APPENDIX-F

WASTEWATER EFFLUENT TEST RESULTS, 2008

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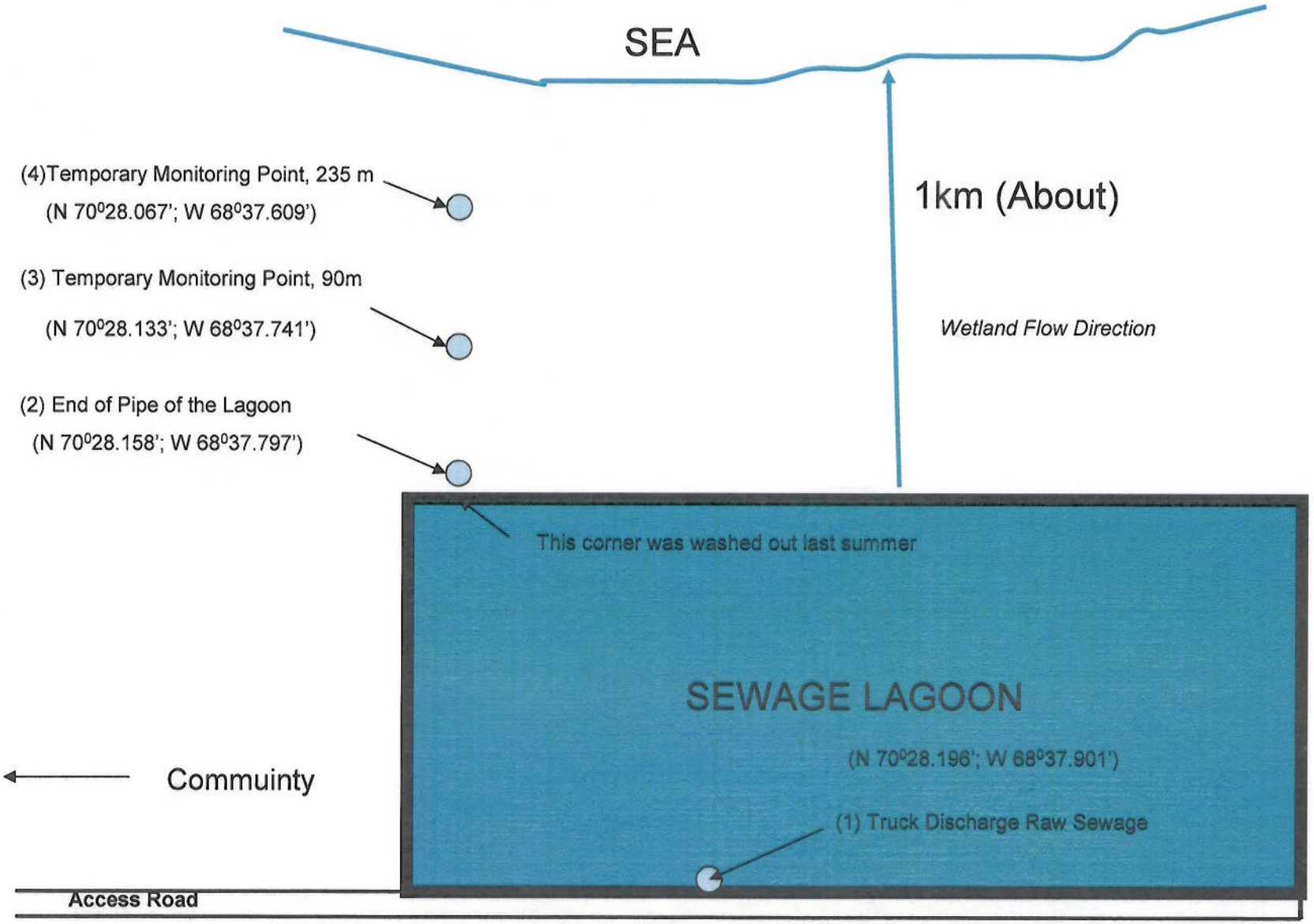
CLYDE RIVER SEWAGE LAGOON



CADUCEON
ENVIRONMENTAL LABORATORIES

☐ Provincial Water Quality Objectives
☐ MISA Guidelines
☐ O.Reg 153/04 (1__ 2__ 3__ 4__ 5__ 6__)
☐ Sewer Use By-Law: _____
☐ O.Reg 558 Leachate Analysis
☐ Other: _____

June 24.08 6 pet

Client: HAMLET of CLYDE RIVER	Address: P.O. Box 89 CLYDE RIVER, NUNAVUT X0A 0E0
Contact: Bill Buckle	
Tel: 867 924 6220	
Fax: 867 924 6293	Quote No.:
Email: Saoclyde2005@qiniq.com	P.O. No.:
	Project Name: Sewage Lagoon
	Additional Info:

ANALYSES REQUESTED (Print Test in Boxes)

BOD | TSS

BOS-19579

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Lab No.	Sample Identification	Sample Matrix *	Date Collected (dd-mm-yy)	Time Collected	# Bottles/ Sample	Field Filtered (Y/N)
	① 3 Samples from overflow line for BOD_5 (Bottles 1, 2, 3)	WW	June 18	10:30am		
	② 3 Samples from overflow line for TSS (Bottles 4, 5, 6)	WW	June 18	10:30am		

Indicate Test For Each Sample By Using A Check Mark In The Box Provided

Samples passed holding time. S2

Sample Submission Information	Turnaround Time Requested	Reporting Format
Sampled By (print): ELISHA SANGUYA	24 Hrs ☐ 48 Hrs ☐	Fax Results ☐
Submitted By (print): BILL BUCKLE	72 Hrs ☐ 5-7 Day ☐	Email ☒
Signature:	Specific Date: _____	No. of Containers Shipped
Date(dd-mm-yy): June 18/08 Time:	Method of Shipment:	

LABORATORY USE ONLY

Received By (print): _____ Signature: _____
Date(dd-mm-yy) Received: June 24/08 Time Received: 9:00
Comments: (Icoe) Laboratory Prepared Bottles: ☐ YES ☐ NO
Page ___ of ___

* Sample Matrix Legend: WW=Waste Water SW=Surface Water GW=Groundwater LS=Liquid Sludge SS=Solid Sludge S=Soil Sed=Sediment PC=Paint Chips F=Filter

Laboratory Locations/Shipping Addresses

Kingston Lab - 285 Dalton Ave., Kingston, ON K7K 6Z1, Tel: (613) 544-2001 Fax: (613) 544-2770, Email: contactkingston@caduceonlabs.com
Ottawa Lab - 2378 Holly Lane, Ottawa, ON K1V 7P1, Tel: (613) 526-0123 Fax: (613) 526-1244, Email: contactottawa@caduceonlabs.com
Peterborough Lab - #206 - 160 Charlotte St., Peterborough, ON K9J 2T8, Tel: (705) 748-1505 Fax: (705) 748-6514, Email: contactpeterborough@caduceonlabs.com
Windsor Lab - 3201 Marentette Ave., Windsor, ON N8X 4G3, Tel: (519) 966-9541 Fax: (519) 966-9567, Email: contactwindsor@caduceonlabs.com
Moncton Lab - 150 Lutz St., Moncton, NB E1C 5E9, Tel: (506) 855-6472 Fax: (506) 855-8294, Email: contactmoncton@caduceonlabs.com

CHARGE SHIPPING NO NO

130046

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CERTIFICATE OF ANALYSIS

Final Report

C.O.C.: 130044

REPORT No. B08-16962

Report To:

Hamlet of Clyde River
Box 89
Clyde River, Nunavut, X0A 0E0
Attention: Bill Buckle

Caduceon Environmental Laboratories
2378 Holly Lane
Ottawa, Ontario, K1V 7P1
Tel: 613-526-0123
Fax: 613-526-1244

DATE RECEIVED: 03-Jun-08
DATE REPORTED: 11-Jun-08
SAMPLE MATRIX: Water

JOB/PROJECT NO.: Lagoon Water
P.O. NUMBER:
WATERWORKS NO.

Parameter:			BOD	Total Suspended Solids			
Units:			mg/L	mg/L			
M.D.L.:			3	3			
Reference Method:			SM 5210	SM 2540			
Date/Site Analyzed:			06-Jun-08/O	05-Jun-08/O			
Client I.D.	**Sample I.D.**	**Date Collected**					
Lagoon Water - Sample #1	B08-16962-1	01-Jun-08	380	--			
Lagoon Water - Sample #2	B08-16962-2	01-Jun-08	420	--			
Lagoon Water - Sample #3	B08-16962-3	01-Jun-08	417	--			
Lagoon Water - Sample #4	B08-16962-4	01-Jun-08	--	72			
Lagoon Water - Sample #5	B08-16962-5	01-Jun-08	--	144			
Lagoon Water - Sample #6	B08-16962-6	01-Jun-08	--	70			

K. Pipin

Krystyna Pipin , M. Sc.
Lab Supervisor

M.D.L. = Method Detection Limit
Site Analyzed=K-Kingston,W-Windsor,O-Ottawa,P-Peterborough,M-Moncton

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CERTIFICATE OF ANALYSIS

Final Report

C.O.C.: 130045

REPORT No. B08-16974

Report To:

Hamlet of Clyde River
Box 89
Clyde River, Nunavut, X0A 0E0
Attention: Bill Buckle

Caduceon Environmental Laboratories
2378 Holly Lane
Ottawa, Ontario, K1V 7P1
Tel: 613-526-0123
Fax: 613-526-1244

DATE RECEIVED: 03-Jun-08
DATE REPORTED: 11-Jun-08
SAMPLE MATRIX: Water

JOB/PROJECT NO.: Wet Land Area
P.O. NUMBER:
WATERWORKS NO.

Parameter:			BOD	Total Suspended Solids			
Units:			mg/L	mg/L			
M.D.L.:			3	3			
Reference Method:			SM 5210	SM 2540			
Date/Site Analyzed:			06-Jun-08/O	05-Jun-08/O			
Client I.D.	**Sample I.D.**	**Date Collected**					
Wet Land Area - Sample #7	B08-16974-1	03-Jun-08	3	--			
Wet Land Area - Sample #8	B08-16974-2	03-Jun-08	3	--			
Wet Land Area - Sample #9	B08-16974-3	03-Jun-08	3	--			
Wet Land Area - Sample #10	B08-16974-4	03-Jun-08	--	52			
Wet Land Area - Sample #11	B08-16974-5	03-Jun-08	--	14			
Wet Land Area - Sample #12	B08-16974-6	03-Jun-08	--	18			

K. Pipin

Krystyna Pipin , M. Sc.
Lab Supervisor

M.D.L. = Method Detection Limit
Site Analyzed=K-Kingston,W-Windsor,O-Ottawa,P-Peterborough,M-Moncton

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CERTIFICATE OF ANALYSIS

Final Report

C.O.C.: ---

REPORT No. B08-19579

Report To:

Hamlet of Clyde River
Box 89
Clyde River, Nunavut, X0A 0E0
Attention: Bill Buckle

Caduceon Environmental Laboratories
2378 Holly Lane
Ottawa, Ontario, K1V 7P1
Tel: 613-526-0123
Fax: 613-526-1244

DATE RECEIVED: 24-Jun-08
DATE REPORTED: 02-Jul-08
SAMPLE MATRIX: Water

JOB/PROJECT NO.:
P.O. NUMBER:
WATERWORKS NO.

	Parameter:		BOD	Total Suspended Solids			
	Units:		mg/L	mg/L			
	M.D.L.:		3	3			
	Reference Method:		SM 5210	SM 2540			
	Date/Site Analyzed:		25-Jun-08/O	02-Jul-08/O			
Client I.D.	Sample I.D.	Date Collected					
Bottle #1	B08-19579-1	18-Jun-08	408 [1]	--			
Bottle #2	B08-19579-2	18-Jun-08	389 [1]	--			
Bottle #3	B08-19579-3	18-Jun-08	399 [1]	--			
Bottle #4	B08-19579-4	18-Jun-08	--	20			
Bottle #5	B08-19579-5	18-Jun-08	--	26			
Bottle #6	B08-19579-6	18-Jun-08	--	24			

1. Passed holding time

K. Pipin

Krystyna Pipin , M. Sc.
Lab Supervisor

M.D.L. = Method Detection Limit
Site Analyzed=K-Kingston,W-Windsor,O-Ottawa,P-Peterborough,M-Moncton

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ENVIRONMENTAL LABORATORIES

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- ☐ MISA Guidelines
- ☐ O.Reg 153/04 (1___ 2___ 3___ 4___ 5___ 6___)
- ☐ Sewer Use By-Law: _____
- ☐ Landfill Analysis
- ☐ O.Reg 558 Leachate Analysis
- ☐ Other: _____

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Client:	Address:	
Contact:		
Tel:		
Fax:	Quote No.:	Project Name:
Email:	P.O. No.:	Additional Info:

ANALYSES REQUESTED (Print Test in Boxes)

REPORT NUMBER:

Lab No.	Sample Identification	Sample Matrix *	Date Collected (dd-mm-yy)	Time Collected	Indicate Test For Each Sample By Using A Check Mark In The Box Provided	# Bottles/ Sample	Field Filtered (Y/N)

Sample Submission Information	Turnaround Time Requested	Reporting Format	LABORATORY USE ONLY
Sampled By (print):	24 Hrs ☐ 48 Hrs ☐	Fax Results ☐	Received By (print): Signature:
Submitted By (print):	72 Hrs ☐ 5-7 Day ☐	Email ☐	Date(dd-mm-yy) Received: Time Received:
Signature:	Specific Date: _____	No. of Containers Shipped	Comments: Laboratory Prepared Bottles: ☐ YES ☐ NO
Date(dd-mm-yy): Time:	Method of Shipment:		Page ___ of ___

* Sample Matrix Legend: WW=Waste Water SW=Surface Water GW=Groundwater LS=Liquid Sludge SS=Solid Sludge S=Soil Sed=Sediment PC=Paint Chips F=Filter

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Peterborough Lab - #206-160 Charlotte St., Peterborough, ON K9J 2T8, Tel: (705) 748-1506 Fax: (705) 748-6514 Email: contactpeterborough@caduceonlabs.com
Windsor Lab - 3201 Marentette Ave., Windsor, ON N8X 4G3, Tel: (519) 966-9541 Fax: (519) 966-9567 Email: contactwindsor@caduceonlabs.com
Moncton Lab - 150 Lutz St., Moncton, NB E1C 5E9, Tel: (506) 855-6472 Fax: (506) 855-8294 Email: contactmoncton@caduceonlabs.com

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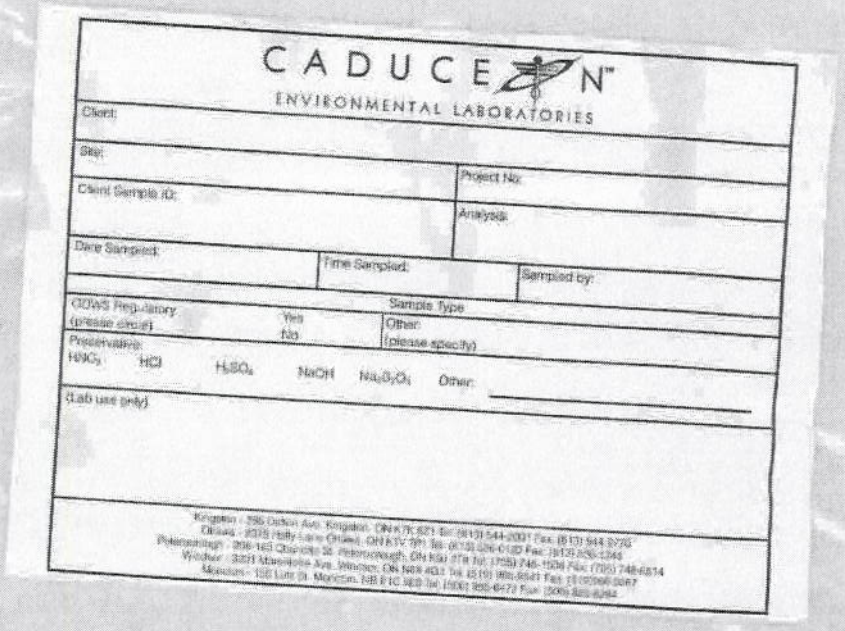

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Client:

Site:

Project No:

Client Sample ID:

Analysis:

Date Sampled:

Time Sampled:

Sampled by:

ODWS Regulatory (please circle)

Yes

No

Sample Type

Other: (please specify)

Preservative:

HNO_3 HCl H_2SO_4 NaOH $Na_2S_2O_3$ Other:

(Lab use only)

Kingston - 36b Oxford Ave, Kingston, ON K7K 6Z1 Tel: (613) 544-2001 Fax: (613) 544-2775

Ottawa - 2378 Holly Lane Ottawa, ON K1V 7P1 Tel: (613) 526-0123 Fax: (613) 526-1244

Peterborough - 208-143 Charlotte St. Peterborough, ON K9J 2T9 Tel: (705) 748-1556 Fax: (705) 748-6314

Windsor - 3339 Mainwaring Ave, Windsor, ON N8X 4G3 Tel: (519) 966-9541 Fax: (519)966-9567

Moncton - 150 Lutz St. Moncton, NB E1C 9B9 Tel: (506) 855-6472 Fax: (506) 855-6944

Biochemical Oxygen Demand

1.0 Scope and Application

1.1 The Biochemical Oxygen Demand (BOD_5) is an indicator of the dissolved oxygen required for the decomposition of organic materials by aerobic bacteria. The BOD_5 is used to assess the oxygen demand of organic wastes, to determine the biodegradable loadings to treatment plants, and to evaluate the efficiency of waste treatments. The test requirement for a five day incubation period imposes a lengthy time delay in establishing the demand of a particular waste. This method is applicable for BOD determination in waters such as ground water, surface water, and waste waters.

1.2 The analytical range for this method is approximately 1 mg/L to 30000 mg/L with a maximum sample volume of 300mL.

1.3 By adding nitrogen inhibitor to analysis bottle, carbonaceous BOD ($CBOD_5$) may be determined. The scope and application is the same as for BOD determination.

2.0 Principle and Theory

2.1 Principles

2.1.1 The BOD_5 is a measure of dissolved oxygen depletion during a 5 day incubation period at a specified temperature (20°C). The units are milligrams per litre as oxygen. It is determined by diluting a suitable sample aliquot with dilution water. The dilution should be such that about 50 % of the dissolved oxygen is depleted after 5 days incubation. The dissolved oxygen is determined using a dissolved oxygen probe, as soon as possible after set-up; and again after the incubation period. The BOD_5 is expressed as the amount of dissolved oxygen in mg utilized by 1 litre of sample during a 5 day incubation period at 20°C. The principle of the oxygen electrode is based on the relationship between the concentration of dissolved oxygen in a sample and the current generated by its reduction under controlled conditions. The electrode probe contains an electrolytic cell separated from test sample by a teflon membrane which is permeable to dissolved oxygen. When the probe is immersed in a sample, a portion of the oxygen in the sample diffuses through the membrane into the electrolytic cell and is reduced at the cathode. The resultant change in current is directly proportional to the oxygen concentration present in the sample, and is read out digitally as mg/L of O_2. A suitable velocity of water across the membrane is maintained by a motorized stirrer and a built-in thermistor compensates for temperature variations.

2.2 Interferences

2.2.1 Most heavy metals, sulphates , and cyanide interfere with biological processes. Any gases, which diffuse through the membrane and enter into a redox reaction, will interfere. Chlorine is the most commonly known gas of this type and its interference can be nullified by raising the pH to 12 and converting the gas to hypochlorous ion.

2.2.2 Prolonged exposure to oily samples will produce a film on the membrane which might retard the diffusion of oxygen. Such film should be removed by placing the electrode membrane in hot water for a short period of time.

2.2.3 Prolonged exposure to samples containing hydrogen sulphide will result in corrosion of the lead anode. Periodic cleaning of the electrodes with 50% HCl solution controls this poisoning problem.

3.0 Safety

3.1 Extreme caution should be exercised when preparing acidic and caustic solutions. A full face shield, an apron and gloves should be worn when working with concentrated solutions. Goggles, gloves and a lab

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coat are suitable for working with diluted solutions. Refer to each chemical MSDS for detailed hazards.

3.2 Refer to Caduceon Safety Manual for general laboratory safety practices and procedures.

4.0 Sample Requirements

4.1 Samples must be collected in plastic or glass bottles, and must be refrigerated as soon as possible after sampling at 4 ± 3°C; and stored in the dark to minimize bacterial decomposition and photosynthetic activity. Store not longer than 96 hours. Preservatives are not employed because they may retard bacterial action during incubation. The minimum sample volume submitted for analysis is 500 milliliters.

4.2 Samples containing caustic alkalinity or acidity are neutralized to pH 5.0 to 8.0 with H_2SO_4 or NaOH using a pH meter.

4.3 Chlorine residuals, if present in a sample, are overcome by dechlorinating the sample by adding Na_2SO_3 solution and seeding the dilution water. The dechlorinating procedure applies for effluent samples and treated drinking water samples. Other samples must be treated if from an industrial process using chlorine in the manufacturing stream.

4.4 Samples supersaturated with dissolved oxygen must have the dissolved oxygen content reduced to saturation, 9.17mg/L at 20°C, by aerating with compressed air or by vigorous shaking of the sample in its container.

5.0 Equipment

5.1 BOD bottles - 300mL glass

5.2 20L carboy

5.3 Incubator, thermostatically controlled at 20°C ± 1°C (temperature reading accuracy verified as per Caduceon SOP-10)

5.4 Winkler titration apparatus

5.5 Dissolved oxygen electrode

5.6 Volumetric flasks, Class A

5.7 Volumetric pipets, Class A

5.8 Disposable graduated pipets, 10mL size

5.9 25.0mL graduated buret, 0.1mL graduation (dispensing volume accuracy verified as per Caduceon SOP-08)

5.10 Filters, Whatman GF/C or equivalent

5.11 Graduated cylinders, various sizes (dispensing volume accuracy verified as per Caduceon SOP-08)

Note: Clean glassware (except BOD bottles) with phosphate-free detergent; rinse thoroughly with reagent grade water, and drain. Dry flasks and pipets before re-use
BOD bottles must be cleaned as follows:

- Place all bottles in the designated dishwasher and wash on normal cycle using phosphate-free detergent;
- Let drain, then rinse well with Reagent-grade water to remove possible copper contamination;
- Allow the bottles to dry before use.

6.0 Reagents

Note: Record all reagent preparation in the appropriate reagent preparation log.

6.1 Reagent grade water, DW (to meet specifications as per Caduceon SOP-04)

6.2 Reagents for sample pretreatment:

6.2.1 1N Sodium hydroxide solution: In a 100mL volumetric flask containing approximately 50mL reagent grade water, dissolve 4.0g NaOH. Dilute to mark. Prepare fresh every six months or as needed. Store at room temperature.

6.2.2 1N Sulfuric acid solution: In a 100mL volumetric flask containing about 50mL reagent grade water, add 2.8mL concentrated H_2SO_4. Dilute to mark. Prepare fresh yearly or as needed. Store at room temperature.

6.2.3 50% Acetic acid solution (v/v): In a 200mL volumetric flask containing approximately 50mL reagent grade water, add 100mL concentrated acetic acid. Dilute to mark. Prepare fresh weekly or as needed. Store at room temperature.

6.2.4 5% Potassium iodide solution (w/v): In a 200mL volumetric flask containing approximately 100mL reagent grade water, dissolve 10g KI. Dilute to mark. Prepare fresh weekly or as needed. Store at room temperature.

6.2.5 Sodium sulphite solution: In a 100mL volumetric flask containing approximately 50mL reagent grade water, dissolve 0.158g Na_2SO_3. Dilute to mark. Make fresh daily. Prepare fresh daily. Store at room temperature.

6.2.6 Nitrogen Inhibitor Hach 2579-24 (2-chloro-6 (trichloro methyl) pyridine). Refer to manufacturer certificate for holding time/expiry date. Store at room temperature.

6.3 Dilution water reagents:

6.3.1 Phosphate buffer solution: In a 500mL volumetric flask, dissolve 4.25g KH_2PO_4, 10.9g K_2HPO_4, 16.7g $Na_2PO_4 \bullet 7H_2O$ and 0.85g NH_4CL in about 500mL reagent grade water. Dilute to mark. Discard reagent if there is any sign of biological growth in the stock bottle. Prepare fresh monthly or as needed. Store at room temperature.

6.3.2 Magnesium sulphate solution: In a 500mL volumetric flask, dissolve 11.25g $MgSO_4 \bullet 7H_2O$ in reagent grade water and dilute to mark. Prepare fresh monthly or as needed. Store at room temperature.

6.3.3 Calcium chloride solution: In a 500mL volumetric flask, dissolve 13.75g $CaCl_2$ in reagent grade water and dilute to mark. Prepare fresh monthly or as needed. Store at room temperature.

6.3.4 Ferric chloride solution: In a 500mL volumetric flask, dissolve 0.075g $FeCl_3$ in reagent grade water and dilute to mark. Prepare fresh monthly or as needed. Store at room temperature.

6.4 Reagents for Winkler Dissolved Oxygen (DO) Determination:

6.4.1 Manganese sulphate solution: Dissolve 364g $MnSO_4 \bullet H_2O$ in reagent grade water. Filter the solution through a Whatman #4 filter and dilute to 1L in a 1.0L volumetric flask. Prepare fresh yearly or as needed. Store at room temperature.

6.4.2 Alkali-Iodide-Azide Reagent: In a 1.0L volumetric flask, dissolve 500g NaOH and 150g KI in 800mL of reagent grade water. To this solution, add 10g NaN_3 (sodium azide) dissolved in 90mL of reagent grade water. Dilute to mark. Prepare fresh yearly or as needed. Store at room temperature.

6.4.3 1:1 Sulphuric acid: To a 200mL volumetric flask containing approximately 75mL reagent grade water, add slowly 100mL concentrated sulfuric acid. Mix thoroughly and allow to cool to room temperature. Dilute to mark with reagent grade water. Prepare fresh yearly or as needed. Store at room temperature.

6.4.4 Starch Solution: Dissolve 3.00g soluble starch arrowroot powder and 0.625g salicylic acid ($C_6H_4(OH)COOH$) with approximately 50mL reagent grade water. Slowly add, with stirring, to

about 400mL of boiling reagent grade water in a 500mL volumetric flask. Dilute to mark; allow to boil for a few minutes, and let settle overnight. Retain supernatant. Prepare fresh weekly or as needed. Store at room temperature.

6.5 Potassium Bi-Iodate Stock Solution 0.10 N: In a 1.0L volumetric flask, dissolve 3.24g of $KH(IO_3)_2$ in reagent grade water and dilute to mark. Prepare fresh every six months or as needed. Keep refrigerated at 4 ± 3°C.

6.6 Potassium Bi-Iodate Working Standard Solution 0.0250 N: Using a 25.0mL volumetric pipet, transfer 25.0mL of potassium bi-iodate stock solution to a 100mL volumetric flask. Dilute to mark with reagent grade water. Prepare fresh daily. Store at room temperature.

6.7 1:10 Sulphuric acid: To a 200mL volumetric flask containing approximately 150mL reagent grade water, add slowly 20mL concentrated sulfuric acid. Mix thoroughly and allow to cool to room temperature. Dilute to mark with reagent grade water. Prepare fresh yearly or as needed. Store at room temperature.

6.8 Sodium Thiosulphate ~0.025 N: In a 1.0 L volumetric flask, dissolve 6.205g $Na_2S_2O_3 \bullet 5H_2O$ in freshly boiled reagent grade water and mix thoroughly. Preserve with 2.0g NaOH. Allow solution to cool to room temperature and dilute to mark with freshly boiled reagent grade water. Prepare fresh monthly or as needed. Store at room temperature.

6.8.1 Standardization of Sodium Thiosulphate solution: Dissolve approximately 2.0g of iodate-free KI in an erlynmeyer flask containing 100 to 150mL distilled water. Using volumetric pipettes, add 2.0mL of 1:10 sulphuric acid solution, followed by 20.0mL potassium bi-iodate working standard solution (section 6.6). Dilute to approximately 200mL with reagent grade water and titrate with sodium thiosulphate solution (section 6.8). When a pale straw colour is reached, add approximately 2mL of starch solution and complete the titration to the colourless end point. The normality of the thiosulphate solution is calculated as:

$$A = \frac{B \times C}{D}$$

A = normality of sodium thiosulphate solution
B = normality of potassium bi-iodate working standard
C = volume (mL) of potassium bi-iodate working standard used
D = volume (mL) of sodium thiosulphate solution added

6.8.2 Record the normality of the sodium thiosulphate solution in the analyst work book. Standardization is performed when the reagent is prepared.

6.9 Seeding Material - must be obtained fresh weekly from RMOC or other sewage facility. Store in a plastic container, labelled with the date obtained and the expiry date. Keep refrigerated at 4 ± 3°C.

6.10 Standard Preparation

6.10.1 Stock Standard, 200mg/L (Glucose-glutamic acid solution): Dry glucose and glutamic acid at 105°C for one hour. In a 1.0L volumetric flask, add 150mg glucose and 150mg glutamic acid. Dilute to mark with reagent grade water. Prepare fresh monthly. Store at 4 ± 3°C.

6.10.2 QC-01 Working Standard, 50mg/L: Take 125mL of stock standard (200mg/L) and dilute to 500mL. Transfer 20mL of this working standard solution into a BOD bottle. Add 2mL of seed and fill with dilution water. Prepare fresh daily.

7.0 Test Procedure

7.1 Preparation of dilution water: Place desired volume of reagent grade water in a suitable bottle and add 1mL each of phosphate buffer, $MgSO_4$, $CaCl_2$ and $FeCl_3$ solutions per liter of water. Saturate with DO by aerating with organic-free filtered air for 15-20 minutes.

7.2 Calibration and Operation of the Oxygen Meter:

7.2.1 The oxygen meter is calibrated against a sample of known DO concentration as determined by the Winkler method. Calibration is routinely performed against dilution water.

7.2.1.1 Fill 4 BOD bottles with dilution water.

7.2.1.2 Determine the Winkler DO concentration in the first two bottles by adding 2mL $MnSO_4 \bullet H_2O$ and 2mL of alkali-azide reagent to each bottle.

7.2.1.3 Close the bottle carefully with the stopper to exclude air bubbles and mix by inverting the bottles several times.

7.2.1.4 When precipitation has sufficiently settled, add 2.0mL H_2SO_4.

7.2.1.5 Close the bottle carefully with the stopper again and mix by inverting several times.

7.2.1.6 A 200mL aliquot of sample is titrated with 0.025 N $Na_2S_2O_3$. Add 2.0mL starch solution towards the end of the titration when a pale straw colour has been reached. Titrate to a clear end point.

7.2.1.7 The volume of sodium thiosulphate standard solution dispensed equals the DO of the aerated water. Correct this value for the true normality of the sodium thiosulphate standard solution (obtained in section 6.8.1) using the following calculation:

$$A = \frac{B \times 0.025}{C}$$

A = corrected DO value
B = volume of $Na_2S_2O_3$ dispensed
C = actual normality of $Na_2S_2O_3$ (section 6.8.1)

Note: The DO meter probe is adjusted based on the average of two DO results.

7.2.1.8 Insert the oxygen probe into one of the two remaining BOD bottles and switch the stirrer on.

7.2.1.9 Switch instrument to zero position and zero the meter with the zero knob.

7.2.1.10 Switch instrument to calibrating position and calibrate meter according to the DO value obtained from titration.

7.2.1.11 Verify the DO measurement with the oxygen probe and meter on the remaining bottle of dilution water and record the result in the analyst workbook.

7.3 pH adjustment for samples with pH outside range 5.0 to 8.0: Using a pH meter (see Caduceon method, A-pH-01), adjust the pH of the sample by adding 1N NaOH (pH < 5.0) or 1N H_2SO_4 (pH > 8.0) dropwise until the sample pH is within the required range. Ensure that the change in sample volume is less than 1 percent and record the volume and type of solution added.

Note: Check the initial pH of each sample prior to set-up with pH paper, and use the pH meter only in cases where pH adjustment is required.

7.4 Removal of residual chlorine: Place 50mL of sample, 5mL of 5% potassium iodide solution, 5mL of 50% acetic acid solution, and about 3mL starch solution into a 250mL erlenmeyer flask. Mix by swirling. If residual chlorine is present in the sample, the colour of the solution will turn to dark blue. Add 0.01N Na_2SO_3 solution dropwise, while swirling, until the the solution turns clear. Record the amount of 0.01N Na_2SO_3 required per 50mL of sample directly onto the sample bottle. The required amount of 0.01N

Na_2SO_3 necessary for neutralization will be added later, to portions of the original sample prior to dilution.
Note: Excess Na_2SO_3 exerts an oxygen demand and reacts slowly with certain organic chloramine compounds that may be present in chlorinated samples.

7.5 Filtration: Samples submitted for filtered BOD_5, are filtered through a Whatman GF/C filter, prior to dilution.

7.6 Sample seeding: For samples needing pH adjustment, add seeding material. For samples containing residual chlorine, add the required amount of 0.01N Na_2SO_3 solution and seeding material (approximately 2mL). All industrial wastes and final effluent samples should be seeded as mentioned above.

7.7 Sample dilutions: Using a wide-tip volumetric pipet or a graduated cylinder, add the desired sample volume to individual BOD bottles of known capacity. Fill bottles with enough dilution water, seeded if necessary, so that insertion of the stopper will displace all air, leaving no bubbles.

7.7.1 For dilutions greater than 1 : 100, make a primary dilution in a graduated cylinder before making final dilution in the bottle.

7.8 Dilution Water Blanks: Use a dilution water blank as a rough check on quality of unseeded dilutions, water and cleanliness of incubation bottles. The DO uptake should not be more than 0.2mg/L.

7.9 Seed Control: Determine BOD of seeding material as for any other sample. The DO uptake of seeded dilution water should be between 0.6 and 1.0mg/L.

7.10 Quality Control Checks: Take 125mL of glucose-glutamic acid (300mg/L) and dilute to 500mL. Transfer 20 mL of glucose-glutamic acid reagent into BOD bottle. Add 2mL of seed and fill with dilution water.

7.11 Matrix Spike Preparation: Transfer 10mL of 50 mg/L working standard (section 6.101.2) to the BOD bottle containing the appropriate amount of diluted sample. The target value is 1.76 mg/L of O_2 depletion.

7.12 Determine the initial DO on all BOD bottles, using the oxygen probe and meter. Stopper tightly; water seal and incubate for 5 days at 20 ± 2°C. Rinse DO electrode between determinations to prevent cross-contamination of samples.

7.13 Determine final DO for each bottle, as in section **7.12**, after 5 days of incubation.

Note: Each set-up must include dilution water blanks, standards, and seeded dilution water. These must be set up in duplicate. Samples are prepared at two to five different dilutions. Duplicate samples are analyzed at a level of at least once after every ten samples and a matrix spike after every thirty samples. If the relative deviation in duplicate and spike results is greater than the control limits (refer to the QC log), the duplicate sample and spike recovery results are reported to the client with a comment to qualify the data as suspect. Sample holding time prevents samples from being re-analyzed if duplicate results are not within the required range.

7.14 Carbonaceous B.O.D.: Requires the addition of ~0.16 g (2 shots from the dispenser) of nitrogen inhibitor which is added to each dilution bottle of the samples requiring C.B.O.D.. The amount of the inhibitor put in each bottle (including standards and blanks) is done with the chemical applicator supplied from Hach.

7.15 Documentation Procedures

7.15.1 Document all required information in the BOD Analysis workbook when analyzing samples and QC solutions.

7.15.2 Document all required information in BOD Standard/Reagent Preparation logs when

preparing Reagents and QC Standards.

7.15.3 Document all maintenance, comments and any changes in the instrument log book.

7.15.4 QC data must be entered into the QC log data file by the analyst.

7.15.5 The QC log data file is found on the Ottawa server: ...QC LOGS\Organic Chemistry\BOD.xls.

7.15.6 Open this file and enter the data in the appropriate fields; Date, Expected Concentration for working QC-01, Found Concentration for working QC-01, Duplicate and Spike results and Blanks.

7.15.7 The excel program will calculate the % recoveries of the QC-01 and spikes and the % difference of the duplicate samples and the average concentration of the blanks.

7.15.8 The excel program files will be maintained by the QA officer.

7.15.9 Control charts will be monitored for trend analysis as per SOP-01 Control Charting.

8.0 Calculations & Reporting

8.1 When sample is not seeded:

$$A = \frac{(B - C) \times 300}{D}$$

A = concentration of BOD_5 (mg/L)
B = initial DO reading (mg/L)
C = final DO reading (mg/L)
D = volume of sample analyzed (mL)

8.2 When sample is seeded:

$$A = \frac{[(B - C) - E] \times 300}{D}$$

A = concentration of BOD_5 (mg/L)
B = initial DO reading (mg/L)
C = final DO reading (mg/L)
D = volume of sample analyzed (mL)
E = DO reading of seed (mg/L)

8.3 When a sample is spiked:

8.3.1 Depletion of working standard = DO (initial) – DO (final). Target result is 1.76 mg/L

8.3.2 Depletion of sample = DO (initial) – DO (final)

8.3.3 Depletion of spiked sample = DO (initial) – DO (final)

8.3.4 Actual Spike amount recovered, as depletion = Depletion (8.3.3) – Depeltion (8.3.2)

8.3.5 % Spike Recovery = $\frac{\text{Result (8.3.4)} \times 100}{\text{Result (8.3.1)}}$

8.4 Criteria for Result Acceptance:

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8.4.1 The following criteria must be met for a result to be accepted as valid.

8.4.1.1 The final DO reading must be ≥ 1mg/L.

8.4.1.2 The difference between the final DO reading and the initial DO reading must be ≥ 1mg/L.

8.4.2.3 There must be no evidence of sample toxicity at higher sample concentrations, or the existance of an obvious anomaly. All acceptable dilution results are averaged to obtain the reportable result.

8.5 Refer to Caduceon SOP-39 LIMS Training for details of the recording of results in the Laboratory Information Management System (LIMS).

8.5.1 The calculated sample result is entered in the Laboratory Run module of the LIMS. The LIMS will display the correct reportable result.

9.0 Method Validation & Method Performance

9.1 Method Validation Data

	Data Points	Calculation (Reporting MDL)
MDL (mg/L)	10	1.1 (1)
Precision (%)*	10	3.8
Accuracy (%) *	10	101

* Based on 10mg/L standard results

9.2 Quality Control Standards

Sample ID	Number of Data Points	Expected (mg/L)	Mean (mg/L)	Average Bias (mg/L)	Standard Deviation	UCL (mg/L)	LCL (mg/L)
QC-01	56	50	50.8	0.8	2.0	57	45
BODSP-01 Spike (O_2 Depletion)	10	1.76	1.76	0.00	0.27	2.56	0.97

9.3 Duplicates

Analytical Range (mg/L)	Number of Data Sets	Acceptable Limits-RPD %
≤ 10	55	100
> 10	70	26

9.4 Method Uncertainty

9.5.1 The expanded uncertainty is determined as per SOP-23 . The data accumulated in the QC log is used to calculate the expanded uncertainty detailed in the following table.

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Typical Concentration (mg/L)	Combined Uncertainty (mg/L)	Expanded Uncertainty* (Percent)
5	0.7	27
50	5.2	20
200	20.3	20

* Uncertainty at 95% confidence interval (coverage factor k=2)

9.5 Method Performance

9.5.1 The Method Performance is monitored by the results of PT sample analysis. Each round's reported results and consensus values are entered in the Method QC log. The % Recovery is calculated on a minimum of 8 sample results. The maximum allowable deviation of a PT result is based on 3sd.

Mean % Recovery	98.4
Standard Deviation (sd)	8.5
3sd (99% confidence level)	25.5
Number of Data Points (n)	14

9.6 Based on the method validation data supplied above, this method has been deemed as fit for its intended use (as stated in Section 1 of this document).

10.0 References

10.1 Standard Methods for the Examination of Water and Wastewater, 5210-B, 21st Ed., 2005

10.2 Caduceon SOP-04, Preparation of De-Ionized Water

10.3 Caduceon SOP-07, Control Charting

10.4 Caduceon SOP-08, Verifying Delivery Volumes

10.5 Caduceon SOP-10, Thermometer Calibration and Verification

10.6 Caduceon SOP-23, Determination of Uncertainty in Measurement

10.7 Caduceon SOP-39, LIMS Training

10.8 Caduceon SOP-43, Non-conformity Logs

10.9 Caduceon Safety Manual