Focused Toxicity Identification Evaluation (TIE)
for
Georgia-Pacific's Paper Mill in Palatka, FL

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Background

Georgia-Pacific Corporation operates a pulp and paper mill in Putnam County, Florida near the city of Palatka. The mill currently discharges approximately 30 mgd of treated wastewater to Rice Creek nearly 5 miles upstream from where it flows into the St. Johns River (see Fig. 1). Effluent quality is governed by NPDES Permit No. FL0002763 and a related Administrative Order No. 039-NE.

The permit requires plant operators to perform periodic whole effluent toxicity (WET) tests and report the results to state officials. Historically, the facility has been unable to pass consistently because there is often a statistically-significant reduction in reproduction among Ceriodaphnia dubia (a freshwater fleas used as the standardized test organism).

Georgia-Pacific Corporation requested that Risk Sciences investigate and determine, if possible, what specific water quality factors are causing the WET tests to fail. In addition, Risk Sciences was asked to recommend to what degree those water quality factors must be changed in order to assure consistent compliance with the NPDES permit conditions.
**Review of Historical Data**

A review of historical WET test results indicates that the Palatka facility routinely passes the acute toxicity test using Ceriodaphnia dubia. The acute toxicity test is a short-term (2-4 day exposure) to undiluted effluent. If there is no statistically-significant difference between survival rates compared to control organisms, then the test "passes" and the sample is deemed "non-toxic." Effluent samples from the Palatka mill also consistently pass the survival endpoint in the chronic toxicity test. The chronic toxicity test is a long-term exposure lasting 6-8 days.

When a WET test failure occurs, it is usually because there is a statistically significant reduction in Ceriodaphnia dubia (water flea) reproduction among organisms exposed to the highest effluent concentrations. The No-Observed-Effect-Concentration (NOEC) is generally in the 25-50% range. This means the effluent is rendered non-toxic if it can be diluted 2:1 - 3:1. However, there is insufficient flow in the receiving water to provide the necessary dilution. The maximum allowed instream waste concentration (IWC) is only 72% effluent.

Previous chemical analyses indicate that all Priority Pollutants, including ammonia, chlorine, heavy metals, and various organic compounds, are well below the level known to cause toxicity. However, total dissolved solids (salinity) is somewhat elevated. Conductivity of the final effluent is 400% higher than the laboratory dilution water used as a control during WET tests.

Ceriodaphnia dubia are extremely sensitive to increasing salinity. The inhibitive effect on reproduction is made worse by ionic imbalance. Ionic imbalance occurs when the ratio of common minerals is substantially altered from the baseline formula used to prepare laboratory dilution water. For example, significantly increasing alkalinity (bicarbonate) in relation to hardness is known to inhibit reproduction in Ceriodaphnia dubia. Normally, the ratio between alkalinity and hardness is approximately 1:1. In the Palatka mill effluent, the ratio is nearly 3:1.

Finally, recent water chemistry samples revealed higher aluminum concentrations in the final effluent (approximately 10-14 mg/L). Alum is used throughout the mill's manufacturing process, so it is not surprising to find that it is present in the wastewater. Scientific literature and our own experience suggests that alum may inhibit reproduction when concentrations increase much above 3 mg/L. This is generally quite rare because, by its nature, alum tends to bind with other substances and is rendered non-toxic as a result. Nevertheless, further investigation is warranted.

After reviewing all available data, we theorized that the following water quality factors were the "most probable" causes of WET test failure (in descending order of importance):

1) High salinity (conductivity) in the effluent
2) Ionic interference caused by unbalanced ratio between alkalinity and hardness.
3) Elevated aluminum in the final effluent.

Additional laboratory experiments were conducted to investigate these and other, less likely, theories.
Focused TIE

Effluent samples, collected from the Palatka mill, were collected and tested to confirm that they inhibited Ceriodaphnia dubia reproduction. Then, the samples were subjected to various treatments designed to increase or decrease the potential toxicity of specific chemicals. The TIE procedure is recommended by U.S. EPA. A focused TIE is preferred where chemical analyses demonstrate that certain pollutants (e.g., ammonia, chlorine) cannot be the source of toxicity in the effluent. A focused TIE eliminates some of the unnecessary standard treatments and adds special treatments for more unusual chemicals (e.g., DhA, alkalinity, aluminum).

Undiluted effluent samples, collected in April and May of 2006, inhibited reproduction by 79-84% compared to controls. When the effluent samples were diluted to the IWC, reproduction was inhibited by only 38-43%. Nevertheless, that was still sufficient to "fail" the test. The reported NOEC was 25%, well below the 72% required in the permit.

Filtering the effluent through granular activated carbon (GAC) did improve reproduction rates among the water fleas. This is important because most organic pollutants will be reduced, if not eliminated, by GAC filtration. The lack of improvement suggests that WET test failure is, most likely caused, by something else.

Spiking studies confirmed that dehydroabeatic acid (DhA) was not contributing to the apparent toxicity test failures. In fact, increasing the DhA concentration by 200% and 400% actually seemed to improve reproduction rates among test organisms to the point where the effluent would not have failed the chronic test.

Spiking studies also revealed that increasing the aluminum concentration did, in fact, inhibit reproduction. Adding just 5 mg/L of aluminum to the effluent reduced reproduction by 94% compared to the control organisms. Baseline effluent samples, without any added aluminum, reduced reproduction by only 43%.

Spiking studies to increase alkalinity had a small, but statistically-significant adverse effect on reproduction. However, this factor does not appear to be as important as the aluminum concentration.

Synthetic effluent samples were created to investigate the degree to which total dissolved solids (salinity) were responsible for inhibiting reproduction. The basic mineral concentration of the synthetic effluent sample was adjusted to match the ionic composition of the real-world effluent sample. The synthetic effluent sample was slightly more toxic than the true effluent sample. When diluted to the maximum allowed instream waste concentration of 72%, the synthetic effluent inhibited reproduction by 55% vs. the control organisms. This suggests that nearly all of the adverse effect on reproduction may be due to general salinity and not some exotic pollutant.

Finally, when humic acid is added, the synthetic effluent no longer inhibits reproduction and is, therefore, not toxic. This is consistent with other published studies which indicate that the presence of simple organic compounds partially mitigates against the biological stress caused by natural minerals in the water.
Interim Conclusions

In order to pass the Ceriodaphnia dubia test consistently, effluent samples should not suppress reproduction by more than 20% at the instream waste concentration. Greater inhibition will nearly always trigger a finding of "statistically-significant adverse effect." At present, the level of inhibition caused by exposure to Palatka mill's effluent is nearly twice that level.

Given the present chemical composition of the effluent, there is inadequate dilution available in Rice Creek to neutralize toxicity in the wastewater discharge. The amount of dilution would need to be twice the current estimated background flow to assure consistent compliance.

It appears that the primary cause of chronic toxicity test failure is the elevated conductivity (salinity) of the effluent. The concentration of total dissolved solids must be reduced to less than 1200 mg/L to assure consistent compliance.

Aluminum also appears to be contributing to the failing chronic toxicity tests. The concentration of aluminum must be reduced by approximately 75% (from 12 to 3 mg/L) to assure consistent compliance.

Comparing toxicity test results from the Palatka mill to other Georgia-Pacific facilities shows that there is not much to be gained by shifting production to be more like that at Cedar Springs or Plattsburg. However, results from the Leaf River mill indicate this type of production may hold more promise for meeting the Palatka permit limits (see Fig. 2).

Fig. 2: Comparison of Chronic Toxicity Results for Georgia Pacific Mills
**Additional Studies**

It is important to emphasize that all of the above analyses were performed using only one or two effluent samples. While we believe the results to be true, they are only valid if the underlying samples and test organisms are representative. Therefore, it would be wise to repeat some of the experiments if greater certainty is required prior to making decisions about future treatment or production options.

In particular, it is important to separate the adverse effects of salinity from the inhibition caused by elevated aluminum levels. It is difficult to remove aluminum without also changing the concentration of total dissolved solids. Nevertheless, we believe it is possible to construct an array of laboratory experiments to determine the relative impact of these two different sources of chronic toxicity.

Ideally, the highest level of confidence can be achieved by manipulating effluent quality at the plant-scale. If the Palatka mill has the ability to temporarily reduce the use of aluminum throughout its manufacturing process, then re-run the toxicity tests, a more robust conclusion may be drawn from the resulting data. Alternatively, aluminum could be added to effluent samples collected from other mills where the aluminum concentration in the effluent is already quite low (e.g. Plattsburgh, Cedar Springs or Leaf River). Running additional toxicity tests on these manipulated samples would aid in affirming or refuting our conclusions.

It may also be useful to perform additional chronic toxicity tests on samples of the source water used at the mill. It is likely that the natural chemical composition of local water supplies will also inhibit Ceriodaphnia dubia reproduction. Data from such studies can be help convince state permitting authorities to allow an "intake credit" or authorize adjustment to the standard test methods to account for natural sources of biological stress that are beyond the control of the discharger.

**Attachments**

Copies of all toxicity test results and other chemical analyses performed by or on behalf of Advent-Environ during our investigation are attached as an appendix to this report.

*Respectfully submitted,*

[Signature]
### Comparative Chemistry and Chronic Toxicity Test Results at Four Paper Mills

<table>
<thead>
<tr>
<th>Sample Source</th>
<th>Toxicity (tox. units)</th>
<th>NOEC Equivalent</th>
<th>Conductivity (μmohs/s)</th>
<th>TDS (mg/L)</th>
<th>Chloride (mg/L)</th>
<th>Alkalinity (mg/L)</th>
<th>Hardness (mg/L)</th>
<th>Alk./Hard. (ratio)</th>
<th>Aluminum (mg/L)</th>
<th>DhA (mg/L)</th>
<th>Pct. Effect @ 72% IWC</th>
<th>Hi. Conf. IWC</th>
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</thead>
<tbody>
<tr>
<td>Culture Water</td>
<td>=1.0 TUc</td>
<td>100%</td>
<td>320</td>
<td>200</td>
<td>2</td>
<td>70</td>
<td>90</td>
<td>0.8 : 1</td>
<td>?</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Leaf River</td>
<td>≈ 1.0 TUc</td>
<td>100%</td>
<td>2400</td>
<td>1600</td>
<td>270</td>
<td>350</td>
<td>140</td>
<td>2.5 : 1</td>
<td>1.1</td>
<td>0.04</td>
<td>-20%</td>
<td>73%</td>
</tr>
<tr>
<td>Plattsburgh</td>
<td>≈ 1.4 TUc</td>
<td>71%</td>
<td>330</td>
<td>210</td>
<td>60</td>
<td>44</td>
<td>41</td>
<td>1.1 : 1</td>
<td>0.21</td>
<td>n/a</td>
<td>-27%</td>
<td>63%</td>
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<tr>
<td>Palatka-Pond 1</td>
<td>≈ 1.7 TUc</td>
<td>59%</td>
<td>2600</td>
<td>1800</td>
<td>160</td>
<td>860</td>
<td>189</td>
<td>4.6 : 1</td>
<td>10.9</td>
<td>1.25</td>
<td>-39%</td>
<td>52%</td>
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<tr>
<td>Cedar Springs</td>
<td>≈ 1.9 TUc</td>
<td>52%</td>
<td>1500</td>
<td>1200</td>
<td>10</td>
<td>350</td>
<td>86</td>
<td>4.1 : 1</td>
<td>2.3</td>
<td>2.97</td>
<td>-47%</td>
<td>47%</td>
</tr>
</tbody>
</table>

**Observations:**

1) Plattsburgh is likely to be least toxic because its ionic chemistry is very similar to that of the lab water used to culture test organisms. However, hardness less than 50 mg/L may inhibit reproduction and hardness less than 25 mg/L may cause excess mortality.
2) Leaf River reportedly exhibits only infrequent and minor toxicity despite conductivity similar to Palatka. However, Leaf River has a much better ionic balance between alkalinity and hardness compared to Palatka. Minor toxicity is most likely due to elevated chloride concentrations at Leaf River.
3) Cedar Springs has much lower conductivity and chloride than any of the other plants. However, the alkalinity to hardness ratio is relatively poor (similar to Palatka's). If the WET test results show higher toxicity, then we can infer that ionic imbalance, not overall salinity, is the most likely cause of toxicity at both Cedar Springs and Palatka.
4) If ionic imbalance is causing WET test failure at Palatka, then compliance could be restored by reducing alkalinity (bicarbonate concentrations) by about 60% provided that the current hardness concentrations remain unchanged. This might be accomplished by adding acid to reduce alkalinity (similar to swimming pool chemistry). Must be careful not to increase overall conductivity or to increase toxic ions such as chloride as a result of the ensuing chemical reactions.
5) If elevated bicarbonate concentrations at Palatka are caused by naturally-occurring conditions in the local groundwater supply wells, then it is likely we can convince state permitting authorities to recognize this as a "test interference" rather than actual effluent toxicity. The test method can be modified to adjust for this natural source of interference. Similar adjustments have been approved by EPA-Region 4 in South Carolina.
6) Toxicity at Palatka is probably not caused by complex organics because filtering effluent thru activated carbon did not improve test results.
7) The difference between 1.4, 1.5, 1.7, & 1.9 TUs is relatively small and well within the error band of C. dubia reproduction test.
8) "NOEC Equivalent" is the Chronic Toxicity Units value converted to the No Effect Concentration.
9) "Percent Effect at 72% IWC" is the estimated reduction in reproduction among organisms exposed to 72% effluent compared to control organisms.
10) "High Confidence Instream Waste Concentration" is the IWC at which there is a very high probability that the effluent will consistently pass the chronic C. dubia test.