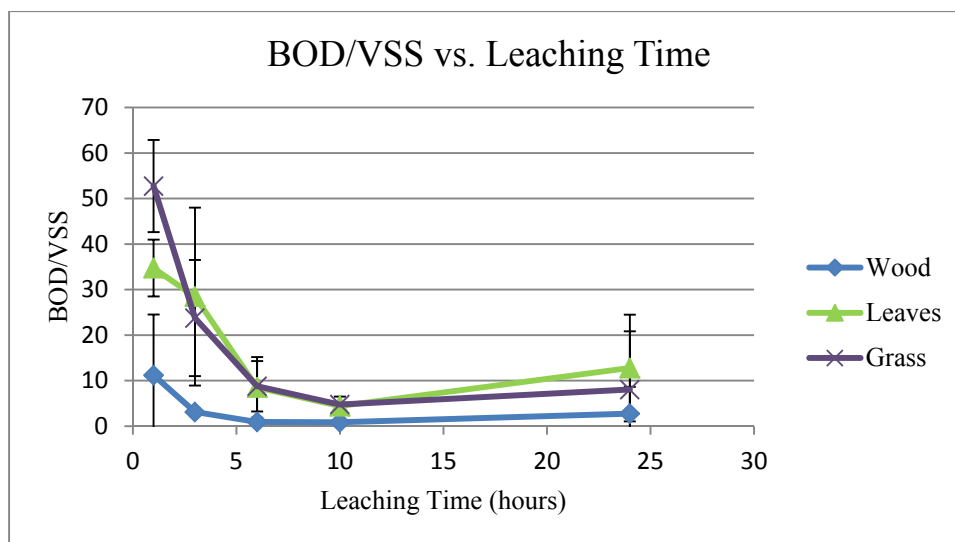
Grass	2	2.8786	195.43	126.48	59.83	29.42	44.27
Grass	3	2.7278	205.58	91.43	39.83	21.67	29.62



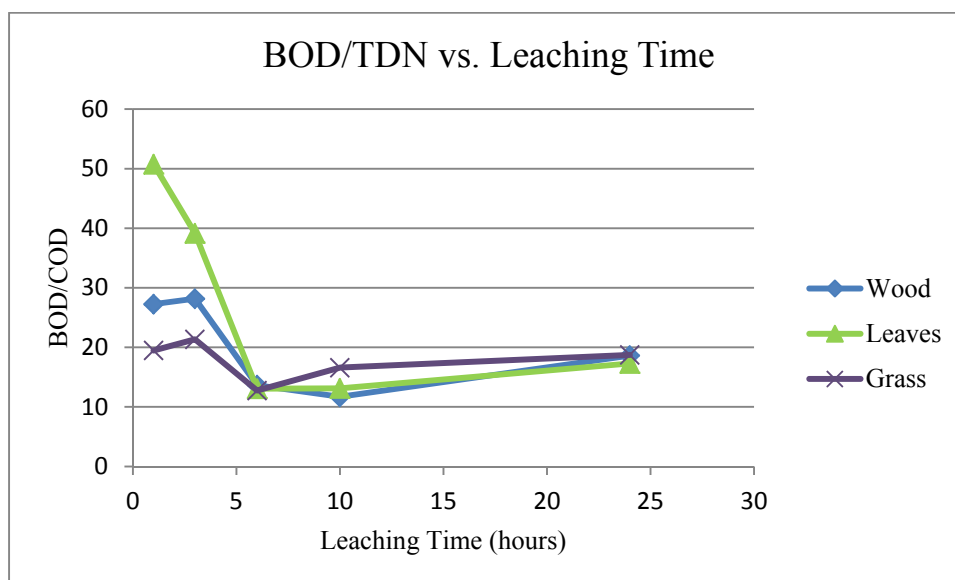
Comparison of VSS to soluble total BODu



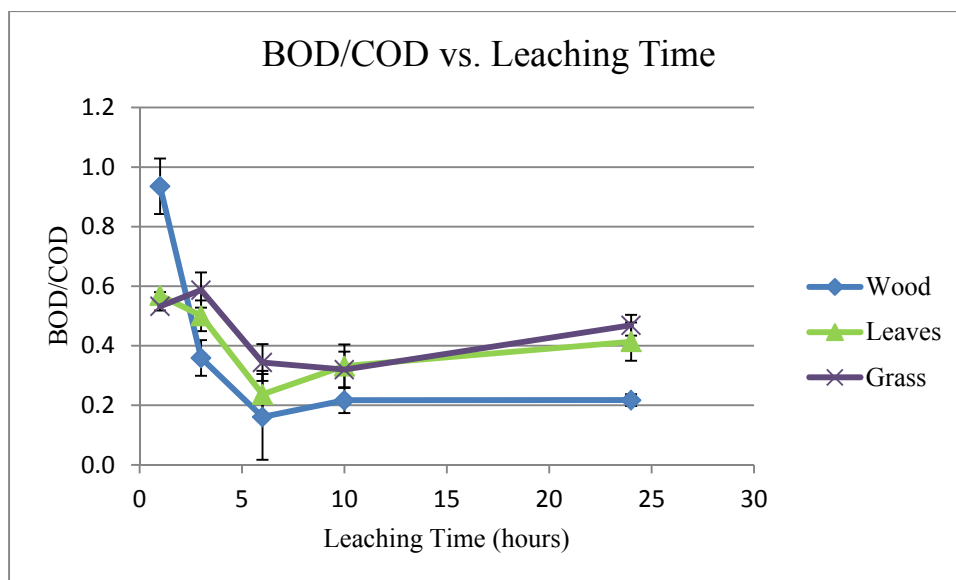
Comparison of TDN to soluble total BODu



BOD to VSS ratio versus leaching time



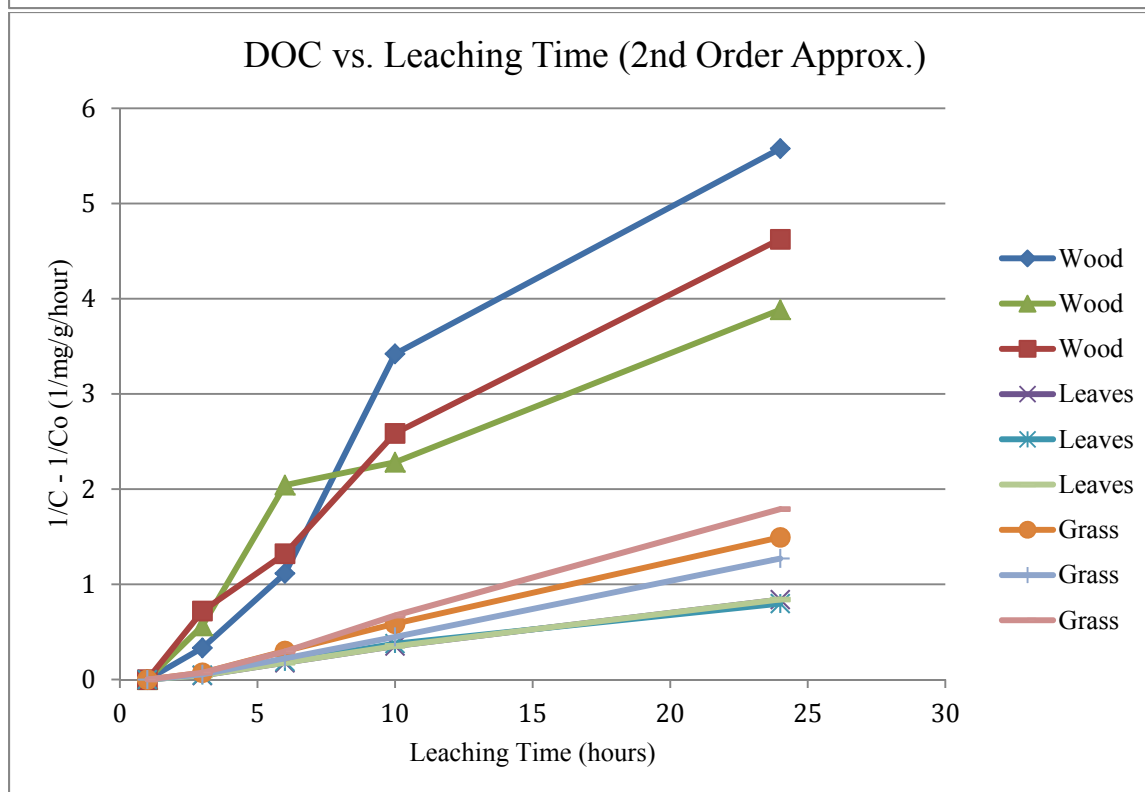
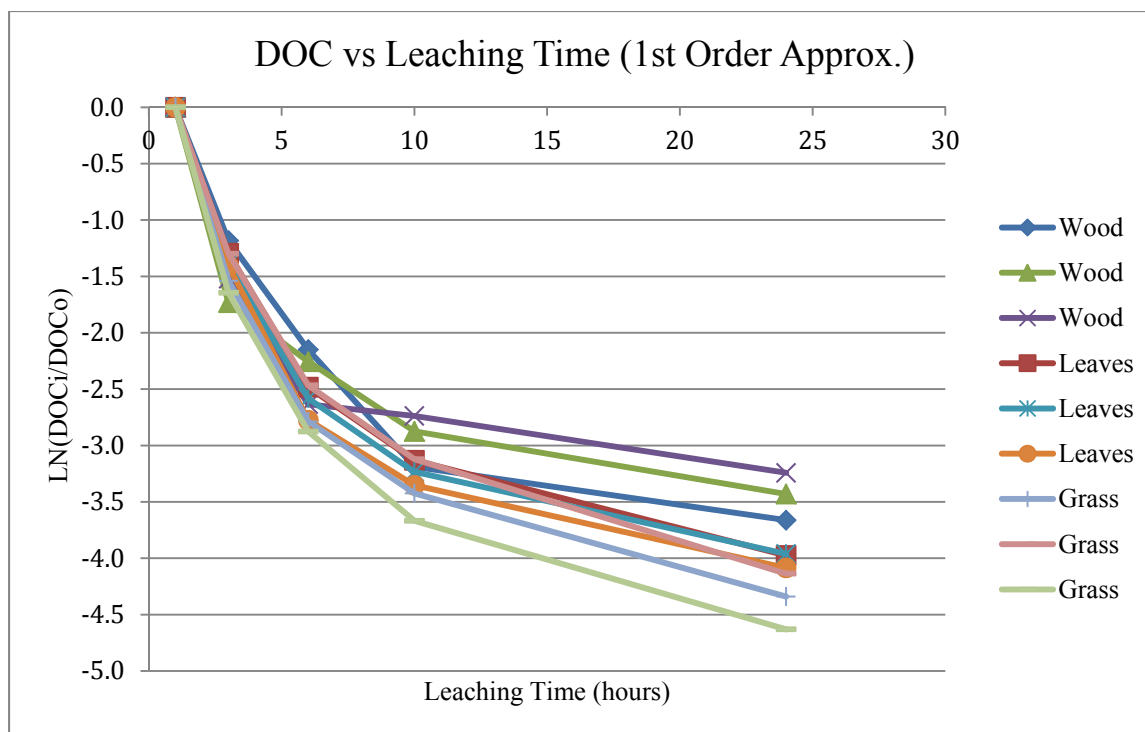
BOD to TDN ratio versus leaching time

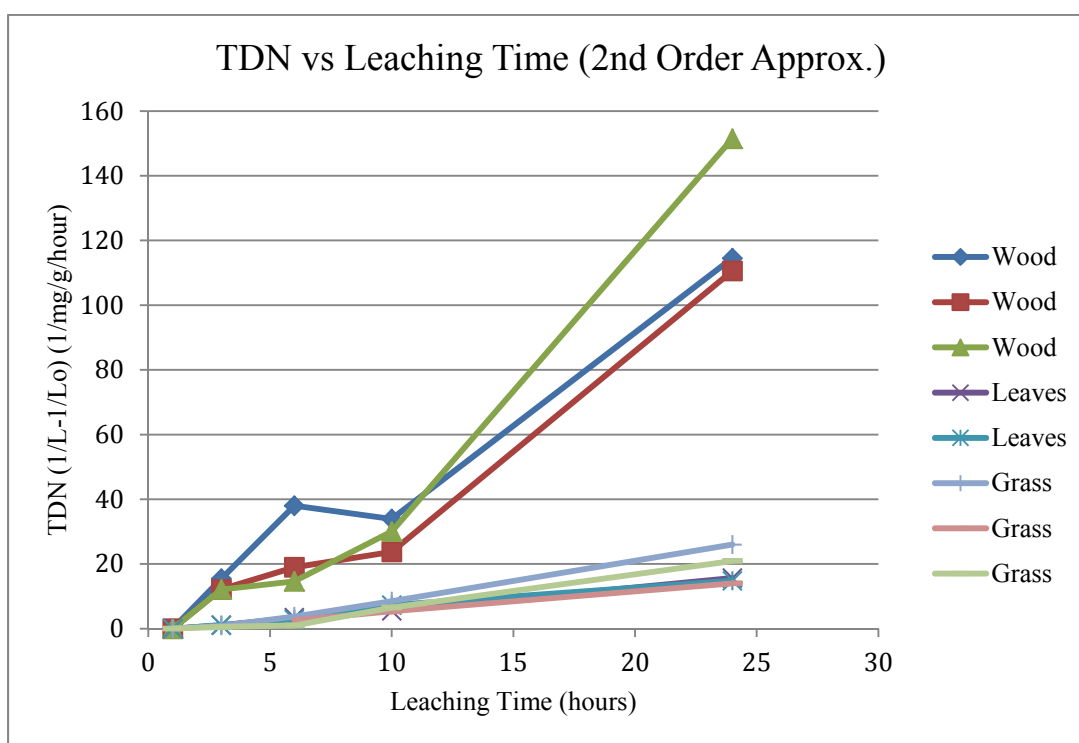
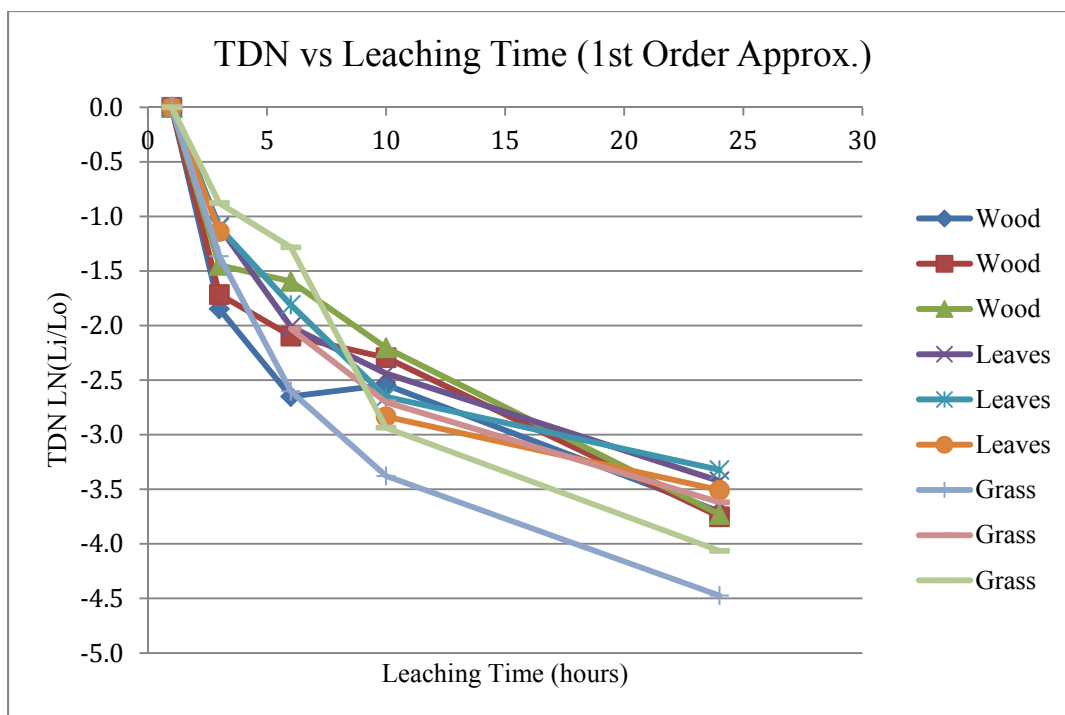


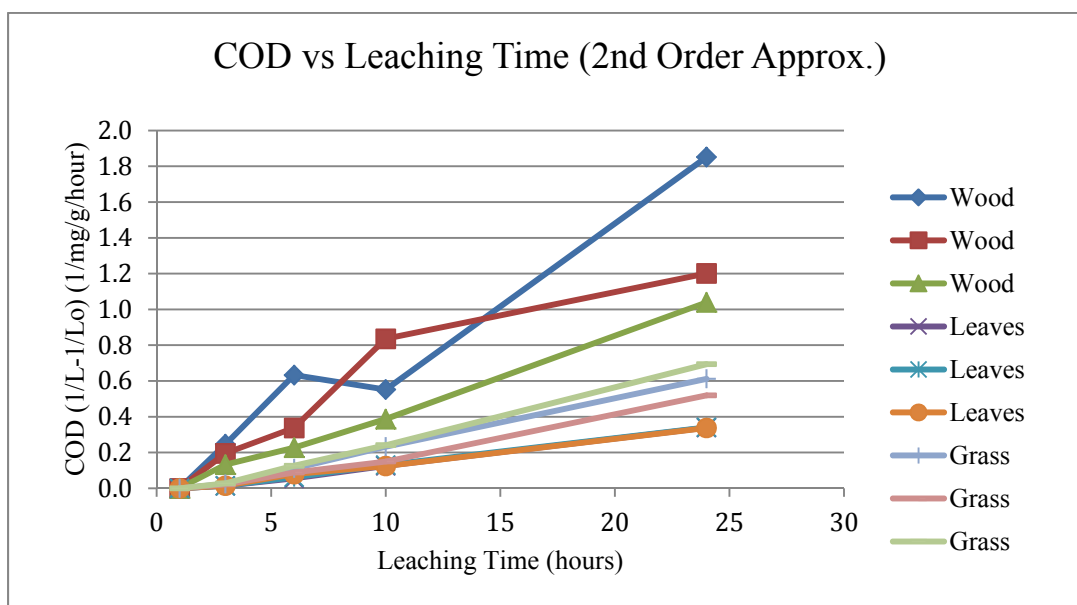
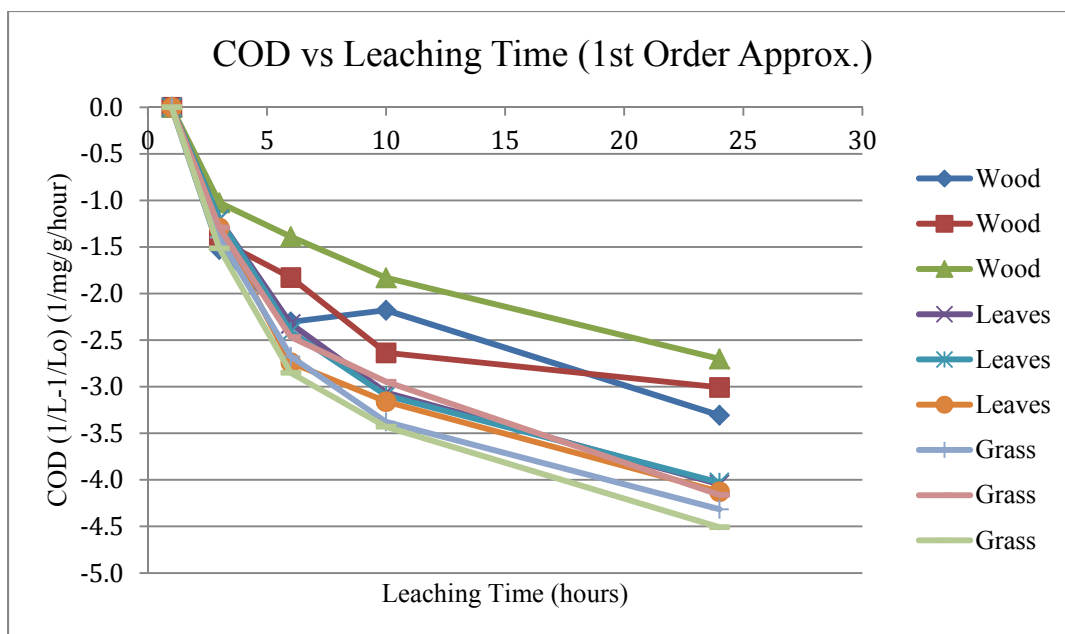
BOD to COD ratio versus leaching time

Appendix E

First order versus second order plots for parameters analyzed in the leaching tests







Appendix F

Summary data from Thomas Method determination of BOD rate constants.

k (1/day) (base e)					
CPOM Type	Leaching Time (hours)				
	1	3	6	10	24
Wood	0.29 ± 0.06	0.04 ± 0.01	-0.29 ± 0.59	0.04 ± 0.02	0.03 ± 0.01
Leaves	0.08 ± 0.01	0.01 ± 0.00	0.02 ± 0.00	0.02 ± 0.01	0.02 ± 0.00
Grass	0.09 ± 0.00	0.01 ± 0.00	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.00

BODu (mg/L)					
CPOM Type	Leaching Time (hours)				
	1	3	6	10	24
Wood	37.3 ± 30.6	13.3 ± 6.5	0.10 ± 1.6	4.7 ± 1.9	11.1 ± 4.1
Leaves	266.9 ± 32.1	97.6 ± 18.4	42.2 ± 17.4	18.6 ± 6.6	36.1 ± 9.2
Grass	244.6 ± 34.8	103.0 ± 31.2	33.3 ± 12.3	19.7 ± 11.0	32.5 ± 5.9

Lag (days)					
CPOM Type	Leaching Time (hours)				
	1	3	6	10	24
Wood	1.96 ± 2.16	4.62 ± 0.27	2.35 ± 2.65	3.48 ± 1.27	2.37 ± 0.07
Leaves	0.53 ± 0.04	0.85 ± 0.15	2.55 ± 0.46	1.82 ± 0.36	2.47 ± 0.09
Grass	0.42 ± 0.31	0.08 ± 0.09	1.50 ± 0.68	1.65 ± 0.25	2.18 ± 0.26

Appendix G

Photos and summary of Chesapeake Bay water wheel trash collector

These photos show a self-powered trash collecting system that was installed in the Inner Harbor of Chesapeake Bay in May of 2014. This is one example of the type of installation that could be used to collect trash at the discharge locations for the Salt Lake City storm drain system.

These photos were retrieved on June 26, 2014 from

<http://www.asce.org/CEMagazine/ArticleNs.aspx?id=23622331108#.U6xSHPldWVM>.

