THE UNIVERSITY OF
NEW SOUTH WALES

Water Research
Laboratory

School of Civil and
Environmental Engineering

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Our Ref: WRL 08068.01 WCG L100201

Gunns Ltd
PO Box 572
LAUNCESTON TAS 7250

Attention: Mr Lawson Harding

Dear Mr Harding,

PARTITIONING STUDY OF CHLORATE AND AOX FROM A NOMINATED BRAZILIAN PULP MILL

The Water Research Laboratory (WRL) was engaged by Gunns Ltd to assist in a partitioning study of dissolved contaminants, namely Chlorate and AOX, within treated pulp mill effluent when diluted with seawater. This letter report outlines the study methodology and results from the laboratory analysis.

1. OBJECTIVE

The objective of this study was to examine the fate of key dissolved contaminants upon initial mixing with seawater. Specifically, a partitioning study was undertaken to seek evidence of additional attenuation (beyond physical dilution) in the dissolved concentration of chlorate and AOX in pulp mill effluent after mixing with seawater.

Information derived from this study can be utilised for interpretation of hydrodynamic modelling outputs that are to be provided by others.

2. BACKGROUND AND METHODS

The methodology of the study was developed in conjunction with NMI Laboratories, Dr Graeme Batley of CSIRO, WRL staff and Gunns Ltd. Sampling containers and QA procedures (i.e. field blanks and spikes) were organised and agreed to by all relevant parties prior to undertaking the onsite sampling. Chlorate samples were analysed at the National Measurement Institute (NMI) using Method NR52 - low concentration in marine waters. AOX tests were undertaken by Levay and Co. Environmental Services, as subcontractors to NMI, using the Standard Method SCAN-W 9:89.

The samples were obtained from a nominated Brazilian pulp mill. The sampling location at the plant was agreed to by Dr William Glamore of WRL and Mr Lawson Harding of Gunns Ltd. This site is the same location used for local compliance monitoring of the Brazilian mill's effluent. AOX samples were unfiltered, whereas chlorate samples were filtered upon sampling with a 20 micron filter. No preservatives or additives were added to the samples collected for the partitioning study.

Samples were obtained on November 17th 2009 and delivered to NMI within the desired holding period (<48 hours). The samples were obtained and transported by Mr Lawson Harding of Gunns Ltd as per the previously agreed sampling procedure. While there were some issues with transferring the travel spikes (see below), all of the samples were collected as per the sampling protocols.

Three discrete samples were collected for chlorate and AOX testing. Each of the raw samples were analysed. Raw samples were then mixed by NMI with Sydney seawater to create 2 additional diluted samples. For the chlorate analysis, the two diluted samples consisted of a 1:10 raw sample:seawater dilution and a spiked sample diluted 1:30 (raw sample:seawater). For the AOX analysis, the dilutions were 1:15 and 1:30 raw sample:seawater. Table 1 summarises the testing program.

Table 1
Testing Program

Sample Date	Sample Analysis	Lab Preparation/sample taken (for Chlorate and AOX)
Nov 17 2009	Chlorate	No dilution (raw sample)
	Chlorate	1 Part Effluent:10 Parts Seawater
	Chlorate	1 Part Effluent: 30 Parts Seawater*
Nov 17 2009	AOX	No dilution (raw sample)
	AOX	1 Part Effluent:15 Parts Seawater
	AOX	1 Part Effluent: 30 Parts Seawater

*Note samples were spiked with 250 ppb chlorate prior to dilution.

3. RESULTS

3.1 Chlorate Analysis

Chlorate QA/QC results are provided in Table 2. These results indicate that the QA/QC samples may have undergone some level of attenuation after sampling. However, discussions with NMI and Gunns Ltd have indicated that these results are likely products of the sampling/analysis techniques.

The poor result with Travel Spike 1 (22% recovery) is likely due to an inability to safely transfer the prearranged chlorate from the ampoule into the sample bottles. Without the use of a pipette, insufficient sample volume could be removed from the ampoule. To correct this problem for Travel Spike 2, the entire ampoule of chlorate was submerged within the sample container. Unfortunately, this sample was not tested until 18th January 2010 (more than 2 months after sampling) and hence, some sample may have decayed. Despite the extended period between sampling and analysis, Travel Spike 2 is a better indicator of chlorate attenuation (68% recovery) as the volume of chlorate spike solution was added with more certainty to the field QA/QC sample.

Table 2
Chlorate QA/QC Results

QA/QC Check	Result (ug/L)	Expected (ug/L)
Travel Spike 1	2.2	10
Travel Spike 2	6.8	10
Blanks	<2	<2

Chlorate analysis results are given in Table 3. Analysis of the raw samples ranged from 47 – 76 μg/L. For the 1:10 dilution, the recovery rates were 100% and 81% for Samples 1 and 2, respectively, but decreased to 54% for Sample 3. For the 1:30 dilution, recovery rates for all samples ranged from 85% - 90%. No apparent trend in recovery rates was evident from the samples analysed.

Table 3
Chlorate Results

Sample	Sample Preparation	Result (ug/L)	Expected (ug/L)	% Recovery
1	Raw	47		
1	1 part sample, 10 parts seawater	4.3	4.3	100
1	1 part sample, 30 parts seawater*	8.6	9.6	90
2	Raw	58		
2	1 part sample, 10 parts seawater	4.3	5.3	81
2	1 part sample, 30 parts seawater*	8.4	9.93	85
3	Raw	76		
3	1 part sample, 10 parts seawater	3.7	6.9	54
3	1 part sample, 30 parts seawater*	8.9	10.5	85

*Note samples were spiked with 250 ppb Chlorate prior to dilution

3.2 AOX Analysis

AOX QA/QC results are provided in Table 4. The results indicate a good recovery of the spiked blank and excellent results for the replicates and blanks.

Table 4
AOX QA/QC Results

QA/QC Check	Achieved Rate	Expected (ug/L)
Spiked Blank Recovery	96%	n/a
Replicate 1	99%	n/a
Replicate 2	97%	n/a
Replicate 3	99%	n/a
Blank	<2	<2

AOX test results are provided in Table 5. Raw samples results ranged from 2245 μg/L – 2320 μg/L. Recovery rates for both dilutions ranged between 98% -100%, indicating no change in solubility with increased ionic strength.

4. SUMMARY

A partitioning study was undertaken to examine the fate of dissolved chlorate and AOX concentrations in pulp mill effluent upon initial mixing with seawater. Prior to sample collection, a Brazilian pulp mill was selected and various sampling and quality assurance/control protocols were agreed to. The sampling was undertaken on November 17th 2009 and samples were received by NMI (Australia) within the allocated holding time.

Table 5
AOX Results

Sample	Sample Preparation	Result (ug/L)	Expected (ug/L)	% Recovery*
1	Raw	2245		
1	1 part sample, 15 parts seawater	147	144	98%
1	1 part sample, 30 parts seawater	76	76	100%
2	Raw	2280		
2	1 part sample, 15 parts seawater	148	146	99%
2	1 part sample, 30 parts seawater	78	77	99%
3	Raw	2320		
3	1 part sample, 15 parts seawater	152	149	98%
3	1 part sample, 30 parts seawater	80	79	99%

*Note pristine seawater samples (from Curl Curl in Sydney) had background AOX concentration of 3.8-4.0 ug/L. A concentration of 4.0 ug/L was assumed for all dilution calculations.

Chlorate sample analysis results are given in Tables 3. Issues concerning sampling and delayed analysis affected the chlorate QA/QC results. In comparison to raw sample concentrations, recovery rates for all seawater dilutions ranged from 54% - 100% with the majority of samples indicating between 80% – 90% recovery. Though no trends are apparent in the results, the data suggests that limited chlorate partitioning may occur when the ionic strength of the solution is increased.

AOX sample analysis results are given in Tables 5. QA/QC results indicated a good recovery of the travel spike and repeatability. Raw sample results varied within 3% and recovery rates were between 98 – 100%. Based on these findings, no attenuation in the dissolved concentration of AOX was apparent after mixing with seawater.

Please contact Dr William Glamore at (02) 8071 9868 or w.glamore@wrl.unsw.edu.au if you have any further questions on the above results.

Yours sincerely,

Brett M Miller
Manager