Second (2nd) Mill-Wide COD Balance to Identify Important COD Point Sources
(Interim Report for IP XL-2 Project)

By

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MANAGEMENT SUMMARY

Introduction

This report summarizes the results of the 2001 mill-wide COD sewer survey, the objective of which was to assess the quantity of COD and Color being discharged from the various unit processes at the Androscoggin mill. Other important objectives of the survey were to assess progress made by process modification projects being conducted under the auspices of the IP XL-2 project, identify additional XL-2 projects for process modification to reduce Color and COD, and lastly to determine the suitability of using COD as a process-monitoring tool.

Experimental Method

In performing the balances reported here, the Androscoggin Mill was divided into three areas. The areas for study were (1) the paper machines and coating preparation facility, (2) unit operations associated with the Black Liquor Cycle and (3) other miscellaneous areas. The paper machine area included five paper machines and the coating preparation facility. Unit operations associated with the Black Liquor Cycle encompassed the digesters, bleach plant and recovery cycle. The miscellaneous area included wastewater from both the groundwood facility and Otis paper mill, as well as backwash coming from the water treatment plant. These areas were selected based upon last year's survey of streams that had sizeable quantities of COD going to the mill wastewater treatment plant.

In this year's survey, measurements were made for the total volumetric flow rate, BOD, COD, Suspended Solids, Dissolved Solids, Specific Conductance, pH, and Color. Samples were taken for seventeen (17) sewer streams comprising the Androscoggin Mill. The selected streams were thought to be the most likely to contain sizable quantities of COD being discharged to the waste treatment system. For each sewer stream, three samples were taken. Of the 17 sewer streams that were sampled, ten (10) were composite and seven (7) were "grab" samples. The sampling was conducted over a four-day period of time in August 2001. For the composite samples, sampling was done periodically over a 24-hour period, while the grab samples were taken randomly once per day.

Results of Sewer Survey

Total Flow Rate Measurements. The sum of the flow rates of all the sources of the mill contributing to the total flow rate at the Bar Screen is approximately 30% lower than the measured flow rate at this location. This significant discrepancy might be the result of inaccuracies in the flow meter calibrations, and the use of estimated rather than measured flow rates for several sewer streams.

Comparison to 2000 Survey. Comparing the 2001 and 2000 sewer surveys, the estimated flow rate emanating from the paper mill is reduced by about 30%, from 15,461 GPM in the 2000 survey to only 10,592 GPM in the 2001 survey. Similarly, the COD measured at the Bar Screen has been reduced by about 20% from 392K lbs/day measured in 2000 to 313K lbs/day in 2001. This was thought to result partially from COD remediation projects implemented under XL-2.

COD and Color. Comparing the Total and Dissolved COD measurements from the various areas of the mill, approximately 53% of the Total COD comes from the Paper Mill, while 37% comes from the Black Liquor Cycle. By contrast 78% of the Dissolved COD and 65% of the Color comes from the Black Liquor Cycle, while only 13% of the Dissolved COD and 33% of the Color comes from the Paper Mill. The bleach plant and the A Pulp Mill General effluent are the largest contributors to the total emission of Dissolved COD and Color from the Black Liquor Cycle. The bleach plant contribution to the Black Liquor Cycle is 63% for Dissolved COD and 55% for Color. The relatively large emission by the A Pulp Mill General is likely related to incomplete closure of the screen room (A sluice filtrate replacement approved by XL-2 must still be implemented) and black liquor carry-over from the undersized flash tanks.

Efficiency in Wastewater Treatment System. The removal efficiencies in the waste treatment system are very high for Total BOD, Dissolved BOD and Suspended Solids, respectively 96, 96 and 95%. The removal efficiency of Dissolved COD is significantly lower at 66%, meaning that 1/3 of the combined Dissolved COD from all production units ends up in the Androscoggin River. The removal efficiency for Color is even lower, only 38%. This value is typical for biological treatment of pulp and paper wastewater, and may be due, at least partially, to the formation of new colored groups when ECF bleach effluents are oxidized in the treatment system.

Color and Dissolved COD as Process Monitoring Parameters. Because most suspended solids are removed in the waste water treatment plant, the appropriate effluent parameter to monitor the impact of mill processes on the final effluent quality is Dissolved COD rather than Total COD. Dissolved BOD is not a good effluent parameter for the Androscoggin mill because the concentration in the final effluent is lower than the raw water taken in by the mill from the river. Since essentially all Dissolved BOD is eliminated in the treatment system, the parameter (Dissolved COD – Dissolved BOD) characterizes the organic material that contributes most to the dissolved COD in the final effluent. Approximately half of the (Dissolved COD-Dissolved BOD) passes through the wastewater treatment system. This compares to 34% for Dissolved COD alone. Therefore, the (Dissolved COD – Dissolved BOD) mass flow rate of effluents released by production units are a good measure of their impact on the COD content of the final mill effluent.

Specific Conductance. The Specific Conductance of the effluent samples correlates well with the Dissolved Solids content for all seventeen sample locations. This can be explained by the fact that much of the dissolved solids are salts that are ionized. More importantly, however, the Specific Conductance measurement gives a good indication of the impact of the Black Liquor Cycle related effluents (except for the Acid Sewer and Evaporator effluents) on the COD content of the final mill effluent. The Specific Conductance is not related to the Color content of the effluents.

Toxicity. Toxicity measurements suggest that the effluent from the paper machines is non-toxic while that from the Black Liquor Cycle is.

Recommendations

It is recommended that existing flow meters be recalibrated, and that new flow meters be installed in the seven (7) sewers which lacked such a device. It is also recommended that the XL-2 team finish closing up the screen room, and reduce black liquor carryover from the A pulp mill flash tanks going to the sewers in order to reduce both the Color and the COD of the final mill effluent. Future efforts of the XL-2 team should be directed at reducing the kappa number going to the bleach plant, since the combined bleach plant effluent is the largest contributor to COD and Color released by the Black Liquor Cycle. Obvious candidates are optimization of the oxygen delignification system on the softwood side, and improved pulp washing.

Installation of conductivity probes in the black liquor cycle related effluents should be of much benefit for monitoring and controlling the COD content of the final mill effluent. It is recommended to use a less sensitive alarm for the conductivity probe installed in the Acid Sewer, and not to install probes in the Evaporator effluents. Finally, measures should be considered that improve the removal efficiency for Color by the wastewater treatment system.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

An XL-2 Project is being conducted at the IP paper mill in Jay, Maine[1]. Six (6) previous reports have been written summarizing the status of this project[2]. Under the terms of the XL agreement, the IP mill is exempt from Best Management Practice (BMP) in the water pollution portion of the Cluster rules. In exchange for this exemption, IP has agreed to take a number of steps designed to improve the quality of the mill effluent for COD and Color beyond the levels likely to be attained through implementation of the BMP requirements.

This report summarizes the second comprehensive COD and Color balance for the Androscoggin mill of International Paper Company in Jay, Maine. The objective of the work reported here was to assess quantitatively the amount of COD and Color being discharged from the various Unit Processes at the mill and to compare the 2001 data to values obtained in the 2000 sewer survey. A second objective was to measure quantitatively the efficiency for removal for suspended solids, BOD, Color and COD in the waste treatment system and to determine the suitability of using COD as a process-monitoring tool.

SECOND (2ND) MILL-WIDE COD AND COLOR BALANCE

Process Sampling and Location

The location in the sewer system of the sampling points used in the 2nd mill-wide COD balance is indicated in Figure 1. Table 1 gives a summary of the sample locations for the sewer survey and lists whether the flow was measured or estimated. Composite samples were obtained at ten (10) locations and grab samples were obtained in seven (7). In the case of the seven grab samples, the flow rates were estimated. For each sewer stream, three samples were taken. The sampling was conducted over a four-day period of time between August 14 and 17, 2001. Composite samples were made once an hour over a 24-hour period while the grab samples were taken once per day.

For performing the balances, the mill was divided into the three distinct areas, (1) the paper mill, (2) the black liquor cycle, and (3) other or miscellaneous. The paper machine area consisted of the No. 1 and No. 2 paper machines (sample 7), the No. 4 and No. 5 paper machines (sample 9) and the No. 3 paper machine and coating preparation area (sample 8). The mass flow rate of the various measured quantities in the appropriate streams (m_{ij}) consisted of the masses for the various substances (i) in stream (j) within the designated process area.

$$(m_{PM})_i = m_{i,Sample1} + m_{i,Sample9} + m_{i,Sample8} = Disch\arg e\ from\ Paper\ Mill$$

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[1] International Paper XL Project: Effluent Improvements", Final Project Agreement, Androscoggin Mill, Jay, Maine (June 29,2000).

[2] Genco, J. M., and van Heiningen, A., "Status Reports on XL-2 Projects at IP Androscoggin Mill", dated October, 25, 2001 (6th report); July, 16, 2001 (5th report); April 25, 2001 (4th report), "Comparative Analysis of XL-2 Projects", December, 28, 2000 (3rd report), "Mill-Wide COD Balance to Identify Important COD Point Sources", October 18, 2000 (2nd report), "First Summary Report for IP XL-2 Project, Initial Evaluation of COD Balance", August 9, 2000 (1st report).

The black liquor cycle consisted of the following units: A Pulp Mill general (sample 12) and caustic sewers (sample 11), the B Pulp Mill general (sample 18) and caustic (sample 14) sewers, the acid sewer (sample 13), the A evaporators (sample 15), the B-evaporators 6th and surface condenser (sample 17). Since the black liquor contained in the B evaporator sewer (sample 16) is already counted in the A Pulp Mill general sample (see Figure 1):

$$(m_{BL\,Cycle})_i = m_{i,Sample12} + m_{i,Sample11} + m_{i,Sample18} + m_{i,14} + m_{i,13} + m_{i,15} + m_{i,17}$$
$$= Discharge\ from\ BL\ Cycle$$

The other or miscellaneous category consisted of the groundwood mill sewer (sample 10), waste from the Otis mill (sample 5) and backwash from treatment of the river water (sample 3).

$$(m_{Other})_i = m_{i,Sample10} + m_{i,Sample5} + m_{i,Sample3} = Discharge\ from\ Misc.Areas$$

Additional samples were taken of the incoming raw water (sample 2), the mill sewer at the bar screen (sample 6), and the final mill effluent (sample 1).

Process Measurements

Table 2 summarizes the tests that were performed on the samples taken at the different locations. The samples were sent to Acheron Laboratory, an environmental testing laboratory located in Newport, Maine. Measurements were made for the total mass flow, BOD, COD, Suspended Solids, Dissolved Solids, Specific Conductance, pH, and Color. BOD and COD measurements were made for the composite sample as obtained directly from the various sewer streams and also after filtering through a 0.8-micron fiberglass filter. The filtered samples were thought to measure dissolved and sub-micron colloidal material and were designated as “Dissolved BOD” and “Dissolved COD” respectively.

Experimental Data

Raw Data. A complete set of samples were taken on August 14, 16, and 17, 2001. The raw data that were collected during the three day sampling period are summarized in Appendix A as Tables A1 through A3. The data for the three (3)-day averages for the flow rate and process parameters are summarized in Table A4 while the standard deviation and coefficient of variation for the measured quantites is summarized in Tables A5 and A6 respectively.

Average Data for Rates of Flow. Table 3 summarizes the calculated mass flow rates for the measured quanties ($m_{i,j}$) in the streams of interest. The flow rate data is given in terms of gpm. The mass flow rate data for the BOD, COD (both Total and Dissolved), Suspended Solids, Dissolved Solids, Total Solids, and Color were calculated in terms of pounds per day. This was done by multiplying the three-day average value for the various concentrations in stream (j) C_{ij}(mg/L) by the flow rate Q_j(gpm) times the conversion factor 0.0120. This was done by using the average data for the concentration (C_{ij}) and flow rate (Q_j) shown in Table A4.

$$m_{i,j} = 0.012032 * C_{i,j}(mg/l) * Qj(gpm) = \frac{lbs}{day}$$

Coefficient of Variation. The COV for each measurement is defined as the standard deviation (S) for each set of three measurements divided by the average X of for the three measurements. The data for the coefficient of variation (COV) are summarized in Table A6 were estimated from the formula.

$$COV_{ij} = (\frac{S}{X_{Ave}})_{ij} * 100 = Coefficient\ of\ Variation\ of\ measurement\ "i"\ in\ stream\ "j"$$

If the COV was smaller than about 30% then it was felt that the data were consistent. It can be seen from Table A6 that many of the data exceed this value. The data for the volumetric flow (gpm) were quite consistent except that seven (7) of the seventeen (7) samples were not measured, but were estimated since there was no flow meter in seven of the sewers of interest. The measurements with the highest coefficients of variation were the BOD (36% on average), the suspended solids (49% on average) and the color test (40% on average). However, except for the suspended solids, the COV values for the samples taken from the Black Liquor Cycle area were generally below 30%.

Mass Balances for the Combined Effluent at the Bar Screen

The sum of the sources from the three primary areas of the mill was summed to give the flow of the various quantities at the bar screen.

$$Sum\ of\ Sources\ at\ Bar\ Screen = m_{PM} + m_{BLCycle} + m_{Other} - m_{i,13}$$

The main flow of the acid sewer, $m_{i,13}$ was not included in the sum of sources because this stream combined with the general sewer after the Bar Screen. The sum of the sources was then compared to the measured value at the bar screen (sample 6).

$$m_{Sum of\ Sources} \cong m_{Bar\ Screen}$$

This permitted an estimate to be made for closure on the mass balance. These results are summarized in Table 4 for eight (8) variables plus the total flow. The percent difference (Δ Difference) shown in Table 4 was taken to be the difference between the measured quantity and the sum of the sources.

$$\Delta Difference = \left(\frac{Measured\ Quantity\ at\ Bar\ Screen - Sum\ of\ Source}{Measured\ Quantity\ at\ Bar\ Screen} \right)_{BarScreen} \text{x } 100$$

From Table 4, the sum of sources leads to an under estimation on every measurement. For the Total COD the sum of the sources was only 2% low compared to the measured quantity but was as high as 51% for the Dissolved Solids. On average the difference was underestimated by 32%. The closure on the mass balances for Dissolved Solids (51%) and Color (49%) are quite large. The question is why are the sum of the sources consistently lower than the measured quantity. Possible explanations are that the measurements are in error, such as Color and Dissolved Solids, or alternatively that the flow measurements are inaccurate. The first hypothesis is unlikely since if the experimental measurements are in error, the estimates for the mass flows would be random rather than consistently low for the sum of the sources. A more likely explanation lies in the flow measurements.

Total Flow

Total Flow Balance. The data for the total mass (flow) balance are summarized in Tables 3 and 4. On the total flow, the sum of the sources is 30% less than what is measured. This observation is consistent with what was seen in the sewer survey taken in August, 2000 in which the underestimated value for the total flow was about 14%.[3]

The measured value at the bar screen for the total flow was 25,717 gpm, which is close to measured values for the flow coming in with the raw water 29,028 gpm and leaving with the effluent 29,537 gpm (see Table 3). By comparison, the sum of the sources is only 18,040 gpm. Thus, clearly the sum of the sources from the various measured point sources is too low. A likely explanation is that the flow measurements are inaccurate or in need of recalibration. This is the likely explanation because seven of the seventeen streams did not have flow meters and were estimated. A bias in the flow measurements would cause all of the measurements to be low by about 30% since the flow rate appears in all of the estimates for mass flow. In general this is true, with the exception being the total COD which is low by only 2%.

Total Flows by Areas. Figure 2 shows the flows divided between the three major areas of the mill. The calculated total flow was 29.75 millions gallons per day. The total flow was estimated to be divided as 51% from the paper mill, 34% from unit operations comprising the black liquor cycle, and 15% from the other areas. By comparison, the flow measured in the 2000 sewer survey from the paper machine area was 66% of the total flow compared to 51% in this year's sewer survey.

An important difference in this year's sewer survey compared to last year is that the total mass flow rate for the paper machines has been reduced significantly. The results of this year's survey indicate that the absolute value from the paper machine area is lower by about 30%. In terms of the absolue values, the flow in the 2000 sewer survey was 15,461 GPM compared to this year's value of 10,592 GPM.

The flow from both the Black Liquor Cycle and the other miscellaneous areas were about the same in this year's survey as last year. For example, the Black Liquor Cycle was only about 6% lower in this year's survey compared to last year, that is about 7075 GPM in 2001 compared to 7489 GPM in year 2000. Similarly, the flow rate or total mass from the other miscellaneous areas of the mill was about 2,993 GPM in 2001 compared to 2719 GPM in year 2000, or an increase of about 10%.

Total COD and BOD Mass Balances -Comparison of the 2000 and 2001 Balance

Figure 3 presents a comparative analysis for the Total COD and BOD mass balances. Data are presented for both the sum of the sources and also for the measured values at the bar screen. This figure compares the data for years 2000 and 2001. The measurements show that both the Total COD and Total BOD are less at the bar screen in the 2001 sewer survey when compared to the data presented in the 2000 survey. The measured Total COD was reduced from 392,000 pounds per day in the 2000 survey to 313,000 pounds per day in the 2001 survey. Similarly, the measured Total BOD was

[3] Genco, J. M., and van Heiningen, A., "Mill-Wide COD Balance to Identify Important COD Point Sources", October 18, 2000 (2nd report).

reduced from 101,000 pounds per day in the 2000 survey to 88,000 pounds per day in the 2001 survey. This represents a 20% reduction in COD and a 13% reduction in BOD.

Removal Efficiencies in the Waste Water Treatment Plant

Efficiencies for removal in the waste water treatment plant were estimated for the Total and Dissolved BOD, Total and Dissolved COD, Color, Total Suspended and Dissolved Solids. The efficiency for the process variable was estimated from the mass flowing to and from the waste treatment facility using an equations of the form:

$$h_i = \left(\frac{m_{Influent} - m_{Effluent}}{m_{Influent}} \right)_i * 100$$

The difference between the total and dissolved samples involves the value for the sample after filtration through a 0.8 micron (μm) filter. The efficiency data are summarized in Table 5 and shown graphically in Figure 4. Table 5 also shows the measured values for the influent and effluent flows from the waste treatment system, 40.8 and 42.5 million gallons per day respectively.

BOD. The efficiency values are 95% or 96% for the Total BOD (96%), Dissolved BOD (96%) and Total Suspended Solids (95%). These are very high values and are indicative of a very efficient waste water treatment system for removal of Suspended Solids and BOD.

COD. For the Total and Dissolved COD, the efficiencies are significantly lower. The efficiency for removal of Dissolved COD is 66% so that approximately one-third ($1/3^{rd}$) of the Dissolved COD in the effluent will go to the river. The removal efficiency for the Total COD, that is COD of the samples before filtration, is 78%. The removal efficiency for the Total COD (78%) is higher than the removal efficiency for the Dissolved COD (66%) because the Total COD involves removal of Suspended Solids, which has a removal efficiency of 95%. The efficiency for removal of the total COD (78%) lies between that of the Suspended Solids (95%) and Dissolved COD (66%).

Dissolved Solids. The removal efficiency for Dissolved Solids involves both removal of organic and inorganic material in the waste treatment plant. The removal efficiency for Dissolved Solids is very low (2.6%). This is understandable because much of the dissolved material is most likely dissolved salts such as Na^+, Cl^-, K^+, $CO_3^=$, HCO_3^-, $SO_4^=$, etc. Even the partially oxidized organic salts such oxylate ion will contribute to the measured Dissolved Solids in the effluent from the waste treatment plant.

Color. Color is primarily a measure of chromophoric groups in organic compounds, usually conjugated carbonyl structures, coming from the bleach plant. Color removal in the waste water treatment system is low, only about 38%. Clearly the waste water treatment system is a poor system for removal of color. Actually, in the literature [4],[5] increases in effluent color of 31 and 22% have been documented, indicating that part of the color in the effluent may be biologically generated. Recent research at the

[4] S.W. Lang and R.L. Miller, "Colour increase of treated kraft effluents", Proceedings of Tappi Environmental Conf. (1977).

[5] T.E. Kemeny and S. Banerjee, "Relationships among effluent constituents in bleached kraft mills", Water Research, 31(7), 1589-1594 (1997).

University of Toronto has confirmed this for ECF bleaching waste water. Therefore, Color should be removed by process modification and avoiding discharge of color containing compounds, and by improving the removal efficiency for Color by the waste water treatment system.

Dissolved COD minus Dissolved BOD. The (Dissolved COD - Dissolved BOD) is a process parameter indicative of recalcitrant material. The influent value to the waste treatment system was 113,000 pounds per day compared to about 54,000 pounds per day in the effluent. This gives a removal efficiency of about 52%. The importance of the (Dissolved COD - Dissolved BOD) will be discussed in more detail later in this report.

Effect of Sample Filtration on BOD and COD

The effect of filtration on the BOD and COD samples is summarized in Figure 5 for BOD and Table 6 for COD.

BOD. In Figure 5, the BOD of the samples before and after filtration are presented for the various process areas and also for the raw water, in the mill sewer at the bar screen and in the mill effluent. The difference in the BOD data reflect that suspended solids are removed during the filtration. Note that there was essentially no difference between the Total and Dissolved BOD for the raw water (6,200 and 5,800 pounds per day respectively. Figure 5 shows that the mill BOD is not an important issue because values for the BOD in the mill effluent are lower than that of the raw water, that is 5,600 pounds per day for the Dissolved BOD in the raw water and 1,900 pounds per day for the Dissolved BOD in the mill effluent. The data of Figure 5 also show that most of the BOD is coming from the black liquor cycle and is in agreement with the findings in the 2000 sewer survey.

COD. Table 6 summarizes the COD removal efficiencies due to sample filtration and are broken down by area. Data are presented for the Total COD, Dissolved COD and the percentage difference between the Total and the Dissolved COD.

$$\Delta COD = \left(\frac{COD_{Total} - COD_{Dissolved}}{COD_{Total}} \right)_{Areai} * 100$$

Sample filtration removes about 91% of the COD from samples obtained in the paper mill effluents and only about 22% from the Total COD in the Black Liquor Cycle. In the other miscellaneous areas, filtration removes about 68% of the COD in the samples.

Dissolved COD as Process Monitoring Parameter. The efficiency for removal of Total Suspended Solids is 95% (see Table 5) and would be expected to correlate roughly with filtration of the samples through the 0.8 micron filter. Consequently, the key step in determining the impact of the mill on the receiving body of water is filtration of the sample. Similarly, a key parameter in assessing impact of a unit process on the environment would be the Dissolved COD since the suspended solids with associated COD would be removed in the waste water treatment system.

COD Release By Area

The COD release by area is summarized in Figures 6, 7 and 8. In Figure 6, the impact of the various parts of the mill is seen in the difference between the incoming raw water and the mill effluent. The data of Figure 6 shows that the mill adds about 52,000 pounds per day of Total COD of ($73.3 \times 10^3 - 21.3 \times 10^3$) to the Androscoggin River. Of the total 52,000 pounds per day of COD that are added to the river, approximately 42,400 pounds per day are added as Dissolved COD. Furthermore, in terms of Dissolved COD, this material is coming primarily from the Black Liquor Cycle (see Figure 6); 15,700 pounds per day of Dissolved COD from the paper mill versus 96,000 pounds per day of Dissolved COD coming from the Black Liquor Cycle.

From the 2001 sewer survey (Figure 7), 53% of the Total COD comes from the paper mill versus 37% of the Total COD comes from the Black Liquor Cycle and 10% from the other areas of the Jay, Maine mill. These findings agree well with the conclusions reached in the sewer survey conducted in 2000. By contrast, 78% of the Dissolved COD originates from the Black Liquor Cycle compared to only 13% from the paper mill and 9% from the other miscellaneous areas of the mill (see Figure 8).

These results further show that the Total COD measurement is not a particularly good parameter for process monitoring because most of the Total COD comes from the paper mill as suspended solids, which are settled and removed in the wastewater treatment plant. To assess the true impact of the mill processes on the environment it would appear that the Dissolved COD would be a more appropriate parameter for process monitoring.

COD Contributions to the Black Liquor Cycle

Figure 9 summarizes the COD contributions of the different production units in the black liquor cycle in terms of daily emissions of Total and Dissolved COD. It shows that except for the B Pulp Mill (General) sewer, the emission of Dissolved COD is only about 5 to 25% lower than that of total COD. Thus, in contrast to the paper machine effluent, filtration of the pulp mill effluent samples through a 0.8 μm filter leads to the removal of only a relatively small fraction of material that is oxidizable.

A Pulp Mill (General). The comparatively high emission of Dissolved COD from the A Pulp Mill (General) sewer relative to that of the B Pulp Mill (General) sewer, that is 3,800 versus 2,600 lbs/day, is thought to result partially from the A sluice filtrate, and from black liquor carry-over from the undersized flash tanks. The replacement of the sluice filtrate, an XL project that was not yet implemented at the time of this study, would lead to an estimated reduction of the Total COD emission of 2,060,000 lbs/year or 5,650 lbs/day. The Total COD contribution of the black liquor carry-over is estimated at 2,100,000 lbs/year or 5,750 lbs/day, giving a sum of 11,400 lbs/day for these two sources to the Total COD emission by the Androscoggin mill. Since the measured Total COD of the A Pulp Mill (General) sewer is 17,900 lbs/day, and the Dissolved COD is about 4/5th or 80% of the Total COD, these two sources are mostly responsible for the Dissolved COD in the A Pulp Mill (General) effluent stream.

B Pulp Mill (General). It can be seen in Figure 9 that only for the B Pulp Mill (General) there is a large difference between the Total COD and Dissolved COD. The likely explanation for this large difference is that the effluent contains a significant amount of fiber due to the fact that at the time of this survey the time dump of the cleaner in the B pulp mill screen room was not yet operational.

Dissolved COD Contributions to the Black Liquor Cycle

Bleach Plant and A Pulp Mill (General). The relative contribution of the different production units to the Black Liquor Cycle in terms of Dissolved COD is seen in Figure 10. It shows that the major contributions are coming from the bleach plant for both the softwood and hardwood pulp, namely the A Pulp Mill (Caustic) sewer (23%), the B Pulp Mill (Caustic) sewer (17%), and the Acid Sewer (23%). The sum of these contributions leads to a total release of Dissolved COD by the bleach plant of 63% of the Black Liquor Cycle. The A Pulp Mill (General) sewer is the next largest contributor and indicative of incomplete closure of the screen room (A sluice filtrate replacement) and black liquor carry over from the undersized flash tanks as discussed earlier.

Evaporators and B Pulp Mill (General). The total contribution of Dissolved COD coming from the Evaporators (including 6^{th} and surface condenser) on the A and B side are 13 and 8% respectively. Although these are smaller values than those from the bleach plant and the A Pulp Mill (General), they still represent significant contributions to the Black Liquor Cycle. However, since the Dissolved COD/Dissolved BOD ratio is small compared to that released from other production units in the Black Liquor Cycle, the relative contribution from the evaporators to the final effluent released to the river will be smaller. Finally, the contribution of the B Pulp Mill (General) sewer is very small (3%), indicative of a relatively well-closed screen room for the hardwood pulp.

COD Minus BOD For Filtered Samples

Significance of (Dissolved COD-Dissolved BOD) Parameter. The removal efficiency of Dissolved BOD by the wastewater treatment system is 96% (see Table 5). Since most of the Dissolved BOD entering the wastewater treatment system originates from the Black Liquor Cycle, it may be concluded that essentially all of the dissolved organic material measured as BOD in the pulp production effluent is eliminated in the treatment system.

Since the Dissolved BOD is a fraction of all the dissolved material measured as Dissolved COD, the difference between Dissolved COD and Dissolved BOD represents the material, a significant fraction of which ends up in the Androscoggin River. Table 5 shows a removal efficiency of 52% for (Dissolved COD-Dissolved BOD). This means that 48%, or approximately half of the (Dissolved COD-Dissolved BOD) passes through the wastewater treatment system. This compares to 34% for Dissolved COD alone, and 4% for Dissolved BOD. Therefore, the value of the parameter (Dissolved COD-Dissolved BOD) characterizes the material that contributes mostly to the COD in the final effluent.

Contributions of All Sources. The contributions of all effluent sources in terms of daily release of (Dissolved COD - Dissolved BOD) are shown in Figure 11. Again it can be seen that the biggest sources are located in the Black Liquor Cycle, with the biggest four contributions coming from the A Pulp Mill (Caustic) sewer, Acid Sewer, A Pulp Mill (General) sewer and B Pulp Mill (Caustic) sewer. It is also interesting to note that the (Dissolved COD - Dissolved BOD) contributions from the three paper machine sources are all about the same, and that their combined total is smaller or similar to that of any of these four separate Black Liquor Cycle sources.

Relative Contributions to the Black Liquor Cycle. Figure 12 and Table 7 show the percentage contributions of the different pulp production units to the Black Liquor Cycle in terms of (Dissolved COD - Dissolved BOD). Similar to Figure 10 for the Dissolved COD, it can be seen that the main contribution to (Dissolved COD - Dissolved BOD) is the bleach plant (Acid Sewer, A Pulp Mill Caustic sewer and B pulp Mill Caustic sewer) representing 68% of the total. After the bleach plant, the next biggest contributor to (Dissolved COD - Dissolved BOD) is the A Pulp Mill General sewer, responsible for 16% of the Black Liquor Cycle. The percentage contribution from the evaporators is 7% for the A side and 5 % for the B side (sum of B Evaps and 6th and SC). The latter contributions to (Dissolved COD - Dissolved BOD) are smaller than the corresponding percentage contributions of Dissolved COD (see Figure 10) because the evaporator effluent has a low ratio of Dissolved COD/Dissolved BOD, and thus is relatively easy to degrade in the wastewater treatment system.

Color Released By Area

The Color emission data are summarized in Figures 13, 14 and 15. The relative contributions to the Color emission by the three areas are displayed in Figure 13. It shows that the Black Liquor Cycle is the largest contributor of Color in the effluent (65%), and is about twice as large as that coming from the paper machines (33%). Since most of the Dissolved COD also originates from the Black Liquor Cycle, these results suggest that a significant fraction of the Dissolved COD is solubilized lignin fragments containing chromophoric groups.

Contributions of All Sources. The contributions to Color by all mill sources are shown in Figure 14. The four largest contributors are the number 4 and 5 paper machines (19,000 pounds per day), followed by A Pulp Mill General sewer (15,800 pounds per day), and the B pulp Mill Caustic sewer (14,200 pounds per day). Thus, although most of the Color is associated with the Black Liquor Cycle, paper machines 4 and 5 also contribute significantly to effluent Color. This most likely arises from the grades of paper being produced on the No. 4 and 5 paper machines. Color bodies containing chromophoric groups arise from the discharge of white water containing dyes and coating solids, especially dissolved starch and latex binders.

Relative Contributions to the Black Liquor Cycle. Figure 15 shows the sources of Color in the Black Liquor Cycle. It can be seen that the bleach plant is the main contributor (56% as the sum of A Pulp Mill Caustic sewer, the Acid sewer, and B Pulp Mill Caustic sewer). The effluent from the A Pulp Mill General sewer is the largest single source of Color and contributes 31 % of the total emission of Color from the Black Liquor Cycle. This large Color emission is likely related to the incomplete closure of the screen room (A sluice filtrate replacement must still be implemented) and the black liquor carry over from the undersized flash tanks. The Color contribution from the B Pulp Mill General sewer is also relatively large (11%), considering that the Dissolved COD or (Dissolved COD - Dissolved BOD) arising from this source is small at 3 and 4% of the total respectively. It is known, however, that Color from the B pulp Mill General sewer will be much smaller with the recent installation of the timed dumping of the cleaner rejects in the B screen room, confirming that a major fraction of Color is associated with raw black liquor. Finally, the data in Figure 15 shows that the Evaporator effluents on both the A and B sides have almost no Color, and contribute only 0.7 and 1.1% to the total Color load in the Black Liquor Cycle.

Comparison of Major Parameters for the Black Liquor Cycle

The percentage contributions of the different Black Liquor Cycle sources to Dissolved COD, (Dissolved COD –Dissolved BOD), Color and also Dissolved Solids are summarized in Table 8. It shows that there is a good agreement between the percentages of (Dissolved COD –Dissolved BOD) and Dissolved Solids for the A Pulp Mill General, B pulp Mill General, A Pulp Mill Caustic and B Pulp Mill Caustic. However, this correlation breaks down for the Acid Sewer and the Evaporators. This may be explained by the high content of (inorganic) spent bleach liquor salts in the Acid Sewer, and the very low concentration of salts in the Evaporator effluent. The Dissolved COD percentages are similar to those of (Dissolved COD – Dissolved BOD), except that the Evaporator contributions of the latter are lower. The Color is not well correlated with the Dissolved Solids. A correlation between the major effluent parameters and Dissolved Solids content is of interest because it will be shown that the latter is well predicted by the Specific Conductance, a property easily monitored on-line for the effluents. Finally, Table 8 shows that the bleach plant contribution to the Black Liquor Cycle is 63% for Dissolved COD, 68% for (Dissolved COD – Dissolved BOD), 55% for Color and 82% for Dissolved Solids.

Correlation of Effluent Parameter with Specific Conductance

It was investigated whether there exists a correlation between the different effluent parameters and the measured Specific Conductance. It was found that the Specific Conductance only correlated with the Dissolved Solids content for all the different samples. This correlation is shown graphically in Figures 16 and 17. The correlation between Dissolved Solids and Specific Conductance can be explained by the fact that much of the dissolved solids are salts that are ionized.

Correlation between Dissolved Solids and Specific Conductance. The dominance of ionized salts as dissolved solids is confirmed by the large daily input to the wastewater treatment system of 377,000 lbs/day (see Table 5) compared to 165,000 lbs/day for the Dissolved COD. The fact that the wastewater treatment removal efficiency for the Dissolved Solids is only 2.6% also agrees with that inorganic salts are not removed by a biological treatment system. The calculated ratio between the Specific Conductance and the Dissolved Solids for all the different sources is shown in Figure 16. It can be seen that the ratio lies between 0.08 and 0.28 μS*L/cm*mg. It is also important to notice that the ratio is very similar (0.09±0.1 μS*L/cm*mg) for the four samples contributing to the Black Liquor Cycle from the A Pulp Mill General sewer, the A Pulp Mill Caustic sewer, the B Pulp Mill General sewer and the B Pulp Mill Caustic sewer. The ratio is higher for the Acid Sewer (0.15 μS*L/cm*mg) and the A Evaporators (0.28 μS*L/cm*mg) and B Evaporators including the 6^{th} effect and surface condenser (0.2 μS*L/cm*mg). The good correlation between the Dissolved Solids and Specific Conductance is also seen in Figure 17, displaying the value of the two parameters at all the sampling points. This means that the Specific Conductance of the Black Liquor Cycle effluents could be used to monitor the discharge of dissolved material from all pulp mill source sources.

Correlation of (Dissolved COD – Dissolved BOD) and Specific Conductance. It was also investigated whether the Specific Conductance was correlated with the (Dissolved COD – Dissolved BOD) or the Color for the various sewer streams in the Black Liquor Cycle. It was found that there was only a correlation between (Dissolved COD–Dissolved BOD) and the Specific Conductance for a limited number of black liquor sources. In Table 9 the ratio of the Specific Conductance and (Dissolved COD–Dissolved BOD) is listed for the different effluents. It can be seen that the ratio is about 0.2 µS*L/cm*mg for the A Pulp Mill (General), A Pulp Mill (Caustic) and B Pulp Mill (Caustic). For the B Pulp Mill (General) and the Acid Sewer the ratio is about half and three times larger, respectively. This means that compared to the former effluents, the Specific Conductance measurement underestimates the (Dissolved COD–Dissolved BOD) content in the B Pulp Mill (General) effluent by a factor of 2. It leads to an overestimation of the (Dissolved COD–Dissolved BOD) content in the Acid Sewer by a factor of 3. For the Evaporators, the Specific Conductance measurement strongly underestimates the (Dissolved COD – Dissolved BOD) content. However, the (Dissolved COD – Dissolved BOD) emissions in lbs/day by the Evaporators and the B Pulp Mill (General) are relatively small percentages of the Black Liquor Cycle (see Figure 12). Therefore, the Specific Conductance is also valuable for monitoring and controlling the impact of Black Liquor Cycle effluents on the COD content of the final mill effluent. The Specific Conductance of the different Black Liquor Cycle effluents is **not** a good indicator of the Color of these streams.

Toxicity Measurements

The toxicity data in terms of the (Ceriodaphnia Dubia) A-NOEC and LC-50 are summarized in Table 10. It shows that the A Pulp Mill (Caustic) effluent is much more toxic than the Acid Sewer, while the effluent from the No. 3 paper machine effluent is non-toxic. As expected, the combined effluent at the Bar Screen is intermediate in toxicity. Therefore the results in Table 10 further confirm that the focus of the present XL project on the Black Liquor Cycle will also have a significant impact on the toxicity of the final effluent.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. The calculated effluent flow rate of the sum of the production units of the entire mill complex (excluding the acid sewer stream) is 30 % less than that measured at the Bar Screen.
2. About 51% of the total effluent flow rate originates from paper mill sources, while 34% comes from the Black Liquor Cycle and 15% from other sources.
3. The Total BOD and Total COD measured at the Bar Screen in the present study have been reduced relative to the survey taken in 2000 by respectively 13 and 20%.
4. The removal efficiencies in the waste treatment system are very high for Total BOD, Dissolved BOD and Suspended Solids, respectively 96, 96 and 95%. The removal efficiency of Dissolved COD is significantly lower at 66%, meaning that 1/3 of the combined Dissolved COD from all production units ends up in the Androscoggin River. The removal efficiency for Color is only 38%. This low value is typical for biological treatment of pulp and paper wastewater, and may be due, at least partially, to the formation of new colored groups when ECF bleach effluent is oxidized in the waster water treatment system.
5. BOD, either Total or Dissolved, is not a good effluent parameter for an integrated mill with an aerated secondary wastewater treatment system since the concentration in the final effluent of the Androscoggin mill is lower than the raw water taken in by the mill from the river.
6. The majority (53%) of the Total COD comes from the paper mill, versus 37% from the Black Liquor Cycle and 10% from other areas of the mill. By contrast, 78% of the Dissolved COD originates from the Black Liquor Cycle, only 13% from the paper mill and 9% from other areas.
7. Because most suspended solids are removed in the waste water treatment plant, the appropriate effluent parameter to monitor the impact of mill processes on the final effluent quality is Dissolved COD rather then Total COD.
8. The bleach plant represents 63% of the Dissolved COD contained by the combined Black Liquor Cycle effluent stream, with contributions coming from the A Pulp Mill (Caustic) sewer (23%), the B Pulp Mill (Caustic) sewer (17%), and the Acid Sewer (23%). The A Pulp Mill (General) sewer is the next largest contributor to Dissolved COD, and is indicative of incomplete closure of the screen room (A sluice filtrate replacement) and black liquor carry over from the undersized flash tanks.
9. Since essentially all Dissolved BOD is eliminated in the treatment system, the parameter (Dissolved COD – Dissolved BOD) characterizes the organic material that contributes most to the dissolved COD in the final effluent. Approximately half of the (Dissolved COD-Dissolved BOD) passes through the wastewater treatment system. This compares to 34% for Dissolved COD alone.

10. The main contribution to (Dissolved COD - Dissolved BOD) in the Black Liquor Cycle effluent is the bleach plant representing 68% of the total. The next biggest contributor to (Dissolved COD - Dissolved BOD) is the A Pulp Mill General effluent, responsible for 16% of the black liquor cycle, followed by the evaporators on the A side (7%) and 5 % for the B side.

11. Similar to Dissolved COD, the black liquor cycle is also the largest contributor of Color in the final mill effluent (65%), and is about twice as large as that coming from the paper machines (33%).

12. The bleach plant and the A Pulp Mill General contribute respectively 56% and 31% to the total emission of Color from the Black Liquor Cycle. This large color emission by the A Pulp Mill General is likely related to the incomplete closure of the screen room (A sluice filtrate replacement must still be implemented) and the black liquor carry over from the undersized flash tanks. The evaporators contribute only 0.7 and 1.1% to the total color load of the Black Liquor Cycle.

13. The Specific Conductance of the effluent samples correlates well with the Dissolved Solids content for all samples. This can be explained by the fact that much of the dissolved solids are salts that are ionized.

14. Except for the Acid Sewer and Evaporator effluents, the Specific Conductance measurement gives a good indication of the impact of the Black Liquor Cycle effluents on the Dissolved COD content of the final mill effluent.

15. The A Pulp Mill (Caustic) effluent is much more toxic than the Acid Sewer, while the effluent from the No. 3 paper machine effluent is non-toxic.

Recommendations

1. Recalibrate existing flow meters, and install new flow meters in the seven (7) sewers for which the flow rate had to be estimated.

2. Use the mass flow rates of Dissolved COD, or even better (Dissolved COD – Dissolved BOD) of effluents at the source as a measure for their impact on the COD content of the final mill effluent.

3. It is recommended that the XL-team finish closing up the screen room, and reduce black liquor carryover from the flash tanks of the softwood pulp mill in order to reduce both Color and COD of the final mill effluent.

4. Longer range effort of the XL-team should be directed at reducing the kappa number to the bleach plant, since the combined bleach plant effluent is the largest contributor to COD and Color released by the Black Liquor Cycle. Obvious candidates are optimization of the oxygen delignification system on the softwood side and improve pulp washing.

5. Install conductivity probes in the black liquor cycle related effluents for monitoring and controlling the COD in the final mill effluent. Use a less sensitive alarm for the probe installed in the Acid Sewer, and do not install probes in the Evaporator effluents.

6. Consider measures that improve the removal efficiency for Color by the wastewater treatment system.

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APPENDIX A.
SUMMARY OF EXPERIMENTAL DATA

Table A 1
8/14/01 Raw Data

Location	Flow Rate (gpm)	Total BOD (mg/L)		Total COD (mg/L)	Dissolved BOD (mg/L)		Dissolved COD (mg/L)	Solids Susp. (mg/L)	Solids Diss. (mg/L)	Spec. Conduc. (mS/cm)	pH	Color (mg/L)
(2) Raw Water - Grab	28611	43			10	a.	38	12	80	0.14	6.13	0
(8) PM #3 & Coating Prep - Composite	3561	15		1200	43	>*	116	972	477	0.74	6.81	92
(9) PM #4 & #5 - Composite	2249	112		940	26		294	412	95	0.167	8.09	1285
(7) PM #1& #2 - Composite	5037	137		886	41		120	535	427	0.592	7.41	11
(12) A Pulp Mill (general) - Composite	1829	223		880	187		800	24	1250	1.1	10.18	865
(11) A Pulp Mill (caustic) - Composite	630	690		2710	726		2640	26	5160	4.84	10.30	1660
(18) B Pulp Mill General	Missing Data											
(14) B Pulp Mill (caustic) - Grab	650	1240		2530	1040	>*	2240	54	2630	3.09	10.56	475
(13) Acid Sewer - Grab	2650	235		790	214		738	11	2220	3.25	3.00	325
(15) A Evaporators - Grab	800	860	>*	1730	933		1380	7	99	0.183	7.85	30
(16) B Evaporators - Grab	494	163		300	103		222	1	38	0.034	8.14	30
(17) B Evaporators 6th & SC - Grab	310	1300		1960	1120		1840	1	94	0.265	8.39	80
(10) Groundwood - Composite	287	136		641	120		292	2290	336	0.628	5.89	220
(5) Otis - Composite	2213	339		991	154		316	259	339	0.32	7.22	0
(3) River Waste - Grab	347	3	<	31	3	<	17	584	389	0.45	6.29	70
(6) Mill Sewer (Bar Screen) - Composite	25833	301		1160	166		464	776	1220	1.23	7.65	460
(1) Mill Effluent - Composite	29653	14		254	5		161	46	959	1.36	7.80	270

a. Raw water COD entry was 696 mg/l. This appears to be a bad data point and was not included in analysis.

Table A 2
8/16/01 Raw Data

Location	Flow Rate (gpm)	Total BOD		Total COD	Dissolved BOD		Dissolved COD	Solids Susp.	Solids Diss.	Spec. Conduc. (mS/cm)	pH	Color (mg/L)
		(mg/L)										
(2) Raw Water - Grab	28958	4	<	66	20	<	64	15	95	0.138	6.35	15
(8) PM #3 & Coating Prep - Composite	3231	83	*	1020	66		148	529	436	0.633	10.04	305
(9) PM #4 & #5 - Composite	2012	211	>*	2250	29		92	1240	298	0.696	7.90	630
(7) PM #1& #2 - Composite	5178	83	*	692	39		80	475	413	0.542	3.30	10
(12) A Pulp Mill (general) - Composite	1710	182		912	146		808	40	1130	0.963	10.22	760
(11) A Pulp Mill (caustic) - Composite	630	804		3160	722		3100	27	5810	5.08	10.96	1805
(18) B Pulp Mill (General)- Composite	219	1370		8520	206		1070	6350	1290	1.04	7.46	2210
(14) B Pulp Mill (caustic) - Grab	660	1000		2200	792		2100	111	2010	1.83	9.87	355
(13) Acid Sewer - Grab	2565	190		684	163		614	5	1890	2.8	3.00	360
(15) A Evaporators - Grab	800	1040	>*	1900	906		1390	5	52	0.172	8.28	35
(16) B Evaporators - Grab	494	146		268	104		226	1	19	0.033	8.24	30
(17) B Evaporators 6th & SC - Grab	310	1300		1900	1120		1840	1	135	0.252	8.74	70
(10) Groundwood - Composite	310	205	>*	780	196		400	827	84	0.137	6.57	275
(5) Otis - Composite	2213	303		640	167		340	302	430	0.359	7.83	35
(3) River Waste - Grab	347	12		596	4		10	359	168	0.769	6.35	20
(6) Mill Sewer (Bar Screen) - Composite	25833	296	>*	1230	152		476	645	966	1.1	9.20	460
(1) Mill Effluent - Composite	29653	9		175	4		149	23	1050	1.32	7.87	240

Table A 3
8/17/01 Raw Data

Location	Flow Rate (gpm)	Total BOD (mg/L)		Total COD (mg/L)	Dissolved BOD (mg/L)		Dissolved COD (mg/L)	Solids Susp. (mg/L)	Solids Diss. (mg/L)	Spec. Conduc. (mS/cm)	pH	Color (mg/L)
(2) Raw Water - Grab	29514	6	<	56	20	<	11	14	84	0.131	6.74	5
(8) PM #3 & Coating Prep - Composite	3683	228	>	3120	76		174	1880	614	0.791	7.05	85
(9) PM #4 & #5 - Composite	1933	371	*	2210	21		116	1360	277	0.698	7.65	305
(7) PM #1& #2 - Composite	4892	155	*	1130	24		70	689	364	0.548	7.63	25
(12) A Pulp Mill (general) - Composite	1970	122		640	98		270	39	813	0.67	9.52	550
(11) A Pulp Mill (caustic) - Composite	630	797		3350	827		3040	35	5620	5.11	10.47	2140
(18) B Pulp Mill (General)- Composite	226	482		2600	153		856	1380	900	0.787	9.11	1880
(14) B Pulp Mill (caustic) - Grab	658	1180		2300	834		1890	139	2180	2.18	10.57	700
(13) Acid Sewer - Grab	2645	187		834	172		722	28	2130	3.46	2.63	290
(15) A Evaporators - Grab	800	921		1500	786		1150	8	37	0.171	8.44	40
(16) B Evaporators - Grab	494	164		486	118		218	17	26	0.029	8.23	70
(17) B Evaporators 6th & SC - Grab	310	1420		2100	1030		1670	2	148	0.239	8.82	90
(10) Groundwood - Composite	226	160		524	154		356	763	105	0.138	5.63	230
(5) Otis - Composite	2688	498	>*	1610	173		364	121	377	0.34	7.69	30
(3) River Waste - Grab	347	9		394	4		34	1220	554	0.595	6.36	20
(6) Mill Sewer (Bar Screen) - Composite	25486	254		646	128		450	644	832	1.06	8.18	370
(1) Mill Effluent - Composite	29306	8		190	7	<	159	28	1090	1.47	7.86	245

Table A 4
Average Values of Experimental Data

Location	Flow Rate (gpm)	Total BOD	Total COD	Dissolved BOD	Dissolved COD	Solids Susp.	Solids Diss.	Spec. Conduc. (mS/cm)	pH	Color (mg/L)
		(mg/L)								
(2) Raw Water - Grab	29028	18	61	17	38	14	86	0.136	6.41	7
(8) PM #3 & Coating Prep - Composite	3492	109	1780	62	146	1127	509	0.721	7.97	161
(9) PM #4 & #5 - Composite	2065	231	1800	25	167	1004	223	0.520	7.88	740
(7) PM #1& #2 - Composite	5036	125	903	35	90	566	401	0.561	6.11	15
(12) A Pulp Mill (general) - Composite	1836	176	811	144	626	34	1064	0.911	9.97	725
(11) A Pulp Mill (caustic) - Composite	*630*	764	3073	758	2927	29	5530	5.010	10.58	1868
(18) B Pulp Mill (General)- Composite	223	926	5560	180	963	3865	1095	0.914	8.29	2045
(14) B Pulp Mill (caustic) - Grab	656	1140	2343	889	2077	101	2273	2.367	10.33	510
(13) Acid Sewer - Grab	2620	204	769	183	691	15	2080	3.170	2.88	325
(15) A Evaporators - Grab	800	940	1710	875	1307	7	63	0.175	8.19	35
(16) B Evaporators - Grab	494	158	351	108	222	6	28	0.032	8.20	43
(17) B Evaporators 6th & SC - Grab	310	1340	1987	1090	1783	1	126	0.252	8.65	80
(10) Groundwood - Composite	274	167	648	157	349	1293	175	0.301	6.03	242
(5) Otis - Composite	2371	380	1080	165	340	227	382	0.340	7.58	22
(3) River Waste - Grab	347	8	340	4	20	721	370	0.605	6.33	37
(6) Mill Sewer (Bar Screen) - Composite	25717	284	1012	149	463	688	1006	1.130	8.34	430
(1) Mill Effluent - Composite	29537	10	206	5	156	32	1033	1.383	7.84	252

Table A 5
Standard Deviation

Location	Flow Rate (gpm)	Total BOD	Total COD	Dissolved BOD	Dissolved COD	Solids Susp.	Solids Diss.	Spec. Conduc. (mS/cm)	pH	Color (mg/L)
		(mg/L)								
(2) Raw Water - Grab	456	22	7	6	27	2	8	0.005	0.31	8
(8) PM #3 & Coating Prep - Composite	234	109	1164	17	29	689	93	0.081	1.80	125
(9) PM #4 & #5 - Composite	164	131	745	4	110	516	112	0.306	0.22	499
(7) PM #1& #2 - Composite	143	37	219	9	26	110	33	0.027	2.44	8
(12) A Pulp Mill (general) - Composite	130	51	149	45	308	9	226	0.220	0.39	160
(11) A Pulp Mill (caustic) - Composite	N.A	64	329	60	250	5	334	0.148	0.34	246
(18) B Pulp Mill (General)- Composite	5	628	4186	37	151	3514	276	0.179	1.17	233
(14) B Pulp Mill (caustic) - Grab	5	125	169	133	176	43	320	0.650	0.40	175
(13) Acid Sewer - Grab	48	27	77	27	67	12	171	0.337	0.21	35
(15) A Evaporators - Grab	N.A	92	201	78	136	2	32	0.007	0.31	5
(16) B Evaporators - Grab	N.A	10	118	8	4	9	10	0.003	0.06	23
(17) B Evaporators 6th & SC - Grab	N.A	69	103	52	98	1	28	0.013	0.23	10
(10) Groundwood - Composite	43	35	128	38	54	864	140	0.283	0.49	29
(5) Otis - Composite	274	104	491	10	24	95	46	0.020	0.32	19
(3) River Waste - Grab	N.A.	5	286	1	12	447	194	0.160	0.04	29
(6) Mill Sewer (Bar Screen) - Composite	200	26	319	19	13	76	197	0.089	0.788	52
(1) Mill Effluent - Composite	200	3	42	2	6	12	67	0.078	0.038	16

N.A = Not Applicable. Only one estimate of the flow was made

Table A 6
Coefficient of Variation

Location	Flow Rate	Total BOD	Total COD	Dissolved BOD	Dissolved COD	Solids Susp.	Solids Diss.	Spec. Conduc.	pH	Color
(2) Raw Water - Grab	2%	124%	12%	35%	70%	11%	9%	3%	5%	115%
(8) PM #3 & Coating Prep - Composite	7%	100%	65%	27%	20%	61%	18%	11%	23%	78%
(9) PM #4 & #5 - Composite	8%	56%	41%	16%	66%	51%	50%	59%	3%	67%
(7) PM #1& #2 - Composite	3%	30%	24%	27%	29%	19%	8%	5%	40%	55%
(12) A Pulp Mill (general) - Composite	7%	29%	18%	31%	49%	26%	21%	24%	4%	22%
(11) A Pulp Mill (caustic) - Composite	N.A.	8%	11%	8%	9%	17%	6%	3%	3%	13%
(18) B Pulp Mill (General)- Composite	2%	68%	75%	21%	16%	91%	25%	20%	14%	11%
(14) B Pulp Mill (caustic) - Grab	1%	11%	7%	15%	8%	43%	14%	27%	4%	34%
(13) Acid Sewer - Grab	2%	13%	10%	15%	10%	81%	8%	11%	7%	11%
(15) A Evaporators - Grab	N.A.	10%	12%	9%	10%	23%	52%	4%	4%	14%
(16) B Evaporators - Grab	N.A.	6%	34%	8%	2%	146%	35%	8%	1%	53%
(17) B Evaporators 6th & SC - Grab	N.A.	5%	5%	5%	6%	43%	22%	5%	3%	13%
(10) Groundwood - Composite	16%	21%	20%	24%	16%	67%	80%	94%	8%	12%
(5) Otis - Composite	12%	27%	45%	6%	7%	42%	12%	6%	4%	87%
(3) River Waste - Grab	N.A.	57%	84%	16%	61%	62%	52%	26%	1%	79%
(6) Mill Sewer (Bar Screen) - Composite	1%	9%	32%	13%	3%	11%	20%	8%	9%	12%
(1) Mill Effluent - Composite	1%	31%	20%	29%	4%	37%	6%	6%	0%	6%
Average	5%	36%	30%	18%	23%	49%	26%	19%	8%	40%