Online Monitoring for Process Control

Los Angeles Glendale Water Reclamation Plant

Draft Interim Report I

April 2001

Applied Research (WESD), LAG, TITP, and EMD
Bureau of Sanitation
Public Works/City of LA

ISCO - STIP

CITY OF LOS ANGELES
INTER-DEPARTMENTAL CORRESPONDENCE

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Subject: **Online Monitoring for Process Control: ISCO/STLP BIOX-lOlO at LAG Draft Report**

This is the first interim report by the Applied Research Group/Wastewater Engineering Services Division (WESD) on the progress of the subject matter. This project has been prepared in collaboration with the staff of Los Angeles Glendale Water Reclamation Plant (LAGWRP), Environmental Monitoring Division (EMD), and ISCO/STIP.

It covers work for online monitoring of biochemical oxygen demand (BOD) at LAGWRP from April 2000 to early January 2000. Thus far, operations and applications have been highly successful. The LAR Biomonitor, the second BOD online instrument, also installed at LAG, has not performed to our expectations. There are also two toxicity meters (ISCO/ST1P and LAR) that are planned for installation in the near future.

For questions and comments please call Reza Iranpour / Dave Bianchi, project managers, at (310) 648-5280 or Miguel Zermeno, project lead, at (310) 648—5440.

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EXECUTIVE SUMMARY

Recommendations/Conclusions

I) A combination of the successful experiments in this report, previous experiences, and applications to plant process control justify our conditional recommendation to purchase the BIOX-1010 instrument from ISCO-STIP, as summarized by the following reasons (with the corresponding sections of the main report).

1. The BIOX-1010 (providing BOD readings every two minutes and operating at primary effluent) has given data agreeing as expected with BOD_5, allowing for a 15% standard deviation of BOD_5(5 day BOD result lab test), as described in *Standard Methods* 5210B. Averages of the machine readings during shock loadings usually agree well with the BOD_5 values for the corresponding 24-hour composite samples ***(Sections 3.1 and 3.2)***.

2. The BIOX-1010 (operating at primary effluent) has picked up many shock loadings from industrial waste dischargers ***(Section 3.2)***.

3. We would like to test the BIOX-1010 instrument at the primary influent (raw influent) using similar protocols developed for the primary effluent. This location would benefit the plant operation the most.

4. Based on past and present experiences with competing instruments and our knowledge of current work in the field, the BIOX-1010 instrument appears to be better than other rapid BOD measurement technologies ***(Sections 1.2 and 6.1)***.

5. The LAG plant management and operation staff have been very satisfied with the performance and results. Since late September they have been using the BIOX-1010 instrument to trigger an alarm to alert them to possible shock loads and activate a flexible action plan that they have developed to determine whether the flow to the plant should be reduced to prevent a process impact ***(Section 3.2)***.

6. Industrial Waste has found this instrument to be very helpful, since it assisted them in identifying industrial waste dischargers that were exceeding their permits for discharges into the waste stream ***(Section 3.2)***.

7. One of the industrial waste dischargers, which is Baxter Hyland Immuno, has already purchased the same unit to control their waste concentration into the collection system and into LAG. The data from such locations could be very valuable to our plant operations as they could help prevent high loading fluctuations of our primary tanks ***(Section 6.1)***.

8. The cost associated with the installation and operation of a BIOX-1010 is estimated to be around $42,000 for capital/installation and startup costs, and over $3000 for annual operation and maintenance costs. Annualizing this cost over ten years gives a cost around $7000 per year per unit *(Section 5.3)*.

9. The cost of biological and chemical actions to recover from a process impact is tens of thousands of dollars, and the total cost may be much more, depending on regulatory fines *(Section 5.4)*.

10. The cost advantage of a BIOX-1010 compared to the approximately $11,000 per year required for daily BOD_5 measurements at one location is less important than the benefits of the speed of the instrument (thousands of times faster than BOD_5) and its ability to produce detailed records of intraday fluctuations of BOD *(Sections 5.1, 5.2 and 5.3)*.

11. It would be very interesting to know how accurate the unit would perform when the BOD concentrations are low (i.e., less than 20 mg/l). This implies that ISCO/STIP should test the unit at the effluent end of the secondary clarifiers, in the future at some plant.

II) Continuing with existing plans to test toxicity meters (ISCO-STIP & LAR) at LAG's primary influent location is recommended and preparation for this work is under way.

III) Inclusion of the BOD and toxicity projects into the Bureau's automation master plan is recommended.

Another interim report is planned that will discuss the remaining results on the BOD online instruments and activities with toxicity meters. **Figure 0, attached to this Executive Summary, is a tentative schedule for planned further work on online instruments.**

Introduction

This is a continuation of the 1995 studies conducted by the Bureau of Sanitation Applied Research Group and TITP staff on Biochemical Oxygen Demand (BOD) measurement instruments, which began in the preceding reports, "Online BOD Measurements, BOD 2000 Instrument Pilot Test Results, 1995" and "Online BOD Measurements BIOX-1010 Pilot Test Results, 1995". The BOD-2000 report presented the background and motivation for the work on BOD instrument technology in terms of its suitability for process control applications in the wastewater treatment facilities.

Although the five-day BOD_5 measurement is suitable for regulatory compliance with the California Water Quality Control Board (CWQCB) in retrospective influent/effluent and treatment process monitoring, it is too slow for process control. A much faster measurement is needed for operators to respond to shock loadings of organic wastes or toxic chemical discharges. Other available measures of organic strength (e.g., chemical oxygen demand, total organic carbon, etc.) cannot substitute for BOD measurements.

The present study is highly encouraging and indicates that this technology is likely to be a reliable method for nearly instantaneous BOD monitoring for plant process applications. Laboratory tests indicate that the technology is already capable of providing quantitative measures in as little as 2 minutes that almost always agree well with BOD_5. The BIOX-1010 has been operating well for the past five months and has produced highly satisfactory results.

Included in the report is a brief description of the instrument technology, tests that were conducted under both laboratory and field conditions, and the conclusions following extensive evaluation of the data.

Management Issues

Assuming a 10-year life cycle for the BIOX-1010 instrument with zero salvage value, and an annual inflation rate of 4%, around $42,000 for capital/installation and startup costs, and around $3000 for annual operation and maintenance costs translate to an annualized cost of around $7,000 per monitoring station. A typical process impact takes three to four weeks to correct. The costs of biological and chemical actions to recover from a process impact total tens of thousands of dollars, and the total cost may be much more, depending on the specific violation to the NPDES permit. Thus, the actual costs to the City of not using a BOD instrument are the costs of the expected number of process impacts. They must be compared with the costs of using an instrument, continuing the legally required minimum BOD_5 testing, and the costs of adapting plant operation to prevent a process impact, taking action at the first warning of abnormal conditions. This latter group of costs is small compared to the costs of impact recovery and probable fines ***(Section 5)***.

Method

Instrument Operation: The BIOX-1010 instrument works by mixing small amounts of wastewater (automatically collected by the online unit) with a large amount of oxygen-saturated tap water,

and using a dissolved oxygen (DO) probe to measure the oxygen consumed as the substrates are metabolized by a bacterial population residing in small cylindrical plastic carriers in the reaction vessel. Knowing the pumping rates for the wastewater and tap water, the oxygen depletion in the bioreactor, and a user-set calibration constant LK allows BOD estimates to be calculated by a simple formula. A microprocessor controls all aspects of operation, measurement, and display. The BOD measurements were recorded in the microprocessor memory every two minutes for this study's analysis, but the BOD value on the instrument display is updated much more frequently, being recalculated from the internal sensor readings at intervals of less than a second. Calibration is an important aspect of the operation of this instrument that is discussed in detail in the full report ***(Section 2.4)***. ***Figures 1 through 4*** show the instrument and how it works.

Maintenance: The success of this instrument in the field depends to a large extent on how well it is maintained. The primary effluent sample contains microbes and substrates, so that slime tends to build up quickly in the strainer and DO probe membrane surface. The instrument is now programmed to wash the membrane with a spray twice a day. Nevertheless, if the membrane is not manually cleaned for more than a week, the instrument BOD values start to trend upward. It was found that with a proper maintenance and service schedule the microbial buildup problem was solved. Based on a combination of information from the manufacturer and experience in this study, the currently recommended service schedule consists of general service (cleaning the strainer and the DO probe membrane surface according to the procedures in the manual) once a week, and providing full service to the unit (calibration and cleaning of the pumps) once a month. The time required to perform the weekly cleaning service is approximately one hour ***(Section 4)***.

Results

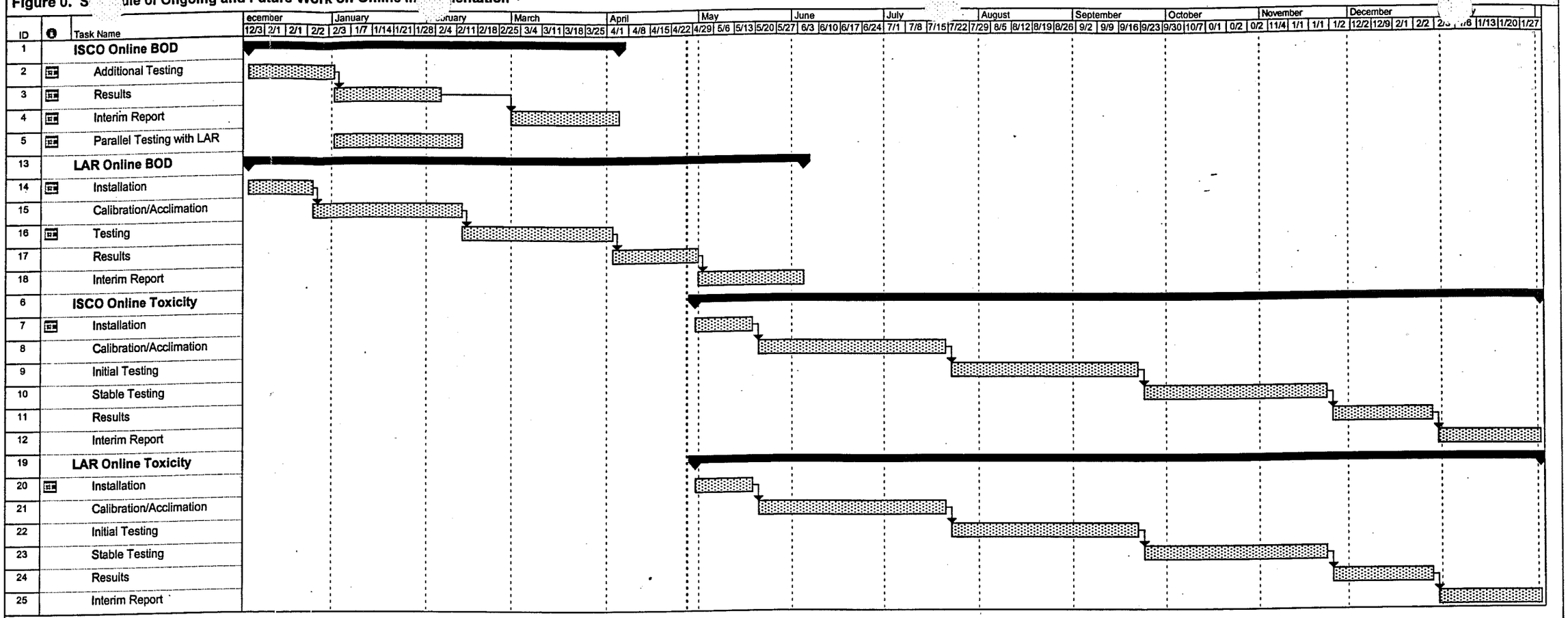
Online BOD vs. BOD_5 Comparison: Ten days of direct comparisons between the online BOD and BOD_5 were performed in the field to evaluate the precision of the online unit. The test days were in September and October, 2000, and January, 2001. The BIOX-1010 readings generally duplicate the BOD_5 time series trends, although the instrument readings were generally less variable than the laboratory results, neither rising as high on the peaks nor sinking as low in the dips. Nevertheless, the disagreements were almost always within the range of uncertainty of the BOD_5 method ***(Section 3.1, Figures 9a – 9e)***.

Detection of Shock Loads: Furthermore, this equipment made it possible for LAG staff to modify process operation nearly 20 times in a period of four months in response to high organic loading events in the plant influent. Since late September the plant management and operation staff have been using the instrument to trigger an alarm to alert them to possible shock loads and activate a

flexible action plan that they have developed to determine whether the flow to the plant should be reduced to prevent a process impact, as was done, for example, on November 4 ***(Section 3.2, Figures 10a – 10m)***.

Instrument vs. BOD_5 Daily Averages: Averages of the machine readings during shock loadings usually agree well with the BOD_5 values for the corresponding 24-hour composite samples (Table 3). In addition, the BIOX has assisted Industrial Wastes Management Division (IWMD) in alerting its staff and collecting wastewater samples to evaluate illegal discharges into our collection system and into LAG. The results to date are highly satisfactory, and appear superior to competing devices and tests, such as the LAR BioMonitor, the Nissin BOD-2000, and the headspace BOD test ***(Section 3.2, Table 3 and Figure 11)***.

Figure 0. S ule of Ongoing and Future Work on Online In mentation



Project: Online BOD and Toxicity at LAG
Date: Fri 4/27/01
Applied Research, LAG, EMD, ISCO, & LAR

Task | Summary | Rolled Up Task

Factor of safety is not included for other priorities and any other situations.

SECTION 0
NOTATIONS AND KEYWORDS

BIOX-1010:	Instrument for BOD measurement provided by ISCO-STIP at Lincoln, Nebraska
BOD:	Biochemical Oxygen Demand
BOD_5:	BOD value obtained from the standard 5-day BOD test
online BOD:	BOD value obtained in a few minutes from an automated respirometric instrument
WESD:	Wastewater Engineering Services Division
LAG:	Los Angeles / Glendale Treatment Plant
DCT:	Donald C. Tillman Water Reclamation Plant
EMD:	Environmental Monitoring Division
COD:	Chemical Oxygen Demand
TOC:	Total Organic Carbon
Sample:	Primary Effluent
Unit:	BIOX-1010
LK factor:	Calibration factor for instrument calculation of online BOD
NPDES:	National Pollutant Discharge Elimination System
DO Probe:	A small electrochemical cell that produces an output current proportional to the dissolved oxygen concentration
CWQCB:	California Water Quality Control Board
RWQCB:	Regional Water Quality Control Board
EPA:	Environmental Protection Agency

SECTION 1

1.1 Background

The Los Angeles Bureau of Sanitation (BOS) is conducting a program to reduce cost and avoid violation to the National Pollutant Discharge Elimination System (NPDES) permit by using online instrumentation. This technology will be able to do much more than traditional laboratory standard tests like the BOD_5 test.

This is the first interim report on the automation project (online BOD, toxicity meter and others) at the Los Angeles / Glendale Treatment Plant (LAG), covering the period up to early January 2001. Work at LAG on process control instrumentation is ongoing. The attachment to the executive summary is a tentative bar chart schedule of planned work for the near future, focusing on toxicity testing and the LAR BioMonitor instrument.

This project is being conducted by a task force composed of personnel from the Applied Research Group of the Wastewater Engineering Services Division (WESD), LAG, Environmental Monitoring Division (EMD), Industrial Waste Management Division (IWMD), Bureau of Sanitation management, and ISCO-STIP vendors. The preparations at LAG began about one year ago with a review of previous studies on this topic by the Bureau of Sanitation and references on online instrumentation.

As described in subsequent sections, the project has been highly successful so far. Laboratory BOD_5 values compared with BOD online results are very close. In addition, approximately twenty shock loadings in the past five months have been detected, allowing the LAG plant staff to respond quickly and modify process operations to avoid a process impact in the aeration basins. It has also allowed IWMD to evaluate the plant influent composition for pollutants and to cross-reference with their permit discharge database to find the industrial waste discharger.

A prompt biochemical oxygen demand (BOD) detection in our wastewater treatment plant influent and primary effluent is essential for process control. As an example of this need, the LAG treatment plant experiences diurnal variations of influent flow rate that range from 6 to 21 mgd, combined with unpredictable discharges from industries, comprising 15-25% of the influent flow, which could possibly cause violations of our wastewater discharge permit. It frequently happens that many BOD shock loadings occur in a month, causing process impacts. Hence, it would be extremely useful to know the plant's influent BOD concentration in a few minutes, preferably by an automated monitoring system that would operate continuously. This would allow plant

would allow plant operators to establish appropriate process control measures during periods of high BOD loadings, and allow IWMD to investigate the discharge source or sources.

Other chemical laboratory tests such as chemical oxygen demand (COD) and total organic carbon (TOC) have been tried to supplement the five day BOD (BOD_5). However, mercuric sulfate ($HgSO_4$), a hazardous chemical, was used as a complexing agent in the COD test, and therefore Sanitation management required the treatment plants to end all COD testing. The TOC analysis test requires only a few hours as compared to the BOD_5 analysis and can be correlated to BOD_5. However, TOC analysis does not measure other organic and inorganic bound elements (such as nitrogen and hydrogen) that can contribute to BOD. Hence, it cannot be considered a suitable replacement for BOD_5. EMD laboratories at LAG performs COD analysis without the use of $HgSO_4$ and the results are still useful to the plant operations.

Competing types of instruments make their measurements either by bioreactors or biosensors. The next section summarizes other existing technologies that have been considered, all of which appear to be inferior to the BIOX for this application.

1.2 Review of Literature and Other Technologies

The BOD_5 test is slow because it waits for the indigenous microbial population in the wastewater to metabolize most of the available nutrients. Thus, the fundamental strategy of all methods that make faster measurements of BOD is to speed up consumption of the nutrients by providing additional biomass and to measure oxygen consumption with some method of respirometry. This strategy was first introduced more than 20 years ago (Leblanc, 1974), but microprocessor control has been the key to the more recent development of automated instruments to carry out the necessary procedures rapidly at low cost. The measurement method in biosensor devices is more recently developed than the method of the bioreactors, but there are many diverse ways to use bioreactors, and they are currently used in several modern instruments.

Biosensor instruments: Two of these instruments are on the market: the Nissin Electric BOD-2000, also available in field model BOD-2200, (CKC Manual, 1994) and the LANGE ARAS Sensor BOD (Riedel, 1994). The biosensor in each is a biomembrane impregnated with well studied microbes, wrapped around an electrode that measures dissolved oxygen. The biosensor is located on the side of a small cell, about 1 cm^3, through which sample flow is pumped.

In Iranpour et al. (1997a) there is a description of additional details of the operation of the BOD-2000 and of the long development process in Japan for the instrument that is discussed in Harita,

et al. (1985), Hikuma, et al. (1979), Karube, et al. (1977a & b). In both the BOD-2000 and the BOD-2200 the membrane is impregnated with *Trichosporon cutaneum* yeast. Good correlations with BOD_5 were observed in results from the BOD-2000, a laboratory instrument that requires operators to insert each sample separately, which is too labor-intensive for process control (Iranpour et al. 1997a).

The LANGE ARAS BOD instrument, from Germany, uses biosensors impregnated with two types of microbes, *Rhodococcus erythropolis* and *Issatchenkia orientalis* (Riedel, 1994). These microbes are claimed to be less of a health hazard to humans than the yeast in the Nissin instrument, so disposing of used membranes needs fewer safeguards. A laboratory model with labor-intensive operation much like the BOD-2000 has been demonstrated on the West Coast (including one day at TITP). An on-line version was planned to be available in late 1995, but there has been no contact with the vendor in recent years, so the availability of the online version is unknown as of the time of this interim report.

Bioreactor instruments: In these instruments the microbes are distributed through a reaction vessel instead of being confined in a membrane, so many configurations have been used and many ways of measuring oxygen consumption. For example, The Columbus Instruments activated sludge respirometer (Columbus Instruments, 1994) uses activated sludge from wastewater treatment plant and measures respiratory activity by detecting both O_2 and CO_2 concentrations in the headspace gas of the reaction chamber, using a special fuel cell for oxygen detection and an infrared spectrometer for CO_2. The respirometer system at the Newark, Ohio, wastewater treatment plant (Loomis 1991) also uses sludge, but uses KOH to scrub CO_2 from the headspace gas, and infers the consumption of O_2 by respiration, based on the pressure reduction in a tightly sealed reaction chamber.

The LAR (formerly Anatel) Biomonitor uses activated sludge from the plant, in two cascades of four bioreactor vessels each, one cascade for the sludge alone and one for sludge plus sample. Measurement of oxygen consumption in each cascade allows endogenous respiration to be determined separately from the respiration of the mixture of sludge and sample (Anatel Corporation, 1996).

Other promising bioreactor procedures to speed up BOD measurements are still being studied, such as the GC-HBOD$_3$ (Logan, et al. 1993 and 1997). However, as this is a three-day test, it also is not suitable for process control.

The BIOX-1010 is a bioreactor instrument, and is described in much more detail in Section 2.1. For this section it is distinguished from other instruments in this class by having its biomass on plastic carriers instead of in sludge, and by detecting dissolved oxygen depletion instead of requiring diffusion between a liquid phase and headspace gas. Riegler (1984, 1987) discusses the background and operation of a respirometer that is an early version or a close precursor to the BIOX-1010, giving some details that do not appear in the Manual (Cosa Instrument Co., 1994). Additional work with the early version is reported by Köhne, et al. (1986), and experience with the BIOX-1010 is reported in one preprint (Teutscher and Grosser, n.d.) for which copies are available from the Applied Research Group office.

1.3 Goals and Objectives

The overall goal is to evaluate the application of the BIOX-1010 for process control in a wastewater treatment plant. The objectives are:

1. To obtain information about the BIOX-1010 under process conditions in LAG:
   a) Quality of the results relative to the standard BOD$_5$ test;
   b) Detection of shock loadings;
   c) Operation and maintenance requirements; and
   d) Application to process control.
   e) Testing the BIOX-1010 unit at the primary influent.

2. To obtain information about similar competing technologies (e.g. LAR BioMonitor):
   a) Dependability of results and process applications under similar field conditions;
   b) Operation and maintenance under similar field conditions.

3. To recommend ~~to management~~ the best technology for process control BOD monitoring for LAG and perhaps other plants ~~in a report~~ containing the following:
   ~~a) Comprehensive~~ concise executive summary;
   ~~b~~) Instrument setup, operation and maintenance issues;

c) Experimental results;

d) Management issues and application to process control; and

e) Economic evaluation.

4. To inform management about ongoing and future work on online instrumentation, emphasizing toxicity detection (Figure 0):

a) Tasks;

b) Schedule;

The following sections summarize the experimental setup and procedures for the ISCO-STIP BIOX instrument at LAG, online BOD results with an analysis of the laboratory BOD_5 and shock loadings, maintenance and operational schedule, preliminary conclusions, and preliminary recommendations. Thus far, our effort at LAG has been highly successful.

SECTION 2
METHODOLOGY

2.1 The BIOX-1010 Analyzer

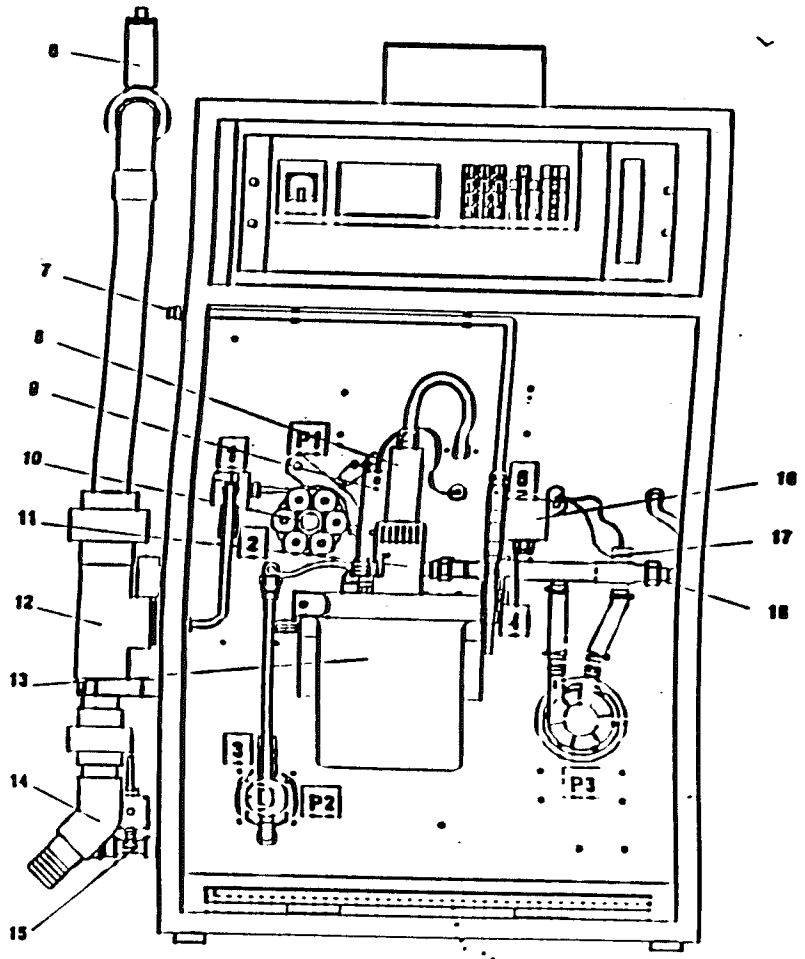
The BIOX-1010 is a field online BOD analyzer instrument. The instrument (Figures 1 and 2a) is enclosed in a weather resistant casing. The casing is divided into four compartments, two in the front and two in the back. The top front compartment (Figure 1a) contains the unit's computer system with a liquid crystal display (LCD) for measurement results and a keypad. The front bottom (Figure 1a) compartment contains the water and sample pumps, dissolved oxygen probe, fluidized bed bioreactor, and tubing for the sample and fresh water. The upper back compartment (Figure 1b) contains all the electrical connections such as the printer, computer, control room connection, etc. The lower back compartment (Figure 1b) contains the air pump, air diffuser system, fresh water container, thermostat, and all other measuring parts. Located on the right side of the casing are the connections for the fresh water, sample wastewater and overflow sample discharge pipes. Inside the 2-inch intake sample PVC pipe is a cylindrical fine strainer with openings of 0.5 mm pores to prevent any clogging to the 3 mm tubing feeding the sample to the bioreactor (Figure 2b). A microprocessor controls all aspects of operation, measurement and display. The sample flow rate range is from 1 to 80 mL/min, the fresh water flow rate range is 5 to 500 mL/min, the reactor total mixed inflow and outflow is constant at 500 mL/min and the operating temperature range is from 27 to 32 degrees Celsius.

The BIOX-1010 performs measurements (Figure 3) by determining and controlling the sample flow rate required to maintain a specified constant rate of respiration by an acclimatized biomass in the fluidized bed reactor. A stable population of microbes is maintained under controlled conditions by using an immobilized biofilm on a multitude of small, hollow, cylindrical plastic carriers. Turbulence in the bioreactor prevents adhesion of the biomass to the external surface of the carriers, but allows the development of an acclimatized biofilm on the interior surface. The quantity of biomass is thus fixed by the surface area to which it adheres.

The unit operates by using computer-controlled pumps to mix a small continuous stream of a nutrient-laden solution (e.g., plant primary influent) with a large amount of tap water, which is saturated with oxygen by the air pump. The mixture is supplied to the bioreactor, where the dissolved oxygen sensor (DO probe) determines the oxygen consumption by measuring oxygen concentration in the bioreactor. The sample and tap water flows to the bioreactor are adjusted by the instrument's computer to maintain the bioreactor dissolved oxygen (DO) as the nutrients and

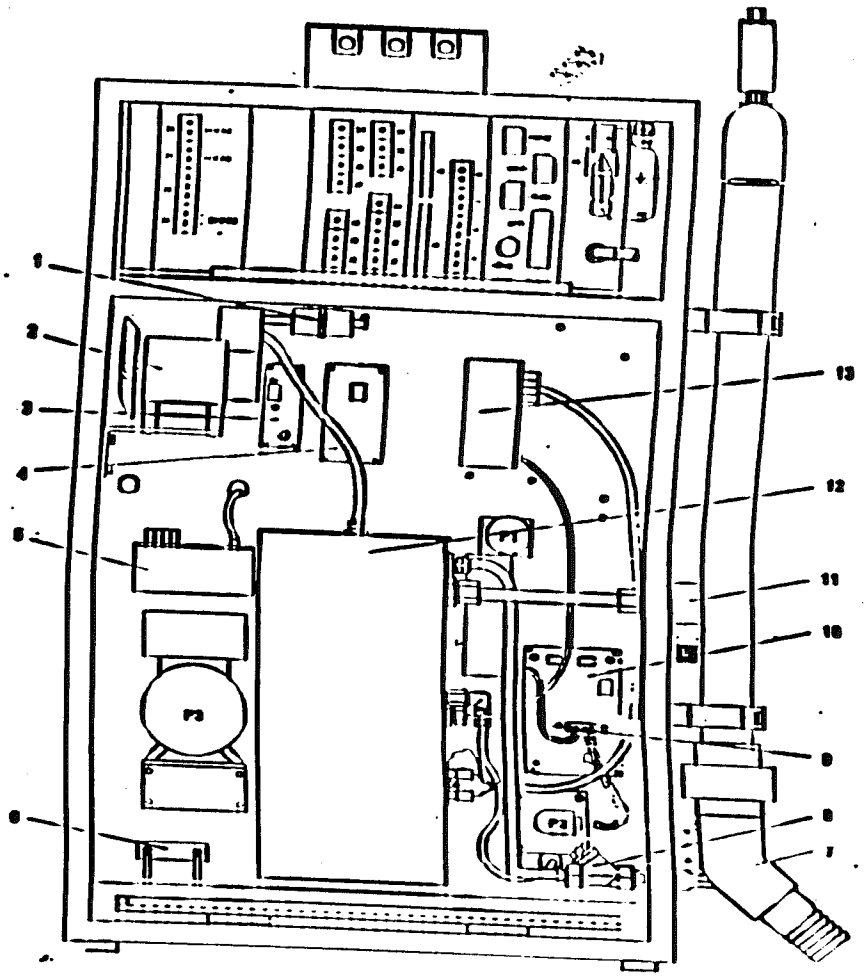
Figure 1. ISCO/STIP BIOX-1010 Instrument BOD Analyzer

a) Front view



1 = Valve 1
2 = Valve 2
3 = Valve 3
4 = Valve 4
5 = Valve 5
6 = Venting valve
7 = Sample discharge
8 = O_2-probe
9 = Sweeper
10 = Roller head P1
11 = Flow armature
12 = Bypass screen
13 = Bio-reactor
14 = Bypass inlet
15 = Fresh water intake
16 = Pressure switch
17 = Temperature sensor, puls controller heating 2
18 = Heating 2, circulation system
P1 = Peristaltic pump
P2 = Gear pump
P3 = Circulating pump

b) Back view



1 = Air filter, compressor
2 = Compressor
3 = Temperature test amplifier (temperature sensor frequency converter)
4 = Oxygen test amplifier
5 = Puls controller, heating 2
6 = Leakage contacts
7 = Bypass outlet
8 = Dirt trap, dilution water supply
9 = Temperature sensor (heating controller 1
10 = Pump control
11 = Tube connector overflow
12 = Fresh water tank
13 = Heating controller 1

Figure 2. ISCO/STIP Biox-1010 Pictures

a) Front view

b) Bioreactor

oxygen are used by the microorganisms, and then a simple formula converts the flow data into a BOD estimate.

For municipal wastewater the sample stream is all the seed culture that is needed. The controlled conditions of oxygen and food permit the rapid reproduction of the microorganisms. The acclimatization period is about 6-7 days and depends on the waste stream constituents and the rate of growth of the microorganisms.

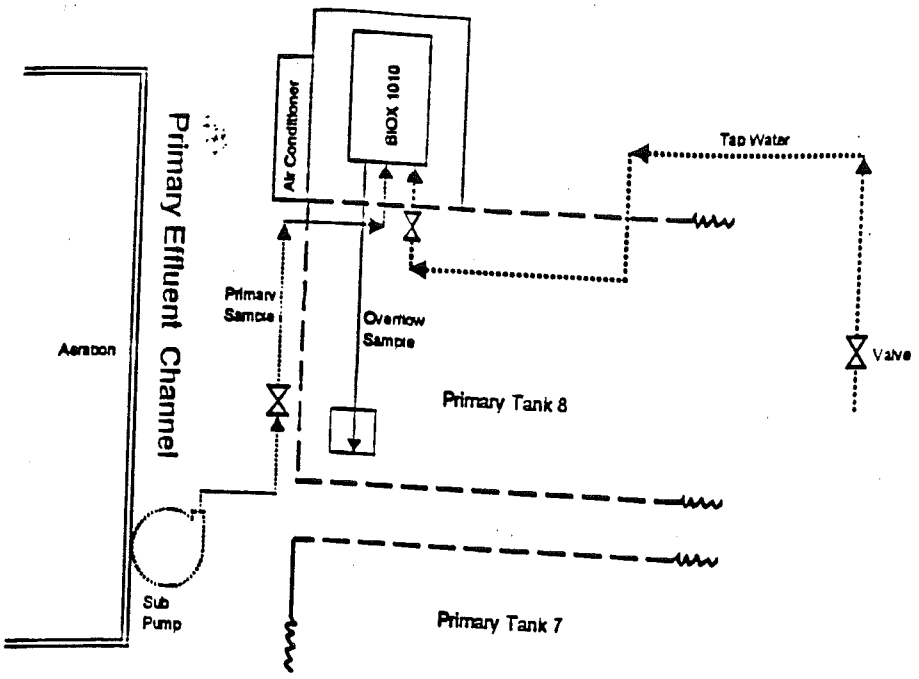
2.2 Equipment setup

In April 2000 a shed was set up to shelter the BIOX-1010 during the field testing. The shed is 5 feet in width and 8 feet in length, with an air conditioner to maintain the temperature at recommended levels for the microorganism culture. It was placed next to the end of Tank number 8 and as near as possible to the primary effluent flow channel to reduce the sample travel distance and prevent changes in the sample BOD strength. Figure 4 is a flow schematic of the BIOX-1010 at LAG. 1 inch and 1-1/2 inch hoses are connected to the BIOX-1010 to deliver and discharge the fresh water and sample, respectively. A submersible pump inside the primary effluent channel pumps the sample from 3 feet below the surface. A 1-1/2 inch PVC pipe is connected to the pump (5 feet) and flexible hose (20 feet) connect the BIOX-1010 to the PVC pipe. 1 inch flexible hose is used to run the fresh water from a distance of 400 feet to the unit, the maximum fresh water required by the unit being 500 mL/min.

2.3 Installation and Startup of Test Units

The first BIOX-1010 was delivered to the site in April 2000. The field test for this unit started on the second week of April and continued until mid-July. The period from April 20, 2000 to May 15, 2000 was used to acclimatize the bacterial population in the bioreactor. The acclimatization period was long because during this period LAG staff was upgrading some of the potable water valves and the equipment had to be placed in standby mode to avoid overheating it. In addition, a few power outages contributed to the acclimatization delay. ... Once the acclimatization of the microbes had been achieved in the bioreactor, BOD measurements started recording every two minutes. However, for a month BOD trends were very unstable. Figure 5 shows BOD measurements varying almost 200 percent within 20 minutes. Efforts were made to correct the equipment's faulty parts by contacting the vendor, but it was determined that major and intensive maintenance was required every day to keep this unit operating properly. Therefore, it was decided to replace the unit with the latest model and upgrade the software program version.

Figure 4. Flow schematic of BIOX-1010 at LAG



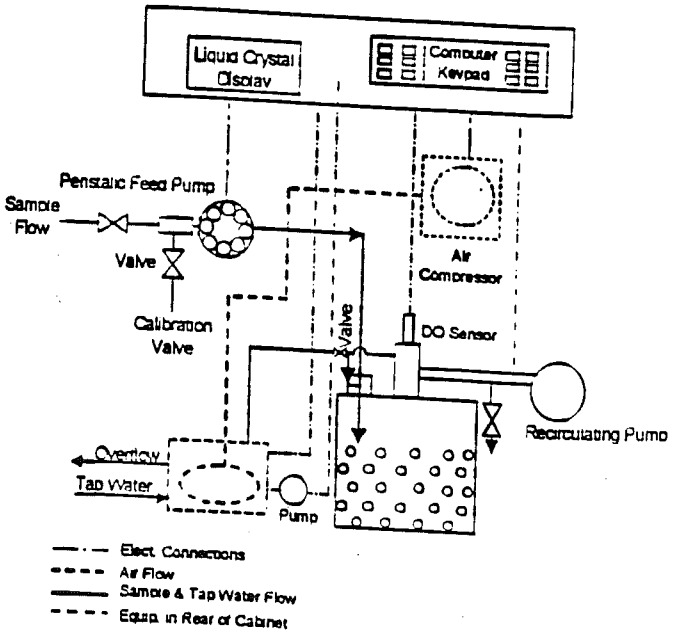
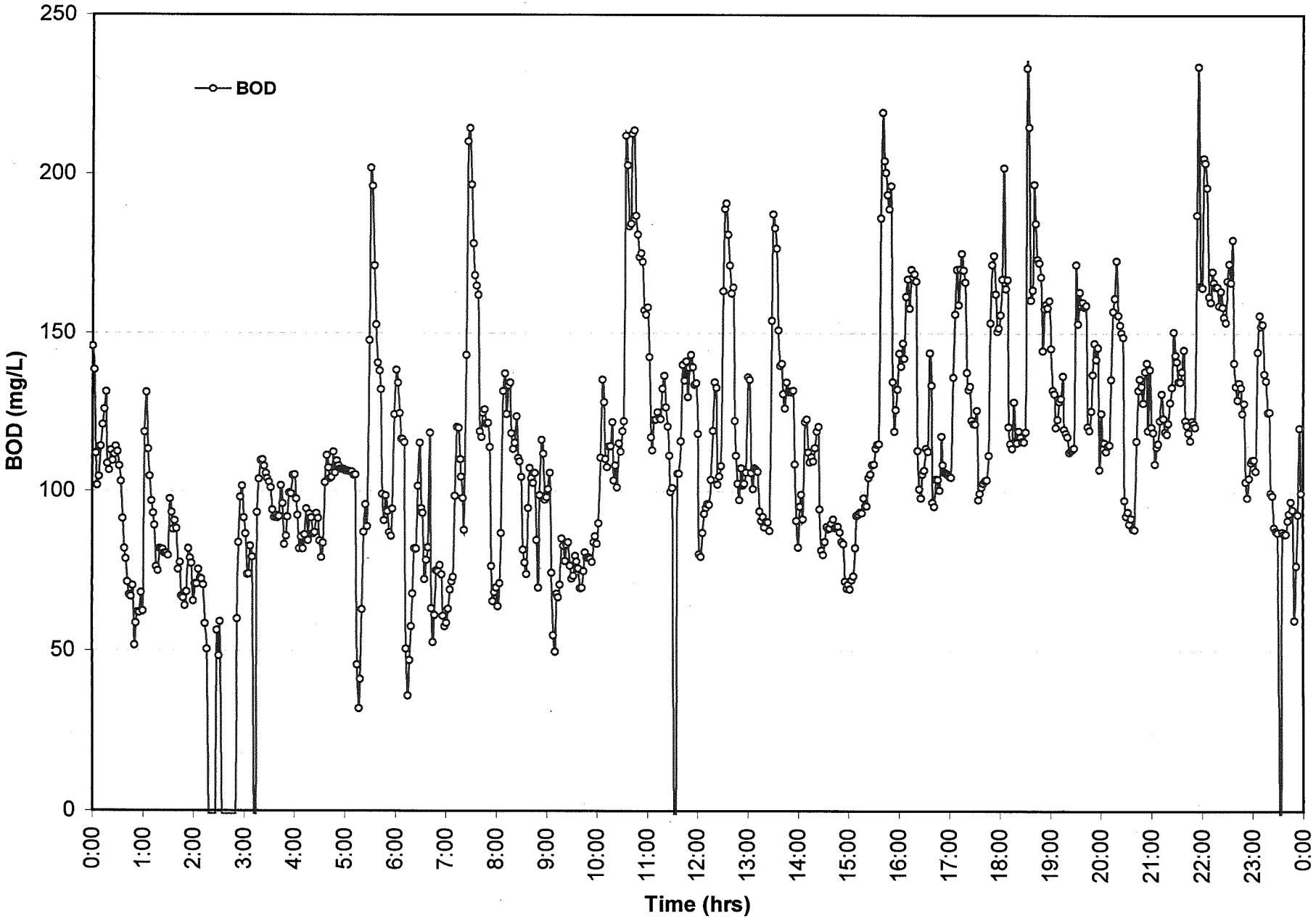


Figure 5. ISCO/STIP BIOX-1010 primary effluent (old set-up), June 15, 2000



The new BIOX-1010 was installed August 5, 2000, and it has been performing very well. The established culture was transferred from the old to the new bioreactor, so the acclimatization period was just a few hours. From August 7, 2000 to August 16, 2000, the unit was being observed and evaluated for performance and maintenance dependency. Figure 6 is an example of a day of data from the new instrument, along with the BIOX-1010 24-hour composite average and the 24-hour composite BOD_5 result. This plot shows that the BOD measurement trends were very stable; no large variations between readings were observed; and the readings were maintained for more than three days without needing maintenance. Based on the excellent performance observed on these days, it was decided that the unit had passed its start-up test and was ready to proceed with the calibration test. After calibration, the new unit has been operating well, and starting August 31, 2000, it began detecting many shock loadings.

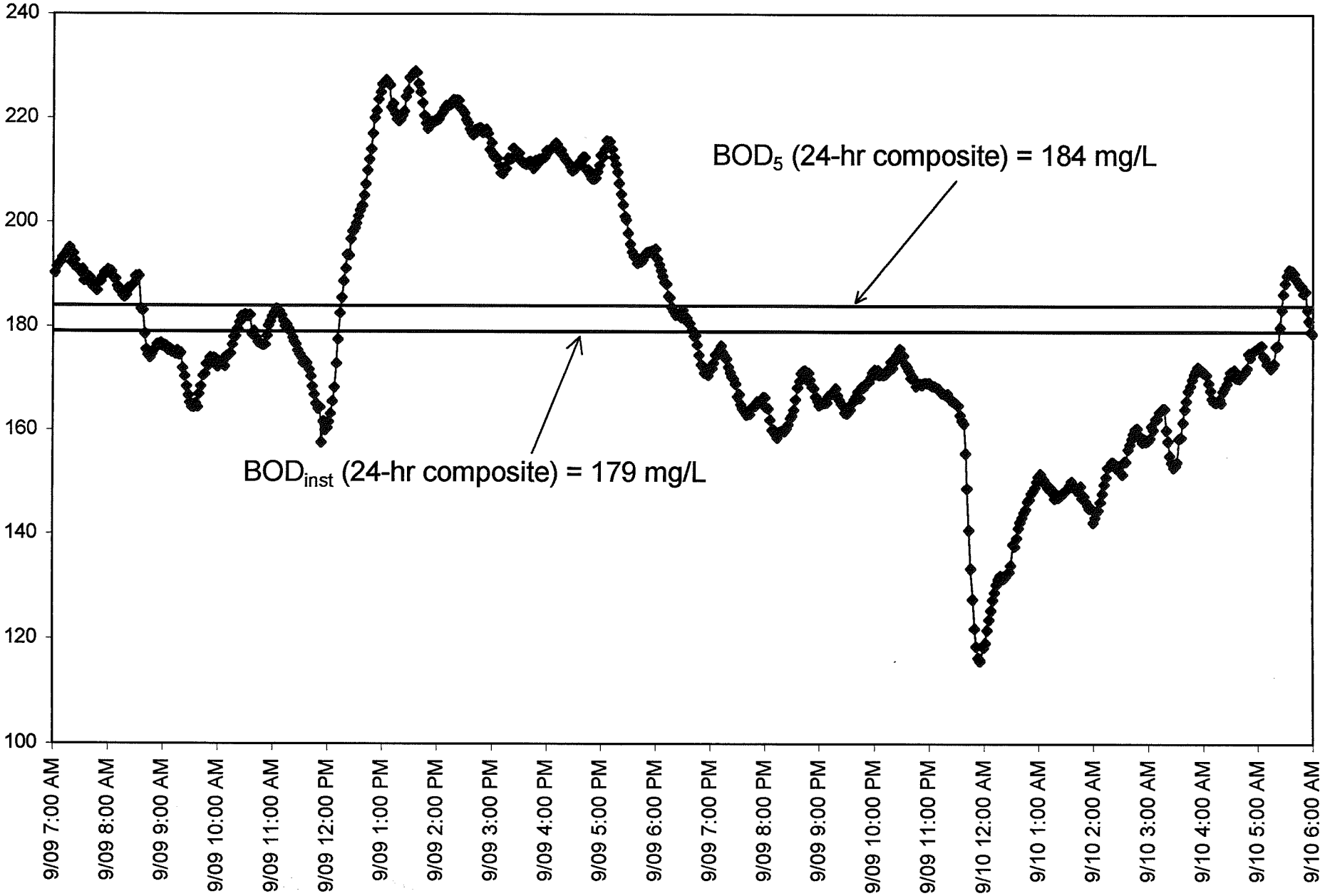
2.4 Instrument Calibration

Because of the simplicity of the operation of the instrument, the accuracy of the outputs depends on only three things: the calibration of the pumps, the accuracy of the DO probe output, and the calibration factor LK.

Pump Calibration. As noted in Section 2.1, the microprocessor uses pump rate readings for aerated tap water and the sample in computing the sample BOD. As these readings are electrically derived from the rotation rates of the pump motors, it is necessary for the pumps to be in good mechanical condition to make the actual pumping rates correspond with the electrical estimates. The principal source of errors in pump calibration is microbial slime buildup in the tubing of the peristaltic pumps, so good mechanical condition is maintained by periodic cleaning and occasional replacement of the pump tubing.

DO Probe Output Accuracy. The DO probe is a small electrochemical cell that produces current proportional to the DO concentration in the water that is in contact with it, so if the cell is good condition (no serious loss of electrolyte or excessive corrosion of electrodes) then it is extremely accurate in measuring the DO concentration in its immediate microenvironment. However, it is protected from direct contact with the microbial population by a plastic membrane, so that microbial slime growth on the membrane interferes with diffusion of DO to the probe, resulting in underestimates of the true DO concentration in the bioreactor, with consequent overestimates of the BOD of the sample. Hence, keeping the membrane clean is the key to good DO probe operation, and the instrument is equipped with a spray device to clean the membrane with fresh water under microprocessor control.

Figure 6. Well behaved BOD_5 trends (new set-up), Sept. 9, 2000



The Calibration Factor LK. Let Q_1 be the flow of aerated tap water and Q_2 be the sample flow rate. Likewise, let S be the soluble BOD of the sample and R be the oxygen depletion in the bioreactor. Since the biomass in the bioreactor is large and the sample is small, with a corresponding small total amount of soluble food, the biomass is assumed to completely consume the soluble food during the hydraulic residence time in the bioreactor. There is of course no food in the tap water, so the oxygen consumption rate for full oxidation of the food is the same in either the diluted or the undiluted sample. In the diluted case it is $(Q_1 + Q_2)R$ and in the undiluted case it is Q_1S, so equating these and solving for S gives $S = (Q_1 + Q_2)R/Q_1$. Since the saturation concentration of oxygen in water at the instrument's operating temperature is around 7 mg/L, using R = 3 mg/L maintains the bioreactor DO at around 4 mg/L, allowing reliable detection of both upward and downward excursions with changing inputs.

Ordinarily, S is expected to be less than BOD_5 in municipal wastewater, since there is usually some edible particulate matter that is broken down and consumed during the five-day test but is not available in the few minutes of residence time in the bioreactor. On the other hand, the DO of the tap water is not measured after aeration, but is simply assumed to be saturated. Since the probes cost nearly $1600, having only the bioreactor probe in the instrument reduces costs, but it opens the possibility that the aerated water may fall short of saturation without the users knowing it. In this case R would be overestimated, with consequent overestimation of S.

For all of these reasons, the instrument is programmed to operate with R = 3 mg/L, as deduced from the DO probe, but the user supplies a calibration factor, LK, that is used in computing the instrument's best feasible approximation to what the BOD_5 test would produce for the corresponding sample, according to the formula $BOD = (Q_1 + Q_2)LK/Q_1$. Thus, it is necessary to start with some plausible LK and then to perform a test to determine whether a corrected value of LK is needed.

The method recommended in the manual uses the obvious approach of taking a large grab sample and feeding part of it into the instrument (through a pipe and valve provided for this operation) and testing part of it by the standard BOD_5 procedure, followed by adjusting the LK value if the instrument result is significantly different from the BOD_5 result. Since the BOD_5 test is known to have an uncertainty of as much as 15%, several replicates of the test are performed on aliquots of the original sample, to improve the statistics. Also, the recommended method includes an internal consistency check for both the instrument results and the BOD_5 results, since all the testing is to be done both on full-strength aliquots of the sample and on diluted aliquots. Dilution

to 1/4 of the original strength is recommended. Figure 7 shows the setup for feeding the calibration sample into the instrument.

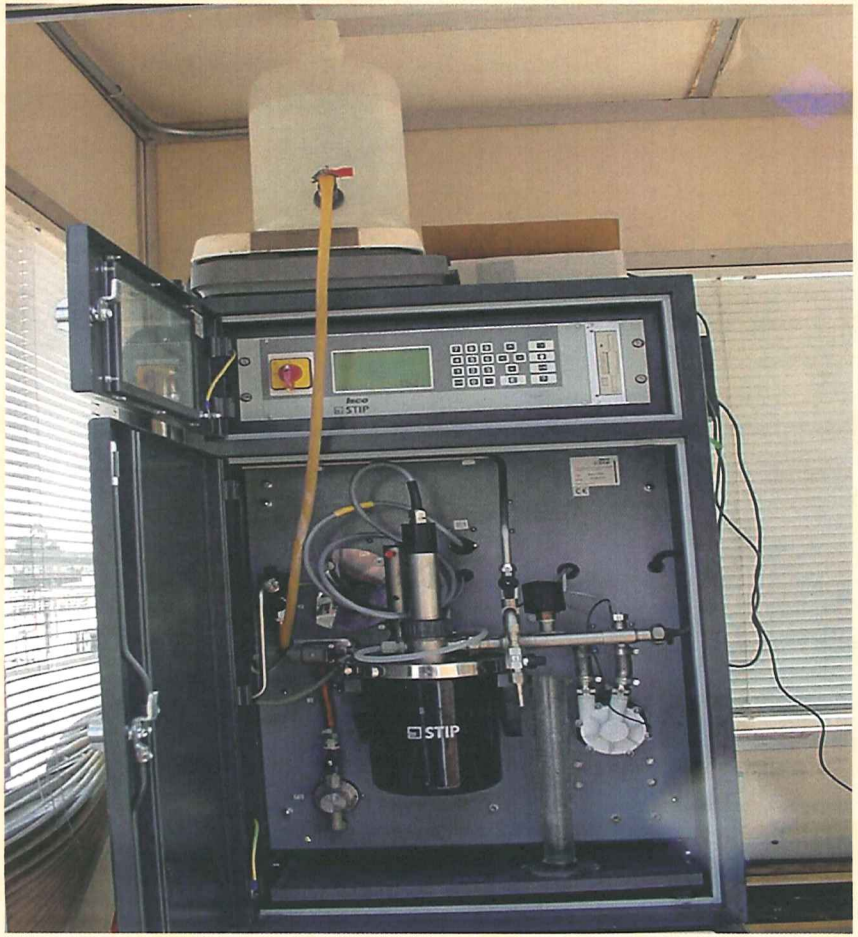
Table 1 shows the calibration test results (BOD_5, online BOD and the calculated LK) immediately after culture acclimation, based on operation with the recommended default value of LK = 5. The ratios obtained for the undiluted and diluted samples were 4.44 and 4.55, respectively, for the EMD lab and online BOD. The percent difference between these ratios was only 2.5%. According to the vendor's recommendations, the data obtained during the comparison test are acceptably consistent, since the percent difference was less than 20%. On the other hand, the instrument outputs were clearly almost exactly twice as large as the BOD_5 results. Therefore, the average was used to calculate the new factor LK = **2.5**.

Figure 8 is a plot of the online BOD trends before and after LK calibration as a function of time from August 20, 2000 to August 31, 2000. The first three days of this figure show that when LK = 5 was used, the online BOD readings were in the range of 300-400 mg/L. On August 23, 2000, the LK factor was set at 2.5. After the new LK factor was set, the online BOD readings were in the range of 180-220 mg/L. Although the new LK factor produced much more accurate results, the BOD still trended upward as a function of time because of rapid bacterial growth on the surface of the DO probe membrane. Several manual cleanings were done, each of which greatly reduced the BOD readings for a short time. On August 29, 2000, the software was commanded to perform the self-cleaning spray on the DO probe membrane twice a day. Since then the unit has operated well, and on August 31, 2000, it detected its first shock loading.

2.5 Test Procedure

The test comparing online BOD with BOD_5 consisted of ten days of sampling for BOD_5 from September 20, 2000 to January 18, 2001, along with continuous operation of the BIOX-1010 since August 29. The samples for BOD_5 were collected with an autosampler set up on top of the primary effluent channel next to the submersible pump suction port from which the samples are being withdrawn. Primary effluent samples were taken every two hours, 24 hours a week (12 samples/day), and the first sampling series started at 12:00 a.m. on September 20, 2000 and ended at 10:00 a.m. on September 21, 2000. The second, third, fourth and fifth sampling series were done on September 26-27, 2000, October 3-4, 2000, January 9-10, 2001 and January 17-18, 2001, respectively. The autosampler was programmed to collect 600 mL of primary effluent every two hours into 1 liter containers and microorganism activity was slowed by keeping the temperature low with ice placed in the middle section of the autosampler carousel. After the last sample was collected, the samples were delivered to the plant's laboratory for BOD_5 analysis.

Figure 7. LK Calibration Test for (ISCO/STIP) BIOX-1010



a) Full Strength Primary Effluent

b) 1:3 Diluted Ratio

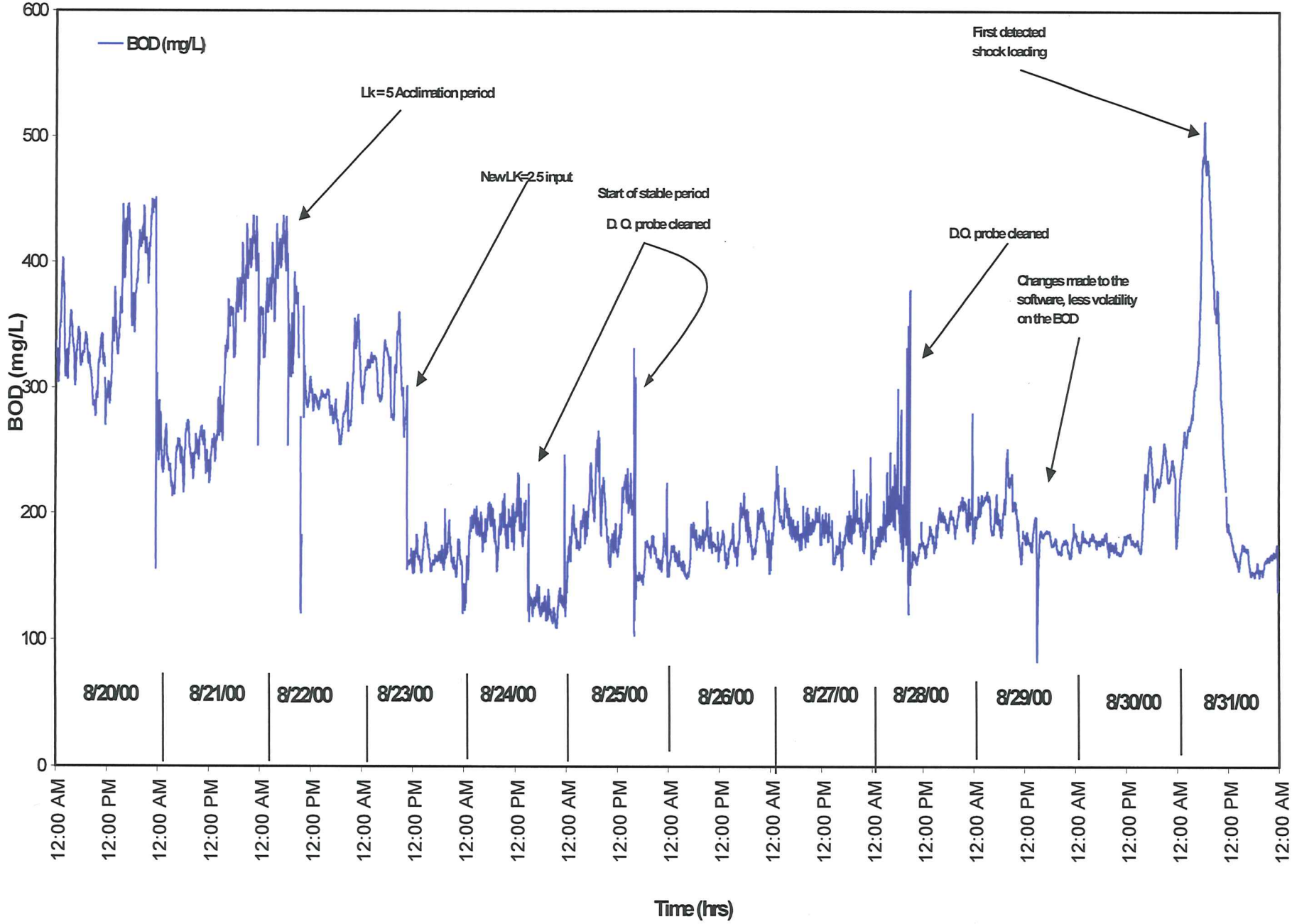
Table 1. Calibration test results (BOD_5, BOD-online, and LK values)

	Full Strength Sample		Dilute Sample (1:3)	
Sample No	$BOD_{5\,(lab)}$ mg/L	Online BOD (BIOX-1010) mg/L	$BOD_{5\,(lab)}$ mg/L	Online BOD (BIOX – 1010) mg/L
1	147	289	32	64
2	144	289	33	63
3	146	289	32	63
4	141	287	33	63
5	146	287		
6	146	286		
Ave	144.3(1)	288(2)	32.5(3)	63.25(4)

BOD_5 ratios	
(1)/ (3)	4.41(5)
(2)/ (4)	4.55(6)

% error	2.5%
Lk (new)	2.5

Figure 8. Online BOD trends before and after LK calibration



SECTION 3
RESULTS

The figures in this section summarize the results that were obtained during work with the BIOX-1010. Two major analyses were done: comparison of the online BOD results with BOD_5, and analyses of the online BOD readings for shock loadings. In both of these the BIOX-1010 equipment has proven to be satisfactory.

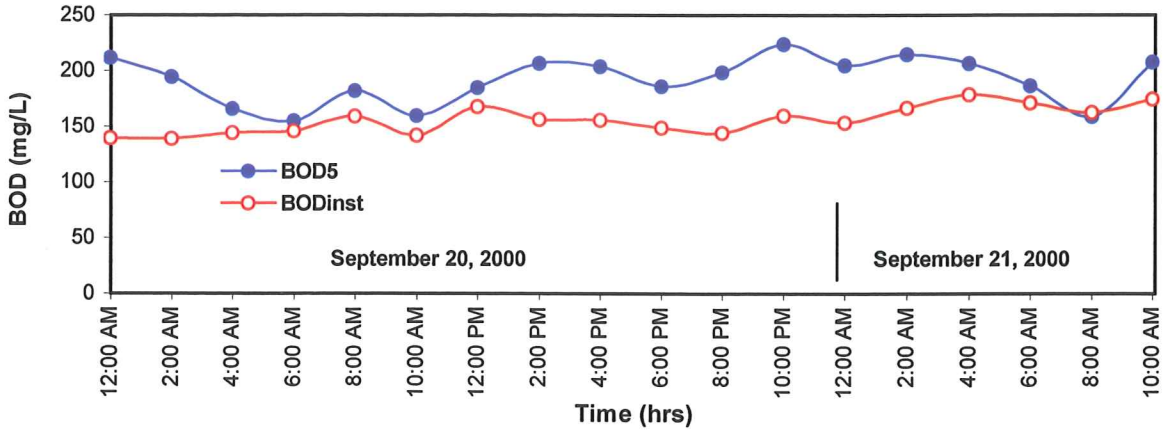
3.1 Test Comparison (Online BOD vs. BOD_5)

Ten days of direct comparisons between the online BOD and BOD_5 were performed in the field to evaluate the precision of the online unit. As described in Section 2.5, the test days were in September and October, 2000, and January, 2001. Figures 9a through 9e and Table 2 show that the BIOX-1010 readings generally duplicate the BOD_5 time series trends.

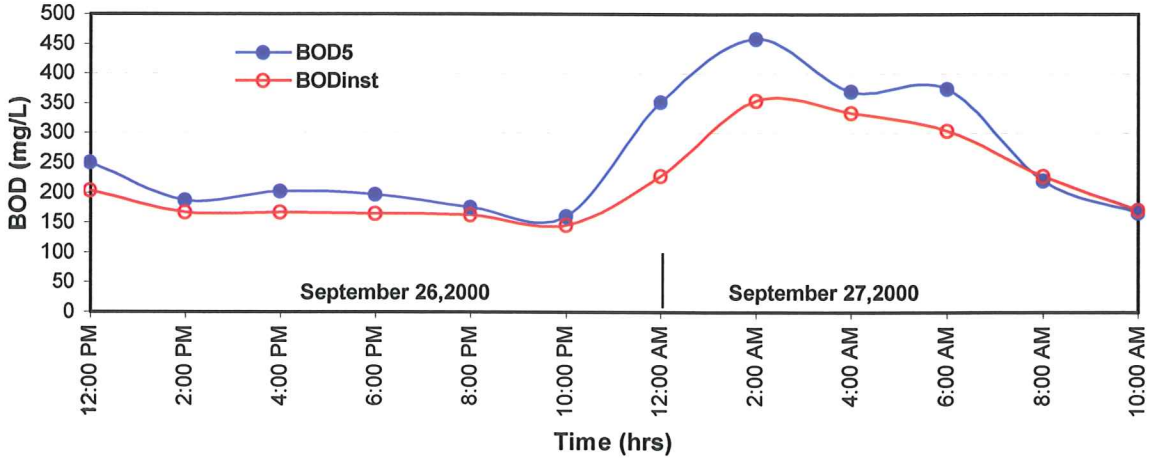
The plots in Figure 9 also suggest that the instrument readings are generally less variable than the laboratory results, neither rising as high on the peaks nor sinking as low in the dips. In particular, during the shock loading event on September 26 and 27, 2000, seen in Figure 9b, the peak BOD reported by the instrument was around 350 mg/L, while the peak BOD_5 was around 450 mg/L. On the other hand, since the daily average percentage deviations calculated in Table 2 show that the instrument readings tended to be below BOD_5 in September, and above BOD_5 in January, it is possible that enough drift occurred in the instrument response after the probe cap was changed on October 14 to account for part of these observations. As this behavior looks like a slower version of the behavior observed before the frequent spray cleanings were programmed for the DO probe membrane, a loss of membrane permeability is a plausible hypothesis to explain it. If so, membrane replacement would restore the behavior observed in September. Part of the rise may also result from increasing LK from 2.5 to 2.65 on November 22.

Although these results do not quite live up to the near-perfect agreement between online BOD and BOD_5 reported by Riegler(1987), the distribution of these disagreements is approximately what would be expected from the typical 15% standard deviation for BOD_5 measurements (*Standard Methods*, 5210B), with only two readings on January 10 (or around 5% of the 67 measurements in Table 2) disagreeing by significantly more than two standard deviations, or 30%, as also seen in Figure 9d. Although this fraction may seem high on initial consideration, the two values are consecutive samples from one event, and hence are not statistically independent. Moreover, these two cases are probable overestimates of low BOD values, not

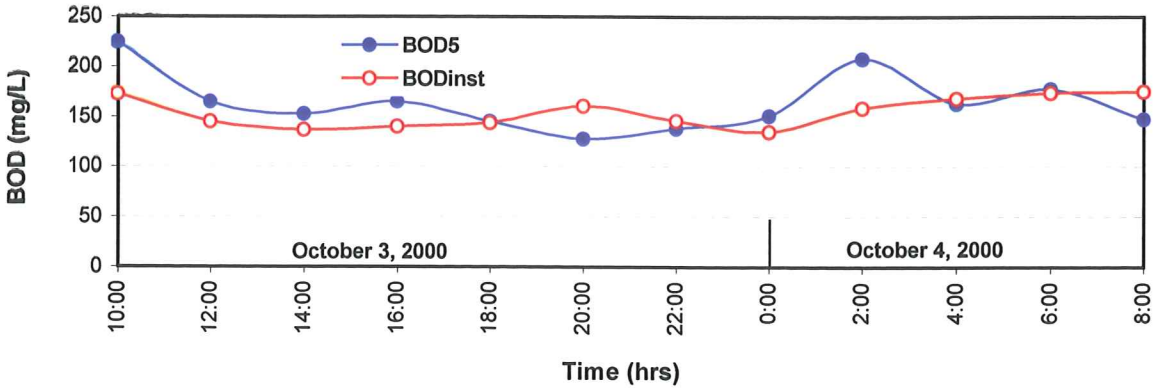
Figure 9. Field test comparison results, BOD_5 vs. BOD- online



(a) September 20-21, 2000

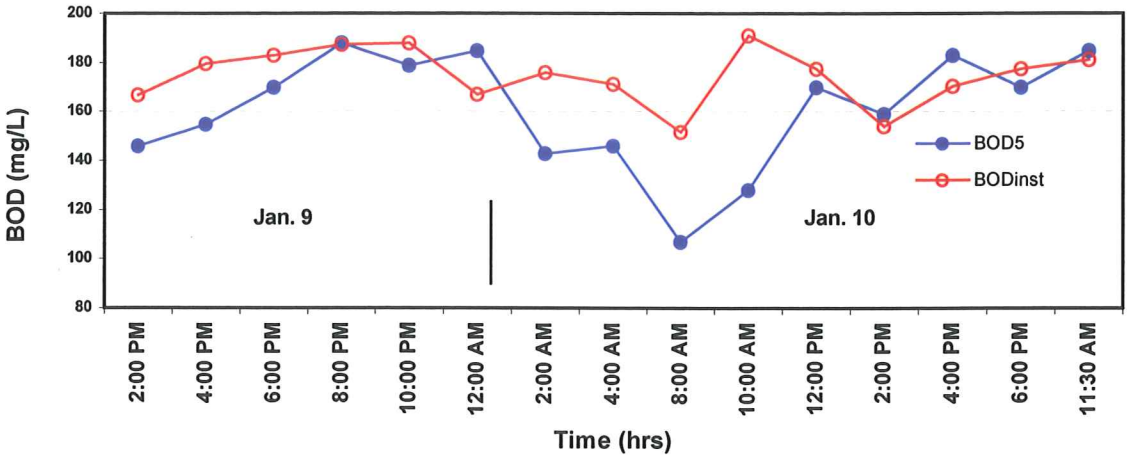


(b) September 26-27, 2000

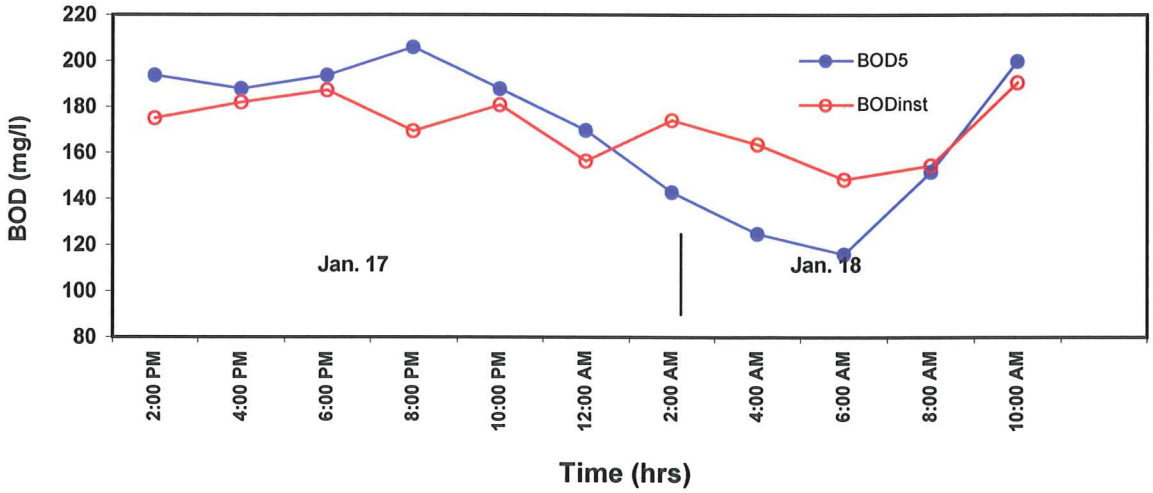


(c) October 3-4, 2000

Figure 9. Continued



(d) January 9-10, 2001



(e) January 17-18, 2001

Table 2. LAG field test comparison results, BOD_5 vs. BOD-online

Date & Time	BOD_5 mg/L	BOD inst	%error BOD_5 vs BOD inst
9/20/00 12:00 AM	212	139.84	34.04
9/20/00 2:00 AM	195	139.05	28.69
9/20/00 4:00 AM	166	144.44	12.99
9/20/00 6:00 AM	155	146.25	5.65
9/20/00 8:00 AM	182	159.21	12.52
9/20/00 10:00 AM	160	142.03	11.23
9/20/00 12:00 PM	185	167.56	9.43
9/20/00 2:00 PM	207	156.06	24.61
9/20/00 4:00 PM	204	155.95	23.55
9/20/00 6:00 PM	186	148.71	20.05
9/20/00 8:00 PM	199	144.15	27.56
9/20/00 10:00 PM	224	160.03	28.56
9/21/00 12:00 AM	205	153.61	25.07
9/21/00 2:00 AM	215	166.71	22.46
9/21/00 4:00 AM	207	178.76	13.64
9/21/00 6:00 AM	187	171.09	8.51
9/21/00 8:00 AM	159	162.70	-2.33
9/21/00 10:00 AM	208	174.61	16.05
		Average==>	**17.90**

(a) September 20-21, 2000

Date & Time	BOD_5 mg/L	BOD inst	%error BOD_5 vs BOD inst
9/26/00 12:00 PM	251	203.9	18.76
9/26/00 2:00 PM	188	167.54	10.88
9/26/00 4:00 PM	203	167.51	17.48
9/26/00 6:00 PM	197	165.33	16.08
9/26/00 8:00 PM	176	163.35	7.19
9/26/00 10:00 PM	161	145.65	9.53
9/27/00 12:00 AM	353	228.01	35.41
9/27/00 2:00 AM	459	355.23	22.61
9/27/00 4:00 AM	371	334.93	9.72
9/27/00 6:00 AM	376	304.28	19.07
9/27/00 8:00 AM	221	228.11	-3.22
9/27/00 10:00 AM	167	171.44	-2.66
		Average==>	**13.41**

(b) September 26-27, 2000

Table 2. Continued

Date & Time	BOD_5 mg/L	BOD inst	%error BOD_5 vs BOD inst
10/3/00 10:00 AM	225	173.07	23.08
10/3/00 12:00 PM	165	145.16	12.02
10/3/00 2:00 PM	153	137.03	10.44
10/3/00 4:00 PM	165	140.33	14.95
10/3/00 6:00 PM	145	144.2	0.55
10/3/00 8:00 PM	128	160.72	-25.56
10/3/00 10:00 PM	138	146.11	-5.88
10/4/00 12:00 AM	151	134.94	10.64
10/4/00 2:00 AM	208	158.85	23.63
10/4/00 4:00 AM	163	168.39	-3.31
10/4/00 6:00 AM	178	174.39	2.03
10/4/00 8:00 AM	148	175.73	-18.74
		Average==>	**3.65**

(c) October 3-4, 2000

Date & Time	BOD_5 mg/L	BOD inst	%error BOD_5 vs BOD inst
1/9/01 2:00 PM	146	166.91	-14.3
1/9/01 4:00 PM	155	179.67	-15.9
1/9/01 6:00 PM	170	183.17	-7.7
1/9/01 8:00 PM	188	187.59	0.2
1/9/01 10:00 PM	179	187.87	-5.0
1/9/01 12:00 AM	185	167.08	9.7
1/10/01 2:00 AM	143	175.95	-23.0
1/10/01 4:00 AM	146	171.3	-17.3
1/10/01 8:00 AM	107	151.61	-41.7
1/10/01 10:00 AM	128	191.15	-49.3
1/10/01 12:00 PM	170	177.47	-4.4
1/10/01 2:00 PM	159	154.13	3.1
1/10/01 4:00 PM	183	170.47	6.8
1/10/01 6:00 PM	170	177.59	-4.5
		Average ==>	**11.7**

(d) January 9-10, 2001

Table 2. Continued

Date & Time	BOD_5 mg/L	BOD inst	%error BOD_5 vs BOD inst
1/17/01 11:30 AM	185	181.13	2.1
1/17/01 2:00 PM	194	175.38	9.6
1/17/01 4:00 PM	188	182.33	3.0
1/17/01 6:00 PM	194	187.48	3.4
1/17/01 8:00 PM	206	169.78	17.6
1/17/01 10:00 PM	188	181.16	3.6
1/18/01 12:00 AM	170	156.64	7.9
1/18/01 2:00 AM	143	174.38	-21.9
1/18/01 4:00 AM	125	163.97	-31.2
1/18/01 6:00 AM	116	148.69	-28.2
1/18/01 8:00 AM	152	154.81	-1.8
1/18/01 10:00 AM	200	190.76	4.6
		Average==>	**2.6**

(e) January 17-18, 2001

underestimates of high ones, and hence are not evidence of a risk of failing to detect a shock loading. Since Figure 9b shows that both measurement methods agree reasonably well on the magnitude of the shock loading, and very well on the eight-hour duration, this is strong evidence that the BIOX-1010 can be used for process control.

3.2 Shock Loading Detection

Much stronger evidence is provided by the many other detections of shock loads that the instrument has produced since the end of August. There has been no difficulty in distinguishing between shock loads and the daily BOD rises that LAG often experiences during the transition of low flow to average flow in the morning, which occurs between 6:00 am to 8:30 am, as seen in Figure 6. These normal BOD rises are short lived, lasting approximately one to two hours. The highest BOD concentrations during the period of flow transition is approximately 230 mg/L. If the BOD concentration rises above 230 mg/L with a duration of 40 minutes or more and the aeration basin DO level decreases to the range 0.0-0.2 then a shock loading is considered to occur.

Table 3 summarizes the shock loadings detected at LAG from August 2000 to January 2001. The averages in the fourth column are the means of the instrument readings made every two minutes during the shock loading, and the values in the fifth column are the BOD_5 readings for the 24-hour composite samples collected routinely to verify regulatory compliance, as described in more detail in Section 5.2. As the table shows, the agreement between the two types of average is usually good, and sometimes perfect. Figure 11 (from Table 3) shows the comparison between BOD_5 of 24-hour composite samples and the corresponding shock loading averages from the BIOX-1010 instrument.

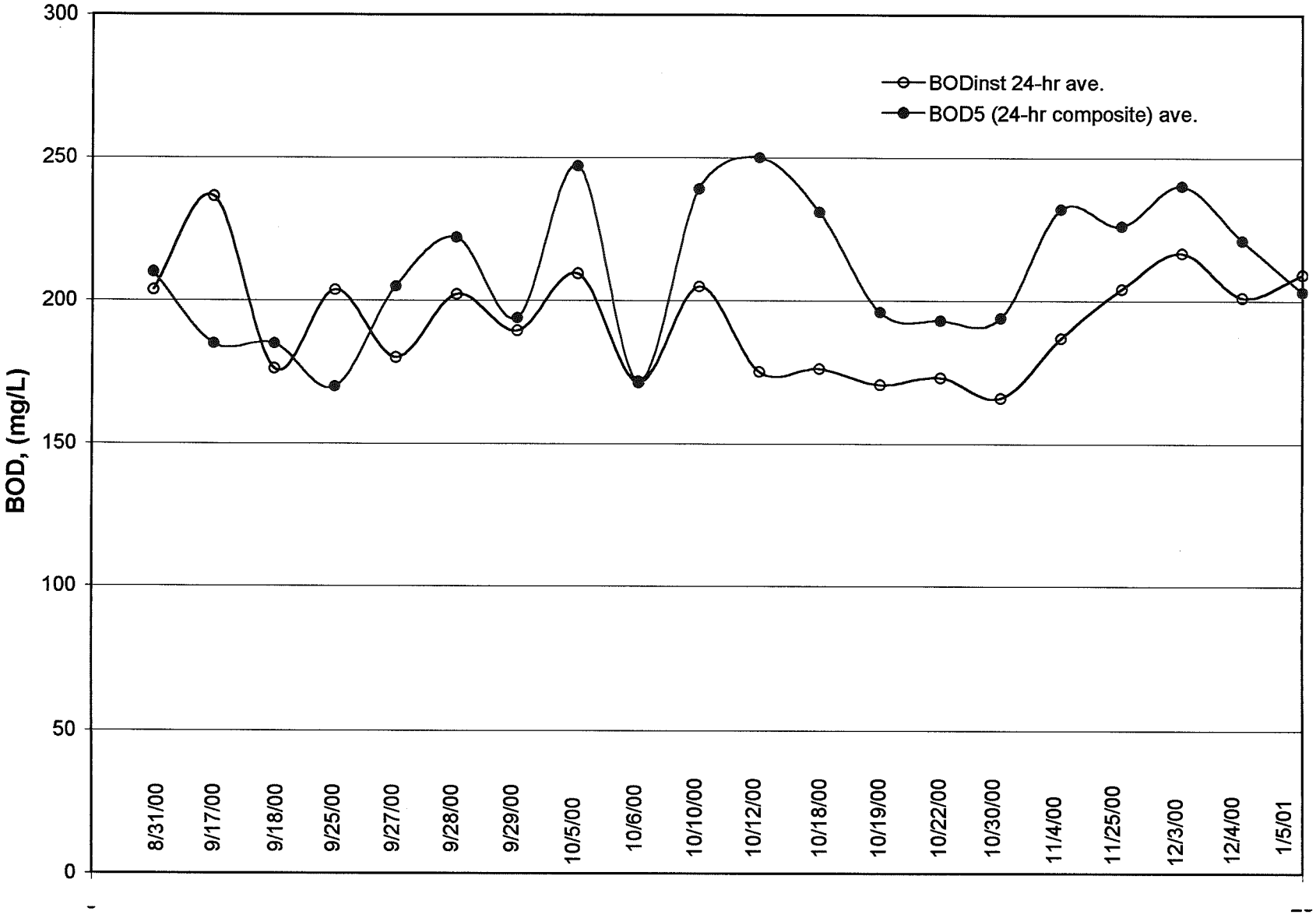
Figures 10a through 10m are time series plots of the online BOD data. They show that before and during a shock loading the BOD concentration can increase by as much as 100 percent for periods of up to 10 hours. For comparison, they also show a number of days of no shock loadings, such as September 1 (Figure 10a) and September 19 (Figure 10b). September 19 is a particularly good example of the normal BOD rises around 6:00 am, and additional examples of daily flow histories are included in Figures 10f and 10g. Another feature of September 19, also seen in some other plots, such as September 22 (Figure 10c), September 26 (Figure 10d), October 6 (Figure 10e) and October 23 (Figure 10i), are sharp transitory drops in the BOD readings around noon. These are artifacts of the programmed probe membrane washing.

Table 3. Summary of shock loadings at LAG from August 2000 to January 2001, primary effluent

Date	BOD instrument Max (mg/L)	BOD instrument Min (mg/L)	BOD instrument 24-hr Ave. (mg/L)	BOD_5 24-hr Composite Ave. (mg/L)
8/31/00	511.91	138.75	203.74	210
9/17/00	345.68	120.55	236.37	185
9/18/00	429.12	86.26	176.26	185
9/25/00	371.65	78.97	203.78	170
9/27/00	376.64	132.49	180.15	205
9/28/00	292.89	129.12	202.15	222
9/29/00	316.85	129.08	189.53	194
10/5/00	390.19	145.11	209.43	247
10/6/00	311.55	93.67	171.46	172
10/10/00	297	129	204.85	239
10/12/00	324	126	175.23	250
10/18/00	387.87	119.33	176.25	231
10/19/00	331.48	109.92	170.67	196
10/22/00	355.31	108.85	173.18	193
10/30/00	343.74	120.5	166	194
11/4/2000*	247	88.3	187	232
11/25/00	342.53	126.04	204.00	226
12/3/00	237.54	143.91	216.55	240
12/4/00	346.59	165.68	201.15	221
1/5/01	315.81	150.17	209.10	203

*Plant influent is reduced to minimize impact to the aeration process.

Figure 11. Comparison of BOD_{inst} Daily Averages with Plant 24-hr Composites for Shock Loadings (8/00-1/01) - Primary effluent



The shock loadings in Table 3 were those during the period of August 30, 2000 to January 5, 2001 that were severe enough for the LAG plant staff to modify process conditions. The average duration of each shock loading was approximately 6 hours and they normally occurred from about midnight until 6 a.m. During this period, when the flow is lowest, the plant is more vulnerable to microbial deterioration by a shock loading, causing sludge settling problems. Since late September the plant management and operation staff have been using the instrument to trigger an alarm to alert them to possible shock loads and activate a flexible action plan that they have developed to determine whether the flow to the plant should be reduced to prevent a process impact. November 4 (Figure 10k) is an example of an occasion when the flow was reduced from the normal daytime rate of around 20 mgd to around 13 mgd, which is why the minimum BOD reading from the instrument was so low on this day.

Figures 10a through 10m clearly show that the shock loadings were not isolated cases, and the time pattern consistency suggested a single source. The ability to determine the BOD concentration allows for a) determination of aeration basin air needs, b) diversion of the flow into the plant, c) evaluation of microbial population, and d) monitoring of turbidity levels. The BIOX-1010 results have assisted IWMD staff to determine the source of the organic loading by cross-referencing the lab results to their permit database and determining that the source of the shock loads was the Baxter pharmaceutical company, located a few hundred feet from LAG.

Putting all of these results together, we conclude that the BIOX-1010 has proven to provide acceptable BOD values for shock loading detection and to observe the diurnal BOD strength patterns for process control. The results to date are highly satisfactory, and appear superior to competing devices and tests, such as the LAR BioMonitor, the Nissin BOD-2000, and the headspace BOD test.

SECTION 4
MAINTENANCE AND SERVICE SCHEDULE

The success of this instrument in the field depends to a large extent on how well it is maintained. As discussed in more detail in Section 2, the primary effluent sample contains microbes and nutrients, so that slime tends to build up quickly in the strainer and DO probe membrane surface. If the membrane is not cleaned for more than a week, the instrument BOD values start to trend upward. It was found that with a proper maintenance and service schedule the microbial buildup problem was solved, allowing the BIOX-1010 to perform to expectations. Table 4a summarizes all the maintenance and services provided to the BIOX-1010 unit since it was installed.

Based on a combination of information from the manufacturer and experience in this study, the currently recommended service schedule consists of general service (cleaning the strainer and the DO probe membrane surface according to the procedures in the manual) once a week, and providing full service to the unit (calibration and cleaning of the pumps) once a month. Table 4a indicates that the time required to perform the weekly cleaning service is approximately one hour. The table also shows that since the beginning of November the actual interval between general services has been more commonly ten days or two weeks. As the possible long-term shift in behavior suggested by the results in Section 3.1 would be consistent with a decrease in permeability of the membrane, it is possible that additional experience will show a need to replace the membrane every six months or so.

Table 4a. LAG Installed BIOX-1010 Maintenance and Service Schedule

Date:	Cleaning Time Start	Cleaning Time Finish	BOD mg/L Before	BOD mg/L After	E1 Before	E1 After	Notes
F[illegible] equipment 6/15/00 to 8/2/00							The first unit was replaced since it had some mechanical and logistics malfunction.
Second equipment place on service (malfunction was fixed)							
8/5/00 Saturday	4:15 PM	5:00 PM	175-180	190	0.67	0.67	Performed cleaning of screen and DO probe. D. O. probe had build up a layer of microbes. No change occurred after membrane cleaning.
8/8/00 Tuesday	8:15 AM	9:47 AM	204	180			Preparation for LK test. Calibrate all pumps. Performed cleaning of screen and DO probe. P1 changed from 40 mL to 42 mL.
8/12/00 Saturday	9:15 AM	10:30 AM	220				(8/9/00, E1=0.71), (8/10/000, E1= 0.76), (8/11/00, E1=0.78). Performed cleaning of screen and DO probe. Screen was very duty.
8/[illegible]/00 Wednesday	9:00 AM	10:00 AM	239				Performed cleaning of screen and DO probe. D. O. probe had build up a layer of microbes. No change occurred after membrane cleaning.
8/18/00 Friday	11:00 AM	12:00 PM					Performed cleaning of screen and DO probe. D. O. probe had build up a layer of microbes. No change occurred after membrane cleaning.
8/22/00 Tuesday	9:06 AM	10:06 AM	334	310	0.89	0.63	Delta O_2 = 2.80. Performed cleaning to screen and DO probe.
8/24/00	3:40 PM						Cleaned Pump #2.
8/25/00	3:20 PM	4:15 PM	210	163-150	0.65	0.62	Cleaned screen and D.O.

Table 4a. LAG Installed BIOX-1010 Maintenance and Service Schedule

	Cleaning Time		BOD mg/L		E1		
Date:	Start	Finish	Before	After	Before	After	Notes
'28/00	8:10 AM	9:30 AM	330-300		0.66	0.62	Cleaned screen and probe . Screen was clogged. D.O. probe surface did not have a lot of build-up XXX E1= 0.65. Something caused the change from E1=0.62 to E2=0.66 20 min after E1was taken.
8/29/00	Changes to the instrument were made during the time of 2:30 PM -3:45 PM. Since then the equipment has shown a cte BOD of 170-179. What were the changes? Ask Scott!						
9/6/00	At 9:10 P.M. power was cut for one minute						
9/7/00	9:10 PM	10:00 PM					Screen and probe cleaned. Calibration done.
9/12/00	2:30 AM **System was down for 12 hrs**						At 14:48 hrs, equipment was out for about 10-12 hrs. Equipment needs to be stable in order to continue its readings.
9/13/00	8:56 AM It took about 24-36 hours for unit to stabilize.						On September 12 through Sept 13, the equipment was down due to high temperature readings. No data was recorded. Maintenance reading. Bypass screen and DO probe were cleaned.
9/19/00	10:30 AM	11:30 AM			0.71	0.63	Cleaned D.O probe and bypass screen. Calibrated pump #1 and pump #2.
9/26/00							Bypass screen and DO probe were cleaned. Auto-sampler was set-up to take samples every 2 hrs. starting at 12:00 PM, from 9/26 and 9/27. Pumps #1 and #2 were calibrated.
10/2/00	9:00 AM	10:20AM					Bypass and DO probe cleaned. Pumps 1 and 2 were calibrated.

Table 4a. LAG Installed BIOX-1010 Maintenance and Service Schedule

	Cleaning Time		BOD mg/L		E1		
Date:	Start	Finish	Before	After	Before	After	Notes
4/00	12:00 PM	3:00 PM					The plant had shock loadings during 10/9,10, and 11 (Mon-Wed), but equipment did not register them. Reason: The equipment has not been cleaned for @ least 12 days. It could have affected the results. Check E1 & BOD values. DO probe cap changed (newly installed). Screws were cleaned. Pumps #1 & #2 were calibrated.
10/25/00	9:00 AM	10:00 AM					Screen and DO probe were cleaned. Pumps #1 & #2 were calibrated.
10/31/00	8:00 AM	10:00 AM					Screen and DO probe were cleaned. Pump #1 & #2 were calibrated. Delta O2 was low after cleaning. Value of delta O2 kept dropping. Data was lost for 2 hrs. Recommendation: clean unit every 5 days. To avoid unsuspected changes to operation - Pause control changed from 180 sec to 3600 sec when time changed. This is caused by the CPU , not a big deal but when this occurs the unit must be reset (recalibrated) to correct this change. Working fine.
1 '00	8:00 AM	10:00 AM	240	94	0.1	0.58	Cleaned DO probe and screen.
11/22/00							Cleaned DO probe and screen. LK was changed from 2.5 to 2.65
12/6/00	9:00 AM	10:00 AM					Cleaned DO probe and screen.
12/19/00	2:00 PM	3:00 PM					Pumps #1 & #2 were calibrated. Screen and DO probe were cleaned.
12/28/00							Machine back on line after 8 hrs of pause mode (from 11:30 p.m. to 7:30 a.m., on 12/28/2000). By 9:00 a.m., machine is responding OK. DO probe and screen were cleaned.

Table 4b. Recommended Maintenance Schedule for ISCO/STIP BIOX-1010

SERVICES		Service Period (days)
CLEANING -	Bypass-screen	1hr. per week
CLEANING -	O_2-Probe	1 hr. per week
O2-PROBE -	Calibration	1 hr. per week
PUMPS -	Calibrate Pump 2	once a month
CLEANING -	Circulating Pump	once a month
CLEANING -	Bio-reactor	as needed
If Necessary:		
O2-probe:	Replace, refurbish	every 2 months
Pump 1:	Replace tube (if broken)	as needed
Fresh water tank:	Delime	as needed
Pump 2:	Replace gear wheels	as needed

SECTION 5
MANAGEMENT ISSUES

5.1 Important Factors

Advancing instrumentation technology is opening possibilities for replacing long-established and often legally mandated laboratory test procedures with quicker or cheaper alternatives using new equipment. That is the case for the five day BOD test which can be replaced with an instrument that provides results in just a few minutes. The test results have shown that the BIOX-1010 provides good enough results that using it can be technically justified; thus, it is appropriate to consider comprehensively the costs and advantages of integrating such instruments into plant operations.

Since a measurement cycle of a few minutes is hundreds of times faster than a five-day laboratory BOD test procedure, using the BIOX-1010 or a similar instrument obviously provides capabilities that are not possible with the standard BOD_5 method. Hence, additional information is needed beyond a simple comparison of the costs of using one or the other in cases where both can be used.

In particular, using an instrument for process control needs to be assessed by estimating money saved resulting from prevention of process impacts due to BOD shock loadings. There are two types of costs involved with process impacts: 1) extra plant operation costs resulting from measures taken to recover from a process impact, and 2) fines assessed by regulatory agencies for violation of effluent standards.

The analysis is further complicated because current governmental regulations mandate that some BOD_5 testing will have to continue in the near future, even if an instrument is installed. The NPDES permit compliance for BOD_5 discharge requires monitoring of the plant final effluent based on the BOD_5 test of flow proportional 24-hour composite samples. Results of these analyses are submitted to the RWQCB monthly. Thus, in the near future, results from a BOD analyzer will not be admissible for the NPDES permit compliance. It is reasonable to hope that the regulatory agencies will eventually reconsider their policies to accept instrument monitoring of final effluent, but for now it is necessary to continue BOD_5 testing at the required rate.

The following sections first give estimates of the direct costs of current BOD_5 testing, and on-line BOD analyzer, and then discuss indirect costs of different ways of dealing with potentially impacting fluctuations in influent quality.

5.2 Costs of Current BOD_5 Testing

As part of the NPDES permit requirements, LAG, DCT and TITP collect and analyze samples for BOD_5 determination. LAG conducts daily 24-hour composite sampling and lab analyses for the primary effluent, and weekly 24-hour composite samples for the raw influent and final effluent. DCT collects a total of six daily samples (one from the raw influent, one from the primary effluent, two from the secondary effluent and two from the tertiary effluent). TITP collects four daily samples (one from the primary influent and effluent, and two from the secondary effluent).

No additional BOD_5 analyses are performed for process requirements, except on occasions when a process impact occurs that could be traced to BOD shock loadings. Such cases are becoming frequent, with approximately 20 shock loadings having been registered at LAG in 2000. The potential for BOD shock loadings remains because of industrial waste discharges in the LAG service area.

Laboratory analyses are performed by the EMD laboratory staff, with each plant maintaining its own satellite analytical laboratory. The average cost of performing a BOD_5 analysis is estimated at $30 per sample. This includes both the lab supplies used and the labor expended from the sample preparation to the final result. A typical BOD_5 analysis requires 0.1 man-hour of chemist time and 0.05 man-hours of supervision by a Senior Chemist. The annual costs of BOD_5 analyses are $21,900 for LAG, $65,700 for DCT and $43,800 for TITP.

5.3 Costs of an Online BOD Analyzer

The costs associated with using an on-line BOD analyzer include equipment acquisition, installation, operation and maintenance. A typical BOD on-line analyzer, such as the BIOX-1010, could cost as much as $39,000. Installation involves plumbing and electrical connections at each site. The availability of these utilities at the site considerably reduces the corresponding cost.

Operation and maintenance of the equipment will involve regular visits to the monitoring station to ensure that the equipment is functioning properly, as described in Section 4. Table 4b presents a list of maintenance requirements that need to be attended to. These items are recommended by the equipment manufacturer for the equipment to function accurately. Time needed to perform

the maintenance activities ranges from 45 minutes to as long as 70 minutes, with an average frequency of once a week, except for cleaning and calibrating the pumps, which may be done on a monthly basis.

The following summarizes the cost associated with the installation and operation of an on-line BOD analyzer:

Installation and Startup Costs		
• Equipment acquisition (includes shipping & handling and sales tax)		$39,000
• Installation (includes labor and materials) / startup		3,250
	TOTAL	**$43,250**
Annual Operation and Maintenance Costs		
• Parts replacement kit		932
• Labor		2,717
	TOTAL	**$3,649**

Assuming a 10-year life cycle for the instrument with zero salvage value, and an annual inflation rate of 4%, the above expenditures translate to an annualized cost of $7,200 per monitoring station.

5.4 **Costs of a Process** Impact

A typical process impact takes three to four weeks to correct. When a process impact occurs, a large amount of extra work must be done to deal with the situation, incurring extra costs.

a. **Fines are typically imposed when a specific violation to the NPDES permit has occurred.**

b. Regulatory agencies must be notified, usually by telephone, with confirming letters, subsequently written and mailed. This imposes a small increase in office expenses.

c. Analytical work at the plant laboratory must be stepped up to monitor the process condition in much finer detail than what is done under normal circumstances. This increases costs for both laboratory personnel and supplies.

d. Experts must review the laboratory results to determine modifications of plant operations to reverse the impact.

e. The changes in plant operation usually impose increased energy costs for additional aeration or pumping of activated sludge or wastewater, and may also require costs for additional chemicals or inoculation of tanks with new cultures. These latter actions often cost tens of thousands of dollars.

f. Other costs might also be incurred, primarily regulatory fines. These may range from many thousands to millions of dollars.

g. Further costs may occur that are not directly charged to the Bureau: harm to wildlife, contamination of beaches, delayed harm to humans or animals from toxins that accumulate in the food chain, etc. These costs are the motivation for regulatory fines.

Thus, the actual costs to the City of not using a BOD instrument are the costs of the expected number of process impacts. They must be compared with the costs of using an instrument, continuing the legally required minimum BOD_5 testing, and the costs of adapting plant operation to prevent a process impact, taking action at the first warning of abnormal conditions. This latter group of costs is small compared to the costs of impact recovery and probable fines.

SECTION 6
CURRENT STATUS AND RECOMMENDATIONS

6.1 Current Status

The BIOX-1010 shows excellent monitoring response to the diurnal variation of BOD in the primary effluent and has assisted LAG staff in process control modifications to handle shock loadings. Field test results after the initial stabilization period agree well with BOD_5. Results from current side-by-side comparison testing between the BIOX-1010 and the LAR BioMonitor suggest that the BIOX produces better results.

It also may be worth noting that the recurrent shock loadings were identified as coming from the Baxter Pharmaceuticals plant, which is located a few hundred feet from LAG. On being informed that their plant had been found to be discharging excessive quantities of wastes, the Baxter managers purchased a BIOX-1010 so that they could monitor and control their waste discharges, preventing future shock loadings and possible fines or other legal action.

The results to date are highly satisfactory, and appear superior to competing devices and tests, such as the LAR BioMonitor, the Nissin BOD-2000, and the headspace BOD test. Hence, it is anticipated that the eventual purchase recommendation will favor the BIOX instrument.

6.2 Recommendations

A) A combination of these experiments, previous experience, and discussions with plant personnel justify our recommendation to purchase the BIOX-1010 instrument from ISCO-STIP.

B) Testing the BIOX and LAR instruments in toxicity detection mode at the primary influent is also recommended, including studying how ordinary BOD measurement is affected if the instrument is switched between one mode and the other.

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SECTION 8
APPENDICES

APPENDIX A Earlier Work Experience With Online BOD Instrumentation

1. Real Time BOD Monitoring For Wastewater Process Control.
2. Issues On Biosensor based BOD Instruments For Online Application.
3. Gas Chromatography-Based Headspace Biochemical Oxygen Demand test.
4. Response Characteristics of a Dead-Cell BOD Sensor

APPENDIX B Standard Method 5210.B 5-Day BOD Test

APPENDIX B
STANDARD METHOD 5210 B. 5-DAY BOD TEST

measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. The seeding and dilution procedures provide an estimate of the BOD at pH 6.5 to 7.5.

Although only the 5-d BOD (BOD_5) is described here, many variations of oxygen demand measurements exist. These include using shorter and longer incubation periods, tests to determine rates of oxygen uptake, and continuous oxygen-uptake measurements by respirometric techniques. Alternative seeding, dilution, and incubation conditions can be chosen to mimic receiving-water conditions, thereby providing an estimate of the environmental effects of wastewaters and effluents.

2. Carbonaceous Versus Nitrogenous BOD

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

Measurements that include nitrogenous demand generally are not useful for assessing the oxygen demand associated with organic material. Nitrogenous demand can be estimated directly from ammonia nitrogen (Section 4500-NH_3); and carbonaceous demand can be estimated by subtracting the theoretical equivalent of the reduced nitrogen oxidation from uninhibited test results. However, this method is cumbersome and is subject to considerable error. Chemical inhibition of nitrogenous demand provides a more direct and more reliable measure of carbonaceous demand.

The extent of oxidation of nitrogenous compounds during the 5-d incubation period depends on the presence of microorganisms capable of carrying out this oxidation. Such organisms usually are not present in raw sewage or primary effluent in sufficient numbers to oxidize significant quantities of reduced nitrogen forms in the 5-d BOD test. Many biological treatment plant effluents contain significant numbers of nitrifying organisms. Because oxidation of nitrogenous compounds can occur in such samples, inhibition of nitrification as directed in ¶ B.4*e*6) is recommended for samples of secondary effluent, for samples seeded with secondary effluent, and for samples of polluted waters.

Report results as $CBOD_5$ when inhibiting the nitrogenous oxygen demand. When nitrification is not inhibited, report results as BOD_5.

3. Dilution Requirements

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

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

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

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5210 B. 5-Day BOD Test

1. General Discussion

a. Principle: The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 d. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined immediately after the dilution is made, all oxygen uptake, including that occurring during the first 15 min, is included in the BOD measurement.

b. Sampling and storage: Samples for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analyzing sample promptly or by cooling it to near-freezing

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

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

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

2. Apparatus

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

b. Air incubator or water bath, thermostatically controlled at 20 ± 1°C. Exclude all light to prevent possibility of photosynthetic production of DO.

3. Reagents

a. Phosphate buffer solution: Dissolve 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g NH_4Cl in about 500 mL distilled water and dilute to 1 L. The pH should be 7.2 without further adjustment. Discard reagent (or any of the following reagents) if there is any sign of biological growth in the stock bottle.

b. Magnesium sulfate solution: Dissolve 22.5 g $MgSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 L.

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

d. Ferric chloride solution: Dissolve 0.25 g $FeCl_3 \cdot 6H_2O$ in distilled water and dilute to 1 L.

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

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

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

f. Sodium sulfite solution: Dissolve 1.575 g Na_2SO_3 in 1000 mL distilled water. This solution is not stable; prepare daily.

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

h. Glucose-glutamic acid solution: Dry reagent-grade glucose and reagent-grade glutamic acid at 103°C for 1 h. Add 150 mg glucose and 150 mg glutamic acid to distilled water and dilute to 1 L. Prepare fresh immediately before use.

i. Ammonium chloride solution: Dissolve 1.15 g NH_4Cl in about 500 mL distilled water, adjust pH to 7.2 with NaOH solution, and dilute to 1 L. Solution contains 0.3 mg N/mL.

4. Procedure

a. Preparation of dilution water: Place desired volume of water in a suitable bottle and add 1 mL each of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solutions/L of water. Seed dilution water, if desired, as described in ¶ 4*d*. Test and store dilution water as described in ¶s 4*b* and *c* so that water of assured quality always is on hand.

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

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

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

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

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

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

d. Seeding:

1) Seed source—It is necessary to have present a population of microorganisms capable of oxidizing the biodegradable organic matter in the sample. Domestic wastewater, unchlorinated or otherwise-undisinfected effluents from biological waste treatment plants, and surface waters receiving wastewater discharges contain satisfactory microbial populations. Some samples do not contain a sufficient microbial population (for example, some untreated industrial wastes, disinfected wastes, high-temperature wastes, or wastes with extreme pH values). For such wastes seed the dilution water by adding a population of microorganisms. The preferred seed is effluent from a biological treatment system processing the waste. Where this is not available, use supernatant from domestic wastewater after settling at room temperature for at least 1 h but no longer than 36 h. When effluent from a biological treatment process is used, inhibition of nitrification is recommended.

Some samples may contain materials not degraded at normal rates by the microorganisms in settled domestic wastewater. Seed such samples with an adapted microbial population obtained from the undisinfected effluent of a biological process treating the waste. In the absence of such a facility, obtain seed from the receiving water below (preferably 3 to 8 km) the point of discharge. When such seed sources also are not available, develop an adapted seed in the laboratory by continuously aerating a sample of settled domestic wastewater and adding small daily increments of waste. Optionally use a soil suspension or activated sludge, or a commercial seed preparation to obtain the initial microbial population. Determine the existence of a satisfactory population by testing the performance of the seed in BOD tests on the sample. BOD values that increase with time of adaptation to a steady high value indicate successful seed adaptation.

2) Seed control—Determine BOD of the seeding material as for any other sample. This is the *seed control*. From the value of the seed control and a knowledge of the seeding material dilution (in the dilution water) determine seed DO uptake. Ideally, make dilutions of seed such that the largest quantity results in at least 50% DO depletion. A plot of DO depletion, in milligrams per liter, versus milliliters seed should present a straight line for which the slope indicates DO depletion per milliliter of seed. The DO-axis intercept is oxygen depletion caused by the dilution water and should be less than 0.1 mg/L (¶ 4*h*). To determine a sample DO uptake subtract seed DO uptake from total DO uptake. The DO uptake of seeded dilution water should be between 0.6 and 1.0 mg/L.

Techniques for adding seeding material to dilution water are described for two sample dilution methods (¶ 4*f*).

e. Sample pretreatment:

1) Samples containing caustic alkalinity or acidity—Neutralize samples to pH 6.5 to 7.5 with a solution of sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) of such strength that the quantity of reagent does not dilute the sample by more than 0.5%. The pH of seeded dilution water should not be affected by the lowest sample dilution.

2) Samples containing residual chlorine compounds—If possible, avoid samples containing residual chlorine by sampling ahead of chlorination processes. If the sample has been chlorinated but no detectable chlorine residual is present, seed the dilution water. If residual chlorine is present, dechlorinate sample and seed the dilution water (¶ 4*f*). Do not test chlorinated/dechlorinated samples without seeding the dilution water. In some samples chlorine will dissipate within 1 to 2 h of standing in the light. This often occurs during sample transport and handling. For samples in which chlorine residual does not dissipate in a reasonably short time, destroy chlorine residual by adding Na_2SO_3 solution. Determine required volume of Na_2SO_3 solution on a 100- to 1000-mL portion of neutralized sample by adding 10 mL of 1 + 1 acetic acid or 1 + 50 H_2SO_4, 10 mL potassium iodide (KI) solution (10 g/100 mL) per 1000 mL portion, and titrating with Na_2SO_3 solution to the starch-iodine end point for residual. Add to neutralized sample the relative volume of Na_2SO_3 solution determined by the above test, mix, and after 10 to 20 min check sample for residual chlorine. (NOTE: Excess Na_2SO_3 exerts an oxygen demand and reacts slowly with certain organic chloramine compounds that may be present in chlorinated samples.)

3) Samples containing other toxic substances—Certain industrial wastes, for example, plating wastes, contain toxic metals. Such samples often require special study and treatment.

4) Samples supersaturated with DO—Samples containing more than 9 mg DO/ L at 20°C may be encountered in cold waters or in water where photosynthesis occurs. To prevent loss of oxygen during incubation of such samples, reduce DO to saturation at 20°C by bringing sample to about 20°C in partially filled bottle while agitating by vigorous shaking or by aerating with clean, filtered compressed air.

5) Sample temperature adjustment—Bring samples to 20 ± 1°C before making dilutions.

6) Nitrification inhibition—If nitrification inhibition is desired add 3 mg 2-chloro-6-(trichloro methyl) pyridine (TCMP) to each 300-mL bottle before capping or add sufficient amounts to the dilution water to make a final concentration of 10 mg/L. (NOTE: Pure TCMP may dissolve slowly and can float on top of the sample. Some commercial formulations dissolve more readily but are not 100% TCMP; adjust dosage accordingly.) Samples that may require nitrification inhibition include, but are not limited to, biologically treated effluents, samples seeded with biologically treated effluents, and river waters. Note the use of nitrogen inhibition in reporting results.

f. Dilution technique: Dilutions that result in a residual DO of at least 1 mg/L and a DO uptake of at least 2 mg/L after 5 d incubation produce the most reliable results. Make several dilutions of prepared sample to obtain DO uptake in this range. Experience with a particular sample will permit use of a smaller number of dilutions. A more rapid analysis, such as COD, may be correlated approximately with BOD and serve as a guide in selecting dilutions. In the absence of prior knowledge, use the following dilutions: 0.0 to 1.0% for strong industrial wastes, 1 to 5% for raw and settled wastewater, 5 to 25% for biologically treated effluent, and 25 to 100% for polluted river waters.

Prepare dilutions either in graduated cylinders and then transfer to BOD bottles or prepare directly in BOD bottles. Either dilution method can be combined with any DO measurement technique. The number of bottles to be prepared for each dilution depends on the DO technique and the number of replicates desired.

When using graduated cylinders to prepare dilutions, and when seeding is necessary, add seed either directly to dilution water or to individual cylinders before dilution. Seeding of individual cylinders avoids a declining ratio of seed to sample as increasing dilutions are made. When dilutions are prepared directly in BOD bottles and when seeding is necessary, add seed directly to dilution water or directly to the BOD bottles.

1) Dilutions prepared in graduated cylinders—If the azide modification of the titrimetric iodometric method (Section 4500-O.C) is used, carefully siphon dilution water, seeded if necessary, into a 1- to 2-L-capacity graduated cylinder. Fill cylinder half full without entraining air. Add desired quantity of carefully mixed sample and dilute to appropriate level with dilution water. Mix well with a plunger-type mixing rod; avoid entraining air. Siphon mixed dilution into two BOD bottles. Determine initial DO on one of these bottles. Stopper the second bottle tightly, water-seal, and incubate for 5 d at 20°C. If the membrane electrode method is used for DO measurement, siphon dilution mixture into one BOD bottle. Determine initial DO on this bottle and replace any displaced contents with sample dilution to fill the bottle. Stopper tightly, water-seal, and incubate for 5 d at 20°C.

2) Dilutions prepared directly in BOD bottles—Using a wide-tip volumetric pipet, add the desired sample volume to individual BOD bottles of known capacity. Add appropriate amounts of seed material to the individual BOD bottles or to the dilution water. Fill bottles with enough dilution water, seeded if necessary, so that insertion of stopper will displace all air, leaving no bubbles. For dilutions greater than 1:100 make a primary dilution in a graduated cylinder before making final dilution in the bottle. When using titrimetric iodometric methods for DO measurement, prepare two bottles at each dilution. Determine initial DO on one bottle. Stopper second bottle tightly, water-seal, and incubate for 5 d at 20°C. If the membrane electrode method is used for DO measurement, prepare only one BOD bottle for each dilution. Determine initial DO on this bottle and replace any displaced contents with dilution water to fill the bottle. Stopper tightly, water-seal, and incubate for 5 d at 20°C. Rinse DO electrode between determinations to prevent cross-contamination of samples.

g. Determination of initial DO: If the sample contains materials that react rapidly with DO, determine initial DO immediately after filling BOD bottle with diluted sample. If rapid initial DO uptake is insignificant, the time period between preparing dilution and measuring initial DO is not critical.

Use the azide modification of the iodometric method (Section 4500-O.C) or the membrane electrode method (Section 4500-O.G) to determine initial DO on all sample dilutions, dilution water blanks, and where appropriate, seed controls.

h. Dilution water blank: Use a dilution water blank as a rough check on quality of unseeded dilution water and cleanliness of incubation bottles. Together with each batch of samples incubate a bottle of unseeded dilution water. Determine initial and final DO as in ¶s 4*g* and *j*. The DO uptake should not be more than 0.2 mg/L and preferably not more than 0.1 mg/L.

i. Incubation: Incubate at 20°C ± 1°C BOD bottles containing desired dilutions, seed controls, dilution water blanks, and glucose-glutamic acid checks. Water-seal bottles as described in ¶ 4*f*.

j. Determination of final DO: After 5 d incubation determine DO in sample dilutions, blanks, and checks as in ¶ 4*g*.

5. Calculation

When dilution water is not seeded:

$$\text{BOD}_5,\ \text{mg/L} = \frac{D_1 - D_2}{P}$$

When dilution water is seeded:

$$\text{BOD}_5,\ \text{mg/L} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

where:

D_1 = DO of diluted sample immediately after preparation, mg/L,
D_2 = DO of diluted sample after 5 d incubation at 20°C, mg/L,
P = decimal volumetric fraction of sample used,
B_1 = DO of seed control before incubation, mg/L (¶ 4*d*),
B_2 = DO of seed control after incubation mg/L (¶ 4*d*), and
f = ratio of seed in diluted sample to seed in seed control = (% seed in diluted sample)/(% seed in seed control).

If seed material is added directly to sample or to seed control bottles:

f = (volume of seed in diluted sample)/(volume of seed in seed control)

Report results as $CBOD_5$ if nitrification is inhibited.

If more than one sample dilution meets the criteria of a residual DO of at least 1 mg/L and a DO depletion of at least 2 mg/L and there is no evidence of toxicity at higher sample concentrations or the existence of an obvious anomaly, average results in the acceptable range.

In these calculations, do not make corrections for DO uptake by the dilution water blank during incubation. This correction is unnecessary if dilution water meets the blank criteria stipulated above. If the dilution water does not meet these criteria, proper corrections are difficult and results become questionable.

6. Precision and Bias

There is no measurement for establishing bias of the BOD procedure. The glucose-glutamic acid check prescribed in ¶ 4*c* is intended to be a reference point for evaluation of dilution water quality, seed effectiveness, and analytical technique. Single-laboratory tests using a 300-mg/L mixed glucose-glutamic acid solution provided the following results:

Number of months:	14	
Number of triplicates:	421	
Average monthly recovery:	204	mg/L
Average monthly standard deviation:	10.4	mg/L

In a series of interlaboratory studies,[1] each involving 2 to 112 laboratories (and as many analysts and seed sources), 5-d BOD measurements were made on synthetic water samples containing a 1:1 mixture of glucose and glutamic acid in the total concentration range of 3.3 to 231 mg/L. The regression equations for mean value, $\bar{X}$, and standard deviation, S, from these studies were:

$\bar{X}$ = 0.658 (added level, mg/L) + 0.280 mg/L
S = 0.100 (added level, mg/L) + 0.547 mg/L

For the 300-mg/L mixed primary standard, the average 5-d BOD would be 198 mg/L with a standard deviation of 30.5 mg/L.

a. Control limits: Because of many factors affecting BOD tests multilaboratory studies and the resulting extreme variability test results, one standard deviation, as determined by interlaboratory tests, is recommended as a control limit for individual laboratories. Alternatively, for each laboratory, establish its control limits by performing a minimum of 25 glucose-glutamic acid checks (¶ 4*c*) over a period of several weeks or months and calculating the mean and standard deviation. Use the mean ± 3 standard deviations as the control limit for future glucose-glutamic acid checks. Compare calculated control limits to the single-laboratory tests presented above and to interlaboratory results. If control limits are outside the range of 198 ± 30.5, re-evaluate the control limits and investigate source of the problem. If measured BOD for a glucose-glutamic acid check is outside the accepted control limit range, reject tests made with that seed and dilution water.

b. Working range and detection limit: The working range is equal to the difference between the maximum initial DO (7 to 9 mg L) and minimum DO residual of 1 mg/L multiplied by the dilution factor. A lower detection limit of 2 mg/L is established by the requirement for a minimum DO depletion of 2 mg/L.

7. References

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5220 CHEMICAL OXYGEN DEMAND (COD)*

5220 A. Introduction

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter. The test is useful for monitoring and control after correlation has been established. The dichromate reflux method is preferred over procedures using other oxidants because of superior oxidizing ability, applicability to a wide variety of samples, and ease of manipulation. Oxidation of most organic compounds is 95 to 100% of the theoretical value. Pyridine and related compounds resist oxidation and volatile organic compounds are oxidized only to the extent that they remain in contact with the oxidant. Ammonia, present either in the waste or liberated from nitrogen-containing organic matter, is not oxidized in the absence of significant concentration of free chloride ions.

1. Selection of Method

The open reflux method (B) is suitable for a wide range of wastes where a large sample size is preferred. The closed reflux methods (C and D) are more economical in the use of metallic salt reagents, but require homogenization of samples containing suspended solids to obtain reproducible results. Ampules and culture tubes with premeasured reagents are available commercially. Follow instructions furnished by the manufacturer.

Determine COD values of >50 mg O_2/L by using procedures 5220B.4*a*, C.4, or D.4. Use procedure 5220B.4*b* to determine, with lesser accuracy, COD values from 5 to 50 mg O_2/L.

2. Interferences and Limitations

Volatile straight-chain aliphatic compounds are not oxidized to any appreciable extent. This failure occurs partly because volatile organics are present in the vapor space and do not come in contact with the oxidizing liquid. Straight-chain aliphatic compounds are oxidized more effectively when silver sulfate (Ag_2SO_4) is added as a catalyst. However, Ag_2SO_4 reacts with chloride, bromide, and iodide to produce precipitates that are oxidized only partially. The difficulties caused by the presence of the halides can be overcome largely, though not completely, by complexing with mercuric sulfate ($HgSO_4$) before the refluxing procedure. Although 1 g $HgSO_4$ is specified for 50 mL sample, a lesser amount may be used where sample chloride concentration is known to be less than 2000 mg/L, as long as a 10:1 ratio of $HgSO_4$:Cl^- is maintained. Do not use the test for samples containing more than 2000 mg Cl^-/L. Techniques designed to measure COD in saline waters are available.[1,2]

Nitrite (NO_2^-) exerts a COD of 1.1 mg O_2/mg NO_2^--N. Because concentrations of NO_2^- in waters rarely exceed 1 or 2 mg NO_2^--N/L, the interference is considered insignificant and usually is ignored. To eliminate a significant interference due to NO_2^-, add 10 mg sulfamic acid for each mg NO_2^--N present in the sample volume used; add the same amount of sulfamic acid to the reflux vessel containing the distilled water blank.

* Approved by Standard Methods Committee, 1990.