A Critique of the Mill Waste Characterization in Paprican Miscellaneous Report MR 324

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Paul MacGillivray for
Reach for Unbleached!
Box 39, Whaletown BC
V0P 1Z0

NOTE: The points made in this critique apply with even greater relevance to the individual mill waste characterizations which accompany various permit applications in the province of BC.

In Paprican Miscellaneous Report MR 324 - Characterization of Pulp & Paper Mill Solid Residues: a Review, (B. J. O’Connor, February 1996) the author sets out to review literature pertaining to the industry’s solid waste, focusing on characterization of the wastes, comparisons to municipal and sewage sludges, and comments on the variability of the available data. This is done to “facilitate the selection of the most appropriate uses for the solid residues.”

The use being considered here is land application of the solids. The mill wastes contain nutrients which could be used as fertilizer, but are also laced with contaminants. (The review confines itself only to Dioxins and Heavy Metals.) The reasoning is that if a typical mill waste can be defined, and contaminant levels are no worse than the guidelines used for municipal sludges, then the case for land application is made stronger. In this evaluation of the review, we take exception to some of the author’s methodology, comparisons and conclusions, based on the data provided.

The author states that “the properties of the residues vary considerably between pulp and paper processes”. It is this variability which should be of concern in both
characterization and uses of these wastes. From the data shown in the Appendices, variability is the predominant characteristic of the residues.

It is useful to examine the data and references in the Appendices before any conclusions or graphs are drawn, or averages (means) calculated. It is the author’s use of graphs and means that are the most problematic aspects of data interpretation in this review since they give the impression of a legitimacy which is not reflected in the data from which they are supposedly derived.

Looking at Appendix 1 for Heavy Metals, it is clear that the number of sludges and ashes sampled is low in relation to the range they exhibit. Typically, \( n = \) about four or five samples - from a low of one to a high of ten. The ranges are often over several orders of magnitude.

This raises the question of the legitimacy of the calculated mean. When attempting to characterize a material known to have widely varying characteristics, it is not enough to merely calculate a mean and assume that it is representative of the whole. Just one data point can have a profound effect on the average. If the data points range widely, as they often do in this review, it would not be correct to give much weight to the calculated mean generated by such low numbers of samples.

The range data here would indicate that the calculated means are a mathematical construct rather than a reasonable approximation of a typical waste. The known variability of mill waste composition, which is reflected in the range data, plus the low number of samples would indicate that there is not enough information here to reach an intelligent conclusion about what constitutes a typical waste.

Despite these warning signs, the author calculates the means, then compounds the problem by bar-graphing the results for comparison with various guidelines.
Unfortunately, we are not supplied with the individual sample concentration data, which would have been useful in evaluating the adequacy of the mean calculation, but we can still draw some conclusions from the range and sample number data. It can be seen in one case that at least one out of five samples had Cadmium results close to or over the limit the author uses as a benchmark. Another case has one out of six ash samples over the limit, with lesser but significant ranges for the other sample groups. Graphing the mean of these groups tends to obscure this information. If the author concludes from the bar-graphs that most samples were of low concentration, he should also conclude that a significant number were not.

Calculating the average “smooths out” the differences between a relatively small number of samples, and tends to lose information by obscuring variability. Small sample groups contain less information than large ones, so every effort should be made to maximize the information available. The conclusion this should lead to is that for both sludges and ashes we should be cautious about relying on few and infrequent analyses to characterize these solid wastes.

When the data for Dioxins is examined, we find that the bar-graph has been generated by only six sludge and three ash samples. While the results are not averaged this time, the variability of the few samples is again the most obvious characteristic of the data set.

The limited data presented show that one out of six sludges (17%) and one out of three ashes (33%) are very close to his benchmark limit1. Again, the variability shown by this limited sampling indicates that highly contaminated solids occur frequently enough to be of serious concern and that more sampling would be required to realistically estimate loadings or the risk entailed in land application. The review deals with this by noting that

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1 It should be noted that the author switches Guidelines from Quebec’s to Ontario’s at this point, which is neither consistent nor helpful. It should also be noted that the high samples (C-2 and F) are considerably higher than the EPA Guidelines in the same table.
"it is difficult to generalize as to whether the dioxin content of all pulp & paper sludge and ash is acceptable for land application."

Nonetheless, he does, saying that "the concentrations of dioxins in most samples were extremely low" and that "dioxin contamination should not be of great concern". It must be remembered that merely "diluting" a highly contaminated waste with a larger amount of lesser-contaminated material just avoids the problem instead of reducing overall contaminant loadings. While dilution may serve to decrease bulk concentrations of solids below some regulatory benchmark, the total environmental loadings (the most important aspect of persistent and bioaccumulative contaminants) still increase.

Several points made in the section on Dioxins should be addressed:

One is that data used in this review come from "current unpublished data" which makes verification of the quality of the data more difficult.

Further, the author has left out older literature reports which would "not reflect accurately on the current situation concerning the concentration of dioxin in sludge." We note this without comment.

Much is made of "the fact that industry has taken steps to vastly decrease its discharge of dioxins" and "expected improvement as a result of changes in pulp bleaching technology". It must be pointed out that this is conjecture and not proof and really has no place in a risk assessment.

The regulatory benchmark the author wishes to use for comparison is worthy of discussion here - the comparison of mill wastes to land application guidelines for municipal and sewage sludges. There is some question as to the fairness of this comparison, since sewage and municipal sludges are complex and usually highly contaminated by the wide variety of materials the population as a whole chooses to throw away. There is no control of the sludge composition as there is in an industrial process where conditions can be changed to minimize pollution. It must be pointed out that municipal and sewage guidelines are often forced higher than the authorities are
comfortable with by the practical considerations of dealing with large quantities of complex and highly contaminated waste

It is the author’s last point on variability which should receive more prominence, as it becomes the controlling factor from which all other decisions should come, including interpretation of analytical results. Most importantly, it affects our ability to realistically characterize the residues and has a profound effect on our ability to judge the risks involved in land application.

Only three papers are cited as research on the variability of the residues chemical composition, focusing on nutrients and some metals. There are no references to dioxin levels or other persistent organochlorines. This information “appears to be lacking in the general literature”.

However, the scant information on variability is instructive. Confining itself to nutrients and metals, these studies show changes over time of 10-20 fold, 3-70 fold and “up to 50-fold.”

It has been shown earlier that a significant number of the samples were close to or over the limits for even the relatively forgiving comparisons to municipal and sewage sludges. Factoring in these variabilities would predict a high probability that a significant number of residues would be highly contaminated.

It is not surprising to find great variability in the wastes of a mill when all of the variables which change, daily and hourly, in the mill operation are considered. It is to be expected that characterization of the waste streams of a complex operation will not be simple. Experience has shown that conclusions reached on the basis of inappropriate use of the average may be not only inaccurate, but wildly inaccurate. It is therefore important not to apply simplistic techniques of data reduction to this task.
It is also important to understand when there is not enough information to reach an intelligent conclusion regarding environmental samples. That perspective seems to be lacking in this review. While circumstances sometimes force decisions based on questionable data, that is not the case here. The characterization data necessary to resolve the questions can be obtained through more sampling, analysis, and research. In this we concur with the author.

*What kinds of analysis do we need for solid wastes?*

It may be that a dual approach is best. On one hand, a proper search of the available analytical data which does exist would reveal which compounds we already know exist, or are likely to exist, in the effluents. On the other word, priority pollutants, or chemicals of concern, should be defined and applied to whatever we find when we search the lit.

First, some things we know we should be looking for are:

- PCDD’s & PCDF’s
- Chlorinated Hydrocarbons
- Chlorobenzenes
- Resin acids
- PAH’s (Naphthalene-like chemicals)
- Chlorinated Phenols, catechols & Guiacols
- Pthalates
- Alkylphenols and other hormone mimics
- Heavy metals

This is by no means a complete list, and would be added to as additional information comes to light, hopefully from a greater effort in comprehensive testing of the waste streams to monitor the waste’s composition. This detailed characterization will not only aid in adjusting mill operating procedures, but will also be a first step in evaluation of synergistic effects.
Further to the testing parameters, the frequency of sampling needs to be increased, until the issue of variability is settled, either by testing of each batch to be land-spread, or by eventual predictability of results due to correlation with operating conditions at the mill in question.