AN EVALUATION OF INTERFERENCE BY PULP MILL EFFLUENT IN THE AZIDE-WINKLER OXYGEN TECHNIQUE

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1. INTRODUCTION

Bleached kraft pulp mill effluent (BKME) contains a wide range of organic and inorganic compounds. It has been suspected that these compounds interfere with the azide-Winkler iodometric method of measuring dissolved oxygen (DO) (Hodgson and Barth 1989). Although such interference is quite clear for undiluted BKME (Environmental Quality Monitoring Branch unpubl. data), the question is whether this affects Winkler DO measurements on rivers receiving BKME. This is very significant for oxygen modelling and waste load allocation studies of receiving rivers. To assess this problem existing data was reviewed and an experiment was carried out on the Wapiti River and the Procter and Gamble Cellulose Ltd. BKME. Factors examined in the experiment were the degree of effluent dilution and length of holding time during sample fixation and titration.

2. METHODS

Effluent was collected by G. Scammell of Standards and Approvals Division, 27 February 1990 from the outflow of the aerated stabilization basin at the Procter and Gamble bleached kraft pulp mill near Grande Prairie. Dilution water was collected from the Wapiti River at Highway #40, upstream of both the P&G effluent and the Grande Prairie sewage effluent. Effluent and dilution water were returned to the field base and, within 3 hours of collection, made up into a series of dilutions: 2%, 5%, 10%, 20%, 50%, and 100% effluent. The dilutions were contained in a 25L pail. A calibrated Hydrolab Corp. Model 4041 meter (membrane-polarographic type) was used to measure DO and temperature. Four Winkler

samples were collected from each dilution with an APHA displacement-type sampler (Clesceri et al 1989) and treated as follows:

1. Held for 1-2 hours, then fixed, acidified and titrated within 20 minutes.
2. Fixed immediately, held about 1 hour, then acidified and titrated immediately.
3. Fixed immediately, refrigerated about 22 hours, then acidified and titrated immediately.
4. Fixed immediately, held about 1 hour then acidified, refrigerated about 21 hours, then titrated.

The azide modification of the Winkler method (Clesceri et al 1989) was used for DO determination. Sodium thiosulphate titrant was standardized and the appropriate correction factor applied to titration results.

3. RESULTS AND DISCUSSION

3.1 Experimental Findings

As compared to the meter, interference in the Winkler method ranged from negligible for the 2% dilution to essentially complete interference on 100% effluent (Table 1, Figure 1). There is some difficulty in knowing the true DO of the 2% dilution, since the meter indicated a lower DO than did the Winkler measurements. However, the discrepancy (about 0.3 mg/L) was very similar to the meter - Winkler discrepancy earlier in the day at sampling sites on the Wapiti River upstream of the mill effluent (i.e. 0% effluent). Thus it is assumed there is no significant interference from the 2% dilution, that the Winkler DO there is accurate, and therefore that the meter values are about 0.3 mg/L too low. Using this assumption, estimated 'true' values are shown on Figure 1, for the dilutions up to 20%. Compared to these,

the Winkler technique reported values that were 0.5-1.2 mg/L too low for 5% effluent, 1.5-2.3 mg/L too low for 10% effluent, and 2.8-4.1 mg/L too low for 20% effluent.

Of the four treatments, #4 consistently resulted in the lowest value for any given dilution (Table 1, Figure 1). This treatment involves early acidification and then a holding period, suggesting that the iodine liberated after acidification may be subject to some loss during the holding period. The normal procedure for Winkler DO samples during field surveys is to fix immediately, then titrate at the end of the field day or in the morning of the following day, with acidification just before titration. This is intermediate between treatments #2 and #3. These treatments gave the highest Winkler DO values, suggesting that the normal field procedure remains the best way to handle Winkler DO samples in cases where BKME interference is a possibility.

3.2 Other Observations

Paired Winkler and meter DO measurements were made at all sampling sites during the Feb-March 1990 synoptic water quality survey on the Wapiti-Smoky rivers (Table 2). Winkler values for the Wapiti River downstream of the pulp mill, which contained about 3.6% BKME, were consistently lower than meter values, supporting the possibility of interference. For other sampling sites there was not a consistent pattern in differences between the meter and Winkler DO values. Meter DO measurements were not taken in the March 1989 survey. Hodgson and Barth (1989) reported even larger discrepancies between meter and Winkler DO measurements for Wapiti River samples taken downstream of the mill in

Table 1. Oxygen and temperature measurements, 27-28 February 1990.

Dilution: % P&G Effluent	Meter Temp. °C	Meter DO mg/L	Winkler DO - mg/L Treatment 1	Treatment 2	Treatment 3	Treatment 4
2%	3.0	11.4	11.6	11.8	11.8	11.7
5	3.4	11.3	10.7	10.9	10.8	10.4
10	4.4	10.8	9.5	9.5	9.6	8.8
20	6.1	9.7	6.8	7.2	7.0	5.9
50	10.7	6.8-7.0*	1.3	2.0	1.7	0.4
100	18.1	6.2-7.0*	0	<0.4	0	0

* DO concentration declined during the 10-15 minute measuring period.

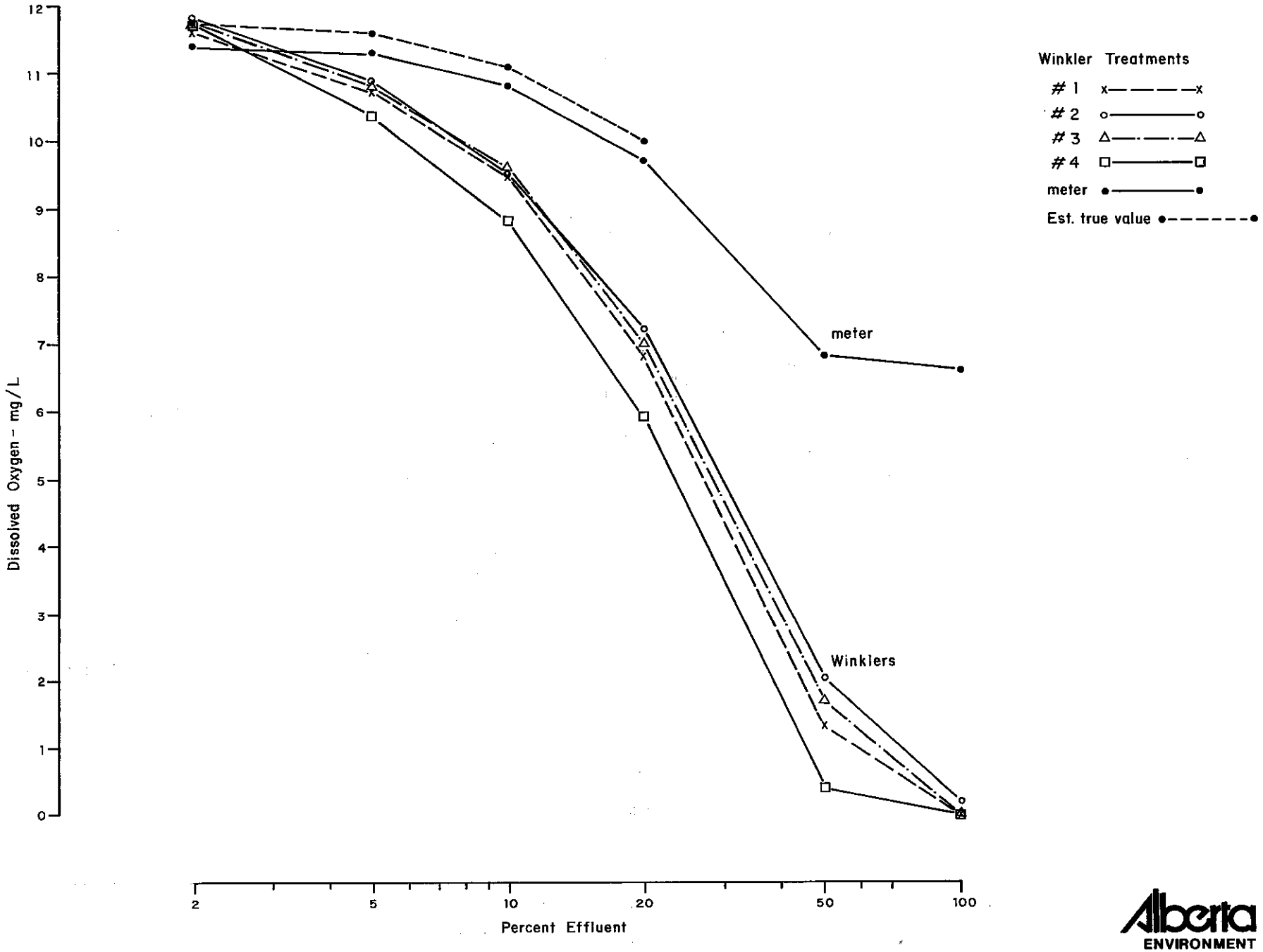

Figure 1. Oxygen measurements in pulp mill effluent dilutions.

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Table 2. Wapiti-Smoky river surveys: percent effluent and dissolved oxygen.

SITE	March 1989 Date	BKME %	Winkler DO - mg/L Measured*	Winkler DO - mg/L Adjusted	Feb - March 1990 Date	BKME %	Meter DO mg/L	Winkler DO - mg/L Measured*	Winkler DO - mg/L Adjusted
Wapiti R. @ Hwy 40	1 March	0	12.3	-	27 Feb	0	11.5	12.01	-
Wapiti R. 5km d/s of Grande Prairie Sewage	-	-	-	-	27 Feb	0	11.5	11.93	-
Wapiti R. d/s Haul Bridge	-	-	-	-	27 Feb	0	11.6	11.91	-
Wapiti R. u/s of Mill Effluent	-	-	-	-	27 Feb	0	11.6	11.92	-
Big Mountain Cr. Mouth	-	-	-	-	27 Feb	0	13.0	12.92	-
Procter & Gamble Final Effluent									
Wapiti R. @ Railroad Bridge - Left Bank	2 March	11.5	9.8	11.6	28 Feb	3.6	11.6	11.20	11.6
- Right Bank			9.8	11.6			11.4	11.31	11.7
Wapiti R. ~ 10km d/s of P&G Effluent	-	-	-	-	28 Feb	3.6	11.9	11.52	11.9
Wapiti R. u/s Bear R.	2 March	11.5	9.2	11.0	28 Feb	3.6	10.7	10.42	10.8
Wapiti R. ~ 10km u/s of mouth	-	-	-	-	28 Feb	3.6	10.0	9.76	10.2
Wapiti R. near mouth	3 March	11.4	6.87	8.7	1 March	3.6	10.1	9.41	9.8
Smoky R. u/s of Wapiti R.	3 March	0	11.4	-	1 March	0	12.3	11.88	-
Simonette R. mouth	3 March	0	10.5	-	1 March	0	10.2	10.76	-
Smoky R. @ Hwy 34	4 March	3.0	9.5		6 March	0.8	11.1	11.01	-
Smoky R. u/s of Puskwaskau R.	5 March	3.0	8.3		6 March	0.8	10.5	10.36	-
Puskwaskau R. mouth	-	-	-		6 March	0	12.9	12.63	-
Bad Heart R. mouth	-	-	-		6 March	0	13.3	12.87	-
Smoky R. @ km 105	6 March	3.4	7.6		7 March	0.8	10.3	10.26	-
Little Smoky R. mouth	7 March	0	5.2		7 March	0	10.3	10.22	-
Smoky R. @ Watino	7 March	3.0	7.3		7 March	0.6	9.9	9.88	-
Smoky R. 1/2 way, Watino to mouth	9 March	3.0	7.1		7 March		9.7	9.77	-
Smoky R. near mouth	9 March	3.0	7.2		7 March	0.6	9.3	9.42	-

* Mean of 2-3 samples

February and March 1989, and also concluded there was interference. Their finding of greater discrepancies than during the experiment here, may reflect their use of different Winkler techniques.

Paired Winkler and meter DO measurements were also made during winter synoptic surveys on the Athabasca River in 1989. The Athabasca River immediately downstream of Hinton contained about 3% BKME during the surveys, but Winkler and meter DO measurements there, and at other locations, were not significantly different (Noton and Shaw 1989). The Hinton BKME in undiluted form is known to interfere strongly with the Winkler test (e.g. meter DO ca. 5 mg/L, Winkler DO ca. 1 mg/L - EQMB unpublished data). The lack of apparent interference in river samples may reflect the fact that the 3% dilution is approaching the level where interference is low (Figure 1) and also that the Hinton BKME contains lower concentrations of many dissolved constituents than does the Procter and Gamble BKME.

Effluent from the chemithermomechanical pulp mill (CTMP) at Whitecourt is known to interfere with the azide-Winkler method, by foaming and/or containing excessive suspended solids during the test (EQMB unpublished data). However, it is lower in flow than the two kraft mills and in winter constitutes less than 1% of Athabasca River flow downstream of its discharge. Winkler and meter DO measurements there have not been significantly different (Noton and Shaw 1989).

3.3 Nature of the Interference

Clesceri *et al* (1989) note the many possibilities for chemical interference in the Winkler iodometric method. They list several

modifications to deal with familiar interferences, of which the azide modification is the one normally used for surface waters. Clesceri et al (1989) note that during the Winkler test "most organic matter is oxidized partially when the oxidized manganese precipitate is acidified, thus causing negative errors." Pulp mill effluent contains high concentrations of dissolved organic carbon (DOC), as well as numerous other solutes. Further, the apparent Winkler interference from BKME in the Wapiti River, and the apparent lack of it in the Athabasca River at similar dilutions, is consistent with the higher concentration of DOC and other solutes in the P&G BKME. McKeown et al (1967) tested spent liquor from a sulfite pulping process and found considerable interference with the azide-Winkler method but negligible interference with the membrane electrode method. Clesceri et al (1989) note that membrane-electrode DO meters are generally less affected by interference than the Winkler techniques since the membrane separates the electrode from the sample water.

4. CONCLUSION AND RECOMMENDATIONS

Interference by pulp mill effluent in the azide-Winkler DO method has been demonstrated here and by other investigators. This interference is great enough to have affected Winkler DO measurements on the Wapiti River downstream of the P&G pulp mill, during winter surveys in 1989 and 1990. Based on experimental measurements, a graph of Winkler, meter, and 'true' DO versus percent effluent (Figure 1) was used to provide an empirical correction factor for Winkler DO values by entering the curve at the percent dilution for the survey in question, measuring the difference between Winkler and 'true' DO, and adding this

amount to the measured values from the field. The resulting adjusted values (Table 2) should be more accurate and this is supported by the fact the 1989 values are similar to Hodgson and Barth's 1989 meter DO values. The adjusted values also result in a much improved mass balance for DO:

Sites	March 1989			Feb-March 1990		
	Flow m^3/s	DO mg/L	DO kg/d	Flow m^3/s	DO mg/L	DO kg/d
Upstream:						
Wapiti R	5.33	12.3	5669	13.8	11.9	14,224
P&G effluent*	0.696	5(est)	300	0.516	5.3	236
Big Mountain Cr.	-			0.172	12.9	192
Total			5970			14,650
Downstream:						
Wapiti @ railroad	6.05	11.6	6060	14.5	11.6	14,530

*Foam pond

Note that this empirical correction factor is specific to the method of Winkler analysis used here (treatments #2 and #3) and is not necessarily valid for other treatments.

Future DO sampling of rivers containing more than about 2% pulp mill effluent should employ reliable membrane-electrode meters.

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