Dear Brian,

As per your recent request, enclosed are some comments regarding the November 25th memo from "Reach for the Unbleached" which deals with the chemical characterization of pulp and paper mill sludge. In her memo, Delores Brotten requests that a number of different compounds, that might be present in primary and secondary sludge, be routinely analyzed as part of a mill's characterization program. While we agree with some of her choices, we also feel that a number of compounds are either present only in trace amounts or should not be of concern.

Compounds that Warrant Characterization

Dioxins and Furans

With the industry's move towards increased chlorine dioxide substitution, most biosolid samples contain low levels of these contaminants which are present well below the guidelines recommended by a number of different authorities. While there have been concerns about the environmental implications of trace concentrations of TCDD and TCDF in slurges, studies of wildlife exposed to land-applied slurges from mills using chlorine bleaching, however, have shown no adverse effects [1-6]. In spite of this information, we believe that the concerns over dioxins and furans in biosolids warrant their characterization in order to continue to demonstrate that our biosolids do not pose a threat from these particular components.
Heavy Metals

Heavy metal concentrations are of concern for land application programs due to their potential toxicity to plants, as well as to animals and humans, if present in excessive amounts. Most municipalities in Canada and the United States have guidelines respecting the permissible levels of heavy metals that are acceptable for land spreading programs and hence require that sludge samples be routinely monitored for these contaminants. To date, the available data suggests that biosolids from pulp and paper mills contain levels of heavy metals that are well below the acceptable guidelines.

Alkylphenols and Alkylphenol Ethoxylates

Nonylphenol ethoxylates (a family of alkylphenol ethoxylates) are currently being assessed under the Canadian Environmental Protection Act (CEPA) to determine whether they should be considered as “toxic” within the meaning of the act. Currently, there are a number of different positions over the risks posed by exposure to alkylphenol ethoxylates and alkylphenols. Some groups state that these compounds are hormone disrupting chemicals while others feel that there is no firm scientific evidence to suggest that alkylphenol ethoxylates or their breakdown products are contributors to reproductive problems.

We are currently working with Dr. Bill Lee of the National Water Research Institute, to survey the industry to determine the levels of nonylphenol ethoxylates (NPE) and nonylphenol that are present in pulp and paper mill effluents and biosolid samples. To date, Dr. Lee has mentioned that the levels of NPE found in pulp and paper mill effluents were much lower than what has been found in municipal treatment plant effluents. While there is limited data available on the levels of nonylphenol in sludges, Dr. Lee has measured levels of 137 and 470 µg/g in sewage treatment plant sludges from a municipality in Toronto (7). The levels found in 6 Canadian pulp mill biosolid samples were approximately 20 times lower than the municipal sludge samples. This work is continuing and Dr. Lee expects to have a report prepared in the spring of 98. Until the report is issued it would probably be a good idea to continue to characterize pulp mill biosolid samples for these parameters in order to broaden the available database.

Compounds that we Feel Should not be Characterized

Chlorolignin Compounds

In the past years, the utilization of modified pulp bleaching technologies involving high levels of chlorine dioxide substitution have been beneficial in drastically reducing the amounts of Adsorbable
Organic Halogen (AOX) in pulp mill effluents. AOX is a good estimate of the chlorinated lignin content of the effluent. Research has shown that the chlorolignin from these bleaching processes does not contain a high level of chlorination and that it does not degrade to become chlorocatechols, chloroguaiacols or chloroveratrole over time (8). Studies have also shown that chlorolignin compounds formed during bleaching are rapidly immobilized in soil and are slowly mineralized to inorganic chloride (1,9,10). Given this information we would not consider it necessary to characterize the chlorolignin content of pulp mill biosolids.

**Chlorinated Phenols, Catechols and Guaiacols**

As mentioned above the industry's increased use of chlorine dioxide substitution has also been beneficial in reducing the amounts of chlorinated phenolic compounds present in pulp and paper mill effluents. The increased use of chlorine dioxide has resulted in a virtual elimination of the more highly substituted chlorinated phenolics (i.e., those with greater than 2 chlorine atoms). At >70% chlorine dioxide substitution, the chlorinated phenolics that are present in the effluent are basically mono- and di-chlorinated phenolic compounds which are much less toxic than their highly chlorinated counterparts and are more easily degradable. Studies have shown that low molecular weight chlorinated degradation products appear to rapidly decompose in soil, and do not accumulate, leach or create a toxic environment for soil bacteria (1,9,10). Therefore we would not consider chlorinated phenolics to be of concern in pulp mill biosolids.

**Resin and Fatty Acids, Sterols, Terpenes and Vanillins**

All of these compounds are naturally occurring components that are present in the extractives of trees. They are easily degraded in the secondary treatment facilities of pulp and paper mills and are not expected to be present in significant quantities in the biosolids from these mills. In the forests, these compounds are released from fallen trees and are degraded in the environment. Given that these compounds are a natural component of the forests there is no indication that their presence in pulp mill biosolids would be detrimental when used for land applications.

**MX**

MX is a component that has been identified in the bleaching effluent from pulp and paper mills. Although it has been shown to have mutagenic activity it is highly unstable and does not survive the treatment system at the mills. MX is not expected to be present in the final mill effluent or in the pulp mill biosolids.
Chlorinated-Acids, Acetones, Benzenes, Terpenes, Thiophenes and Halogenated Alkanes

I am not aware of these components being present in pulp mill biosolid samples. If they are present their concentrations would be expected to be very low. The reason for this is that chlorine dioxide tends to oxidize organic material instead of adding chlorine atoms to the compound. Also the secondary-treatment system would likely degrade any of these compounds to very low levels. In the memo it is mentioned that "benzene is known to the State of California to cause cancer". To my knowledge it is impossible for chlorobenzenes to be degraded to benzene under the conditions that are present in the treatment system or in the environment.

Phthalate Esters

Phthalate esters are not a by-product of the pulping process. These esters are ubiquitous in nature and since they tend to be found in a variety of different places we would not suggest that they be routinely characterized in pulp mill biosolid samples.

Chlorate (ClO₃⁻)

Chlorate is formed during the bleaching process and can be present in the effluent after secondary treatment. Chlorate, however, is very water soluble and should therefore remain in the effluent. If some of the chlorate was transferred to the biosolids, we would expect that it would be converted to chloride, which occurs quickly under anaerobic conditions.

References
