University of Alberta

Sediment Oxygen Demand Investigation and CE-QUAL-W2 Model Calibration in the Athabasca River

by

Miao Yu ©

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in

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Abstract

Mathematical modeling of dissolved oxygen (DO) concentrations in the Athabasca River has been used to set effluent standards for pulp mills. Sediment Oxygen Demand (SOD) is a component of the oxygen balance that has previously been poorly understood and represented in the Athabasca River. In order to achieve more acurate DO predictions, a sediment core incubation method was developed in this study and compared to the *in situ* closed chamber method commonly employed in most SOD evaluations. The study showed that the sediment core incubation method provided convenient, reliable, yet cost-effective means for quantifying SOD in some habitats.

This study indicated that the largest source of error in SOD determinations is correctly representing turbulence in the water column. The sediment core incubation method developed in this study allowed the opportunity to test the effects of mixing rates on SOD determination. This study further indicated that actual SOD rates could be as much as 2-fold higher than originally reported due to inadequate mixing in chamber methods.

Changes in SOD rates resulting from nutrient additions were evaluated with *in vivo* incubations of sediment cores. Oxygen depletion rates at the sediment interface were used to estimate SOD using oxygen microelectrodes. The results indicated that organic carbon loading resulted in significant SOD increases while addition of nitrogen and phosphorus resulted in increases only when organic carbon was added. SOD in the Athabasca River appears to be carbon limited.

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A distributed parameter model (CE–QUAL–W2) was implemented for the Athabasca River, representing a large improvement over previous modeling efforts. Where previous efforts failed to produce predictive capabilities the new approach can predict dissolved oxygen concentrations in the Athabasca River because it incorporates more accurate ice-cover, hydrodynamic, nutrient, and algal regimes in the Athabasca River.

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1 Introduction

The Athabasca River originates in the Rocky Mountains of Jasper National Park and flows in a northeasterly direction for some 1400km to Lake Athabasca. The river extends from the Rocky Mountains through foothills, boreal forest, and agricultural land, to the Canadian Shield in the northeast. The drainage areas for Jasper, Athabasca, and Fort McMurray are 3,880 km^2, 74,600 km^2 and 133,000 km^2 respectively (Alberta Environment, 2005). Factors in the basin that are relevant to Athabasca River water quality include the headwater flow, inflows from several sizeable tributaries, and effluent from several pulp mills and several municipalities.

Concentrations of dissolved oxygen (DO) needed for fish and other aquatic organisms have been considered as an important index in the Athabasca River. During winter months, when ice cover blocks contact with the air and DO levels dwindle, a potential reduction in DO concentration was identified as a primary concern in the Athabasca River. Modeling of DO concentrations is currently used to predict the impacts of effluent from pulp mills and other sources on the Athabasca River and is used to set effluent discharge limits for pulp mills. Computer modeling of the water quality and the oxygen balance in the Athabasca River began in 1987, with the initial expansion of pulp mills from one to five. Models used for the Athabasca River had been developed from steady-state modules, such as the Dissolved Oxygen Stochastic Model (DOSTOC) (HydroQual, 1988; MacDonald and Hamilton, 1989), to dynamic modules, such as the US EPA Water Quality Analysis Simulation Program (WASP) (Golder, 1995; Stantec, 2001a). In recent

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years, mid-winter DO concentrations have declined below 6.5 mg/L and have approached 5 mg/L. These low DO concentrations were not predicted in the DO models that had been in use over the last decade. Understanding and modeling the factors controlling DO were considered to be urgent needs to manage effluent discharge from pulp mills and municipalities on the Athabasca River and to ensure sustainable development in the watershed.

The factors that result in the low DO in winter include Biochemical Oxygen Demand (BOD), Sediment Oxygen Demand (SOD), and reaeration. The major driver of DO, the water column oxygen demand, or BOD, has been the focus of previous studies in the Athabasca River (Golder, 1995; Stantec, 2001a). SOD was incorporated into the WASP model, and a sensitivity analysis showed that the prediction of DO levels was sensitive to the SOD term (Stantec, 2001c; Tian, 2005). Although SOD in the Athabasca River had been investigated since 1989 (Casey and Noton, 1989; HBT 1993; Monenco, 1993; Tian et al., 2004), data were limited spatially and temporally due to the time consuming and expensive SOD measurement methods and an inadequate understanding of the factors influencing SOD values. Few researchers have published SOD research under winter conditions in cold regions such as Northern Canada, although some work on SOD has been done in warm regions and in oceanic sedimentary environments. Hence, more reliable and updated SOD values and further study on the impacts of various factors were required in order to provide more accurate inputs for the water quality model.

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Re-aeration, the major source of DO, is limited during the winter when rivers are ice-covered. The impact of ice coverage on re-aeration was incorporated into the WASP model by applying a factor, the open water surface area to ice cover ratio. However, the factor was insufficiently quantified due to the limitation of the model. Tian (2005) found that the failure to adequately represent limitations on re-aeration due to ice cover during winter may be one of the key factors contributing to the lack of fit in the simulation of DO concentrations. An empirical approach to predict the ice cover from the air temperature provided an improvement but was crude compared to heat balance models used for ice-process modeling (Tian, 2005). A recommendation from Tian's study was to replace WASP with a model with a dynamic ice module. At the same time, another limitation of WASP, its inability to simulate hydrodynamics for situations when the flow rates varied rapidly, were noticed when more accurate predictions were needed.

The purpose of this project is to quantify the role of SOD on low DO conditions in the Athabasca River and follow on the recommendations of Tian et al. (2004) to model the Athabasca River using the CE-QUAL-W2 model. The improvements generated in this study can be used to improve management of the Athabasca River. The project will result in improvements for management of industrial and urban growth in Alberta's river basins. One is developing an understanding of the impacts from nutrient and organic carbon enrichment on SOD and ultimately on DO. The other deliverable is a calibrated CE-QUAL-W2 model of the Athabasca River. The results of this study are essential in determining loading limits for pulp mills. The study is broadly applicable and will allow the SOD components to be applied to other rivers in Alberta.

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In this study, a sediment core incubation method for easily and ecomomically quantifying SOD was refined and developed based on the previous sediment core apparatus used in SOD measurements in the Athabasca River (Monenco, 1992; HBT Agra Ltd., 1994; Tian et al., 2004). New local SOD values along the river were obtained using the sediment core incubation method during a winter survey of the Athabasca River in 2004, work which was a part of the study. The sediment core incubation method was compared to the closed chamber method and microelectrode method in order to evaluate its accuracy and practicability. In addition, the impacts of several factors including organic carbon, nutrient, DO, temperature, and current velocity on SOD were investigated. All these efforts better quantified the SOD parameter. The data were then used to develop and calibrate the water quality model into a predictive tool. In order to achieve more accurate predictions, in this study a two-dimensional hydrodynamic and water quality model, CE-QUAL–W2, was employed to model the Athabasca River. The model had the ability to characterize adequately the hydraulics and water quality. Furthermore, the ice cover on the river was predicted by the CE-QUAL-W2 model based on the inputted meteorological and hydrodynamic information. In this study, the CE-QUAL-W2 model was calibrated with the inclusion of SOD values and other water quality and hydrodynamic parameters determined in the river survey.

The thesis consists primarily of two parts: The SOD study and the CE-QUAL-W2 model calibration.

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2 Literature Review

2.1 Sediment Oxygen Demand (SOD)

2.1.1 SOD and Factors Influencing SOD

Oxygen demand by benthic sediments and organisms can represent a large fraction of oxygen consumption in surface waters. SOD is due to the oxidation of organic matter in bottom sediments. These benthic deposits or sludge beds derive from several sources. Wastewater particulates as well as other allochthonous particulates (leaf litter and eroded organic-rich soils) can result in sediments with high organic content. In addition, in highly productive environment such as eutrophic lakes, estuaries, and rivers, photosynthetically produced plant matter can settle and accumulated organic matter will result in a SOD. The importance of sedimentary oxygen consumption in the oxygen balance of natural waters has been recognized since the beginning of the development of stream oxygen balance models (Hatcher, 1986). During the early period, the procedure was simply to measure the SOD as an areal flux of oxygen to the sediment and use that consumption rate as a sink in the mass balance models. However, the control of combined sewer overflows and the removal of nutrients from point sources reduced the supply of particulate organic matter to the sediment. Hence an important issue addressed in latter's studies was the effect the reduction has on the resulting SOD. Di Toro et al. (1990) presented a model that predicts SOD as a function of the rate of sedimentary particulate organic matter (POM) decay and mass transport and oxidation kinetics of

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dissolved methane and ammonia. As depicted in Figure 1 the sediments are divided into an aerobic layer and an anaerobic layer. Within these layers both organic carbon and nitrogen transformations ultimately create SOD.

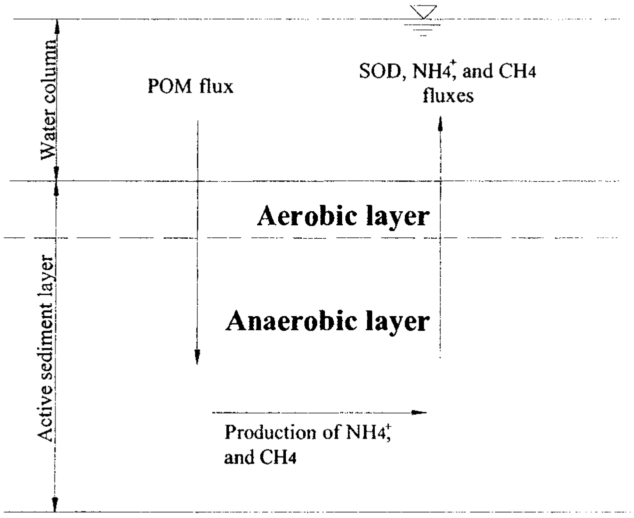

Figure 1 Schematic diagram of SOD model framework (Redrawn from Di Toro et al., 1990)

According to Di Toro et al. (1990), POM is delivered to the sediments by settling. Within the anaerobic sediments, the organic carbon decomposes to yield dissolved methane. The methane diffuses upward to the aerobic zone where it is oxidized. In the process an SOD is generated.

$$CH_2O \rightarrow \frac{1}{2}CO_2 + \frac{1}{2}CH_4 \qquad (2\text{-}1)$$

$$\frac{1}{2}CH_4 + O_2 \rightarrow \frac{1}{2}CO_2 + H_2O \qquad (2\text{-}2)$$

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At the same time, ammonium is generated via ammonification of organic N in the anaerobic zone. In the aerobic zone, nitrification of the ammonium serves as an oxygen-demanding reaction that exerts Nitrogen SOD.

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O \qquad (2\text{-}3)$$

The various factors that influence oxygen depletion by sediments are well documented in the literature. Despite many studies, however, there is still considerable discussion concerning the effects of these factors on SOD. A brief review of some of these factors is provided here.

Oxygen concentration

Clearly, if water oxygen concentration goes to zero the SOD will cease. Conversely above a certain level, it is usually assumed that the SOD is independent of the oxygen concentration in the overlying waters. Many early investigators agreed that SOD is independent of DO concentration in the overlying water in the range of approx. 3-8mg/L DO (Edwards and Rolley, 1965; Hargrave, 1969; Knowles *et al.,* 1962; Martin and Bella, 1971; McKeown *et al.,* 1968; Pamatmat *et al,* 1973). However, a number of previous investigators of the Athabasca River found that the SOD rate decreased during the sediment incubation period although the DO concentration in the overlying water was higher than 3mg/L. They attributed the decreasing rate to progressively more depletive DO concentrations over the course of the incubation period. (Monenco Inc., 1993; Casey and Noton, 1989). The dependence of SOD on DO has been the subject of several

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laboratory and field investigations (Porcella et al., 1986). Walker and Snodgrass (1986) proposed a mechanistic relationship of DO, temperature, and SOD. The explicit dependence of SOD on overlying water DO concentration has been examined experimentally and incorporated in several SOD models (Di Toro et al., 1990).

Sediment resuspension

Essentially all investigators who have commented on this factor observed that SOD increases as sediments are resuspended (Butts, 1974; Hargrave, 1969; Martin and Bella, 1971; Baumgartner & Palotas, 1970). James (1974) found a linear increase in oxygen consumption with increasing water velocity. With higher velocities, the rate of increase became exponential. The effect was apparently due to increased sediment resuspension, leading to increased surface area. In 1994, Nakamura and Stefan published a theory relating SOD to flow velocity using boundary layer concepts. Mackenthun and Stefan, (1998) validated and extended the results. They verified that SOD increases linearly with the velocity of the water above the sediments when the velocities are low. As the velocity increases, the SOD reaches an upper bound. SOD is approximated by linear and Michaelis-Menten type equations with velocity being the independent variable. Jorgensen and Revsbech (1985) measured a decrease of 50% in the thickness of diffusive boundary layers (DBL) above a mat of *beggiatoa spp.* When the flow velocity was increased from 0.01-0.02 m/s to 0.1-0.2 m/s, the subsequent oxygen uptake rate increased from 1.5 to 3.1 g $O_2 m^{-2} \cdot d^{-1}$.

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Organic content of the sediment

Baity (1938) and Fair et al. (1941) provided the first evidence of how the organic content of the sediments affected SOD. Their work suggests a square-root relationship between the SOD and the sediment volatile solids. A similar effect was found between SOD and sediment COD. The square-root relationship leads to the general conclusion that there is less SOD per mass/moles organic carbon as the sediment becomes more enriched. In their paper, Di Toro et al. (1990) developed a model of the SOD process that mechanistically arrives at the same square-root relationship between SOD and sediment organic carbon. He also explained the relationship. In essence when the organic carbon content of the sediment gets high, the amount of methane produced in the anaerobic sediments can exceed its solubility and bubbles form. These bubbles advect upward due to their buoyancy and consequently represent a loss of organic carbon that does not exert a SOD. This loss is one component of the observed square-root relationship between SOD and sediment organic carbon content. Rabouille et al. (2003) also stated that increasing in quality and quantity of organic matter deposited or increasing generation of reduced chemical species could cause an increase of the oxygen demand of the sediment.

Temperature

The effect of temperature on SOD has been well documented in the literature. Increases in temperature result in increased rates of bacterial respiration, yielding higher SOD rates. McDonnell & Hall (1969), for example, reported that biological processes increase two-fold for each 10 °C rise in temperature. The effect of temperature on SOD can be

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represented by $S_B' = S'_{B,20}\,\theta^{T-20}$ (Chapra, 1997). In addition the SOD for temperatures below 10 ^{0}C typically declines faster than indicated by the equation (Chapra, 1997).

Other factors, which affect SOD, include photosynthetic activity, invertebrate activity, pH, and salinity. The impacts of these factors on SOD were not included in this study.

2.1.2 State of the Art Technologies of SOD Measurement

Analytical systems and techniques used to evaluate sediment including SOD measurement techniques have been rapidly developed during the last 20 years. Most of these technologies were developed from oceanographic research. Analytical techniques used by many investigators to evaluate sediment biogeochemistry, which are currently available, include (1) sediment chambers (closed chamber) (2) sediment core incubation (3) electrochemical sensors, (4) other techniques (optical sensors, gel probes, etc.)

Sediment chambers

Sediment chambers have been used since the mid-1960s to study rates of sediment respiration and sediment–water solute exchange *in situ*. A sediment chamber is a device that is placed on the sediment, enclosing a known area of the sediment surface together with a known volume of ambient overlying bottom water. Concentration changes in the enclosed overlying water over time are used to calculate fluxes of oxygen into the sediment. These flux calculations are based on three assumptions: (1) steady state conditions are valid during the *in situ* incubation period with respect to solute exchange (i.e., with respect to concentration gradients within the sediment and between the

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sediment and the overlying water); (2) the hydrodynamic regime inside the chamber does not alter solute exchange across the sediment–water interface as compared to natural conditions; and (3) the size of the sampling/ measurements area is representative for a larger sediment area (Viollier et al., 2003).

Historically, sediment chamber method has been considered as the most reliable measure of total benthic carbon degradation in sediments. These methods also have been utilized for a range of analyses, including inorganic constituents and nutrients, natural and anthropogenic trace metals, and are currently being adapted for organic contaminants. In oceanographic research in order to achieve continuous measurements at the surface of impermeable sediments, benthic chambers have also been equipped with different sensors, such as oxygen electrodes and optodes. Also pH and H_2S electrodes have been used in chambers to obtain measurements other than oxygen.

Sediment chambers have been constructed in many shapes: square, rectangular, cylindrical, and variations of each of these configurations. Sediment chambers are generally constructed of synthetic materials such as plexiglass, acrylic plastic, fiberglass, and perspex. Some chambers were constructed of metal and glass. Much effort has focused on the construction of an ideal chamber and on the characterization of chambers in use with respect to hydrodynamic regime, diffusive boundary layer thickness, as well as pressure and shear stress distribution (Santschi et al., 1983; Opdyke et al., 1987; Buchholtztenbrink et al., 1989; Glud et al., 1995). There are countless choices that can be made in sediment chamber design, to address specific research questions or to make

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chambers more "realistic". However, it is also clear that all design choices cannot be applied to a single chamber, and that chamber design parameters such as oxygen control, size, replication, flexibility, should be carefully tailored to the study site and goals (Viollier et al., 2003).

Sediment core incubation

The principle of sediment core incubation is similar to sediment chamber. Sediment chambers that are used *in situ* are direct measurements made in the field under ambient conditions. Sediment core incubation method requires the collection of undisturbed sediment cores or dredge samples that are obtained with a variety of coring devices for later analysis in the laboratory under controlled conditions.

Sediment core incubation is a common method to measure SOD in the laboratory. The system consists of sealed chambers containing sediment of a known surface area and overlying water of a known volume. The water is generally circulated within the chamber and the DO is monitored. The resulting DO decrease over time is used to calculate the SOD, which is usually expressed as oxygen demand per unit area of sediment.

Water circulation in most cores was maintained either by an internal mixing device or an external pump to provide uniform distribution of DO. DO measurements were made either continuously, periodically, or at the beginning and end of each SOD measurement. The DO probe was the predominant method used to monitor DO concentrations, although some investigators used the Winkler titration technique.

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The laboratory vs. *in situ* issue has long been discussed in the literature. Both SOD measurement approaches have certain advantages and disadvantages. *In situ* techniques are desirable since they are employed under approximately ambient conditions. Yet, they present distinct disadvantages. Investigators must tolerate a variety of natural conditions. Local weather conditions determine when, and for how long, *in situ* measurements can be performed. For example, rapid and substantial changes in the hydrological conditions of a river might interrupt *in situ* studies. In North America, measurements are usually made during the ice-free months. Surveys made during the ice cover period can be difficult; particularly in terms of installing SOD devices and most importantly, in keeping the equipment functioning properly in below-freezing conditions. Variables that can affect SOD and are uncontrollable include: temperature, turbulence, light and current velocity. Thus, there are many factors which must be controlled during measurement in order to collect accurate and reproducible SOD data, which are not always easily accomplished *in situ.* Furthermore, logistical and field labor costs can limit the total number of SOD measurements made under a given research budget. Initially, laboratory techniques might appear to be less desirable since they do not precisely reproduce natural conditions. Also, it may be more difficult to interpret and compare the results of laboratory SOD systems with those developed from field studies. Laboratory variables, though, can be controlled more easily, thereby allowing improved precision among replicates. For example, temperature, light, degree of agitation, and DO concentration can be controlled over a range to better provide modeling inputs based on the likely

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range in these physical factors that occur through a year rather than at the time of *in situ* incubation.

Microelectrodes (microsensors)

Microelectrodes, or microsensors, can be used to investigate sediment in both the laboratory and *in situ*. The highest biochemical activity in sediments occurs close to the sediment–water interface (often within millimeters). This narrow spatial scale is extremely susceptible to sample perturbation. Electrochemical microelectrodes minimize sediment–water interface distortions (mixing), leaving natural gradients of metabolites and substrates intact and allowing for sub-millimeter scale resolution. Additionally, data acquisition can be rapid, providing quantitative information in real or near real time, which can, in turn, guide subsequent sampling and analysis. This approach increases the probability of obtaining meaningful results.

Compared to microelectrode method sediment cores or benthic chambers incubations provide the total oxygen demand, while oxygen microprofiles, coupled with estimation of the formation factor, yield diffusive oxygen demand. Yet, the estimates of the two techniques show contrasted results (Rabouille et al., 2003). Archer and Devol (1992) found an excess of the total oxygen demand compared to the diffusive flux by a factor of 2-3 on the continental shelf.

The most common sensor used to measure SOD is the Clark electrode. The introduction of "Clark-type" amperometric oxygen microelectrodes has provided a powerful and

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reliable electrochemical tool to gain insight into chemical and biological reactions processes of carbon and oxygen within the sediment environment (Jørgensen and Revsbech, 1985; Jørgensen and Des Marais, 1990; Jørgensen and Boudreau, 2001; Revsbech and Jørgensen, 1980; 1986a; 1986b; Revsbech et al., 1988; 1998). These sensors have been deployed to measure concentrations of oxygen in sediments and overlying waters at sub-millimeter scales in oceanographic research.

2.1.3 SOD Measurement in the Athabasca River

Given a significant fraction of the total oxygen demand of the Athabasc River (Macdonald and Radermacher 1993), SOD investigation in the Athabasca River began in 1989 (Casey and Noton, 1989) and SOD measurement have been investigated in several winters since then (Casey 1990; Monenco 1992; HBT AGRA Ltd, 1993; HBT AGRA Ltd 1994; Noton 1995; Tian et. al., 2004). The main method used was closed chamber method, which has been to enclosed sediment in stainless steel chambers *in situ*, and measures the decline in DO in the overlying chamber water during deployment. However, the sediment in the chamber could not be considered as intact. If the majority of SOD occurs on fine organic particles that cover with cobbles, losses of these particles during sediment transfer will lead to underestimate of SOD rate. Also, the water vanes on the chamber lid, which uses to provide water mixing inside the chambers, were not always proportional to river velocities outside the chambers. The reduced mixing in the chambers may cause an underestimate of SOD (Tian et al., 2004).

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Some additional measurements have been done by incubating sediment cores (Monenco, 1992; HBT Agra Ltd., 1994; Tian et al., 2004). As a laboratory SOD measurement, sediment cores were first used in the Athabasca River to determine SOD during the winter 1992 study by Monenco Consultants Ltd. and Alberta Environment. This method, which was based on that developed by McLeod and Gannon (1986), enables intact sediment to be collected and incubated in the same tube. Once connected to a peristaltic pump, constant water circulation at the water-substrate interface could be maintained to simulate the natural river condition and avoid stratification. After that, the sediment core method was developed and modified by Alberta Environment. The main problem encountered with this method was diffusion of oxygen into the system through the pump circulation system (Tian et al., 2004). Given the potential for leaking during external circulating and the lack of comparison to other methods, the results obtained from sediment core assessments were not as reliable as those from the closed chamber method.

Although SOD had been measured in previous years, several questions remained concerning SOD and factors controlling it. These questions include whether SOD accumulates downstream of effluents inputs during winter, and whether SOD is influenced by nutrient loads from effluents. In addition, there is a general need to have regular monitoring of SOD (Noton, 1996), thus a convenient and reliable SOD measuring method is needed to satisfy the regular monitoring requirement.

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2.2 Water Quality Modeling

Water quality models simulate the fate of pollutants and the state of selected water quality variables in water bodies. River water quality models are used extensively in research as well as in the design and assessment of water quality management measures. The application of mathematical models for that purpose dates back to the initial studies of oxygen depletion due to organic waste pollution. Since then, models have been constantly refined and updated to meet new and emerging problems of surface water pollution, such as eutrophication, acute and chronic toxicity. River water quality models seek to describe the spatial and temporal changes of constituents of concern. Components or state variables have been gradually incorporated into models over the past several decades following the evolution of water quality problems. The complexity covers a broad range from the simple Streeter-Phelps model (Streeter and Phelps, 1925) with two state variables to models describing comprehensively O, N, and P cycling with about ten state variables, to ecosystem models that may consider suspended solids, several classes of algae, zooplankton, invertebrates, plants, and fish. The model choice depends on many different factors such as the objectives of the analysis, as well as data and time availability (Rauch et al., 1998).

Water quality changes in river due to physical exchange and transport processes (such as advection and diffusion/ dispersion, the description of which requires one way or another the application of a hydraulic model as an input) and biological, chemical, biochemical, and physical conversion processes (Rauch et al, 1998). These processes are governed by

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a set of well-known extended transport equations. A well-known partial differential equation offers the basic governing equation of water quality models.

$$\frac{\partial c}{\partial t}=\left[-u\frac{\partial c}{\partial x}-v\frac{\partial c}{\partial y}-w\frac{\partial c}{\partial z}\right]+\left[\frac{\partial}{\partial x}(\varepsilon_x\frac{\partial c}{\partial x})\right]+\left[\frac{\partial}{\partial y}(\varepsilon_y\frac{\partial c}{\partial y})\right]+\left[\frac{\partial}{\partial z}(\varepsilon_z\frac{\partial c}{\partial z})\right]+r(c,p) \tag{2-4}$$

The equation also specifies useful framework and the main model elements (Rauch et al., 1998). These are the following:

- The hydrodynamic model for deriving velocity components μ, υ and ω, and turbulent diffusion coefficients ε_x, ε_y, and ε_z.
- The conversion sub-model, r(c, p). It has much less solid theoretical grounds than hydrodynamics and, thus, for its development an adequate combination of theoretical and empirical knowledge is needed.
- Methodologies such as calibration, validation, identification, sensitivity, and uncertainty analysis are required, which aid model selection and testing.
- The model designed on the basis of the above steps and elements should be implemented on a computer, which raises a number of software issues.

Some water quality models focus on particular problem contexts. Other models are more general, and can be used to simulate different water quality problems. Each water quality model has its own set of characteristics and requirements. However, water quality models can rarely represent DO concentration in all seasons (Makinia et al., 2001). Discrepancies during winter months, particularly predictions of elevated DO relative to actual conditions, are common (Makinia et al., 2001).

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The currently available models for river domains were tabulated in Table 1.

Table 1 A list of models, their characteristics, and applications

	Name	Type*	GUI**	Domains
Flow Only	BRANCH	1-D	no	rivers, estuaries, channel networks
	CH3D-WES	3-D	yes	rivers, lakes, estuaries, reservoirs, coastal areas
	DAFLOW	1-D	U	rivers, channel networks
	DYNHYD5	1-D	W	rivers, estuaries
	FEQ	1-D	W	rivers, channel networks
	FESWMS	2-D (h)	U/W	rivers, lakes, estuaries, reservoirs, coastal areas
	FourPt	1-D	no	rivers, channel networks
	HEC-RAS	1-D	W	rivers, channel networks
	RMA2	2-D (h)	U/W	rivers, lakes, estuaries, reservoirs, coastal areas
	UNET	1-D	W	rivers, channel networks
Transport Only	BLTM	1-D	no	rivers, estuaries
	CE-QUAL-ICM	1,2,3-D	U/W	rivers, lakes, estuaries, reservoirs, coastal areas
	OTEQ	1-D (l)	no	rivers
	OTIS	1-D (l)	no	rivers
	RMA4	2-D (h)	U/W	rivers, lakes, estuaries, reservoirs, coastal areas
	SED-2D	2-D (h)	U/W	rivers, lakes, estuaries, reservoirs, coastal areas
	WASP	1, 2, 3-D	W	rivers, lakes, estuaries, reservoirs, coastal areas
Flow and Constituent Transport	CE-QUAL-RIV1	1-D (l)	no	rivers, channel networks
	CE-QUAL-W2	2-D (v)	U/W	rivers, reservoirs, estuaries
	EFDC/HEM3D	1,2,3-D	W	rivers, lakes, estuaries, reservoirs, coastal areas
	MIKE 11	1-D (l)	W	estuaries, rivers, channel networks
	MIKE 3	3-D	U/W	rivers, lakes, estuaries, reservoirs, coastal areas
	QUAL2E	1-D (l)	W	rivers, channel networks
	RMA10	3-D	U/W	rivers, lakes, estuaries, reservoirs, coastal areas
	SNTEMP	1-D (l)	no	rivers, channel networks
	SSTEMP	1-D (l)	W	rivers, channel networks
Model Systems	BASINS	System	W	watersheds, rivers, channel networks
	GenScn	System	W	watersheds, rivers, channel networks
	SMS	System	U/W	rivers, lakes, estuaries, reservoirs, coastal areas

Type*: (l)=longitudinal, (v)=vertical, (h)=horizontal

GUI (Graphical User Interfaces) **: W, runs on Windows OS; U, runs on Unix OS;

(Adapt from USGS, 2005)

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2.2.1 Water Quality Analysis Simulation Program (WASP)

WASP is a generalized framework for modeling contaminant fate and transport in surface waters. Based on the flexible compartment modeling approach, it is designed to permit easy substitution of user-written routines into program structure. Problems studied using WASP include BOD and DO dynamics nutrients and eutrophication, bacterial contamination, and organic chemical and heavy metal contamination (U.S. EPA, 2004).

WASP vision 6 (WASP6) is an enhancement of the original WASP (Di Toro et al., 1983; Connolly and Winfield, 1984; Ambrose et al., 1988), this model helps users interpret and predict water quality responses to natural phenomena and man-made pollution for various pollution management decisions. WASP6 is a dynamic compartment-modeling program for aquatic systems, including both the water column and the underlying benthos. WASP allows the user to investigate 1, 2, and 3-dimensional systems, and a variety of pollutant types. For problems of conventional pollution, involving DO, BOD, nutrients and eutrophication, WASP6 is capable 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 (U.S. EPA, 2004).

The WASP6 system consists of two stand-alone computer programs, DYNHYD5 and WASP6, which can be run in conjunction or separately. The hydrodynamic program, DYNHYD5, simulates the movement of water while the water quality program, WASP6,

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simulates the movement and interaction of pollutants within the water (Wool et al, 2003). While DYNHYD5 is delivered with WASP6, other hydrodynamic programs can also be linked with WASP, for example, EFDC, ECOM, and CH3D.

WASP has been used to examine eutrophication of Tampa Bay, FL; phosphorus loading to Lake Okeechobee, FL; eutrophication of the Neuse River Estuary, NC; eutrophication Coosa River and Reservoirs, AL; PCB pollution of the Great Lakes, eutrophication of the Potomac Estuary; kepone pollution of the James River Estuary; volatile organic pollution of the Delaware Estuary; heavy metal pollution of the Deep River, North Carolina; and mercury in the Savannah River, GA. (U.S. EPA, 2004).

2.2.2 CE-QUAL-W2

CE-QUAL-W2 is a water quality and hydrodynamic model in two-dimensions (longitudinal-vertical) for rivers, estuaries, lakes, reservoirs and river basin systems. This model is supported by U. S. Army Corps of Engineers and Portland State University.

CE-QUAL-W2 models basic eutrophication processes such as temperature-nutrient-algae-dissolved oxygen-organic matter and sediment relationships. CE-QUAL-W2 accurately reproduces vertical and longitudinal water quality gradients. CE-QUAL-W2 presently includes water quality routines for 22 parameters: suspended solids, coliforms, total dissolved solids, labile DOM, refractory DOM, algae, detritus, phosphorous, ammonia, nitrate-nitrite, dissolved oxygen, CBOD, sediment, inorganic carbon, alkalinity, pH, carbon dioxide, bicarbonate, carbonate, iron, and a numerical tracer. CE-

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QUAL-W2 is based on the laterally averaged equations of momentum, continuity, and transport. The formulation includes the vertically varying, longitudinal momentum balance, vertical momentum in the form of the hydrostatic approximation, local continuity, the free-water surface condition based on vertically integrated continuity, and longitudinal and vertical transport of any number of constituents (JEEAI, 2005).

The time-varying solution technique of the model is based on an implicit, finite difference scheme that results from the simultaneous solution of the horizontal momentum equation and the free-water surface equation of vertically integrated continuity. This technique results in the surface long wave equation that is solved on each time step to give the water surface profile, from which the vertical pressure distribution can be determined. The horizontal momentum is then computed, followed by internal continuity and then constituent transport. The QUICKEST finite difference scheme is used for the advective processes in the constituent transport balances. Vertical turbulent transfer of momentum and constituents is determined from the vertical shear of horizontal velocity and a density gradient dependent Richardson number function.

The boundary conditions at the open ends of the branches can be any combination of either elevation or flux conditions. The elevations or fluxes are specified from boundary data. The elevation boundary condition enters the formulation through the implicit long wave surface equation. Fluxes at the elevation boundary are computed from a reduced form of the longitudinal and vertical momentum equations, which include the baroclinic, barotropic, vertical shear, and local acceleration terms but do not include the longitudinal

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spatial acceleration (JEEAI, 2005).

The constituent comparison between CE-QUAL –W2 and WASP is tabulated in Table 2.

Table 2 Constituent comparison between CE-QUAL-W2 and WASP*

Constituent	*CE-QUAL-W2*	*WASP*
Temperature	✓	✓
Coliform bacteria	✓	✓
Dissolved oxygen	✓	✓
Inorganic suspended sediments	✓	
Cohesive sediments		✓
Noncohesive sediment		✓
Salinity		✓
Total dissolved solids	✓	
Dissolved organic matter	✓	
Bottom sediments	✓	
Sediment diagenesis		✓
BOD	✓	✓
Detritus	✓	
Nitrogen	✓	✓
Phosphorus	✓	✓
Silica		✓
Algae	✓	✓
Iron	✓	
Alkalinity	✓	
pH	✓	
User-defined constituent		✓
Conservative tracer		✓
Pesticides		✓
Synthetic organics		✓

* Adapt from USGS (2005)

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2.2.3 DO Models of the Athabasca River

Computer modeling of the water quality and the oxygen balance in the Athabasca River began in 1987 with the initial expansion of pulp mills (HydroQual, 1988; MacDonald et al., 1989; MacDonald and Hamilton, 1989). The DOSTOC model was used to make an initial attempt to quantify the natural processes that govern DO levels in the Athabasca River. DOSTOC model was a steady-state, one-dimensional model based on the system of ordinary differential equations developed by Streeter and Phelps. The DOSTOC model was 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 simulating 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. DOSTOC was considered inadequate because it did not represent the feedback of the effects of photosynthesis, respiration, and nitrogenous BOD into the DO balance and it did not simulate the linkage between effluent discharges and benthic component oxygen demand (Tian, 2005). US EPA WASP was the subsequent model employed for appropriate modeling of DO dynamics in the Athabasca River, because it contained the necessary routines to simulate DO dynamics in the water column and shallow sediments of a river system. Golder (1995) used WASP2 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

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the calibration years 1989 and 1991, but could not represent DO conditions for 1993 at several important sites on the Athabasca River.

In 2001, Stantec (2001a) demonstrated that SOD, which was not included in the previous model simulation, was another important factor that contributed to the DO depletion in the Athabasca River when they conducted the simulation based on the previous model configuration by Golder in 1995. 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 modeling with WASP5, and to include the SOD effect in the modeling was made by Stantec (2001c). An SOD sensitivity analysis (Stantec, 2001b) on the modeling 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 simulated 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. The impact of the pulp mills on DO in the Athabasca River was tested as well. The simulation results showed 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 lowest flows on record occurred in the Athabasca River during the winter of 2002

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and 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 (Tian et al., 2004). Since WAPS5 model failed to predict the observed low DO concentrations, Tian et al. (2004) updated the WASP5 to WASP6 and recalibrated WASP6 by adopting the updated SOD, UBOD, and winter low flow rate in the winter of 2002-2003. The sensitivity analysis using WASP 6.0 indicated that 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 simulated DO fitted with the observed DO well by adjusting ice-cover-ratios. However, the ice-cover-ratio was insufficiently quantified due to the lack of related information. Tian (2005) found that the failure to adequately represent limitations on reaeration due to ice cover during winter may be one of the key factors producing lack of fit in the simulation of DO concentration. She also tried to find the relationship between ice cover and air temperature. However, WASP in its current configuration provided no predictive capacity for determining appropriate ice cover ratio. At the same time another limitation of WASP, inability on simulating hydrodynamics for the situations when the flow rates varied rapidly, were noticed when more accurate predictions were needed. To obtain the best prediction results, hydrodynamic modeling was recommended for use (Tian et al, 2004).

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3. SOD study

Given the important role of SOD in the DO balance, more accurate and updated measurements were required in order to provide more accurate inputs for the water quality model. In order to obtain the SOD values, which can meet both the quality and quantity requirements of modeling, sediment core incubation method was developed in this study during the Athabasca River synoptic survey period in 2004, which was part of the study. The reliability of this SOD measurement method was then investigated by comparison to the SOD measurements from closed chamber method, which had been used to determine SOD rates in the Athabasca River in previous studies since 1989 (Casey and Noton, 1989; Casey 1990; Monenco 1992; HBT Agra 1993; HBT Agra 1994; Noton 1996, Tian et al., 2004). Meanwhile, several factors affecting SOD measurements were discussed. Microelectrode method was employed to further investigate the impacts of two important factors: Organic Carbon and Nutrients. In addition, the SOD measurements obtained by using microelectrode method were compared to those using sediment core incubation method.

3.1 Methodology

3.1.1 Sediment Core Incubation Method Development

The sediment core incubation method was developed during the Athabasca River winter synoptic survey period from October 28 to November 5, 2004.

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The sediment core apparatus is shown in Figure 2 (a). The sediment cores used in this study were developed based on the sediment core apparatus used in previous SOD measurements, which were developed by Monenco and Alberta Environment (Monenco, 1993). The core device consisted of 60 cm lengths of clear polycarbonate tube with inside diameter of 6.0 cm and wall thickness of 0.3 cm. Clear polycarbonate enabled the operator to determine whether an undisturbed sediment core of suitable thickness had been obtained during sampling. Two rubber stoppers (Fisher Scientific, Cat. #14-130s #11 ½) were fastened to both ends of the tube. In previous designs the top stoppers contained two ports allowing the connection of the external circulation pumps (Figure 2(b)), which allowed too many opportunities for leakage, the pumps, the ports in the stoppers, the joints of circulation pipes (Tian et al., 2004). In this study external circulation system was replaced with intact stoppers and an internal stirring mechanism.

To provide uniform distribution of DO in water column, a magnetic stir bar (Fisher Scientific, Cat. #14-513-51 3/8") was wrapped in closed cell polyurethane foam (for floatation) and placed in each core. A stir plate was inverted and placed on the top of each core to provide the drive for the stir bar. Water circulation in the sediment core incubation apparatus used in this study was maintained by an internal mixing device (floating stirring mechanism) to provide uniform distribution of DO. Compared to the previous sediment core (Figure 2(b)), the new one has less leaking sources (e.g. external pump, circulating tubes, and joints). In addition, the new device is more flexible. It can be set up in various conditions and the only external material is a magnetic stirrer. The flexibility made it possible to obtain series of SOD measurements along the river and to

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carry out regular monitoring of SOD rates in the Athabasca River or even other rivers in Alberta.

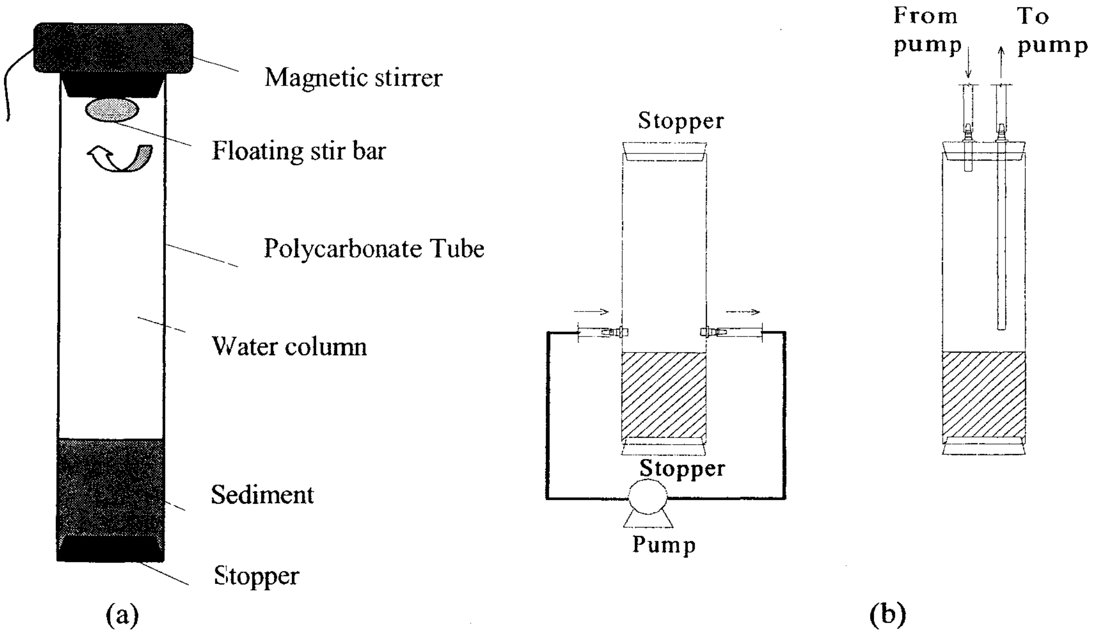

Figure 2 Sediment core apparatus (a) SOD incubation apparatus used in this study. (b) Sediment core apparatuses used in previous SOD measurements (Redrawn from Monenco, 1992)

To test mixing efficiency of the internal stirring mechanism, 1% wt Rhodamine dye was introduced to the tubes with mixing and without mixing respectively as a tracer. The test results showed that the time required for complete mixing were 3 minutes and 24 minutes for with and without the internal stirring mechanism setups, respectively (See Figure 3). Obviously, the internal stirring mechanism provided an efficient mixing for the water column within the tube.

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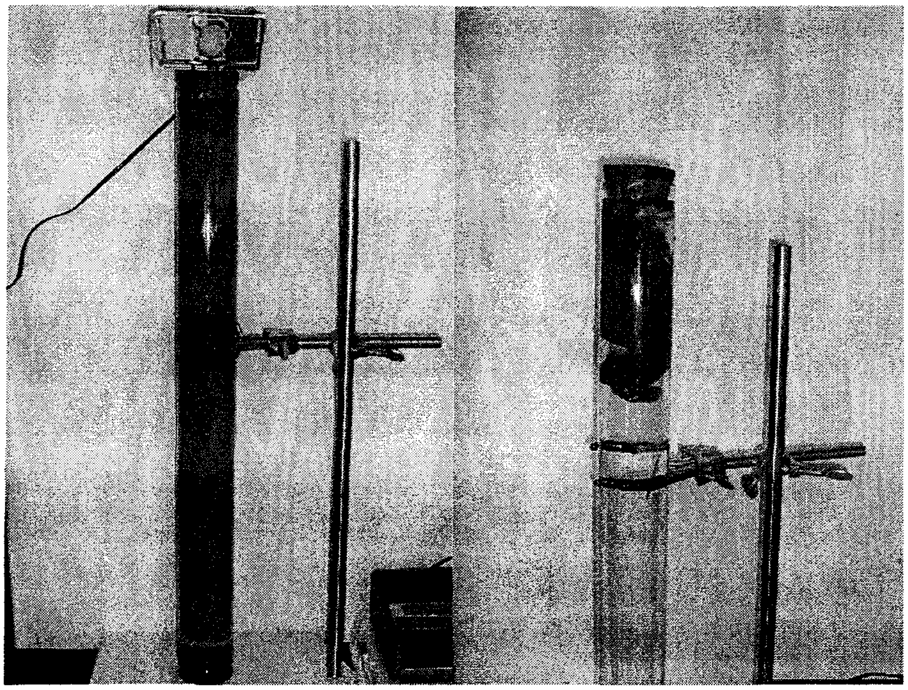

(a) (b)

Figure 3 Mixing efficiency test of the internal stirring mechanism (a) Core with mixing mechanism (b) Core without mixing mechanism

For successful collection of core samples, fine sediments ranging in depth from 5 to 15 cm were required.

After the disturbance of substrate was avoided, the polycarbonate coring tube was pressed firmly into the fine sediment until the undisturbed top of sediment core was 5 to 15 cm from the bottom of the tube. Then floating stir bar was gently put into the top of the core. The top was sealed and the core was gently extracted and the bottom sealed prior to removal from the river. Once the coring device was gently rotated out of the substrate; a rubber stopper was inserted in the bottom of the tube immediately. Water

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was added to the tube where the water depth of the river was less than the length of the tube. River water was collected with the same device to make blank samples. DO concentration was measured at the same time and the same site using Winkler titration and DO meter. Both the core and blank samples were placed on a rack in a cooler.

Sample temperature was maintained at 0 °C throughout incubation for most sediment core by packing the cores in ice. In order to detect the influence of temperature on SOD, two cores were incubated in a 10 °C water bath. Light penetration and possible photosynthetic activity were provented.

To investigate the impact of stratification on SOD measurement, some paired cores were incubated with and without mixing.

After 24 or 48 hours of incubation, average depth of water overlying the sediment in the each tube was measured. Water samples were collected from the cores into 300ml BOD bottles. Manganous sulfate and alkaline-iodide-azide reagent (APHA, 1992) were added immediately to the sample and mixed. Winkler titrations were conducted within 6 hours.

SOD was calculated using the following formula:

$$\mathrm{SOD}(\mathrm{gO_2\,m^{-2}\,d^{-1}}) = 0.024\,D\,(b1-b2) \qquad (3\text{-}1)$$

where, 0.024 is a constant for converting mg L^{-1} h^{-1} to g m^{-2} d^{-1}; D is the depth of water column (m); b1 is the change in DO inside core with sediment (mg O_2 L^{-1} h^{-1}); b2 is the change in DO inside blank core without sediment (mgO_2 L^{-1} h^{-1}).

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3.1.2 Comparison Between Sediment Core and Closed Chamber Methods

The comparison of two SOD measurement methods (sediment core method and closed chamber method) was conducted at a site on the North Saskatchewan River near E. L. Smith water treatment plant on December 2, 2004.

The closed chamber method Figure 4 used in the Athabasca River was developed by Casey and Noton (1989). The basic design was a stainless steel base with a removable lid. The base had a flat rim welded on the top with a rubber gasket attached. On the underside of the lid, a gasket made of closed-cell foam was attached. The foam and rubber gasket made a complete seal between the base and lid of the chamber. Four snap-down clips welded around the top of the chamber secured the lid in a watertight seal (Casey and Noton, 1989).

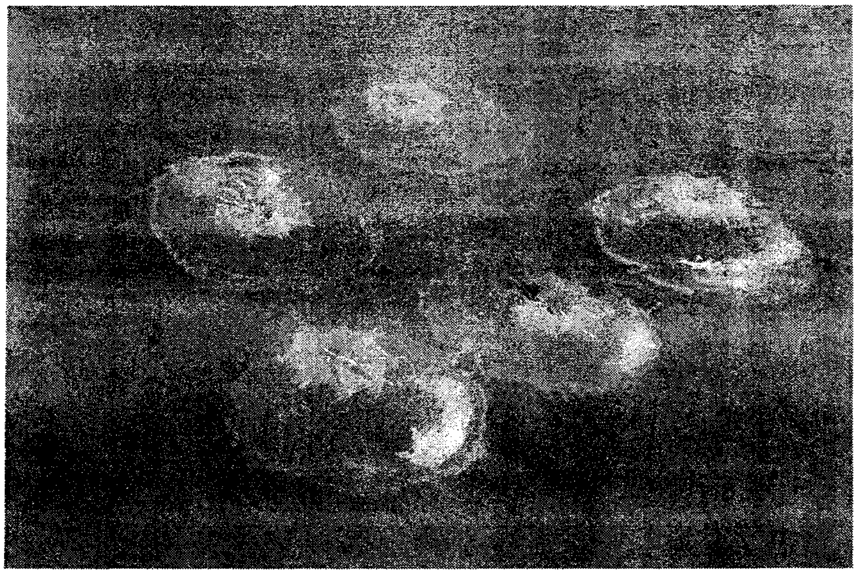

Figure 4 Closed chambers

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In order to maintain mixing of the water inside the chamber, a mixing mechanism (termed a water vane) was mounted in the lid of the chamber. The water vane was constructed of stainless steel and included a central rod and axle, with spokes on either end. Polypropylene funnels were fitted onto the spokes to serve as cones on the water vane. Three portholes in the lid were used to obtain measurements and water samples from inside the chamber (Casey and Noton, 1989).

Sediment core is same as described in section 3.1.1.

The location was selected suitable for both closed chamber and sediment core. The spot selected to deploy both methods was dictated by limitations of substratum, water depth, and velocity. The maximum depth and velocity in which both chambers and cores could be safely deployed was 60cm and 60cm/s, respectively.

Sediment was placed in the chamber carefully in a similar condition as that found *in situ*. Chambers containing substratum were gently filled with river water and placed on the riverbed without the lid. The chambers were left in position, without the lid, to allow the suspended sediment to settle in the chamber or flush clear in the current. The lids, with the porthole stoppers removed, were placed gently on the chamber so as not to trap air. The foam gasket was checked to insure it was fitted correctly around the edge of the lid (Casey and Noton, 1989). A control chamber without sediment was as a reference for water column oxygen demand.

Chambers were left in the river for 24 hours. After the incubation, dissolved oxygen was

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measured by the Winkler method. Samples were obtained through the tube on the top of chamber. Before taking a sample, the water vane was rotated several times to ensure the chamber contents were mixed. Water was withdrawn from the chamber into a 300 ml BOD bottle. Manganese sulfate and alkali-iodide-azide reagent were added immediately to the samples and mixed. The samples were taken back to lab and titrated within 6 hours (APHA, 1992). Oxygen demand of the water column was obtained by the controlled chamber.

Sediment oxygen demand was calculated using the following formula:

$$\text{SOD}\ (\text{g}\ O_2\ \text{m}^{-2}\ \text{d}^{-1}) = 0.024\ D\ (b1-b2) \qquad (3\text{-}3)$$

where, 0.024 is constant, converting mg/L/h to g/m^2/day. D is the average depth of water column (m) in the chamber. b1 is change in DO inside chamber with sediment (mgO_2/L/h). b2 is change in DO inside control chamber without sediment (mgO_2/L/h).

At the same location and same time, the samples were collected using sediment cores; the procedures were same as that described in section 3.1.1. The incubation was conducted in cold room (4 ^{o}C) after transported from the sampling site.

3.1.3 Investigation of the Impact of Organic Carbon and Nutrients Using Microelectrode Method

The study described in section 3.1.1 suggested the organic carbon content and nutrient content in sediment might influence oxygen depletion by sediments. In addition, the

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impacts of adding nutrients and organic carbon alone and in combination on the sediment oxygen demand are essential in determining loading limits for pulp mills on Northern Rivers in Alberta. Oxygen microelectrodes can be used in the laboratory to measure SOD under controlled conditions and was chosen as the method to investigate the impacts of organic carbon and nutrient enrichment on SOD.

A short sediment core sampling device consisting of an acrylic tube (150 mm diameter, 100mm long), an acrylic flat plate (15mm in diameter, 3 mm in thickness), and a glass petri dish (Fisher Scientific, 08-747F 150×20mm) were used to collect a sediment sample suitable for microsensor work.

Combined oxygen microelectrodes were fabricated in the laboratory before short sediment cores were sampled. The fabrication followed the procedure described by Lu and Yu (2002). An additional step was added to coat a protein layer on the microelectrode tip in order to enhance its mechanical strength. The protein coating followed the procedure described by Li (2001) and Tian (2005). Eight oxygen microelectrodes were fabricated and utilized in this study. The tip diameter ranged from 15 to 40 μm and, therefore, created almost no physical or chemical distortion when they were inserted into the sediment.

A micromanipulator (World Precision Instruments Inc., Sarasota, FL, USA; Model M3301R) was used to provide precision control on the movement of the microelectrodes. And a picoammeter (Unisense, Denmark, Model No. PA2000) was used to measure and convert the low-level current signal from the microelectrode. The DO concentrations at

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certain depths of sediment were determined after the proportionality between current signal and oxygen partial pressure was obtained by microelectrode calibration.

The soluble organic carbon stock solution was the mixture of 5000 mg/L glucose and 5000 mg/l glutamic acid. It was prepared by dissolving 1 g glucose and 1g glutamic acid in 200 ml distilled water (APHA, 1992). The solution contained 4 mg /ml total organic carbon (TOC). The particulate organic carbon source was cooking starch (Tapioca starch, Erawan Marketing CO. LTD, Product of Thailand). The nutrients (N and P) stock solutions were a) phosphate buffer solution made by dissolving 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4.7H_2O$, and 1.7 g NH_4Cl in 1 L distilled water, and b) ammonium chloride solution made by dissolve 1.15g NH_4Cl in 500ml distilled water, the NH_4CL solution was adjusted to pH of 7.2 with NaOH solution, and dilute to 1 L. The nutrients stock solutions contained 9.68mg/ml total phosphor (TP) and1.5 mg/mL total nitrogen (TN)(APHA, 1992).

In order to determine the appropriate incubation time, which can show the effects of the additions of organic carbon and nutrients, experiments (Experiment 1 and Experiment 2) were designed and conducted.

Short sediment cores were sampled from the Athabasca River at the location of upstream of Al-Pac on September 2, 2005. For successful collection of short core samples, fine sediments ranging in depth from 5 to 8 cm was required. A plastic bucket was filled with river sediment about 100 mm in height. After the disturbance of substrate was avoided, the acrylic tube was pressed firmly into the fine sediment in the river until the

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undisturbed top of sediment was over 5 cm from the bottom of the core. The core and the sediment around the core were shoveled out the river. An acrylic flat plate was inserted carefully onto the bottom of the core under sediment. The short sediment core and the plate were gently taken off the shovel and put in a glass dish. The glass dish containing sediment core and plate was put into the plastic bucket filled with 100 mm height sediment. And they were pushed into the sediment to minimize disturbance during transportation. The river water was added to the bucket. More river water was collected in carboys. Four sediments were collected for this set of experiments.

After the sediment cores were transported back to the laboratory at the university, two short cores with sediment were put into empty desiccators filled with 6.85 L of the river water. The water column of each desiccator was aerated with compressed air to keep the DO concentration constant. After overnight aeration the DO concentration reached saturate level. The incubation setup is shown in Figure 5.

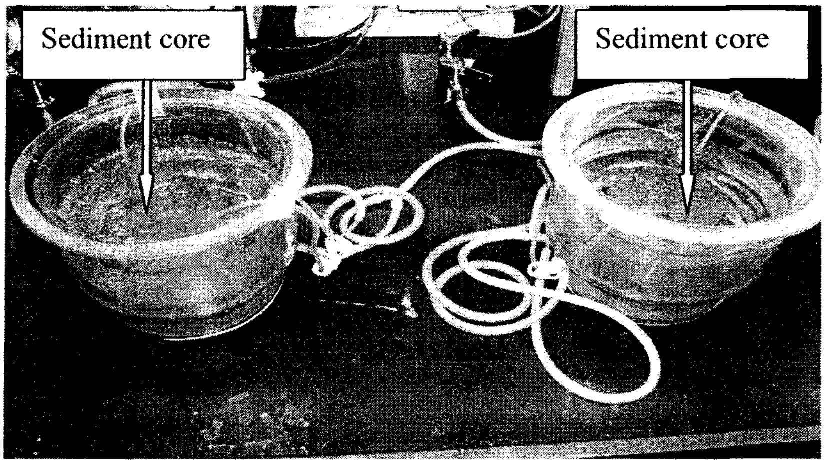

Figure 5 Short sediment core incubation setup

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Three oxygen profiles were measured for each sediment core. The three profiles were acquired at 3 random points within the same core as described in Figure 6 Locations of three oxygen profiles obtained Figure 6.

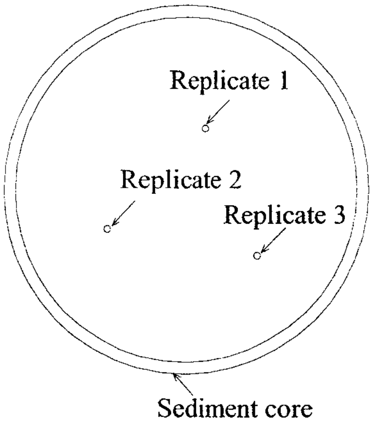

Figure 6 Locations of three oxygen profiles obtained

After the initial profile measurements, 1.5 mL of nutrient stock solution a, 45 mL of nutrient stock solution b, and 100 mL soluble organic carbon stock solution were added into the desiccator (Experiment 1). The concentrations of organic carbon and nutrients in the desiccator were 3 times of background concentrations. The background concentration was obtained based on the highest historical monitoring record of concentrations of organic carbon and nutrients in the Athabasca River. The temperature during the incubation and measurement period was 21.4-±0.3 °C. The overlying water was aerated at all times.

The profiles of oxygen concentration along sediment depth were measured using oxygen microelectrodes, which were fabricated and calibrated before sampling. The microelectrodes were polarized in de-ionized water overnight and calibrated again in raw

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river water using a picoammeter before the measurements. The short sediment core with the plate and bottom dish within a desiccator was put on the bench, which was equipped with manipulator and picoammmeter. The sediment core was raised from the bottom of the desiccator to the level where the tip of the microelectrode could reach to 3 mm below the sediment water interface within the desiccator before the profile measurement. The water depth above the sediment water interface was kept at least 3 cm during the measurement. The setup was shown in Figure 7. The electrode was introduced stepwise into the sediment from above with the aid of a micromanipulator, and the oxygen concentrations readings were taken at 0.1mm to 0.5 mm intervals. The water above the sediment was stirred and kept saturated with air by bubbling before and after measurement. The stirring was stopped when the electrode reached 2 mm above the sediment water interface. The measurement was completed in 15 to 25 minutes without stirring. As the electrode tip was hardly visible in the water, the interface between water and sediment was first approximately determined by the observation obtained from both naked eyes and under the microscope; and the interface level was then confirmed from the oxygen profiles. The position of the maximum gradient was adapted as the sediment water interface (Rabouille et al., 2003). The electrodes were calibrated for each oxygen profile in air saturated raw water, thus excluding the error of current drift during experiment. The oxygen profiles were obtained on Day 0, Day 2, Day 4, Day 8, Day 10, and Day 16 from the sediment core with additions of nutrients and organic carbon. The oxygen profiles on Day 4, and Day 10 were obtained from the control core, to which no addition of nutrients and organic carbon was applied.

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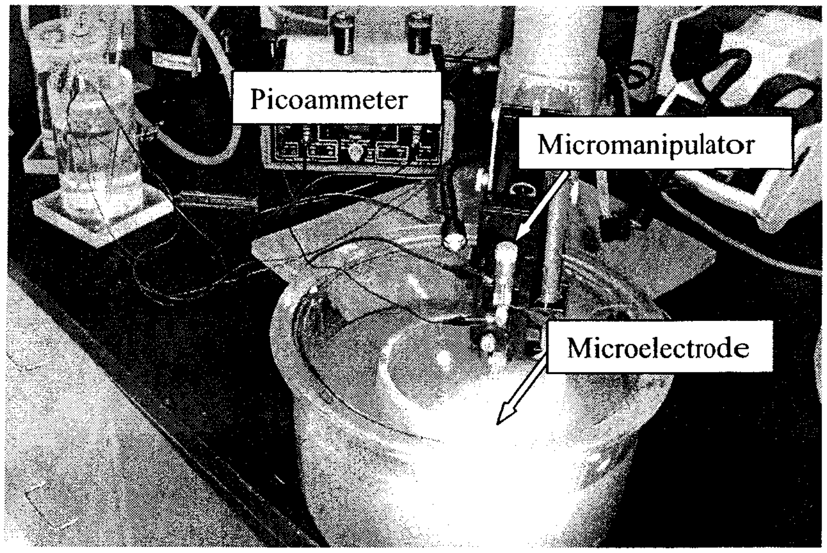

Figure 7 Microelectrode profile method setup

Another experiment (Experiment 2) was conducted by adding particulate organic carbon into a short sediment core as an extra addition besides soluble organic carbon and nutrients. Another sediment core was incubated in the same room temperature and aeration without addition of nutrients and organic carbon as control core. After the initial oxygen profiles were obtained in a sediment core before the addition, the same amount of soluble addition of nutrients and organic carbon as mentioned above in Experiment 1 and 1 g cooking starch were mixed with the raw river water which was withdrawn from the water column above the sediment core. Then the mixied solution was carefully injected back to the top of the sediment core. Thirty minutes late, the short sediment core was lowered down to the bottom of the desiccator. The oxygen profiles of the sediment were measured at 3 hours, 45 hours, 92 hours, and 240 hours after the addition. The oxygen profiles were also obtained from the control core at 0 hour and 92 hours.

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A proper approach to calculate a diffusive oxygen flux from a concentration profile is still in question and should be standardized (Viollier et al., 2003). Most researchers calculated the flux from the oxygen gradients in the diffusive boundary layer (DBL) using Fick's first law of diffusion (Revsbech, 1980a; 1980b; 1988; Jorgensen and Revsbech, 1985; Sweerts et al., 1988; Archer and Devol, 1992; House, 2002; Rabouille et al., 2003).

$$\mathrm{SOD} = J = 8460 D_s \Phi \, dC/dx \qquad (3\text{-}4)$$

where J is oxygen flux (g O_2 m^{-2} d^{-1}) and Φ is the porosity of the sediment. D_s is apparent diffusion coefficient of oxygen in the pore water (cm^2/sec). dC/dx is oxygen concentration gradient in the DBL, estimated from the oxygen profiles (mg L^{-1} mm^{-1}).

In this study, the porosity Φ, determined as the weight loss of a known volume of sediment dried to constant weight at 105 °C (Revsbech, 1980a), was 55% for the upper 0.5 cm of the sediment cores. The raw data of the porosity measurement was attached in Appendix A. D_s was interpolated from Broecker and Peng (1974) according to the bulk temperature, ranged from 2.13×10^{-5} cm^2/sec to 2.16×10^{-5} cm^2/sec. dC/dx, oxygen concentration gradient, was estimated by the maximum gradients near sediment-water interface from the oxygen profiles. The SOD values were calculated based on the oxygen profiles.

The SOD values versus incubation time curve (Figure 12), which was obtained from Experiment 2, indicated that the maximum SOD measurement was obtained after 4 days

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incubation. Therefore, the appropriate incubation time was about 4 days.

Eight short cores were collected and set up in the laboratory following the same procedure described above in Experiment 1 and 2. After overnight aeration the DO concentration reached saturation level. Three oxygen profiles for each of the eight sediment cores were measured following the procedure described above in Experiment 1 and Experiment 2. Nutrients and organic carbon were added alone and in combination into the six desiccators respectively (Experiment 3 to Experiment 6). The concentration was three times of the background concentration and tabulated in Table 3. The other two cores were used as control sediment cores. The desiccators with short sediment cores were incubated in the laboratory at room temperature for 4 days. Three oxygen profiles were measured for each of the eight sediments at the end of the incubation period.

Table 3 Concentrations of additions of nutrients and organic carbon

	The historically highest concentration (Background concentration) (mg/L)	Location	Date	Concentration of addition (mg/L)
TP (mg/L)	0.682	Athabasca	4/29/1991	2
TN (mg/L)	3.4	U/S of Confluence Pelican River	2/24/1992	10
TOC (mg/L)	19	Athabasca	7/12/1988	57

Four long sediment cores and two control cores with blank water samples were sampled following the procedure described in section 3.1. The long cores and control cores were incubated in the same conditions as the short cores for 24 hours. Two of the long

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sediment cores were incubated with mixing using the internal stirring mechanism as described in section 3.1. The other two was incubated without mixing. SOD values were measured and calculated. SOD rates were compared to those obtained from microelectrode profile method.

3.2 Results

3.2.1 Sediment Core Incubation Method Development

The survey was carried out from October 28 to November 5, 2004. Measurements of SOD were obtained at six study locations using the sediment core incubation method. They were Maskuta Ck Station (upstream of Hinton), Knight Bridge, Fort. Assiniboine, Calling River, Chisholm, and Pelican Landing. The parameters of the river in each sample site is shown in Table A1 in Appendix A. At the majority of study locations, substrates were dominated by pebble-cobble mixtures, which had only patchy deposits of fine sediment on their surfaces. The deep fine sediments located in side channels. The sediment cores were sampled from sites with fine sediment.

SOD rates measured in the Athabasca River during the period of 28 October to 5 November is presented in Table 4.

Table 4 presents mean values of several sediment cores at the same site during 24-hour and 48-hour incubation periods. The highest SOD occurred at Pelican landing and Fort Assiniboine, while, the SOD rates of Knight Bridge (24h) and Hinton upstream (48h) were low and possibly due to extreme cold conditions at the time of incubation.

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Table 4 Summary of the Athabasca River SOD rates (without mixing) during the period of 28 October to 5 November 2004

Sample Site	SOD (24h) $g/m^2/day$	SOD (48h) $g/m^2/day$
Hinton upstream	0.17	0.14
Knight Bridge	0.12	
Fort Assiniboine	0.32	
Chisholm	0.08	0.04
Calling River	0.21	0.14
Pelican Landing	0.33	0.23

3.2.2 Comparison Between Sediment Core and Closed Chamber Methods

Substratum was dominated by sand and slit mixtures at the sampling location. The atmospheric temperature was 7 °C. The water temperature was 0 °C. The river was covered by floating ice.

The SOD measurement results are presented in Table 5. The chambers provided higher SOD estimates than unmixed cores; however, they underestimated SOD rates with adequate mixing. No information is available as to the true boundary conditions experienced in the river at different flow velocities and which mixing speeds best mimic these conditions. It is likely that the *in situ* chambers do not adequately mimic mixing conditions because the mixing vanes will often not turn under winter flow velocities according to the communication with Alberta Environment staff.

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Table 5: Summary of SOD rates obtained in North Saskachwen River

SOD Measurement Method	Replicate	SOD ($gO_2\ m^{-2}\ d^{-1}$)	SOD(ave) ($gO_2\ m^{-2}\ d^{-1}$)
Cores w/o mixing	1	0.13	
	2	0.21	0.17
Cores w/ mixing	1	0.27	
	2	0.37	
	3	0.54	0.39
Closed chamber	1	0.19	
	2	0.24	
	3	0.18	0.20

3.2.3 Investigation of the Impact of Organic Carbon and Nutrients Using Microelectrode Method

Incubation time

The oxygen profiles obtained from the short sediment core with soluble additions of nutrients and organic carbon (Experiment 1) were presented in Figure 8. The penetration depth of oxygen ranged from 1.1 to 1.9 mm. The zero in depth in all profiles presents the location of water sediment interface, and negative direction presented water phase.

The profile comparison between the short sediment core with soluble additions of nutrients and organic carbon and the control core (without addition) indicated that the soluble additions (organic carbon and nutrients) did not result in an obvious change on the oxygen profiles, thus no obvious SOD change. The profile comparisons are presented in Figure 9.

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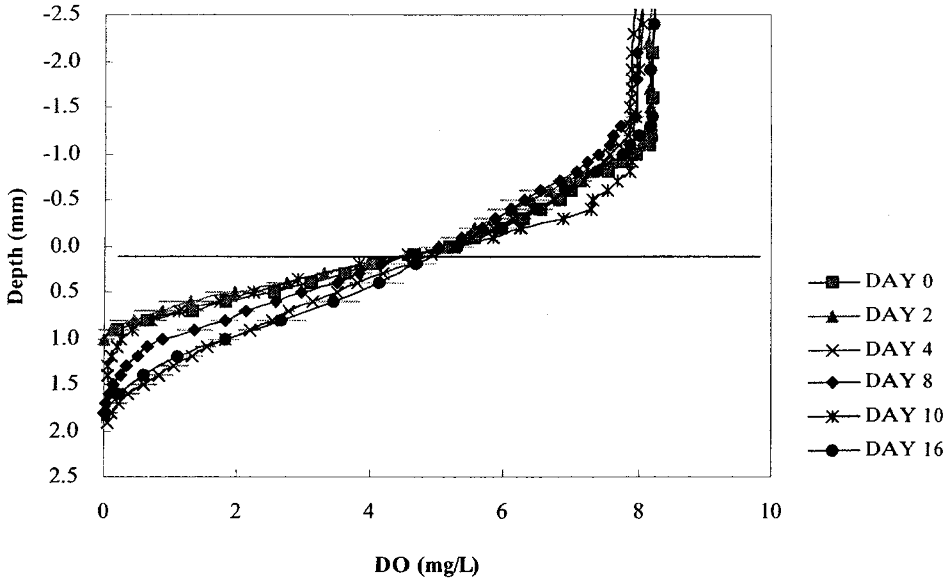
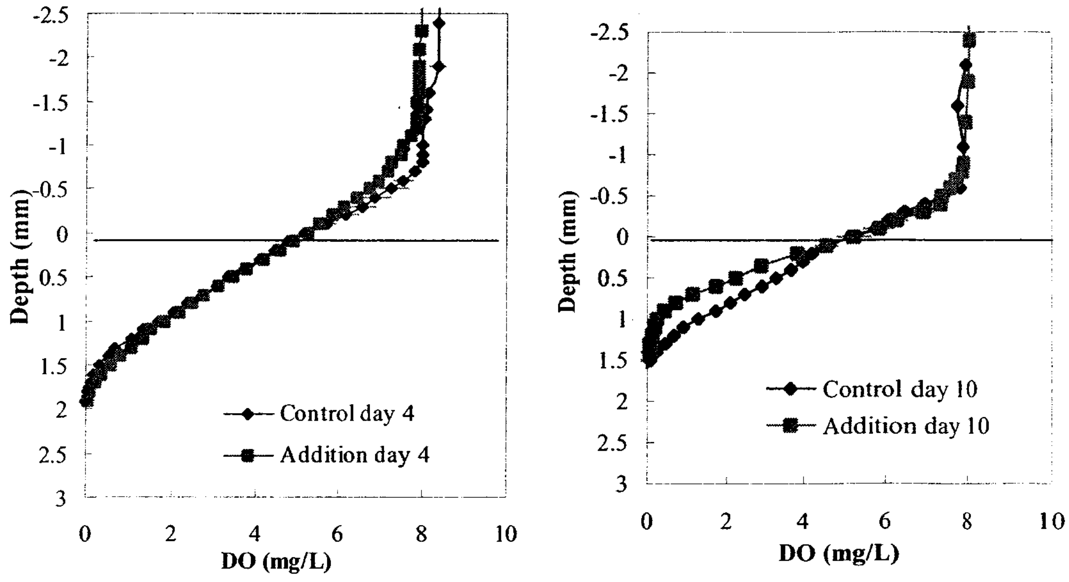


Figure 8 Oxygen profiles obtained from the short core with soluble additions



(a) (b)

Figure 9 Comparisons of profiles with and without soluble additions of organic carbon and nutrients (a) Day 4 (b) Day 10.

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The oxygen profiles were also obtained from another sediment core measurement where particulate organic carbon was added into the water column (Experiment 2). The DO concentration was plotted against the penetration depth in Figure 10. The comparison of the profiles between with additions of nutrient and organic carbon and the control core (without addition of nutrient and organic carbon) indicated that the addition of particulate organic carbon changed the oxygen profiles obviously. The profile comparisons are shown in Figure 11.

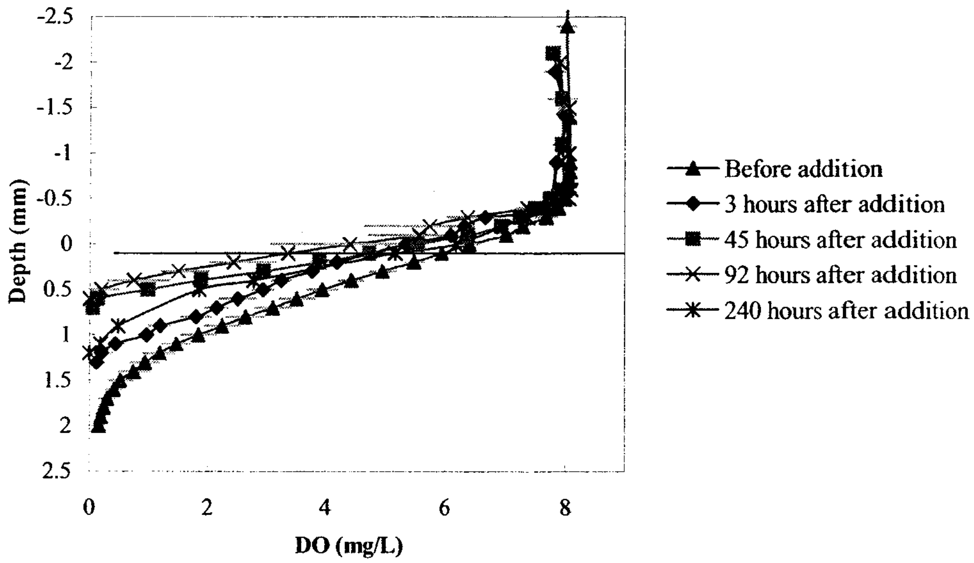

Figure 10 Oxygen profiles obtained from the short sediment core with particulate organic carbon additions

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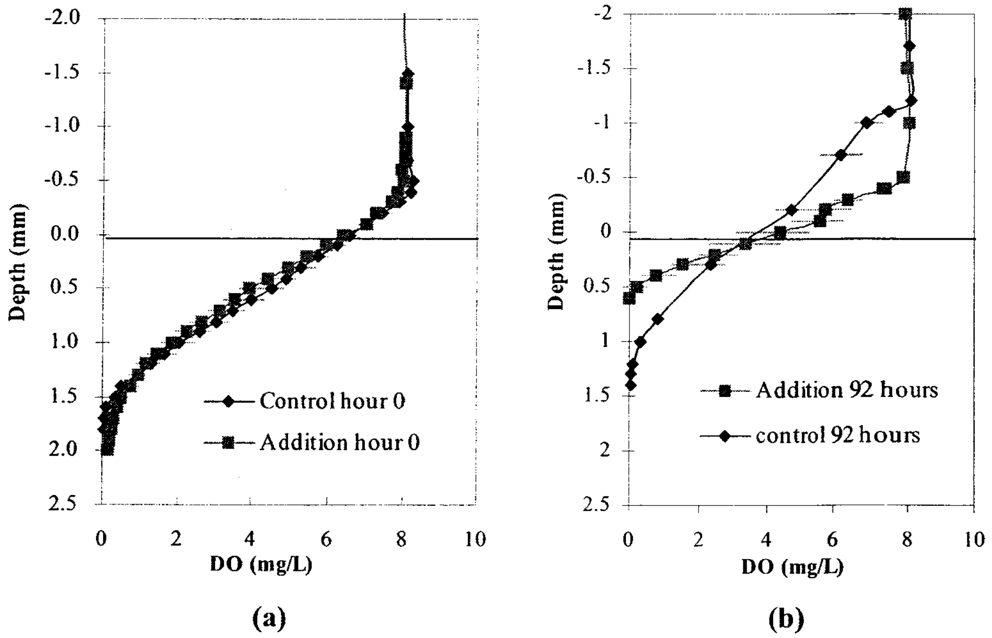

Figure 11 Comparisons of profiles with and without particulate organic carbon additions (a) Hour 0; (b) Hour 92 (Day 4)

The SOD values were calculated based on the oxygen profiles shown in Figure 11 .The curve of SOD values versus incubation time for the short sediment core with soluble and particulate organic carbon addition was plotted in Figure 12.

Figure 12 shows the trend of SOD change after organic carbon and nutrients were added into the water above the sediment. The curve indicated that the SOD value reached the highest at day 4 after the addition within the incubation period of 10 days. Hence the incubation time was determined to be 4 days for the following experiments, which were designed to further investigate the effect of the organic carbon and nutrient additions.

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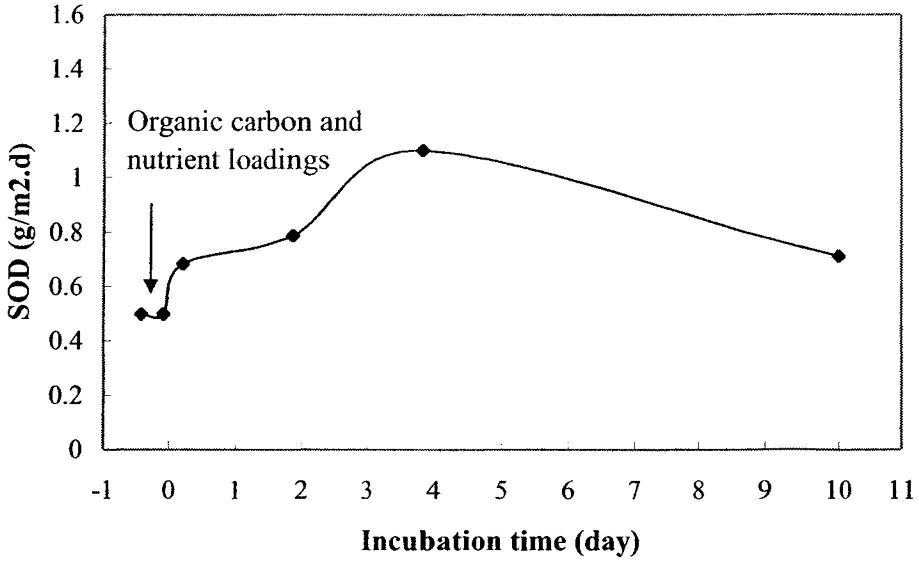

Figure 12 Curve of SOD rates vs. incubation time for the short sediment core with particulate organic carbon addition

Impact of the organic carbon and nutrients

Analyses of oxygen profiles in Figure 13, which were measured from 8 sediment cores under different organic carbon and nutrient addition conditions, indicated that the oxygen profiles did not change significantly within the 4-day incubation period for the control cores (Figure 13 a and b, Experiment 3) and the cores with soluble nutrient addition (Figure 13 c and d, Experiment 4).

Significant oxygen profile changes were observed in the cores with particulate organic carbon addition (e and f, Experiment 5) and combined addition of particulate organic carbon and nutrients (g and h, Experiment 6).

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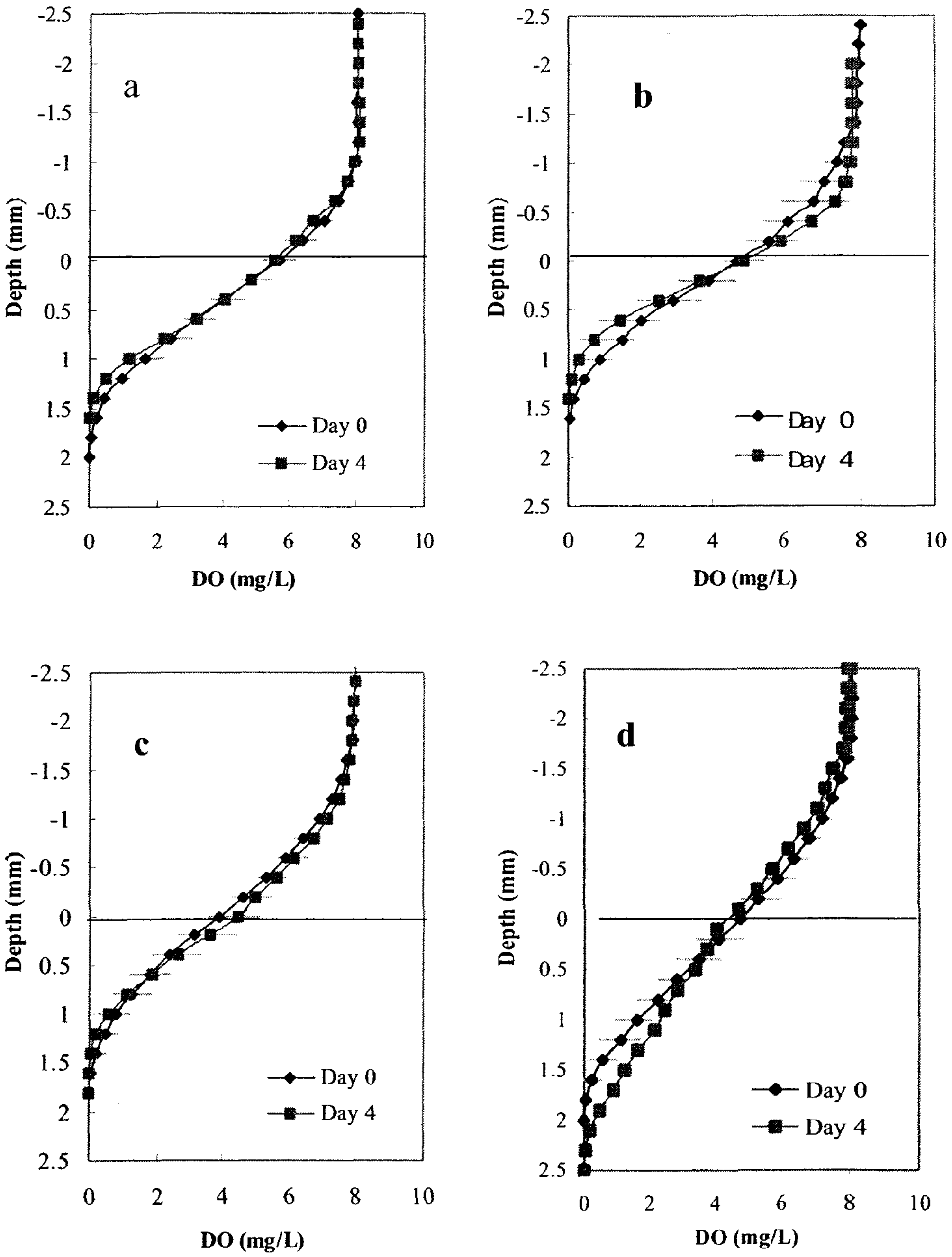
The SOD rates were calculated from these oxygen profiles by using the method explained in section 3.1.3. The SOD rates and SOD change are presented in Figure 14.



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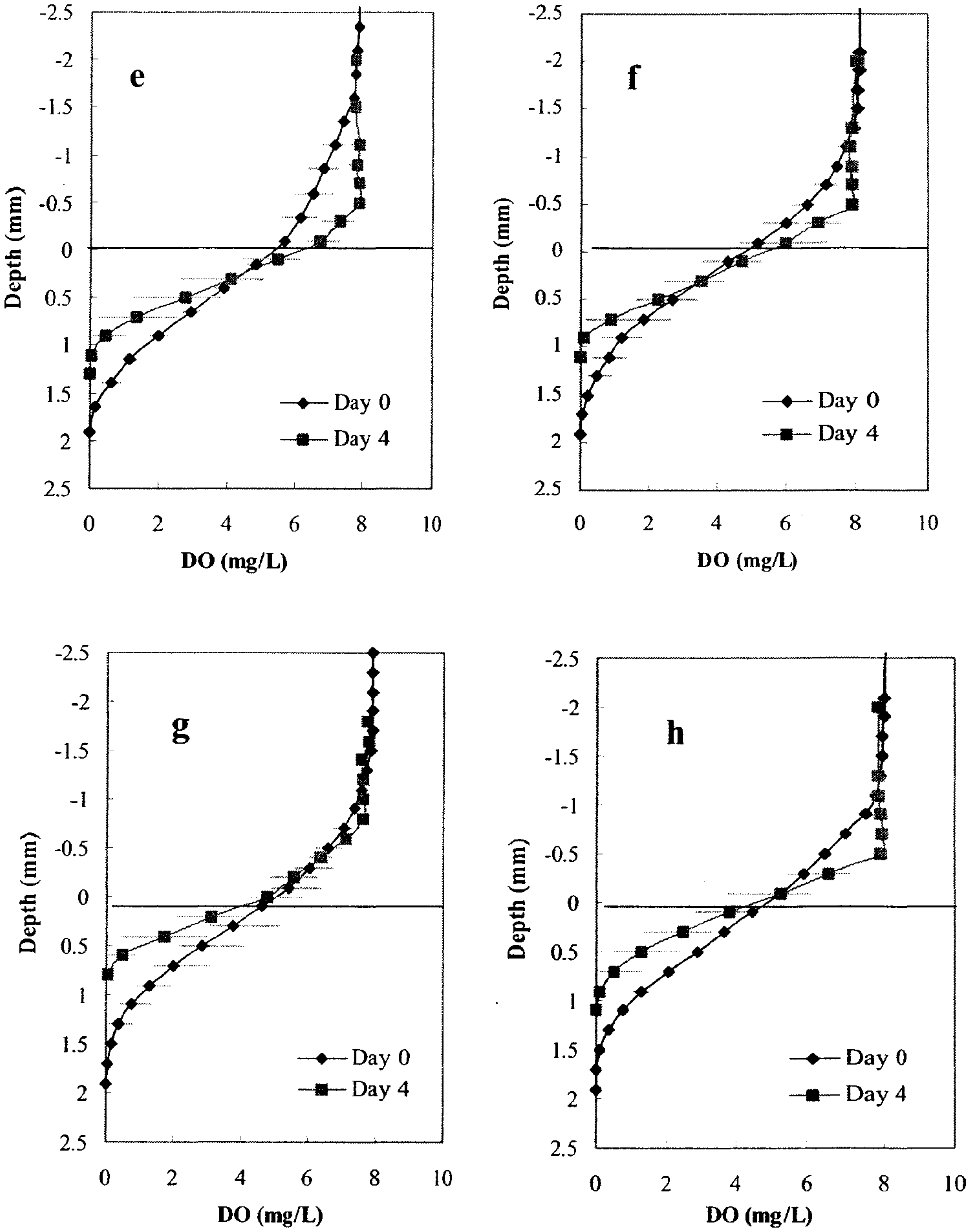

Figure 13 Profile changes in the 4-day incubation period. (a) and (b): Control cores. (c) and (d): Soluble nutrient addition (e) and (f): Particulate and soluble organic carbon addition. (g) and (h) Particulate and soluble organic carbon and soluble nutrient addition.

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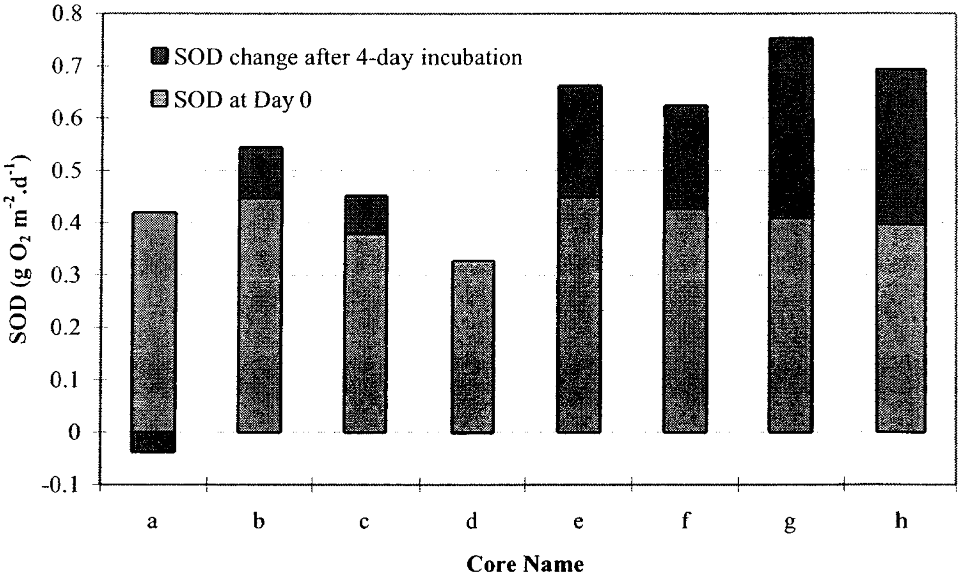

Figure 14 SOD rates and SOD change obtained using microelectrode profile method from eight cores. (a) and (b): Control cores. (c) and (d): Soluble nutrient addition (e) and (f): Particulate and soluble organic carbon addition. (g) and (h) Particulate and soluble organic carbon and soluble nutrient addition.

Comparison of the microelectrode profile method with the sediment core incubation method

Eight short sediment cores and 4 long sediment cores were sampled from the same location in the Athabasca River in the same day. Twenty-four oxygen profiles were obtained from the measurements in the eight short sediment cores (3 profiles for each core). Four SOD values were obtained from the measurements in four long sediment cores by using sediment core incubation method. Two of the long sediment cores were incubated with mixing using the internal stirring mechanism as described in section 3.1.1.

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The other two long sediment cores were incubated without mixing. The SOD rates estimated by the long sediment core incubation method were presented in Figure 15.

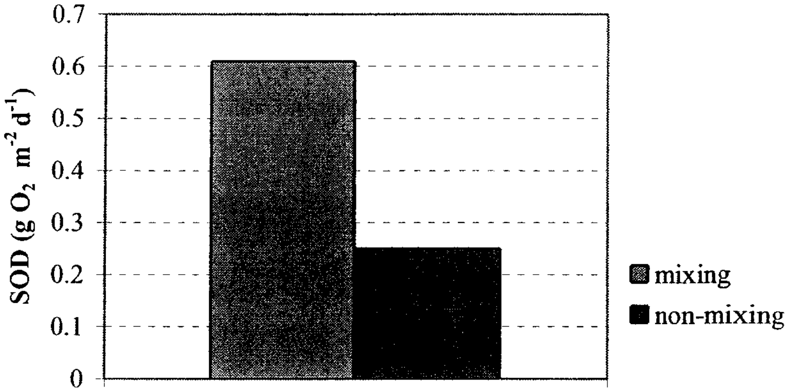

Figure 15 SOD rates obtained using long sediment core incubation method.

Figure 15 confirmed the significant impact of mixing on SOD rate as discussed in section 3.3.1 and 3.3.2.

The SOD rates estimated by microelectrode profile method were presented in Figure 16. The SOD rate for each core was calculated from the average of the three oxygen profiles. The spread of the SOD distribution was low with a factor of 1.4 between the lowest (0.33 g O_2 $m^{-2} \cdot d^{-1}$) and highest (0.45 g O_2 $m^{-2} \cdot d^{-1}$) SOD. The average SOD estimated from microelectrode method was 0.41g $O_2/m^2 \cdot d$, whereas the averages for the long sediment core incubation method with and without mixing were 0.25 and 0.61 O_2 $m^{-2} \cdot d^{-1}$, respectively (Figure 17).

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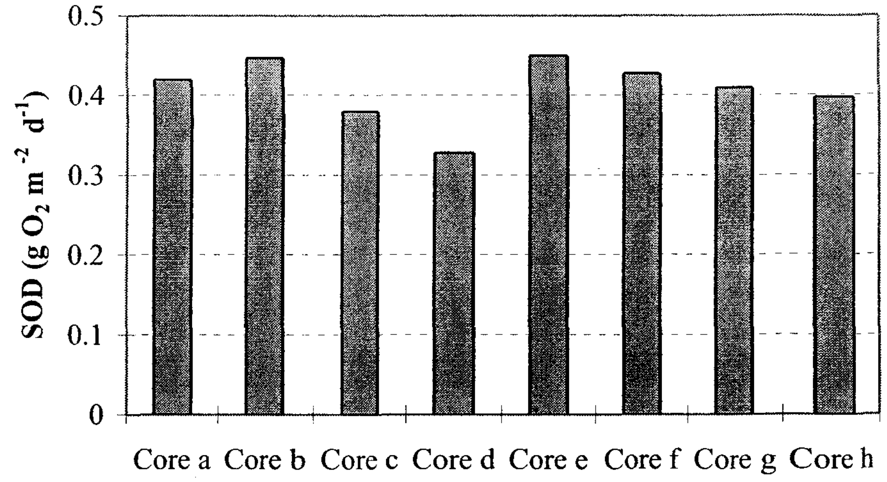

Figure 16 SOD rates obtained using microelectrode profile method (Day 0)

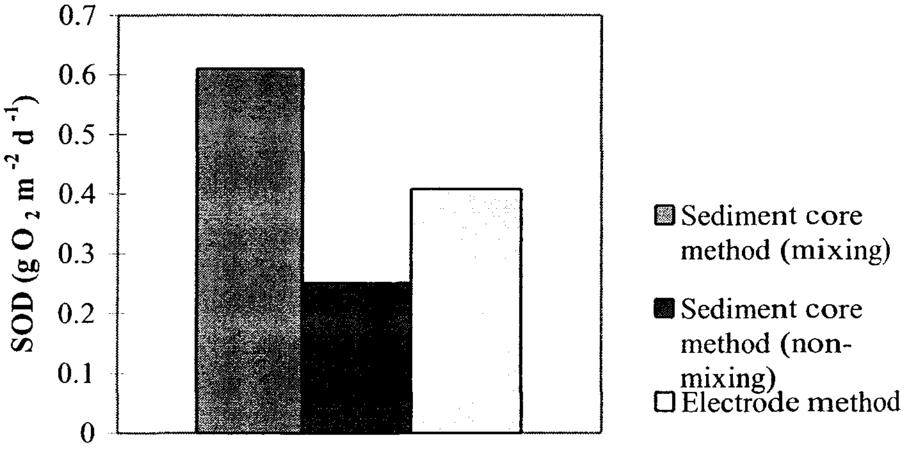

Figure 17 Comparison of SOD rates obtained from sediment core incubation method and microelectrode method

3.3 Discussion

3.3.1 Sediment Core Incubation Method Development

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Trends in SOD during the incubation period

SOD rates declined with time from 24 hours to 48 hours (Table 4). Decreasing SOD rates with time in incubation experiments can be expected due to a decrease of DO concentrations in water column (Porcella et al., 1986; Walker et al.,1986). The explicit dependence of SOD on overlying water DO concentration has also been examined experimentally and incorporated in several SOD models by other researchers (Di Toro et al., 1990). A number of investigators of the Athabasca River have attributed decreasing rate to progressively more depleted dissolved oxygen concentrations over the course of the incubation period (Monenco, 1993; Casey and Noton, 1989).

Another possible reason for the decreasing SOD rate was the decreasing biodegradable organic matter concentration and nutrient concentration in the sediments over the course of the incubation period. Previous investigators of the Athabasca River suspected that the SOD should be related to organic content of sediment. However, no relationship has been observed in the data collected to date from the Athabasca River (Noton, 1996). Given the potential relationship between SOD and sediment organic matter in the Athabasca River, as well as the potential relationship between SOD and nutrient concentration in the sediment, two depositional-zone sediment samples at each survey site were collected and analyzed for TOC/organic matter, continuous particle size spectrum, available NO_3^-, NH_4^+, and PO_4^{3-}. The trends of SOD and TOC along the river were shown in Figure 18. Figure 19 presents the relationship between SOD rate and nutrients (sum of NO_3^-, NH_4^+,

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and PO_4^{3-}), NO_3^-, NH_4^+, and PO_4^{3-}. The correlation analysis of SOD, TOC, and Nutrients is tableted in Table 6.

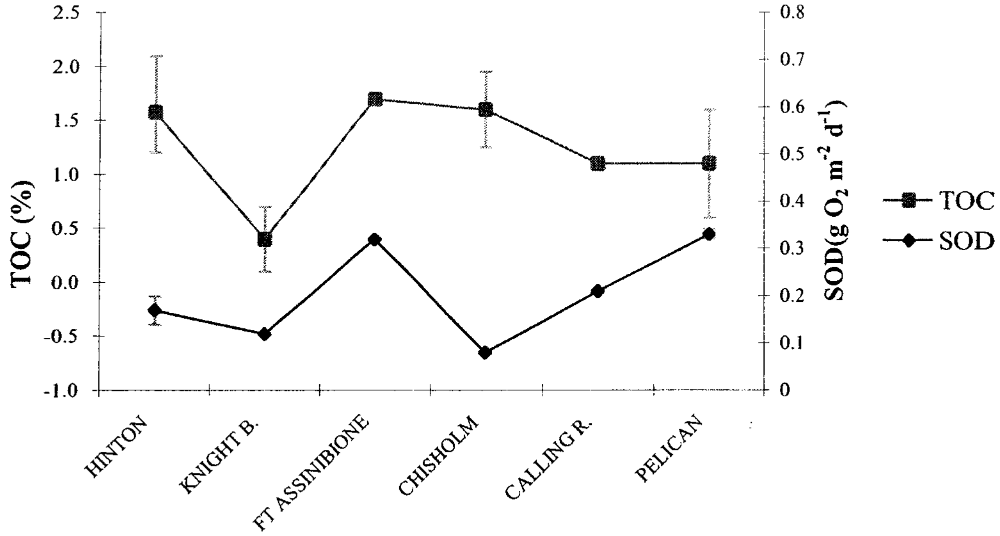

Figure 18 Comparison SOD values to TOC concentration

Figure 18 and Figure 19 showed that the highest TOC and nutrient concentrations occurred in Fort Assinibione where the SOD was high as well. The impact of organic carbon and nutrient concentration in sediment on the SOD rate required further investigation, which was carried out later in laboratory analysis as described in Section 3.3.

Table 6 Correlation analysis of SOD, TOC and nutrients

	SOD	TOC	NH_4^+,NO_3^-,PO_4^{3-}	NH_4^+	NO_3^-	PO_4^{3-}
SOD	1.00					
TOC	0.20	1.00				
NH_4^+,NO_3^-,PO_4^{3-}	0.27	0.68	1.00			
NH_4^+	0.20	0.65	0.99	1.00		
NO_3^-	0.35	-0.03	-0.55	-0.65	1.00	
PO_4^{3-}	0.31	-0.04	-0.10	-0.21	0.66	1.00

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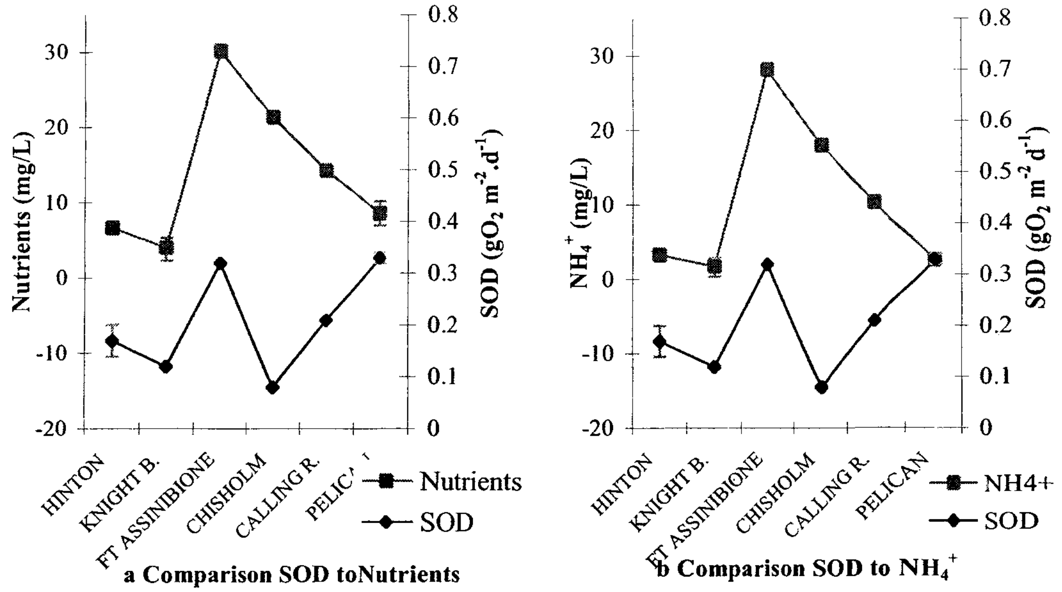
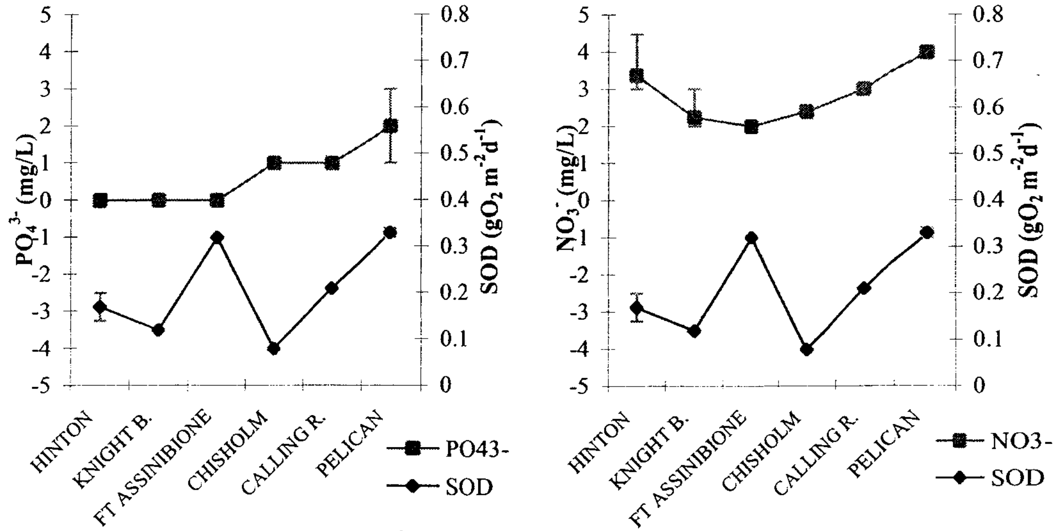


a Comparison SOD toNutrients

b Comparison SOD to NH_4^+



c Comparison SOD to PO_4^{3-}

d Comparison SOD to NO_3^-

Figure 19 SOD rate vs. nutrients (available NO_3^-, NH_4^+, and PO_4^{3-})

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Stratification of water column and the influence of mixing

Many observations showed the influence of stirring conditions of the overlying water on sediment characteristics. As demonstrated by Sweerts et al, (1988), the oxygen concentration at the sediment–water interface and the penetration depth of oxygen in the sediments decreased considerably when the overlying water was not stirred. Increases in SOD at higher flow velocity have been attributed to an increased flux of either oxygen or dissolved organic material to the sediment (Whittemore, 1986). The comparison of SOD values obtained with and without stir bar is shown in Table 7.

Table 7 Comparison of SOD values with and without mixing

Location	**SOD(gO_2 $m^{-2}d^{-1}$) without mixing**	**SOD(gO_2 m^{-2} d^{-1}) with mixing**	**Difference (gO_2 m^{-2} d^{-1})**	**Difference (%)**
Hinton	0.3	0.56	0.26	87
Fort. Assiniboine	0.58	0.81	0.23	40

The differences between mixed and unmixed incubations were over 0.23 gO_2 m^{-2} d^{-1}. With SOD calculations increasing by 40% and 87% at Fort Assiniboine and Hinton, respectively, if cores were mixed the effect of the stirring was important and brings into question the efficacy of in situ chamber incubations where stirring mechanisms often function poorly. Stirring is necessary in order to obtain accurate SOD rates. Therefore it is recommended that mixing be controlled, the relationship between mixing speed in the lab and river flow be calibrated and all previous in situ measurements made in the Athabasca River be viewed as possible underestimates of true SOD values.

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Impact of temperature

The effect of temperature on SOD has been well documented in the literature. Increases in temperature result in increased rates of bacterial respiration, yielding higher SOD rates. The effect of temperature on SOD can be represented by

$$S_B' = S'_{B,20}\,\theta^{T-20} \tag{3-2}$$

Where, S_B' is SOD rate at T °C, θ is Arrehnius relationship coefficient.

In this study, the impact of temperature on the SOD values was investigated. The influence of temperature is tabulated in Table 8.

Table 8 Comparison of SOD values obtained 0°C and 10°C

location	**SOD at 0° C incubation ($gO_2\ m^{-2}\ d^{-1}$)**	**SOD at 10° C incubation ($gO_2\ m^{-2}\ d^{-1}$)**	**Difference ($gO_2m^{-2}\ d^{-1}$)**	**Increasing %**
Hinton	0.17	0.3	0.13	76%
Fort Assiniboine	0.32	0.58	0.26	81%

In order to detect the influence of temperature on SOD, some cores were incubated at 10 °C water bath although most of the cores were incubated at 0 °C. Facilities were not available to maintain exact temperatures for the 10 °C incubation so these results should be viewed only as confirmation of the large increase in SOD that could accompany a shift in temperature from winter to early Summer and Fall temperatures, or approximately the mid range for open water conditions. Future model development should calibrate the temperature effect in the Athabasca River if open water modeling becomes important.

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Comparison to previous results

The SOD values for the Athabasca River in past years are summarized in Table 9. Most of the locations where the SOD was measured this late fall were different from the locations where we had the SOD measurements in past years (Casey, 1990; Monenco, 1992; HBT AGRA Ltd, 1993; HBT AGRA Ltd, 1994; Noton, 1995, Tian et al., 2004). The comparable locations were upstream Hinton and Calling River. For both locations, higher SOD rates were determined in this study compared to previous work. The SOD rates of previous years were obtained by *in-situ* close chamber method rather than sediment core incubation method. Therefore, a comparison between the two methods was conducted and the results were shown in the next section.

Table 9 Summary of SOD for the Athabasca River

Site	**1990**	**1992**	**1993**	**1994**	**1995**	**2004 (winter)**	Ave.	**2004 (fall)**
Hinton upstream					0.05		0.05	**0.17**
Hinton downstream		0.31		0.12	0.31		0.25	
Emerson Bridge								**0.12**
Windfall	0.01	0	0.01	0.04			0.02	
US. of McLeod River					0.12		0.12	
DS. of McLeod River	0.23	0.26		0.28	0.57		0.34	
Fort Assiniboine								**0.32**
Chisholm								**0.08**
Smith	0.08	0.15	0.11	0.1	0.2		0.13	
DS. of Lesser Slave River				0.59			0.59	
Athabasca		0.21	0.17		0.15	0.18	0.18	
Calling River					0.09	0.12	0.11	**0.21**
Pelican Landing								**0.33**

(Casey 1990; Monenco, 1992; HBT AGRA Ltd, 1993; HBT AGRA Ltd, 1994; Noton ,1995, Tian et al., 2004)

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3.3.2 Comparison Between Sediment Core and Closed Chamber Methods

Stratification of water column and the influence of mixing

In this study, in order to verify the impact of stratification which was detected during the sediment core incubation method development in Athabasca River, the same magnetic floating stir bars were deployed to stir the overlying water inside some cores to simulate the flow of river. The results showed that the mean SOD values measured from the cores with mixing were almost double the mean SOD values measured from the cores without mixing. The data both from this comparing study and from the survey in the Athabasca River during late fall of 2004 were analyzed by paired t-test. The data are tabulated in Table 10.

Table 10: Statistical test of hypothesis that mixing effects SOD determination

Pair No.	Location	SOD without mixing	SOD with mixing	Difference
1	North Saskatchwan River at E.L. Smith WTP	0.21	0.37	0.16
2	North Saskatchwan River at E.L. Smith WTP	0.13	0.27	0.14
3	Athabasca River at Hinton	0.3	0.57	0.27
4	Athabasca River at Fort Assiniboine	0.58	0.81	0.23
			Mean difference	0.20
			Total Pairs* n	4
			Degree of freedom	3
			Standard deviation	0.06
			t_0	6.61
			α	0.05
			$t_{critical} = t_{(0.05, n)}$	4.18

* 1 pair = 2 measurements

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The statistic analysis showed a significant difference between the values obtained with and without mixing.

Effect of flow velocity on SOD

In this study, three sediment cores (with internal mixing mechenism as described in Section 3.1) were incubated in a cold room. The mixing speeds of the three cores were different during incubation period. The SOD values obtained from cores are shown in Table 11.

Table 11: Summary of the effect of mixing speed on SOD determination*

Core No.	SOD (g O_2 m^{-2} d^{-1})	Mixing Rate
1	0.27	Mixed gently and stopped before incubation end
2	0.37	Mixed gently
3	0.54	Mixed rapidly

* All cores are from North Saskatchwan River and incubated in a same cold room with mixing.

Core 1 and Core 2 were initially mixed at the same speed; however, the stir bar stopped in core 1 sometime during the incubation. A more powerful stirrer was used to stir the Core 3, which produced a higher SOD (0.54 g O_2 m^{-2} d^{-1}) compared to the SOD values obtained from Core 1 and 2. These results indicated the mixing speed is an important factor on SOD measurement.

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Impact of temperature

In this investigation, the incubation temperature of chambers was 0 °C degree; the cores were incubated in a 4 °C cold room. In order to eliminate the effect of the temperature, the SOD values were adjusted according to the Arrehnius relationship (3-2). Various values of θ have been reported in the literature. The most common reported value of θ is 1.065 (Truax et al., 1995) which is the value used in the calculation. The SOD values before and after modification are presented in Table 11. And the adjusted SOD values obtained from core method were compared to the SOD obtained from closed chamber method. The comparison shows that sediment cores with mixing provided higher SOD estimates than the closed chambers, whereas sediment core without mixing provided lower SOD values. Therefore, the sediment core incubation method is comparable to the closed chamber method. Furthermore, core method allows adjusting flow and temperature to match actual ambient conditions in a river.

Table 12 SOD values before and after the adjustment for tempature

Method	**SOD (ave) (g O_2m^{-2} d^{-1}) 4°C**	**SOD (ave) (g O_2m^{-2} d^{-1}) 0°C**
Cores w/o mixing	0.17	0.13*
Cores w/ mixing	0.39	0.29*
Closed chamber		0.20

* Adjusted SOD values obtained from core method.

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3.3.3 Investigation of the Impact of Organic Carbon and Nutrients Using Microelectrode Method

Potential biases on the determination of SOD rate by microelectrode method

Some methodological issues that have the potential to introduce biases into the results are addressed in this section. The observed variation of the SOD rates determined from oxygen profiles could partially be attributable to the method used to determine the sediment-water interface. Since the diffusive boundary layer could not be observed directly by naked eyes or by using microscope, the sediment-water interface was determined to be at the position of the maximum gradient near the approximate interface, which was estimated by direct observation. The SOD rate was then determined using this maximum gradient with two successive oxygen concentrations readings at the sediment-water interface. Although this method of determination of the sediment-water interface was used by many researchers (Revsbech, 1980a; 1988b; Jorgensen and Revsbech, 1985; Sweerts et al, 1988; Archer and Devol, 1992; House, 2003; Rabouille et al., 2003), it has the potential to introduce biases into the results, contributing to the observed variability. Therefore, the SOD rates obtained in this study were determined using the average of three profiles measured at three random points within a core to minimize the potential bias. Furthermore, The SOD values obtained in this study exhibited low variation and small error bars in all oxygen profiles. Three repeated measurements of oxygen profiles at different points within the same sediment core demonstrated that the gradient was reproducible.

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The heterogeneity of the sedimentary environment could be another source of potential bias. The variability of the SOD rates obtained from the eight sediment cores, although not significant, was linked to the heterogeneity. In order to further minimize the bias introduced from heterogeneity, the sediment cores were sampled at the same location of the river. Moreover, the three oxygen profiles measured at three random points within a core were averaged to minimize the bias due to the heterogeneity within a core. Figure 17 shows the heterogeneity among different cores. It suggests the degree of heterogeneity was insignificant.

Comparison of the SOD values obtained from microelectrode method and sediment core incubation method

The two techniques (sediment core incubation and microelectrode profiles) used during this study to determinate the SOD provided different insight on the diagenetic system. The core incubation method is primarily associated with the surface area of the core (28 cm^2, in this study). The SOD rate estimated by core incubation integrated all processes related to oxygen transfer within the incubation period (24 hours in this study), which include diffusion and advective movement of pore water induced by faunal activity. Hence, it was considered as total flux, or total SOD rate (Rabouille et al., 2003). In contrast, the microelectrode method is primarily associated with the trasport of chemical species accomplished by molecular diffusion excluding the other traport processes.

Previous studies (Lindeboom et al., 1985; Archer and Dveol, 1992; Rasmussen and Jorgensen, 1992; Glud et al., 1994; Rabouille et al., 2003) have found a factor of 1 to 4

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between total and diffusive oxygen demand in different oceanic sedimentary environments. However, to my knowledge, there has been no report of this factor in river sedimentary environment in the literature. In this study, the diffusive flux (SOD rate obtained from microelectrode method) was between the SOD rates obtained from the incubation cores with mixing and incubation cores without mixing. Since the incubation method without mixing underestimated the SOD rate as discussed in section 3.1 and 3.2, the SOD rates obtained from the incubation cores with mixing were considered more accurate SOD rate estimates. Based on these experimental results, a factor of 1.4 between the total oxygen demand obtained by using sediment core incubation method and diffusive oxygen demand obtained by using microelectrode method was found in this study.

Effect of organic carbon and nutrients

In this study, experiments were performed under different organic carbon and nutrients addition conditions. Table **13** summarizes the addition conditions of these experiments and the changes of SOD rate and penetration depth resulted from different additions in 4 days of incubation.

The comparison between Experiment 1 and Experiment 2 revealed that the addition of particulate OC produced a significant increase of SOD rate (0.48 g O_2 m^{-2} d^{-1}) and a significant decrease of penetration depth (1.2 mm). In contrast, the decrease of 0.06 g O_2 m^{-2} d^{-1} in SOD rate and increase of 0.5 mm in penetration depth were found for Experiment 1 in which soluble organic carbon was added into the water column. That the

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addition of soluble organic carbon did not change the oxygen profiles was probably a result of organic carbon consumption in water column rather than in sediment. Once the organic carbon was added to the water column, the organic carbon was easily consumed by the aerobic microorganisms in the water column where DO was near saturation. As a result, very limited organic carbon could reach the pore water or settle down on the surface of sediment to contribute to the SOD. In contrast, the particulate organic carbon was not easily utilized instantly. Most particulate organic carbon added settled down on the surface of sediment and degraded gradually by the microbial communities in the sediment. Hence, it is more likely that the particulate organic carbon contributed to the SOD. Although some researchers have reported increased SOD rates and decreased penetration depth with increasing amount of organic matter (House, 2003; Sayles et al. 1994; Steeby et al., 2004; Tahey et al., 1994), there has been no report of SOD changes under different organic carbon conditions in river sedimentary environment in the literature to my knowledge.

Sediments used in Experiment 3 to Experiment 6 were sampled at the same location and on the same date; and the experiments were conducted at the same temperature. Experiment 3 was control experiment without any additional load. Both the SOD rate (0.03 $gO_2/m_2 \cdot d$) and penetration depth (-0.15mm) did not change significantly in the 4 days.

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Table 13 Addition conditions and the changes of SOD rate and penetration depth

	Sampling date	Concentrations of additions			SOD change after 4 days (g O_2m^{-2} d^{-1})	Penetration depth change after 4 days (mm)
		Particulate organic carbon (mg/L)	Soluble organic carbon (mg/L)	Nutrients (mg/L)		
Experiment 1 (SC+N)*	Sept. 2	0	57	2, 10**	-0.06	0.5
Experiment 2 (SC+PC+N)*	Sept. 2	57	57	2, 10	0.48	-1.2
Experiment 3 (Control)*	Sept. 23	0	0	0, 0	0.03	-0.15
Experiment 4 (N)*	Sept. 23	0	0	2, 10	0.04	0.15
Experiment 5 (SC+PC)*	Sept. 23	57	57	0, 0	0.21	-0.85
Experiment 6 (SC+PC+N)*	Sept. 23	57	57	2, 14	0.32	-0.85

** Concentration of TN, Concentration of TP

* SC: Soluble organic carbon. PC: Particulate organic carbon. N: Nutrients

The Experiment 4 was conducted with addition of 2 mg/L soluble TP and 10 mg/L soluble TN addition. No major change on the oxygen profiles was found. The possible reason was soluble nutrients was consumed in water column instead of in sediment. Hence, particulate nutrient additions were recommended in future's investigation.

Obviously, the changes of SOD rate and penetration depth were significant in Experiment 5 and Experiment 6, where particulate and soluble organic carbon additions were used in the former and particulate and soluble organic carbon plus soluble nutrient additions were used in the later. The SOD rates increased by 0.21 g O_2 $m^{-2}\cdot d^{-1}$ (47%) and 0.32 g O_2 $m^{-2}\cdot d^{-1}$ (79%), respectively; and the penetration depth decreased by 0.85 mm in both experiments. Since neither the addition of soluble organic carbon alone, soluble

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nutrients alone, or the combination of both produced significant change on the SOD and penetration depth of oxygen, the conclusion is drawn that it is the particulate OC that caused the significant change of SOD in the sediment.

3.4 Summary

3.4.1 Sediment Core Incubation Method Development

The sediment core method provided easy and cheap means for quantifying SOD in small substrate sized habitats. The SOD rate decreased during incubation. The decreasing rate was attributed to progressively more depleted DO concentrations over the course of the incubation period. It is believed that the 24-hr incubation better represents the continuous replenishment of DO and organic material in a flowing river. Hence 24-hr measurements should be the basis for modeling inputs while 48-hr estimates should be adjusted by a proportionate factor to better represent the true SOD. While other studies were inconclusive, our study indicates relationships between SOD and sediment nutrient concentrations are likely. Further investigation is recommended. All future SOD estimates should be made under controlled mixing conditions. The increasing temperature produced a higher SOD. In order to obtain an accurate measurement, the temperature control during incubation period is necessary.

3.4.2 Comparison Between Sediment Core and Closed Chamber Methods

Several factors influenced SOD rates and their determination. As such the best method for determining SOD should allow for the control of these factors. While the core and

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closed chamber methods are roughly comparable, only the core method allows for a determination where flow and temperature can be adjusted to match actual ambient conditions or a range of potential conditions in a river. The sediment core method provided accurate, yet cost-effective means for SOD determination in small substrate sized habitats. Future SOD measurements made for modeling purposes are recommented to include sediment core incubation with mixing method developed in this project.

3.4.3 Investigation of the Impact of Organic Carbon and Nutrients Using Microelectrode Method

Fifty-seven oxygen profiles were measured in this study. A factor of 1.4 was found between the total oxygen demand and diffusive oxygen demand for the Athabasca River sediment at the location of upstream of Al-Pac in September 2005. The concentration of particulate organic carbon of 57 mg/L produced significant impact on SOD rate and oxygen penetration depth in the sediment. No significant impact was detected by adding soluble nutrients (2 mg/L TP and 10mg/L TN) and soluble organic carbon (57mg/L) in the water column. Particulate nutrient addition was recommended to further investigate the impact of nutrient addition.

Organic carbon and nutrients were recommended to be considered as important constituents in the effluents from municipalities and industries, which can affect the SOD rate, thus affect the DO balance of the Athabasca River. Therefore, the amount of organic carbon and nutrients entering the river should be limited.

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4 CE-QUAL-W2 Model Calibration

During the Athabasca River simulation using WASP by Tian (2005), the limitations of WASP were noticed when more accurate predictions were needed. The limitations include the inability on predicting the ice cover that was critical for the reaeration. Furthermore, WASP was unable to simulate hydrodynamics for the situations when the flow rates varied rapidly. As a result, when WASP was used in the multi-dimensional schematization, another hydrodynamic model would be needed. Through a thorough analysis on a variety of water quality models, a two-dimensional hydrodynamic and water quality model, CE–QUAL–W2, was employed to model the Athabasca River in this study.

In this study, simulations were undertaken for the winter period only, which was defined as October to April. The modeling in this study was intended to determine the suitability of the CE-QUAL-W2 model to provide continuous winter DO simulation capacities for the Athabasca River.

4.1 Model Preparation and Data Input

According to the past years monitoring of the DO concentration in the Tabasco River, the lowest DO concentration occurred at upstream of Grand Rapids (Noton and Allan, 1994) where it serves as a major spawning area for fish, such as lake whitefish and walleye (Alberta Environment, 2005). Hence, accurate DO concentration prediction is critical in order to satisfy the levels of dissolved oxygen needed for fish and other aquatic

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organisms, especially during the winter months, when ice cover blocks contact with the air and DO levels dwindle.

Therefore, the modeled section should include the upstream of Grand Rapids. Considering other factors, e.g. the availability of data, the modeled section of the Athabasca River was chosen from Athabasca to Grand Rapids, as shown in Figure 18. The length of the section is 259.63 kilometers.

In order to model the system, the following data are required and input:

- Bathymetry of the river;
- Flow, temperature, and water quality characteristics for boundary conditions, major tributaries, and point sources;
- Meteorological conditions.

Alberta Environment has been collecting data on the Athabasca River and has provided them to this study. The available data were reviewed and analyzed to determine the model simulation periods and assemble model boundary conditions and tributary data.

4.1.1 Model Geometry

Bathymetry data

Alberta Environment provided riverbank and channel elevations and cross-sections from the river survey conducted in 1974-1975.

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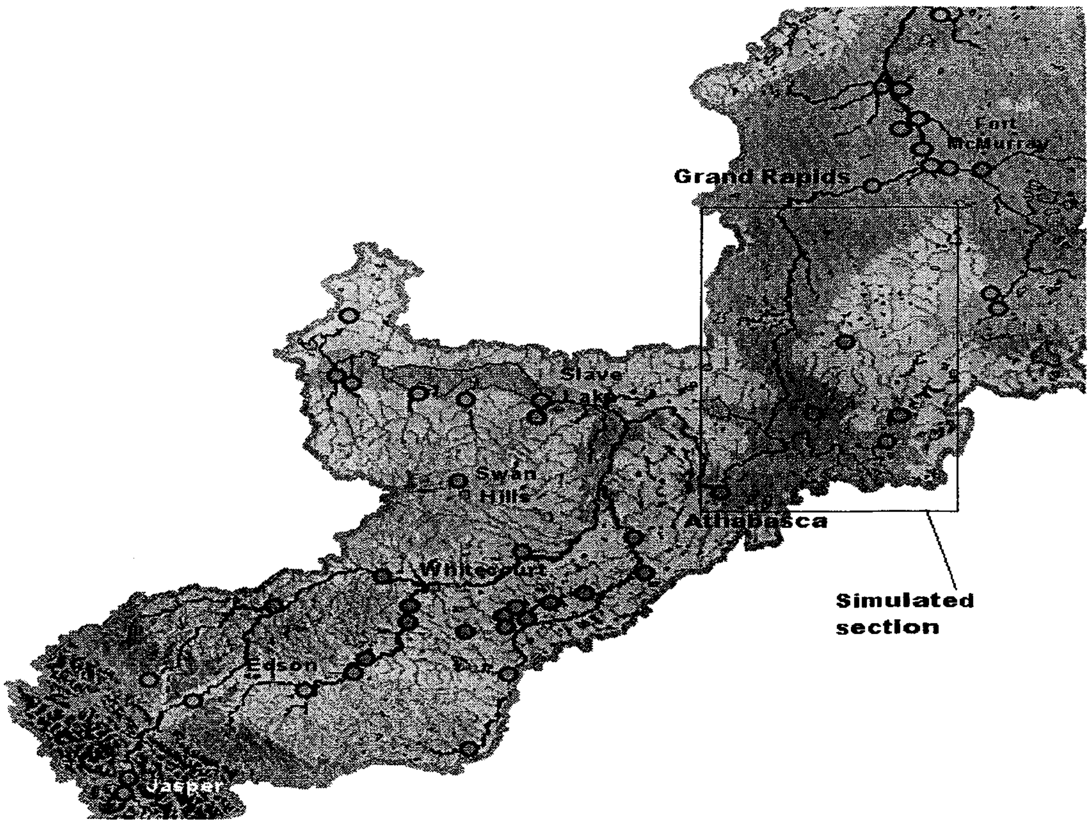

Figure 20 Athabasca River basin and simulated section (Adapt from Alberta Environment, 2005)

Model grid development

The river was modeled with 102 longitudinal segments, each 1630 to 5300 meters long. Vertical grid layers were set at a thickness of 1.5 to 2.0 meters (Figure 21). Figure C1 (in Appendix C) and Figure 22 show the model segments and branch locations, and Figure 23 shows a vertical profile of the river bottom. As this figure shows, the river has four distinct slopes through the section being modeled. From river meter 0 to 118800, the slope is 0.00026, and 0.00058 from 118800 to 162630. The slope from 162630 to 200630 is 0.00085. The 0.00056 is the slope from 200630 to 259630. According to the slope

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breaks and the locations of tributaries and some municipal and industrial discharge, the modeled section of the river was modeled as nine separate water bodies. Each water body contains a branch.

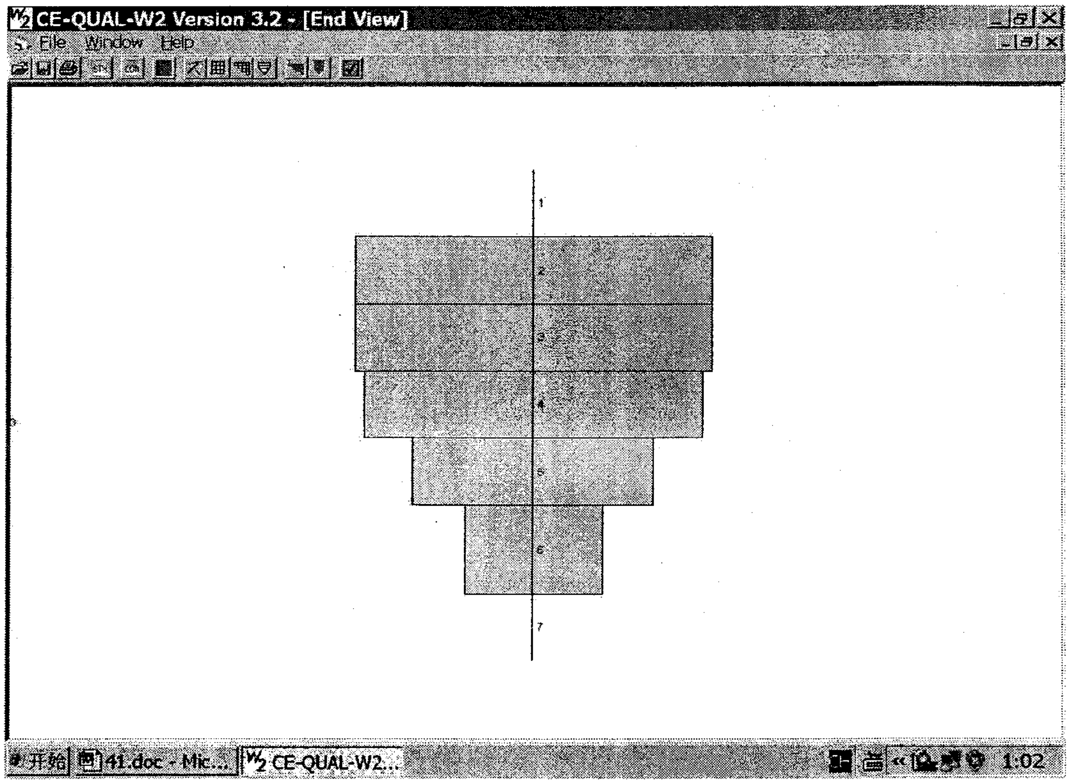

Figure 21 Vertical grid layers

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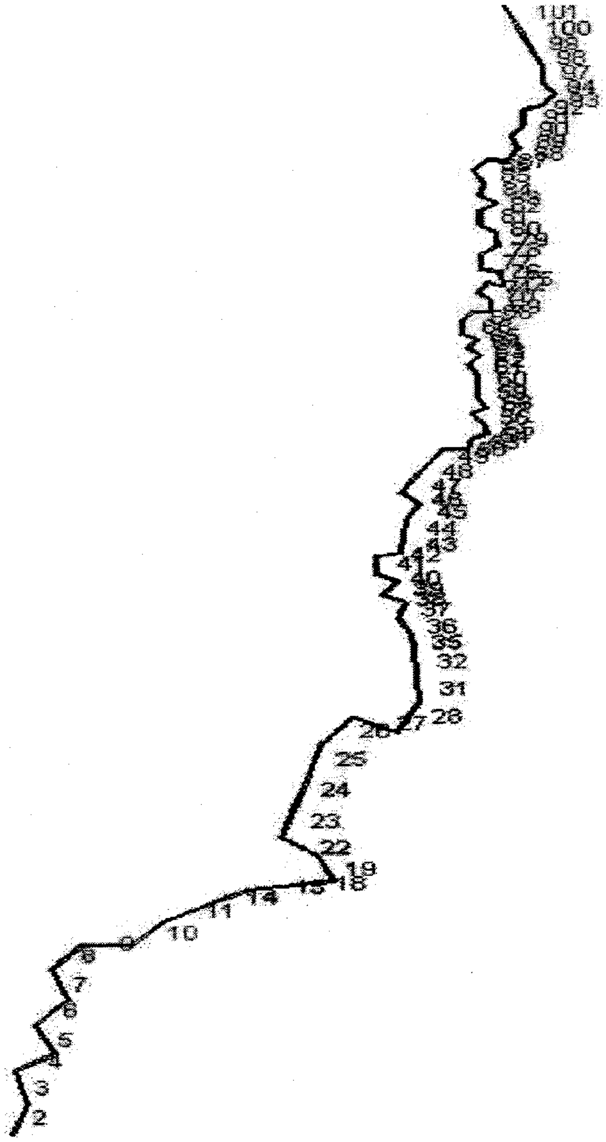

Figure 22 Model segments locations

Table 14 provides a breakdown of the water bodies and segments. The segment numbers in the table include the “null” segments that divide each branch.

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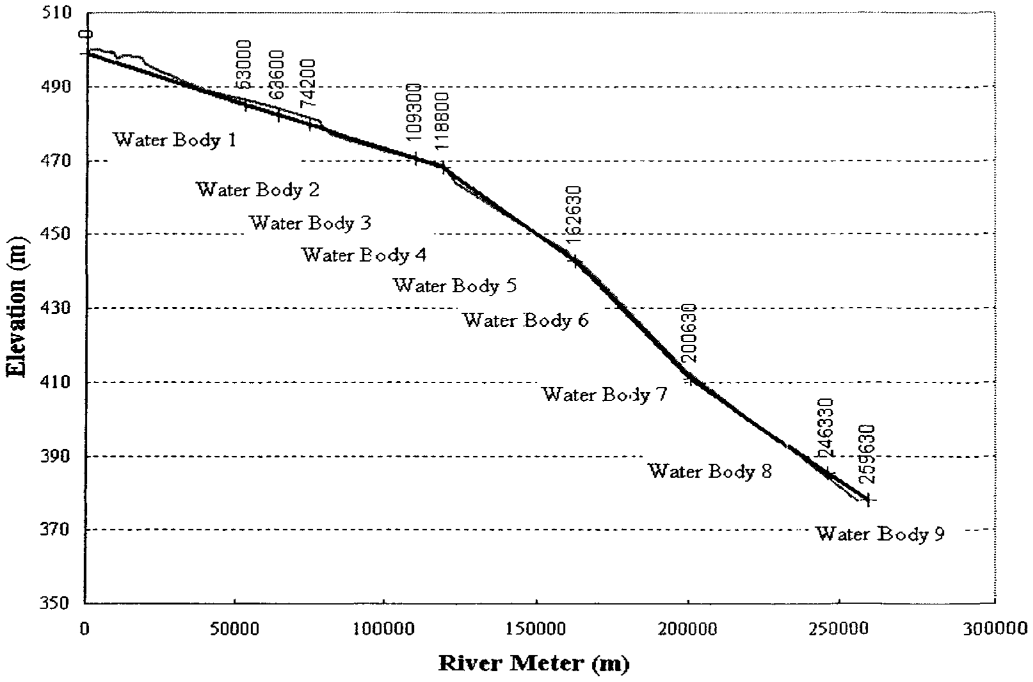

Figure 23 Profile of actual and averaged Athabasca River channel bottom

Table 14 Water body characteristics

Water Body	Description	Segment Start	Segment End	Number of Segment	Average Slope
1	From the Town of Athabasca	1	12	12	0.00026
2	The location of Alpac discharge	13	16	4	0.00026
3	Downstream of Alpac	17	20	4	0.00026
4	Calling River Confluence	21	29	9	0.00026
5		30	33	4	0.00026
6		34	51	18	0.00058
7	Pelican River Confluence	52	73	22	0.00083
8	House River Confluence	74	95	22	0.00056
9	Upsream of Grand Rapids	96	102	7	0.00056

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4.1.2 Model Simulation Time Period

Criteria for choosing modeling run times included (Kraft et al., 2004):

- Availability of upstream and downstream boundary condition data.
- Availability of data for tributaries.
- Encompassing as many variations and extreme as possible.
- Comparability to other models (e.g. WASP)

There are two long-term monitoring stations within or near the modeled section in the Athabasca River which recorded the water quality data from 1987 to March 2003. The flowrate of the Athabasca River are available from 1958 to 2003 in the Athabsaca and below Fort McMurry. Some meteorological data are available from 1957 to 2005 in Athabasca and Fort McMurry. The winter 2002-2003 was an extreme winter with low flowrate and low DO concentration and low air temperature.

Based on the available data and the objects of the project, the model run period were from October 18 through May 1 in four different years: 1999-2000, 2000-2001, 2001-2002, and 2002-2003 respectively.

4.1.3 Boundary Conditions

The upstream boundary is at the long-term water quality monitoring station at Athabasca, which is considered River Meter 0 in this model. The downstream boundary was upstream of Grand Rapids.

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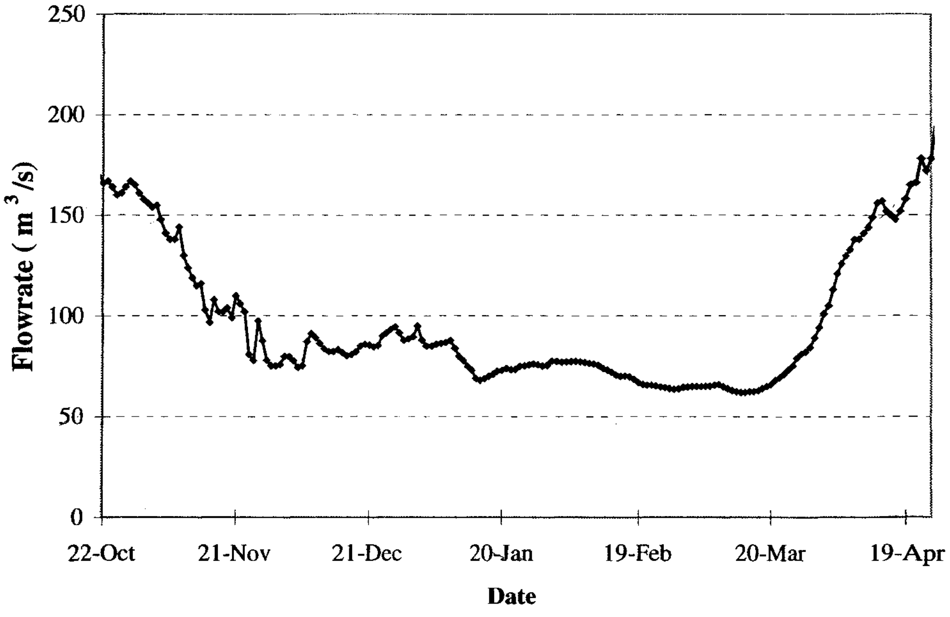
The upstream boundary condition was characterized by flow, temperature, and water quality; and the downstream boundary is characterized by water surface elevation, temperature, and water quality.

The main reason that the upstream boundary was chosen at Athabasca was that the water quality and meteorological and hydrodynamic data were relatively complete at Athabasca.

Flow

The closest flow gage to the upstream boundary was the hydrometric station of Athabasca River at Athabasca (07BE001)-(AB). Daily flow data were obtained from this gage from October 1999 to May 2003. Flow data from this gage were directly used as the flow of the upstream boundary inflow (Figure 24).



a. 1999-2000

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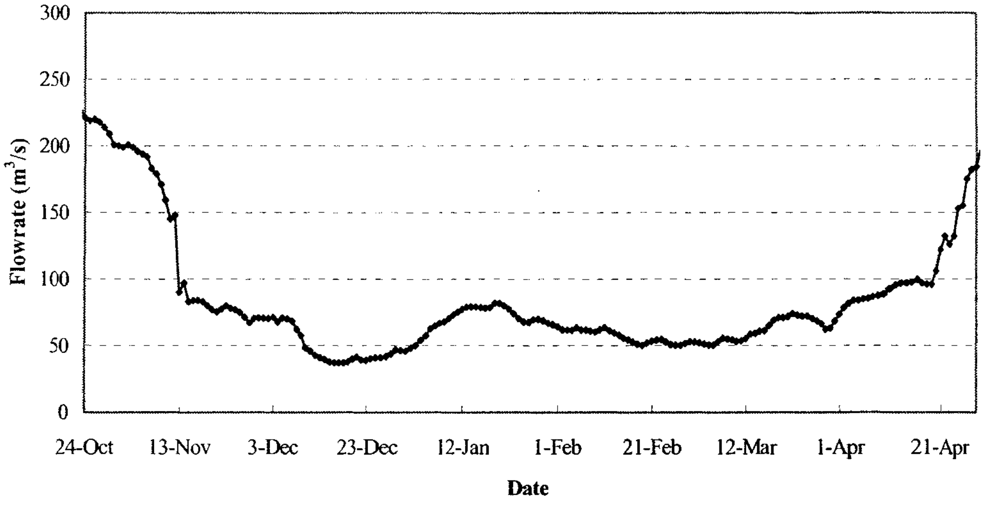
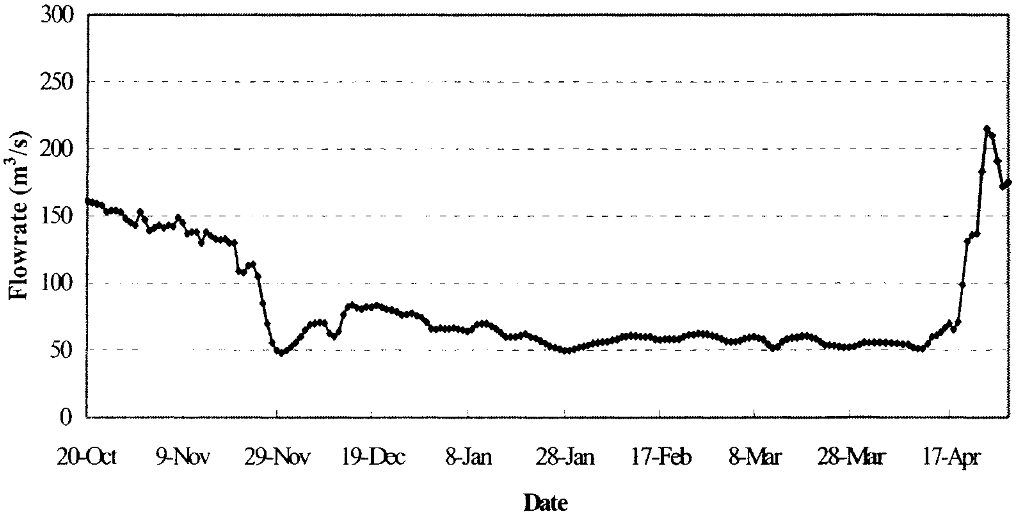


b. 2000-2001



c. 2001-2002

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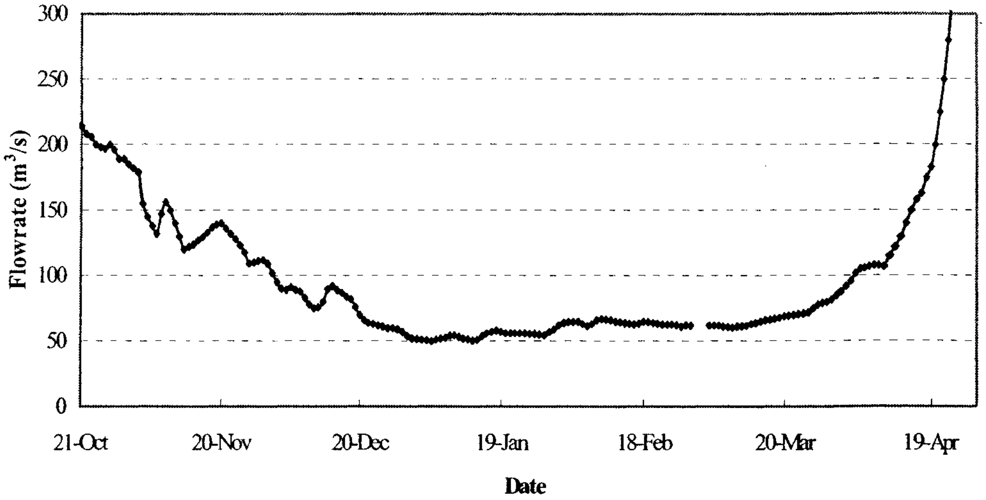

d. 2002-2003

Figure 24 Upstream boundary flow input

Temperature

The water temperature data were recorded at the long term monitoring station at Athabasca. The temperature data from October 1999 to May 2003 were used to describe the upstream boundary condition.

Water quality

Water quality data from the long-term station at Athabasca was used as the upstream boundary condition. The constituents in Table 14 were available and modeled. Interpolation or extrapolation were used to fill the data gaps. The input data used as the water quality of the upstream boundary inflow is list in Table 16, Table 17, Table 18, and Table 19.

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Table 15 Water quality constituents included in the model

Constituent	Constituent Name
TDS	Total dissolved solids or salinity (mg/L)
COND	Conductivity (μs/cm)
SS	Suspended solid
PO4	Dissolved inorganic phosphorus (mg/L)
NH4	Ammonia (mg/L)
NO3	Nitrate-nitrite (mg/L)
FE	Dissolved iron (mg/L)
LDOM	Labile dissolved organic matter (mg/L)
RDOM	Refractory dissolved organic matter (mg/L)
LPOM	Labile particulate organic matter (mg/l)
RPOM	Refractory particulate organic matter (mg/L)
CBOD	CBOD (mg/L)
algal	Algal group
DO	Dissolved oxygen
TIC	Total inorganic carbon (mg/L)
ALK	Alkalinity (mg/L)

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Table 16 Upstream boundary inflow 1999-2000

JDAY	18- Oct	23- Oct	26- Oct	25- Nov	4- Dec	20- Dec	8- Jan	17- Jan	24- Jan	5- Feb	22- Feb	6- Mar	23- Mar	10- Apr	23- Apr	3- May
TDS	200	214	214	257	257	302	302	295	295	295	285	285	281	281	192	192
COND	298	298	353	392	3392	491	491	476	476	484	484	484	454	454	328	328
SSOLID	7	6	5.8	4	4	1	1	1	1	1	1	1	10	7	7	7
PO4	0	0	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.04	0.04	0.05	0.05	0.02	0.01
NH4	0.01	0.01	0.01	0.01	0.01	0.01	0.06	0.06	0.06	0.04	0.03	0.01	0.01	0.01	0.01	0.01
NO3	0.05	0.05	0	0.06	0.06	0.14	0.14	0.18	0.18	0.23	0.23	0.23	0.22	0.22	0	0
FE	0.51	0.51	0.51	0.51	0.23	0.23	0.23	0.23	0.11	0.11	0.11	0.13	0.13	0.5	0.8	2
LDOM	2.85	2.85	2.7	2.93	2.93	3.83	3.83	3.3	3.3	3.3	3.98	3.98	3.83	3.83	3.3	3.3
RDOM	0.95	0.95	0.9	0.98	0.98	1.28	1.28	1.1	1.1	1.1	1.33	1.33	1.28	1.28	1.1	1.1
LPOM	0.3	0.3	0.45	0.23	0.23	0.6	0.6	1.13	1.13	1.13	0.45	0.45	0.6	0.6	1.13	1.13
RPOM	0.1	0.1	0.15	0.08	0.08	0.2	0.2	0.38	0.38	0.38	0.15	0.15	0.2	0.2	0.38	0.38
CBOD	1.5	1.5	1.5	1.5	1.5	1.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2
ALG1	0.03	0.03	0.03	0.03	0.03	0.06	0.06	0.02	0.02	0.02	0.03	0.03	0.11	0.11	0.28	0.28
ALG2	0.03	0.03	0.03	0.03	0.03	0.06	0.06	0.02	0.02	0.02	0.03	0.03	0.11	0.11	0.28	0.28
DO	11.5	11.5	12	14	14	12.1	11.1	10.4	10.4	9.53	8.53	9.13	9.96	9.96	11	11
TIC	29.4	29.4	29.4	29.4	29.4	41.3	41.3	41.3	41.3	41.3	41.3	41.3	41.3	41.3	41.3	41.3
ALK	152	152	152	186	186	222	222	209	209	209	167	167	194	194	135	135

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Table 17 Upstream boundary inflow 2000-2001

JDAY	18-Oct	23-Oct	27-Nov	18-Dec	17-Jan	14-Feb	3-Mar	13-Mar	9-Apr	10-May
TDS	230	230	316	292	266	328	328	280	240	240
COND	332	332	457	504	429	454	454	481	367	272
SSOLID	7	5	1	1	1	1	1	8	2	7
PO4	0	0	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
NH4	0.01	0.01	0.01	0.04	0.04	0.03	0.03	0.01	0.01	0.01
NO3	0.05	0.05	0	0.06	0.06	0.14	0.14	0.14	0.14	0.14
FE	0.51	0.51	0.51	0.51	0.23	0.23	0.23	0.23	0.23	0.11
LDOM	2.85	2.85	2.7	2.93	2.93	3.83	3.83	3.83	3.3	3.3
RDOM	0.95	0.95	0.9	0.98	0.98	1.28	1.28	1.28	1.1	1.1
LPOM	0.9	0.9	1.05	0.83	0.83	0.6	0.6	0.6	1.13	1.13
RPOM	0.3	0.3	0.35	0.28	0.28	0.2	0.2	0.2	0.38	0.38
CBOD	1.5	1.5	1.5	1.5	1.5	1.5	2.5	2.5	2.5	2.5
ALG1	0.04	0.04	0.12	0.03	0.05	0.28	0.28	0.4	0.17	0.12
ALG2	0.04	0.04	0.12	0.03	0.05	0.28	0.28	0.4	0.17	0.12
DO	12.35	12.35	13.32	12.96	10.04	10.07	11.07	13.54	15.8	10.46
TIC	35	35	35	35	35	41.3	41.3	41.3	41.3	41.3
ALK	147	147	207	213	193	200	200	182	145	117

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Table 18 Upstream boundary inflow 2001-2002

Date	18-Oct	14-Nov	16-Jan	12-Feb	12-Mar	10-Apr	7-May
TDS	199	225	296	283	284	279	127
COND	334	384	485	468	483	464	206
SSOLID	1	2	1	1	1	1	33.7
PO4	0	0.01	0.01	0.01	0.01	0.02	0.02
NH4	0.01	0.01	0.13	0.16	0.01	0.03	0.04
NO3	0.05	0.05	0.06	0.06	0.14	0.14	0.14
FE	0.51	0.51	0.51	0.23	0.23	0.23	0.23
LDOM	2.85	2.7	2.93	3.83	3.83	3.3	3.3
RDOM	0.95	0.9	0.98	1.28	1.28	1.1	1.1
LPOM	0.9	1.05	0.83	0.6	0.6	1.13	1.13
RPOM	0.3	0.35	0.28	0.2	0.2	0.38	0.38
CBOD	1.5	1.5	1.5	1.5	2.5	2.5	2.5
ALG1	0.05	0.07	0.02	0.02	0.06	0.15	0.45
ALG2	0.05	0.07	0.02	0.02	0.06	0.15	0.45
DO	12.16	11.64	8.86	8.05	9.62	8.78	11.83
TIC	35	35	35	41.3	41.3	41.3	41.3
ALK	139	161	202	192	202	186	95.2

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Table 19 Upstream boundary inflow 2002-2003

Date	18-Oct	6-Nov	11-Dec	8-Jan	5-Feb	5-Feb	5-Feb	3-Mar	4-May
TDS	214	214	268	328	298	302	292	296	296
COND	358	358	427	528	511	514	510	505	505
SSOLID	1	1	1	1	1	1	1	2	2
PO4	0	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02
NH4	0.01	0.01	0.06	0.04	0.17	0.16	0.15	0.07	0.07
NO3	0.05	0.05	0.06	0.06	0.14	0.14	0.14	0.14	0.14
FE	0.51	0.51	0.51	0.23	0.23	0.23	0.23	0.23	0.23
LDOM	3.9	3.98	7.13	4.58	4.35	4.05	4.28	3.38	3.38
RDOM	1.3	1.33	2.38	1.53	1.45	1.35	1.43	1.13	1.13
LPOM	0.9	0.9	0.83	0.83	0.6	0.6	0.6	1.13	1.13
RPOM	0.3	0.3	0.28	0.28	0.2	0.2	0.2	0.38	0.38
CBOD	1	1	1	1.2	1.2	1.2	1.2	0.6	0.6
ALG1	0.04	0.013	0.04	0.03	0.026	0.028	0.028	0.017	0.017
ALG2	0.04	0.013	0.04	0.03	0.026	0.028	0.028	0.017	0.017
DO	13.03	13.03	13.24	11.65	7.19	7.19	7.19	7.42	7.42
TIC	35	35	35	35	41.3	41.3	41.3	41.3	41.3
ALK	150	180	220	193	192	193	193	193	193

4.1.4 Tributaries

There were six tributaries to be included in this model: The effluent from sewer treatment plant (STP) of Ahtabasca, the effluent from Alberta Pacific (Al-Pac), La Biche River,

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Calling River, Pelican River, and House River. Each tributary was characterized by flow, temperature, and water quality.

Flow

The STP and Al-Pac have flow gages to record the discharge. Four tributaries (La Biche River, Calling River, Pelican River, and House River) have no gage near the confluence locations. The flows of the four tributaries were estimated according to the discharge areas (Table 20).

Table 20 Drainage area estimates of tributaries (from Alberta Environment, unpublished data)

River Name	**Drainage Areas (km2)**
Athabasca River at Athabasca	74,600
La Biche River	4,860
Calling River	1,000
Pellican River	4,000
House river	8,000
Other tributary (Distributed discharge)	9,328

Temperature

The temperature data of the four tributaries (La Biche River, Calling River, Pelican River, and House River) were only available from 1989 to 1996. They were averaged and used as boundary conditions.

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Water quality

The water quality data from 1989 to 1996 were the only available data for the four tributaries (La Biche River, Calling River, Pelican River, and House River). They were averaged to characterize the tributary boundary conditions.

4.1.5 Distributed Tributaries

To address non-point flow and flow contributions from a series of small tributaries along the modeled section, distributed tributary flow was estimated according to the discharge areas (Table 20). The estimated daily average flow was divided among the segments according to the lengths of the segments in six branches (1, 4, 6, 7, 8, and 9).

4.1.6 Meteorological Data

The daily climate data were obtained from the station at Athabasca. The meteorological data used in the model include air temperature, dew point temperature, air pressure, wind speed, and wind direction. Data were obtained and used in the model in daily intervals. The air temperature which was input into the model is shown in Figure 25.

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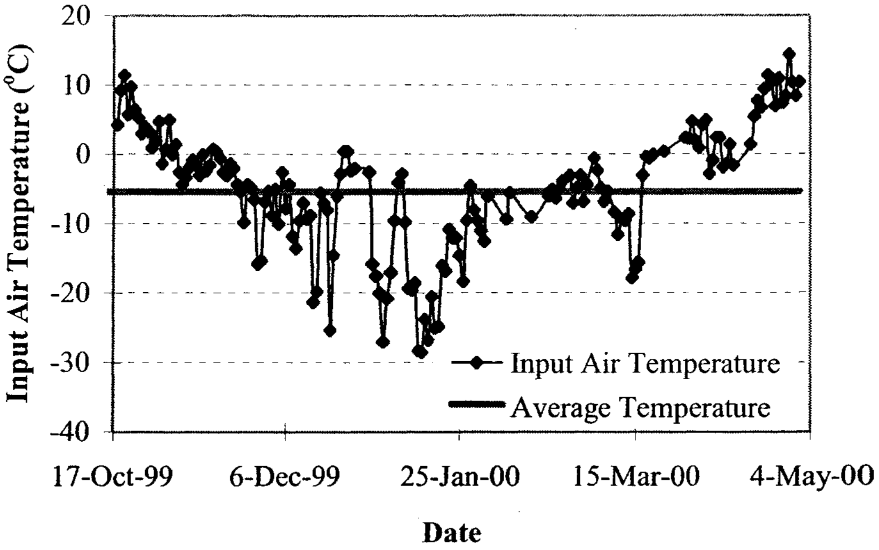

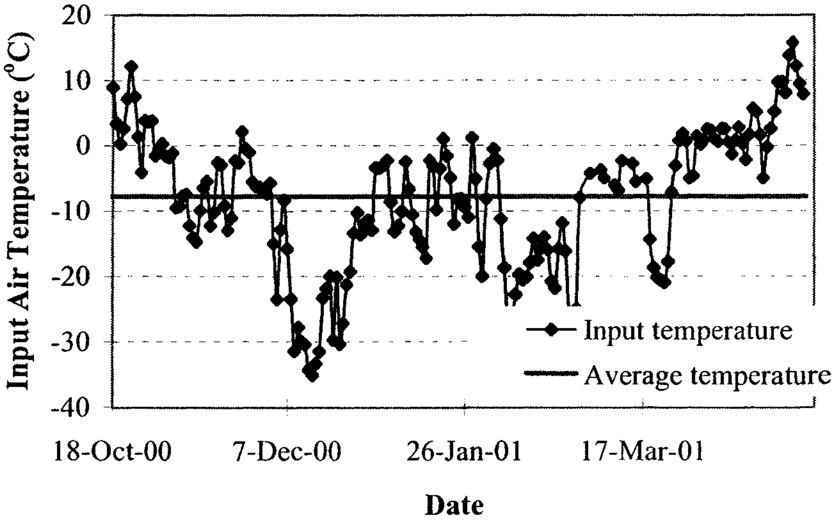

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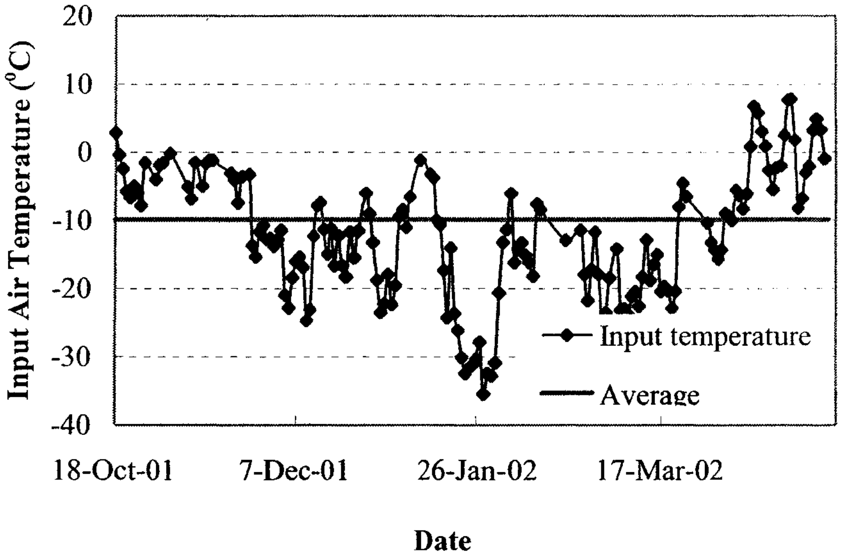

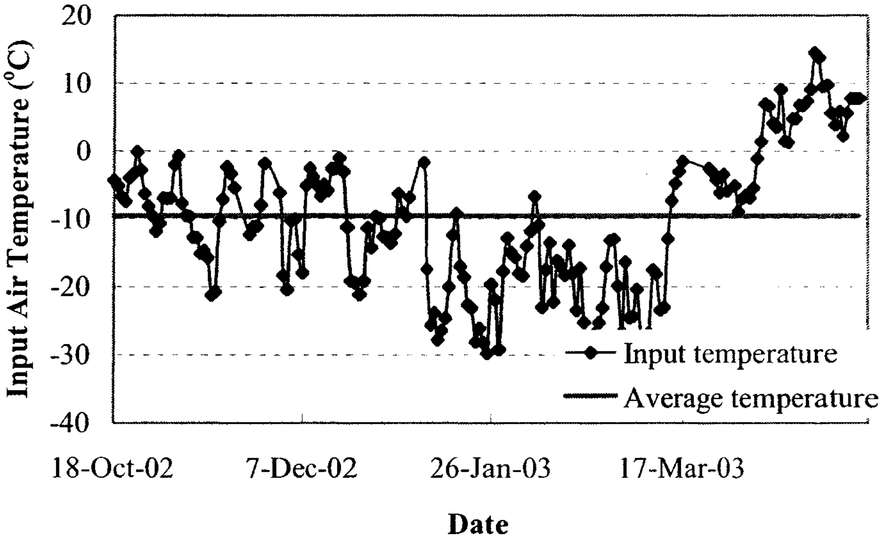

Figure 25 Air temperature input

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4.2 Model Calibration

The calibration effort focused on model prediction of hydrodynamics (flow), temperature, and eutrophication parameters (such as DO, nutrients, and algae). The model calibration periods were focused on winter and early spring periods for four years from 1999 to 2003, including the winter of 2002-2003 which was an extreme winter with low flowrate, low DO concentration and low air temperature.

4.2.1 Hydrodynamic Calibration

There was no gage station between Athabasca and Fort McMurray. Grand Rapids was in the middle of Athabasca and Fort McMurray. The discharge area of the Athabasca River at Grand Rapids was the average of the discharge areas at Athabasca and at Fort McMurry. The flowrate at Grand Rapids was assumed to be between the flows at Athabasca and Fort McMurry. Figure 26 showed the model results and data for flow.

The simulated flowrates at upstream of Grand Rapids are between the flowrates at Athabasca and Ft. McMurry for the four simulated period. This indicates that the hydrodynamic simulation is acceptable.

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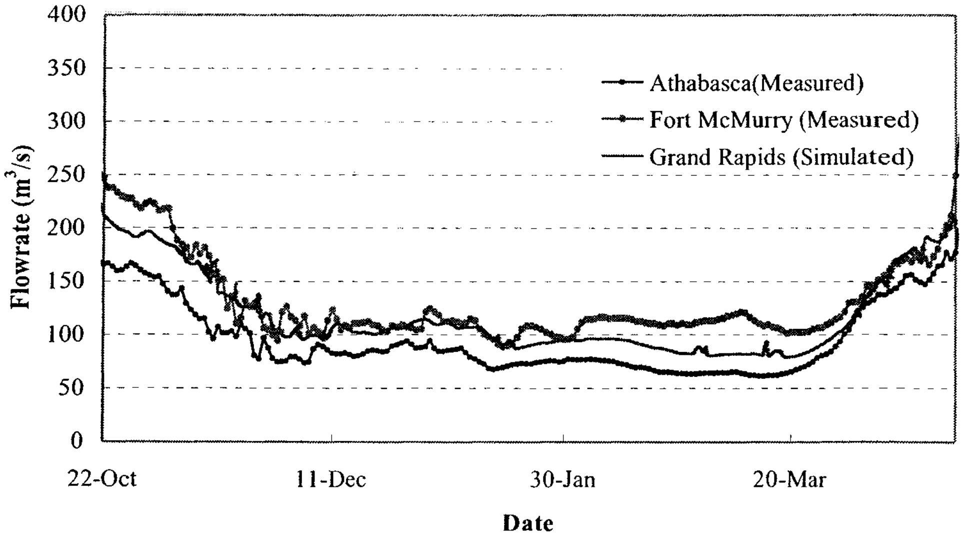
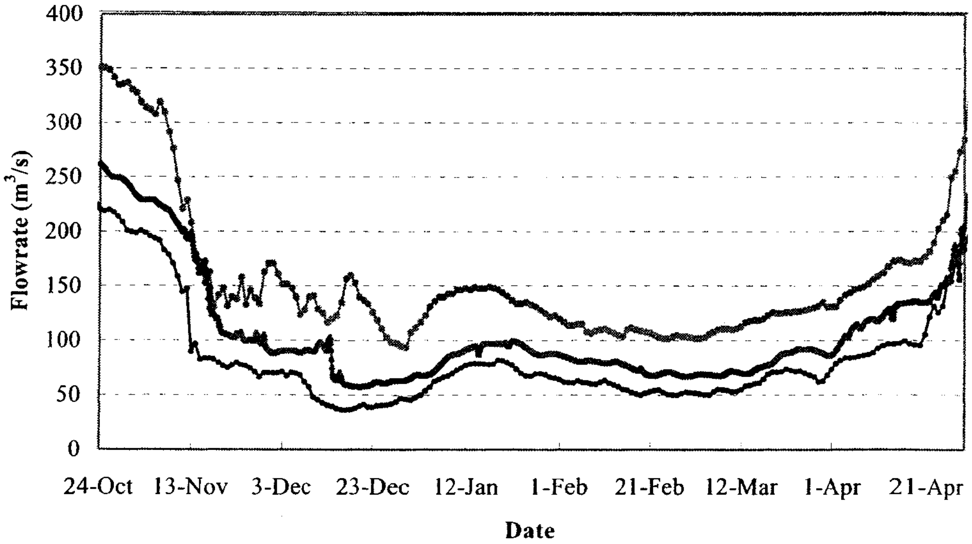


a. Flowrate Simulation 1999-2000



b. Flowrate Simulation 2000-2001

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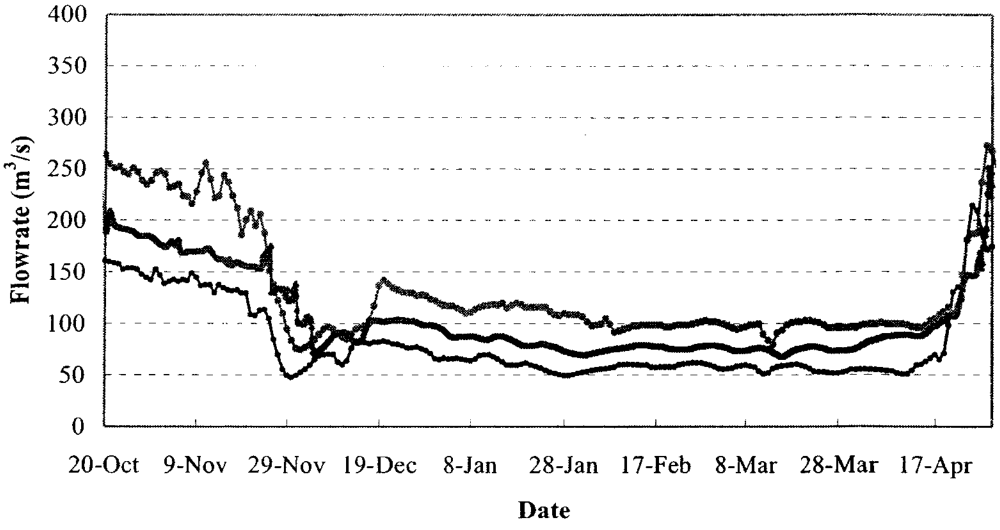
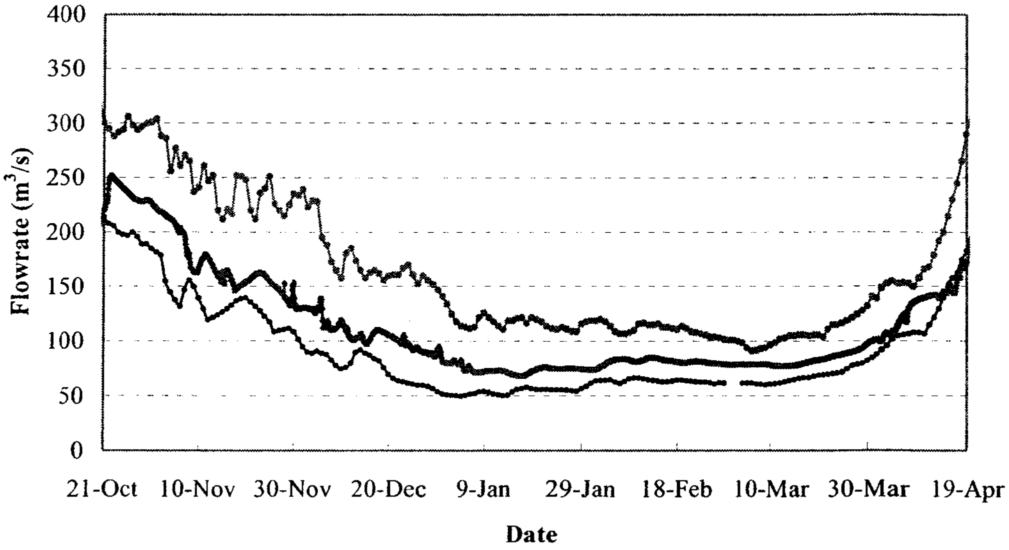


c. Flow Simulation 2001-2002



d. Flowrate simulation 2002-2003

Figure 26 Flowrate simulation at upstream of Grand Rapids

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4.2.2 Temperature Calibration

Within the simulation section of the main stream, the water temperature data between 2001 and 2003 was only available at the location of the Town of Athabasca. The water temperature at Grand Rapids was supposed to be between the temperatures of Athabasca and Fort McMurry. In this simulation the average values of the water temperatures of Athabasca and Fort McMurry were adopted to represent the water temperature data at Grand Rapids for 2001 to 2003. Figure 27 compares the model simulated values with measured data for temperature. The statistics on related error analysis can be found in Table 21.

For water temperature, the model simulated values compared well with the measured data between October and March for the four winters, but did not compare well in late March and early April in 2000, when significant temperature swings predicted by the model were not observed in real situations. The inability of the model to simulate this transition period will be discussed in section 4.3.

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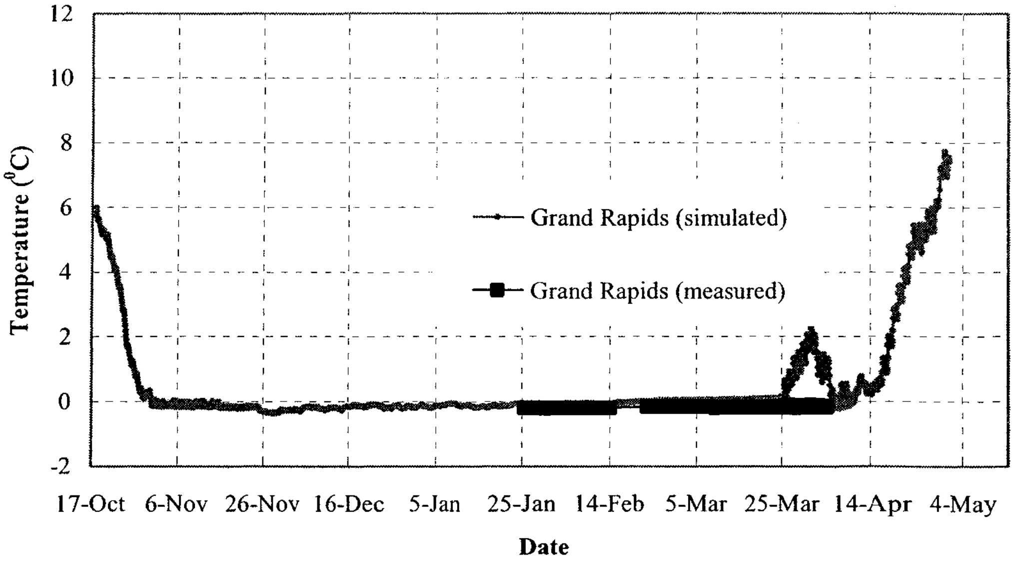
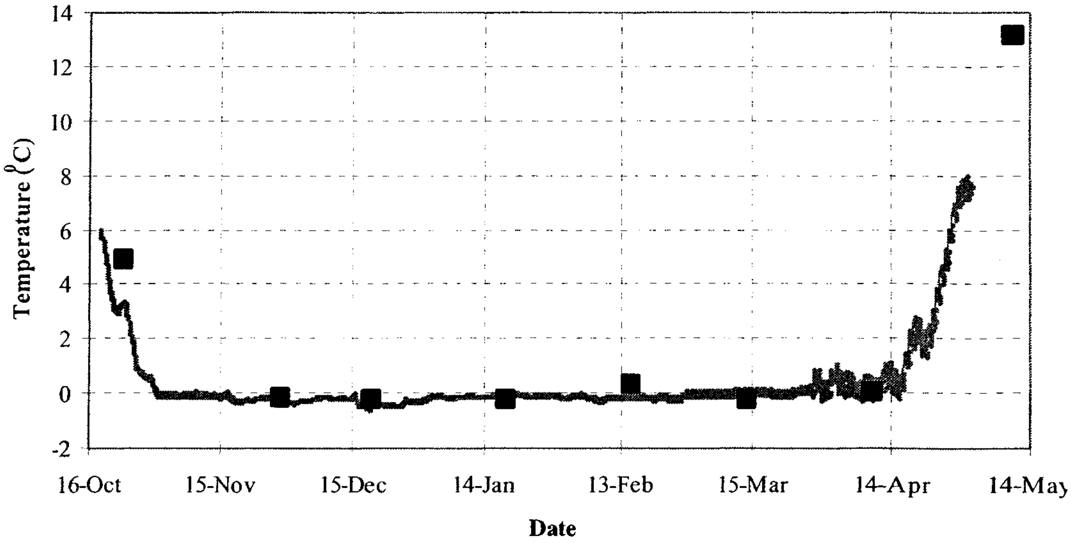


a. Water Temperature Simulation 1999-2000



b. Water Temperature Simualtion 2000-2001

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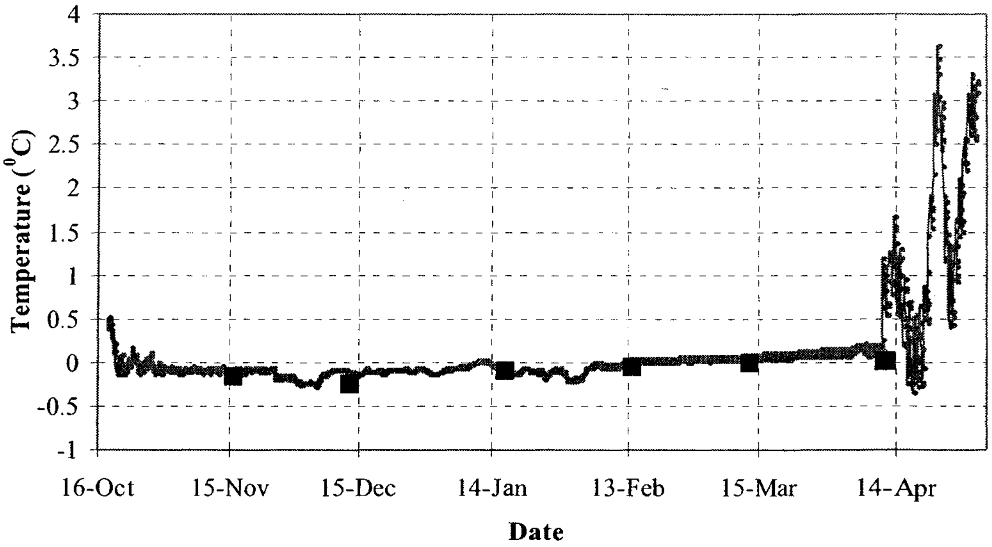
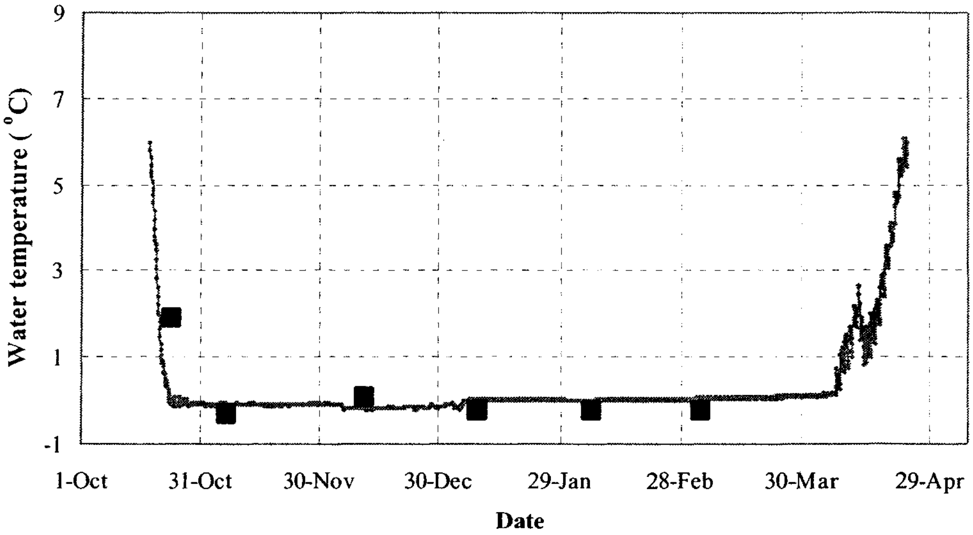


c. Water Temperature Simulation 2001-2002



d.Water Temperature Simulation 2002-2003

Figure 27 Water temperature simulation at upstream Grand Rapids

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Table 21 Water temperature error statistics

Year	No. of data comparisons	Mean Error (^{0}C)	AME	RMSE
1999-2000	1878	0.01	0.01	0.01
2000-2001	7	-0.33	0.45	0.67
2001-2002	6	0.18	0.19	0.37
2002-2003	6	-0.04	0.06	0.08

AME: Absolute Mean Error

RMSE: Root Mean Square Error

4.2.3 Water Quality Calibration

Dissolved oxygen

Dissolved oxygen data were available at upstream of Grand Rapids from 1999 to 2003. And upstream of Grand Rapids was a critical location to simulate DO concentrations, where the lowest DO concentrations were reported during winters.

CE-QUAL-W2 has nine reaeration formulations that can be used for river systems. The Churchill, Elmore and Buckingham(1962) equation was used in model runs. Both zero order and first-order sediment demands were used to describe the SOD in this calibration.

Ice cover prevents reaeration, which is a major source of DO. Ice cover is modeled in CE-QUAL-W2. CE-QUAL-W2 assumes that the ice covers a whole segment with the same ice thickness, and the heat exchange only change the thickness of the ice instead of ice cover ratio. In real situations, some open water zones exist even in mid-winter due to the effluent temperature. The recent data collected from the Athabasca River showed that

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the open water lead due to the effluent ranges from a few hundred meters to several kilometers long (Lima-Neto et al. 2005) and varies mainly as a function of air temperature and effluent temperature. In order to mimic the real open lead, two extra water bodies, waterbody 2 (5.3 km long) and waterbody 3 (5.3 km long) were added in this study. The waterbody 2 and waterbody 3 were located downstream of Al-Pac. They were forced to be open water zone for the whole simulated winter of 1999-2000 by positive air temperature input for the two waterbodies. The waterbody 2 was forced to be open during the whole simulated winter of 2000-2001. The waterbody 2 was forced to be open before January and after March simulated winter of 2001-2002. And the real air temperature data were input for all segments in 2002-2003.

Figure 28 shows the DO simulation by using this approach, and Table 22 shows the statistics of error analysis (mean, AME, and RMS). The model-simulated DO values compared well with the measured data in mid-winter for the four simulated years, including the winter of 2002-2003, which the WASP failed to simulate. The model simulateded DO data had also similar fluctuation as the measured DO data. The similarity in fluctuation indicated that the model successfully simulated the impact of the algae and epiphyte. Similar to the temperature simulation, owever, the model simulated DO values did not compare well with the measured DO data in early and late winters when the ice was forming or melting.

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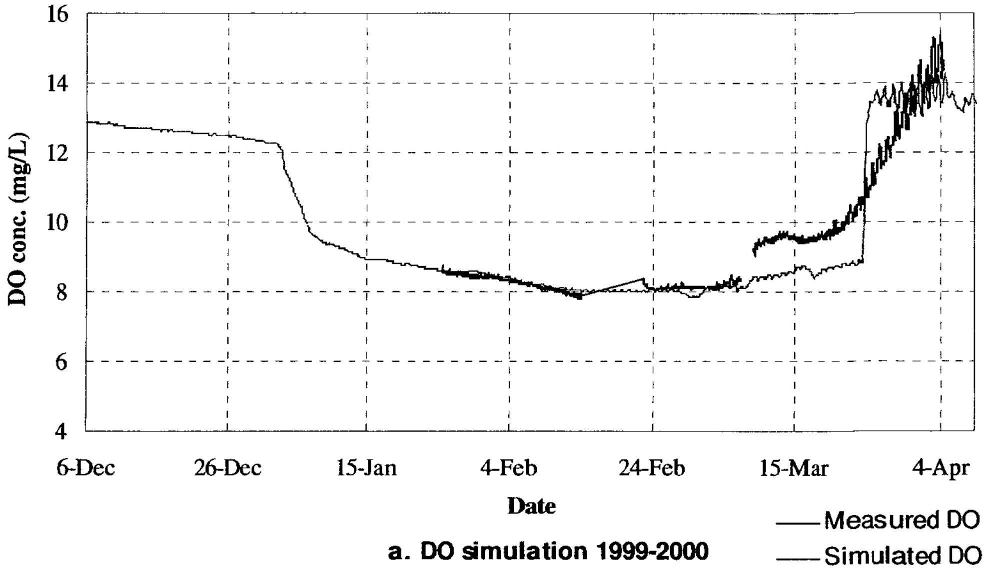
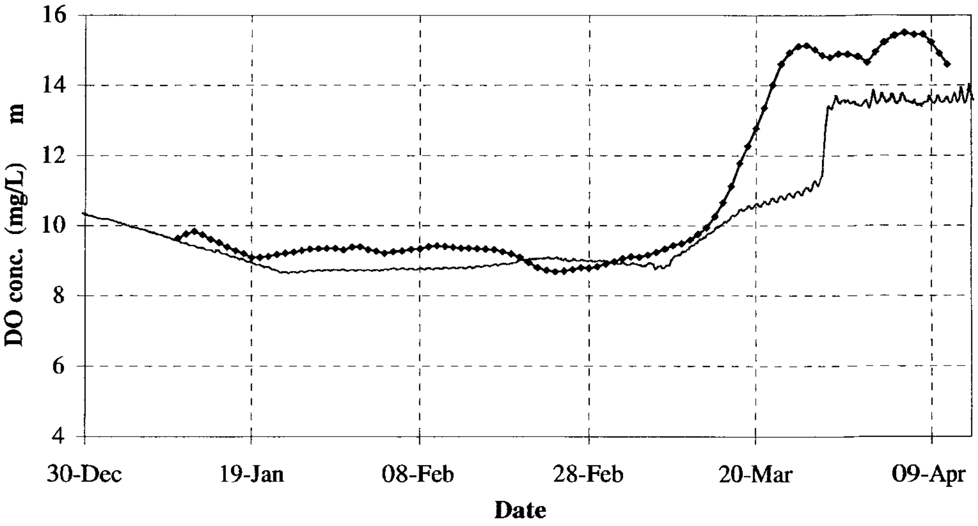


a. DO simulation 1999-2000



b. DO simulation 2000-2001

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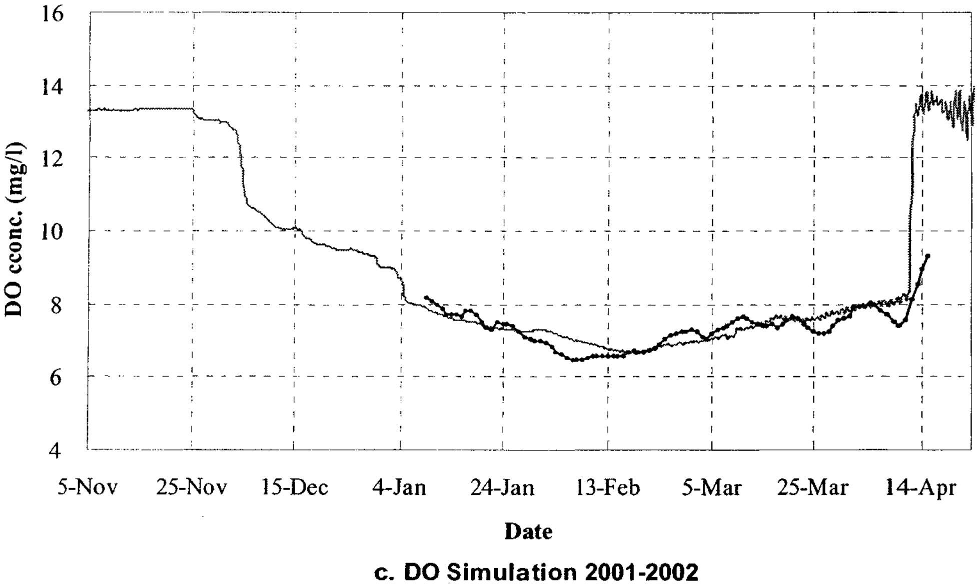
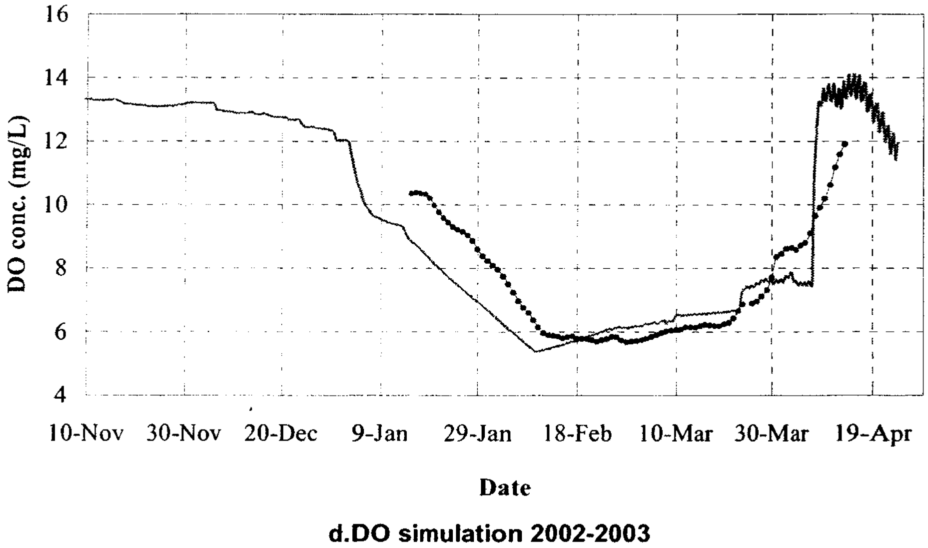


c. DO Simulation 2001-2002



d.DO simulation 2002-2003

Figure 28 DO simulation at upstream Grand Rapids

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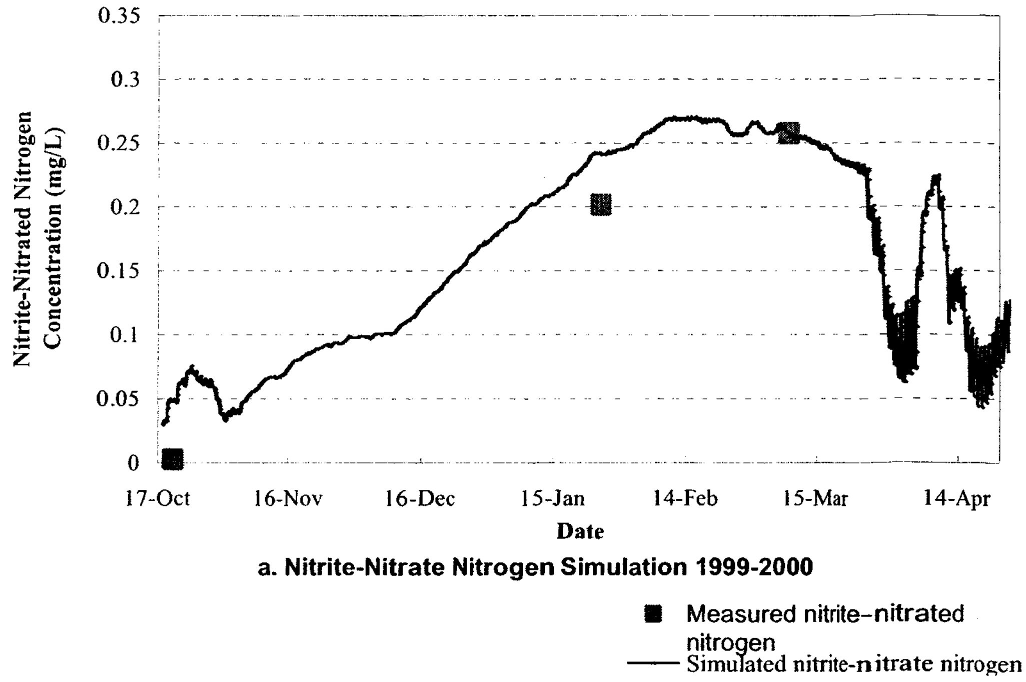
Table 22 DO error statistics

Year	No. of data comparisons	Mean Error (mg/L)	AME (mg/L)	RMSE (mg/L)	Period (y/m/d)
1999-2000	2199	0.05	0.09	0.21	2000/1/10 to 2000/3/7
2000-2001	64	-0.3	0.38	0.42	2001/1/10 to 2001/3/14
2001-2002	82	0.03	0.21	0.27	2002/1/9 to 2002/4/6
2002-2003	52	-0.1	0.52	0.66	2003/1/31 to 2003/3/23

Nitrite-nitrate nitrogen

Nitrite-nitrate concentration in the river water influences and is influenced by the growth of epiphyte and algae. There is no nitrite-nitrate data available at Grand Rapids. The nitrite-nitrate data at Fort McMurray were adopted. Figure 29 compares the field data to model simulated values; and Table 23 shows the statistics of error analysis.



a. Nitrite-Nitrate Nitrogen Simulation 1999-2000

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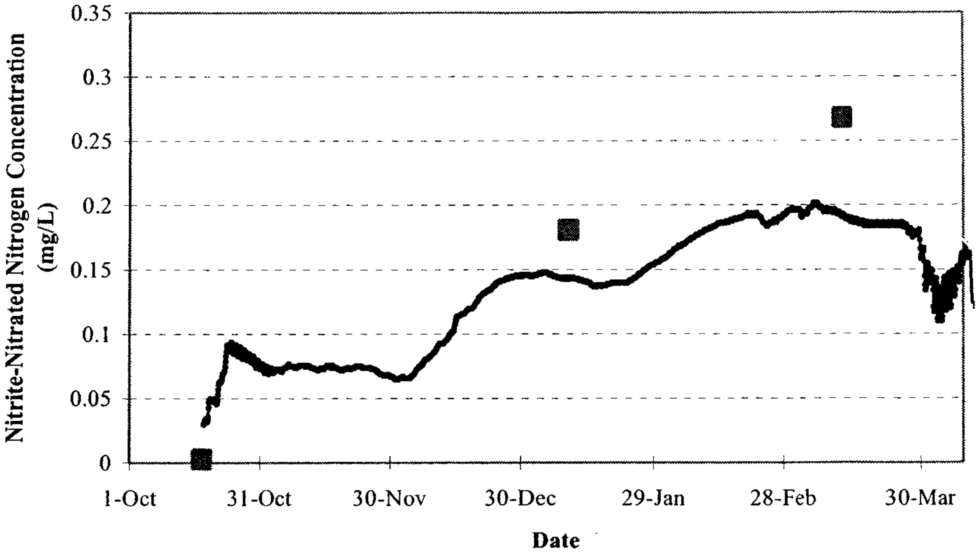
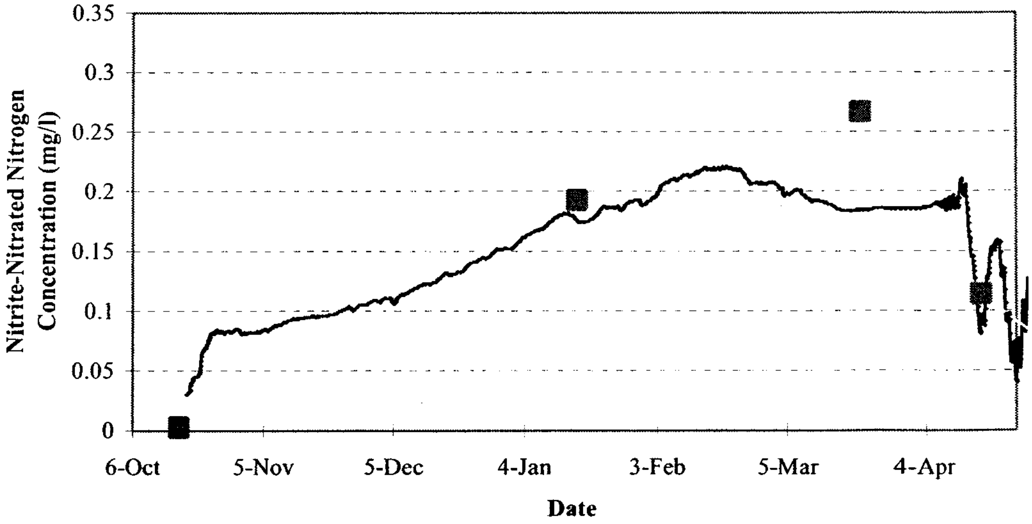


b. Nitrite-Nitrate Nitrogen Simulation 2000-2001



c. Nitrite-Nitrate Nitrogen Simulation 2001-2002

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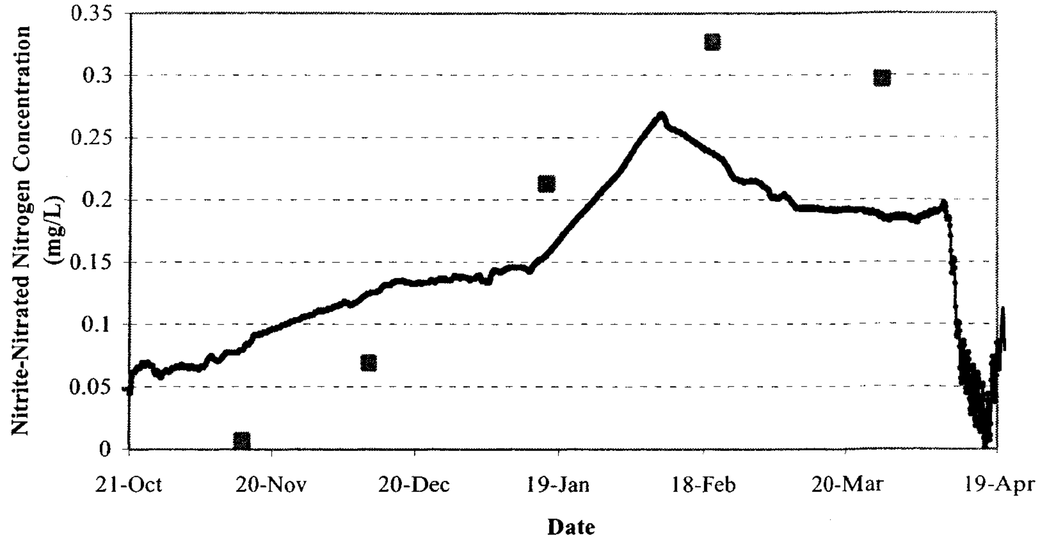

d. Nitritr-Nitrate Nitrogen Simulation 2002-2003

Figure 29 Nitrite-nitrate nitrogen simulation at upstream Grand Rapids

Table 23 Nitrite- Nitrate nitrogen error statistics

Year	No. of data comparisons	Mean Error (mg/L)	AME (mg/L)	RMSE (mg/L)
1999-2000	3	0.028	0.028	0.035
2000-2001	3	-0.028	0.046	0.05
2001-2002	4	-0.021	0.034	0.044
2002-2003	5	-0.03	0.077	0.079

Ammonia nitrogen

The ammonia nitrogen data at Fort McMurry were adopted to represent the ammonia nigrogen data at upstream of Grand Rapids. Figure 30 compares the field data to model simulated values; and Table 19 shows the statistics of error analysis.

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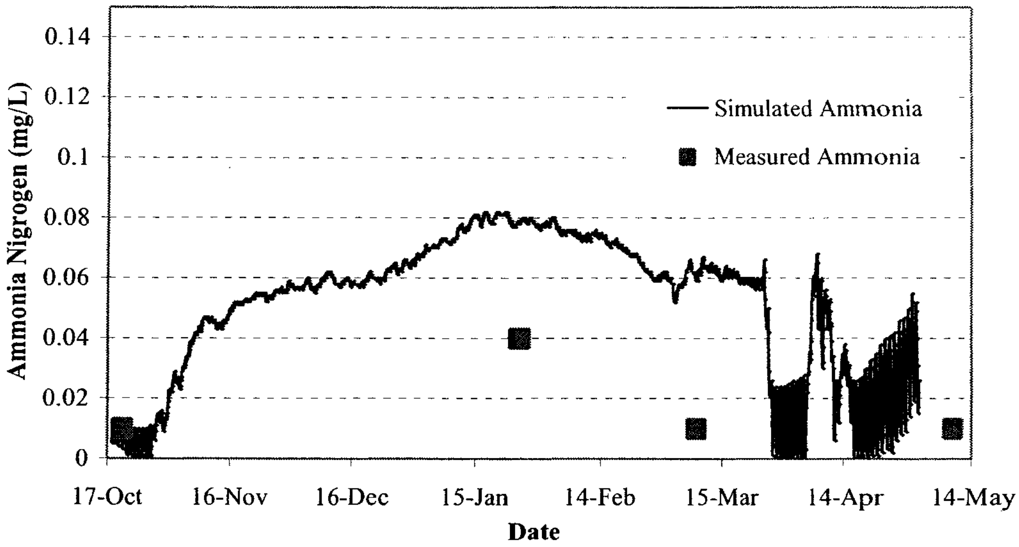
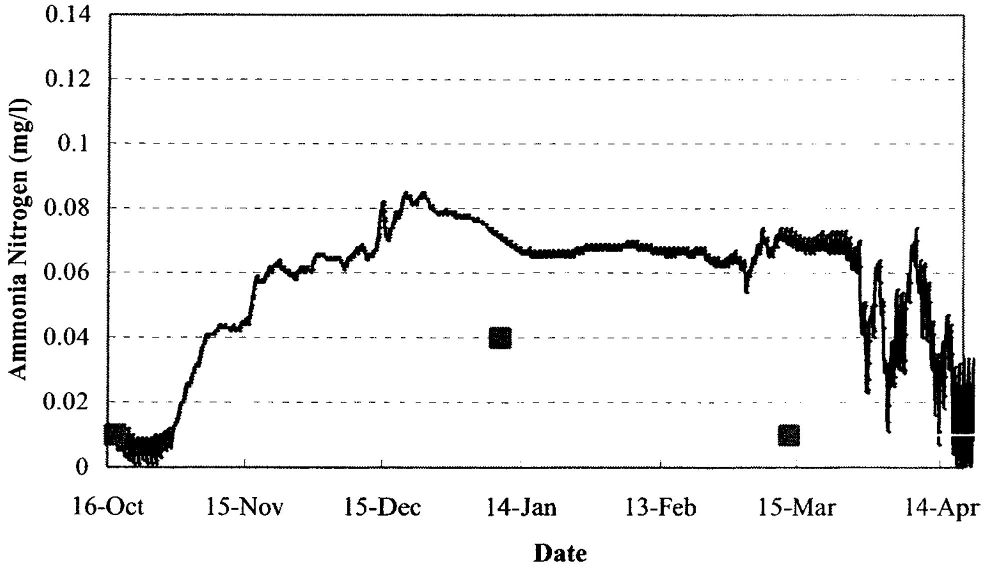


a. Ammonia Nitrogen Simulation 1999-2000



b. Ammonia Nitrogen Simulation 2000-2001

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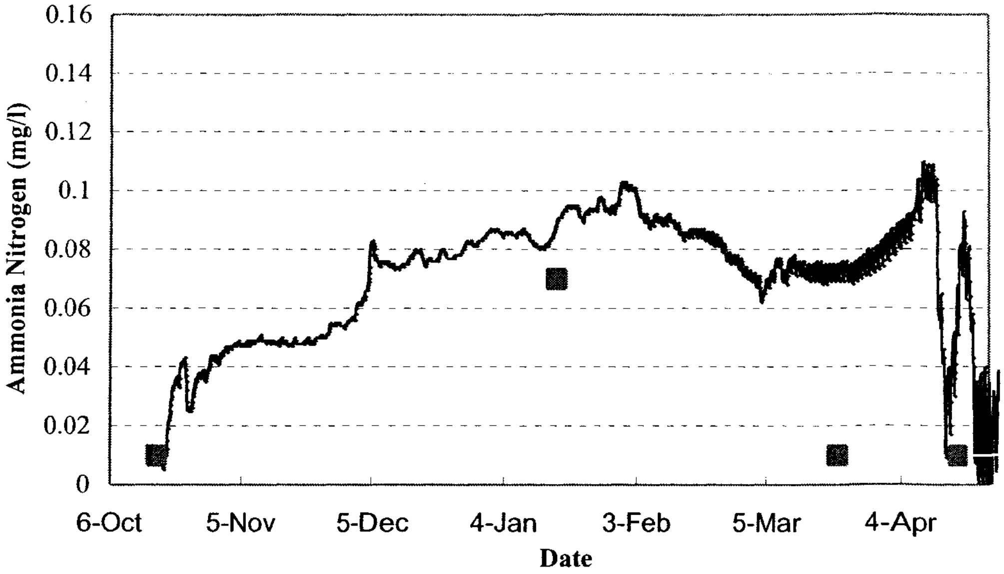
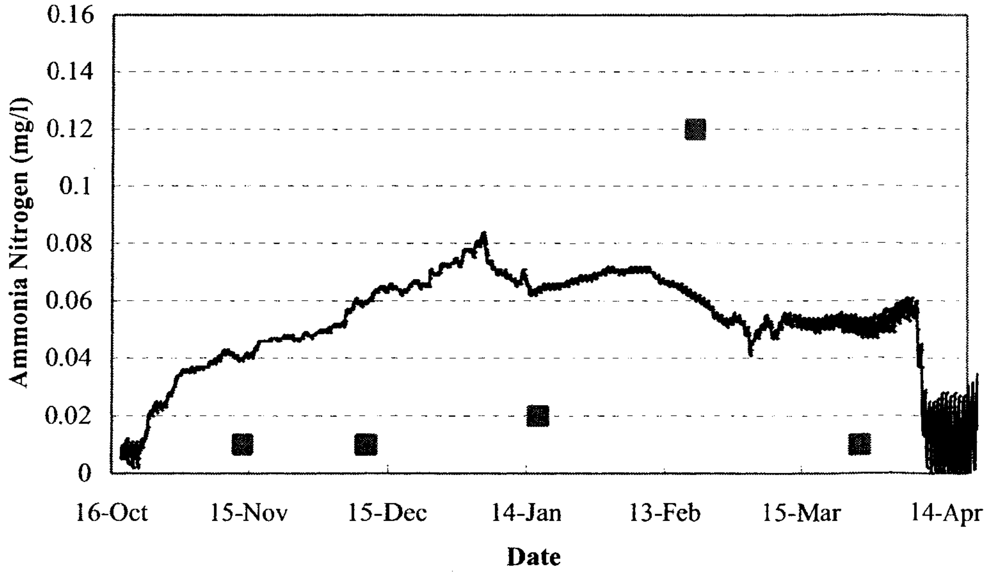


c. Ammonia Nitrogen Simulation 2001-2002



d. Ammonia Nitrogen Simulation 2002-2003

Figure 30 Ammonia nitrogen simulation at upstream of Grand Rapids.

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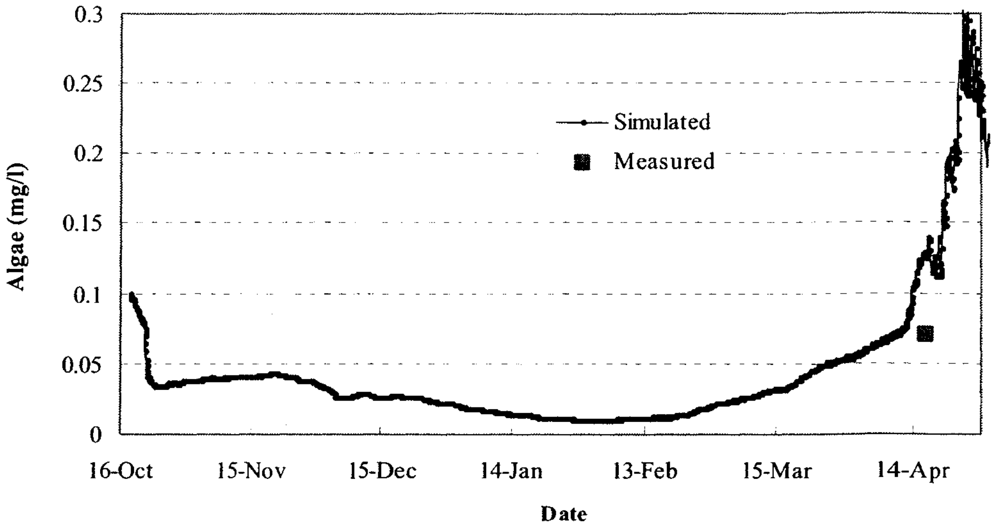
Table 24 Ammonia nitrogen error statistics

Year	No. of data comparisons	Mean Error (mg/L)	AME (mg/L)	RMSE (mg/L)
1999-2000	3	0.029	0.029	0.036
2000-2001	3	0.03	0.03	0.04
2001-2002	4	0.025	0.025	0.034
2002-2003	5	0.02	0.044	0.045

Algae

Figure 31 shows the comparisons of field data with model simulated values for year 2001-2002 and 2002-2003, respectively. Table 25 shows the statistics of error analysis.

The algae biomass to chlorophyll-a ratio was used to calibrate the model to the sampled data. An algae biomass to chlorophyll-a ratio of 65 was used in the model, along with an algal growth rate of 1 d^{-1}.



a. Algae Simulation 2001-2002

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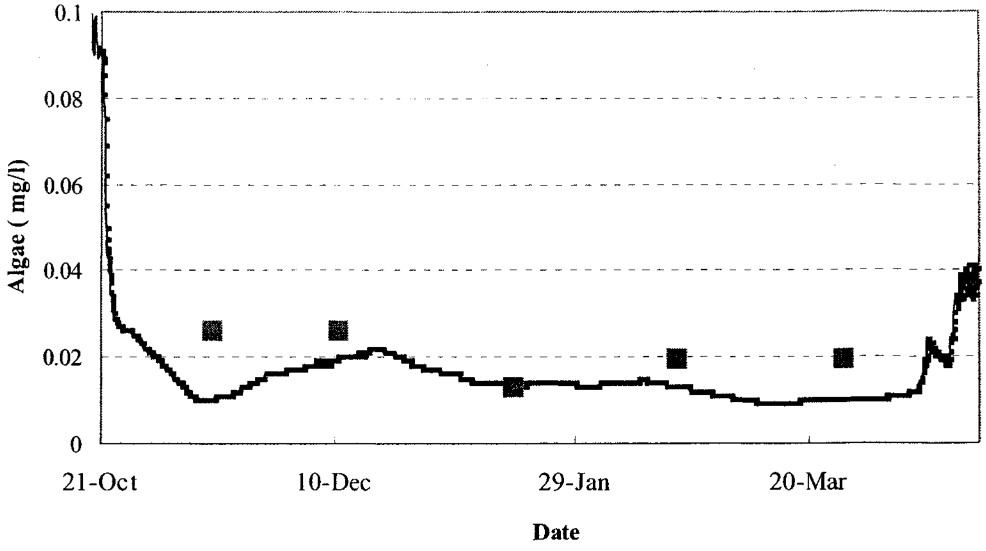

b. Algae Simulation 2002-2003

Figure 31 Algae simulation at upstream of Grand Rapids

Table 25 Algae error statistics

Year	No. of data comparisons	Mean Error (mg/L)	AME (mg/L)	RMSE (mg/L)
2001-2002	1	0.055		
2002-2003	5	-0.0074	0.0078	0.0092

4.3 Discussion on the Suitability of CE-QUAL-W2

4.3.1 Hydrodynamic

In contrast to WASP, which relies on hydraulic model for hydrodynamics, CE-QUAL-W2, as a two-dimensional (longitudinal/vertical) hydrodynamic and water quality model, predicted both hydrodynamic and water quality characteristics of the simulated section of

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the Athabasca River in this study. CE-QUAL-W2, although capable of handling narrow systems that stratifies, was found with limitations for river modeling. In the development of CE-QUAL-W2, vertical accelerations were considered negligible compared to gravity forces. This assumption leads to the approximation of hydrostatic pressure for the z-momentum equation. In sloping channels, the assumption is not always valid because the vertical accelerations cannot be neglected if the x and z axes are aligned with an elevation datum and gravity, respectively (Cole and Wells, 2005). Also, the current CE-QUAL-W2 algorithm does not allow the upstream bed elevation to be above the downstream water surface elevation. Therefore, the sloping section had to be broken into multiple small branches. In this study, the Athabasca River modeling was found to be a challenging endeavor by using CE-QUAL-W2, although the river channel is not very sloping. This is because: a) Shear and bottom friction effects are significant, requiring a considerable calibration effort; b) The change in river bathymetry could dramatically affect the velocity field; c) Dynamic flowrates at low flows could dry up segments, causing the model to stop running. Even with these inherited difficulties, however, the calibration results of flowrates for the four winters (including the low flowrate periods), as presented in Figure 23, still showed that the CE-QUAL-W2 has the capacity to simulate the modeled section of the Athabasca River.

4.3.2 DO

DO is the biggest concern and the most important element in the Athabasca River aquatic ecosystems. The DO was modeled using CE-QUAL-W2 as described in Figure 32.

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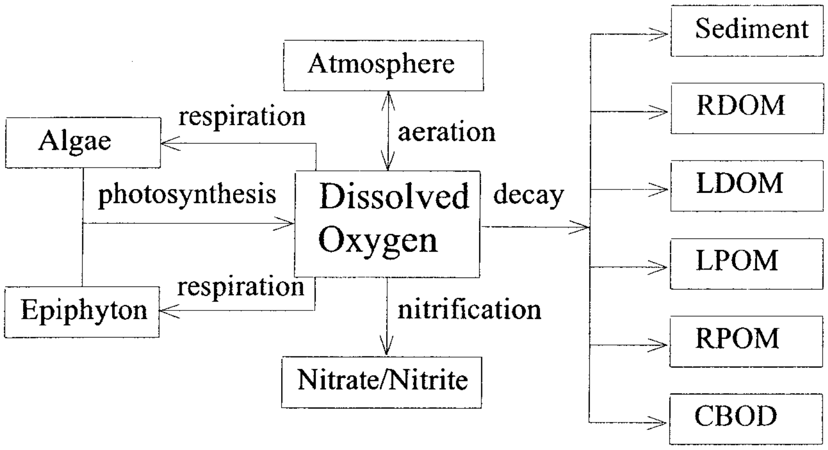

Figure 32 Internal flux between DO and other compartments. (Redrawn from Cole and Wells, 2005)

All the rates, parameters, and constants related to DO and other compartments for the Athabasca River modeling were selected according to measured data and literatures and presented in the control file in Appendix C.

Figure 28 illustrates the models ability to reproduce changes in DO over the winter periods. The DO concentration started dropping in the late fall and reached the lowest in February, which was consistent with the observation. After that, in early April the DO concentrations increased to a relatively stable level.

The model also reproduced changes on a diel basis on the Athabasca River. The model has captured not only the diel swings in dissolved oxygen due to the photosynthesis and respiration of the algae and epiphyton, but also the change in the magnitude of the diel

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variation. The variation was 0.05 mg/L during the mid-winter when the river was covered by ice and the activities of the algae and epiphytons were very limited and increased to up to 1 mg/L in early spring in the simulation year 1999-2000, in which the variation of DO was observed clearly through the measured data. The DO predictions were in close agreement with the observed variations. These simulation results indicated that the model was accurately reproducing algae and epiphyton primary production. This was reinforced in Figure 29 through Figure 31. In Figure 29 the algae were accurately modeled. In Figure 29 and Figure 30, ammonia and nitrite-nitrated nitrogen were simulated since they serve as the primary nutrients for the growth of algae and epiphytons. Algae use ammonium and nitrate-nitrite during photosynthesis to form proteins. In many applications, nitrogen is the limiting nutrient for algae growth (Cole and Wells, 2005). The significant variations of nitrogen in the early springs due to the growth of the algae were reproduced.

Another important factor influencing DO simulation is reaeration, which is limited by ice cover during winter. Figure 33 shows both the ice cover simulation and DO simulation. Obviously, the sudden DO changes related to the ice forming and melting. The lowest DO (less than 6 mg/L) occurred in 2003, which is the year with the longest ice cover period in the Athabasca River (from October to April). All these facts indicate that the ice cover is crucial to reaeration and, therefore, to DO balance in winter. Although the DO predictions were in close agreement with the observed data in most simulation periods, the model failed to simulate the transition periods in spring, when ice cover was

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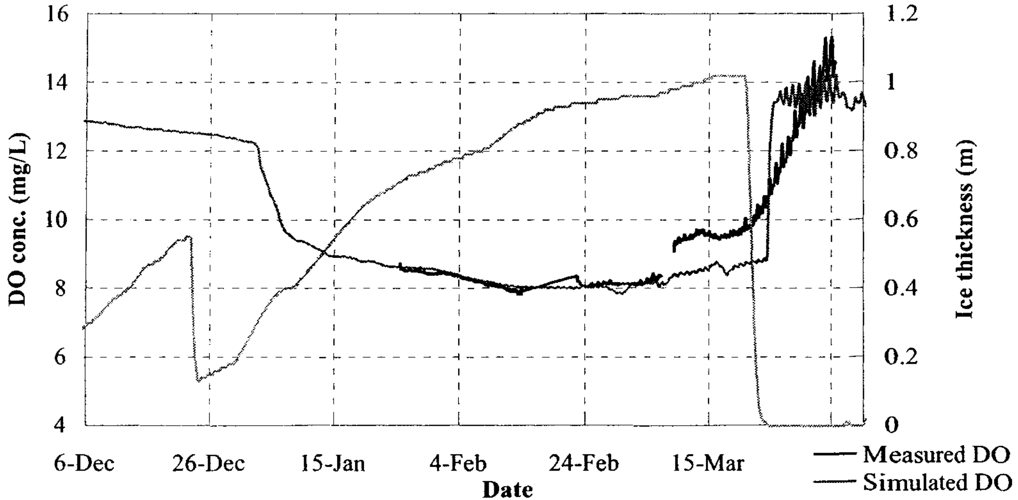
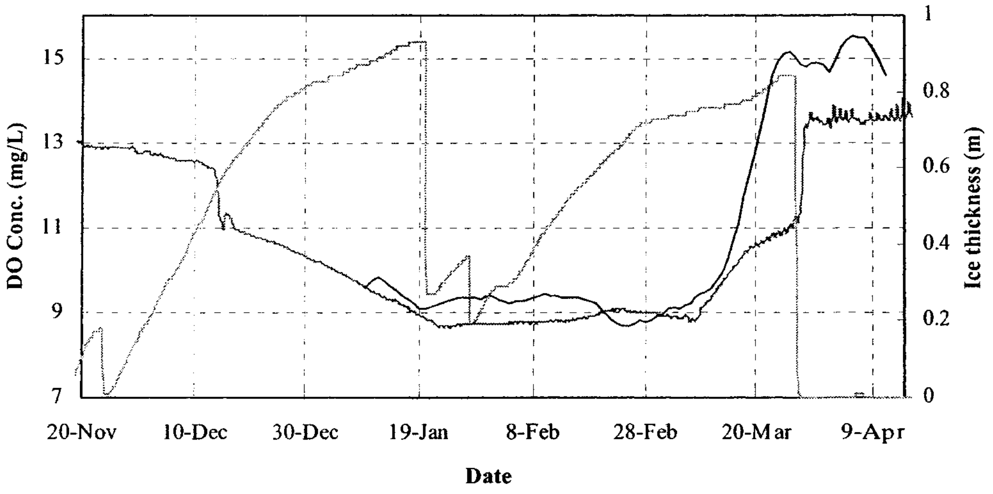
broken and reaeration became significant. This is considered as a limitation of CE-QUAL-W2 when it is used to model ice covered rivers in cold region.



a. Ice simulation 1999-2000



b. Ice Simualtion 2000-2001

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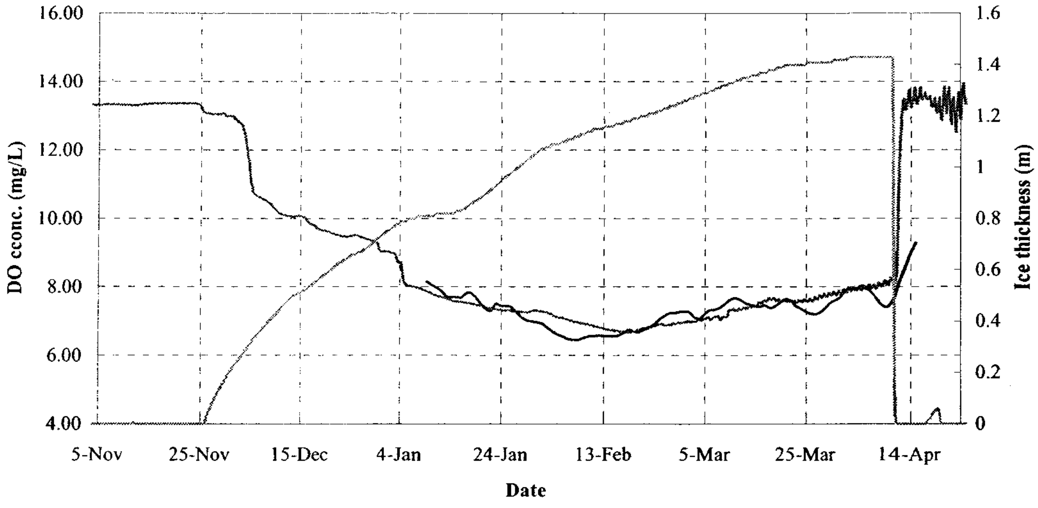
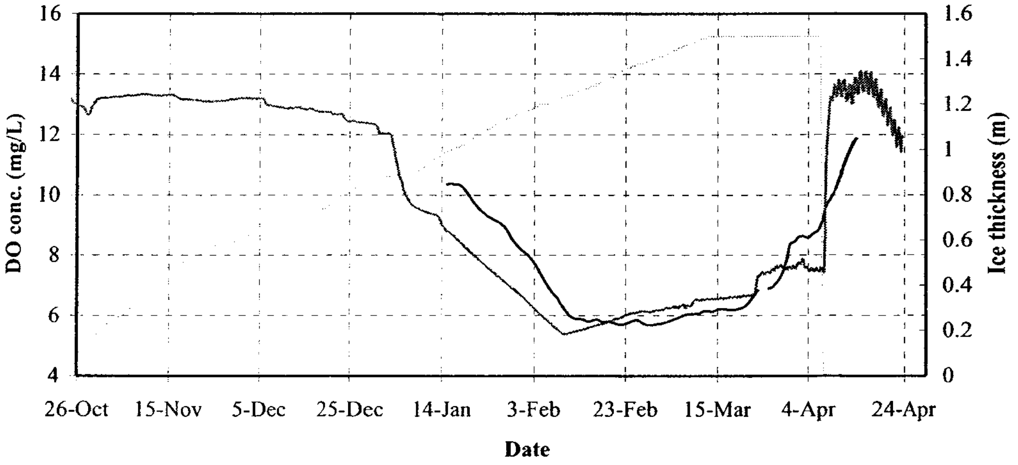


c. Ice Simulation 2001-2002



d. Ice Simulation 2002-2003

Figure 33 Comparison ice simulation to DO simulation at upstream of Grand Rapids

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4.3.3 Ice Cover and Reaeration

Ice cover plays an important role in the heat budget of northern water bodies (e.g. Athabasca River). Moreover ice cover prevents reaeration, which is a major source of DO. Ice cover is modeled in CE-QUAL-W2 base on an ice cover with ice-to-air heat exchange, conduction through the ice, conduction between underlying water and a melt temperature layer on the ice bottom (Ashton, 1979). CE-QUAL-W2 is capable of modeling the ice thickness according to the meteorological information (e.g. air temperatures and wind speed) and other information (e.g. solar radiation, effluent temperatures). CE-QUAL-W2 assumes that the ice covers a whole segment with the same ice thickness, and the heat exchange only change the thickness of the ice instead of ice cover ratio. In real situations, some open water zones exist even in mid-winter due to the effluent temperature. The open water zone is critical to the reaeration in winter. The recent data collected from the Athabasca River showed that the effluent temperature of Al-Pac is 20-23^{0}C; and the open water lead due to the effluent ranges from a few hundred meters to several kilometers long (Lima-Neto et al. 2005). The combined effect of air temperature, wind velocity and effluent discharge temperature at each year leads to a varied ice-cover-ratio (Tian, 2005). Therefore, the limitation of CE-QUAL-W2 in terms of ice cover modeling was found when it was used to model rivers with significant width in comparison to the width of the open water lead.

In order to minimize the impact of this limitation, different length of water segment were forced to be open water zone by positive air temperature input. The DO simulation by

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using this approach reproduced accurate predictions in mid-winter as illustrated in Figure 28, which indicates that the model can be used to predict reaeration rates by forcing a certain water body open.

The data of ice thickness downstream of Al-Pac in Athabasca River were obtained in Feburary 2004. The ice thickness ranges from 0.3 m to 2.0 m from the mid-channels to banks. The simulated ice thickness (Figure 33) is within the range.

4.3.4 SOD

Organic sediment contributions to nutrients and dissolved oxygen demand are simulated using two methods in CE-QUAL-W2. The first method uses a constant, or zero-order, release and demand. It does not depend on sediment concentrations or require a separate sediment compartment. However, the formulation is not predictive, as the rates do not vary over time except as a result of temperature dependence of the decay rate. The second method uses a sediment compartment to accumulate organic sediments and allow their decay. But the first-order sediment compartment in CE-QUAL-W2 is not a true sediment diagenesis compartment as it does not keep track of organic nutrient delivery to the sediments, their decay, and subsequent release back into the water column during hypoxic/anoxic conditions. However, it does keep track of organic matter delivery to the sediments via particulate organic matter and dead algal cells, and the subsequent water column oxygen demand that is exerted. The inclusion of the first–order sediment compartment makes the model more predictive in that any increase of organic matter delivery to the sediments will have an affect on SOD (Cole and Wells, 2005).

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In this simulation, both zero-order and first-order SOD were used to describe SOD rates. The newest SOD rates obtained from this study were used to describe the zero-order SOD. The SOD rates and other parameters are presented in the control file in Appendix C.

4.4 Summary

The most recent SOD data were used in the model in order to achieve more accurate DO predictions in the Athabasca River.

Despite the fact that assumptions had to be made in both the calibration and scenario evaluations, the model predictions are made with reasonable certainty. As the preceding figures illustrated, CE-QUAL-W2 is capable of modeling hydrodynamics, temperature, dissolved oxygen, nutrient, algae and epiphyton regimes in the Athabasca River for mid-winter, even though some limitations of the model were found during the simulation study. For example, the model failed to simulation the transition periods in spring.

CE-QUAL-W2 is capable of modeling ice thickness according to the meteorological information. CE-QUAL-W2 assumes that the ice covers a whole segment with the same ice thickness, and the heat exchange only change the thickness of the ice instead of ice cover ratio. This is considered a limitation of the CE-QUAL-W2. In order to simulate the real ice cover and reaeration situation a certain area of water body has to be open by using positive air temperature input.

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Moving the downstream boundary to downstream of Fort McMurray or moving the upstream boundary to a gage station up the Athabasca would provide more measured flow, temperature and water quality data to verify the simulation in more locations. Therefore, In order to obtain more complete and accurate simulation, it is recommended to apply CE-QUAL-W2 to a longer section of the Athabasca River.

Sensitivity analysis may be required to evaluate the sensitivity of DO concentration in the Athabasca River to changes in SOD in the river, BOD, TOC and nutrients loadings from the pulp mills and DO injection.

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5. Conclusions and Recommendations

5.1 Conclusions

In this thesis, a series of field studies (including a river survey) were conducted in fall and winter 2004 along the Athabasca River, to obtain accurate SOD rates along the river. A sediment core incubation method with floating magnetic stirring was developed during the field work to provide realistic estimates of SOD. The sediment core incubation method was compared to the closed chamber method and the microelectrode method. The impact of organic carbon and nutrients on SOD was investigated using the microelectrode method. The new SOD values obtained in this study were input into CE-QUAL-W2; and the model was calibrated for the section from the town of Athabasca to just upstream of Grand Rapids.

The following conclusions can be drawn in this study:

1) The sediment core incubation method developed in this study provided a convenient, reliable, yet cost-effective means for SOD determination in some habitats in the Athabasca River.
2) The SOD rate decreased during incubation. The decreasing rate was attributed to progressive depletion of dissolved oxygen and organic carbon concentrations over the course of the incubation.
3) SOD rates were correlated to temperature.

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4) Mixing speed is an important factor for SOD measurement. Sediment core incubation method allows for more accurate SOD estimation because mixing can be controled.

5) A factor of 1.4 was found between the total oxygen demand and diffusive oxygen demand for the Athabasca River sediment at the location of upstream of Al-Pac in September 2005.

6) Particulate organic carbon addition produced significant increase in SOD rate and reduced oxygen penetration depth. No significant change was detected by adding soluble nutrients (2 mg/L TP and 10 mg/L TN) and soluble organic carbon (57 mg/L) in the water column on their own.

7) CE-QUAL-W2 is capable of modeling ice cover using meteorological information. CE-QUAL-W2 assumes that the ice covers a whole segment with the same ice thickness; and the heat exchange only changes the thickness of the ice instead of ice cover ratio. In order to simulate the real ice cover and reaeration situation, a certain area of water body has to be open by using positive air temperature input.

8) CE-QUAL-W2 is capable of modeling hydrodynamics, temperature, DO, nutrients, algae regimes in mid-winter.

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5.2 Recommendations

1) The sediment core incubation method with internal mixing, developed in this project, is recommended for future SOD measurement made for modeling purposes in Alberta rivers.
2) Further work is needed to calibrate mixing speed with the boundary dynamics occurring in rivers at given flow and roughness conditions.
3) In order to obtain accurate SOD measurements, temperature must be accurately controled during incubation.
4) Organic carbon imputs caused significant increase in SOD. Therefore, the amount of organic carbon entering the river should be managed to reduce DO depletion.
5) Future work using particulate nutrient addition is recommended in order to investigate the impact of nutrient addition on SOD.
6) In order to obtain more complete and accurate simulation, CE-QUAL-W2 should be applied to the Athabasca River over its entire length.
7) Sensitivity analysis should be performed to evaluate relationships between DO concentration and changes in SOD, BOD, TOC and nutrient loadings from pulp mills.
8) This thesis represents an initial attempt at representing the Athabasca River. A more thorough modeling approach should be undertaken at which point management options such as DO injection can be assessed.

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Appendices

Appendix A Raw data of the field work

Table A1 Athabasca River Survey Field Parameters

Station	Location	Date	Time	Temp (^{0}C)	D.O. (titration) (mg/l)	D.O. (YSI) (mg/l)	pH	EC (μs/cm)
Maskuka Ck	MidChan	29/10/04	1115h	0.62		11.57	8	161
Emerson Bridge	LDB	30/10/04		0.83	12.08		8.23	133
	RDB			0.75	13.05		8.14	144
Knight Bridge	LDB	30/10/04	1700h	-0.61	12.62	13.3	8.5	170
	RDB			1.04	14.01	13.6	8.3	177
U/S McLeod R.	LDB	31/10/04	1200h	0.08		13.3	7.75	174
	RDB		1210h	0.06	13.22	13.37	7.73	140
McLeod R.	MidChan	31/10/04	1200h	0.03		13.47	7.18	145
D/S McLeod R.	LDB	31/10/04		Not accessible due to river ice				
	RDB			Not accessible due to river ice				
Blue Ridge	LDB	1/11/04	1000h	0.04		12.45	8.33	180
	RDB		1010h	0.02	13.25	12.9	8.36	157
Ft. Assiniboine	LDB	1/11/04	1400h	0.09	13.58	13.3	8.5	177
	RDB			0.05		13.04	8.56	176
Chisholm	LDB	2/11/04	1130h	0.09		13.33	8.2	174
	MidChan			0.07		12.93	8.29	175
	RDB			0.39	13.07	12.24	8.05	176
Pembina R.	MidChan	2/11/04	1530h	No Data				
Athabasca	LDB	3/11/04	0900h	0.05	13.45	13.67	8.44	156
	RDB		1045h	0.02	13.32	13.9	8.37	162
Calling River	LDB	3/11/04		Not accessible due to river ice				
	RDB		1430h	0.16	13.55	12.95	8.48	160
Pelican Landing	LDB	4/11/04	1240h	0.19		13.76	8.49	154
	RDB		1130h	0.14	13.27	13.72	8.49	156

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Table A2 Raw data and SOD calculation in Athabasca River during the river survey using the sediment core incubation method

Date	Location			Incubation time (h)	DO (mg/l)	Height of water (cm)	SOD (g $O_2/m^2.d$)	SOD(ave) (g $O_2/m^2.d$)	Incubation condition
Day2 10/29	Hinton upstream	RDB	24h blank	25.1	11.78				
			24h	25.1	11.29	42.0	0.20	0.17	
			24h	25.1	11.39	36.7	0.14		
			24h	25.1	10.30	39.7	0.56		mixed
			24h	25.1	10.20	37.5	0.57	0.57	mixed
		LDB	24h	25.1	11.14	48.7	0.30	0.30	10°C
		RDB	48h blank	47.3	12.13				frozen
			48h	47.3	11.44	34.0	0.12	0.14	frozen
			48h	47.3	11.29	36.5	0.16		frozen
Day3 10/30	Emerson bridge	island	24h blank	24.1	12.72				frozen
			24h	24.1	13.02	42.5	-0.13		frozen
	Knight bridge	LDB	24h blank	23	12.28				frozen
			24h	23	12.62	46.0	-0.17		frozen
			24h	23	12.57	52.0	-0.16		frozen
		island	24h	22.5	12.03	46.0	0.12	0.12	frozen
Day4 10/31	McLeod River		No fine sediment						
Day5 11/01	Blue Ridge		No fine sediment						
	Fort Assiniboine	LDB	24h blank	26	12.48				
			24h	25.6	11.93	46.5	0.32	0.32	
			24h	26	11.14	46.8	0.58		10°C
			24h	25.6	10.76	45.5	0.81		10 °C mixed

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			48h blank	49.8	12.40				
			48h	49.8	12.26	44.7	0.03		bar down
Day6 11/02	Chisholm	RDB	24h blank	25.8	12.41				
			24h	25.8	12.18	49.0	0.10	0.08	
			24h	25.8	12.28	49.0	0.06		
			24h	25.8	12.23	44.4	0.07		no bar
			48h blank	51.5	11.88				
			48h	51.5	11.58	46.2	0.06	0.04	
			48h	51.5	11.83	47.0	0.01		
Day7 11/03	Athabasca		No fine sediment						
	Calling River	RDB	24h blank	27.5	12.60				
			24h	27.5	12.13	50.0	0.21	0.21	
			24h	27.5	11.93	36.5	0.21		
			48h blank	47.8	12.36				
			48h	47.8	11.87	42.0	0.10	0.14	
			48h	47.8	11.60	45.5	0.17		
Day8 11/04	Pelican Landing	RDB	24h blank	27.8	12.57				
			24h	27.8	11.79	50.0	0.34	0.33	
		LDB	24h	27.8	11.77	46.5	0.32		
			48h	48.2	11.65	54.5	0.24	0.23	mixed
			48h	48.2	11.68	52.0	0.22		

░ 24h SOD

▓

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Table A3 Raw data and SOD calculation in North Saskatchewan River using closed chamber and sediment core incubation methods

Date	Location	Method	Core or chamber No.		Incubation time (h)	DO (mg/l)	Height of water column (cm)	SOD (g $O_2/m^2.d$)	Note
02-Dec-04	North Saskatchewan River	cores	3	24h blank	22.8	12.19			
			16	24h blank	22.8	12.17			
			10	24h w/o mixing	22.6	11.62	36.0	0.21	
			6	24h w/o mixing	22.5	11.85	36.0	0.13	
			13	24h w/o mixing	22.5	12.16	48.2	0.01	Stir bar out of order*
			9	24h w/mixing	22.2	11.64	46.0	0.27	
			20	24h w/mixing	22.3	11.24	36.3	0.37	
			8	24h w/mixing	22.3	10.72	34.5	0.54	mixed strongly**
		close chamber	8	24h blank	23	13.30			
			4	24h blank	23	13.22			
			9	24h	23	11.96	13.7	0.19	
			7	24h	23	11.22	11.5	0.24	
			11	24h	23	11.62	10.7	0.18	

* the stir bar droped to the surface of the sediment, so the result was not reliable

** this core was stirred by a more powerful stirrer,the rotary speed was higher than the others

Appendix B Raw data of the laboratory experiments

B.1 Determination of porosity of sediment

Table B1 Raw data and calculation of sediment porosity

Replicate	Volume of sediment (mL)	Wet weight (g)	Weight after dried (g)	loss of weight (g)	Porosity
1	120	326.45	261.04	65.41	0.55
2	58	136	103.32	32.68	0.56
3	42	118.94	95.91	23.03	0.55
Average					0.55

B.2 SOD calculation using microelectrode method.

B.2.1 Microelectrode calibration

The calibration equation was regressed from the calibration line, which was constructed according to the microelectrode calibration result in raw river water.

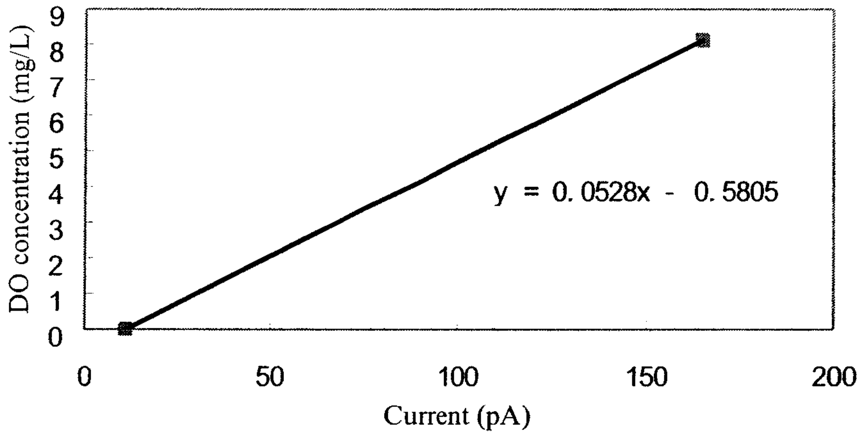

Figure B 1 Calibration line and calibration equation

B.2.1 DO concentration measurement along the depth of sediment

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The currents were transferred to DO concentration using calibration equation. A measurement example is showed in Table B 2. An oxygen profile was plotted using DO concentration versus depth of sediment.

Table B 2. Raw data of a measurement using microelectrode method

Depth of sediment (mm)	Current (read from picoammeter) (pA)	DO concentration (mg/L)
-3.4	164	8.0787
-2.4	160	7.8675
-1.4	163	8.0259
-0.9	163	8.0259
-0.8	163	8.0259
-0.7	165	8.1315
-0.6	164	8.0787
-0.5	163	8.0259
-0.4	162	7.9731
-0.3	160	7.8675
-0.2	149	7.2867
-0.1	143	6.9699
0	130	6.2835
0.1	121	5.8083
0.2	112	5.3331
0.3	101	4.7523
0.4	91	4.2243
0.5	81	3.6963
0.6	72	3.2211
0.7	64	2.7987
0.8	55	2.3235
0.9	48	1.9539
1	40	1.5315
1.1	34	1.2147
1.2	28	0.8979
1.3	24	0.6867
1.4	20	0.4755
1.5	17	0.3171
1.6	16	0.2643
1.7	14	0.1587
1.8	14	0.1587
1.9	13	0.1059
2	13	0.1059

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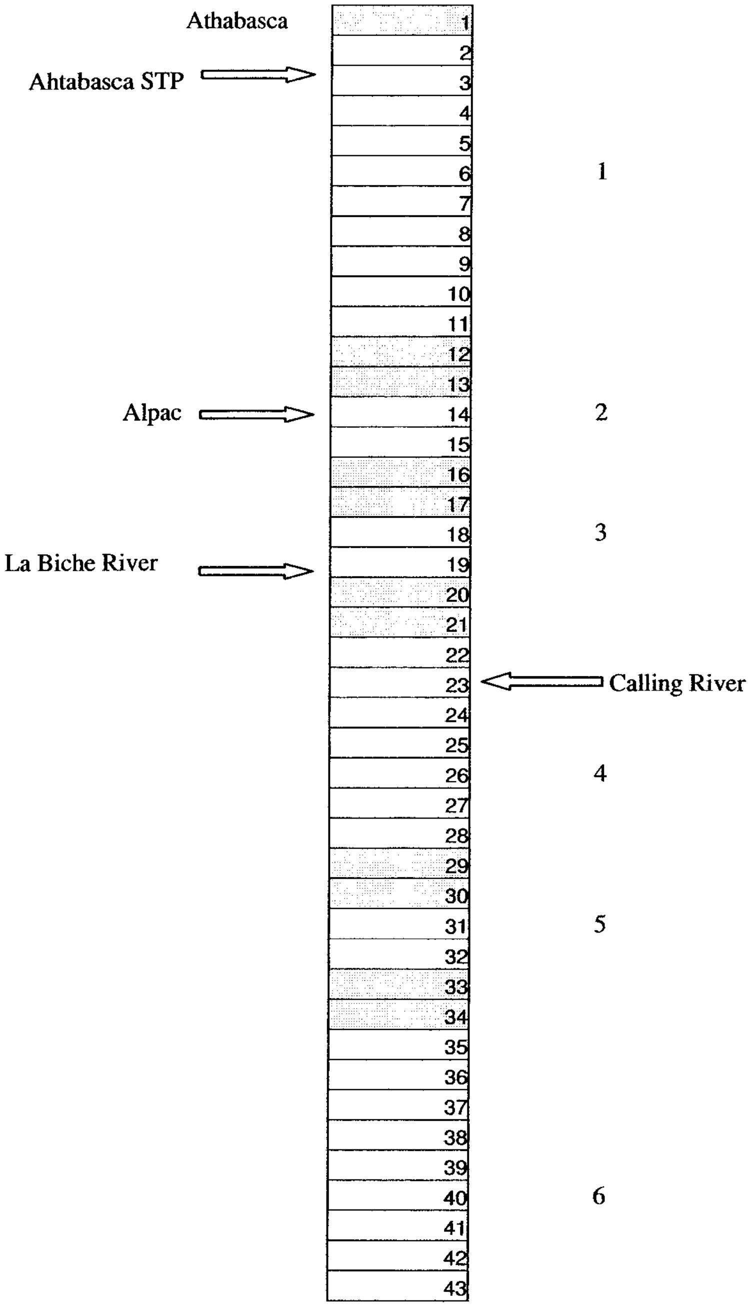
Appendix C Data of CE-QUAL-W2

C.1 Model segments and branch locations



	No. of Branch	Length of the segment (m
1		5300
2		5300
3		5300
4		5300
5		5300
6	1	5300
7		5300
8		5300
9		5300
10		5300
11		5300
12		5300
13		5300
14	2	5300
15		5300
16		5300
17		5300
18	3	5300
19		5300
20		5300
21		5300
22		5300
23	Calling River	5300
24		5300
25		5300
26	4	5300
27		4300
28		4300
29		4300
30		4500
31	5	4500
32		5000
33		4000
34		2740
35		2740
36		2740
37		2740
38		2740
39		2740
40	6	2740
41		2740
42		2740
43		2740

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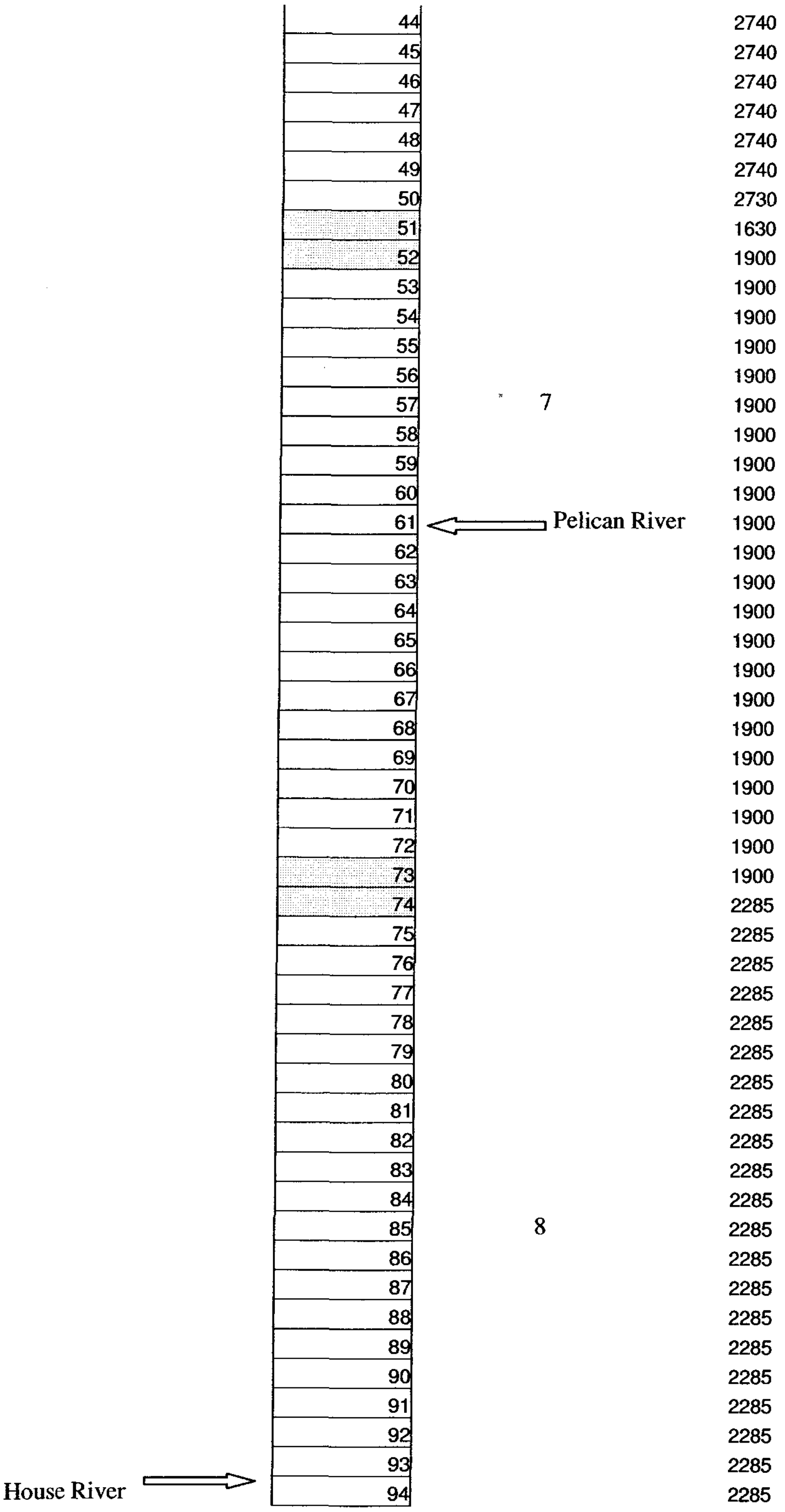

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45	2740
46	2740
47	2740
48	2740
49	2740
50	2730
51	1630
52	1900
53	1900
54	1900
55	1900
56	1900
57	1900
58	1900
59	1900
60	1900
61	1900
62	1900
63	1900
64	1900
65	1900
66	1900
67	1900
68	1900
69	1900
70	1900
71	1900
72	1900
73	1900
74	2285
75	2285
76	2285
77	2285
78	2285
79	2285
80	2285
81	2285
82	2285
83	2285
84	2285
85	2285
86	2285
87	2285
88	2285
89	2285
90	2285
91	2285
92	2285
93	2285
94	2285

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	95		2285
	96		2660
	97		2660
	98		2660
	99		2660
	100	9	2660
	101		2660
Grand Rapids	102		2660

Figure C3 Model segments and branch locations

C.2 Control file of CE-QUAL-W2

The parameters and constants used in this simulation were contained in control files.

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```
W2 Model Version 3.2

TITLE C ..............................TITLE..................................
     CE-QUAl-W2 v3.2 Control File

     Athabasca River
     River Model with Sloping Channels - 9Branches


     water quality simulation




GRID      NWB   NBR   IMX   KMX
            9     9   102     7

IN/OUTFL    NTR   NST   NIW   NWD   NGT   NSP   NPI   NPU
            6     0     0     0     0     0     0     0

CONSTITU    NGC   NSS   NAL   NEP  NBOD
            3     1     2     1     1

MISCELL    NDAY
           1000

TIME CON TMSTRT  TMEND   YEAR
     291.000 487.000   1999

DLT CON     NDT  DLTMIN
            2 0.10000

DLT DATE   DLTD    DLTD    DLTD    DLTD    DLTD    DLTD    DLTD    DLTD    DLTD
     1.00000 3.00000

DLT MAX  DLTMAX DLTMAX DLTMAX DLTMAX DLTMAX DLTMAX DLTMAX DLTMAX DLTMAX
     10.0000 50.0000

DLT FRN    DLTF    DLTF    DLTF    DLTF    DLTF    DLTF    DLTF    DLTF    DLTF
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WB 4        OFF    OFF
WB 5        OFF    OFF
WB 6        OFF    OFF
WB 7        OFF    OFF
WB 8        OFF    OFF
WB 9        OFF    OFF

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BR2      14    15    11    18     0     0     1 0.00026
BR3      18    19    15    22     0     0     1 0.00026
BR4      22    28    19    31     0     0     1 0.00026
BR5      31    32    28    35     0     0     1 0.00026
BR6      35    50    32    53     0     0     1 0.00058
BR7      53    72    50    75     0     0     1 0.00083
BR8      75    94    72    97     0     0     1 0.00056
BR9      97   101    94    -1     0     0     1 0.00056

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WB 2     54.7000 113.000 482.230     2     2     2
WB 3     54.7000 113.000 480.000     3     3     3
WB 4     54.7000 113.000 470.350     4     4     4
WB 5     55.0000 112.000 468.140     5     5     5
WB 6     55.0000 112.000 442.720     6     6     6
WB 7     56.0000 112.000 411.040     7     7     7
WB 8     56.0000 112.000 385.450     8     8     8
WB 9     56.0000 112.000 378.000     9     9     9

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WB 4       OFF    OFF    OFF    OFF     ON    OFF
WB 5       OFF    OFF    OFF    OFF     ON    OFF
WB 6       OFF    OFF    OFF    OFF     ON    OFF
WB 7       OFF    OFF    OFF    OFF     ON    OFF
WB 8       OFF    OFF    OFF    OFF     ON    OFF
WB 9       OFF    OFF    OFF    OFF     ON    OFF

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WB 9       ON     ON     ON     ON

INTERPOL  QINIC  DTRIC   HDIC
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BR3       ON     ON     ON
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WB 2      TERM    OFF    OFF     ON    OFF 9.20000 0.46000 2.00000 2.00000
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WB 4      TERM    OFF    OFF     ON    OFF 9.20000 0.46000 2.00000 2.00000
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WB 8      TERM    OFF    OFF     ON     OFF 9.20000 0.46000 2.00000 2.00000
WB 9      TERM    OFF    OFF     ON     OFF 9.20000 0.46000 2.00000 2.00000

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WB 2         ON  DETAIL 0.80000 70.0000 0.60000 0.10000 0.10000 0.00000
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WB 6    ULTIMATE 0.55000
WB 7    ULTIMATE 0.55000
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WB 9    ULTIMATE 0.55000

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WB 2     1.00000 1.00000 0.30000 3.00000 0.01000 0.90000    MANN
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WB 8     1.00000 1.00000 0.30000 3.00000 0.01000 0.90000    MANN
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WB 6      NICK    IMP 1.00000
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BR2        0
BR3        0
BR4        0
BR5        0
BR6        0
BR7        0
BR8        0
BR9        0

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BR 1
BR 2
BR 3
BR 4
BR 5
BR 6
BR 7
BR 8
BR 9

STR TOP   KTSTR  KTSTR  KTSTR  KTSTR  KTSTR  KTSTR  KTSTR  KTSTR  KTSTR
BR1
BR2
BR3
BR4
BR5
BR6
BR7
BR8
BR9
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BR2									
BR3									
BR4									
BR5									
BR6									
BR7									
BR8									
BR9									

STR SINK	SINKC	SINKC	SINKC	SINKC	SINKC	SINKC	SINKC	SINKC	SINKC
BR1									
BR2									
BR3									
BR4									
BR5									
BR6									
BR7									
BR8									
BR9									

STR ELEV	ESTR	ESTR	ESTR	ESTR	ESTR	ESTR	ESTR	ESTR	ESTR
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BR2									
BR3									
BR4									
BR5									
BR6									
BR7									
BR8									
BR9									

STR WIDT	WSTR	WSTR	WSTR	WSTR	WSTR	WSTR	WSTR	WSTR	WSTR
BR1									
BR2									
BR3									
BR4									
BR5									
BR6									

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BR7
BR8
BR9

PIPES IUPI IDPI EUPI EDPI WPI DLXPI FPI FMINPI WTHLC

PIPE UP PUPIC ETUPI EBUPI KTUPI KBUPI

PIPE DOWN PDPIC ETDPI EBDPI KTDPI KBDPI

SPILLWAY IUSP IDSP ESP A1SP B1SP A2SP B2SP WTHLC

SPILL UP PUSPC ETUSP EBUSP KTUSP KBUSP

SPILL DOWN PDSPC ETUSP EBUSP KTDSP KBDSP

SPILL GAS GASSPC EQSP AGASSP BGASSP CGASSP

GATES IUGT IDGT EGT A1GT B1GT G1GT A2GT B2GT G2GT WTHLC

GATE WEIR GTA1 GTB1 GTA2 GTB2 DYNVAR

GATE UP PUGTC ETUGT EBUGT KTUGT KBUGT

GATE DOWN PDGTC ETDGT EBDGT KTDGT KBDGT

GATE GAS GASGTC EQGT AGASGT BGASGT CGASGT

PUMPS 1 IUPU IDPU EPU STRTPU ENDPU EONPU EOFFPU QPU WTHLC

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WEIR BOT   KBWR   KBWR   KBWR   KBWR   KBWR   KBWR   KBWR   KBWR   KBWR

WD INT     WDIC   WDIC   WDIC   WDIC   WDIC   WDIC   WDIC   WDIC   WDIC

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WD BOT     KBWD   KBWD   KBWD   KBWD   KBWD   KBWD   KBWD   KBWD   KBWD

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BR 2       OFF
BR 3       OFF
BR 4       ON
BR 5       OFF
BR 6       ON
BR 7       ON
BR 8       ON
BR 9       ON

PUMPBACK    JBG    KTG    KBG    JBP    KTP    KBP
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PRINTER     LJC
            IV

HYD PRIN  HPRWBC  HPRWBC  HPRWBC  HPRWBC  HPRWBC  HPRWBC  HPRWBC  HPRWBC
HPRWBC
NVIOL     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
U       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
W        OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
T       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
RHO       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
AZ       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
SHEAR     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ST       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
SB       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ADMX      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DM        OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
HDG       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ADMZ      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
HPG       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
GRAV      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF

SNP PRINT   SNPC   NSNP   NISNP
WB 1       OFF     1      1
WB 2       OFF     1      1
```

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WB 3     OFF    1    1
WB 4     OFF    1    1
WB 5     OFF    1    1
WB 6     OFF    0    0
WB 7     OFF    0    0
WB 8     OFF    0    0
WB 9     OFF    0    0

SNP DATE   SNPD   SNPD   SNPD   SNPD   SNPD   SNPD   SNPD   SNPD   SNPD
WB 1   1.00000
WB 2   1.00000
WB 3   1.00000
WB 4   1.00000
WB 5   1.00000
WB 6
WB 7
WB 8
WB 9

SNP FREQ   SNPF   SNPF   SNPF   SNPF   SNPF   SNPF   SNPF   SNPF   SNPF
WB 1   14.5000
WB 2   14.5000
WB 3   14.5000
WB 4   14.5000
WB 5   14.5000
WB 6
WB 7
WB 8
WB 9

SNP SEG   ISNP   ISNP   ISNP   ISNP   ISNP   ISNP   ISNP   ISNP   ISNP
WB 1      24
WB 2      42
WB 3      64
WB 4      86
WB 5      93
WB 6
WB 7
WB 8
WB 9
```

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```
SCR PRINT   SCRC    NSCR
WB 1        OFF     1
WB 2        OFF     1
WB 3        OFF     1
WB 4        OFF     1
WB 5         ON     1
WB 6        OFF     0
WB 7        OFF     0
WB 8        OFF     0
WB 9        OFF     0

SCR DATE    SCRD    SCRD    SCRD    SCRD    SCRD    SCRD    SCRD    SCRD    SCRD
WB 1    1.00000
WB 2    1.00000
WB 3    1.00000
WB 4    1.00000
WB 5    1.00000
WB 6
WB 7
WB 8
WB 9

SCR FREQ    SCRF    SCRF    SCRF    SCRF    SCRF    SCRF    SCRF    SCRF    SCRF
WB 1    1.00000
WB 2    1.00000
WB 3    1.00000
WB 4    1.00000
WB 5    0.50000
WB 6
WB 7
WB 8
WB 9

PRF PLOT    PRFC    NPRF    NIPRF
WB 1        OFF     0       0
WB 2        OFF     0       0
WB 3        OFF     0       0
WB 4        OFF     0       0
WB 5        OFF     0       0
WB 6        OFF     0       0
WB 7        OFF     0       0
```

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```
WB 8      OFF    0    0
WB 9      OFF    0    0

PRF DATE   PRFD   PRFD   PRFD   PRFD   PRFD   PRFD   PRFD   PRFD   PRFD
WB 1
WB 2
WB 3
WB 4
WB 5
WB 6
WB 7
WB 8
WB 9

PRF FREQ   PRFF   PRFF   PRFF   PRFF   PRFF   PRFF   PRFF   PRFF   PRFF
WB 1
WB 2
WB 3
WB 4
WB 5
WB 6
WB 7
WB 8
WB 9

PRF SEG   IPRF   IPRF   IPRF   IPRF   IPRF   IPRF   IPRF   IPRF   IPRF
WB 1
WB 2
WB 3
WB 4
WB 5
WB 6
WB 7
WB 8
WB 9

SPR PLOT   SPRC   NSPR   NISPR
WB 1      OFF      1     23
WB 2      OFF      1     16
WB 3      OFF      1     20
WB 4      OFF      1     20
```

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```
WB 5      OFF    1    5
WB 6      OFF    0    0
WB 7      OFF    0    0
WB 8      OFF    0    0
WB 9      OFF    0    0

SPR DATE  SPRD   SPRD   SPRD   SPRD   SPRD   SPRD   SPRD   SPRD   SPRD
WB 1    0.10000
WB 2    0.10000
WB 3    0.10000
WB 4    0.10000
WB 5    0.10000
WB 6
WB 7
WB 8
WB 9

SPR FREQ  SPRF   SPRF   SPRF   SPRF   SPRF   SPRF   SPRF   SPRF   SPRF
WB 1    12.0000
WB 2    12.0000
WB 3    12.0000
WB 4    12.0000
WB 5    12.0000
WB 6
WB 7
WB 8
WB 9

SPR SEG    ISPR   ISPR   ISPR   ISPR   ISPR   ISPR   ISPR   ISPR   ISPR
WB 1        2      3      4      5      6      7      8      9     10
           11     12     13     14     15     16     17     18     19
           20     21     22     23     24
WB 2       27     28     29     30     31     32     33     34     35
           36     37     38     39     40     41     42
WB 3       45     46     47     48     49     50     51     52     53
           54     55     56     57     58     59     60     61     62
           63     64
WB 4       67     68     69     70     71     72     73     74     75
           76     77     78     79     80     81     82     83     84
           85     86
WB 5       89     90     91     92     93
```

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```
WB 6
WB 7
WB 8
WB 9

VPL PLOT   VPLC   NVPL
WB 1       OFF    0
WB 2       OFF    0
WB 3       OFF    0
WB 4       OFF    0
WB 5       OFF    0
WB 6       OFF    0
WB 7       OFF    0
WB 8       OFF    0
WB 9       OFF    0

VPL DATE   VPLD   VPLD   VPLD   VPLD   VPLD   VPLD   VPLD   VPLD   VPLD
WB 1
WB 2
WB 3
WB 4
WB 5
WB 6
WB 7
WB 8
WB 9

VPL FREQ   VPLF   VPLF   VPLF   VPLF   VPLF   VPLF   VPLF   VPLF   VPLF
WB 1
WB 2
WB 3
WB 4
WB 5
WB 6
WB 7
WB 8
WB 9

CPL PLOT   CPLC   NCPL
WB 1       OFF    1
WB 2       OFF    0
```

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```
WB 3      OFF     0
WB 4      OFF     0
WB 5      OFF     0
WB 6      OFF     0
WB 7      OFF     0
WB 8      OFF     0
WB 9      OFF     0

CPL DATE   CPLD    CPLD    CPLD    CPLD    CPLD    CPLD    CPLD    CPLD    CPLD
WB 1    1.00000
WB 2
WB 3
WB 4
WB 5
WB 6
WB 7
WB 8
WB 9

CPL FREQ   CPLF    CPLF    CPLF    CPLF    CPLF    CPLF    CPLF    CPLF    CPLF
WB 1    0.20000
WB 2
WB 3
WB 4
WB 5
WB 6
WB 7
WB 8
WB 9

FLUXES     FLXC   NFLX
WB 1      OFF     0
WB 2      OFF     0
WB 3      OFF     0
WB 4      OFF     0
WB 5      OFF     0
WB 6      OFF     0
WB 7      OFF     0
WB 8      OFF     0
WB 9      OFF     0
```

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```
FLX DATE   FLXD   FLXD   FLXD   FLXD   FLXD   FLXD   FLXD   FLXD   FLXD
WB 1
WB 2
WB 3
WB 4
WB 5
WB 6
WB 7
WB 8
WB 9

FLX FREQ   FLXF   FLXF   FLXF   FLXF   FLXF   FLXF   FLXF   FLXF   FLXF
WB 1
WB 2
WB 3
WB 4
WB 5
WB 6
WB 7
WB 8
WB 9

TSR PLOT   TSRC   NTSR  NITSR
             ON      1     50

TSR DATE   TSRD   TSRD   TSRD   TSRD   TSRD   TSRD   TSRD   TSRD   TSRD
        1.00000

TSR FREQ   TSRF   TSRF   TSRF   TSRF   TSRF   TSRF   TSRF   TSRF   TSRF
        0.10000

TSR SEG    ITSR   ITSR   ITSR   ITSR   ITSR   ITSR   ITSR   ITSR   ITSR
            101    100     97     94     88     86     85     84     83
             82     80     78     74     72     70     68     66     65
             64     62     60     58     56     55     54     53     52
             51     49     47     40     37     35     33     31     29
             27     25     23     20     18     16     15     14     13
             12     11      9      5      2

TSR LAYE   ETSR   ETSR   ETSR   ETSR   ETSR   ETSR   ETSR   ETSR   ETSR
        -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000
```

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```
        -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000
        -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000
        -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000
        -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000 -6.0000
        -6.0000 -6.0000 -6.0000 -6.0000 -6.0000

WITH OUT   WDOC   NWDO   NIWDO
        OFF      0      0

WITH DAT   WDOD   WDOD   WDOD   WDOD   WDOD   WDOD   WDOD   WDOD   WDOD


WITH FRE   WDOF   WDOF   WDOF   WDOF   WDOF   WDOF   WDOF   WDOF   WDOF


WITH SEG   IWDO   IWDO   IWDO   IWDO   IWDO   IWDO   IWDO   IWDO   IWDO


RESTART    RSOC   NRSO   RSIC
        OFF      0    OFF

RSO DATE   RSOD   RSOD   RSOD   RSOD   RSOD   RSOD   RSOD   RSOD   RSOD


RSO FREQ   RSOF   RSOF   RSOF   RSOF   RSOF   RSOF   RSOF   RSOF   RSOF


CST COMP    CCC   LIMC    CUF
        ON     ON     7

CST ACTIVE  CAC
TDS         ON
Gen1       OFF
Gen2       OFF
Gen3        ON
ISS1        ON
PO4         ON
NH4         ON
NO3         ON
DSI        OFF
PSI        OFF
```

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```
FE       ON
LDOM      ON
RDOM      ON
LPOM      ON
RPOM      ON
BOD1      ON
ALG1      ON
ALG2      ON
DO       ON
TIC      ON
ALK      ON

CST DERI  CDWBC  CDWBC  CDWBC  CDWBC  CDWBC  CDWBC  CDWBC  CDWBC  CDWBC
DOC       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
POC       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
TOC       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DON       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
PON       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
TON       OFF   OFF   OFF   OFF   OFF OFF   OFF   OFF   OFF
TKN       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
TN       ON    ON    ON    ON    ON    ON    ON    ON    ON
DOP       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
POP       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
TOP       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
TP       ON    ON    ON    ON    ON    ON    ON    ON    ON
APR       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
CHLA      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ATOT      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
%DO       ON    ON    ON    ON    ON    ON    ON    ON    ON
TSS      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
TISS     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
CBOD      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
pH       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
CO2      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
HCO3      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
CO3      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF

CST FLUX  CFWBC  CFWBC  CFWBC  CFWBC  CFWBC  CFWBC  CFWBC  CFWBC  CFWBC
TISSIN    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
TISSOUT    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
PO4AR     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
```

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PO4AG	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PO4AP	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PO4ER	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PO4EG	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PO4EP	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PO4POM	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PO4DOM	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PO4OM	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PO4SED	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PO4SOD	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PO4SET	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4NITR	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4AR	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4AG	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4AP	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4ER	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4EG	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4EP	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4POM	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4DOM	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4OM	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4SED	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NH4SOD	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NO3DEN	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NO3AG	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NO3EG	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
NO3SED	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
DSIAG	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
DSIEG	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
DSIPIS	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
DSISED	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
DSISOD	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
DSISET	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PSIAM	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PSINET	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PSIDK	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
FESET	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
FESED	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
LDOMDK	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
LRDOM	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
RDOMDK	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF

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```
LDOMAP    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
LDOMEP    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
LPOMDK    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
LRPOM     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
RPOMDK    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
LPOMAP    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
LPOMEP    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
LPOMSET   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
RPOMSET   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
CBODDK    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DOAP      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DOAR      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DOEP      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DOER      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DOPOM     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DODOM     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DOOM      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DONITR    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DOCBOD    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DOREAR    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DOSED     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DOSOD     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
TICAG     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
TICEG     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
SEDDK     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
SEDAS     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
SEDLPOM   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
SEDSET    OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
SODDK     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF

CST ICON  C2IWB  C2IWB  C2IWB  C2IWB  C2IWB  C2IWB  C2IWB  C2IWB  C2IWB
TDS     200.000 200.000 200.000 200.000 200.000 200.000 200.000 200.000 200.000
Gen1    0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
Gen2    0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
Gen3    298.000 300.000 300.000 300.000 300.000 300.000 300.000 300.000 300.000
ISS1    5.00000 5.00000 5.00000 5.00000 5.00000 5.00000 5.00000 5.00000 5.00000
PO4     0.00300 0.00500 0.00500 0.00500 0.00500 0.00500 0.00500 0.00500 0.00500
NH4     0.00500 0.00500 0.00500 0.00500 0.00500 0.00500 0.00500 0.00500 0.00500
NO3     0.03000 0.03000 0.03000 0.03000 0.03000 0.03000 0.03000 0.03000 0.03000
DSI     0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
```

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```
PSI     0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
FE      0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
LDOM     2.85000 2.85000 2.85000 2.85000 2.85000 2.85000 2.85000 2.85000 2.85000
RDOM     0.95000 0.95000 0.95000 0.95000 0.95000 0.95000 0.95000 0.95000 0.95000
LPOM     0.30000 0.30000 0.30000 0.30000 0.30000 0.30000 0.30000 0.30000 0.30000
RPOM     0.10000 0.10000 0.10000 0.10000 0.10000 0.10000 0.10000 0.10000 0.10000
BOD1     1.50000 1.50000 1.50000 1.50000 1.50000 1.50000 1.50000 1.50000 1.50000
ALG1    0.05000 0.10000 0.10000 0.10000 0.10000 0.10000 0.10000 0.10000 0.10000
ALG2    0.05000 0.10000 0.10000 0.10000 0.10000 0.10000 0.10000 0.10000 0.10000
DO      11.5300 11.5300 11.5300 11.5300 11.5300 11.5300 11.5300 11.5300 11.5300
TIC     29.4000 29.4000 29.4000 29.4000 29.4000 29.4000 29.4000 29.4000 29.4000
ALK     152.000 152.000 152.000 152.000 152.000 152.000 152.000 152.000 152.000

CST PRIN  CPRWBC  CPRWBC  CPRWBC  CPRWBC  CPRWBC  CPRWBC  CPRWBC
CPRWBC  CPRWBC
TDS       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
Gen1      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
Gen2      ON    ON    ON    ON    ON    ON    ON    ON    ON
Gen3      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ISS1      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
PO4       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
NH4       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
NO3       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DSI       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
PSI       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
FE        OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
LDOM       ON   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
RDOM       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
LPOM      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
RPOM       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
BOD1       ON    ON    ON    ON    ON    ON    ON    ON    ON
ALG1      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ALG2      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DO        ON    ON    ON    ON    ON    ON    ON    ON    ON
TIC       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ALK       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
```

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CIN CON	CINBRC	CINBRC	CINBRC	CINBRC	CINBRC	CINBRC	CINBRC	CINBRC	CINBRC
TDS	ON	ON	ON	ON	ON	ON	ON	ON	ON
Gen1	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
Gen2	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
Gen3	ON	ON	ON	ON	ON	ON	ON	ON	ON
ISS1	ON	ON	ON	ON	ON	ON	ON	ON	ON
PO4	ON	ON	ON	ON	ON	ON	ON	ON	ON
NH4	ON	ON	ON	ON	ON	ON	ON	ON	ON
NO3	ON	ON	ON	ON	ON	ON	ON	ON	ON
DSI	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
PSI	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
FE	ON	ON	ON	ON	ON	ON	ON	ON	ON
LDOM	ON	ON	ON	ON	ON	ON	ON	ON	ON
RDOM	ON	ON	ON	ON	ON	ON	ON	ON	ON
LPOM	ON	ON	ON	ON	ON	ON	ON	ON	ON
RPOM	ON	ON	ON	ON	ON	ON	ON	ON	ON
BOD1	ON	ON	ON	ON	ON	ON	ON	ON	ON
ALG1	ON	ON	ON	ON	ON	ON	ON	ON	ON
ALG2	ON	ON	ON	ON	ON	ON	ON	ON	ON
DO	ON	ON	ON	ON	ON	ON	ON	ON	ON
TIC	ON	ON	ON	ON	ON	ON	ON	ON	ON
ALK	ON	ON	ON	ON	ON	ON	ON	ON	ON

CTR CON	CTRTRC	CTRTRC	CTRTRC	CTRTRC	CTRTRC	CTRTRC	CTRTRC	CTRTRC	CTRTRC
TDS	OFF	ON	ON	ON	ON	ON			
Gen1	OFF	OFF	OFF	OFF	OFF	OFF			
Gen2	OFF	OFF	OFF	OFF	OFF	OFF			
Gen3	ON	ON	ON	ON	ON	ON			
ISS1	OFF	OFF	ON	OFF	OFF	OFF			
PO4	OFF	ON	ON	ON	OFF	ON			
NH4	ON	ON	ON	ON	ON	ON			
NO3	ON	ON	ON	ON	ON	OFF			
DSI	OFF	OFF	OFF	OFF	OFF	OFF			
PSI	OFF	OFF	OFF	OFF	OFF	OFF			
FE	OFF	ON	OFF	OFF	OFF	OFF			

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```
LDOM     ON    ON    ON    ON    ON    ON
RDOM     ON    ON    ON    ON    ON    ON
LPOM     ON    ON    OFF   OFF   OFF   OFF
RPOM     ON    ON    OFF   OFF   OFF   OFF
BOD1     ON    ON    ON    ON    ON    ON
ALG1     OFF   OFF   ON    OFF   OFF   OFF
ALG2     OFF   OFF   ON    OFF   OFF   OFF
DO       ON    ON    ON    ON    ON    ON
TIC      OFF   ON    OFF   OFF   OFF   OFF
ALK      ON    ON    ON    OFF   OFF   OFF

CDT CON  CDTBRC CDTBRC CDTBRC CDTBRC CDTBRC CDTBRC CDTBRC CDTBRC
CDTBRC
TDS      ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
Gen1     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
Gen2     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
Gen3     ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
ISS1     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
PO4      ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
NH4      ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
NO3      ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
DSI      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
PSI      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
FE       ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
LDOM     ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
RDOM     ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
LPOM     ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
RPOM     ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
BOD1     ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
ALG1     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ALG2     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DO       ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
TIC      ON    OFF   OFF   ON    OFF   ON    ON    ON    ON
ALK      ON    OFF   OFF   ON    OFF   ON    ON    ON    ON

CPR CON  CPRBRC CPRBRC CPRBRC CPRBRC CPRBRC CPRBRC CPRBRC CPRBRC
CPRBRC
```

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```
TDS      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
Gen1     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
Gen2     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
Gen3     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ISS1     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
PO4      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
NH4      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
NO3      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DSI      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
PSI      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
FE       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
LDOM     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
RDOM     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
LPOM     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
RPOM     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
BOD1     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ALG1     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ALG2     OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
DO       OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
TIC      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF
ALK      OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF   OFF

EX COEF   EXH2O   EXSS   EXOM   BETA    EXC   EXIC
WB 1    0.45000 0.10000 0.10000 0.25000   OFF   OFF
WB 2    0.45000 0.10000 0.10000 0.25000   OFF   OFF
WB 3    0.45000 0.10000 0.10000 0.25000   OFF   OFF
WB 4    0.45000 0.10000 0.10000 0.25000   OFF   OFF
WB 5    0.45000 0.10000 0.10000 0.25000   OFF   OFF
WB 6    0.45000 0.10000 0.10000 0.25000   OFF   OFF
WB 7    0.45000 0.10000 0.10000 0.25000   OFF   OFF
WB 8    0.45000 0.10000 0.10000 0.25000   OFF   OFF
WB 9    0.45000 0.10000 0.10000 0.25000   OFF   OFF

ALG EX     EXA    EXA    EXA    EXA    EXA    EXA
        0.30000 0.30000

GENERIC   CGQ10  CG0DK  CG1DK   CGS
```

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```
CG 1     0.00000 0.00000 0.00000 0.00000
CG 2     0.00000 0.00000 0.00000 0.00000
CG 3     0.00000 0.00000 0.00000 0.00000

S SOLIDS     SSS   SEDRC   TAUCR
SS# 1    0.25000      ON 0.10000

ALGAL RATE    AG      AR      AE      AM      AS    AHSP    AHSN   AHSSI    ASAT
ALG1     1.00000 0.02000 0.02000 0.10000 0.10000 0.00300 0.01000 0.00000 100.000
ALG2     1.00000 0.02000 0.02000 0.10000 0.10000 0.00300 0.01000 0.00000 100.000

ALGAL TEMP   AT1     AT2     AT3     AT4     AK1     AK2     AK3     AK4
ALG1     1.00000 3.00000 25.0000 30.0000 0.10000 0.90000 0.90000 0.10000
ALG2     0.00000 1.00000 2.00000 4.00000 0.10000 0.90000 0.90000 0.10000

ALG STOI   ALGP    ALGN    ALGC   ALGSI   ACHLA   ALPOM   ANEQN    ANPR
ALG1     0.00500 0.08000 0.45000 0.00000 65.0000 0.80000       1 0.00100
ALG2     0.00500 0.08000 0.45000 0.00000 65.0000 0.80000       1 0.00100

EPIPHYTE    EPIC    EPIC    EPIC    EPIC    EPIC    EPIC    EPIC    EPIC    EPIC
EPI1          ON      ON      ON      ON      ON      ON      ON      ON      ON

EPI PRIN    EPRC    EPRC    EPRC    EPRC    EPRC    EPRC    EPRC    EPRC    EPRC
EPI1          ON      ON      ON      ON      ON      ON      ON      ON      ON

EPI INIT   EPICI   EPICI   EPICI   EPICI   EPICI   EPICI   EPICI   EPICI   EPICI
EPI1     2.00000 2.00000 2.00000 2.00000 2.00000 2.00000 2.00000 2.00000 2.00000

EPI RATE      EG      ER      EE      EM      EB    EHSP    EHSN   EHSSI
EPI1     1.00000 0.02000 0.02000 0.05000 0.00005 0.00200 0.00200 0.00000

EPI HALF    ESAT     EHS   ENEQN    ENPR
EPI1     75.0000 8.00000       2 0.00100

EPI TEMP     ET1     ET2     ET3     ET4     EK1     EK2     EK3     EK4
EPI1     0.00000 1.00000 2.00000 24.0000 0.15000 0.90000 0.99000 0.10000
```

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```
EPI STOI    EP      EN      EC      ESI   ECHLA    EPOM
EPI1     0.00500 0.08000 0.45000 0.00000 85.0000 0.80000

DOM       LDOMDK  RDOMDK  LRDDK
WB 1     0.05000 0.00050 0.00500
WB 2     0.05000 0.00050 0.00500
WB 3     0.05000 0.00050 0.00500
WB 4     0.05000 0.00050 0.00500
WB 5     0.05000 0.00050 0.00500
WB 6     0.05000 0.00050 0.00500
WB 7     0.05000 0.00050 0.00500
WB 8     0.05000 0.00050 0.00500
WB 9     0.05000 0.00050 0.00500

POM       LPOMDK  RPOMDK  LRPDK    POMS
WB 1     0.04000 0.00100 0.00500 0.10000
WB 2     0.04000 0.00100 0.00500 0.10000
WB 3     0.04000 0.00100 0.00500 0.10000
WB 4     0.04000 0.00100 0.00500 0.10000
WB 5     0.04000 0.00100 0.00500 0.10000
WB 6     0.04000 0.00100 0.00500 0.10000
WB 7     0.04000 0.00100 0.00500 0.10000
WB 8     0.04000 0.00100 0.00500 0.10000
WB 9     0.04000 0.00100 0.00500 0.10000

OM STOIC    ORGP    ORGN    ORGC   ORGSI
WB 1     0.00500 0.08000 0.45000 0.18000
WB 2     0.00500 0.08000 0.45000 0.18000
WB 3     0.00500 0.08000 0.45000 0.18000
WB 4     0.00500 0.08000 0.45000 0.18000
WB 5     0.00500 0.08000 0.45000 0.18000
WB 6     0.00500 0.08000 0.45000 0.18000
WB 7     0.00500 0.08000 0.45000 0.18000
WB 8     0.00500 0.08000 0.45000 0.18000
WB 9     0.00500 0.08000 0.45000 0.18000

OM RATE    OMT1    OMT2    OMK1    OMK2
```

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```
WB 1    0.00000 26.0000 0.10000 0.99000
WB 2    0.00000 26.0000 0.10000 0.99000
WB 3    0.00000 26.0000 0.10000 0.99000
WB 4    0.00000 26.0000 0.10000 0.99000
WB 5    0.00000 26.0000 0.10000 0.99000
WB 6    0.00000 26.0000 0.10000 0.99000
WB 7    0.00000 26.0000 0.10000 0.99000
WB 8    0.00000 26.0000 0.10000 0.99000
WB 9    0.00000 26.0000 0.10000 0.99000

CBOD       KBOD   TBOD    RBOD
BOD 1    0.20000 1.01470 1.85000

CBOD STOIC  BODP    BODN    BODC
BOD 1    0.00400 0.06000 0.32000

PHOSPHOR    PO4R   PARTP
WB 1    0.00100 0.00000
WB 2    0.00100 0.00000
WB 3    0.00100 0.00000
WB 4    0.00100 0.00000
WB 5    0.00100 0.00000
WB 6    0.00100 0.00000
WB 7    0.00100 0.00000
WB 8    0.00100 0.00000
WB 9    0.00100 0.00000

AMMONIUM    NH4R   NH4DK
WB 1     0.0010 1.80000
WB 2     0.0010 1.80000
WB 3     0.0010 1.80000
WB 4     0.0010 1.80000
WB 5     0.0010 1.80000
WB 6     0.0010 1.80000
WB 7     0.0010 1.80000
WB 8     0.0010 1.80000
WB 9     0.0010 1.80000
```

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```
NH4 RATE   NH4T1   NH4T2   NH4K1   NH4K2
WB 1     0.00000  3.0000 0.20000 0.99000
WB 2     0.00000  3.0000 0.20000 0.99000
WB 3     0.00000  3.0000 0.20000 0.99000
WB 4     0.00000  3.0000 0.20000 0.99000
WB 5     0.00000  3.0000 0.20000 0.99000
WB 6     0.00000  3.0000 0.20000 0.99000
WB 7     0.00000  3.0000 0.20000 0.99000
WB 8     0.00000  3.0000 0.20000 0.99000
WB 9     0.00000  3.0000 0.20000 0.99000

NITRATE    NO3DK    NO3S
WB 1      0.0500 0.50000
WB 2      0.0500 0.50000
WB 3      0.0500 0.50000
WB 4      0.0500 0.50000
WB 5      0.0500 0.50000
WB 6      0.0500 0.50000
WB 7      0.0500 0.50000
WB 8      0.0500 0.50000
WB 9      0.0500 0.50000

NO3 RATE   NO3T1   NO3T2   NO3K1   NO3K2
WB 1    0.00000 25.0000 0.10000 0.99000
WB 2    0.00000 25.0000 0.10000 0.99000
WB 3    0.00000 25.0000 0.10000 0.99000
WB 4    0.00000 25.0000 0.10000 0.99000
WB 5    0.00000 25.0000 0.10000 0.99000
WB 6    0.00000 25.0000 0.10000 0.99000
WB 7    0.00000 25.0000 0.10000 0.99000
WB 8    0.00000 25.0000 0.10000 0.99000
WB 9    0.00000 25.0000 0.10000 0.99000

SILICA     DSIR    PSIS   PSIDK  PARTSI
WB 1    0.10000 0.00000 0.30000 0.00000
WB 2    0.10000 0.00000 0.30000 0.00000
```

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```
WB 3    0.10000 0.00000 0.30000 0.00000
WB 4    0.10000 0.00000 0.30000 0.00000
WB 5    0.10000 0.00000 0.30000 0.00000
WB 6    0.10000 0.00000 0.30000 0.00000
WB 7    0.10000 0.00000 0.30000 0.00000
WB 8    0.10000 0.00000 0.30000 0.00000
WB 9    0.10000 0.00000 0.30000 0.00000

IRON       FER    FES
WB 1    0.30000 1.00000
WB 2    0.30000 1.00000
WB 3    0.30000 1.00000
WB 4    0.30000 1.00000
WB 5    0.30000 1.00000
WB 6    0.30000 1.00000
WB 7    0.30000 1.00000
WB 8    0.30000 1.00000
WB 9    0.30000 1.00000

SED CO2    CO2R
WB 1    0.10000
WB 2    0.10000
WB 3    0.10000
WB 4    0.10000
WB 5    0.10000
WB 6    0.10000
WB 7    0.10000
WB 8    0.10000
WB 9    0.10000

STOICH 1   O2NH4   O2OM
WB 1    4.57000 1.40000
WB 2    4.57000 1.40000
WB 3    4.57000 1.40000
WB 4    4.57000 1.40000
WB 5    4.57000 1.40000
WB 6    4.57000 1.40000
```

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```
WB 7    4.57000 1.40000
WB 8    4.57000 1.40000
WB 9    4.57000 1.40000

STOICH 2   O2AR   O2AG
ALG1    1.10000 1.40000
ALG2    1.10000 1.40000

STOICH 3   O2ER   O2EG
EPI1    1.10000 1.40000

O2 LIMIT   O2LIM
     0.10000

SEDIMENT   SEDC  SEDPRC  SEDCI   SEDK   FSOD   FSED
WB 1        ON     ON 0.20000 0.05000 2.00000 1.00000
WB 2        ON     ON 0.20000 0.05000 2.00000 1.00000
WB 3        ON     ON 0.20000 0.05000 2.00000 1.00000
WB 4        ON     ON 0.20000 0.10000 2.00000 1.00000
WB 5        ON     ON 0.30000 0.10000 2.00000 1.00000
WB 6        ON     ON 0.30000 0.10000 2.00000 1.00000
WB 7        ON     ON 0.30000 0.10000 2.00000 1.00000
WB 8        ON     ON 0.30000 0.10000 2.00000 1.00000
WB 9        ON     ON 0.30000 0.10000 2.00000 1.00000

SOD RATE   SODT1   SODT2   SODK1   SODK2
WB 1    0.00000 8.00000 0.10000 0.99000
WB 2    0.00000 8.00000 0.10000 0.90000
WB 3    0.00000 8.00000 0.10000 0.90000
WB 4    0.00000 8.00000 0.10000 0.90000
WB 5    0.00000 8.00000 0.10000 0.90000
WB 6    0.00000 8.00000 0.10000 0.90000
WB 7    0.00000 8.00000 0.10000 0.90000
WB 8    0.00000 8.00000 0.10000 0.90000
WB 9    0.00000 8.00000 0.10000 0.90000

S DEMAND    SOD    SOD    SOD    SOD    SOD    SOD    SOD    SOD    SOD
```

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```
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000 0.15000
0.15000 0.15000 0.15000

REAERATION TYPE  EQN#  COEF1   COEF2   COEF3   COEF4
WB 1     RIVER     2 0.00000 0.00000 0.00000 0.00000
WB 2     RIVER     2 0.00000 0.00000 0.00000 0.00000
WB 3     RIVER     2 0.00000 0.00000 0.00000 0.00000
WB 4     RIVER     2 0.00000 0.00000 0.00000 0.00000
WB 5     RIVER     2 0.00000 0.00000 0.00000 0.00000
WB 6     RIVER     2 0.00000 0.00000 0.00000 0.00000
WB 7     RIVER     2 0.00000 0.00000 0.00000 0.00000
WB 8     RIVER     2 0.00000 0.00000 0.00000 0.00000
WB 9     RIVER     2 0.00000 0.00000 0.00000 0.00000

RSI FILE.................................RSIFN.................................
     rsi.npt - not used

QWD FILE.................................QWDFN.................................
     qwd.npt

QGT FILE.................................QGTFN.................................
     qgt.npt - not used

WSC FILE.................................WSCFN.................................
     wsc.npt

SHD FILE.................................SHDFN.................................
```

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```
    shd.npt

BTH FILE................................BTHFN................................
WB 1   Bth_wb1.npt
WB 2   Bth_wb2.npt
WB 3   Bth_wb3.npt
WB 4   Bth_wb4.npt
WB 5   Bth_wb5.npt
WB 6   Bth_wb6.npt
WB 7   bth_wb7.npt
WB 8   bth_wb8.npt
WB 9   bth_wb9.npt

MET FILE................................METFN................................
WB 1   Met_wb1.npt
WB 2   Met_wb2.npt
WB 3   Met_wb3.npt
WB 4   Met_wb4.npt
WB 5   Met_wb5.npt
WB 6   met_wb6.npt
WB 7   met_wb7.npt
WB 8   met_wb8.npt
WB 9   met_wb9.npt

EXT FILE................................EXTFN................................
WB 1   ext_1.npt
WB 2   ext_2.npt
WB 3   ext_3.npt
WB 4   ext_4.npt
WB 5   ext_5.npt
WB 6   ext_6.npt
WB 7   ext_7.npt
WB 8   ext_8.npt
WB 9   ext_9.npt

VPR FILE................................VPRFN................................
WB 1   vpr1.npt - not used
```

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WB 2	vpr2.npt - not used
WB 3	vpr3.npt - not used
WB 4	vpr4.npt - not used
WB 5	vpr5.npt- not used
WB 6	vpr_6.npt- not used
WB 7	vpr_7.npt- not used
WB 8	vpr_8.npt- not used
WB 9	vpr_9.npt- not used

LPR FILE.................................LPRFN.................................

WB 1	lpr1.npt - not used
WB 2	lpr2.npt - not used
WB 3	lpr3.npt - not used
WB 4	lpr4.npt - not used
WB 5	lpr5.npt - not used
WB 6	lpr6.npt - not used
WB 7	lpr_7.npt- not used
WB 8	lpr_8.npt- not used
WB 9	lpr_9.npt- not used

QIN FILE.................................QINFN.................................

BR1	qin_br1.npt
BR2	qin_br2.npt
BR3	qin_br3.npt
BR4	qin_br4.npt
BR5	qin_br5.npt
BR6	qin_br6.npt
BR7	qin_br7.npt
BR8	qin_br8.npt
BR9	qin_br9.npt

TIN FILE.................................TINFN.................................

BR1	tin_br1.npt
BR2	tin_br2.npt
BR3	tin_br3.npt
BR4	tin_br4.npt
BR5	tin_br5.npt

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BR6	tin_br6.npt
BR7	tin_br7.npt
BR8	tin_br8.npt
BR9	tin_br9.npt

CIN FILE..................................CINFN.................................

BR1	cin_br1.npt
BR2	cin_br2.npt
BR3	cin_br3.npt
BR4	cin_br4.npt
BR5	cin_br5.npt
BR6	cin_br6.npt
BR7	cin_br7.npt
BR8	cin_br8.npt
BR9	cin_br9.npt

QOT FILE..................................QOTFN.................................

BR1	qot_br1.npt - not used
BR2	qot_br2.npt - not used
BR3	qot_br3.npt - not used
BR4	qot_br4.npt - not used
BR5	qot_br5.npt - not used
BR6	qot_br6.npt- not used
BR7	qot_br7.npt- not used
BR8	qot_br8.npt- not used
BR9	qot_br9.npt- not used

QTR FILE..................................QTRFN.................................

TR1	Qtr_1.npt
TR2	Qtr_2.npt
TR3	Qtr_3.npt
TR4	Qtr_4.npt
TR5	Qtr_5.npt
TR6	Qtr_6.npt

TTR FILE..................................TTRFN.................................

TR1	Ttr_1.npt

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```
TR2    Ttr_2.npt
TR3    Ttr_3.npt
TR4    Ttr_4.npt
TR5    Ttr_5.npt
TR6    Ttr_6.npt

CTR FILE.................................CTRFN.................................
TR1    ctr_1.npt
TR2    ctr_2.npt
TR3    ctr_3.npt
TR4    ctr_4.npt
TR5    ctr_5.npt
TR6    ctr_6.npt

QDT FILE.................................QDTFN.................................
BR1    qdt_br1.npt
BR2    qdt_br2.npt
BR3    qdt_br3.npt
BR4    qdt_br4.npt
BR5    qdt_br5.npt
BR6    qdt_br6.npt
BR7    qdt_br7.npt
BR8    qdt_br8.npt
BR9    qdt_br9.npt

TDT FILE.................................TDTFN.................................
BR1    tdt_br1.npt
BR2    tdt_br2.npt
BR3    tdt_br3.npt
BR4    tdt_br4.npt
BR5    tdt_br5.npt
BR6    tdt_br6.npt
BR7    tdt_br7.npt
BR8    tdt_br8.npt
BR9    tdt_br9.npt

CDT FILE.................................CDTFN.................................
```

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BR1	cdt_br1.npt
BR2	cdt_br2.npt
BR3	cdt_br3.npt
BR4	cdt_br4.npt
BR5	cdt_br5.npt
BR6	cdt_br6.npt
BR7	cdt_br7.npt
BR8	cdt_br8.npt
BR9	cdt_br9.npt

PRE FILE.................................PREFN................................

BR1	pre_br1.npt - not used
BR2	pre_br2.npt - not used
BR3	pre_br3.npt - not used
BR4	pre_br4.npt - not used
BR5	pre_br5.npt - not used
BR6	pre_br6.npt- not used
BR7	pre_br7.npt- not used
BR8	pre_br8.npt- not used
BR9	pre_br9.npt- not used

TPR FILE.................................TPRFN................................

BR1	tpr_br1.npt - not used
BR2	tpr_br2.npt - not used
BR3	tpr_br3.npt- not used
BR4	tpr_br4.npt- not used
BR5	tpr_br5.npt- not used
BR6	tpr_br6.npt- not used
BR7	tpr_br7.npt- not used
BR8	tpr_br8.npt- not used
BR9	tpr_br9.npt- not used

CPR FILE.................................CPRFN................................

BR1	cpr_br1.npt - not used
BR2	cpr_br2.npt - not used
BR3	cpr_br3.npt - not used
BR4	cpr_br4.npt - not used

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BR5 cpr_br5.npt - not used
BR6 cpr_br6.npt- not used
BR7 cpr_br7.npt- not used
BR8 cpr_br8.npt- not used
BR9 cpr_br9.npt- not used

EUH FILE.................................EUHFN.................................
BR1 euh_br1.npt - not used
BR2 euh_br2.npt - not used
BR3 euh_br3.npt - not used
BR4 euh_br4.npt - not used
BR5 euh_br5.npt - not used
BR6 euh_br6.npt- not used
BR7 euh_br7.npt- not used
BR8 euh_br8.npt- not used
BR9 euh_br9.npt- not used

TUH FILE.................................TUHFN.................................
BR1 tuh_br1.npt - not used
BR2 tuh_br2.npt - not used
BR3 tuh_br3.npt - not used
BR4 tuh_br4.npt - not used
BR5 tuh_br5.npt - not used
BR6 tuh_br6.npt- not used
BR7 tuh_br7.npt- not used
BR8 tuh_br8.npt- not used
BR9 tuh_br9.npt- not used

CUH FILE.................................CUHFN.................................
BR1 cuh_br1.npt - not used
BR2 cuh_br2.npt - not used
BR3 cuh_br3.npt - not used
BR4 cuh_br4.npt - not used
BR5 cuh_br5.npt - not used
BR6 cuh_br6.npt- not used
BR7 cuh_br7.npt- not used
BR8 cuh_br8.npt- not used

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BR9 cuh_br9.npt- not used

EDH FILE..................................EDHFN..................................
BR1 edh_br1.npt - not used
BR2 edh_br2.npt - not used
BR3 edh_br3.npt - not used
BR4 edh_br4.npt - not used
BR5 edh_br5.npt- not used
BR6 edh_br6.npt- not used
BR7 edh_br7.npt- not used
BR8 edh_br8.npt- not used
BR9 edh_br9.npt

TDH FILE..................................TDHFN..................................
BR1 tdh_br1.npt - not used
BR2 tdh_br2.npt - not used
BR3 tdh_br3.npt - not used
BR4 tdh_br4.npt - not used
BR5 tdh_br5.npt- not used
BR6 tdh_br6.npt- not used
BR7 tdh_br7.npt- not used
BR8 tdh_br8.npt- not used
BR9 tdh_br9.npt

CDH FILE..................................CDHFN..................................
BR1 cdh_br1.npt - not used
BR2 cdh_br2.npt - not used
BR3 cdh_br3.npt - not used
BR4 cdh_br4.npt - not used
BR5 cdh_br5.npt- not used
BR6 cdh_br6.npt- not used
BR7 cdh_br7.npt- not used
BR8 cdh_br8.npt- not used
BR9 cdh_br9.npt

SNP FILE..................................SNPFN..................................
WB 1 snp_wb1.opt

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WB 2	snp_wb2.opt
WB 3	snp_wb3.opt
WB 4	snp_wb4.opt
WB 5	snp_wb5.opt
WB 6	snp_br6.opt
WB 7	snp_br7.opt
WB 8	snp_br8.opt
WB 9	snp_br9.opt

PRF FILE.................................PRFFN.................................

WB 1	prf_wb1.opt
WB 2	prf_wb2.opt
WB 3	prf_wb3.opt
WB 4	prf_wb4.opt
WB 5	prf_wb5.opt
WB 6	prf_wb6.opt
WB 7	prf_7.opt
WB 8	prf_8.opt
WB 9	prf_9.opt

VPL FILE.................................VPLFN.................................

WB 1	vpl_wb1.opt
WB 2	vpl_wb2.opt
WB 3	vpl_wb3.opt
WB 4	vpl_wb4.opt
WB 5	vpl_wb5.opt
WB 6	vpl_wb6.opt
WB 7	vpl_7.opt
WB 8	vpl_8.opt
WB 9	vpl_9.opt

CPL FILE.................................CPLFN.................................

WB 1	cpl_wb1.opt
WB 2	cpl_wb2.opt
WB 3	cpl_wb3.opt
WB 4	cpl_wb4.opt
WB 5	cpl_wb5.opt

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WB 6	cpl_wb6.opt
WB 7	cpl_7.opt
WB 8	cpl_8.opt
WB 9	cpl_9.opt

SPR FILE.................................SPRFN.................................

WB 1	spr_wb1.opt
WB 2	spr_wb2.opt
WB 3	spr_wb3.opt
WB 4	spr_wb4.opt
WB 5	spr_wb5.opt
WB 6	spr_wb6.opt
WB 7	spr_7.opt
WB 8	spr_8.opt
WB 9	spr_9.opt

FLX FILE.................................FLXFN.................................

WB 1	flx_wb1.opt
WB 2	flx_wb2.opt
WB 3	flx_wb3.opt
WB 4	flx_wb4.opt
WB 5	flx_wb5.opt
WB 6	flx_wb6.opt
WB 7	flx_7.opt
WB 8	flx_8.opt
WB 9	flx_9.opt

TSR FILE.................................TSRFN.................................

tsr.opt

WDO FILE.................................WDOFN.................................

wdo.opt - not used

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