THE INFLUENCE OF MINOR COMPONENTS ON THE DIOXIN CONTENT OF UNITED STATES DAIRY FEEDS

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Introduction

The United States Environmental Protection Agency (USEPA) has completed a survey of dioxin-like compounds in dairy feeds from ten dairy research facilities around the US, sampling the overall feed mixtures, and the major and minor components of dairy feeds. The design of the survey, the analytical methods used, and resulting dioxin concentrations of the total feed mixtures and the major components of the feed were reported on earlier in Dioxin 2004[1]. Low levels of dioxin were found in all feed mixtures, with an average concentration of 0.05 pg/g toxic equivalent dry weight (ppt TEQ dwt), with all samples less than 0.1 ppt TEQ dwt. This included the 17 dioxin and furan (CDD/F) congeners and the 12 dioxin-like polychlorinated biphenyls (PCBs). Another key finding concerned the role of "leafy" major components of the feed, such as the hays and silages of the dairy feed, versus the "non-leafy" major components, such as the corn grain and other protected or bulky vegetations of the feed. The TEQ concentrations of all major feed components ranged from 0.02 to 0.15 ppt TEQ, with the highest concentrations being the leafy vegetation of alfalfa and grass, and the lowest being the cottonseed and pulp products. Generally, the leafy vegetations were, in fact, higher in concentration than the non-leafy vegetations. This finding is consistent with the hypothesis that air-to-leaf transfers of dioxins would lead to higher concentrations in leafy as compared to bulky/protected vegetation. Also, leafy vegetation comprised a greater percentage of the total mass of mixed feed: on average, leafy vegetation made up 66% of total mixed feed. Because they were also higher in concentration compared to bulky vegetation, it was estimated that the leafy vegetation delivered 81% of TEQ to the dairy cows. This earlier paper did not address the concentrations and impacts of the minor components of the feeds, since they had not yet been analyzed. This paper reports on the concentrations of the minor components and the influence they have on overall feed dioxin concentrations.

Materials and Methods

This study entailed the collection of the dairy feed total mixed feed, major feed components (including forages, grains, and concentrates), and minor components (including vitamins, animal fat additives, and others) at ten US government and state university research facilities which raise dairy cattle in a manner similar to commercial dairy operations. The purpose of this study is to determine the relative contribution of various feed components to the total dioxin content of dairy feeds. The facilities were sampled between April, 2002 and January, 2003. EPA traveled to each facility, and over the course of a few days, collected, boxed and shipped the samples to be prepared (dried and ground to a fine powder) at one of the 10 participating facilities. Then, samples were packed tightly in dry ice in coolers and shipped to the EPA laboratory for refrigeration storage until chemical analysis.

Analysis generally followed a modified EPA's Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, with modifications designed to achieve the lowest possible detection limits. Approximately 30 grams of dried and homogenized feed sample were weighted into an extraction thimble and mixed with anhydrous sodium sulfate. All sample types were fortified with a mixture containing each of the 17, ^{13}C labeled 2,3,7,8,-Cl substituted dioxins/furans and the 12, ^{13}C WHO PCBs. The samples were extracted with 75/25 hexane/methylene chloride in a soxhlet for 24 hours. Limits of detection (LOD) for CDD/Fs ranged from 0.01 pg/g

for the lower chlorinated congeners to 0.20 pg/g for OCDD, and LODs for the PCBs ranged from 0.01 pg/g for PCB 169, 0.02 pg/g for the most toxic PCB congener, PCB 126, to 4.5 pg/g for PCB 118.

Dioxin TEQ concentrations were determined using the 1998 WHO toxic equivalency factor scheme, and assuming ND = ½ LOD. Congener profiles were determined by summing the absolute (not TEQ adjusted) concentrations of each of the 17 CDD/F congeners, in this case assuming ND = 0, and then determining the percentage each congener contributed to this sum total.

Results and Discussion

There were a total of 42 minor components measured, with about 4 minor components per feed mixture in each of the 10 research facilities. Minor components averaged 4% of the feed mixture by weight, and included such products as minerals/vitamins, yeast, animal fat additives, limestone, sodium bicarbonate, and molasses. Because they comprised such a small percentage of the overall feed mixtures, even high concentrations of dioxins in the minor components might have little effect on overall feed mixture concentrations. In fact, the TEQ concentrations of most minor components were near or less than 0.10 ppt TEQ dwt, similar to the feed mixtures themselves and the major components of the feed. There were a few components at concentrations higher than 0.5 ppt TEQ dwt, including megalac at 0.7 ppt TEQ dwt, three different vitamin/complex products at 0.7, 0.9 and 5.1 ppt TEQ dwt, and one animal fat additive at 0.6 ppt TEQ dwt.

One minor component was significantly higher than this range. This minor component was called, “Flo-bond”, and it had a concentration of 38.5 ppt TEQ dwt. According to the manufacturer of this product, Flo-bond is a “select, high affinity sorbent Hydrated Sodium Calcium Aluminosilicate (HSCAS) which is used in animal feeds and ingredients. It's use has been proven world wide when molds, caking, and flowability are problems.” (http://www.brookside-agra.com/Flobnd.html). The high TEQ concentration found is reminiscent of ball clay, which had been added to poultry feed in the 1990s as a flowability agent as well. High TEQ concentrations found in poultry samples during a national joint survey between USDA and EPA in the mid-1990s were traced back to the ball clay in the poultry feed. With TEQ concentrations in ball clay well into the hundreds to thousands of parts per trillion, this minor component influenced the dioxin content of the feed and subsequently the quality of the poultry meat[2]. Poultry samples originating from poultry consuming this feed were found to have concentrations near 30 ppt TEQ lipid weight. This compares to the more normal poultry concentrations less than 1 pg/g TEQ lipid weight.

Not only is the TEQ concentration of Flobond unusually high as a minor component, in fact the congener profiles of Flobond and ball clay are similar. Figure 1 shows the congener profiles of ball clay and Flobond, and, for comparison, the profile of corn silage, one of the major components of the dairy feeds of this survey. Common to both Flobond and ball clay are the overwhelming dominance of dioxin congeners and the virtual absence of furan congeners. The PCB congeners in Flobond were also not remarkable; they were not found at elevated levels in ball clay and they were found in Flobond at similar low levels as in other minor and major components of this survey. The highest congener found in Flobound is the hepta dioxin congener, 1234678-HpCDD, while the highest congener typically found in the ball clay was OCDD. The corn silage profile is typical of all the mixed feeds in this survey, as well as the major components of the feed, and is essentially the archtype background profile of dioxins in furans in soil, air, vegetation, and food products of terrestrial origin. Four congeners dominate this archtype background profile: the hepta and octa dioxins, and the hepta and octa furans congeners.

Even at 38.5 pg/g TEQ, the question remains as to whether this would influence the overall quality of the feed. It comprised only 0.1% of the overall feed mixture it came from, so this would suggest the possibility of having little effect on the final feed mixture concentration. The potential effect it could have on the final feed concentration can be ascertained by determining the weighted average concentration of the mixed feed, as a function of the feed components, both with and without flo-bond. Deriving a mixed feed concentration from the major and minor

components is possible in this survey because all components were individually measured, in addition to the mixed feed itself. For the feed mixture containing the flobond, the following components that were individually measured, the percentage they made of the overall feed mixture, and the TEQ concentrations were: 1) corn silage – 51%, 0.02 ppt TEQ, 2) alfalfa hay/silage – 21%; 0.08 ppt TEQ, 3) high moisture corn – 15%, 0.09 ppt TEQ, 4) soybean meal – 8%; 0.02 ppt TEQ, 5) grass hay – 3%; 0.06 ppt TEQ; 6) minerals/vitamins – 0.6%; 0.02 ppt TEQ; 7) limestone – 0.6%; 0.02 ppt TEQ; 8) sodium bicarbonate – 0.6%; 0.02 ppt TEQ, 9) dicalcium phosphate – 0.1%; 0.12 ppt TEQ; and 10) flo-bond – 0.1%; 38.5 ppt TEQ. A simple weighted average calculation results in a total mixed feed concentration of 0.083 ppt TEQ. If you calculate the total mixed feed concentration without the flo-bond, it would be 0.044 ppt TEQ. Actually, this weighted average concentration is close to the actual measurement of the mixed feed itself, which was 0.05 ppt TEQ. This discrepancy between the total mixed feed measured 0.05 ppt TEQ and the weighted average mixed feed concentration of 0.083 ppt TEQ could be a simple matter of variability in content of the mixed feed - the inhomogenous mixture that was measured may not have had the flo-bond in it, since it was a minor component estimated to be mixed in at the low amount of 0.1%. In any case, this calculation suggests that the flobond could as much as double the average concentration of the mixed feed.

In summary, the analysis of minor components in this dairy feed survey suggest that mostly they are at low concentrations of 0.10 ppt TEQ and less, and that they do not influence the final feed concentrations. However, in one instance a minor component measured 38.5 ppt TEQ and could effectively have doubled the concentration of the feed into which it was mixed, despite comprising less than 1% of the feed mass. Together with past evidence of ball clay, this suggests that, in certain circumstances, the minor components of animal feeds could be as important if not more important than major components in delivering dioxins to food animals.

Disclaimer

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References

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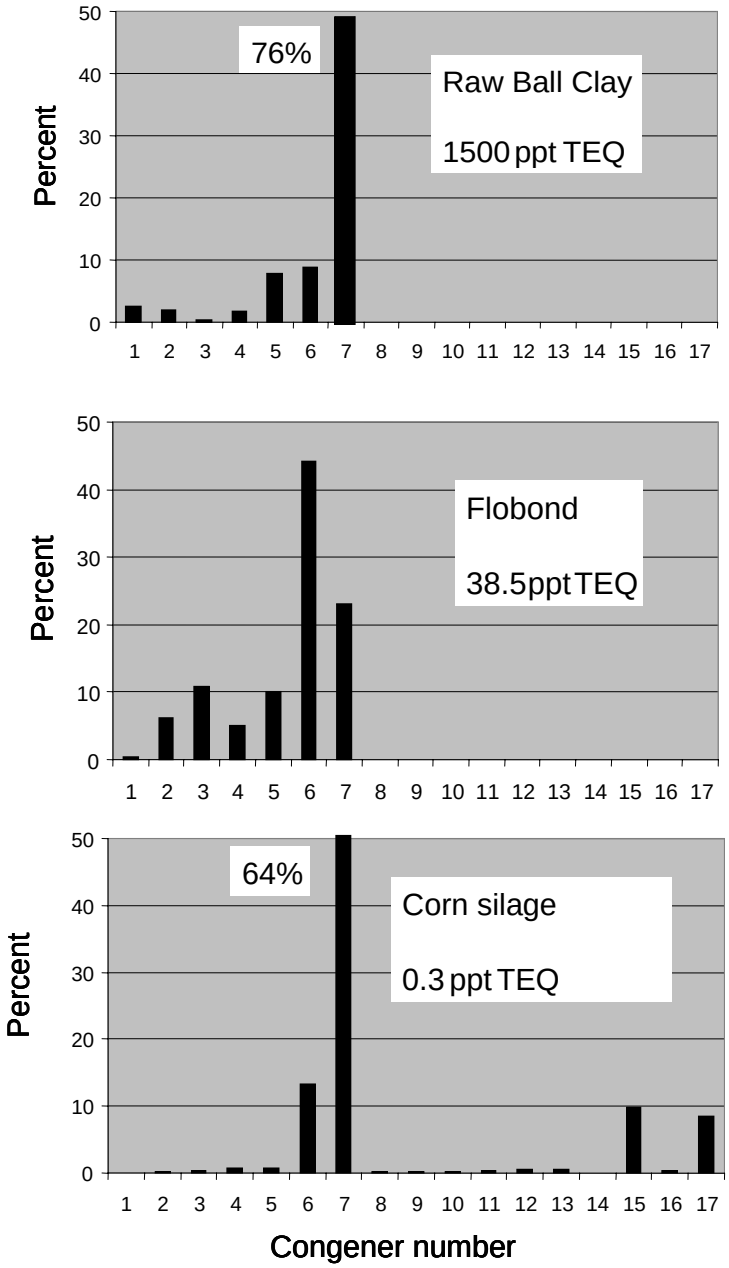

Key

1	2,3,7,8-TCDD
2	1,2,3,7,8-PeCDD
3	1,2,3,4,7,8-HxCDD
4	1,2,3,6,7,8-HxCDD
5	1,2,3,7,8,9-HxCDD
6	1,2,3,4,6,7,8-HpCDD
7	OCDD
8	2,3,7,8-TCDF
9	1,2,3,7,8-PeCDF
10	2,3,4,7,8-PeCDF
11	1,2,3,4,7,8-HxCDF
12	1,2,3,6,7,8-HxCDF
13	2,3,4,6,7,8-HxCDF
14	1,2,3,7,8,9-HxCDF
15	1,2,3,4,6,7,8-HpCDF
16	1,2,3,4,7,8,9-HpCDF
17	OCDF

Figure 1. Comparison of the dioxin and furan congener profile of raw ball clay to the "Flobond" minor component and the Michigan corn silage profiles.