University of Alberta

A DISSOLVED OXYGEN MODEL AND SEDIMENT OXYGEN DEMAND STUDY IN THE ATHABASCA RIVER

by

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ABSTRACT

This study seeks to identify factors controlling dissolved oxygen (DO) concentrations in the Athabasca River. The work has three components: field measurement, laboratory study and computer modeling. The field study was conducted in the Athabasca River during the winter of 2004. Sediment oxygen demand (SOD) values were obtained under ice using a closed chamber method; oxygen microsensors were fabricated to both determine the oxygen dynamics at the sediment/water interface and its potential use as an alternative to *in situ* SOD incubations. The USEPA Water Analysis Simulation Program (WASP6) was chosen as the predictive tool for modeling. The model was calibrated using data from extreme low-flow, low DO years (2002 to 2003) and field and laboratory quantification of SOD. This study provided insight into the role of SOD in northern rivers, and improved the accuracy of dissolved oxygen modeling.

Key words: dissolved oxygen, sediment oxygen demand (SOD), biochemical oxygen demand (BOD), modeling, microsensor, river, ice cover, pulp mill effluent

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1. Introduction

Since the late 1980s, pulp mills along the Athabasca River have been under various stages of development or expansion. Effluents from the mills containing readily oxidizable organic matter create high levels of biochemical oxygen demand (BOD) in the river. In addition to natural and municipal discharges, BOD loadings from the mills have been shown to cause a pronounced decline in dissolved oxygen (DO) concentrations progressively downstream in the river (Chambers et al. 2000; Pietroniro et al. 1998). There is a growing concern that increased development combined with reduced river flows in recent years will cause DO concentration to fall below critical levels for aquatic biota during winter months. The current guidelines for the maintenance of DO in Alberta rivers are 5.0 mg/L for acute exposure and 6.5 mg/L for 7-day chronic exposure (Alberta Environment 1999). These thresholds have been confirmed by recent studies of low DO effects on benthic invertebrate communities in the Athabasca River (Golder 2004). The lowest flows on record occurred in the Athabasca River during the winter of 2002 and 2003 (Environment Canada 2003). As a result, very low DO concentration that fell below chronic threshold values was observed. In 2002, DO concentration in the Athabasca River declined to 5.7 mg/L for a 28-day period. Given the potential role of pulp mills in causing reduced DO, understanding and modeling the factors controlling DO was considered an urgent need to manage effluent discharges from pulp mills and municipalities on the Athabasca River and ensure sustainable development in the watershed.

Computer modeling of the oxygen balance in the Athabasca River began in 1987 with the initial expansion of pulp mills. Models used for the Athabasca River have been developed from steady-state modules, such as the Dissolved Oxygen Stochastic Model, DOSTOC, by Pietroniro et al. (1998), to dynamic modules, such as USEPA Water Quality Analysis Simulation Program (WASP), by Golder (1995) and Stantec (2001b). However, these modeling efforts failed to predict the recently observed low DO concentrations and a re-calibration was required.

Three factors appear to be the principle drivers of DO in the Athabasca River; the biochemical oxygen demand in the water column, or BOD, the proportion of ice cover limiting re-aeration, and the sediment oxygen demand (SOD). BOD is the major driver of DO and has been well documented in previous studies in the Athabasca River. Re-aeration, the major source of DO, is limited during the ice-covered winter. Although SOD in the Athabasca River was investigated in 1993, data were limited spatially and temporally (HBT 1993; Monenco 1993). Modeling efforts on the Athabasca River were thus hindered by poor quantification of two parameters, re-aeration and SOD. Hence, quantifying re-aeration was the major concern of model updates between 1995 and 2000. The impact of ice cover on re-aeration was incorporated into the WASP model by applying a factor that is calculated as the open water surface area to ice cover ratio. However, due to the lack of related information, the factor could not be predicted in the model and was therefore calibrated.

In this study, more comprehensive biochemical mechanisms that influence DO conditions in the river were also added to the model. Ice-cover-ratio was further related to air temperature at three sites along the river, experimental regression equations were obtained based on the data. SOD was incorporated into the model and a sensitivity analysis showed that the prediction of DO levels was sensitive to the SOD term. In this study difficulties in estimating SOD were addressed, new methods for its quantification that may simplify data collection were proposed, and 2004 values with those collected in the early and mid-1990s were compared.

In this thesis the following questions are addressed: a) how does SOD affect the oxygen balance in the Athabasca River since 2000; b) is there any correlation between DO level in water column (river) and SOD rate; c) is there any correlation between ice-cover-ratio and air temperature on the river; d) what effects does nutrient loading have on periphyton growth and how do the algal mats contribute to SOD. Using data developed in this project, the WASP6 model was calibrated and provided DO predictions within reaches of the Athabasca River from Hinton to Athabasca.

As SOD was found to be one of the important parameters for the evaluation of the DO level in the Athabasca River, field measurement of SOD was carried out in winter of 2004 in this project. Two field sites (Al-Pac and Calling River confluence) were selected to conduct SOD *in situ* measurement. Both closed chamber and laboratory sediment core methods were used to measure SOD rate.

Extra intact sediment core was collected and transported to the University of Alberta laboratory to conduct oxygen profile measurements with oxygen microsensors, fabricated at the University of Alberta. The oxygen microsensors were used to accurately measure the oxygen profile in river sediment as a third method for determining SOD and more accurately model oxygen demand in the river. The SOD received by the three methods were compared and discussed. It is suggested that an alternative, labor-reduced SOD measurement technique – oxygen microsensor be developed for the Athabasca

River. Correlation between SOD rates and DO concentrations in the overlying water was also established based on microsensor measurement.

In order to identify causes of the low DO level on the Athabasca River and to improve the model simulation and prediction ability, this study on DO conditions of the Athabasca River was conducted, including recalibration of the model with the inclusion of field and laboratory determined values for BOD and SOD. A sensitivity study of model inputs and particularly the influence of total maximum monthly BOD discharge from the pulp mills was conducted.

This thesis is mainly composed of two parts: the results of the SOD study and the re-calibration of the model, simulation and sensitivity analysis.

2. Literature Review -- the Role of SOD in Dissolved Oxygen Modeling

2.1 Introduction

The DO concentration in water is controlled by temperature, atmospheric pressure, reaeration, photosynthesis, respiration BOD and SOD. For a given river, the DO budget is composed of the following major components:

Sources: Reaeration at the surface
Photosynthesis by aquatic plants
Inflow from upstream

Sinks: Water column oxygen demand
Sediment oxygen demand (SOD)
Outflow to the downstream

The water column oxygen demand is mainly composed of BOD due to detritus suspended in the water column and including bacterial respiration and plant respiration (Stefan 1992). In ice-covered rivers, the oxygen sources are drastically reduced because ice cover prevents reaeration, and because snow on the ice can reduce light penetration and photosynthesis to near zero.

SOD, which is defined as the rate of consumption of dissolved oxygen from the water column by the substratum, is an important variable in the oxygen balance of water systems. SOD is also a major contributor to low DO levels in water column. DO concentrations and SOD-related processes at the sediment-water interface regulate the movement of reduced biological or chemical species (which are considered as B-SOD and C-SOD, respectively, and are reviewed in a later section of this thesis) from the sediment surface to the overlying water. The understanding and quantification of SOD processes are important in order to assess the effects on sediment-water interactions and ultimately on water quality.

Factors influencing the SOD rates include benthic bacterial, algal and invertebrate communities, sediment nutrient concentrations, the presence of chemical reducing agents (for example, bacterial by-products such as sulphide, nitrogen), and the water velocity. The water temperatures and the DO concentration also influence oxygen uptake by the sediments.

Based on the DO budget above, dissolved oxygen modeling has been used in water quality studies to simulate oxygen concentration changes in water bodies and to predict the potential environmental impacts on waters. In some northern rivers, however, many developed models cannot predict the DO concentrations well; one possible reason is that the accumulation of organic matter and nutrients in sediments and its resulting increases in SOD has not been properly understood, particularly under ice-cover condition.

2.2 Dissolved Oxygen Modeling

The Clean Water Act of 1972 in the United States prompted the use and development of water quality models to manage wastewater discharges from a receiving water perspective. Receiving water models have been used frequently since 1972 to represent the assimilative capacity of receiving waters, assign waste load allocations, and quantify additional waste treatment needs for water quality limited rivers. The maintenance of dissolved oxygen concentrations has been one of the focuses of water quality management due to its obvious need by aquatic organisms. Major contributions of water quality modeling to the water quality management in the areas of input parameter estimation techniques, model calibration and verification efficiency will be reviewed below.

2.2.1 Modeling for Dissolved Oxygen Concentrations in Fresh Waters

DiToro and Connolly (1980) were among the earliest to report their research on the development and application of a mathematical model of the water quality in large lakes in the US. The mathematical model was developed for analysis of the interactions between nutrient discharges (primarily phosphorus and nitrogen) to Lake Erie, the response of phytoplankton to these discharges, and the DO depletion that occurred as a consequence. In this study, DO, phytoplankton chlorophyll for diatoms and nondiatoms, zooplankton biomass, nutrient concentrations in available and unavailable forms and inorganic carbon were considered in the model. An understanding of sediment geochemistry expanded, and the role of SOD was included within the framework of DO mass balances.

In 1986, a one dimensional, steady state water quality model QUAL2E was developed to describe the DO concentration during low-flow periods for the Du Page River in the US (Freeman et al. 1986). Stream discharge, river stage, water temperature, and chemical constituent concentrations were the parameters that were considered to calibrate the model. The simulations in their study indicated that although ammonia oxidation played a role in the DO depletion, the primary factor was SOD.

In another study by Chaudhury et al. (1998), QUAL2E was calibrated and validated for the Blackstone River in the US. The profiles of flow change on the water surface was developed on the River. These flow profiles had been verified by the model to simulate a conservative parameter, chloride and independent flow measurements. It assumed that the major transport mechanisms were significant only in the direction of flow. To calibrate and validate the model, atmospheric reaeration and oxygen depletion were the key factors chosen; carbonaceous BOD, nitrification, SOD and algal photosynthesis and respiration were also considered to influence oxygen depletion.

The QUAL2E model, assumes steady-state conditions and is only applicable to well mixed streams. It simulates the major reactions of nutrient cycles, algal production, benthic and carbonaceous oxygen demand, atmospheric reaeration and their effects on the dissolved oxygen balance under a single set of environmental conditions. It is intended as a water quality-planning tool, for developing total maximum daily loads (TMDLs) under worst-case conditions. The effect of dynamic forcing functions (e.g. the record of variable changes with time) cannot be modeled (USEPA 2003).

In 2001, another model, River Water Quality Model No. 1 (RWQM1) was adopted for the Lahn River in Germany (Borchardt and Reichert 2001). This modeling quantified the SOD and the spatial and temporal extent of sediment zones with oxygen depletion. However, the spatially averaged approach does not account for heterogeneity in the sediment. Furthermore, this model is not as popular as QUAL2E.

An oxygen budget model was developed to analyze the diurnal water-quality data from a series of surveys combined with a series of field measurements aimed at studying short-term DO variability in a marine fish culture zone in Hong Kong (Lee et al. 1991).

The model formulation included phytoplankton dynamics and photosynthetic production, SOD, fish respiration, carbonaceous and nitrogenous oxidation, and atmospheric oxygen transfer. The model was used to determine the components of oxygen consumption and production, in particular, the SOD and carbon-to-chlorophyll (C: CHL) ratio. It was found in this study that SOD and algal respiration were major oxygen consumption items, and the C: CHL ratio of the river water was much higher than reported in previous mathematical model studies.

Apart from the studies of SOD influence on DO modeling, researchers also developed direct SOD models to simulate SOD kinetics (Ditoro et al. 1990; DiToro et al. 1992; Walker and Snodgrass 1986). In the Athabasca River, these SOD models are beyond the scope of available data.

The Water Quality Analysis Simulation Program (WASP), which was used as the prediction model in this research project, is a generalized framework for modelling contaminant fate and transport in surface waters. Based on the flexible compartment modelling approach, it can be applied in one to three dimensions and is designed to permit easy substitution of user-written routines into program structure. Variables studied using the WASP framework include BOD and DO dynamics of nutrients and eutrophication, bacterial contamination, organic chemical and heavy metal contamination (Wool et al. 2003a). WASP has become one of the most popular water quality modelling tools in the past several years.

WASP6 is an enhanced Windows version of WASP. Within the model, the eutrophication module of WASP was used to simulate the complex nutrient transport and cycling in the Neuse River Estuary in the US. It showed that the response in chlorophyll-a and DO concentrations as a function of nutrient loadings and transport throughout the estuary could be successfully predicted (Wool et al. 2003b).

Overall, WASP is one of the most popular models used in water quality simulations. "It helps users interpret and predict water quality responses to natural phenomena and man-made pollution for various pollution management decisions" (Wool et al. 2003a). Due to its precision and flexibility on water quality simulation, WASP has been selected as predictive tool and been used on the Athabasca River for 10 years.

2.2.2 Studies on the Athabasca River

The modelling of dissolved oxygen concentration began in 1987 with the expansion of the pulp mill industry and the recognized need for understanding the impacts on the Athabasca River (HydroQual 1988; HydroQual Consultants Inc. 1988; MacDonald and Hamilton 1989). The dissolved oxygen stocastic (DOSTOC) model was used to make an initial attempt to quantify the natural processes that govern dissolved oxygen levels in the Athabasca River. DOSTOC is a steady state, one-dimensional model based on the system of ordinary differential equations developed by Streeter and Phelps. The equations were modified to include the major sources and sinks of oxygen in river processes, but nitrogenous oxygen demand and feedback of DO concentration to the related terms were not included. This model was relatively successful in predicting large-scale trends in average oxygen concentrations for the Athabasca River, but was unable to capture local oxygen sags downstream of certain pulp mills in some winters. The reason DOSTOC was considered inadequate was that it did not represent the feedback of the effects of photosynthesis and respiration, nitrogenous BOD into the DO balance. In other words, it did not simulate the linkage between effluent discharges and benthic component oxygen demand. It is clear that a nutrient model for the northern river systems was required for appropriate modeling of DO dynamics.

Subsequent modeling shifted to USEPA WASP because it contained the necessary routines to simulate DO dynamics in the water column and shallow sediments of a river system. Nevertheless, the knowledge generated by DOSTOC was used to optimize the WASP model on the Athabasca River.

Golder (1995) used WASP 2 to simulate the oxygen demand in the Athabasca River. Monte Carlo simulation was employed to create representative parameter distributions for calibration. The calibration provided a reasonable representation of observed DO concentrations for the calibration years 1989 and 1991, but could not represent DO conditions for 1993 at several important sites on the Athabasca River.

In order to evaluate the relative contribution of the Alberta Newsprint Corporation (ANC)'s pulp mill discharge to the potential DO depletion in the river as compared with the other four pulp mills: Alberta Pacific Forest Industries Inc. (Al-Pac), Slave Lake Pulp (SLP), Millar Western, and Weldwood of Canada, the WASP5 model was used by Stantec (2001a) to conduct the simulation based on the previous model configuration by Golder in 1995. The results showed that the effects of the ANC effluent discharge on DO concentrations in the Athabasca River were insignificant compared to the other pulp mills and sewage treatment plants. The BOD discharge from ANC comprised less than 2 % of the total BOD loadings into the river. The relative change of DO concentrations resulting from the ANC discharge was less than 0.1 %. However, SOD, which was not included in the model simulation, was another important factor that contributed to the DO depletion in the river. It was suggested that the exclusion of SOD and other biological processes in the model resulted in the under-estimation of the effects of the pulp mills on DO levels in the river.

An effort to update previous versions of WASP modelling with WASP5, and to include the SOD effect in the modelling was made by Stantec (2001c). An SOD sensitivity analysis on the modelling was tested. The model simulation results showed that reducing SOD by 50 % would result in an average increase of DO in the river of 0.6 mg/L. If SOD was doubled, DO would decrease on average by 1.6 mg/L below the present situation at Grand Rapids. The maximum decrease in DO with doubling SOD would be 3.8 mg/L at Grand Rapids. It was demonstrated that when SOD was doubled, the water quality would deteriorate significantly; but if SOD decreased to half of its original value, water quality only improved moderately.

Stantec (2001b) conducted another simulation study to test the influence from the pulp mills on DO in the river. It was demonstrated that the pulp mills contribute to DO reduction by a range of 0.1 to 1.5 mg/L. The average DO reduction is 0.6 mg/L over the winter season.

The summary of SOD values incorporated in the model ranged from 0.01 to 0.59 mg/L (Table 1, except for the SOD values in year 2004). Table 1 also included most recent SOD results from the fieldwork of this research project. These SOD values were selected from literature and the available data on the Athabasca River. As a comparison, the summary of typical SOD values in the world is shown in Table 2. SOD estimated in previous studies in the Athabasca River is low compared with other water bodies in the world.

Table 1. Summary of SOD values from 1990 to 2004 on the Athabasca River.

	SOD Rate (g $O_2/m^2 \cdot d$)						
Site	1990	1992	1993	1994	1995	2004	Average
Up stream of Hinton at entrance					0.05		0.05
Down stream of Hinton		0.31		0.12	0.31		0.25
Windfall	0.01	0.00	0.01	0.04			0.01
Up stream of McLeod River					0.12		0.12
2 km down stream of McLeod River	0.23	0.26		0.28	0.57		0.34
4 km down stream of McLeod River					0.15		0.15
Smith	0.08	0.15	0.11	0.10	0.20		0.13
Down stream of Lesser Slave River				0.59			0.59
Athabasca (upstream of Al-Pac discharge)		0.21	0.17		0.15	0.18	0.17
Upstream of Calling River					0.09	0.12	0.11

(Casey 1990b; HBT 1993; HBT 1994; Moneco 1993; Noton 1996)

Based on the previous model sensitivity analysis, it is clear that the Athabasca River is very sensitive to SOD effect. However, the SOD data were insufficient and possibly contributed to the inability for the previous WASP implementation to represent recent DO concentrations. In order to acquire a more accurate DO prediction on the river by WASP, obtaining updated SOD values on the Athabasca River was important.

Table 2. Typical SOD rates from various waters found in literature.

	SOD (gO_2 /m^2 ·day)	Environment/ Location	Measurement Methods	Sources
1	0.34 - 9.02	Lakes - Southwest USA	*In situ* sealed chamber, respirometer	(Veenstra and Nolen 1991)
2	1.24	Lake Ton-Ton - Uruguay	Sediment core	(Sommaruga 1991)
3	4.44	Ponds - Mississippi USA	*In situ* respirometers	(Berthelson et al. 1996)
4	0.3	Lake Erie - OH USA	*In situ* chamber with DO probe	(Adams et al. 1982)
5	0.14 - 0.38	Lake Walker - USA	Laboratory chambers	(Beutel 2001)
6	0.5	Chesapeake Bay - RI USA	Benthic flux measurement – sediment core	(Garber 1992)
7	1.12-2.24	Onondage Lake - US	Sediment core	(Gelda et al. 1995)
8	0.30 - 0.40	Hiroshima Bay - Japan	*In situ* chamber (bell jar) with DO probe, laboratory respirometer	(Seiki et al. 1994)
9	0.5 – 1.5	Tennessee-Tombigbee - US	Laboratory sealed chamber	(Truax et al. 1995)
10	0.91	Tolo Harbour - HK	Sediment Core	(Chau 2002)
11	0 - 2.43	Passaic River - NJ USA	*In situ* respirometer with DO probe	(Uchrin and Ahlert 1985)
12	0.62	Aroyo Colorado River - US	*In situ* chamber	(Matlock et al. 2003)

2.3 Sediment Oxygen Demand (SOD)

2.3.1 Factors Affecting SOD

(1) Chemical Processes

Most of the chemical reactions taking place in sediments are associated with the decomposition of organic matter by microbes and other inorganic components such as C, N, Mn, Fe. The reaction rates are highly dependent on microbial activity and temperature. The typical chemical reactions are listed as follows (Vigil 1992):

Aerobic Respiration:

$CH_2O + O_2 = CO_2 + H_2O$

Nitrification and Denitrification:

$NH_4^+ + 2O_2 = NO_3^- + 2H^+$

$4NO_3^- + 5CH_2O + 4H^+ = 5\ CO_2 + 2N_2 + 7H_2O$

Manganese Oxidation and Reduction:

$2Mn^{2+} + O_2 + 2H_2O = 2MnO_2 + 4H^+$

$MnO_2 + CH_2O + 4H^+ = CO_2 + 2Mn^{2+} + 3H_2O$

Iron Oxidation and Reduction:

$4Fe^{2+} + O_2 + 6H_2O = 4\ FeOOH + 8H^+$

$4FeOOH + CH_2O + 8H^+ = CO_2 + 4Fe^{2+} + 7H_2O$

Sulphide Oxidation and Sulphate Reduction:

$H_2S + 2O_2 = SO_4^{2-} + 2H^+$

$SO_4^{2-} + 2CH_2O + 2H^+ = 2CO_2 + H_2S + 2H_2O$

When studying sediment oxygen demand, the above chemical reactions should be considered accordingly.

In an SOD component study in New York by Gelda et al. (1995), it was found that more than 70% of the SOD was explained by the oxidation of organic matter and production of reduced chemical species. Reduced chemical species considered include: sulfide, methane, ammonia, and ferrous iron. They contributed 50, 42, 7, and <1% of the total sediment flux, respectively. These findings suggested that recovery of the oxygen resources of the lake would be mediated primarily through reductions in the delivery of particulate organic matter to the sediments and the rate at which in-place reserves of particulate organic matter were stabilized. In this case, the oxidation of sulfide and methane species occupies the most part of the SOD flux, where, the organic components were first reduced to inorganic components (CH_4, S etc.), and the inorganic components were subsequently oxidized. The processes of algal respiration and aerobic mineralization of organic matter in the water column, which exhibited a more rapid response to remediation measures, would play a lesser role. Such findings are uncommon due to the fact of the sulfate-rich nature of the lake. In freshwater systems however, the sulfide percentage is usually low.

By studying the oxidation of iron (Fe^{2+}) on the surface of the sediment as a result of an inhibition effect, Wang (1981) perceived an empirical relationship between SOD and sediment mass. It was found that for small quantities of sediment, SOD is independent of the initial DO concentration. An inhibition effect that occurs through the oxidation of iron (Fe2+) on the sediment surface was also found. After an insoluble coating was formed (Fe3+), the rate of oxidation was presumably decreased, reducing the oxygen uptake at the surface of the sediment.

Not only inorganic components, organic compounds can also affect SOD rate. Krantzberg (1994), Krantzberg and Boyd (1992) found that SOD can play an important role in sub-lethal and/or lethal effects when sediments are contaminated with metals or poly-aromatic hydrocarbons (PAHs). The biological and chemical significance of contaminants in sediment from Hamilton Harbor in Lake Ontario were studied and concluded that the suitability for colonization by benthic invertebrates of sediment was apparently limited both by contaminants and by high SOD. Remedial options were recommended by providing suitable oxygen regimes, and decreasing metal bioavailability to reduce SOD rate in the harbor.

(2) Physical Processes

The major physical processes affecting SOD are sediment re-suspension, temperature effect, and flow velocity in the overlying water. Photosynthesis and micro-faunal activity are physical and biochemical combined process, are reviewed too.

In a study conducted on the Milwaukee river, the effect of combined sewer overflow on the river was investigated (Kreutzberger et al. 1980). Field investigations monitored DO, river temperature, disturbed and undisturbed sediments, and water velocity. Data were analysed using multiple linear regressions. The measured SOD rates indicated that the river was a significant sink for DO both in dry and wet weathers. Velocity measurements in the vicinity of combined sewer outfalls indicated that the scouring of sediments by combined sewer overflow discharges was the probable mechanism by which the sediments cause rapid drops in DO levels.

SOD has also been considered to have two states - diffusion limited SOD and potential SOD (pSOD), expressed when sediment was resuspended through increased flow or other disturbances. A research was done to measure SOD in the Arroyo Colorado River *in situ*, estimate pSOD *ex situ*, and evaluate the relationship between SOD and the depositional environment (Matlock et al. 2003). It was found that sites with high sediment deposition potential had high SOD rate.

Another study conducted on the Kaskaskia River in 1981 evaluated the effects of channelization on DO and SOD in a cutoff meander of the river. The research found that when stagnant or no-flow conditions prevailed, anoxic conditions created by SOD were in a significant part of the water. SOD rates in this river were more closely related to temperature than to sediment consistency or benthic macroinvertebrate numbers (Mathis and Butts 1981).

In a study on the dependence of SOD on other basic physical and biological parameters, Stefan (1992) verified that photosynthesis may lead to DO super saturation in the water column in winter if photosynthetically active radiation can penetrate the ice cover. The dependence of SOD on three parameters: temperature, availability of DO, and flow velocity were investigated too. A remedy of low oxygen concentration was tested in order to prevent the winter fish-kill phenomena. It was also found that air bubble plumes and cascade aerators were the most common remedy methods.

Studies were carried out also to investigate the relationship between SOD and flow velocities. The results verified that SOD increased linearly with the velocity of the water above the sediments when the velocities were low. As the velocity was increased, the SOD reached an upper bound. Both the rates of increase with velocity as well as the upper bound of SOD were found to depend strongly on the sediment material, the benthic biology, and the temperature. SOD was approximated by linear and Michaelis-Menten type equations with velocity being the independent variable (Chau 2002; Mackenthun and Stefan 1998; Park and Jaffe 1999).

Josiam and Stefan (1999) studied the effect of flow velocity on SOD by comparing theoretically and experimentally. Theoretical equations were used to model the experimental data for the three types of sediments. The values used for the parameters in the theoretical equations were determined by iteration until a best fit was obtained for the relationship of SOD to flow velocity from both the theoretical model and experimental data.

Chau (2002) found that the SOD rate at Tolo Harbour, Hong Kong increased with the increase of temperature in the range of 10 to 30°C. But SOD values were independent of the degree of salinity of the overlying water. This conclusion suggests that the SOD studies conducted both on the sea water and on fresh waters are compatible.

(3) C-SOD and B-SOD

In an effort to fractionate lake sediment Wang (1980) separated SOD into biological and chemical processes by applying several biological inhibitors. Chemical SOD (C-SOD) was further differenced into ferrous, sulfide, and manganous demand. The results showed that the major component of the SOD in his study was chemical in contrast to biological (B-SOD) and that the demand due to iron predominates in this lake system.

Considering the effects of environmental factors, Seiki et al. (1994) found that the depth of sediment, reducing substance, oxygen concentration and temperature had apparent effects on SOD. The SOD rates varied with sediment depths, which was attributed to the reducing substances in sediments. In this study, temperature revealed the most marked effect among these factors, and SOD rates increased linearly with temperature in the range of 10 to 30°C. Another conclusion is oxygen concentration in overlying water did not influence the SOD rate when it was over 2-3 mg/l, but influenced below this concentration. The author explained that the results were due to the fact that SOD rates in Hiroshima Bay were mainly controlled by biological consumptions from summer to autumn and by chemical consumption of the reducing substances during winter and spring. The SOD measurement in this study was conducted by *in situ* chamber and laboratory respirometer. Oxygen microsensor that can accurately observe the oxygen profile changes was not applied.

Nevertheless, different results were published regarding the relationship between SOD rates and overlying water DO concentration. For example, Hargrave (1978) reported that SOD rates have no relation to the oxygen concentration at all. Edberg and Hofsten (1973) found that SOD depends on the oxygen concentration in the overlying water, and expressed as an exponential function. Similar results with Edberg and Hofsten's were found in Walker and Snodgrass' (1986) research work and most recently, in Arega and Lee (2005)'s research work. The relationship between SOD and overlying water DO needs to be further studied due to the scientific dispute.

A study on sediment metabolism was carried out in 1986 in Lake Ton-Ton Uruguay (Sommaruga 1991). It was found that during stratification, C-SOD accounted for 69-87% of total SOD, while B-SOD was dominating for the rest of the year, except in July. Biological respiration was principally of microbial origin. Hypolimnetic temperature was the main factor controlling SOD rates ($r = 0.771$, $p < 0.001$). Nevertheless, freshly deposited phytodetritus from an Anabaena bloom, together with a renewed input of oxygen to bottom water were responsible for the maximum SOD values.

Accurate estimates of SOD rates are needed in the water quality models to correctly design the allowable waste loads for discharge permits. In spite of historical documented evidence that SOD can be responsible for a large portion of observed DO deficits, the use of measured SOD data for computation of waste load allocations and permit limits is important although, there is not a standard procedure to conduct. Thus the SOD measurement techniques are reviewed in the following section.

2.3.2 SOD Measurement Techniques

The first guidance for sampling, preservation, and analyses of dredged and filled material was provided by an US EPA's technical report (Plumb 1981). It gave details of analytical techniques for 44 parameters, including SOD. The National Council in the US also conducted a review of *in situ* and laboratory SOD measurement comparisons as early as in 1982 (Blosser 1982). However, the descriptions of the measurement techniques and procedures as well as the physical and chemical characteristics of the sediment had not been consistently reported. The correlation of 65 *in situ* and laboratory core measurements was poor. It was suggested that future research should be directed at quantification of the physical, chemical, and biological characteristics of sediments and their relationship to both in-situ and laboratory measurements of SOD.

In the past 20 years, researchers have developed many different measurement methods. Among them, there are four general techniques used to measure SOD rate according to the chemical and physical processes related. These techniques are based on recording of the DO concentration changes with either time or sediment depth.

(1) Laboratory Core Measurement

By this method, SOD is measured by enclosing an area of sediment in a Plexiglas coring tube of known volume and measuring the change in dissolved oxygen in overlying water over time. A control core, which contains only river water, is often used to correct for oxygen demand by the water BOD. Once initial DO samples are withdrawn, sediment core samples are returned to lab for incubation at simulated *in situ* temperatures. In order to simulate the water velocity and to ensure continuous mixing, a peristaltic pump is used during the entire incubation period (Monenco Inc. 1993).

This method is popular due to the fact that it can access the sediment in deep water. Nevertheless, their use is limited to fine sediment into which the cores can be pressed. If the sediment is attached to the surface of cobbles or gravels, other measuring methods are needed. When used *in situ*, one of the method to solve the problem of leakage is by plugging the core and incubating it in a rack under the water instead of using peristaltic pump in the laboratory. When incubated in the laboratory, temperature and light can be manipulated to mimic *in situ* conditions or test other potential conditions.

Photosynthesis is generally discouraged by low-light conditions because most computer models estimate the oxygen concentration separately from the contribution of sediments.

(2) *In situ* Respirometer

It has a known sediment area and a regulated continuous flow of water circulating over the sediment. *In situ* field measurements are believed to minimize the manipulation of sediment and other ambient field conditions and are therefore more reliable than lab measurements. The *in situ* respirometer has been developed from without mixing devices to with mixing devices in the water (Snodgrass 1987). Wu (1990) made an improved respirometer suitable for continuous *in situ* SOD measurement under a wide range of conditions. However, the *in situ* respirometer method is more suitable for measuring a deep river and relatively deep sediment. It is relatively expensive and sometimes boat and SCUBA are needed to lower the device onto the riverbed.

(3) *In situ* Chambers

This method differs from cores in size but is methodologically similar. Both open and closed chambers are used for measurement depending on whether the bottom of the chamber is sealed or not. The open chamber is usually pressed onto the sediment by force and stayed on the riverbed for incubation after the lid is carefully closed. When using closed chambers, representative sediment is shoveled into the chamber by a spade. The amount of the sediment usually occupies one third of the chamber and river water fills to the top of it. Then the chamber is kept on the riverbed for incubation (HBT 1993). SOD is calculated based on the difference in dissolved oxygen concentrations at the start and end of the incubation, corrected for the BOD of the water within the chamber. Compared to open chambers, closed chambers are more popular because they remove the problem of leakage through the bottom, however, they are more difficult to install and the effect on SOD determination of placing disturbed sediment in the chamber must be evaluated. The chamber measurement can be an alternative to the core measurement when the cobbles or other large particles are the main components of the sediment. However, this method cannot be used in deep water for safety reasons.

From the late 1960s to the 1990s, efforts to measure SOD rates in Environmental Protection Agency Region IV in the US (Kentucky, Tennessee, North Carolina, South Carolina, Georgia, Florida, Alabama, and Mississippi) had been with *in situ* chambers. Later the water bodies of interest were changed from mainly large rivers, lakes and estuaries to small wadeable streams. For the small streams, boulders, rubble, gravel, bedrock, submerged logs, stumps, and other irregular substrates were the predominant component of the streambed. With these substrates, or when DO concentrations were absent or generally less than 1 mg/L near the bottom, the use of *in situ* chambers was considered not practical although the chambers can deal with certain amount of cobbles in the sediment. This reflects the limitation of using closed chamber method.

It is reported that a modified Shelby tube apparatus can solve the limitation of closed chamber. The tube was used to characterize the oxygen demand in the benthos of Tennessee-Tombigbee in the US. By this method, the collection of samples at depths of more than 7 m was conducted without the use of divers (Truax et al. 1995).

(4) Microsensors

The use of microsensors has been increased in the past twenty years. Microsensors are more sensitive. A high-resolution profile with depth can be produced if microsensors are applied (Revsbech 1983; Sweerts et al. 1989). Microsensors determine the concentration of solutes by reducing the volume of the surrounding pore water and measuring the voltage or current generated. Sedimentary solute profiles are used to calculate the flux into or out of the sediment. Microsensors operate differently from the previous three methods in that SOD is calculated from the slope of the linear concentration profile through the diffusive boundary layer between the sediment and the water by Fick's first law of diffusion. This method requires only that equilibrium be established at the sediment water interface and not an extended incubation to detect change.

The advantages of using microsensors for oxygen measurement have been described by Revsbech et al. (1980), which includes short response time, excellent spatial resolution, very low oxygen consumption by the microsensor itself, and linear calibration curve in the range of 0 – 100% oxygen concentration. Poisoning of the microsensors can occur, which will desensitize the sensors and make the zero current less stable. Hydrogen sulfide (Revsbech et al.1980) and dissolved organic carbon (Reimers et al. 1984) are the main causes of poisoning. Reimers et al. (1984) adopted a routine conditioning procedure during which each new microsensor was inserted into the upper layer of the sediment for several minutes before it was used. Once poisoned, microsensors can then operate in a stable fashion; however, an alternate approach that avoided poisoning would be preferred. The microsensor tip can be coated with a thin layer of cross-linked protein.

According to De Beer et al. (1997), this layer can not only reduce the poisoning effect of certain agents, but also enhance the strength of the microsensor tip.

Microsensor technology has been developed, adapted and utilized to study marine sediments (Revsbech et al. 1980), lake sediments (Sweerts 1990) and river sediments (Christensen et al. 1989). In a study on fishpond sediments, oxygen microsensor was used to study the oxygen penetration into the sediment layer (Meijer and Avnimelech 1999). SOD rates were calculated by this method according to the oxygen depletion at the diffusive boundary layer. Change in water temperature and the addition of formaldehyde showed that most of the oxygen consumption in the sediment surface layer was related to biological activity.

2.3.3 Affecting Parameters on SOD

In order to justify the mixing effect on the SOD, there are some comparisons made on the *in situ* respirometer and the laboratory core method. One comparison was made at two river locations (Whittemore 1992). With considerably different sediment characteristics and river hydraulics, sediment samples were collected from New England in 70 mm diameter Plexiglas containers 150 to 200 mm deep. Six to eight cores were collected at a stream site within 1 to 3 m radius. Laboratory testing involved the adjustment of circulation rates to achieve turnover times comparable to the *in situ* tests, DO depletion of at least 1 mg/L during tests, determination of background water BOD, and placement of the device in water to minimize both the air leaks and temperature variations caused by room temperature changes and heat input from the circulation pump. It was found that SOD rates using both measurement procedures increased with increasing mixing in the chambers. The results suggested that there was some justification for using laboratory cores methods as surrogates for *in situ* respirometer. However, laboratory tests were easier to conduct, it utilized fewer field personnel, and generally required less expensive equipment than *in situ* testing.

Hicks (1992) studied the effect of DO concentrations in the overlying water and the effect of temperature on the SOD rates regardless of the ambient state of the oxygen regime at the sediment-water interface. It involved the DiToro model framework that considered the COD flux of the sediment-interstitial water interactions. The DO concentrations in the overlying water were considered a factor affecting SOD rates in a mathematical model. The observed effects were that the SOD rate decreased with reduced concentrations of DO. In most instances, the temperature effects on SOD were described in a mathematical formulation, which generally showed direct proportional response of SOD to a measured increase or decrease in temperature. It is also found that if only temperature compensation effects were used to describe seasonal responses, SOD would appear to be inappropriate since SOD rates were also dependent on DO concentration.

Nakamura and Stefan (1994) reported similar findings about the relationship between DO and DO concentration in the overlying water. Also, oxygen consumption in the sediment can be expressed as the sum of B-SOD with Michaelis-Menten kinetics, and C-SOD assumed to be a first order reaction of oxygen. At very low flow velocities, transport through the diffusive boundary layer is the limiting factor; SOD can be expressed as a linear increasing function of velocity. On the other hand, when flow velocities are increased, SOD becomes independent of velocity, since the reactions in the sediment become a rate-limiting factor.

Using *in situ* enclosed chambers, Suplee and Cotner (1996) found a reasonably strong correlation between organic matter content and sulfate reduction rates in the shrimp pond sediments. Using benthic flux chambers, Berelson and Hammond (1992) found that stirring effects did not play an important role in the boundary layer effects in the SOD measurement.

2.3.4 SOD Study on the Athabasca River

On the Athabasca River, SOD studies can be found back to the 1980s. From the investigation on SOD conducted in 1989 and 1990, despite the apparent changes in pulp mill BOD loading, SOD measurement results were similar between years, which did not support earlier assumptions that SOD increased with BOD loadings (Casey 1990a).

In 1992 and 1993, from the SOD investigations conducted by HBT AGRA (1993), it was found that the rates of SOD at individual study sites were similar to those reported from previous studies. The changes in river gradient and velocity that promoted the settling of particulate material on the riverbed would lead to higher SOD rates. A high proportion of settleable organic particles would be expected to increase the SOD rates as well.

In 1994, HBT AGRA (1994) found that epilithic chlorophyll-a was not correlated to SOD. Total organic carbon (TOC) of cobbled areas was positively correlated with SOD but SOD of fine sediment was not related to TOC. SOD was not correlated with velocity of flow at either site. These conclusions needs further study because the above observations were based on field work only, laboratory analysis will provide a better understanding on the relationships between SOD and TOD and river velocity.

In another study in 1996, it was found that SOD was positively related to epilithic chlorophyll-*a* at open-water sites and to a lesser extent at ice-covered sites. SOD was also positively related to water velocity at all sites. Since the opaque SOD chambers prevented photosynthesis and, therefore, it is the gross benthic respiration, not net oxygen consumption or production that was measured. Thus the measured SOD rates may overestimate net oxygen consumption (Noton 1996).

3. SOD Measurement on the Athabasca River

3.1 Introduction

SOD measurement on the Athabasca River has been conducted since the 1980s. The main measurement devices used in the previous studies were sediment chambers (both open and closed bottom) and sediment cores. Prior to this research work, the most recent SOD measurements along the river were conducted in 1995. No updated SOD data were available since that time. In order to better validate the computer modeling on the river, *in-situ* and laboratory measurement of SOD rates were conducted in this research work. Closed chambers were selected because the problem of sediment leakage during the incubation period can be eliminated, thus the measurement results can be obtained more reliably. Sediment core devices used in the Athabasca River have been in an evolutionary process in the past. Some of them were successful while others were not. In order to provide consistent mixing above the sediment, plastics tubing that were connected with peristaltic pumps through the plungers were adopted in this research work. This device was used as back-up SOD measurement method in order to test the effectiveness of the newly updated device.

The fieldwork was conducted in February 2004, when the ambient air temperature was in the range of −11.5 to −3.8 °C. Sediment was taken at two sampling sites: Calling River confluence and 500 m upstream of Al-Pac discharge pumping station. The river was mostly covered with 30 cm thick ice, with sporadic open water around the effluent discharge points. The water temperature under the ice was close to 0°C. The river flew slowly, with average flow velocity of 0.3 m/s at mainstream. At the sampling sites, which were close to the bank, almost stagnant river water was observed.

All of the time zero water samples were collected right after the chambers or the cores were completely installed to commence incubation. The water samples were stabilized immediately by the addition of Winkler reagents (the addition of manganous sulfate $MnSO_4$ quickly followed by Alkali-iodide-azide). In the presence of the strong base, each oxygen atom in the water sample was bonded with a manganese ion to form a manganous hydroxide complex. So that phytoplankton, bacteria, and other organisms in the sample can no longer change the oxygen content of the sample through photosynthesis and respiration during the transportation period to the laboratory. The stabilized samples were delivered to the laboratory to conduct Winkler titration (APHA 1992) within 6 hours.

3.2 Materials and Methods

3.2.1 Closed Chamber Method

Four stainless steel chambers containing river sediment and a fifth control chamber containing river water only were incubated under ice in the Athabasca River. The DO change over time inside the control chamber determined the correction for oxygen demand from the water column. The difference between the test and control chambers was calculated as the SOD rate in g $O_2/m^2 \cdot d$.

$$\text{SOD } (g\ O_2 / m^2 \cdot d) = 0.024\ (b_1 - b_2)\ V / A \qquad \text{(Equation 1)}$$

where, 0.024 = converting coefficient from mg/L•h to $g/m^2 \cdot d$

b_1 = DO change inside the chamber with sediment (mg O_2/L•h)

b_2 = DO change inside the control chamber (without sediment) (mg O_2/L•h)

V = water volume in the chamber (L)

A = cross-sectional area of the chamber (m^2)

Representative sampling sites were selected of the river reach. The maximum depth for the chambers to be safely deployed was approximately 1 m. At ice-covered areas, a series of exploratory holes were drilled with an ice auger to choose the desired depth. When a location was chosen based on safety reasons, a 2 m × 2 m section of ice was removed to expose the *in situ* sites (Figure 1).

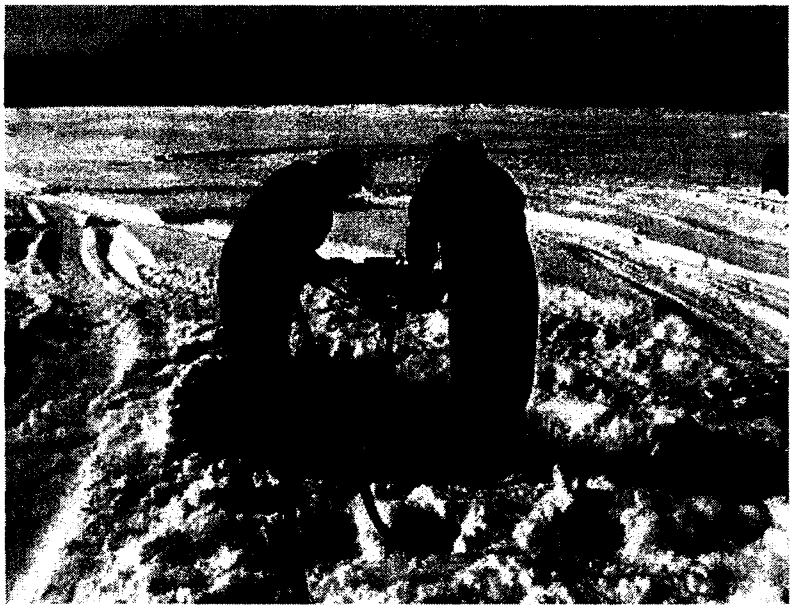


Figure 1. Removal of ice cover with auger and chainsaw.

Representative sediments were placed into the chambers to a depth of 5 to 10 cm by carefully lifting a layer using a flat spade. Rocks, as representative of the site, were placed on the fine sediments with epilithic cover facing up. The chambers (without lids) were carefully placed into the water, allowing the river water to fill the chambers gradually to reduce the water turbulence and avoid the disturbance of the sediment. Once in position, the lids were clamped tightly onto the chambers (Figure 2). The time of lid closure was recorded for each chamber to the nearest minute. Time zero water samples were collected from the river and treated with Winkler reagents immediately in order to stabilize the oxygen concentration. After *in situ* incubation for 24 hours, the chambers were removed from the river. Water samples were siphoned from each chamber through a valve directly into DO bottles and were treated immediately with Winkler reagents. The chamber lids were then opened and the sediment depths in each chamber were recorded. All water samples were titrated by the azide modification of the Winkler method (APHA 1992) within six hours in the laboratory after stabilization by Winkler reagents on-site.

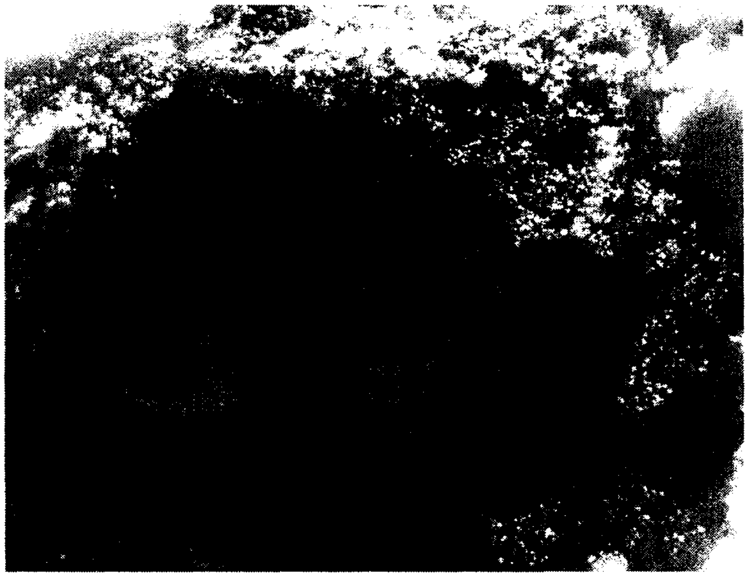


Figure 2. Closed chambers were placed on the riverbed to conduct *in situ* incubation.

3.2.2 Sediment Core Method

The sediment core method was used for areas with deeper water where silt, sand and clay sediments occur. Six transparent plastic tubes (Φ 75 mm, length 600 mm) were used as coring device. The ice holes were exposed the same way as used for closed chamber method. The tubes were shoved manually into the sediment through ice holes. Approximately 15 cm of sediment was obtained and the top of the sediment was filled with overlying water. Rubber stoppers were inserted on the bottom, gasket plungers were inserted on the top of the tubes. Circulation tubing on the plungers was connected under water to make sure no air bubbles were entrained inside the cores and the tubing. Time zero water samples were collected from the river and treated immediately with Winkler reagents. The time for the set-up of core tubes was recorded to the nearest minute. The sealed cores were covered with black plastic to protect them from light and transported on ice pack to the laboratory. The tubes were incubated at near 0 °C for 24 hours with continuous circulation provided by peristaltic pumps (Cole Parmer Masterflex, Model 7553-80, 1-100RPM). Water samples were taken after 24 hours incubation and titrated following the Winkler method within six hours.

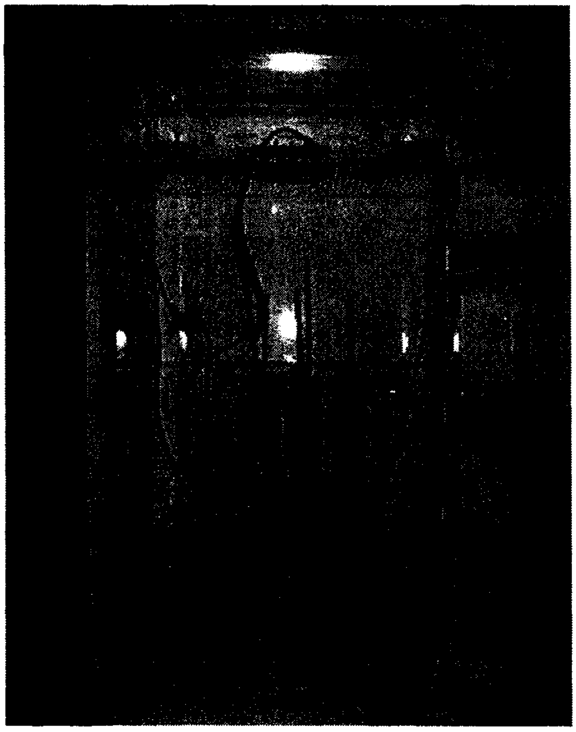


Figure 3. Sediment cores were incubated in the fridge with overlying water circulated by peristaltic pumps.

3.2.3 Microsensor Method

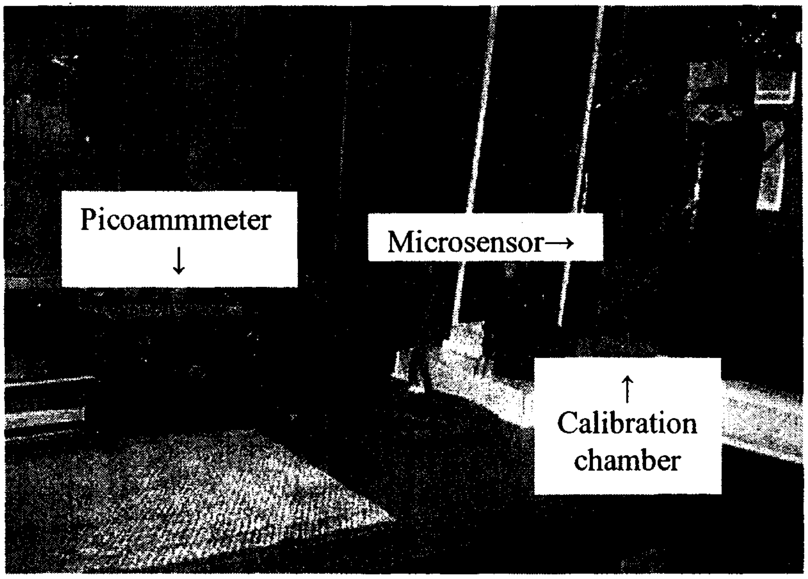
An intact sediment core sample (Φ = 150 mm, H = 100 mm) was collected in Plexiglas tubes at Calling River confluence site for oxygen profile measurements using microsensors. The cores were transported back to the University of Alberta laboratory right after they were taken out of the river and were stored in a 4°C cold room with raw river water above the sediment until oxygen profile measurements were conducted. The river BOD measured by Alberta Environment in February 2004 was in the range of 0.1 to 0.5 mg/L. The measured BOD of overlying water above the sediment in the laboratory was in the range of 2 to 3 mg/L. The laboratory-measured values were greater than the observed values by Alberta Environment in the field. This is most likely due to the fact that the overlying water taken for laboratory analysis was very close to the sediment. There is more organic matter dissolved into the water close to the sediment than far from the sediment.

The combined oxygen microsensors used in the measurements were fabricated in the University of Alberta laboratory. In general, the fabrication followed the procedure described by Lu and Yu (2002). An additional step was added to coat a layer of protein to the tip of each microsensor to decrease the interference from poisoning agents (e.g. dissolved organic carbon) and improve mechanical strength of the tip of the microsensor. The details of this step are described as follows (Li 2001).

After the oxygen microsensor was fabricated and air-dried for at least 5 hours, the tip of the microsensor was dipped into a 10% (w/w) cellulose acetate solution in acetone for 2 to 3 seconds. The tip of the microsensor was then examined under a vertical microscope with a built-in scale (Carl Zeiss, Model Axioskop 2 Plus). Afterward, the tip of a Pasteur pipette was dipped into a mixture of 1 mL protein solution, which contains 10% (w/v) bovine serum albumin (BSA) in 50 mM sodium phosphate (Na_2HPO_4) and 10 μl of 50% glutaraldehyde, so that the tip of pipette was filled with the protein mixture. The pipette was then fastened onto a micromanipulator (World Precision Instruments Inc., Sarasota, FL, USA; Model M3301R). The oxygen microsensor was secured on the stage of the vertical microscope with its tip, coated with the cellulose acetate layer, pointing toward the tip of the pipette. While observed under the microscope, the tip of the microsensor was carefully inserted, for about 500 μm, into the protein mixture, which was inside the tip of the pipette, and stayed there for 10 seconds for the protein layer to be coated onto the tip of the microsensor. Afterward, the tip of the microsensor was carefully and slowly withdrawn from the tip of the pipette. The protein-coated microsensor was then air dried for at least 4 hours and to allow a water insoluble protein layer to be firmly fixed onto the tip of the microsensor before it is calibrated. In this step, the protein layer was tightly coated onto the tip of the microsensor, so there was no obvious shrink observed during the microsensor measurements.

This microsensor, with its tip coated with the protein layer, and after dried for hours, was polarized in de-ionized water overnight and calibrated in chilled raw river water using a picoammeter (Unisense, Denmark, Model No. PA2000) before the measurements. After all the measurements were finished, the microsensor was calibrated again in order to track the signal shifting effect during the measurement. The polarization and calibration strictly followed the procedures described by Lu and Yu (2002). Figure 4 shows the calibration of an oxygen microsensor, in connection with a picoammeter, in a Plexiglas calibration chamber.

The sediment core sample, with raw river water above it, was set on the laboratory bench. Ice cubes were packed around the sediment core to keep the low temperature in the sediment. The oxygen microsensor was fastened onto a micromanipulator. The working anode, guard anode and the reference cathode of the microsensor were all connected to the picoammeter. The height of the sediment core sample and the initial position of the microsensor were set such that the entire oxygen profile measured in the sediment core sample was within the movement range of the micromanipulator. Figure 5 shows the setup for the oxygen profile measurements in the sediment core sample. Using the tip of the microsensor, with good illumination (Fiber optic lighting Carl Zeiss KL 1500), the location of the water-sediment interface was observed and recorded. While the oxygen microsensor was advanced into the sediment core sample, the current readings on the picoammeter that was connected to the microsensor were recorded. When consecutive and stable zero readings were reached, the oxygen profile measurement was terminated. The measured temperatures in the overlying water above the sediment core sample were recorded and were all under 11°C during the experiment process. All of the measurements were conducted under atmospheric pressure.



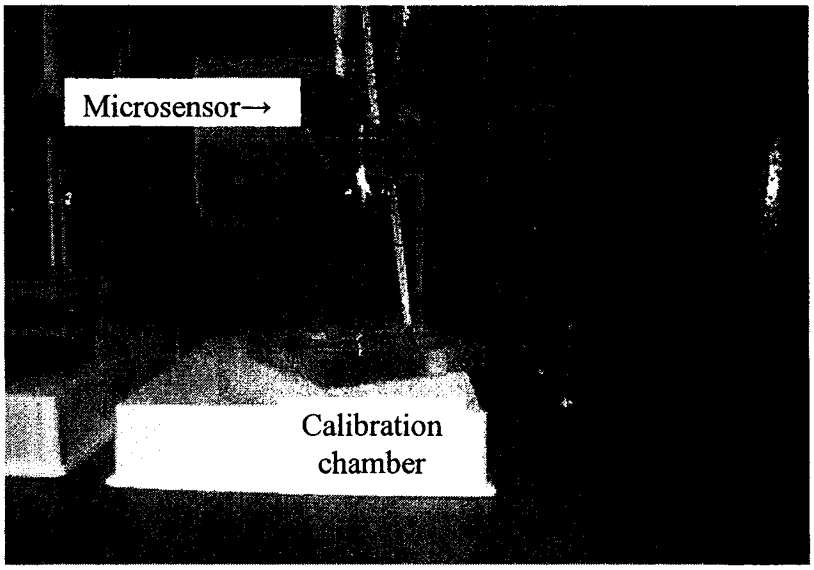


Figure 4. The microsensor was calibrated in the chamber after polarization. Up: calibration setup; down: calibration chamber.

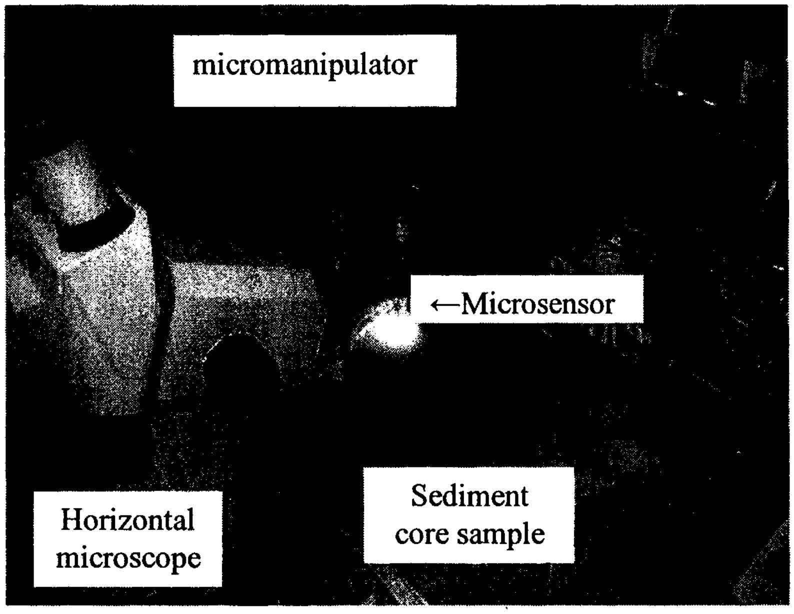


Figure 5. Setup of the sediment oxygen profile measurement.

There were three environmental conditions for the oxygen profile measurements. Under the first condition, oxygen profiles were measured with natural DO concentrations in the overlying water, which was 10.9 mg/L. Under the second condition, N_2 gas was induced into the overlying water of the same sediment core sample in order to lower the DO concentration. YSI 50B DO probe and DO meter was used to monitor the DO concentration in the overlying water while the N_2 gas was induced. When the converted current reading in the picoammeter reached a DO concentration around 7 mg/L and was stable, the N_2 gas injection was stopped. The surface of the sediment core sample was then covered tightly with a plastic wrap to minimize oxygen exchange between ambient air and the water. The profile measurement started after 5 minutes, when the overlying water became static, so that no disturbance on the sediment surface was observed. This is to minimize the influence of turbulence from the introduction of the N_2 gas on the boundary layer. Under the third condition, more N_2 gas was introduced into the overlying water to decrease the DO concentration further to around 4 mg/L. The monitoring procedure was the same with the previous condition. All the measurement points were randomly selected.

In each oxygen profile measurement, the current readings from the picoammeter were recorded while the oxygen microsensor was advanced into the sediment core sample. Each measurement started when the tip of the microsensor was 2 to 3 mm above the sediment water interface. This process was observed under a horizontal microscope (Carl Zeiss, Jena, Germany, Model Stemi SV11). The advancement of the oxygen microsensor into the sediment core sample was controlled manually through the micromanipulator and the step-size was 100 μm. The recording of the current readings from the picoammeter was started when the readings were stable; and the recording was stopped when consecutive and stable minimum readings were reached, which means the oxygen concentration reached zero inside the sediment core sample. The microsensor was then withdrawn in one step-size each time until the tip was back to the original position in the overlying water. The same procedure was repeated again at another randomly selected location in the sediment core sample. Thus, the oxygen profile measurement under one environmental condition was considered completed.

3.3 Results and Discussion on SOD Measurement

3.3.1 Closed Chamber Method and Sediment Core Test

Twenty-four-hour SOD rates measured by closed chambers in February 2004 are presented in Table 3. The mean SOD rate at Al-Pac and Calling River confluence locations were 0.18 and 0.12 g $O_2/m^2 \cdot d$, respectively. The very low standard deviation on the results indicates the method was precise and likely accurate at each of the sites.

Table 3. Twenty-four hour SOD rates as measured with closed chambers in 2004.

Sampling site	Period of SOD measurement	Number of samples	Standard deviation	SOD rate after 24 h incubation ($g\ O_2/m^2 \cdot d$)	
				Range	Mean
Athabasca (Al-Pac location)	Feb 16 – 17	4	0.06	0.12 – 0.24	0.18
Calling River confluence	Feb 12 – 13	4	0.02	0.11 – 0.15	0.12

Sediment incubated core measurement was also conducted in this study. The results are listed in Table 4. By this method, the measured SOD rates are (– 0.06) and 0.03 g $O_2/m^2 \cdot d$, at ALPac and Calling River confluence locations, respectively. These results are likely wrong and cannot represent the real SOD rates at the two sites because numerous air bubbles were observed inside the tubing and sediment cores during the incubation process. The results indicated an underestimate of SOD. A seal problem existed likely due to the design for water circulation apparatus. The inlet and outlet ports for water circulation, the moveable plunger to allow water withdraw at 24 hours and the joints required to connect the circulator tubing to the peristaltic pump all provide potential locations for oxygen leakage. Further development of the sediment core method should be pursued as it is a convenient alternative way to assess SOD from deep waters (Sommaruga 1991; Witte and Graf 1996).

Table 4. Twenty-four hour SOD rates as measured with incubation cores in 2004.

Sampling site	Period of SOD measurement	Number of samples	Standard deviation	SOD rate after 24 h incubation ($g\ O_2/m^2 \cdot d$)	
				Range	Mean
Athabasca (Al-Pac location)	Feb 16 – 17	4	0.02	(– 0.08) – (– 0.04)	(– 0.06)
Calling River confluence	Feb 12 – 13	4	0.03	0.00 – 0.07	0.04

The closed chamber method is more reliable but labor-intensive, especially during cold winter months. The sediment is disturbed when it is placed in the chamber. If the majority of SOD occurs as fine organic particles that cover cobbles, losses of these particles during sediment transfer could lead to underestimate of the SOD rate. In addition, the water vanes on the chamber lid, which provide water mixing inside the chambers, were not always proportional to river velocities outside the chambers. Disproportional mixing in the chambers compared to the rivers would cause an underestimate of SOD as well.

3.3.2 Oxygen Microsensor Method

Since the optimum working temperature for the oxygen microsensor and related instruments is the room temperature, in order to protect the expensive instruments, all the measurements were conducted under regular laboratory conditions instead of in the 4°C cold room. Although packed with ice cubes around the sediment core, the temperature change during the measuring process existed and thus was recorded. In order to compensate the temperature effect on the measured SOD rate by the oxygen microsensor method, the oxygen microsensor was calibrated under two temperatures, 11°C and 4°. So that the real temperature change during the measurement process laid within this range. The calibration results are shown in Figure 6. There is a slope discrepancy between the linear equations obtained under the two temperature conditions. The slope discrepancy is due to the difference in saturated dissolved oxygen concentration in water under different temperature conditions, and by the effect of current signal shift during the measurement process. Since the peak current reading of the microsensor decreased from 811 pA (for 11°C) to 787 pA (for 4°C), which were the worst case scenarios, the slope change with temperature effect and signal shift during the experience will always lay between the two known slopes. Thus the effect of current signal shift and the temperature change was blocked together. Since the difference is small (the overall effect for the worst case is less than 2.9% of the maximum signal reading), a linear interpolation of the slope with temperature change was used during the data processing to approximate the temperature and the current signal shift effect. The adjusted calibration equations for different temperatures were listed in Table 5. In the calibration equations, y represents current (pA) and x represents DO (mg/L).

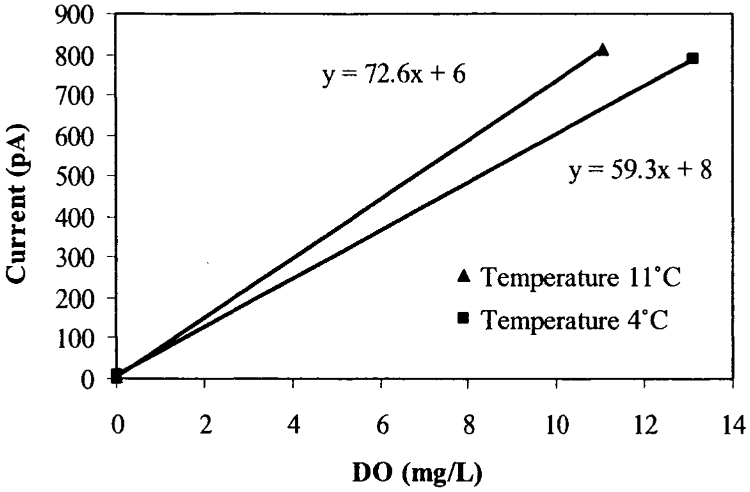


Figure 6. Calibration results of oxygen microsensor under two temperature conditions.

Table 5. Adjusted calibration equations for different temperatures for oxygen microsensor measurement.

Temperature (°C)	Slope	Equation
11	72.6	y=72.6x+6
10	70.7	y=70.7x+6
9	68.8	y=68.8x+6
8	66.9	y=66.9x+7
7	65.0	y=65.0x+7
6	63.1	y=63.1x+7
5	61.2	y=61.2x+8
4	59.3	y=59.3x+8

The oxygen profiles and the changes of oxygen penetration depths with different DO concentrations in the overlying water were shown in Figure 7. The oxygen penetration depth is defined as the distance between sediment water interface and the point inside the sediment where the current reading from the microsensor becomes zero. Negative numbers on the y-axis represent the depth that oxygen penetrated into the sediment. The average oxygen penetration depth was greatest (3.7 mm) when the DO concentration in the bulk water was the highest (10.9 mg/L). The average oxygen penetration depth was the smallest (2.6 mm) when the DO concentration in the bulk water was the lowest (3.9 mg/L). We induced a dissolved oxygen concentration of 7.7 mg/L in the water above the sediment to correspond with the average measured DO concentration in the Athabasca River in February 2004 (7.3 mg/L). Under this matching overlying water condition, the average penetration depth was 3.6 mm. Deeper penetration depth indicates more oxygen available for the metabolic activities of the microorganisms inside the sediment. With lower dissolved oxygen concentration in the overlying water and reduced microbial activity associated with low temperature in winter months at the Athabasca River, the oxygen penetration depth in the sediment decreased relative to summer conditions. Therefore, the aerobic activity of the sediment decreased; while anoxic and anaerobic activities increased.

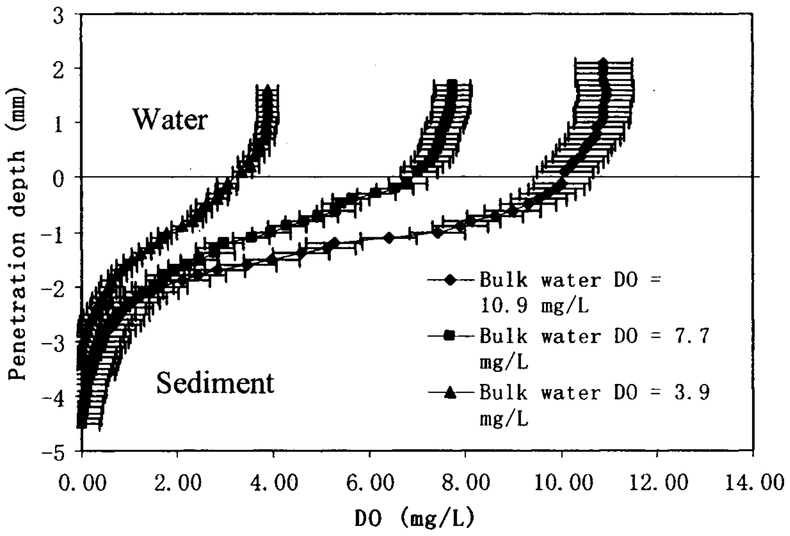


Figure 7. Oxygen profiles and penetration depths under different DO concentrations in the bulk water.

The oxygen transfer in the bulk water is controlled by eddy diffusion. Near the sediment-water interface, oxygen transfer is controlled by molecular diffusion (Santschi et al. 1983) due to the viscous forces, which form a diffusive boundary layer (DBL). The dissolved oxygen uptake rate at DBL is due to mass transport; the oxygen penetration depth is due to biochemical reactions. It was found that at high flow velocity of the water, both oxygen transfer through the DBL and microbial/chemical processes inside the sediment are rate-limiting; whereas at low flow velocity, only oxygen transfer through the DBL is rate limiting (Higashino et al. 2004). In this study, the SOD measurements were conducted to simulate the very low flow velocity condition in the Athabasca River in winter months, with observed nearly stagnant overlying water when the sediment core sample was taken. Thus the calculation of SOD was based on the oxygen uptake rate through the DBL.

The thickness of the DBL was measured with oxygen microsensors by determining the depth of the water layer with a linear oxygen concentration decrease above the sediment (Jorgensen and Revsbech 1985). The sediment-water interface, defining the lower boundary of the DBL, was determined as the position where maximum DO gradient occurring within the first millimeter below the change of slope at the lower end of the DBL (Revsbech et al. 1980). In this study, the DBLs were 1.18, 0.90, and 0.85 mm for the DO concentrations of 10.9, 7.7, and 3.9 mg/L in the overlying water, respectively. This observation tells that at increased temperature, the boundary layer becomes thinner. SOD was assumed equivalent to oxygen uptake rate and was calculated from Fick's first law of diffusion:

$$\mathrm{SOD} = J = D_s \Phi \, dC/dx \qquad \text{(Equation 2)}$$

Where, J = Oxygen flux (g $O_2/m^2 \bullet day$)

D_s = Apparent diffusion coefficient of oxygen in the pore water (cm^2/sec)

Φ = Porosity in the sediment

dC/dx = oxygen concentration gradient, estimated from the oxygen profiles measured using the oxygen microsensor (mg/L·mm).

Within the DBL, we assumed D_s equals to D_0, the temperature dependent diffusion coefficient of oxygen in water, due to the fact that the DBL consists of water. Different D_0 values were adopted by interpolation of Broecker and Peng (1974)'s results of D_0 which was reported with 5°C intervals. The modified temperature dependent diffusion coefficients D_0 are 1.39×10^{-5}, 1.54×10^{-5} and 1.62×10^{-5} cm^2/sec at 6, 9 and 11 °C, respectively. A $\Phi = 0.82$ was also adopted for the porosity of the sediment (Meijer and Avnimelech 1999; Nakamura et al. 2004). Oxygen flux toward the sediment under the laboratory measurement conditions was calculated based on equation 2. Thus the calculated average SOD values are 0.103, 0.082, and 0.079 g $O_2/m^2 \bullet day$ for the 10.9, 7.7, and 3.9 mg/L DO concentrations in the overlying water, respectively (Table 6). From equation 2, it clearly shows that with the increase of DBL and decrease of DO change the SOD rate will decrease. In this study, it is verified that both the DBL and the DO concentration change are significant factors used to determine the SOD change. The calculated SOD rates decreased with the decrease of DO concentration in the bulk water.

It has been verified by many studies that temperature is one of the most important factors affecting SOD; the change in SOD with temperature is generally expressed by Arrhenius relationship: $SOD_T = SOD_{20°C} \times \theta^{(T-20)}$, where SOD_T is the SOD rate at temperature T, θ is the temperature correction coefficient, the value of θ used for the experimental data is 1.065 (Thomann and Mueller 1987). However, this relationship only applies to the temperature range that is above 10°C. This conclusion has been verified by many researchers. For example, Fisher et al. (1982) and Uchirin and Ahlert (1985) reported that 15°C was the temperature threshold in SOD for non-detectability. Seiki et al. (1994) found that SOD rates increased linearly with temperature in the range of 10 to 30°C. It thus can be induced that if the temperatures are close to or lower than the critical values (10 to 15°C), the temperature effect on SOD rate is insignificant. In this study, since all the measurements conducted at the laboratory were controlled between 7 to 11°C, it is reasonably believed that the SOD rates measured by the oxygen microsensors in the laboratory were comparable with the SOD rates measured using the closed chamber method under the field conditions. Although the SOD rate differences among the laboratory measurements exist, the differences are small and are therefore negligible due to the same reason. For the purpose of comparison, all the laboratory measured SOD rates were converted to 20°C using the Arrhenius relationship. And the results are shown in Table 6. The increase of SOD rate with temperature is apparent. The decrease in temperature resulted in the decreased rates of microbial activity, yielding lower SOD rates is valid at higher temperatures, at winter field conditions however, no evidence shows that the SOD rate decreased with temperature significantly.

Table 6. SOD rates as measured using oxygen microsensors.

	Replicate number	Water Depth (cm)	Temp (°C)	DO (mg/L)	Ds	DsΦ	dC (mg/L)	dx (mm)	Measured SOD (g O_2/m^2·d)	SOD (20°C) (g O_2/m^2·d)	Penetration Depth (mm)
Environmental condition 1⁽¹⁾	1	3.2	7	11.26	1.44×10^{-5}	1.18×10^{-5}	1.43	1.29	0.11	0.26	4.8
	2	3.4	9	10.52	1.53×10^{-5}	1.25×10^{-5}	0.92	1.07	0.09	0.19	2.6
	Average	3.3	8	10.89	1.49×10^{-5}	1.22×10^{-5}	1.18	1.18	0.10	0.21	3.7
Environmental condition 2⁽²⁾	1	3.3	9	7.94	1.53×10^{-5}	1.25×10^{-5}	0.34	0.56	0.07	0.13	2.7
	2	3.3	10	7.51	1.57×10^{-5}	1.29×10^{-5}	1.08	1.23	0.10	0.18	4.5
	Average	3.3	10	7.73	1.55×10^{-5}	1.27×10^{-5}	0.71	0.90	0.09	0.16	3.6
Environmental condition 3⁽³⁾	1	3.0	11	3.88	1.62×10^{-5}	1.33×10^{-5}	0.56	0.79	0.08	0.14	3.1
	2	3.3	11	3.90	1.62×10^{-5}	1.33×10^{-5}	0.60	0.91	0.08	0.13	2.0
	Average	3.2	11	3.89	1.62×10^{-5}	$1.33\times10\text{-}^{5}$	0.58	0.85	0.08	0.14	2.6

(1) DO at overlying water was measured at an average of 10.89 mg/L under standard laboratory conditions (20°C room temperature, 1 atmospheric pressure).

(2) DO at overlying water was reduced to an average of 7.73 mg/L by introducing N_2 gas under standard laboratory conditions.

(3) DO at overlying water was reduced to an average of 3.89 mg/L by introducing N_2 gas under standard laboratory conditions.

Figure 8 shows the relationship between the measured SOD rates based on oxygen microsensor measurements and the DO concentrations in the overlying water. Obviously, the SOD rates increased with the increase of DO concentration in the water, which demonstrated an explicit dependence of SOD on DO concentration in the overlying water. An approximate exponential relationship can be found both at laboratory-measured condition and at converted 20 °C. The exponential curve is rather flat at low temperature, compared to a steeper curve at high temperature. This conclusion is consistent with previous studies (Edberg and Hofsten 1973; Edwards and Rolley 1965). A recent study is also verified that for a given sediment type, the SOD is a function of the bulk DO concentration and chamber flow rate (Arega and Lee 2005). Figure 8 also demonstrates that a SOD dependency on DO concentration exists even when the DO concentrations are higher than the critical value that is known to protect aquatic life (as stated before, the current guidelines for the maintenance of DO in Alberta rivers are 5.0 mg/L for acute exposure). This result is consistent with previous studies on SOD as well (Di Toro et al, 1990; McDonnell and Hall, 1969).

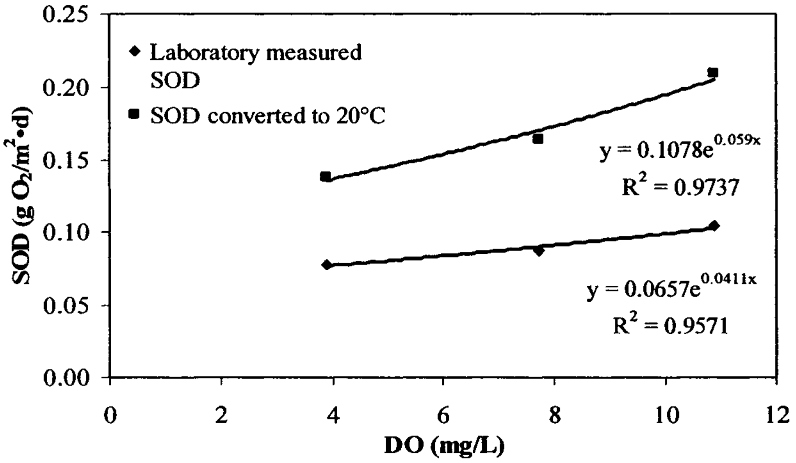


Figure 8. Relationship between SOD and DO in the overlying water.

The non-linear response of SOD to DO concentration is partially a result of non-equilibrium induced by the lower diffusive forces through the boundary layer compared to the demand from the microbial activities. Reimer *et al.* (1984) reported that for pelagic sediments at 5°C, it takes approximately 6 hr for a detectable amount of oxygen to penetrate 1 cm depth; at 25°C, the penetration rate is faster. Meanwhile, steady state condition is reached faster at high than low SOD values (Higashino et al. 2004). For the sediment core sample from the Athabasca River, the relatively low SOD rate is very likely one of the reasons making it difficult to reach steady state condition. As mentioned before, due to the consideration of the temperature requirement for the precision instruments used in the microsensor measurements, this experiment was conducted at standard laboratory temperature, with ice cubes placed around the sediment core sample to maintain low temperature in the sediment. When the DO concentration is relatively low in the overlying water, the low DO concentration and inadequate equilibrium time could inhibit the microbial activities and the biological/chemical reactions that consume oxygen in the sediment. Therefore, the SOD rate decreased with the decrease of DO concentration in the overlying water. And this is one of the possible reasons that the SOD rates obtained by oxygen microsensor method are smaller than the SOD rates obtained from closed chamber method.

3.3.3 Comparison between the Closed Chamber and Microsensor Measurements

SOD rates can vary significantly with the nature of the sediment. Heterogeneity of the sediment interface and differences in microorganisms between the closed chambers and cores for microsensor analysis in this research project are variables that limit direct comparison. However, the two techniques provide different insight on the sediment. The SOD calculated from oxygen profiles measured using microsensors represents diffusive SOD; and the SOD calculated from DO change within closed chambers provides a measurement of total SOD. Diffusive SOD assumes that the limitation of sediment oxygen uptake rate is governed by molecular diffusion across the DBL. Total SOD combines all the processes related to oxygen transfer: which can include diffusion and advective movement of pore water induced by faunal activity, bio-diffusion due to the movements of the fauna, and active pumping within burrows (Reimers et al. 1984). In ice-covered rivers, diffusive processes likely provide the main control on SOD rates even for the closed chamber method because micro biotic activities are low and turbulence during low flow is reduced. However, the low micro biotic activities still likely contribute part of the SOD differences obtained by the two methods. When conducting microsensor measurement, disturbance was avoided to the most possible extent to ensure no disturbance to the microsensor measurement; while in the field, simulated mixing was adopted to mimic the river water movement. Although the observed mixing by water veins was not always effective, and the quantitative effect of mixing factor should be further studied, apparently it is another reason for the relatively lower SOD values from the microsensor method. Based on the above understanding, the SOD values obtained by closed chamber method were utilized in the DO modelling calibration and simulation.

The measured SOD values in the present study and other data collected along the Athabasca River in previous studies were summarized in Table 1, which was placed in the earlier section in this thesis. The range of SOD rates along the river is from 0.01 to

0.59 g $O_2/m^2 \cdot d$. When compared with the SOD rates reported in the literature from other rivers, the SOD rates in the Athabasca River are moderate (Chau 2002; Matlock et al. 2003). The SOD rates at many sites were elevated in 1995. The increase through the early 1990s is consistent with the expansion of pulp mills with four new mills beginning operations through 1994. The SOD values determined in this study were elevated by 0.03 g $O_2/m^2 \cdot d$ at both sites. While more data are required, however, this suggests that SOD rates have not declined in recent years. If the SOD rates have indeed increased by 0.03 g $O_2/m^2 \cdot d$, the added SOD consumption could contribute to a 0.7 mg/L oxygen decrease in the river when it reaches the Calling River site, assuming representative winter river velocity (0.3 m/s) and depth (1.3 m). When the river is covered with ice and thick snow, which diminish re-aeration, the oxygen consumption by SOD itself becomes more important. Clearly, further studies on the impact of SOD, with more measurements at different sites in the Athabasca River, are needed.

4. Modeling of Dissolved Oxygen on the Athabasca River

4.1 Introduction

WASP is a dynamic, generalized framework for modeling water quality. It "permits the user to structure one, two and three dimensional models, allows the specification of time-variable exchange coefficients, advective flows, waste loads and water quality boundary conditions; and permits tailored structuring of the kinetic process" (Wool et al. 2003a). WASP simulates the movement and interaction of pollutants within the water by the principle of mass conservation. The water body is represented as a series of computational elements (segments); each segment is treated as a completely mixed reactor. The water volume and water-quality constituent masses are tracked and accounted for over time and space using a series of mass balance equations. For problems of conventional pollution, involving DO, BOD, nutrients and eutrophication, WASP6 is able to simulate the transport and transformation of up to nine state variables in the water column and sediment bed. The state variables include DO, BOD, phytoplankton carbon (as chlorophyll-a), ammonia, nitrate, organic nitrogen, inorganic phosphorus, organic phosphorus, and salinity. In this study, WASP6 was applied in one-dimension (transverse and vertical mixing assumed to be instantaneous) to an 800 km section of the Athabasca River from Hinton to Grand Rapids, Alberta. The modeling involved 15 major tributaries and effluent loads from five pulp mills along the river. Originally constructed by Golder (1995), shown in Figure 9, the model consists of 39 segments. Based on the current available data collected on the river, five of the nine state variables were simulated in the model, including BOD, DO, ammonia, nitrate and organic nitrogen. Table 7 summarizes the variables used in the model simulation.

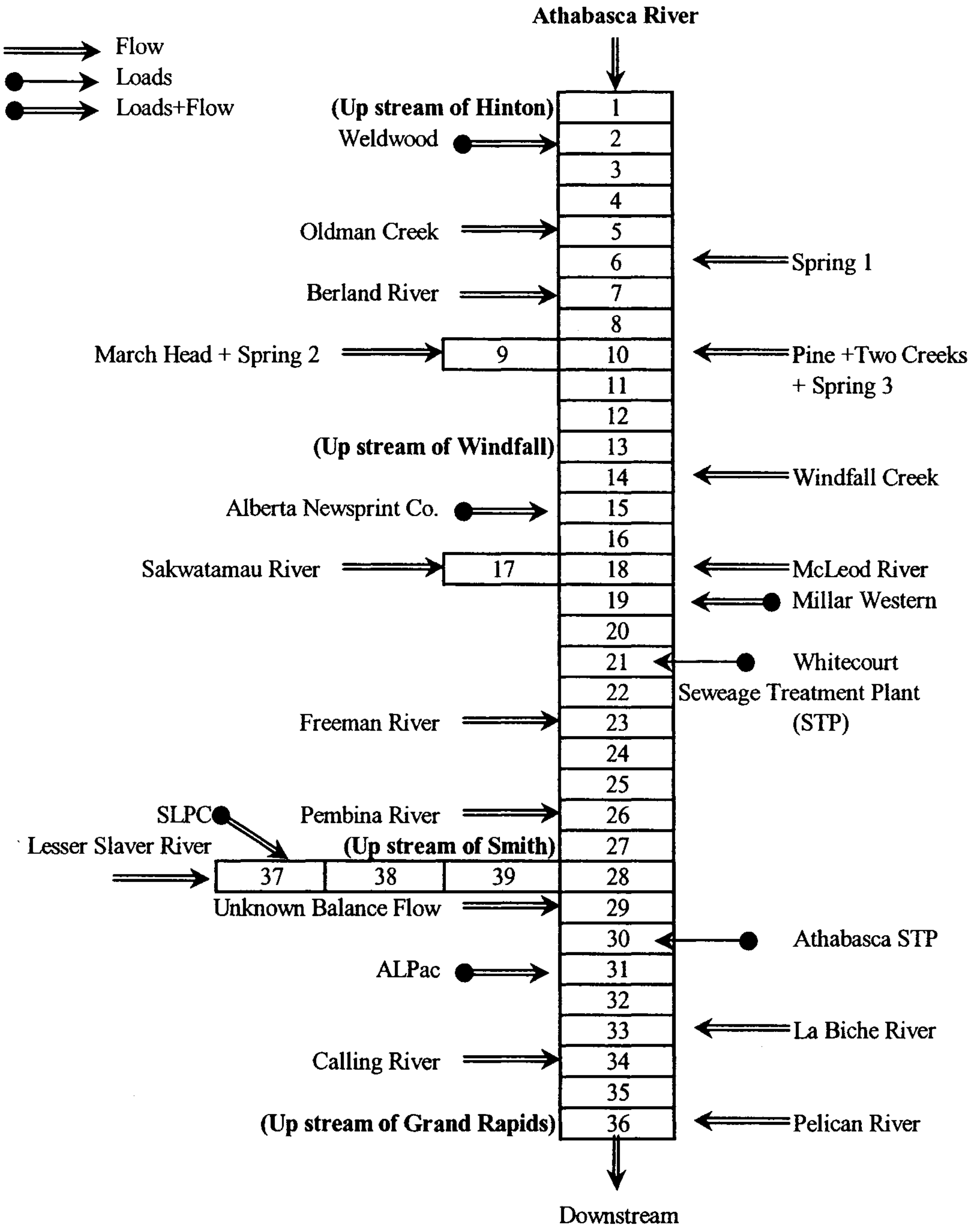


Figure 9. Schematic of Athabasca River dissolved oxygen model setup (after Golder, 1995).

Table 7. Summary of state variables used in the dissolved oxygen balance in model application.

State variables (kg/d)	River segment at pulp mills or sewage treatment plants (STP)						
	Weldwood	Alberta Newsprint	Millar Western	Al-Pac	Lesser Slave River	White-court STP	Athabasca STP
Ultimate BOD	16080	600	3096	1716	3942	189.5	4.3
DO*	7.20	7.99	3.97	4.30	12.00	n/a	n/a
NH_4^+-N	220.8	30.0	14.5	16.2	1.7	1.7	2.2
NO_3^--N	56.0	19.0	21.6	77.2	1.0	5.2	0.4
Organic-N	290.3	38.0	146.9	86.1	138.2	1.7	0.6

* The unit for DO is mg/L.

The WASP water quality model requires a series of inputs to conduct the DO simulations. The winter low flows are one of the conditions that lead to the low DO concentrations in the river. The historical (1961-2002) lowest mean monthly flow at the town of Hinton is 16.9 m^3/s in March 1963; the highest mean monthly flow is 672 m^3/s in June 1991 (Environment Canada 2003). The lowest DO concentration on record (5.7 mg/L at Grand Rapids) was observed during February 2003. Under the winter low flow conditions, BOD and SOD are the primary drivers considered in the modeling simulation. In this study, BOD and SOD were examined in the river. The monthly average discharged BOD_5 loadings in winter of 2002/2003 were collected from the pulp mills. Five-day BOD (BOD_5) from the mill discharges was converted to ultimate BOD (UBOD) by a multiplying a factor of 6 (Pietroniro et al. 1998) to satisfy the model input requirement and the objectives of this modeling exercise which includes a more than 20-day residence time. SOD data in the past 14 years were summarized and the most current data were obtained from the field and laboratory work in this study.

4.2 Model Evaluation and Validation

For various requirements, WASP identified four levels of complexity for DO modeling: Streeter-Phelps, modified Streeter-Phelps, full linear DO balance, and nonlinear DO balance. In this study, the forth level, nonlinear DO balance was adopted. In this scheme, the full DO balance equations divided the nitrogenous BOD (NBOD) process into mineralization (where organic-N was converted to NH_4^+-N) and nitrification (where NH_4^+-N was converted to NO_3^--N), and the effects of photosynthesis and respiration from given phytoplankton levels were added; in addition, feedback from DO concentrations to related terms, such as re-aeration, SOD, carbonaceous de-oxygenation, settling and deposition of particulate organic material in the DO balance were counted in, which became important in inhibiting nitrification and carbonaceous oxidation and in promoting denitrification at low DO conditions.

This DO model was originally calibrated in WASP6 based on observed DO data in the winter of 1999/2000 as conducted by Stantec (2001b). The simulated DO concentrations compare reasonably well with observed data at Grand Rapids in 2000, where the lowest DO concentrations occurred in late February at 8 mg/L. With the same calibrated parameters, however, the predicted DO concentrations during the winter of 2002/2003 with the measured flow data failed to represent the observed decline in DO, and overestimated the DO concentration by more than 2 mg/L.

In the previous studies, carbonaceous BOD_5 loading from the mills was used, which under-estimates the influence of BOD on the river over the 20 to 30-day travel time. In this study, the model inputs were based on the best available estimates of UBOD. This conversion factor was estimated from the winter water quality surveys conducted on the Athabasca River from 1980s to 1990s. The recorded UBOD: BOD_5 ratios in the surveys were in the range of 2.6 to 9.8 for a seven-year period of time. Thus an average of the ratios was used in this research project.

According to the field and laboratory SOD measurements in this study, the SOD data as input parameters in the model evaluation were updated. The same boundary DO concentrations used by Stantec (2001 a, b, c) were chosen. The model was re-calibrated with the converted UBOD loadings, updated SOD rates and ice-cover-ratio re-calibration. Figure 10 represent the SOD rate changes at each segment along the river. The SOD rates were updated based on field measurements conducted in this research work; the other rates adopted the same values used in the previous WASP studies by Stantec (2001b). These SOD input data were used in the model validation process. It can be seen that the SOD rates along the river varied significantly. One of the reasons for the varied SOD rate is due to the different sediment characteristic at different sampling site. Figure 11 shows the river flow rate changes in 2002/2003. The peak flow rate in May was usually due to the spring runoff, where, the melt snow water along the river accumulated towards downstream. Based on the above model evaluation, calibration was evaluated for performance based on other sites on the Athabasca River. Figure 12 demonstrates the model validation results. The best-fit results of the simulated versus observed DO in the winter of 2002/2003 at Grand Rapids indicated the confidence in the modeling simulation process. The results demonstrate that the simulated DO curve fit with the observed DO points very well. The calibrated input parameters were thus used in the model sensitivity studies below.

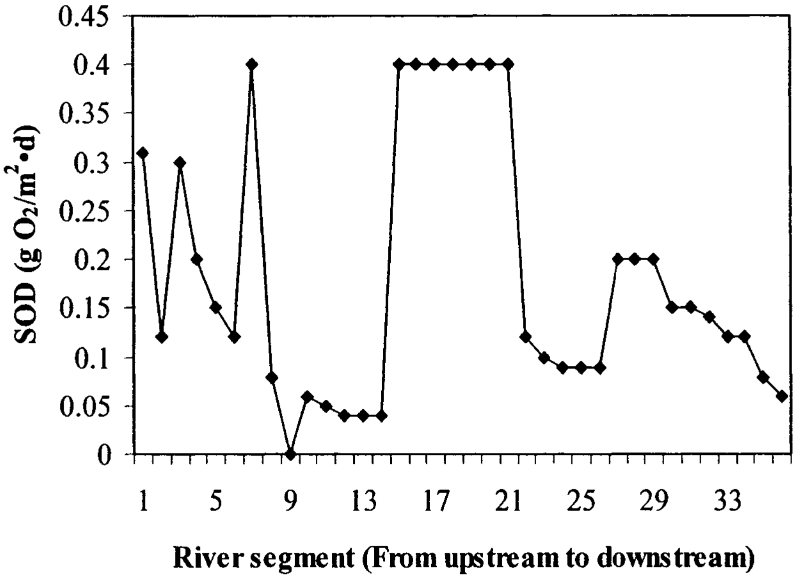


Figure 10. Input SOD rates along the river used in model validation in 2002/2003.

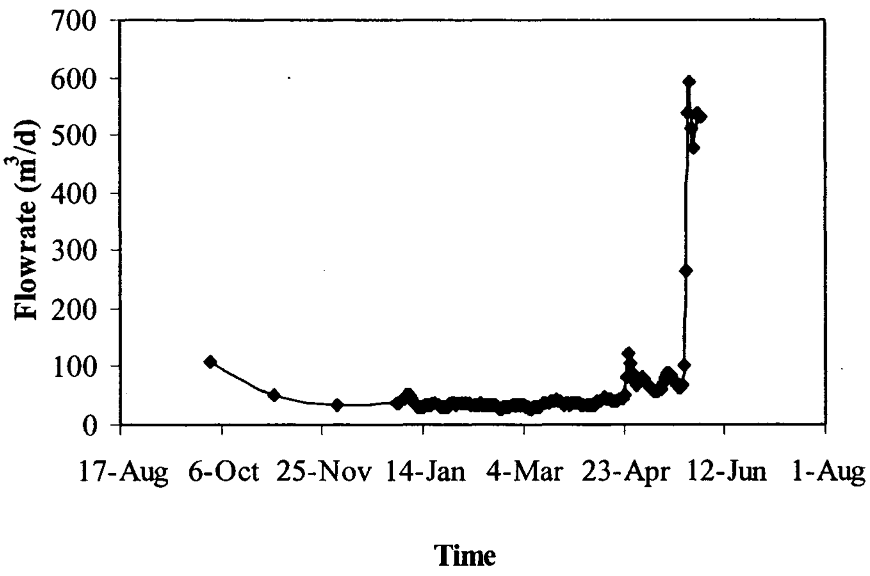


Figure 11. River flow rate changes at upstream of Hinton in 2002/2003.

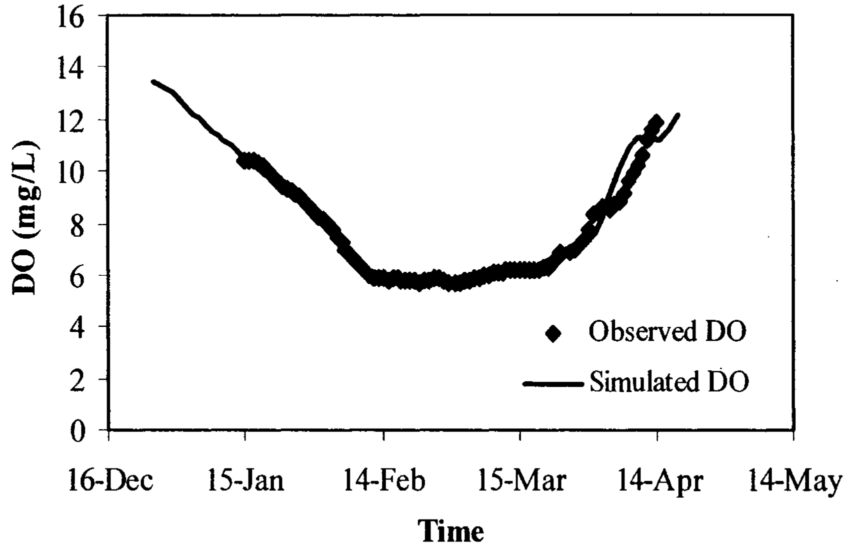


Figure 12. Re-calibration of dissolved oxygen concentration at Grand Rapids in 2003.

4.3 Model Sensitivity Study and Licensed BOD Loading Scenarios

Sensitivity analysis was undertaken in order to understand the factors that are important in revealing the cause of low DO concentrations in the winter river, and to determine potential sources of error in the model that could explain the failure of the model in predicting low DO conditions in the previous studies. The sensitivity analysis included iteratively increasing and decreasing input variables (forcing functions) for BOD, UBOD, SOD, tributary DO and ice cover. From the BOD sensitivity analysis, the results, as shown in Figure 13 a, indicates that the effect of an increase of 1.5 times actual UBOD loading from the mills on the simulated DO concentrations at Grand Rapids is around 1 mg/L. The model appeared to be more sensitive to SOD (Figure 13 b) where an increase of the SOD resulted in a proportional decrease in DO (1.5 times SOD increase results in DO decrease of 1.5 mg/L). The model was also sensitive to the DO concentration in pulp mill effluent (Figure 13 c). The DO at Grand Rapids declined by 0.5 mg/L when DO concentrations in pulp mill effluents were halved.

Ice cover on the river surface during winter months is another important factor that cannot be overlooked. Ice cover condition in the model is represented by an open area ratio, which is defined as 1 for total water surface and 0 for completely ice-covered. This factor, used by Golder (1995) and Stantec (2001b), was determined by a trial-and-error approach to calibrate previous versions of the model. Values adopted varied from 0.02 to 0.2 in the period of December to March. In the present study, the same approach was used for 2002/2003 river DO at Grand Rapids with the updated data (BOD, SOD, flow rate). A potential weakness of WASP is that ice cover is assumed to be consistent among all reaches while the reality is that ice cover varies among segments.

The DO conditions under a range of potential pulp mills BOD_5 loading (Table 8) were simulated after conversion to UBOD. The predicted DO results (Figure 14) indicate that regardless of other factors, the DO at Grand Rapids would decrease to less than 4 mg/L if all the mills currently discharge at their licensed limits under the Athabasca River winter conditions in 2003. Chambers et al. (2000) found that at 6.5 mg/L DO, the hatch of mountain whitefish eggs would be delayed; at 5 mg/L DO, the mass of bull trout alevins post-hatch would be decreased, and the mayfly *Baetis tricaudatus* would be adversely affected. In order to maintain DO concentrations above the 7-day chronic threshold value (6.5 mg/L) at Grand Rapids under the 2002/2003 winter conditions. The total maximum monthly discharge loads (TMML) for all the mills (Figure 15) were simulated based on trial-and-error approach. Many combinations of pulp mill discharge BOD_5 loadings were selected and simulated in order to meet the Alberta guideline on DO concentrations. Figure 15 shows one of the combinations. It is suggested the average licensed monthly BOD_5 loading from Weldwood's discharge should be decreased by 60%, while other pulp mills should decrease their licensed BOD_5 loading by 20%. The environmentally sustainable BOD loads from the mills and from other municipal sources on the river needs to be further studied.

Table 8. Comparison of actual discharged BOD_5 loading and the licensed BOD_5 loading.

Pulp mills	Actual BOD_5 loading (kg/d)	Licensed BOD_5 loading (kg/d)
Weldwood	2680	3300
Alberta Newsprint	100	2100
Millar Western	516	2040
Al-Pac	286	2250
Lesser Slave River	657	1050

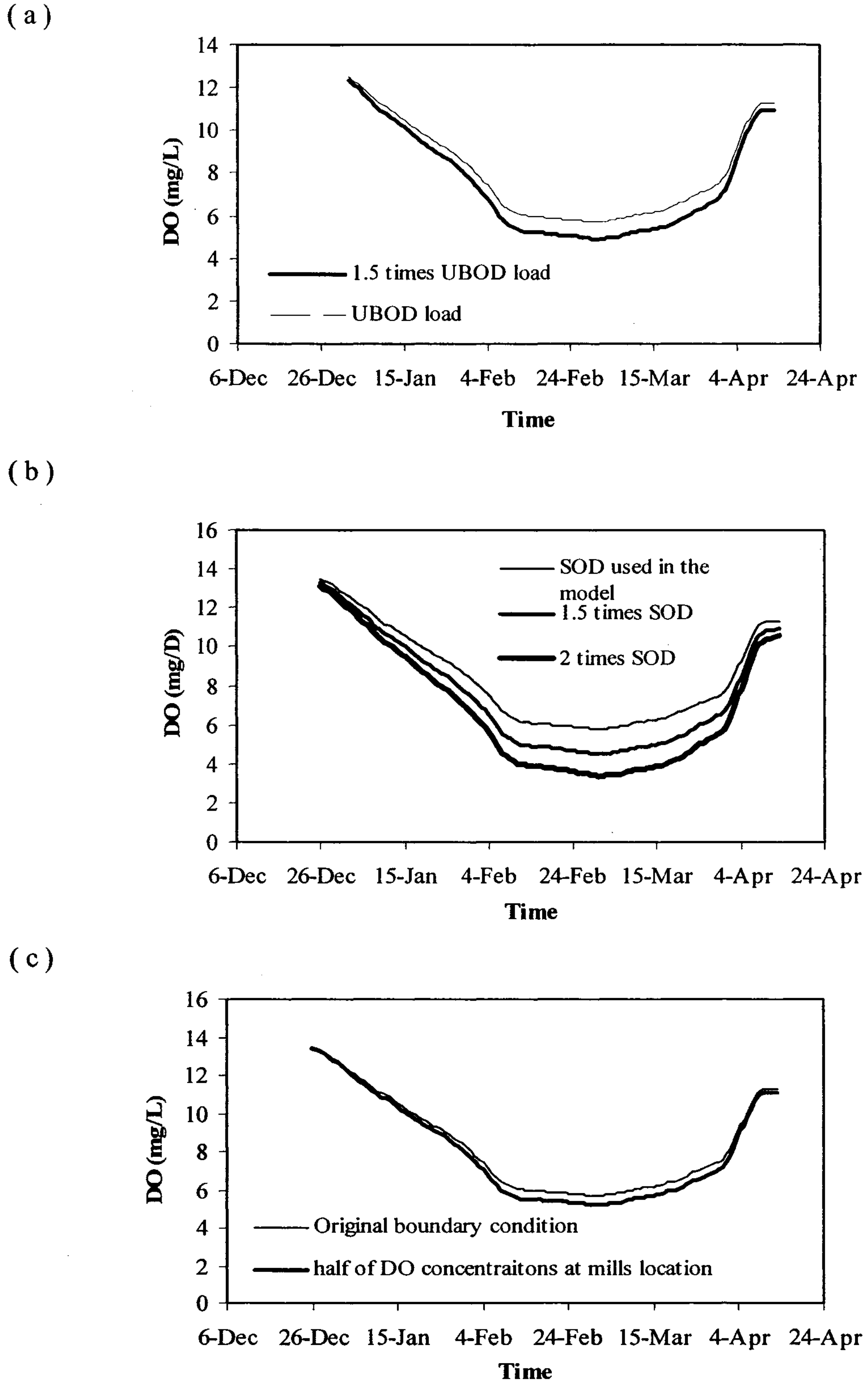


Figure 13. Sensitivity of DO concentrations at Grand Rapids in 2003 (a) BOD (b) SOD (c) boundary DO at pulp mill locations.

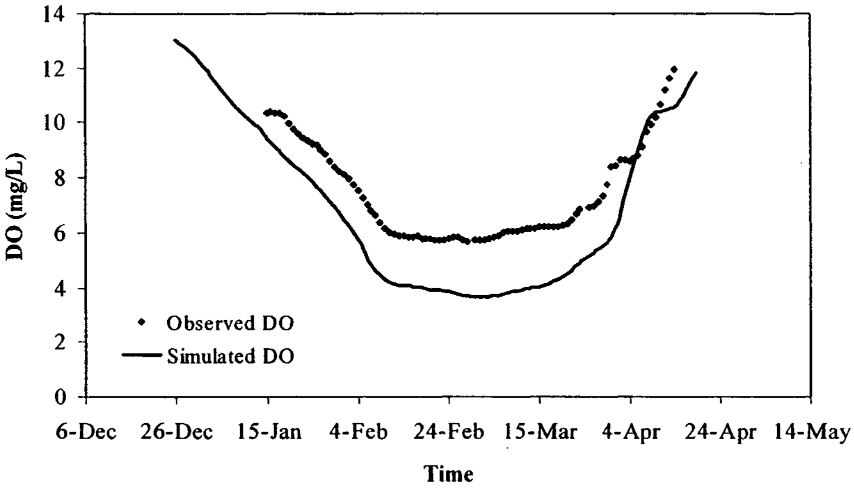


Figure 14. Simulation of 2002/2003 DO at Grand Rapids under licensed pulp mill UBOD load.

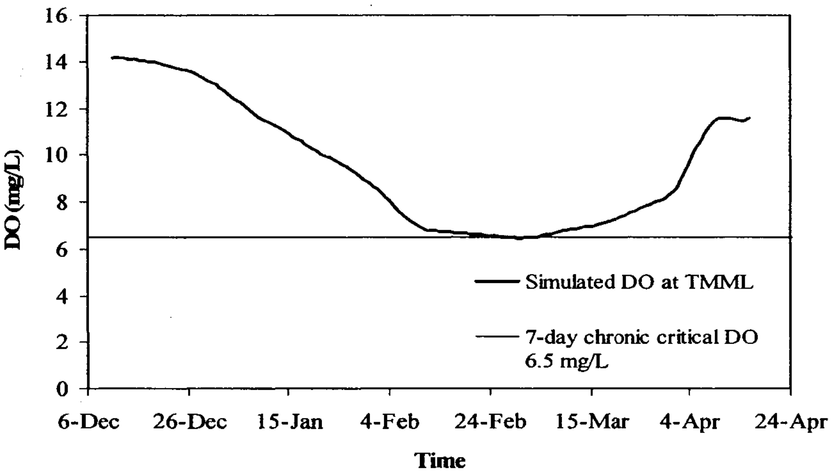


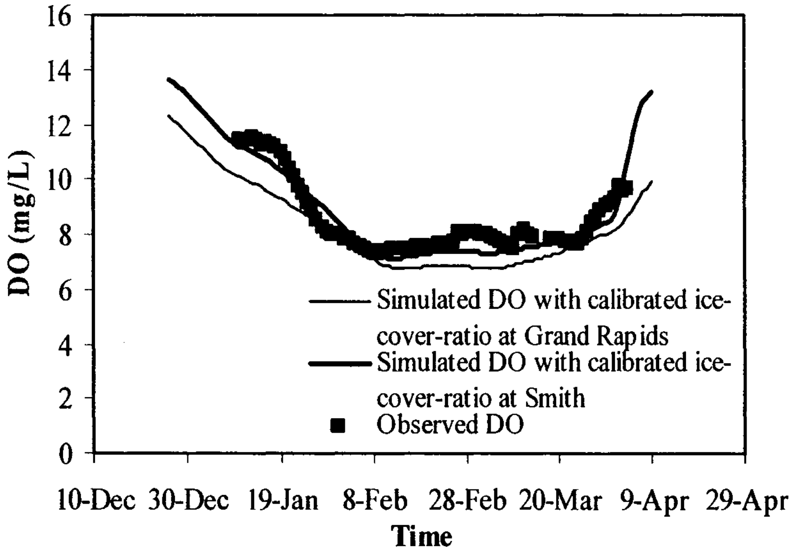
Figure 15. Simulation of total maximum monthly BOD_5 loading (TMML) for the pulp mills.

4.4 Ice-cover-ratio and Air Temperature

Based on this model validation results and with the calibrated ice-cover-ratio at Grand Rapids, two other segments, Smith and Windfall, which are located upstream of Grand Rapids, were chosen as comparisons (Figure 16 a, b). The simulated DO concentrations fit moderately well with observed data at segments where continuous DO monitoring data were available. However, the simulation results for Windfall and Smith sites slightly over-estimate DO in the middle of February. A better fit can be created by adopting adjusted ice-cover-ratios at Windfall and Smith respectively.

By adjusting the ice-cover ratio, the DO level can be quite well simulated, even under the model constraint that only one ratio is allowed for the whole reach of 800 km. Figure 17 compares the ice-cover required to provide the best fit at Windfall, Smith and Grand Rapids, respectively. It appears that the required ice-cover ratio decreases along the river, with the value for the Grand Rapids being the smallest, which means the river freezes earlier downstream than upstream. Although the river flows northward, the temperature at downstream may be slightly lower than the temperature at upstream, this finding is more likely due to the fact that downstream of the river is wider and thus it flows slower than the upper stream. Another finding is that even in the deep winter, there is some open water lead in the river with the ratio being about 0.018 when averaged over the entire 800 km. This is consistent with the observation that open water leads exist downstream of effluent discharge sites. For example, the open water lead downstream of the Al-Pac's outfall is typically about 6 km long when the air temperature is about -15°C (Mark Spafford personal communication).

(a)



(b)

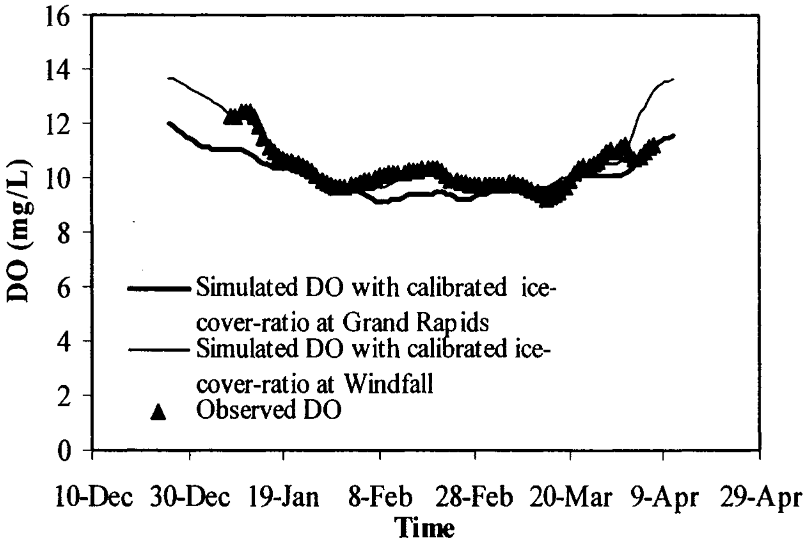


Figure 16. (a) Comparison of simulated and observed dissolved oxygen concentration at Smith in 2003; (b) Comparison of simulated and observed dissolved oxygen concentration at Windfall in 2003.

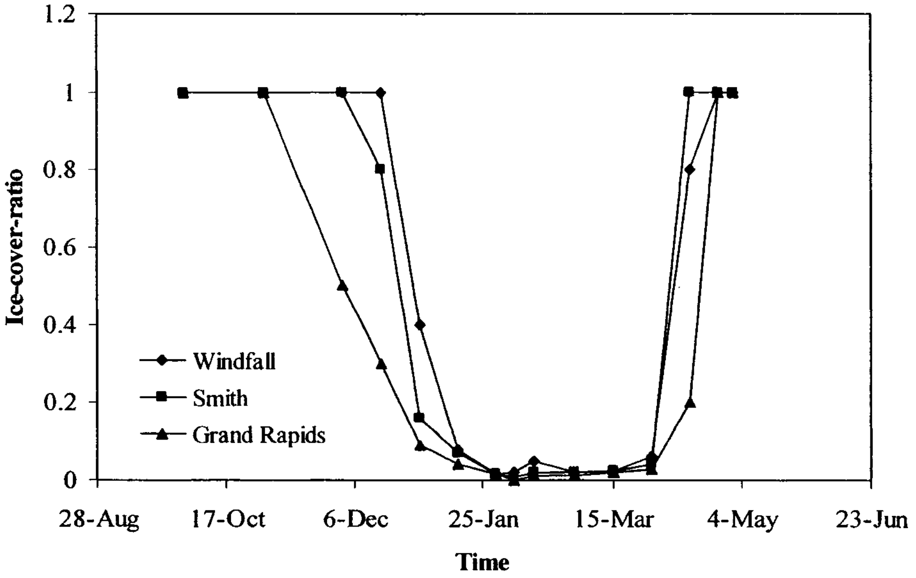


Figure 17. Comparison of calibrated ice-cover-ratio at Windfall, Smith and Grand Rapids.

With the model being most sensitive to the primary calibration terms, WASP in its current configuration provided no predictive capability without some external relationship for determining the appropriate ice-cover-ratio.

Figure 18 shows the apparent relationship between air temperature and ice-cover-ratio at each site. In order to make the best-fit curves with the variation trend of ice-cover-ratio, the moving trend lines of air temperature were adjusted to the 14, 19 and 21 days averaged at Windfall, Smith and Grand Rapids, respectively. This implies that there is a lag between air temperature change and ice cover conditions on the river that becomes more pronounced downstream of the river.

The calibrated ice-cover-ratios determined in 2002/2003 at different sites with the matched air temperatures were compared in an attempt to formulate an empirical relationship for predicting ice-cover-ratios (Figure 19 a, b, and Figure 20). Ice cover varies logarithmically with air temperature adjusted for a suitable moving average to account for thermal transfer from the water mass. Although at Smith, the linear relationship is not very clear, the relationships at the other two sites are moderate. Using a statistical software SPSS® the upper and lower 95% contour curves were added along the regression equation on each figure. From the point of view of statistics, more data points are needed in order to obtain a more accurate regression model. With more studies conducted on this issue in the future, it is expected such relationship may be used to predict future ice cover conditions if air temperatures are provided.

Except for the air temperatures, it is believed that the ice-cover-ratio (in other words, open water lead) in cold winters is also related to the effluent temperatures at pulp mill discharge points and the wind velocity. The most recent data collected showed that the effluent temperature of Al-Pac is 20-23 °C, and the length of open water lead downstream of Al-Pac's diffuser ranges from a few hundred meters to several kilometers (Lima-Neto et al. 2005). The combined effect of air temperature, wind velocity and effluent discharge temperature at each year leads to the varied ice-cover-ratio obtained in the model calibration process to best fit with the observed DO concentrations in the river. The information of the discharges from all other pulp mills along the river and the information on the wind velocity are unavailable for the current research work; such topic needs to be further investigated in the future studies.

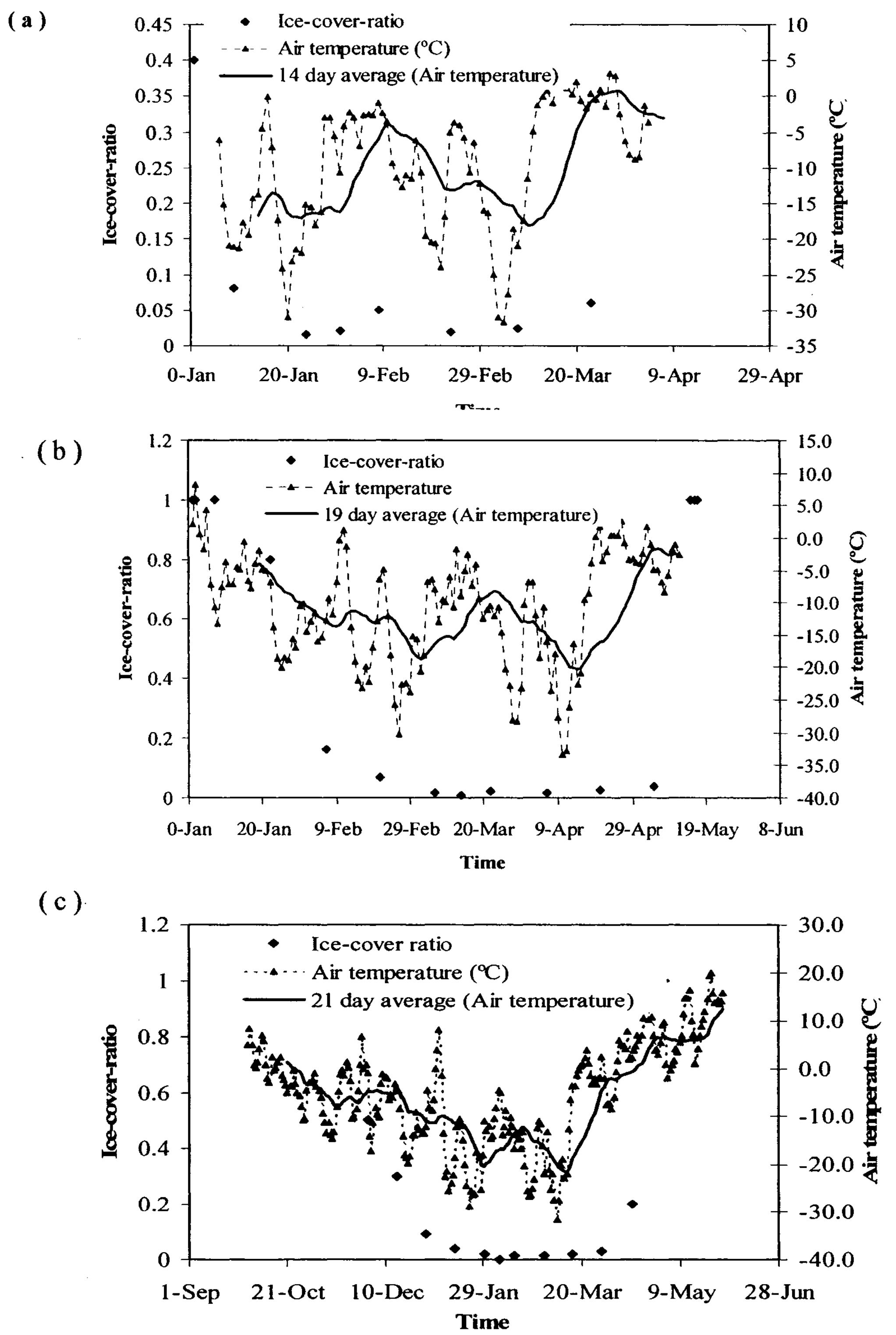


Figure 18. Comparison of ice-cover-ratio versus air temperatures at (a) Windfall (b) Smith (c) Grand Rapids in 2002/2003.

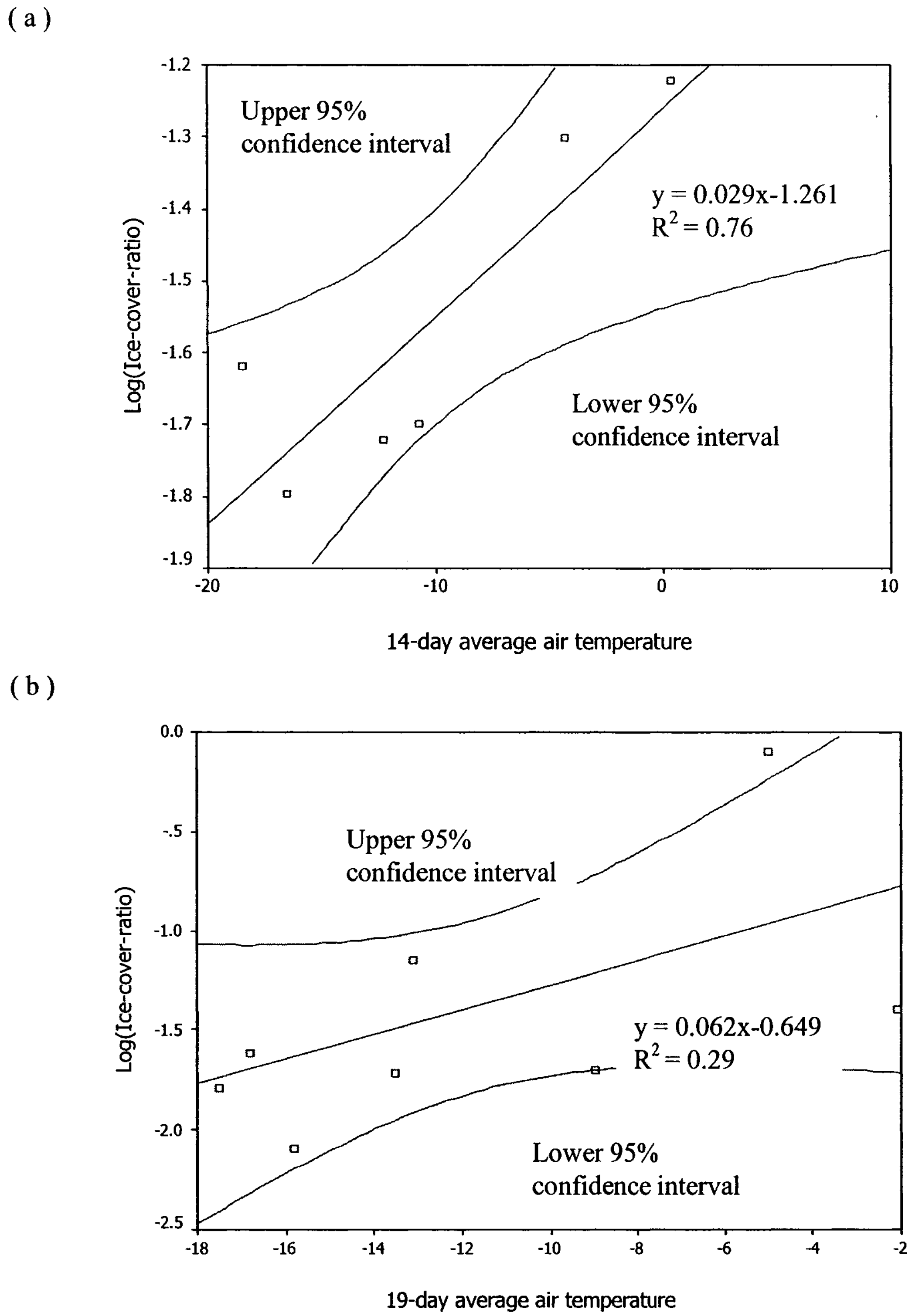


Figure 19. Empirical relationships between Log (Ice-cover-ratio) and moving average air temperatures at (a) Windfall (b) Smith in 2002/2003.

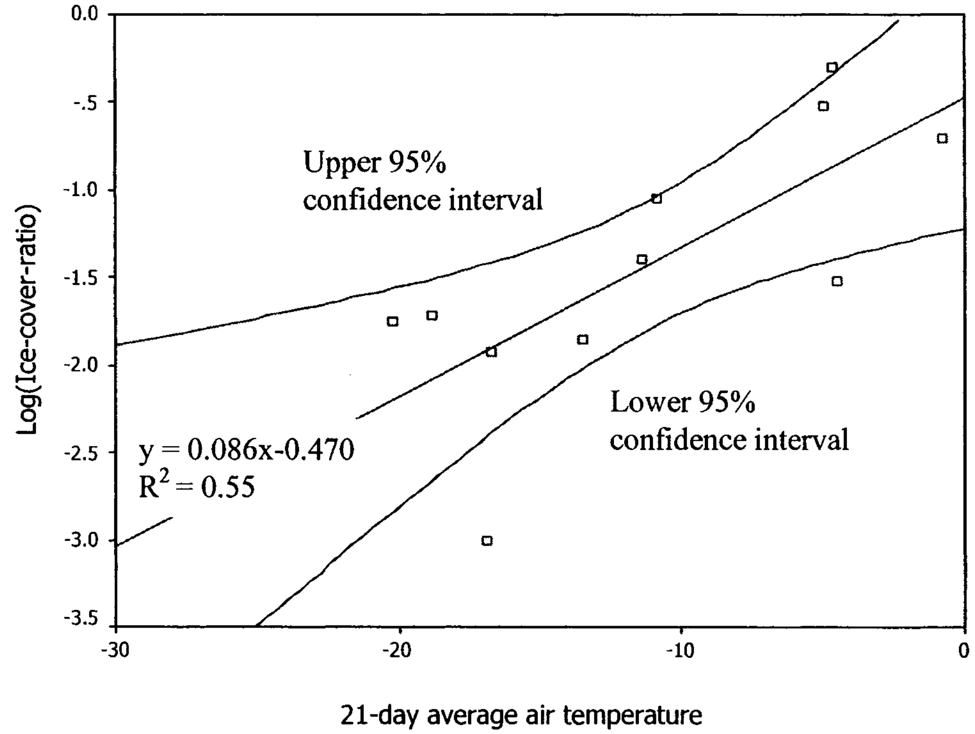


Figure 20. Empirical relationships between Log (Ice-cover-ratio) and moving average air temperatures at Grand Rapids in 2002/2003.

5. Conclusions and Recommendations

5.1 Conclusions

Fieldwork was successfully conducted in winter of 2004 to investigate SOD on the Athabasca River with closed chamber method. Sediment cores were studied in the laboratory with improved oxygen microsensors. The SOD rates are compared between the two methods. The updated SOD rates, as well as BOD, ice-cover-ratio and flow rates were incorporated into WASP6 model to calibrate and simulate DO concentrations in the river. The conclusions are:

(1) The measured mean SOD rates range from 0.12 g $O_2/m^2 \cdot d$ at Calling River confluence and 0.18 g $O_2/m^2 \cdot d$ at Athabasca in the Athabasca River. The increase of SOD from 1995 to 2004 at the two sites is 0.03 g $O_2/m^2 \cdot d$. This change may be due to SOD estimated methods, different *in situ* conditions (mixing) or may represent real change.

(2) The application of oxygen microsensor technology for measuring SOD was compared to *in situ* closed chamber method. Microsensor method can provide more labor effective and easily implemented alternative to *in situ* chamber method. The microsensor technology also gives a chance to study the SOD in a microscopic view, which may assist in forming a better understanding the physical and chemical characteristics inside the sediment.

(3) By oxygen microsensor method, it is verified that SOD rate is dependent with overlying DO concentration and diffusive boundary layer thickness, which are consistent with other studies in this field.

(4) By adopting the updated SOD, UBOD and winter low flow rate in winter of 2002/2003, the recalibrated WASP model simulation and prediction indicated that licensed pulp mill loading may be excessive during low flow years.

(5) Failure to adequately represent limitations on re-aeration due to ice cover during winter may be one of the key factors producing lack of fit in the simulation of DO concentrations in the Athabasca River.

(6) A logarithmic relationship between ice-cover-ratio and air temperature was found on the Athabasca River, this relationship may be used as a prediction tool in the future.

5.2 Recommendations

(1) The water circulation system above the sediment in the cores needs to be redesigned to provide air tightness, so the incubated sediment core method should be improved in future studies because the method itself is an excellent one as it is labor effective as compared with the closed chamber method and, can be used when the water is deep, where the closed chamber method cannot be used.

(2) In order to obtain more current SOD values along the river, more sampling sites need to be investigated during winter months. These SOD values can then be incorporated into the modeling and thus can allow the model to better predict DO concentrations in the river in the future years.

(3) Due to the differences between the closed chamber and oxygen microsensor method, mixing is a topic that needs to be studied further.

(4) Improving the representation of river segment volume is recommended for the computer modeling. When winter low flow rates are incorporated in the model, the volumes for each segment should be changed accordingly. To obtain the best prediction results, hydrodynamic modeling such as EFDC released by USEPA is recommended for use with WASP6 in the future.

(5) It is suggested that the ice cover as well as air temperature, discharge effluent temperature, and wind velocity in winter months along the river need to be monitored. In the future WASP modeling simulations, the ice-cover-ratio should be calibrated at different segments on a yearly basis and the above-mentioned variables should be related to the ice-cover-ratio.

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7. Appendices

Appendix A. Summary of Devices and Chemicals for SOD Measurement

A.1. Closed Chamber Measurement

(1) List of devices and miscellaneous equipment used in the *in situ* measurement:

SOD chambers
YSI 50B DO meter (if possible)
Extra stoppers and wire
Rubber curtains (inner-tubes)
Gear clamps
Screw driver and pliers
Bungee cords
T-posts
0.35 M NaCl solution
Conductivity meter
Hypodermic syringe (50ml or greater)
Thermometer
Flow meter
Meter stick
Ice chisels
Ice auger
Axe and file
Chainsaw
Steel rod/rebar
Shovel
Sledgehammer
Miscellaneous rope
Data sheets

(2) Winkler titration apparatus and chemicals

Refer to the Standard Method of APHA (1992)

A. 2. Sediment Core Measurement

(1) Devices and miscellaneous equipment used in the *in situ* measurement:

SOD Coring Devices
YSI so DO meter (if possible)
Peristaltic pump
Thermometer
Flow meter
Meter stick
Extra Neoprene Stoppers
Cooler (with transport rack)
Ice
Indelible felt pen
Ice Auger
Axe
Chainsaw
Steel rod/rebar
Scrub-brushes
Data sheets
100 ml sample bottles (for sediment cores)
Pipets (in lab)

(2) Winkler apparatus and chemicals

Refer to Standard Method of APHA (1992)

Appendix B. Raw Data for SOD measurement

B.1. SOD Calculation for Closed Chamber Method

The SOD rate in g $O_2/m^2 \bullet d$ is the difference between the test and control chambers:

$$\text{SOD} \ (\text{g } O_2 / m^2 \bullet d) = 0.024 \ (b_1 - b_2) \ V / A \qquad \text{(Equation 1)}$$

where, 0.024 = conversion coefficient from mg/L•h to $g/m^2 \bullet d$

b_1 = DO change inside the chamber with sediment (mg O_2/L•h)

b_2 = DO change inside the control chamber (without sediment) (mg O_2/L•h)

V = water volume in the chamber (L)

A = cross-sectional area in the chamber (m^2)

Table B 1. SOD calculation results from the closed chamber method (g $O_2 / m^2 \bullet d$).

Site	Calling River confluence			500 m upstream of Al-Pac discharge		
Count	$b_1 - b_2$	V/A	SOD	$b_1 - b_2$	V/A	SOD
1	0.04	0.15	0.15	0.05	0.20	0.22
2	0.03	0.16	0.11	0.03	0.19	0.14
3	0.02	0.19	0.11	0.03	0.20	0.12
4	0.03	0.17	0.13	0.05	0.19	0.24
Average			0.12			0.18

B.2. SOD Calculation for Sediment Core Method

The calculation rationale is the same as the closed chamber method and didn't repeat here.

. Table B 2. SOD calculation results from the closed chamber method (g O_2 / m^2 • d).

Site	Calling River confluence			500 m upstream of Al-Pac discharge		
Count	$b_1 - b_2$	V/A	SOD	$b_1 - b_2$	V/A	SOD
1	-0.17	0.01	0.05	0.00	0.41	-0.04
2	-0.24	0.01	0.07	-0.01	0.36	-0.08
3	-0.21	0.01	0.05	-0.01	0.44	-0.07
4	-0.24	0.00	0.00			
Average			0.04			-0.06

B.3. SOD Calculation for Microsensor Method

B.3.1 Microsensor calibration record

Current (pA)	Time (s)	Current (pA)	Time (s)	Current (pA)	Time (s)	Current (pA)	Time (s)	Current (pA)	Time (s)
779	0	6	260	772	520	49	780	767	1040
628	10	6	270	772	530	42	790	780	1050
511	20	6	280	772	540	37	800	793	1060
457	30	6	290	772	550	29	810	811	1070
386	40	60	300	772	560	23	820	811	1080
322	50	268	310	772	570	18	830	811	1090
294	60	420	320	811	580	14	840	811	1100
249	70	514	330	811	590	11	850	811	1110
209	80	618	340	811	600	9	860	811	1120
178	90	650	350	811	610	9	870	811	1130
157	100	671	360	811	620	9	880	811	1140
133	110	691	370	811	630	6	890	772	1150
95	120	702	380	811	640	6	900	772	1160
78	130	723	390	811	650	6	910	772	1170
63	140	750	400	639	660	6	920	772	1180
49	150	768	410	421	670	253	930	772	1190
36	160	774	420	314	680	467	940	772	1200
33	170	783	430	279	690	543	950	772	1210
29	180	803	440	217	700	588	960	811	1220
20	190	811	450	180	710	619	970	811	1230
17	200	811	460	149	720	650	980	811	1240
13	210	811	470	123	730	687	990	811	1250
11	220	811	480	104	740	701	1000	811	1260
9	230	811	490	90	750	719	1010	811	1270
6	240	811	500	72	760	731	1020	811	1280
6	250	811	510	63	770	754	1030	811	1290

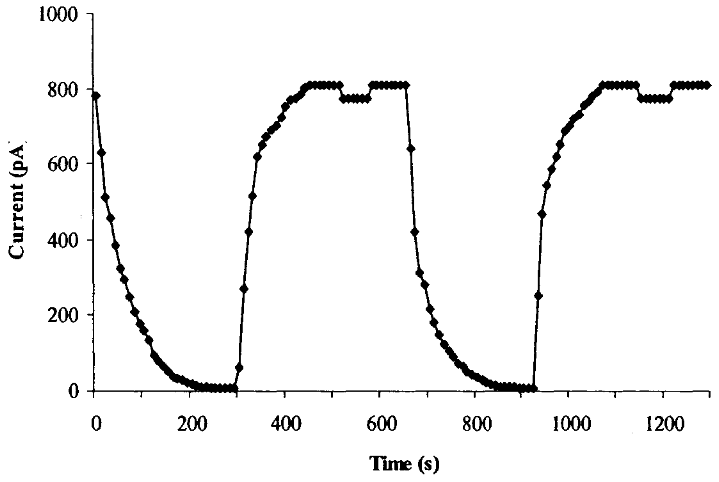

Figure B 1. Calibration curve for the oxygen microsensor used for sediment measurement.

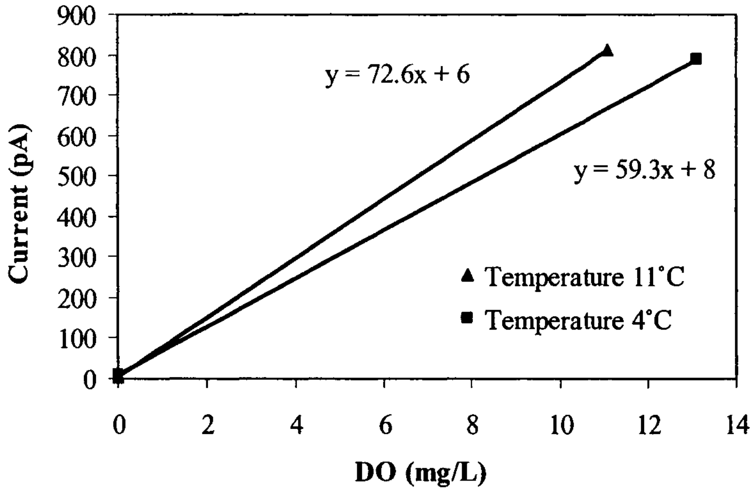

Figure B 2. Calibration equations for oxygen microsensor used for sediment measurement.

Take one of the calibration equations for example. The adjusted saturated dissolved oxygen (DO) in water at 11°C (calibration conducted temperature) can be calculated as S' = (11.07× (791.09 – 9.21))/(760 – 9.21) = 11.09 mg/L, which was reflected by the maximum current 811 pA; the minimum current 6 pA reflected 0 mg/L DO. The calibration lines are shown in Figure B 2. The calibration equation is: Current (pA) = 72.6 × DO (mg/L) + 6.

B.3.2. Oxygen profiles measurement

(1) Environmental condition 1: DO in the overlying water is 10 mg/L

Table B2. Raw data and calculated DO for environmental condition 1.

Replicate 1			Replicate 2			Average	
Water Depth (mm)	Current (pA)	DO (mg/L)	Water Depth (mm)	Current (pA)	DO (mg/L)	Water Depth (mm)	DO (mg/L)
2.3	739	11.26	2.1	730	10.52	2.1	10.89
2.2	740	11.27	2	730	10.52	2	10.89
2.1	739	11.26	1.9	730	10.52	1.9	10.89
2	739	11.26	1.8	730	10.52	1.8	10.89
1.9	739	11.26	1.7	730	10.52	1.7	10.93
1.8	739	11.26	1.6	730	10.52	1.6	10.95
1.7	744	11.33	1.5	730	10.52	1.5	10.94
1.6	747	11.38	1.4	730	10.52	1.4	10.92
1.5	746	11.36	1.3	730	10.52	1.3	10.87
1.4	743	11.32	1.2	730	10.52	1.2	10.86
1.3	736	11.21	1.1	726	10.46	1.1	10.86
1.2	735	11.20	1	720	10.37	1	10.83
1.1	739	11.26	0.9	710	10.23	0.9	10.74
1	741	11.29	0.8	704	10.14	0.8	10.72
0.9	738	11.24	0.7	695	10.01	0.7	10.64
0.8	741	11.29	0.6	687	9.90	0.6	10.55
0.7	740	11.27	0.5	679	9.78	0.5	10.46
0.6	736	11.21	0.4	684	9.85	0.4	10.41
0.5	732	11.15	0.3	680	9.79	0.3	10.27
0.4	720	10.97	0.2	674	9.71	0.2	10.17
0.3	706	10.75	0.1	666	9.59	0.1	10.08
0.2	699	10.64	-0.1	662	9.53	-0.1	9.99
0.1	694	10.57	-0.2	652	9.39	-0.2	9.88

-0.1	686	10.44	-0.3	635	9.14	-0.3	9.72
-0.2	682	10.38	-0.4	619	8.91	-0.4	9.54
-0.3	677	10.30	-0.5	603	8.67	-0.5	9.32
-0.4	668	10.17	-0.6	572	8.22	-0.6	8.98
-0.5	655	9.97	-0.7	545	7.83	-0.7	8.62
-0.6	640	9.73	-0.8	504	7.24	-0.8	8.12
-0.7	619	9.41	-0.9	488	7.00	-0.9	7.90
-0.8	593	9.01	-1	450	6.45	-1	7.42
-0.9	579	8.80	-1.1	370	5.29	-1.1	6.40
-1	552	8.38	-1.2	290	4.13	-1.2	5.26
-1.1	495	7.50	-1.3	280	3.98	-1.3	5.13
-1.2	423	6.40	-1.4	246	3.49	-1.4	4.58
-1.3	415	6.27	-1.5	210	2.96	-1.5	3.95
-1.4	376	5.67	-1.6	163	2.28	-1.6	3.47
-1.5	328	4.94	-1.7	116	1.60	-1.7	2.83
-1.6	310	4.66	-1.8	88	1.19	-1.8	2.43
-1.7	271	4.06	-1.9	71	0.94	-1.9	2.11
-1.8	245	3.66	-2	43	0.54	-2	1.64
-1.9	220	3.28	-2.1	30	0.35	-2.1	1.45
-2	185	2.74	-2.2	20	0.20	-2.2	1.19
-2.1	173	2.55	-2.3	11	0.07	-2.3	1.04
-2.2	148	2.17	-2.4	8	0.03	-2.4	0.91
-2.3	138	2.01	-2.5	5	-0.01	-2.5	0.82
-2.4	123	1.78	-2.6	4	-0.03	-2.6	0.73
-2.5	114	1.65	-2.7	4	-0.03	-2.7	0.65
-2.6	102	1.46	-2.8	4	-0.03	-2.8	0.57
-2.7	93	1.32	-2.9	4	-0.03	-2.9	0.49
-2.8	80	1.12	-3	4	-0.03	-3	0.41
-2.9	67	0.92	-3.1	4	-0.03	-3.1	0.33
-3	58	0.78	-3.2	4	-0.03	-3.2	0.24
-3.1	49	0.65	-3.3	4	-0.03	-3.3	0.16

-3.2	42	0.54	-3.4	4	-0.03	-3.4	0.08
-3.3	35	0.43	-3.5	4	-0.03	-3.5	0.00
-3.4	31	0.37	-3.6	4	-0.03	-3.6	0.00
-3.5	25	0.28	-3.7	4	-0.03		
-3.6	23	0.25	-3.8	4	-0.03		
-3.7	19	0.18	-3.9	4	-0.03		
-3.8	17	0.15	-4	4	-0.03		
-3.9	15	0.12	-4.1	4	-0.03		
-4	13	0.09	-4.2	4	-0.03		
-4.1	11	0.06	-4.3	4	-0.03		
-4.2	10	0.05	-4.4	4	-0.03		
-4.3	9	0.03	-4.5	4	-0.03		
-4.4	9	0.03					
-4.5	8	0.02					
-4.6	7	0.00					
-4.7	6	-0.02					
-4.8	5	-0.03					
-4.9	5	-0.03					
-5	5	-0.03					

(2) Environmental condition 2: DO in the overlying water is 7 mg/L

Table B3. Raw data and calculated DO for environmental condition 2.

Replicate 1			Replicate 2			Average	
Water Depth (mm)	Current (pA)	DO (mg/L)	Water Depth (mm)	Current (pA)	DO (mg/L)	Water Depth (mm)	DO (mg/L)
2	523	7.94	1.7	537	7.51	1.7	7.73
1.9	523	7.94	1.6	538	7.52	1.6	7.76
1.8	524	7.95	1.5	535	7.48	1.5	7.73
1.7	524	7.95	1.4	534	7.47	1.4	7.72
1.6	527	8.00	1.3	532	7.44	1.3	7.70
1.5	526	7.98	1.2	530	7.41	1.2	7.69
1.4	525	7.97	1.1	525	7.34	1.1	7.65
1.3	525	7.97	1	518	7.24	1	7.60
1.2	525	7.97	0.9	512	7.16	0.9	7.56
1.1	525	7.97	0.8	506	7.07	0.8	7.50
1	525	7.97	0.7	503	7.03	0.7	7.48
0.9	525	7.97	0.6	500	6.99	0.6	7.46
0.8	522	7.92	0.5	494	6.90	0.5	7.41
0.7	523	7.94	0.4	487	6.80	0.4	7.34
0.6	523	7.94	0.3	482	6.73	0.3	7.28
0.5	522	7.92	0.2	468	6.53	0.2	7.13
0.4	519	7.87	0.1	458	6.39	0.1	7.03
0.3	516	7.83	-0.1	437	6.09	-0.1	6.81
0.2	509	7.72	-0.2	412	5.74	-0.2	6.53
0.1	506	7.67	-0.3	375	5.22	-0.3	6.15
-0.1	496	7.52	-0.4	321	4.45	-0.4	5.63
-0.2	483	7.32	-0.5	310	4.30	-0.5	5.43
-0.3	467	7.07	-0.6	314	4.36	-0.6	5.31
-0.4	449	6.80	-0.7	285	3.95	-0.7	4.95

-0.5	433	6.55	-0.8	285	3.95	-0.8	4.65
-0.6	414	6.26	-0.9	278	3.85	-0.9	4.29
-0.7	394	5.95	-1	267	3.69	-1	3.97
-0.8	355	5.35	-1.1	262	3.62	-1.1	3.55
-0.9	315	4.74	-1.2	206	2.83	-1.2	2.99
-1	283	4.24	-1.3	192	2.63	-1.3	2.81
-1.1	233	3.48	-1.4	212	2.91	-1.4	2.82
-1.2	212	3.15	-1.5	195	2.67	-1.5	2.46
-1.3	201	2.98	-1.6	181	2.47	-1.6	2.21
-1.4	184	2.72	-1.7	172	2.35	-1.7	1.98
-1.5	153	2.25	-1.8	154	2.09	-1.8	1.74
-1.6	133	1.94	-1.9	166	2.26	-1.9	1.72
-1.7	112	1.61	-2	156	2.12	-2	1.53
-1.8	97	1.38	-2.1	142	1.92	-2.1	1.32
-1.9	84	1.18	-2.2	136	1.84	-2.2	1.20
-2	68	0.94	-2.3	123	1.65	-2.3	1.03
-2.1	53	0.71	-2.4	119	1.60	-2.4	0.94
-2.2	43	0.55	-2.5	103	1.37	-2.5	0.75
-2.3	33	0.40	-2.6	97	1.29	-2.6	0.67
-2.4	25	0.28	-2.7	88	1.16	-2.7	0.58
-2.5	15	0.12	-2.8	79	1.03	-2.8	0.51
-2.6	10	0.05	-2.9	74	0.96	-2.9	0.47
-2.7	7	0.00	-3	68	0.88	-3	0.42
-2.8	6	-0.02	-3.1	64	0.82	-3.1	0.39
-2.9	6	-0.02	-3.2	55	0.69	-3.2	0.33
-3	5	-0.03	-3.3	53	0.66	-3.3	0.32
-3.1	5	-0.03	-3.4	46	0.57	-3.4	0.27
-3.2	5	-0.03	-3.5	39	0.47	-3.5	0.22
-3.3	5	-0.03	-3.6	36	0.42	-3.6	0.20
-3.4	5	-0.03	-3.7	31	0.35	-3.7	0.16
-3.5	5	-0.03	-3.8	26	0.28	-3.8	0.13

	-3.9	24	0.25	-3.9	0.11
	-4	21	0.21	-4	0.09
	-4.1	16	0.14	-4.1	0.06
	-4.2	13	0.10	-4.2	0.03
	-4.3	11	0.07	-4.3	0.02
	-4.4	9	0.04	-4.4	0.01
	-4.5	6	0.00	-4.5	0.02
	-4.6	5	-0.01		
	-4.7	4	-0.03		

(3) Environmental condition 3: DO in the overlying water is 4 mg/L

Table B4. Raw data and calculated DO for environmental condition 3.

Replicate 1			Replicate 2			Average of replicate	
Water Depth (mm)	Current (pA)	DO (mg/L)	Water Depth (mm)	Current (pA)	DO (mg/L)	Water Depth (mm)	DO (mg/L)
1.7	288	3.88	1.6	282	3.90	1.60	3.89
1.6	288	3.88	1.5	282	3.90	1.50	3.89
1.5	288	3.88	1.4	282	3.90	1.40	3.89
1.4	288	3.88	1.3	282	3.90	1.30	3.89
1.3	288	3.88	1.2	282	3.90	1.20	3.89
1.2	287	3.87	1.1	282	3.90	1.10	3.89
1.1	287	3.87	1	280	3.87	1.00	3.87
1	287	3.87	0.9	280	3.87	0.90	3.87
0.9	286	3.86	0.8	276	3.82	0.80	3.84
0.8	286	3.86	0.7	275	3.80	0.70	3.81
0.7	283	3.81	0.6	272	3.76	0.60	3.73
0.6	274	3.69	0.5	270	3.73	0.50	3.70
0.5	272	3.66	0.4	265	3.66	0.40	3.59
0.4	262	3.53	0.3	259	3.58	0.30	3.50
0.3	254	3.42	0.2	254	3.51	0.20	3.51
0.2	261	3.51	0.1	242	3.34	0.10	3.36
0.1	252	3.39	-0.1	231	3.18	-0.10	3.06
-0.1	220	2.95	-0.2	220	3.03	-0.20	3.03
-0.2	226	3.03	-0.3	205	2.81	-0.30	2.88
-0.3	220	2.95	-0.4	194	2.66	-0.40	2.83
-0.4	224	3.00	-0.5	172	2.35	-0.50	2.62
-0.5	216	2.89	-0.6	157	2.14	-0.60	2.51
-0.6	215	2.88	-0.7	142	1.92	-0.70	2.41

-0.7	217	2.91	-0.8	133	1.80	-0.80	2.32
-0.8	213	2.85	-0.9	105	1.40	-0.90	2.10
-0.9	209	2.80	-1	88	1.16	-1.00	1.80
-1	183	2.44	-1.1	73	0.95	-1.10	1.67
-1.1	180	2.40	-1.2	63	0.81	-1.20	1.60
-1.2	180	2.40	-1.3	53	0.66	-1.30	1.41
-1.3	163	2.16	-1.4	37	0.44	-1.40	1.25
-1.4	156	2.07	-1.5	25	0.27	-1.50	1.07
-1.5	142	1.87	-1.6	19	0.18	-1.60	0.95
-1.6	131	1.72	-1.7	16	0.14	-1.70	0.83
-1.7	116	1.51	-1.8	11	0.07	-1.80	0.74
-1.8	109	1.42	-1.9	8	0.03	-1.90	0.63
-1.9	95	1.23	-2	5	-0.01	-2.00	0.57
-2	90	1.16	-2.1	5	-0.01	-2.10	0.50
-2.1	80	1.02	-2.2	5	-0.01	-2.20	0.42
-2.2	68	0.85	-2.3	5	-0.01	-2.30	0.38
-2.3	62	0.77	-2.4	5	-0.01	-2.40	0.31
-2.4	52	0.63	-2.5	5	-0.01	-2.50	0.24
-2.5	42	0.50				-2.60	0.19
-2.6	35	0.40				-2.70	0.14
-2.7	28	0.30				-2.80	0.11
-2.8	23	0.23				-2.90	0.06
-2.9	16	0.14				-3.00	0.03
-3	12	0.08				-3.10	-0.01
-3.1	6	0.00				-3.20	-0.01
-3.2	5	-0.01				-3.30	-0.01
-3.3	5	-0.01				-3.40	-0.01
-3.4	5	-0.01					
-3.5	5	-0.01					
-3.6	5	-0.01					
-3.7	5	-0.01					

-3.8	5	-0.01		
-3.9	5	-0.01		

Appendix C. Raw Data for WASP Model Simulation

Table C1. BOD loading used in model calibration and simulations.

Pulp Mills	2002 Actual BOD_5 load (kg/d)	6 times of 2002 actual BOD_5 load (kg/d)	Licensed monthly BOD_5 load (kg/d)	6 times of Licensed monthly BOD_5 load (kg/d)
Weldwood	2680	16080	3300	19800
Alberta Newsprint Co.	100	600	2100	12600
Millar Western	516	3096	2040	12240
Al-pac	286	1716	2250	13500
Lesser Slave Lake	657	3942	1050	6300

Table C2. Observed dissolved oxygen concentration (mg/L) in winter at Windfall, Smith and Grand Rapids, data were measured and provided by Alberta Environment, monitoring branch.

Date	Windfall	Smith	Grand Rapids
8-Jan-03	12.30		
9-Jan-03	12.22		
10-Jan-03	12.40	11.43	
11-Jan-03	12.47	11.42	
12-Jan-03	12.43	11.44	
13-Jan-03	12.25	11.48	
14-Jan-03	11.89	11.45	
15-Jan-03	11.48	11.28	10.36
16-Jan-03	11.14	11.30	10.39
17-Jan-03	10.93	11.26	10.36
18-Jan-03	10.79	11.17	10.34
19-Jan-03	10.69	11.00	10.22
20-Jan-03	10.62	10.70	9.99
21-Jan-03	10.59	10.40	9.77
22-Jan-03	10.51	10.14	9.59
23-Jan-03	10.44	9.78	9.45
24-Jan-03	10.32	9.46	9.31
25-Jan-03	10.22	9.15	9.23
26-Jan-03	10.08	8.85	9.15
27-Jan-03	9.95	8.55	9.04
28-Jan-03	9.82	8.29	8.88
29-Jan-03	9.72	8.11	8.61
30-Jan-03	9.69	8.03	8.39
31-Jan-03	9.64		8.24
1-Feb-03	9.69	7.98	8.10

2-Feb-03	9.71	7.85	7.96
3-Feb-03	9.74	7.79	7.75
4-Feb-03	9.84	7.67	7.51
5-Feb-03	9.87	7.58	7.24
6-Feb-03	9.95	7.48	6.98
7-Feb-03	9.99	7.39	6.77
8-Feb-03	10.07	7.33	6.61
9-Feb-03	10.10	7.34	6.37
10-Feb-03	10.17	7.38	6.15
11-Feb-03	10.13	7.41	5.98
12-Feb-03	10.17	7.47	5.92
13-Feb-03	10.17	7.50	5.89
14-Feb-03	10.24	7.49	5.86
15-Feb-03	10.25	7.47	5.81
16-Feb-03	10.30	7.50	5.85
17-Feb-03	10.34	7.52	5.87
18-Feb-03	10.36	7.57	5.80
19-Feb-03	10.37	7.58	5.80
20-Feb-03	10.32	7.59	5.79
21-Feb-03	10.22	7.60	5.75
22-Feb-03	10.09	7.64	5.70
23-Feb-03	9.94	7.65	5.75
24-Feb-03	9.92	7.64	5.79
25-Feb-03	9.87	7.70	5.85
26-Feb-03	9.81	8.07	5.84
27-Feb-03	9.78	8.04	5.74
28-Feb-03	9.74	8.07	5.69
1-Mar-03	9.73	8.09	5.70
2-Mar-03	9.75	8.07	5.72
3-Mar-03	9.75	8.04	5.75
4-Mar-03	9.75	7.98	5.80

5-Mar-03	9.77	7.89	5.85
6-Mar-03	9.74	7.79	5.91
7-Mar-03	9.83	7.70	5.97
8-Mar-03	9.81	7.61	6.03
9-Mar-03	9.76	7.54	6.05
10-Mar-03	9.73	7.46	6.07
11-Mar-03	9.62	7.96	6.08
12-Mar-03	9.53	8.18	6.15
13-Mar-03	9.44	8.03	6.16
14-Mar-03	9.35	7.94	6.14
15-Mar-03	9.26		6.20
16-Mar-03	9.28		6.23
17-Mar-03	9.36		6.21
18-Mar-03	9.48	7.84	6.19
19-Mar-03	9.68	7.80	6.20
20-Mar-03	9.91	7.79	6.25
21-Mar-03	10.14	7.75	6.30
22-Mar-03	10.32	7.70	6.44
23-Mar-03	10.42	7.69	6.66
24-Mar-03	10.47	7.68	6.86
25-Mar-03	10.55	7.86	6.90
26-Mar-03	10.60	8.10	6.96
27-Mar-03	10.81	8.40	7.12
28-Mar-03	10.99	8.64	7.33
29-Mar-03	11.00	8.86	7.73
30-Mar-03	10.98	9.06	8.36
31-Mar-03	11.15	9.19	8.46
1-Apr-03	11.19	9.29	8.62
2-Apr-03	10.88	9.73	8.65
3-Apr-03	10.69	9.62	8.58
4-Apr-03	10.80	9.68	8.72

5-Apr-03	10.98	8.81
6-Apr-03	11.15	9.11
7-Apr-03	11.24	9.66
8-Apr-03		9.91
9-Apr-03		10.19
10-Apr-03		10.64
11-Apr-03		11.18

C. 1. Raw Input Data for Model Sensitivity Study

C.1.1 BOD sensitivity study

The compared BOD values used are 1.5 times of licensed UBOD load.

Table C3. UBOD loading used in the BOD sensitivity study.

Pulp Mills	UBOD, that is 6 times of Licensed BOD_5 load (kg/d)	1.5 times UBOD load for sensitivity study (kg/d)
WeldWood	16080	24120
Alberta Newsprint	600	900
Millar Western	3096	4644
Al-pac	1716	2574
Lesser Slave	3942	5913

C.1.2 SOD sensitivity study

Table C4. SOD values used during model sensitivity study (mg/L).

Segment	SOD used in previous studies	Adjusted SOD in this research (use summarized data)	1.5 times SOD for sensitivity study	2 times SOD for sensitivity study
1	0.31	0.31	0.47	0.62
2	0.12	0.25	0.18	0.24
3	0.30	0.30	0.45	0.60
4	0.20	0.20	0.30	0.40
5	0.15	0.15	0.23	0.30
6	0.12	0.12	0.18	0.24
7	0.40	0.40	0.60	0.80
8	0.08	0.08	0.12	0.16
9	0.00	0.00	0.00	0.00
10	0.06	0.06	0.09	0.12
11	0.05	0.05	0.08	0.10
12	0.04	0.04	0.06	0.08
13	0.04	0.04	0.06	0.08
14	0.04	0.01	0.06	0.08
15	0.40	0.40	0.60	0.80
16	0.40	0.12	0.60	0.80
17	0.40	0.40	0.60	0.80
18	0.40	0.40	0.60	0.80
19	0.40	0.34	0.60	0.80
20	0.40	0.15	0.60	0.80
21	0.40	0.40	0.60	0.80
22	0.12	0.12	0.18	0.24
23	0.10	0.10	0.15	0.20
24	0.09	0.09	0.14	0.18
25	0.09	0.09	0.14	0.18

26	0.09	0.09	0.14	0.18
27	0.20	0.13	0.30	0.40
28	0.20	0.20	0.30	0.40
29	0.20	0.59	0.30	0.40

C.1.3. Boundary DO sensitivity study

Table C5. Boundary DO values used in model sensitivity study (mg/L).

Pulp Mills	Original DO at pulp mill discharge locations	Half of original DO for sensitivity study
Weldwood	7.20	3.60
Alberta Newsprint	8.23	4.12
Millar Western	3.97	1.99
Al-Pac	4.30	2.20
Lesser Slave	12.00	6.00

C. 2. Raw Input Data for Model Evaluation and Simulation

Table C6. Segment volumes in the Athabasca River.

Segment	Volume (m^3)
Upstream of Hinton	1.59×10^5
Weldwood	1.01×10^6
Wasp Segment	2.25×10^6
Wasp Segment	1.62×10^6
Oldman Creek	1.96×10^6
Spring 1	2.63×10^6
Berland River	1.42×10^6
Wasp Segment	1.47×10^6
Marsh Head	5.26×10^4
Pine	1.53×10^6
Wasp Segment	1.06×10^6
Wasp Segment	9.20×10^5
Upstream of Windfall	8.05×10^5
Windfall Creek	3.79×10^6
Alberta Newsprint	2.37×10^5
Wasp Segment	7.94×10
Sakwatamau River	5.41×10^4
McLeod River	1.61×10^5
Millar Western	2.02×10^5
Wasp Segment	2.83×10^5
Whitecourt Sewer Treatment Plant	2.84×10^6
Wasp Segment	1.18×10^7
Freeman River	1.10×10^7
Wasp Segment	8.45×10^6

Wasp Segment	2.87×10^{6}
Pembina River	5.39×10^{6}
Upstream of Smith	9.74×10^{6}
Wasp Segment	1.38×10^{7}
Unknown Balance	1.67×10^{7}
Athabasca Sewer Treatment Plant	1.40×10^{7}
Al-Pac	2.66×10^{5}
Wasp Segment	1.97×10^{6}
La Biche River	4.13×10^{6}
Calling River	1.64×10^{7}
Wasp Segment	1.04×10^{7}
Upstream of Grand Rapid (Pelican River)	1.28×10^{7}
SLP (Lesser Slave River)	2.35×10^{5}
Wasp Segment	6.28×10^{5}
Wasp Segment	4.63×10^{5}

Table C7. Organic loading at pulp mills and sewerage treatment plant (kg/d).

Point source	Ammonia	Nitrate	Organic Nitrogen
Weldwood	220.8	56.0	290.3
Alberta Newsprint	30.0	19.0	38.0
Millar Western	14.5	21.6	149.6
Al-Pac	16.2	77.2	86.1
Lesser Slave Lake	1.7	1.0	138.2
Whitecourt Sewer Treatment Plant	1.7	5.2	1.7
Athabasca Sewer Treatment Plant	2.2	0.04	0.6

Table C8. Boundary conditions along the river (mg/L).

Segment	Ammonia	Nitrate	UBOD	DO	Organic Nitrogen
Upstream of Hinton	0.02	0.08	2.85	11.77	0.10
Weldwood				7.20	
Oldman Creek	0.02	0.13	5.95	12.30	0.10
Spring 1	0.02	0.10	3.67	7.80	0.10
Berland River	0.01	0.07	4.30	10.00	0.10
Marsh Head	0.03	0.11	3.48	12.00	0.15
Pine	0.02	0.09	4.53	11.5	0.06
Windfall Creek	0.03	0.07	2.27	7.10	0.20
Alberta Newsprint				7.99	
Sakwatamau River	0.08	0.02	3.55	10.60	0.15
McLeod River	0.06	0.25	4.05	7.70	0.30
Millar Western				3.97	
Freeman River	0.08	0.07	0.76	8.80	0.30
Pembina River	0.10	0.20	1.42	3.10	0.40
Unknown Balance	0.13	0.30	0.10	4.00	0.49
Al-Pac				4.30	
La Biche River	0.15	0.40	2.46	3.30	0.58
Calling River	0.15	0.25	0.63	11.40	0.50
Upstream of Grand Rapids (Pelican River)	0.80	0.02	2.00	12.70	2.00
SLP (Lesser Slave River)	0.03	0.03	2.41	12.00	0.45

Table C9. Constants used in the model execution (Adopted from Stantec 2001b).

Variable	Constant	Value
Ammonia	Nitrification Rate @20c	0.015
	Nitrification Temperature Coefficient	1.05
	Half Saturation: Nitrification Oxygen Limit	2
Nitrate	Denitrificatin Rate @20c	0.015
	Denitrification Temperature Coefficient	1.05
	Half Saturaturation:Denitrification Oxygen Limit	0.1
Chlorophyll-a	Phytoplankton Maximum Growth Rate @20c	2
	Phytoplankton Growth Temperature Coefficient	1.05
	Phytoplankton Light Formulation Switch (1=DiToro, 2=Smith)	2
	Phytoplankton Maximum Quantum Yield Constant	1000
	Phytoplankton Self Shading Extinction	0.016
	Phytoplankton Half-Saturation Constant for Nitrogen	0.007
	Phytoplankton Half-Saturation Constant for Phosphorus	0.001
	Phytoplankton Endogenous Respiration Rate @20c	0.5
	Phytoplankton Respiration Temperature Coefficient	1.05
	Phytoplankton Death Rate Non-Zooplankton Predation	0.02
	Phytoplankton Phosphorus::Carbon Ratio	0.015
	Phytoplankton Nitrogen::Carbon Ratio	0.15
	Phytoplankton Half-Sat. for Recycle of Nitrogen and Phosphorus	0.2
BOD	BOD Decay Rate @20c	0.21
	BOD Decay Rate Temperature Correction	1.07
	BOD Decay Rate in Sediments	0.0004
	BOD Decay Rate in Sediments Temperature Correction	1
	BOD Half Saturation Oxygen Limit	0.5

DO	Waterbody Type Used for Wind Driven Reaeration Rate	1
	Oxygen: Carbon Stoichiometeric Ratio	2.6
Organic nitrogen	Dissolved Organic Nitrogen Mineralization Rate @20c	0.05
	Dissolved Organic Nitrogen Mineralization Temperature Coefficient	1.08
	Fraction of Phytoplankton Death Recycled to Organic Nitrogen	1
Organic phosphorus	Mineralization Rate of Dissolved Organic Phosphorus @20c	0.1
	Dissolved Organic Phosphorus Mineralization Temperature Coefficient	1.08
	Fraction of Phytoplankton Death Recycled to Organic Phosphorus	1