Method development and measurement of sediment oxygen demand during the winter on the Athabasca River

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SUMMARY

Computer modelling of the oxygen balance of the Athabasca River is being used to assess the potential water quality impacts of expanding pulp mill development and to set appropriate effluent standards for the mills. Sediment oxygen demand (SOD) is an important variable in the oxygen balance of the river, particularily during ice cover when re-aeration is minimal. The objective of this study was to develop a method to measure SOD and to use this procedure to obtain SOD measurements during the winter on the Athabasca River.

We used stainless steel chambers covering or containing river substratum and measured oxygen depletion therein. Chambers had current-driven 'water vanes' to provide some internal current and mixing. Chamber leakage was checked by Monitoring conductance after a salt injection.

The estimates of SOD were obtained for five locations: Hinton, Knight bridge, Windfall bridge, Whitecourt, and Fort Assiniboine. Two of these locations were about 1 km downstream of the existing pulp mills, at Hinton and Whitecourt. Several factors were identified which may have caused underestimates of the SOD rates: (1) reduced dissolved oxygen (DO) concentration in the chamber due to oxygen consumption, extraction of water samples and water exchange during sampling, (2) reduced water velocity at the substratum-water interface, (3) reduced mixing of water in the chamber, and (4) at some sites, an overestimation of the oxygen demand of the water column. In contrast, only one factor would have led to overestimates: error in estimating chamber volumes. This was only suspected at two of the sites.

Highest SOD rates were recorded at sites immediately downstream of the two pulp mills. At Hinton the study sites were located downstream of the combined pulp mill/municipal effluent, and at Whitecourt the site was downstream of the pulp mill effluent but upstream of the municipal effluent. Lowest rates of SOD were recorded at the study sites at the greatest distances downstream of the pulp mills. The rates were:

Study site	Mean SOD (g/m^2/d)	n	Coefficient of variation(%)
Hinton, site 1:	0.357	3	19
Hinton, site 2:	0.174	4	63
Hinton, site 3:	0.185	2	44
	0.116	1	--
	0.127	1	--
Knight bridge:	0.058	3	40
	0.074	3	29
Windfall bridge:	0.015	2	NA
	0.001	3	NA

Study site	Mean SOD ($g/m^2/d$)	n	Coefficient of variation(%)
Whitecourt:	0.515	2	2
	0.457	3	29
Fort Assiniboine:	0.188	6	58

This work had a number of limitations including the fact that sampling could only be done in a limited range of depths and velocities, and that only 33 measurements were obtained. Despite this, the SOD rates for the Athabasca River were similar to rates reported in the literature where SOD was measured in flowing waters and at temperatures close to freezing. As well, the rates had a predictable pattern in that they were highest immediately downstream of the two pulp mills, likely due to organic and inorganic enrichment from their effluent. As a result we consider the data to be a reasonable representation of at least the relative rates from place to place.

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1. INTRODUCTION

Pulp mill capacity is expanding rapidly on the Athabasca River system. New pulp mills are in the planning stages, under construction, or recently built, and the existing mill at Hinton is increasing its capacity. Water quality modelling is being used to predict potential impacts and aid in setting appropriate effluent standards for the mills. The oxygen demand of the river bed, or sediment oxygen demand, is an important variable in the oxygen balance of the river and in the oxygen modelling.

The definition of sediment oxygen demand (SOD) varies between researchers (e.g. see the collection of papers edited by Hatcher 1986). However, SOD can be considered as the rate of oxygen consumption from the water column by the substratum in aquatic systems. Processes resulting in SOD include decomposition and chemical oxidation of settled organic material, and respiration of benthic organisms. Environmental factors, such as settling, scour, burial of organic material, water velocity and turbulence, and the oxygen concentration gradient in the substrata (e.g. see Hatcher 1986a) will also influence the rate of oxygen consumption by the substratum. Many attempts have been made to predict SOD using simple equations based on abiotic and biotic parameters, however, this has been very difficult due to the many interrelated factors involved (Hatcher 1986b).

In our study, we considered SOD to include all oxygen consuming processes in, or on the river bed. We used a change in dissolved oxygen (DO) in chambers placed in situ, as a measure of SOD. Little work has been done on SOD in Alberta rivers, in particular during the winter, and none has been done on the Athabasca River. Oxygen demand of the sediment is probably a very important mechanism depleting DO in ice-covered rivers (e.g., Babin and Trew 1985). A large part of this study was directed at developing a satisfactory technique to measure oxygen demand of the river bed. From a survey of the literature on SOD it appears that there has been little work on measuring the oxygen demand of rocky substrata, as opposed to sand-silt substrata. Rocks were common at the proposed study sites on the Athabasca River.

The objective of this study was to develop a method to measure SOD for rivers, and to use this procedure on the upper Athabasca River. We used stainless steel chambers either covering or containing substratum from the river to obtain measurements of SOD.

2. DESCRIPTION OF STUDY SITES

Five locations were sampled for this study: Hinton, Knight bridge, Windfall bridge, Whitecourt, and Fort Assiniboine (Figure 1). At Hinton, 3 study sites of different substrata were sampled. The Hinton study sites were located about 1 km downstream of the combined pulp mill and municipal effluent, and were ice-free. At Whitecourt 2 sites about 80 m apart were sampled but were considered as 1 site because of the

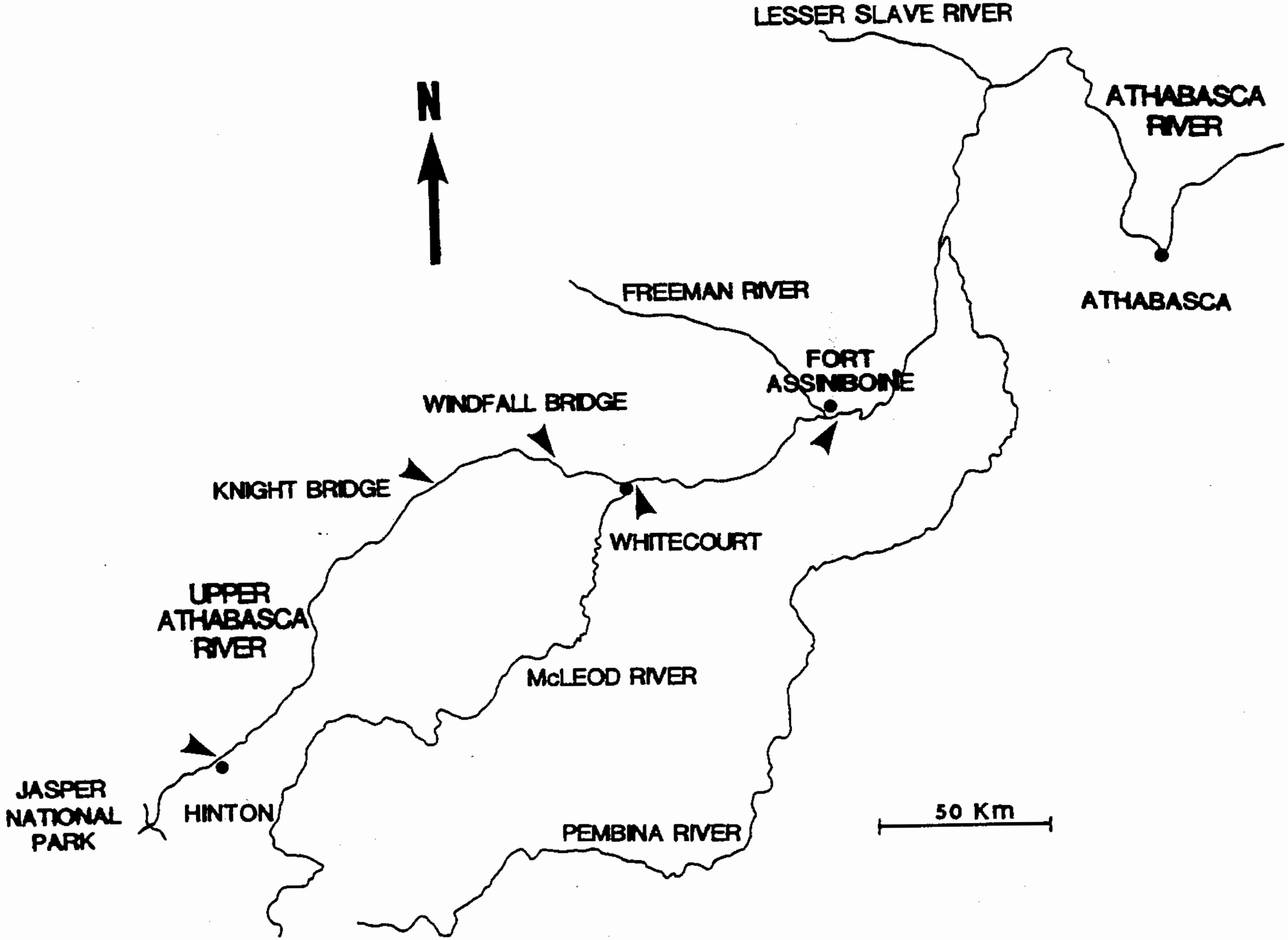

Figure 1. Sediment oxygen demand study sites on the Athabasca River.

similarity in substratum. The Whitecourt study site was located about 1 km downstream of the Millar Western Pulp Ltd. mill effluent and upstream of the Whitecourt sewage effluent. The river edge where chambers were installed was completely ice covered. All other sites were also ice covered.

Important characteristics for each study site with a grid reference to the nearest 100 m are given in Table 1. For all study sites the main substratum was a cobble and pebble mixture, however, at Hinton, (sites 2 and 3), and Fort Assiniboine the rocks were overlain by a thick layer of fine sediment (up to 5 cm); water velocity was lowest at these sites. Water quality data for some of these locations may be found in Hamilton et al (1985) and Noton and Shaw (1989).

3. MATERIALS AND METHODS

In this study, we assumed that SOD included all oxygen-consuming processes in or on the river bed. We measured the rate of depletion of DO in specially designed chambers (see below) which either contained substrate or were placed directly on top of substrate and compared these with rates measured either in chambers without substrate or in dark BOD bottles in situ. Differences between these depletion rates were estimates of SOD ($g/m^2/d$; see Appendix I).

3.1 Description of SOD chamber

The sediment oxygen demand chambers were constructed according to specifications in Figure 2. The basic design was a stainless steel base (thickness = 0.16 cm) with a removable lid (thickness = 0.32 cm). The base had a flat rim (thickness = 0.32 cm, width = 2.5 cm) welded on the top with a rubber gasket (thickness = 0.35 cm, width = 2.5 cm) attached. On the underside of the lid, a gasket made of closed-cell foam (thickness = 0.95 cm, width = 5 cm) was attached. The foam and rubber gasket made a complete seal between the base and the lid of the chamber. Four snap-down clips welded around the top of the chamber secured the lid in a water-tight seal (Figure 2).

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 or axle, (diameter = 0.9 cm) with spokes (diameter = 0.45 cm) on either end. Eight spokes were welded onto the top of axle. Six spokes were welded to a nut that could be screwed onto the bottom end of the axle, on the inside of the chamber. The water vane was held securely in the lid using a pipe fitting which was screwed into the top of the lid (Figure 2). Between the bottom of the lid and the spokes inside the chamber, there was a metal pipe spacer (length = 4.5 cm, inner diameter = 1.1 cm) placed onto the axle to form a casing.

Polypropylene funnels (top diameter = 65 mm), with the stem removed and sealed, were fitted onto the spokes to serve as cones on the water vane (Figure 2). Three portholes in the lid were used to obtain measurements and water samples from inside the chamber. The portholes were closed using rubber stoppers which were attached to the lid of the chamber. The porthole used to obtain water samples was made from a 6 cm length of stainless steel tubing (outer diameter = 0.95 cm, inner diameter = 0.75 cm) welded into the lid. The other two portholes were 1.5 cm and 3 cm in diameter.

3.1.1 Type of SOD chamber

Two types of chamber design were used for this study, open, and closed. Open chambers were used where a satisfactory seal with the substrate could be obtained, usually on mud. They were constructed from a cylinder which was serrated with 2 cm teeth around the lower edge (Figure 2). The teeth and handles on the base of the chamber were used to aid in manually rotating the chamber into the substratum. Around the outside of the chamber, just above the teeth, half of a 13 inch inner-tube (cut along the circumference) was secured with gear clamps to form a curtain over the base of the chamber, to impede 'leakage' of the chambers, Closed chambers were similar to open ones except that the bottom was completely sealed, to form a water-tight chamber. They were used where a seal with the substrate could not be obtained, usually on gravel or coarser material.

Table 1. Characteristics of the study sites for the Athabasca River.

Study site, Latitude, and Longitude	Ice Conditions	Water velocity mean and (range) cm/s	Substratum		
			Predominent Particle size: mean & (range) cm	Epilithic growth	Deposits
Hinton, site 1 53° 25' N, 117° 34' W	Open water	37 (36-38)	6 (5-8)	Small amount, patchy	Patchy fine sediment
Hinton, site 2	Open water	15 (4-21)	10 (4-20)	Small amount, patchy	Abundant fine sediment
Hinton, site 3	Open water	8 (0-13)	Fine sediment	None visible	Up to 5 cm, fine sediment
Knight bridge 54° 9' N, 116° 35' W	Thin ice cover	32 (14-43)	11 (4-14)	Fairly uniform cover	Patchy fine sediment
Windfall bridge 54° 12' N, 116° 3' W	Up to 1 m ice cover	27 (14-34)	15 (2-20)	Small amount, patchy	Patchy fine sediment
Whitecourt 54° 9' N, 115° 40' W	Ice cover 6 days before incubation	58 (54-61)	12 (2-20)	Abundant	Patchy fine sediment
Fort Assiniboine 54° 19' N, 114° 46' W	Up to 1 m ice cover	2 (2-2)	18 (5-24)	None visible	Abundant fine sediment

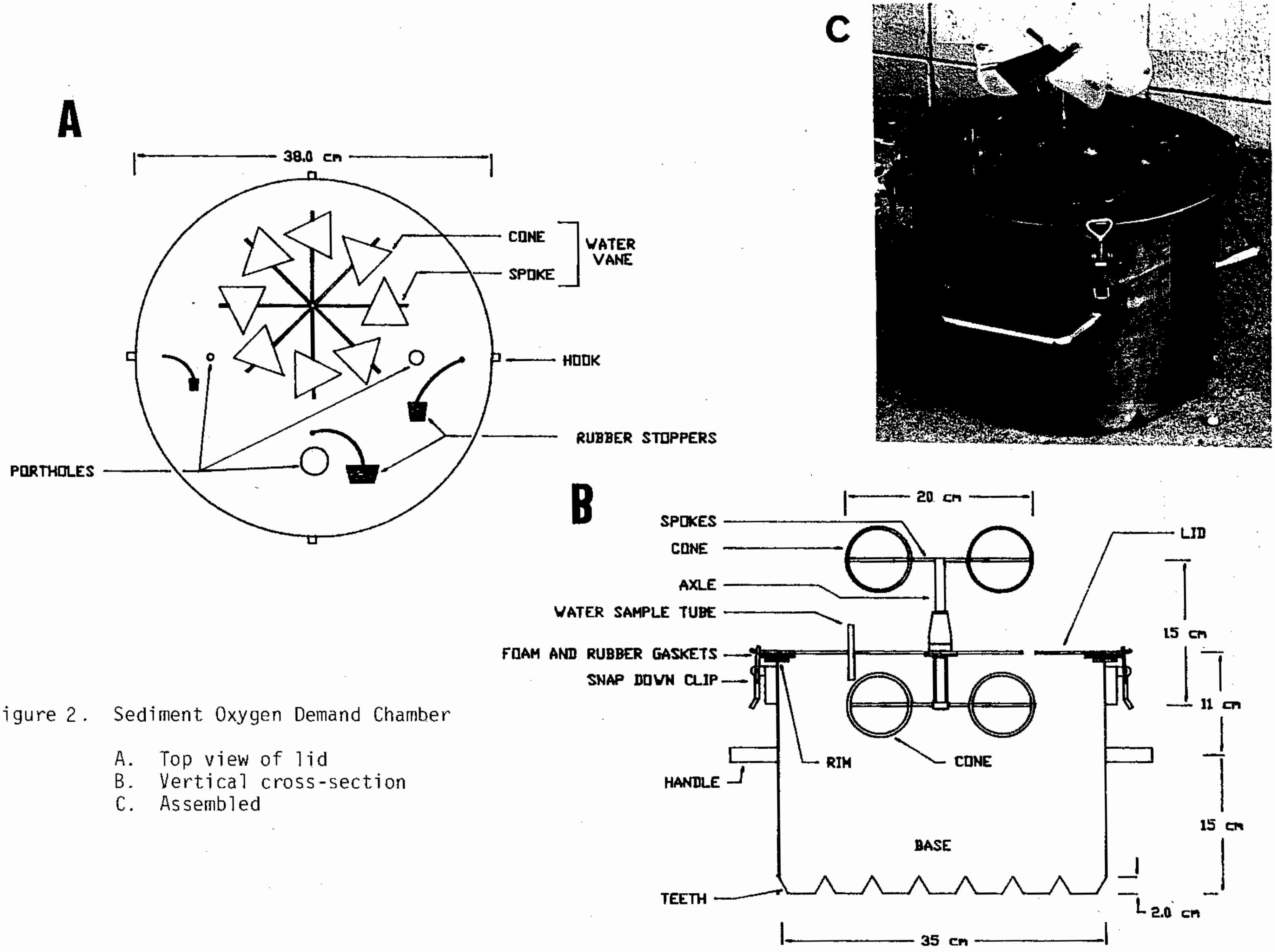

Figure 2. Sediment Oxygen Demand Chamber

A. Top view of lid
B. Vertical cross-section
C. Assembled

A 'blocked' chamber was an open chamber sealed temporarily with a galvanised steel plug (diameter 35 cm), to serve as a closed chamber. The steel plug had a 5 cm vertical lip that fitted snugly inside the chamber bottom, against the inside surface of the 2 cm teeth. Also, around the outside edge of the plug, there was a rim (about 0.5 cm wide) in contact with the end of the teeth. The rubber curtain was attached at the tip of the teeth, touching the rim of the plug. These 'blocked' chambers were used temporarily, during construction of closed chambers. They performed as closed 'chambers' and are not differentiated from them in subsequent sections of the report.

3.2 Field techniques

All chambers were washed thoroughly before each deployment, to remove any material or organisms that might exert an oxygen demand.

3.2.1 Choice of location for the chamber

The actual spot selected to deploy the chambers was dictated by limitations of substrate, water depth, and velocity. Substrate that appeared representative of the overall site was required, and the maximum depth and velocity in which the chambers could be safely deployed was about 56 cm and 60 cm/s, respectively . At open-water study sites (Hinton and Whitecourt) a location for the chambers was found with relatively little difficulty compared to ice-covered areas (Figure 3 and 4). At ice-covered areas, a series of exploratory holes were drilled with an ice auger to locate representative substratum with suitable water velocity and depth. Because water depth was an important limiting factor, all of our study sites were close to shore. In several cases the water velocity at a site was low compared to the flow in the main channel of the river. When a location was chosen a section of the ice was quarried using an ice auger, a chain saw and ice chisels (Figure 4). At Knight bridge a satisfactory study site was found where the ice was only about 11 cm thick (Figure 5). The operator was able to enter the hole and install the SOD chamber on the river bed. For the closed chambers, several could be placed in the same ice opening.

3.2.2 Positioning of the chamber

Disturbance to the natural substratum was kept to a minimum when open chambers were used. The chamber was positioned over the selected substrate, then forced as deep as possible into it. The inside wall of the chamber was checked by hand to determine if adequate penetration of the substrate was obtained. Subsequently, the outer rubber curtain was spread around the chamber base over the substratum. Rocks and sediment were shovelled and placed by hand onto the curtain to the level of the handles. The seal between the chamber and the substratum could then be checked after the lid was secured to the chamber (see section 3.2.3.1). In many cases the chambers were then anchored to the river bed with cords and stakes (Figure 3).

Figure 3. Open water at Hinton, Site 1. Anchoring stakes indicate four SOD chambers *in situ*

Figure 4. Ice opening at Windfall Bridge, and two chamber bases. The opening is large enough to enter and work in.

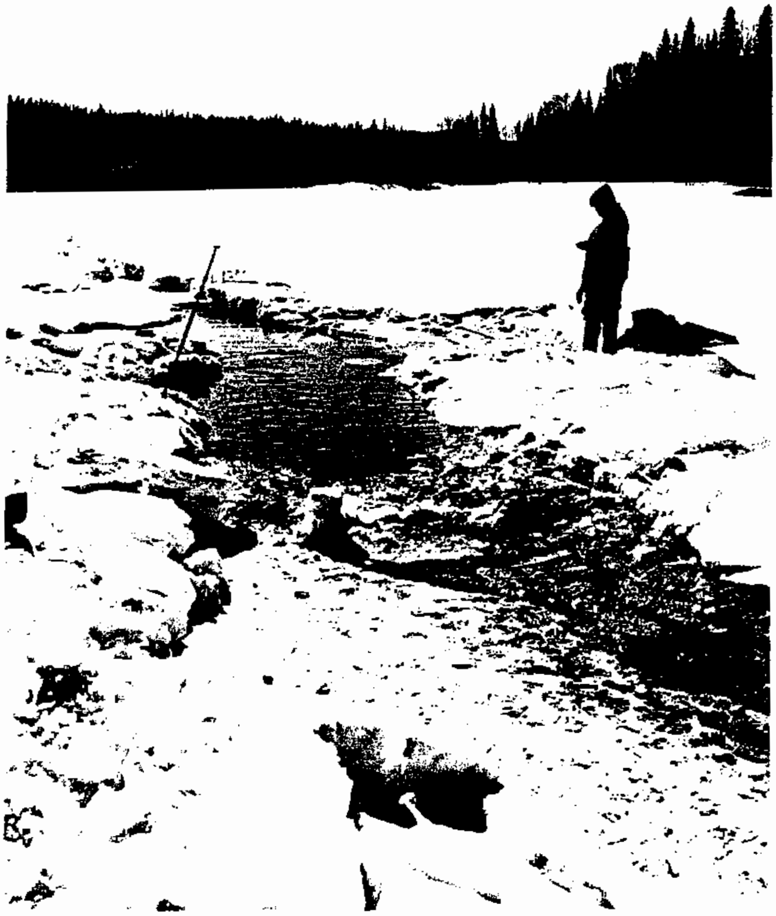

Figure 5. Knight bridge study site. Ice cover at this spot was thin (about 11 cm) relative to the other ice covered sites.

Using closed chambers necessitated disturbance to the substratum. Representative rocks and/or sediment were chosen at each location and placed in the chamber. Rocks were placed in the chamber in a similar position as that found in situ, i.e. with any epilithic growth facing upwards. Sediment was added to the chambers and washed into interstices before placing the chamber in the river. When filling the chamber, the substratum was kept submerged in the river water as much as possible to reduce freezing of the epilithic growth and sediment. Chambers containing substratum were gently filled with river water and placed on the river bed 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.

3.2.3 Measurements

3.2.3.1 Chamber-substrate seal

Obtaining a seal between the chamber and the substratum was essential. To check for leakage 50 ml of 0.35 M NaCl solution was injected into the chamber with a hypodermic syringe through the water sample tube. Conductivity was measured about 5 minutes after injecting the NaCl solution and each time measurements were taken in the chamber, using a portable meter (Hanna Instruments, HI 8033). When measuring conductivity, the water vane was revolved at about 1 revolution per 2 seconds while holding the conductivity probe inside the chamber. The porthole was covered by hand while holding the probe inside, to reduce interchange with water outside the chamber.

3.2.3.2 Dissolved oxygen in the chamber

Dissolved oxygen (DO) was measured by the azide Winkler method (NAQUADAT no. 08101L). Samples were obtained through the tube on the top of the chamber using a hand vacuum pump to extract the water. Before taking a sample, the water vane was rotated several times to ensure the chamber contents were mixed. When water samples were extracted using the hand pump, the 1.5 cm porthole was partially opened to break the seal and allow the sample to be withdrawn. This was especially necessary when closed chambers were used. Water was pumped from the chamber into a 300 mL BOD bottle and then into a graduated 1 L filtering flask with a side-arm. The vacuum pump was attached to the side arm of the filtering flask. At least 300 mL was allowed to accumulate in the flask so that the BOD bottle was well flushed. When necessary, the entire water sampling apparatus including tubing was kept submerged in the river to avoid ice build-up. While taking a sample, the BOD bottle was rotated and tapped lightly to dislodge air bubbles. Manganese sulphate and alkali-iodide-azide reagent powder were added immediately to the samples and mixed. Samples were preserved with sulphuric acid at the end of a field day and titrated within 24 hours of collection. Sediment oxygen demand ($g/m^2/day$) was calculated according to the formulae in Appendix 1.

3.2.3.3 Dissolved oxygen in the water column

Oxygen demand of the water column was also measured at the study sites, except Knight and Windfall bridges where the water column demand was considered to be negligible. Oxygen demand of the water column was measured using a closed chamber or a sealed dark, 300 mL BOD bottle containing water and no substratum. These containers were placed at the same location and left generally for the same time period as chambers containing substratum. Corrections for water column BOD were incorporated in the formulae used to calculate SOD (Appendix 1).

3.2.3.4 Volume of the chamber

At the end of an incubation period, the water volume of each chamber containing substratum was calculated using a depth-profile measuring device (Figure 6). This instrument was positioned on the chamber in place of the lid and twelve steel rods were inserted to contact the substratum, then held in position by "clips". The Plexiglas plate, with the rods inserted, was held in place on the chamber using permanently secured alignment rods. The depth of each rod in the chamber was measured and a mean depth was calculated, so that the volume of water in each chamber could be estimated (Figure 7).

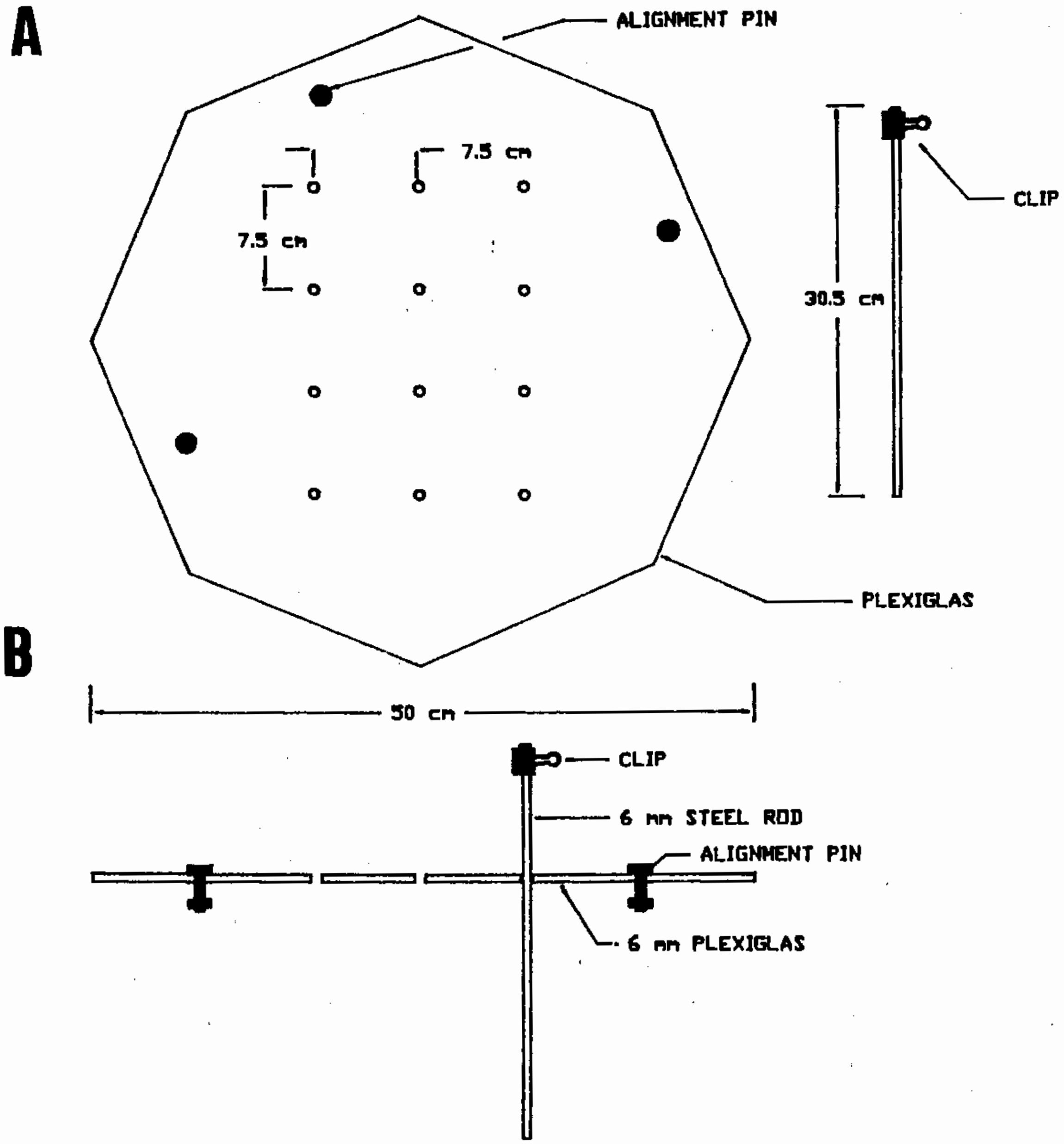

Figure 6. Depth-profile measuring device. A. Top view with a rod alongside. B. Cross-section showing a rod in position.

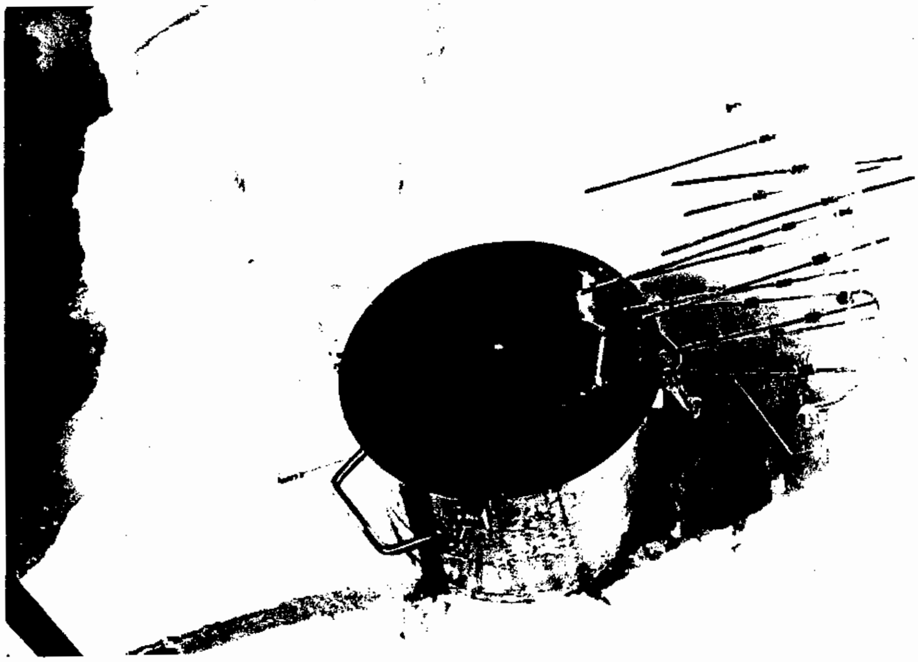

Figure 7. Depth-profile measuring device with rods adjusted to measure the volume in a closed chamber.

3.2.3.5 Other pertinent variables

A number of other variables were also recorded during the SOD measurements. These included the velocity of the water vane which would give an indication of mixing of the water in the chambers. For each location, the water velocity and depth were recorded beside the chambers. In open water areas, water velocity was recorded at 0.6 x depth (i.e. mean velocity). At ice-covered areas, velocity was measured half-way between the bottom of the ice and the substratum. Notes were also made on substratum size and epilithic deposits and growth. An example of the data sheet used in this study is given in Appendix 2.

At each location, the substratum used in the chamber was sampled for chlorophyll a or organic content. These analyses were conducted at the Millwoods field facility, Environmental Assessment Division. At locations where fine sediment was abundant, the sediment was collected by scraping the upper surface of sediment (to about a depth of 5 cm) into a plastic vial (volume = 31 ml). The samples were frozen and subsequently analysed for percent organic content. Percent organic content was calculated by drying a subsample of the sediment to a constant weight 105 °C and then igniting the sample at 550 °C for 1 hour and calculating the percent change in weight.

Where fine sediment was not abundant, the epilithic material on the rocks was sampled by scraping off the material from within a 3 x 3 cm plastic template. Rocks were sampled either in the field or kept frozen and sampled later in the laboratory. The sample was placed in alumimium foil with $MgCO_3$ and frozen, then analysed for chlorophyll a and phaeophytin a. A spectrophotometric technique based on the method of Moss (1967a, 1967b) was used to analyze the samples.

4. RESULTS AND DISCUSSION

4.1 Evaluation of techniques

4.1.1 Use of SOD chamber

The *in situ* method is generally considered superior to transporting the substratum to the laboratory, even though the laboratory situation allows close monitoring of experimental conditions (e.g. see references in Hatcher 1986c). Another *in situ* method is to use a long opaque tunnel, open at either end, placed parallel to the water flow, on the substratum. Dissolved oxygen is measured at the entrance and exit of the tunnel to estimate benthal respiration (SOD). Such an apparatus has been used successfully by James (1974) in 3 separate lotic systems. He compared the results from a tunnel apparatus with an open chamber in the field and in the laboratory, and with the calculation of total oxygen balance. The tunnel method gave the closest agreement to the oxygen balance method, and the chambers in situ (although close to the values obtained by the tunnel) underestimated SOD values, based on the oxygen balance. This suggests that the Athabasca River results may be underestimates of SOD.

4.1.2 Use of NaCl solution

Using the NaCl solution as a check for leaks in the chambers seems unlikely to have affected the results since only small increases in NaCl concentration were involved. The volume and concentration of solution in our method caused the conductivity to increase by about 100 uS/cm, depending on the volume of the chamber. This increased the conductivity of the water in the chamber by about 20 per cent. Potassium chloride has been used successfully for this by other workers (Murphy and Hicks 1986; Whittemore 1986a). One group of researchers used a salt solution and increased conductivity 20-fold in a southern U.S. stream with no apparent effect on SOD (Mancini et al 1986).

4.1.3 Water velocity in the chamber

In order to estimate SOD, the in situ method should replicate the natural environment as much as possible. The water vane was included to provide mixing and water movement inside, in rough proportion to velocity outside the chamber (the vane was driven by outside velocity). There was a general correspondence between the river velocity at a study site and the velocity of the water vane (Table 2). At Windfall bridge and Fort Assiniboine, water velocity was measured below the ice, and the bottom of the ice was below the level of the water vane spokes. Water velocity was most likely lower inside the chamber than outside since no mechanical device can be 100% efficient. Mixing of water inside the chamber most likely did not occur at low velocities in the river, because in several cases under these conditions the spokes were stationary

Table 2. Mean number and range of revolutions of the water vane and the water velocity for each group of chambers and study site. Number of measurements per group used to calculate the mean is shown in parentheses beside the mean value.

Study site	Date	Revolutions per 30 s		Water velocity cm/s	
	d m y	Mean	Range	Mean	Range
Hinton, site 1	22.02.89	5.9 (3)	5.5 - 6.25	37 (3)	36 - 38
Hinton, site 2	21.02.89	2.1 (4)	0.0 - 4.5	15 (4)	4 - 21
Hinton, site 3	28.02.89	0.0 (3)	0.0 - 0.0	8 (5)	0 - 13
	28.02.89	0.0 (1)	-- --		
Knight bridge	17.03.89	2.2 (3)	0.0 - 3.5	32 (6)	14 - 43
	20.03.89	0.25 (3)	0.0 - 0.75		
Windfall bridge	09.03.89	0.4 (2)	0.25 - 0.5	27 (5)	14 - 34
	14.03.89	1.25(3)	0.0 - 3.25		
Whitecourt	21.03.89	9.5 (2)	8.0 - 11.0	58 (6)	54 - 61
	22.03.89	3.75 (3)	2.5 - 5.75		
Fort Assiniboine	29.03.89	0.0 (6)	0.0 - 0.0	2 (2)	2 - 2

(Table 2). For example, at Hinton, site 3, and at Fort Assiniboine, the spokes were not observed to move throughout the time chambers were in situ. However, they were turned manually just before sampling to ensure that the chamber contents were mixed.

Water velocity at the substratum-water interface is considered to have an important effect on the measurement of SOD (James 1974; Hickey 1986; Whittemore, 1986a). Whittemore (1986a) found that an increase in water velocity at the substratum-water interface was directly related to SOD and he concluded that the velocity at the sediment-water interface should be simulated when measuring SOD. Whittemore (1986a) postulated that increased turbulence due to velocity increased transport of soluble organic material to the sediment-water interface causing high SOD. James (1974) also found that oxygen uptake by mud was directly related to velocity, even at low velocities of 5-8 cm/s (similar to the low velocities in our study); at higher velocities this relationship was exponential. Since the water velocity in our chambers was lower than river velocity an underestimation of SOD likely resulted.

4.1.4 Disturbance of sediment in the chamber

Disturbance and mixing of the substratum can potentially increase SOD by bringing a greater amount of oxygen demanding sediment in close contact with water. However, this effect was not apparent in the data. When open and closed chambers were used at the same site, similar SOD rates and trends in the data were obtained (see section 4.2.1).

According to a review by Walker and Snodgrass (1986), disturbance and mixing of the sediment in a chamber did not appear to affect SOD, however resuspension did affect it. Resuspension due to scouring would lead to increased surface area for reaction causing increased oxygen demand (Edwards and Rolley 1965; Hargrave 1969; James 1974; Whittemore 1986a). Murphy and Hicks (1986) were able to demonstrate a drop in DO of greater than 1 mg/L in a chamber over 20 minutes due to resuspension.

In our data it is not possible to determine the effect of resuspension since oxygen was consumed only very slowly and DO measurements could not be taken over short intervals. For our study sites, resuspension was probably not an important factor affecting SOD rates because the chambers were left _in situ_ to allow resuspended sediment to settle or flush out in the current, before securing the lid. However, resuspension was observed at one study site. At Fort Assiniboine when the water vane was revolved at the end of the incubation resuspension was clearly evident. This was most likely due to the sediment being less compact than at the other study sites. However, resuspension probably did not affect the results because DO was measured immediately.

4.1.5 Dissolved oxygen concentration in the chamber

When we extracted water samples _in situ_ by vacuum pump, replacement water from the river entered the chamber via a porthole. The chamber was thus 'contaminated' with river water whose DO concentration was higher than that of water inside the chamber. This was not a problem unless duplicate samples were taken per chamber. In these instances the [DO] of the second sample was consistently higher than that of the first (difference of from 0.2 to 0.65 mg O_2/L); consequently, the mean DO measurements were biased and undoubtedly led to underestimates of SOD in this study.

Some exchange of water would also be expected to occur each time stoppers were removed from the lid. This introduction of river water with high [DO] would also lead to underestimated SOD values. Finally, the use of a chamber rather than an open-ended system (see section 4.1.1 above) where a decrease in DO concentration due to the SOD will be continuously replenished by ambient water, may result in underestimated SOD (see also section 4.2.1.2). This is because once DO is depleted it can not be replaced and if DO declines enough it may begin to limit oxidation rates.

4.1.6 Oxygen demand of the water column

As noted in the methods section, the SOD values reported here are corrected for oxygen demand of the water column (except for Knight and Windfall bridges). The water column oxygen demand is due to the respiration of organisms and material which were suspended in the water. The 300 ml BOD bottles (2 bottles per site) used for our study as controls (or blanks) may not be appropriate. In a study by Murphy and Hicks (1986), the use of BOD bottles instead of blank chambers tended to overestimate the water column respiration rate.

The corrected SOD values for Hinton, site 3, are based on the use of a control chamber. Water column demand ranged from 0.011 to 0.013 mg O_2/L/h. For sites 1 and 2 at Hinton, estimated values of oxygen demand by the water column were based on this control chamber. The SOD data for the Hinton study sites were collected within an 11 day period. For Whitecourt and Fort Assiniboine the SOD values were corrected using BOD bottles as controls, so these SOD rates may be underestimates of the actual SOD. The measured oxygen demand of the water column at Whitecourt was 0.010, 0.020, and 0.035 mg O_2/L/h and at Fort Assiniboine it was 0.016 mg O_2/L/h. The mean percentage change in DO in the water column relative to the DO change in a chamber with substratum was 34% (range = 14-100%) at Hinton, 17% (range = 7-26%) at Whitecourt, and 32% (range = 17-47%) at Fort Assiniboine.

4.1.7 Volume of water in chamber

At Hinton, site 2, and Fort Assiniboine for chambers with soft sediment, there was a possible source of error in calculation of the mean depth, or volume, of the chambers. This was because it was difficult to determine when the rods in the depth-profile measuring device were touching the top of the soft substratum. Turbid water at Hinton, site 2, and resuspension of sediment at Fort Assiniboine confounded this problem. This would result in a potential overestimate in SOD since the rods were likely to be pushed down somewhat past the surface of the sediment. For site 3 at Hinton (the only other area where fine sediment was abundant) it was possible to measure the volume more accurately using a metre stick since the water was clear.

4.1.8 Summary

Most potential errors in our results appeared to suggest that SOD values were underestimated, rather than overestimated (Table 3). Only 1 potential error suggested the SOD rates were overestimated.

4.2 General findings

4.2.1 SOD rates for the Athabasca River

The length of time that the chambers were left in the river (the incubation period) depended on the time required for a change in DO to occur and upon the logistics at a particular site. Dissolved oxygen was often measured more than once during the incubation period (Table 4). Results for SOD ($g/m^2/day$) are presented in Table 5 and Figure 8. The highest rates of SOD were found at Whitecourt, Hinton, and Fort Assiniboine. Lowest rates were at Knight bridge and Windfall bridge. When chambers were left in situ for a longer incubation period to calculate a second SOD rate, there was generally a drop in SOD. There was one exception, at Windfall bridge, where there was a small increase in mean SOD of 0.0083 $g/m^2/day$.

Table 3. Potential factors affecting SOD rates for the Athabasca River.

Factors affecting SOD rates	Probable Effect on SOD rate
Use of chambers versus measuring the oxygen balance of the river	Underestimate
Reduced water mixing in the chamber and reduced water velocity at substratum-water interface	Underestimate
Disturbance and mixing of sediment	No effect
Resuspension of sediment	No effect
Reduced DO concentration in chamber due to extraction of samples and use of portholes	Underestimate
Use of BOD bottles instead of blank chambers as controls for Whitecourt and Fort Assiniboine	Underestimate
Measurement error of volume of water in chamber at Hinton, site 2, and Fort Assiniboine	Overestimate

Table 4. Number of chambers and the date when they were placed in situ for each study site. The length of time after which DO was measured during an incubation period is also shown for each group of chambers placed in the river.

Study site	Date d m y	No. of chambers	Time (h) DO measured
Hinton, site 1	22.02.89	3	19 and 43
Hinton, site 2	21.02.89	4	46 and 66
Hinton, site 3	28.02.89	3	46 and 64
	28.02.89	1	46
Knight bridge	17.03.89	3	72
	20.03.89	3	41
Windfall bridge	09.03.89	2	21 and 114
	14.03.89	3	41 and 65
Whitecourt	21.03.89	2	27 and 45
	22.03.89	3	18
Fort Assiniboine	29.03.89	6	42

4.2.1.1 Variation in SOD rates

In order to obtain an indication of the variability in groups of chambers for which mean SOD rates were calculated at study sites, the coefficient of variation (CV) was calculated (Table 5). A wide range of CV were observed between study sites (CV range = 1-140%), with the higher CV tending to occur with the lower SOD rates. This high CV most likely results from imprecision in the Winkler method which is proportionately large for low SOD rates. This measurement error may also have caused the negative SOD values for Windfall bridge (Table 5, Appendix 3). It was not appropriate to calculate a CV for sets containing negative values.

Whittemore (1986b) surveyed the literature and calculated the CV for relevant SOD measurements made with <u>in situ</u> chambers. For 21 sites, the CV ranged from 0 to 150% with a mean value of 44%. Our results were similar: the CV values ranged from 1 to 140% and averaged 48%.

4.2.1.2 Change in SOD rates during incubation

SOD rates appeared to decrease over time at most of the study sites (Figure 8). Others have also noted this trend and have suggested that the decrease in SOD rates merely reflects the progressively more depleted DO levels in the chamber over the course of the incubation period, since there is a direct relationship between DO concentrations and SOD rates (Edwards and Rolley 1965; Hargrave 1969; Edberg and Hofsten 1973; Newrkla and Guatilaka 1982; Hickey 1986). This is a severe limitation of the closed chamber design for situations where SOD rates

Table 5. Sediment oxygen demand (SOD) for each chamber and study site for different time periods. Mean SOD and coefficient of variation (CV), in parentheses are also given. Two types of chambers were used, open (O), and closed (C). A hatched line between SOD values indicates chambers were left in situ to obtain a second SOD value.

Study site	Chamber type	SOD ($g/m^2/day$) at indicated time period (h)			
		18 - 27	41 - 46	64 - 72	114
Hinton, site 1	C	0.320 ---	0.145		
	C	0.316 ---	0.116		
	C	0.435 ---	0.308		
Mean (CV-%)		0.357 (19)	0.190 (55)		
Hinton, site 2	O		0.322 ---	0.245	
	O		0.074 ---	0.054	
	O		0.112 ---	0.168	
	O		0.186 ---	0.214	
Mean (CV-%)			0.174(63)	0.170 (49)	
Hinton, site 3	O		0.127 ---	0.000	
	O		0.243 ---	0.054	
Mean (CV-%)			0.185 (44)	0.027 (140)	
	C		0.127 ---	0.091	
	O		0.116		
Knight bridge	C			0.084	
	C			0.047	
	C			0.042	
Mean (CV-%)				0.058 (40)	
	C		0.051		
	C		0.093		
	C		0.078		
Mean (CV-%)			0.074 (29)		
Windfall bridge	C	-0.010 ---	---	---	-0.003
	C	0.040 ---	---	---	0.023
Mean (CV-5)		0.015 (NA)			0.010 (NA)
	C		0.015 ---	0.016	
	C		0.022 ---	0.010	
	C		-0.035 ---	0.000	
Mean (CV-%)			0.001 (NA)	0.009 (93)	
Whitecourt	C	0.520 ---	0.316		
	C	0.509 ---	0.321		
Mean (CV-%)		0.515(2)	0.319 (1)		
	C	0.611			
	C	0.373			
	C	0.386			
Mean (CV-%)		0.457 (29)			
Fort Assiniboine	C		0.174		
	C		0.398		
	C		0.197		
	C		0.121		
	C		0.091		
	C		0.147		
Mean (CV-%)			0.188 (58)		

NA - CV was not calculated for data with negative values.

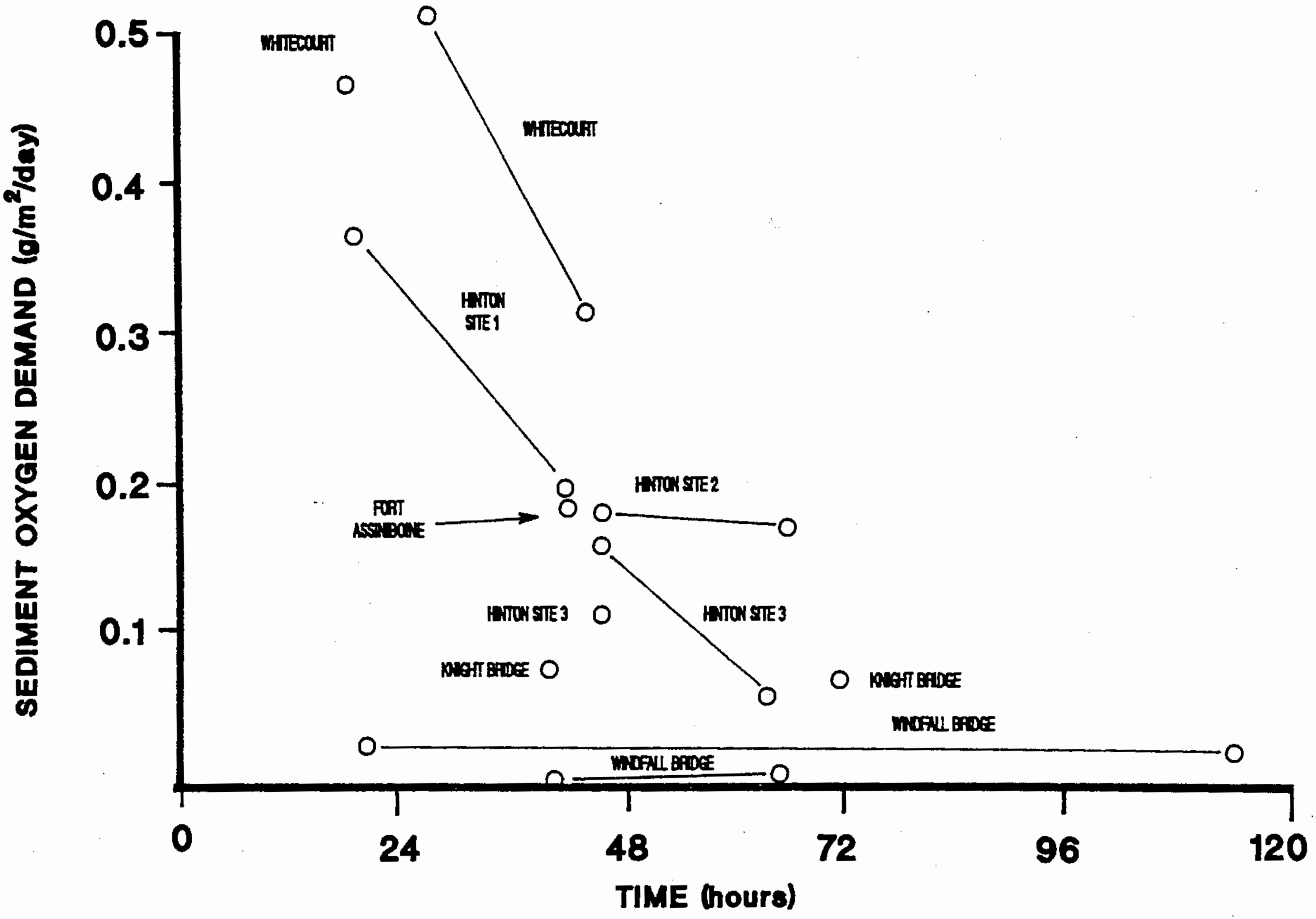

Figure 8. Mean sediment oxygen demand for each group of chambers at a study site over time.

are expected to be high. For example, SOD measurements obtained at Whitecourt and Hinton, site 1, were initially high (0.49 and 0.32 g/m²/d, respectively), but dropped rapidly over the next 24 h (0.32 and 0.13 g/m²/d, respectively). By contrast, at Windfall Bridge, where SOD rates were initially low (0.015 g/m²/d), the final measurement did not decrease appreciably even after 93 h (0.010 g/m²/d). Because of this bias, where SOD rates were measured sequentially, the initial value should be more representative of the actual in situ SOD rate.

4.2.1.3 Influence of substrate type on SOD rates

There was not a clear-cut influence of substrate type on the SOD rate, although a rigorous comparison of types was not carried out. Only 2 basic types of substrate were found at the study sites, i.e. a cobble and pebble mixture or fine sediment (Table 1). Study sites where fine sediment was abundant, covering the bottom of the chambers (sites 2 and 3 at Hinton, and at Fort Assiniboine), had SOD rates in the mid-range of values for the Athabasca River (Figure 8). SOD rates for rocky substrata were grouped at the high and low ends of the range. At Hinton where SOD was measured for both rocky and abundant fine sediment (sites 2 and 3), SOD was apparently greater on the rocky substrata (Table 5, Figure 8). The reason for this was not investigated, although the greater surface area of rocks versus the smooth silt surface, and possibly the greater biomass of algae, bacteria, fungi, and other benthos on the more stable rocks, may be factors.

4.2.2 Sediment organic content

Fine sediment was not present at all sampling sites such that a thorough comparison of sediment organic content among all study sites was not possible. For the 4 sites where samples could be obtained the percent organic content of the sediment was statistically different among sites (ANOVA, $p = 0.04$)(Table 6). Using Scheffe's multiple comparison test ($p = 0.05$), only site 2 at Hinton and Fort Assiniboine, were significantly different, although none of the sites had a high organic content. The higher organic content at Hinton could be due to input from the Hinton combined effluent. From the literature on SOD it appears that organic content per se is not clearly related to SOD (e.g., Rolley and Owens 1967; Edberg and Hofsten 1973) most likely because there are many factors affecting SOD. For example, the type of organic material may have an effect on the amount of oxygen uptake (Edberg and Hofsten 1973). There was no apparent relationship between organic content and SOD in our results, where Windfall bridge with the lowest SOD rates had similar organic content to Hinton and Fort Assiniboine, which had much higher.

Table 6. Percent organic content and mean value for 4 study sites where fine sediment was present.

Study site	Percent organic content	Mean
Hinton, site 2	4.18	3.42
	2.98	
	3.00	
	3.80	
	3.12	
Hinton, site 3	3.11	3.08
	3.33	
	3.54	
	2.94	
	2.50	
Windfall bridge	1.70	2.84
	2.86	
	2.87	
	4.21	
	2.58	
Fort Assiniboine	2.44	2.28
	1.85	
	2.43	
	2.41	
	2.25	

Organic content as % of dry weight of sediment.

4.2.3 Epilithic chlorophyll

Samples for epilithic chlorophyll *a* analysis were obtained at 2 study sites, Knight bridge and Whitecourt (Appendix 4). At other sites it was not possible to obtain a sample to process (using our method of scraping a rock), although epilithic growth was present (Table 1). The Whitecourt substratum had more abundant epilithic cover (chlorophyll *a*) than at Knight bridge. Chlorophyll *a* may have been greater downstream of Whitecourt due to a fertilising effect of the nearby pulp mill effluent. SOD was also greater and the higher chlorophyll there may be indicative of an overall higher biomass and organic content on the rock substrate at that site.

4.2.4 Macroinvertebrates

Macroinvertebrates were not considered to be an important factor in our study. They did not appear to be common at any of the study sites on the Athabasca River, and were only occasionally observed on the substratum. Where macroinvertebrates are abundant they would be expected to influence SOD values (e.g., see Bowman and Delfino 1980). Whatever amount of respiration they account for, is incorporated in the total SOD measured here.

4.2.5 Comparison of SOD rates with published results

Winter conditions are probably the least variable environmental conditions to conduct SOD measurements *in situ*. Water temperature is constant, water discharge and velocity are low and stable, and the substratum would be expected to be most stable relative to other seasons. From a survey of the literature, there appears to be few SOD estimates using *in situ* methods during the winter. Also, there is no accepted standard method available to measure SOD (see Bowman and Delfino 1980; Hatcher 1986c) which may complicate comparisons of data. Comparisons of laboratory and *in situ* results have shown considerable differences (Edberg and Hofsten 1973; James 1974; Bowman and Delfino 1980; Whittemore 1986). Laboratory results are not directly comparable to our data.

Duncan and Brusven (1985) used closed Plexiglas chambers (about half the volume of our chambers and with a recirculating mechanism) into which they placed rocks (5-20 cm) but no sediment. The chambers were positioned in 3 Alaskan streams of different primary productivity. Duncan and Brusven measured respiration (by covering the Plexiglas) and production in succession after leaving the chambers overnight *in situ* to 'stabilize'. They were able to measure respiration over a relatively short time period (4-6 h), then production was measured, and DO concentration in the water was allowed to reach 100% saturation before respiration was measured a second time. For each chamber at a study stream, they calculated a mean SOD rate from all respiration values measured.

For water temperatures less than 0.5° C (October in Duncan and Brusven's study) mean SOD was 0.102, 0.472, and 0.664 g O_2/m^2/day for the least to most productive stream respectively. This range of SOD values is similar to the range in our data, although Duncan and Brusven's average rates are higher. For example at Windfall bridge on the Athabasca, SOD was much lower.

In a Swedish study, Edberg and Hofsten (1973) reported SOD for open Plexiglas chambers in running water at 0° C to be 0.31 g O_2/m^2/day. The substratum appears to have been soft sediment (with organic content of 8-72%). Organic content was higher than for the Athabasca sediment, however SOD values were similar between these 2 studies. For the Alaskan and Swedish studies, higher SOD values were obtained at higher temperatures in situ (Edberg and Hofsten 1973; Duncan and Brusven 1985). Unfortunately where other workers reported SOD data during the winter, they brought the substratum into the laboratory and measured SOD at temperatures of 10-20° C (e.g. Edwards and Rolley 1965; Rolley and Owens 1967).

Despite the small sample size, our results suggest that there is a direct relationship between SOD rates and proximity to the pulp mill on the Athabasca River. SOD rates were greatest immediately downstream of the mills, especially at Whitecourt. For the reasons discussed earlier, the measurements are most probably underestimates of true SOD rates.

5. REFERENCES

Babin, J., and D. O. Trew. 1985. The impact of the proposed Sand River reservoir on winter dissolved oxygen levels in the Beaver and Sand Rivers. Alberta Environment, Pollution Control Division, Water Quality Control Branch. 82 p.

Bowman, G. T., and J. J. Delfino. 1980. Sediment oxygen demand techniques: a review of laboratory and in situ systems. Water Research 14: 491-499.

Duncan, W. F. A., and M. A. Brusven. 1985. Energy dynamics of three low-order southeast Alaska streams: autochthonous production. Journal of Freshwater Ecology 3: 155-166.

Edberg, N., and B. V. Hofsten. 1973. Oxygen uptake of bottom sediments studied in situ and in the laboratory. Water Research 7: 1285-1294.

Edwards, R. W., and H. L. J. Rolley. 1965. Oxygen consumption of river muds. Journal of Ecology 53: 1-19.

Hamilton, H. R., M. V. Thompson, and L. Corkum. 1985. Water quality overview of Athabasca River basin. Alberta Environment, Planning Division. 117 p.

Hargrave, B. T. 1969. Similarity of oxygen uptake by benthic communities. Limnology and Oceanography 14: 801-805.

Hatcher, K. (ed) 1986. Sediment oxygen demand processes, modeling, and measurement. Institute of Natural Resources, University of Georgia U.S.A. 447 p.

Hatcher, K. 1986a. Sediment oxygen demand processes. In Hatcher, K. (1986), p 3-8.

Hatcher, K. 1986b. Sediment oxygen demand modeling. In Hatcher (1986), p 113-120.

Hatcher, K. 1986c. Sediment oxygen demand measurement. In Hatcher (1986), p 301-305.

Hickey, C. W. 1986. Chamber studies of benthic oxygen uptake kinetics in the Waioptapu River, New Zealand. In Hatcher, K. (1986), p 37-61.

James, A. 1974. The measurement of benthal respiration. Water Research 8: 955-959.

Mancini, J. L., P. H. Gruene, and F. B. Winslow. 1986. Dissolved oxygen analysis and sediment interactions. In Hatcher, K. (ed), above, p 259-280.

Moss, B. 1967a. A spectrophotometric method for the estimation of percentage degradation of chlorophylls to pheo-pigments in extracts of algae. Limnology and Oceanography 12: 335-340.

Moss, B. 1967b. A note on the estimation of chlorophyll a in freshwater algal communities. Limnology and Oceanography 12: 340-342.

Murphy, P. J., and D. B. Hicks. 1986. In-situ method for measuring sediment oxygen demand. In Hatcher, K. (1986), p 307-322.

Newrkla, P., and A. Gunatilaka. 1982. Benthic community metabolism of three Austrian pre-alpine lakes of different trophic conditions and its oxygen dependency. Hydrobiologia 92: 531-536.

Noton, L. R. and R. D. Shaw. 1989. Winter water quality in the Athabasca River system 1988 and 1989. Alberta Environment, Environmental Assessment Division 200 pp.

Rolley, H. S., and M. Owens. 1967. Oxygen consumption rates and some chemical properties of river muds. Water Research 1: 759-766.

Walker, R. R.. and W. J. Snodgrass. 1986. Modelling sediment oxygen demand in Hamilton Harbour. In Hatcher, K. (1986), p 209-234.

Weber, C. I. (ed) 1981. Biological field and laboratory methods for measuring the quality of surface waters and effluents. National Environmental Research Center, Office of Research and Development, U.S.E.P.A., Cincinnati, Ohio. EPA-670-4-73001.

Whittemore, R. C. 1986a. The significance of interfacial water velocity on the measurement of sediment oxygen demand. In Hatcher, K. (1986), p 63-74.

Whittemore, R. C. 1986b. Problems with in-situ and laboratory S.O.D. measurements and their implementation in water quality modeling studies. In Hatcher, K. (1986), p 331-341

6. APPENDICES

Appendix 1. Calculation of sediment oxygen demand (SOD)

$$\text{SOD } (g/m^2/day) = 0.024 \ \frac{V}{A} \ (b_1 - b_2)$$

where,

0.024 = constant, converting mg/L/h to $g/m^2/day$

$$= \frac{24 \text{ (h)}}{1000 \text{ (mg)}}$$

V = volume of water in chamber (litres)

= area of base (m^2) x mean depth (m) x 1000

A = area of chamber base in square meters

b_1 = change in DO inside chamber with substratum (mg O_2/L/h)

b_2 = change in DO inside "blank" chamber (control for water column) containing no substratum (mg O_2/L/h).

Appendix 2. Sediment oxygen demand field data sheet.

Sediment oxygen demand study: ____________ Date: ________

Location __________ Sheet no. ___ Grid reference: _______

Substratum: -epilithic growth (colour, % cover, other) _______

-epilithic deposit (colour, size, thickness, other)

-rock size (range, mean size, other) ____________

Time (1)install chambers: start ____ end ____(2)inject NaCl ____

Position of chambers (by no.): upstream ____________downstream

Variable	Chamber no. and type
Conductivity (uS)	
Winkler bottle no.	
Water -velocity -depth	
Funnel velocity	
Depth profile	
Epilithic sample	

Comments: ____

Appendix 3. Dissolved oxygen concentration (DO, mg/L) in the water column at a study site on the date when chambers were installed and the decrease in DO in chambers after the incubation period.

Study site	Date d m y	Water column DO mg/L	Decrease in DO in each chamber (after incubation, h) mg/L	 mg/L
Hinton, site 1	22.02.89	10.55	1.29 (19)	1.60 (43)
			1.29	1.40
			1.62	2.75
Hinton, site2	21.02.89	9.55	3.03 (46)	3.49 (66)
			1.10	1.37
			1.91	2.74
			2.07	3.30
Hinton, site 3	28.02.89	10.72	1.59 (46)	1.90 (64)
			1.59	0.82
			2.53	1.44
	28.02.89		1.49 (46)	
Knight bridge	17.03.89	9.03	1.35 (72)	
			0.72	
			0.67	
	20.03.89	9.23	0.49 (41)	
			0.87	
			0.83	
Windfall bridge	09.03.89	8.68	-0.05 (21)	-0.09 (114)
			0.20	0.60
	14.03.89	8.52	0.15 (41)	0.25 (65)
			0.20	0.15
			-0.35	0.00
Whitecourt	21.03.89	7.87	3.62 (27)	4.3 (45)
			4.00	4.82
	22.03.89	7.78	3.90 (18)	
			2.69	
			2.43	
Fort Assiniboine	29.03.89	7.56	2.14 (42)	
			4.09	
			2.34	
			2.00	
			1.44	
			1.94	

Appendix 4. Epilithic chlorophyll a and phaeophytin a and mean values for 2 study sites.

Study site	Chlorophyll a (mg/m²)	Mean	Phaeophytin a (mg/m²)	Mean
Knight bridge	1.0*	8.3	1.0*	3.8
	13.6		5.7	
	1.5		1.0*	
	17.5		8.2	
	8.0		3.3	
Whitecourt	60.4	48.9	19.1	15.9
	55.5		27.8	
	55.1		14.6	
	34.0		7.6	
	39.3		10.3	

* indicates values are less than or equal to 1.0