

October 13, 2011

Dear Neil,

This letter is a follow-up to our discussion about why I believe that 2,3,7,8-TCDD in Georgia-Pacific Palatka effluent could be discharged at levels that exceed the water quality criterion of 0.014 part per quadrillion (picogram /L or 10^{-12} g dioxin per liter of water) . My reasoning is based on the reports from the 2009 USEPA High Volume Sampling study and from the 2009 Georgia-Pacific Legacy Solids study.

It is important to understand the unique problems associated with analytical limitations and regulation of dioxins .The USEPA acknowledges that Method 1613 (the approved method) for measuring dioxins and furans is not sensitive enough to detect concentrations as low as the 2,3,7,8-TCDD water quality criterion. The detection limit is 10 pg/L while the criterion is 0.014 pg/L. This means that the criterion is 1000 times lower than the lowest concentration that can be detected using the approved method. Thus, an entity can discharge up to 1000 times more dioxin than is permissible without detection and consequence if only Method 1613 is used. However, USEPA also has indicated that it “will continue to explore new measurement techniques to develop methods that yield [minimum detectable limits] that will allow determination of 2,3,7,8-TCDD at the ambient criteria level” (Federal Register: September 15, 1997 (Volume 62, Number 178). It is my assumption that the HVS method (implemented by the EPA Region 4 Science and Ecosystem Support Division) was utilized in order to overcome the analytical limitations of Method 1613 since the HVS method has an adequate detection limit of 0.002 pg/L.

Data from the HVS study clearly and unequivocally show that the effluent contains dioxins at levels that exceed water quality criterion for 2,3,7,8-TCDD by a factor of four to five. The researchers’ quality assurance methods showed that there was no contamination that could have caused erroneously high levels to be reported. The nondetect values found in the Orange Creek reference site confirms this. In fact, there are reasons to believe that this study underreports the concentrations. First, an error during part of the collection of the duplicate effluent sample may have limited the amount of particulates that were collected and therefore the level of solids-phase dioxins determined; the data values for the two G-P particulates samples supports this assumption. Second, the quality control resin retention data indicate that retention of dioxins on and recovery from the XAD-8 resin (used to capture dissolved phase compounds) may have been very low. As noted by the EPA authors, this would cause a low bias in the values reported. Replication of the study would certainly improve the data quality, as with any other analytical technique, and is particularly appropriate because of the sampling error mentioned above.

Data from the Legacy Solids study conducted by Georgia-Pacific also clearly indicate a very high potential for the discharge of 2,3,7,8-TCDD at concentrations that exceed the water quality criterion. Using G-P’s debatable assumption that all dioxins are present in solid phase, the data in the Legacy Solids report indicates that the average concentration of TCDD in all of the solids in all of the ponds is 39 ng/kg (nanograms of dioxin per kilogram of solids), omitting an unusually high outlier in Pond 3. Using the latter average TCDD value as well as total suspended solids (TSS) for January 2009-September 2009 provided by Brown and Caldwell’s Technical Memorandum #3 (6.7 mg solids/L daily average; daily

maximum = 23 mg/L), we can estimate the level of dioxins discharged in the form of solids:

$$\frac{39 \text{ ng TCDD}}{\text{kg solids}} \times \frac{6.7 \text{ mg solids}}{\text{L water}} \times \frac{10^{-6} \text{ kg}}{\text{mg}} \times \frac{10^3 \text{ pg}}{\text{ng}} = \frac{0.26 \text{ pg TCDD}}{\text{L water}}$$

The calculated concentration of TCDD in the effluent is 0.26 pg/L which is nearly 20 times the water quality criterion. During maximum daily TSS discharges, 0.9 pg TCDD/L would be discharged which is more than 60 times the water quality criterion. It should be noted that this data analysis assumes that suspended solids are similar to the solids that were collected near the bottom of the ponds during the legacy solids study. I believe this acceptable because there is a high degree of mixing during aeration, the solids are very flocculent, a high number of the samples were largely aqueous, and there was little difference in concentrations between interface and core samples (which refers to different depths at which samples were collected).

Though we did not discuss them in great detail, please recall there are at least two other issues that I believe may lead to an inaccurate assessment of risk and fate of dioxins in the ponds. First, the exclusive focus on particulate phase dioxins in various reports may be erroneous because there is evidence from the HVS study, the legacy solids study results, and other pulp and paper researchers (e.g. Amendola et al. 1989) that aqueous phase dioxins exist. Second, while only 2,3,7,8-TCDD is restricted in the permit, other types of dioxins also contribute to total dioxin toxicity, particularly 2,3,7,8-TCDF which historically has been high in pulp and paper mill effluents. The legacy solids data indicate that while 2,3,7,8-TCDD is responsible for almost 60% of the total dioxin toxicity, 2,3,7,8-TCDF is responsible for about 30%.

In summary, using methods acceptable by G-P it is physically impossible to determine if their effluent exceeds water quality criterion for 2,3,7,8-TCDD unless the effluent concentrations are more than 1000 times higher than the criterion. Data from two different methods indicate that there is a high probability that 2,3,7,8-TCDD is being discharged at levels that exceed the criterion. Finally, exclusive focus on particulates and TCDD tends to minimize the potential risk from dioxins.

I am happy to discuss these issues with you or anyone else who wishes to do so.

Best Regards,

Lucy

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