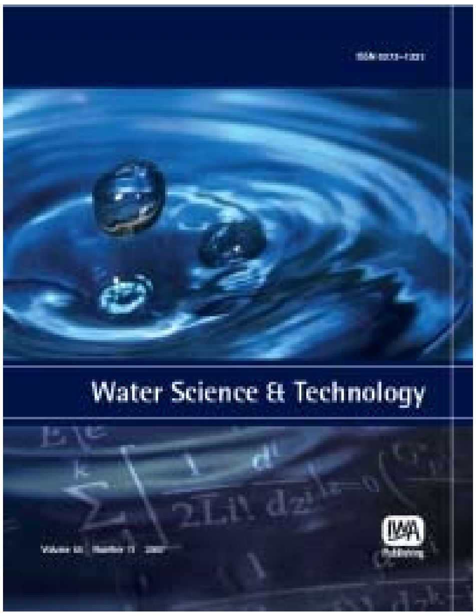

Effluent carbonaceous biochemical oxygen demand (CBOD) characterization for modern pulp and paper facilities

J. E. Palumbo, L. C. Brown, C. V. Maltby and L. Eppstein

ABSTRACT

As receiving water quality models are being used to address dissolved oxygen issues requiring an increased degree of resolution, a more refined characterization of effluent CBOD can become an important aspect of the analysis. The selection and use of kinetic models to identify effluent specific parameters can have a significant impact on this characterization. This study modeled effluents from six pulp and paper facilities in order to reassess the kinetic models, the data, and experimental design used for a typical effluent characterization. The dual first order model fit these effluents with significantly less error than the traditional first order model suggesting a significant fraction of the CBOD is slowly degradable. Because the dual first order model produces a more refined characterization of CBOD kinetics than the first order model, it places an increased demand upon the data used to inform the parameter estimates. Therefore, analysis of the precision of the parameter estimates and methods for improving estimation precision via experimental design are also discussed.

Key words | carbonaceous biochemical oxygen demand, kinetic models, parameter estimation, pulp and paper effluents

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INTRODUCTION

The attainment of an adequate concentration of dissolved oxygen is critical to the health of aquatic ecosystems. In order to maintain ecosystem health, numeric criteria have been established for dissolved oxygen concentrations protective of sensitive species. Receiving water quality models are often called upon to quantitatively link the attainment of dissolved oxygen criteria with point and non-point loadings of oxygen demanding materials. In cases of naturally occurring depressed oxygen levels, the numeric criteria can target very small changes in oxygen, often on the order of 0.1 mg/L of oxygen (SCDHEC 1999; GADNR 2008). The receiving water quality model must have a high degree of resolution in order to accurately link source loads to these small changes in oxygen. One approach to improve the resolution of the receiving water quality model is to develop a more refined characterization of the major model inputs and the most significant model input to a dissolved oxygen model is often the loading of carbonaceous oxygen demanding (CBOD) materials.

Historically, the pulp and paper industry has been diligent in developing accurate representations of pulp and paper CBOD kinetics. (McKeown *et al.* 1981; NCASI 1982). However, upgrades to both the pulping and paper making process and wastewater treatment operations across the industry have likely altered pulp and paper CBOD characteristics and kinetics since the last industry survey nearly 30 years ago. Thus, the objectives of this paper are to reassess the kinetic models used to describe CBOD in pulp and paper effluents and report on

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experimental design issues that may allow for more precise estimation of kinetic model parameters.

CBOD kinetic models

CBOD characteristics are typically defined by the parameters of kinetic models fit to oxygen consumption data from long term BOD tests. Generally, the fitted model parameters provide estimates of the ultimate CBOD (CBOD_u) concentration and the rate of decay. The ratio of CBOD_u to 5-day BOD (sometimes referred to as the *f*-ratio) is widely used in waste load allocation studies and can be determined from the model results. It has been recognized that the values of these parameters can vary significantly across the type of discharge (USEPA 1995); therefore, it can be important that all CBOD sources are uniquely characterized prior to application of the receiving water quality model.

Traditionally, CBOD parameters have been estimated using a first order kinetic model (Equation (1)).

$$y = L_0 - L = L_0(1 - e^{-kt}) \tag{1}$$

where y = oxygen consumed through time t (mg/L); L_0 = ultimate CBOD (mg/L); L = CBOD remaining (mg/L); k = decay rate coefficient (day^{-1}); t = time (days).

While the first order model is widely used, many investigators have shown that the expression does not adequately describe the CBOD decay of many effluents (Adrian & Sanders 1992; Borsuk & Stow 2000; Mason *et al.* 2006).

Alternative models have been proposed to capture the inadequacies of the first order model. These include half-order (Adrian & Sanders 1998), second order (Young & Clark 1965; Tebbutt & Berkun 1976; Adrian & Sanders 1998), mixed order (Borsuk & Stow 2000; Adrian *et al.* 2004) and dual first order (McKeown *et al.* 1981; Mason *et al.* 2006) kinetics. Recent studies have suggested that the mixed order (Borsuk & Stow 2000; Adrian *et al.* 2004) and dual first order (Mason *et al.* 2006) models may be able to represent CBOD decay in a wide variety of effluents.

In 1982 NCASI showed that the dual first order model (sometimes referred to as *sum of first order* or a *double exponential model*) adequately fits many pulp and paper effluents (NCASI 1982). More recently, Mason *et al.* (2006) found that the model compared favorably to the mixed order model when applied to the dataset of Borsuk & Stow (2000).

The dual first order model has the form:

$$y = L_0 - L = L_{10}(1 - e^{-k_1 t}) + L_{20}(1 - e^{-k_2 t}) \tag{2}$$

where k_1 = rapid CBOD rate coefficient (day^{-1}); k_2 = slow CBOD rate coefficient (day^{-1}); L_{10} = ultimate rapid CBOD (mg/L); L_{20} = ultimate slow CBOD (mg/L); $L_0 = L_{10} + L_{20}$ = sum of rapidly and slowly degradable CBOD (mg/L); $L = L_1 + L_2$ = sum of rapidly and slowly degradable CBOD remaining (mg/L).

Mechanistically, the dual first order model is based on the concept that there are multiple first order substrate decay reactions occurring in the effluent. These reactions proceed concurrently but at different rates based on the reactivity of the individual substrate. The model separates these substrates into two fractions based on relatively rapid or slow decay and assigns a lumped rate coefficient to each fraction. Mason *et al.* (2006) summarizes the support for the concept and notes the evidence indicating that heterotrophic organisms simultaneously utilize the substrates available to them while growing under both carbon limited and carbon sufficient conditions (Kovarova-Kovar & Egli 1998). Additionally, pulp and paper wastewater characterizations for treatment plant modeling (Brault *et al.* 2006) have divided organic material into readily degradable (i.e. VFAs, resin acids) and inert (i.e. lignin) fractions providing some support for the selection of two first order expressions. Other practical advantages include the intuitive concept of simultaneous fast and slow first order reactions and the direct application of the parameter estimates to many commonly used receiving water quality models.

In this paper we present the results of modeling studies from long term BOD studies from six pulp and paper facilities. The studies include a comparison between the commonly used first order model and the dual first order model. Parameter estimates are presented and evaluated. The joint confidence regions of the parameter estimates are examined to demonstrate how they reveal the extent of parameter precision and correlation which are then related to specific data quality issues.

METHODS

Laboratory

Effluent selection

Mills for the study were chosen to be representative of modern pulp and paper industry operations. The selection emphasis was on covering major mill production categories while avoiding mills with unique or unusual wastewater or wastewater treatment technologies. Information regarding the selected mills is included in Table 1.

Sample collection and preparation

Samples were collected from the final effluent discharge points at the selected facilities, cooled to 4°C and shipped on ice overnight to the NCASI laboratory at Western Michigan University in Kalamazoo, MI. Upon receipt at the laboratory, the sample was gradually warmed to 20°C in a water bath. The warmed samples were mixed in 30-gal Nalgene tanks and stirred continually during removal via spigot into graduated cylinders for dilution preparations. Each sample dilution was prepared in a dedicated Nalgene container. All were aerated and stirred with a magbar, then transferred to Kimax 4.8-L heavy duty serum bottles (Mfg. No. 14960). A similar reservoir bottle was filled for each sample bottle. Dilutions were designed to provide an expected total oxygen consumption of 20 to 30 mg/L over the course of the experiment. River water from a source local to the laboratory was used as dilution water. Reactor and initial effluent characteristics are presented in Table 2.

Table 1 | Mill process category and treatment technology

Mill identification	Process category	Treatment category
A	Bleached Kraft	AS
B	Unbleached Kraft	ASB
C	De-ink/Recycle	AS
D	Mechanical	AS
E	Bleached Kraft	ASB
F	Unbleached Kraft	AS

Note: AS = Activated sludge; ASB = Aerated stabilization basin.

Table 2 | Effluent description and initial characterization

Mill	Date sampled	pH	TOC (mg/L)	Filtered TOC (mg/L)	COD (mg/L)
A	July 2007	8.3	78.7	71.8	197
B	July 2007	8.3	124.2	56.7	402
C	February 2008	8.4	21.8	20.5	57
D	February 2008	8.4	59.2	56.4	163
E	July 2008	8.2	173.7	115.4	ND
F	July 2008	7.9	17.9	14.7	ND

Note: ND = Not determined.

Procedure

The laboratory procedures for this study followed the procedures outlined in Standard Methods 5210 C (1998). After the reactor preparations had been made, the reactors were sampled for initial TKN (EPA method 351.2), NH_4 (EPA method 350.1), NO_2-NO_3 (EPA method 353.2) using a Bran and Luebbe Auto Analyzer 3. Total organic carbon was measured using EPA method 415.1 (combustion method, NDIR detector). Initial temperature and dissolved oxygen measurements were taken with a luminescent dissolved oxygen probe (Model LDO10103) attached to a Hach multi meter model HQ40d. Conductivity was measured with a YSI Model 32 probe and pH was measured with a Hach probe (Model PHC10103f) attached to the Hach multi-meter. The reactors were then placed in a dark incubator which held the temperature constant (20 ± 1°C).

At periodic intervals the reactors were removed from the incubator and a dissolved oxygen measurement was recorded along with temperature, conductivity, and pH. The dissolved oxygen was maintained above 3.0 mg/L by re-aerating the reactor as needed. Dissolved oxygen was re-measured after each aeration or sizable sample removal. The reactor was topped off with sample from the reservoir bottle to make up for the volume lost due to sampling/ measuring. Periodically, nitrogen series measurements were taken in order to characterize oxygen uptake by nitrification.

Analytical

Data preparation

The amount of oxygen consumed as measured in the reactor must be corrected for any oxygen consumption from the dilution water and from the oxidation of nitrogen compounds. The result of this calculation is the sample's carbonaceous biochemical oxygen demand.

The calculation is performed according to Equation (3) for a single measurement interval:

$$\mathrm{CBOD_{Sample}} = \frac{(\mathrm{BOD_{Obs}} - f * \mathrm{BOD_{Blank}})}{1 - f} - \mathrm{NBOD_{Obs}} \tag{3}$$

where $\mathrm{CBOD_{Sample}}$ = CBOD of the sample wastewater at time t (mg/L); f = percentage of dilution water in reactor; $\mathrm{BOD_{Obs}} = O_2$ consumed by the sample bottle at time t (mg/L); $\mathrm{BOD_{Blank}} = O_2$ consumed by the dilution water blank at time t (mg/L); $\mathrm{NBOD_{Obs}} = O_2$ consumed by the sample due to nitrification at time t (mg/L).

The cumulative sample CBOD is calculated by summing the CBOD over all measurement intervals. Typical results of the calculation procedure are shown graphically in Figure 1. This figure demonstrates the potential magnitude of the dilution and NBOD correction.

The observed NBOD was calculated as the increase in nitrate multiplied by 4.57 mg O/mg nitrate. The CBOD contribution of the river water was measured in blank reactors.

Data replication

Each effluent was run in duplicate in order to assess experimental error between the reactors. Figure 2 shows replicated reactor runs from three effluents. These reactors showed a pattern that was typical of all effluents sampled. Oxygen uptake was relatively rapid during the first 20–25 days, and then increased more slowly until the test was terminated between day 140 and 180. The observed pattern of oxygen uptake in these experiments is similar to those reported by others for pulp and paper effluents (Martone 1976) and other effluent types (Borsuk & Stow 2000).

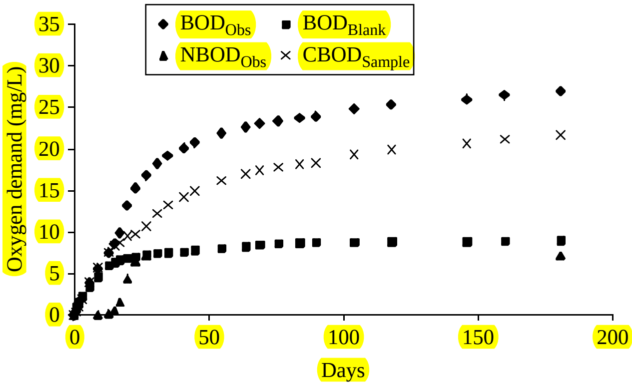

Figure 1 | Oxygen demand components of observed BOD.

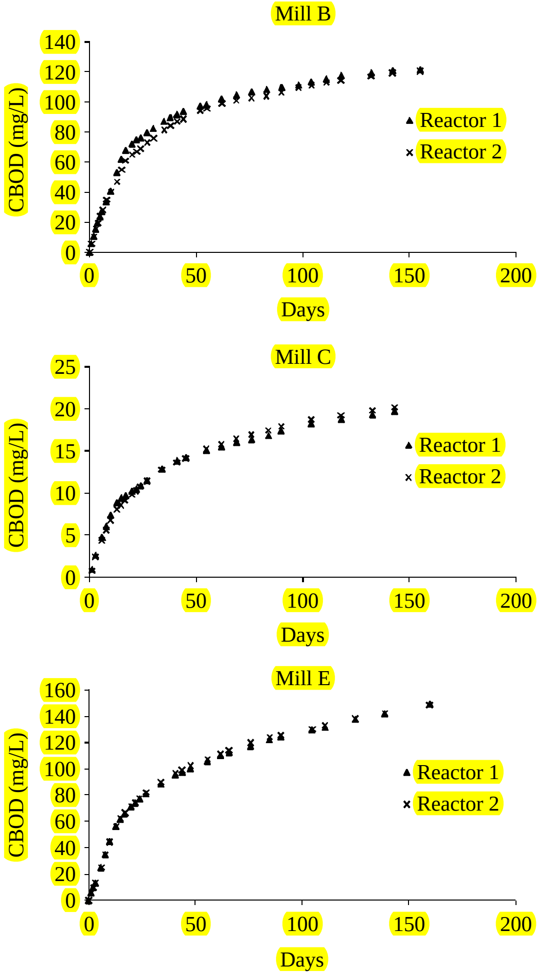

Figure 2 | CBOD time series from Mill B, C and E replicate reactors.

Figure 2 also illustrates some of the primary data related issues associated with fitting models to CBOD time series. The Mill B CBOD time series shows good agreement between the replicates until about day 20 at which point the time series diverge. This divergence is likely caused by the manner in which the nitrification correction to the BOD time series is made. For example, small errors in measuring changes in nitrate concentration can lead to large errors in the nitrification correction ($\Delta 1.0$ mg NO_3-N = $\Delta 4.57$ mg O). Because the onset of the nitrification reaction may be sudden and proceed rapidly, the timing and frequency of nitrogen measurements may be inadequate to obtain a complete nitrogen materials balance. The Mill E replicates show good agreement throughout the time series but illustrate another data oriented problem. The uptake rate over the first few days is lagged, indicating it is likely that the bacteria in the reactors were not yet acclimated to the wastewater. This type of data behavior is not captured by the model and will obscure precise parameter estimation. In contrast, Mill C shows neither of these problems and is likely to provide more precise parameter estimates for the dual first order model.

Model fitting procedure

Both the single first order and dual first order kinetic models were fit to the combined replicate CBOD time series for each wastewater with software utilizing the least squares minimization method of Marquardt (1963). The program provides least squares estimates of the parameters as well as their confidence intervals and correlations. The software was also written to prepare graphical displays of the approximate 95% joint confidence regions for each pair of parameter estimates. These plots are shown to be useful in assessing both the precision of the parameter estimates as well as the correlations among them.

RESULTS AND DISCUSSION

Evaluation of single and dual first order model

Figure 3 shows model fits and the residual plot for the first and dual first order model fitted to the results of a single Mill B replicate reactor. The superior fit of the dual order model to this data can clearly be observed in these plots. In particular, the residuals plot indicates the first order model residuals are large and severely correlated. In contrast, the dual first order model error is small, generally less than 1 mg/L.

The fit of the model can also be examined statistically using a lack of fit test (Faraway 2005). The residual sum of squares (RSSQ) for each effluent and the F-statistic calculated from the lack of fit test are presented for the effluents in Table 3.

Table 3 demonstrates the marked improvement in RSSQ by fitting the dual first order model relative to the first order model for these data. The null hypothesis for the lack of fit test is that the model is correct. This null can be rejected for all first order model fits to the data; however it cannot be rejected for the dual first order model fitted to effluents A, B, C, and D. The null is rejected for the dual order model in effluents E and F ($F_{crit\,95\%} = 2.0$). This occurs in effluent E because of the already discussed lag at the beginning of the time series. For Mill F, the model fit is relatively good as judged by the RSSQ, however significant lack of fit occurs during NBOD exertion.

Dual first order model fits to pulp and paper effluent data

Fitted dual first order model parameters and the associated 95% confidence intervals for the experimental effluents are presented in Table 4. Estimates of L_1 range from 8.1 to 78.8 mg/L, while estimates of L_2 range from 14.4 to 134.1 mg/L. The variability in CBOD concentrations

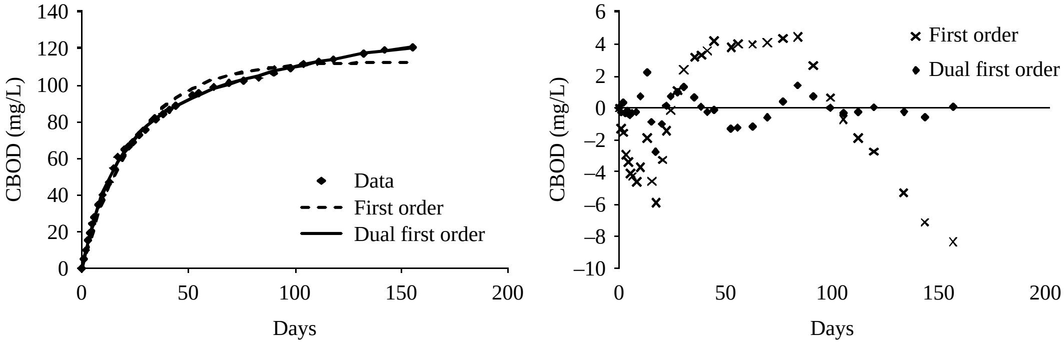

Figure 3 | First order and dual first order model fits and residuals for Mill B.

Table 3 | Residual sum of squares and lack of fit test results

	Residual sum of squares		Lack-of fit F-statistic	
Mill	First order	Dual first order	First order	Dual first order
A	146.5	23.8	10.7	0.9
B	1250.2	371.1	3.5	0.3
C	38.7	3.6	16.1	0.6
D	188.6	13.6	34.1	1.6
E	1997.8	153.5	125.1	9.4
F	20.2	7.8	8.7	2.9

observed across the effluents likely represents the wide range of paper making processes, raw materials, and wastewater treatment technologies employed by the sampled facilities. Estimates of k_1 range from 0.051 to 0.11 day^{-1} and estimates of k_2 range from 0.005 to 0.017 day^{-1}. While the slow CBOD coefficient estimates may not be as statistically precise as desired, they are suggestive of persistent, low rates of oxygen demand as they are consistent and in agreement across several different sources of effluent.

Analysis of parameter estimates

The confidence intervals associated with the dual first order parameter estimates in Table 4 show varying degrees of precision. Parameters for effluents C and D appear to be precisely estimated while Mills A, B, E and F, to varying degrees, are less so. The reasons for the relative imprecision are related to data quality. As already mentioned, materials balance issues with NBOD correction and bacterial lag can impart trends into the CBOD time series that cannot be accounted for with the dual order model resulting in parameter imprecision. Methods are available to adjust the data to address these trends such as removing the lag from the data or modeling rather than calculating NBOD. When these techniques were attempted on this dataset, the parameter estimates did not change, but the precision of the estimates increased noticeably. The confidence intervals are reported in Table 4 with no data correction and therefore represent conservative estimates.

In Mills A, B, E and F much of the imprecision is associated with the slow CBOD parameter estimates. This occurs for two primary reasons; the length of the test and error in the data. The estimates of the slow CBOD rate coefficient are very small with time constants on the order of 200 days. These small coefficients are difficult to estimate precisely at test lengths less than the time constant and any error in the existing data magnifies the estimation difficulty. In contrast, slow CBOD parameters were estimated with precision for Mills C and D likely because of the higher data quality and smaller time constants (83 and 58 days respectively) associated with these effluents.

Parameter precision issues can be explored graphically using joint confidence regions (JCRs) (Boyle *et al.* 1974; Berthouex & Brown 2002). Representative JCRs from a well estimated effluent (Mill C) and a poorly estimated effluent (Mill B) are presented in Figure 4.

In general, the JCRs for Mill C are well conditioned, elliptical, and indicative of precise, low correlated parameter estimates. In contrast, Mill B JCRs are elongated and distorted ellipses indicating imprecision and strong correlation associated with the slow CBOD parameters. The contrast is especially noticeable in the JCR between L_2 and k_2. In mill B, the parameter estimates for L_2 can range up to 800 mg/L provided the rate coefficient is very small.

Table 4 | Parameter estimates and 95% confidence intervals for pulp and paper effluents

Mill	L_1	k_1	L_2	k_2
A	19.5 (14.0, 24.9)	0.051 (0.040, 0.062)	54.9 (44.2, 65.5)	0.006 (0.003, 0.009)
B	78.8 (64.3, 93.2)	0.067 (0.056, 0.079)	68.8 (38.2, 99.4)	0.006 (−0.002, 0.015)
C	8.1 (6.8, 9.3)	0.11 (0.088, 0.126)	14.4 (13.7, 15.2)	0.012 (0.009, 0.016)
D	18.7 (15.0, 22.4)	0.10 (0.083, 0.118)	63.6 (61.2, 66.0)	0.017 (0.015, 0.019)
E	78.0 (68.6, 87.4)	0.069 (0.061, 0.077)	134.1 (81.4, 186.7)	0.005 (0.001, 0.008)
F	11.5 (5.5, 17.6)	0.051 (0.032, 0.068)	12.3 (9.1, 15.6)	0.01 (0.0006, 0.02)

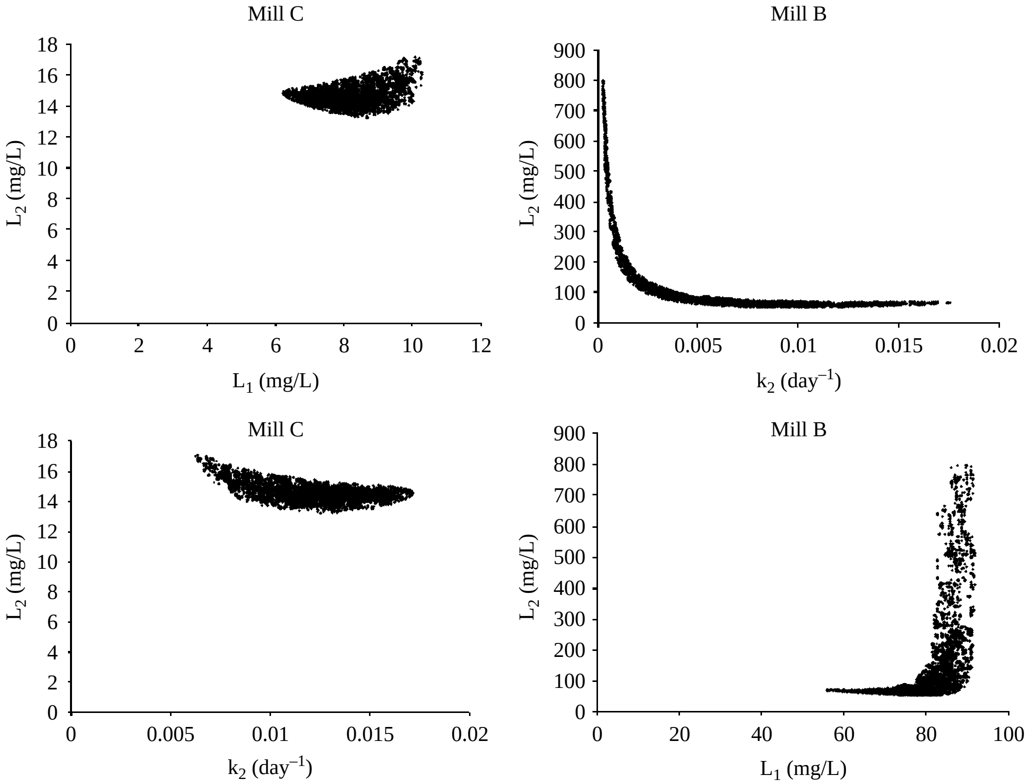

Figure 4 | Joint Confidence intervals from Mill B and Mill C effluents.

In practice the COD of this sample (400 mg/L) provides an upper boundary for CBOD, but the imprecision in the estimate remains problematic for receiving water quality modeling. The imprecision and parameter correlation observed in mill B are likely due to less than adequate test length and a relatively large error correcting for nitrification.

SUMMARY AND CONCLUSIONS

As receiving water quality models are being used to address dissolved oxygen issues of increasing degrees of resolution, the refined characterization of effluent CBOD becomes an important aspect of aquatic ecosystem analysis. Kinetic models which are used to characterize CBOD must be chosen and applied carefully as additional and sometimes difficult to identify information is derived from long term CBOD experiments. This study modeled effluents from six facilities in order to reassess the kinetic models, the data and experimental design used for CBOD characterization of pulp and paper effluents.

The dual first order kinetic model has previously been identified as well suited to pulp and paper effluents. In this study, it was shown that the dual order model could fit these effluents with significantly less error than the traditional first order model. The major advantage of the dual order model is that it divides CBOD into slow and fast reacting fractions based on the data. It seems likely that a similar fractioning of the CBOD load as inputs in a receiving water quality model would lead to a more accurate and robust aquatic ecosystem analysis. In these six pulp and paper effluents strong evidence was found to suggest the presence of a significant fraction of slowly degrading CBOD.

Because the dual first order model produces a more refined characterization of CBOD kinetics than the first order model, it also places an increased demand upon the quality of the data that inform the parameter estimates. In this study, the precision of the parameter estimates was tied directly to data quality. Oxygen uptake lags due to acclimation and the inability to make precise NBOD corrections caused difficulty with estimation precision in several effluents. Reactor replication and complete, frequent nitrogen series sampling will help to address many of these difficulties. The most critical aspect for estimating precise values of slow CBOD is the length of the test. Many of the effluents in this study indicated slow rate coefficients on the order of $0.005-0.01\,\mathrm{day}^{-1}$. In these effluents, minimizing parameter imprecision and correlation requires test lengths approaching or exceeding 200 days. While test lengths of this duration are cumbersome, they may be justified in cases where significant management and resource allocation decisions are to be based on very small changes to the dissolved oxygen concentration of the receiving water.

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