

NATURAL FORMATION - A NEGLECTED SOURCE OF POLYCHLORINATED DIOXINS AND DIBENZOFURANS

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INTRODUCTION

Polychlorinated dioxins (PCDDs) and dibenzofurans (PCDFs) enter the environment primarily as a result of anthropogenic activity. These compounds occur as by-products of chemical manufacturing and as a result of combustion processes of municipal, hazardous and medical waste. PCDDs and PCDFs also can be formed by natural formation processes. Although less focus has been given to the natural formation of these compounds, such a formation has been proven and this abstract summarizes much of that work.

In 1984, Lamparski et al. (1) reported that they had analyzed a sealed sample of dried municipal sewage sludge from 1933. They also analyzed two other sludges from 1981 and 1982 and found almost exactly the same pattern for hexa-, hepta- and octa CDDs that they observed in the 1933 sludge. The authors suggested a natural chlorination reaction to be the source, especially because the production of pentachlorophenol (PCP) did not commence until 1938.

In 1989, Svenson et al. (2) reported an enzyme mediated formation of 2,3,7,8-tetra CDD and other dioxins and dibenzofurans from 2,4,5-trichlorophenol, hydrogen peroxide and horseradish peroxidases. Similar results were reported by Öberg et al. (3), which also included other chlorinated phenols and other peroxidases, such as lactoperoxidase.

In 1992, Öberg et al. (4) reported that the addition of $^{13}\text{C}_6$ -PCP to normal sewage sludge increased the amount of $^{13}\text{C}_{12}$ -octa CDD and $^{13}\text{C}_{12}$ -hepta CDD found in the sludge. This study shows that the *dimerization* of chlorinated phenols to dioxins

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takes place under these conditions. We reanalyzed two of these samples and discuss the results here.

In 1994, Sievers *et al.* (5) reported a dramatic increase in the concentrations of chlorophenols during composting. The concentrations of PCP increased 14-fold after two weeks. The lower chlorinated phenols originally could not be measured but were detected after two weeks of composting. Similarly, Öberg *et al.* (6) reported an almost hundred-fold increase of octa CDD after ten months in a grass compost.

From 1994-1999, a very extensive study of PCDDs and PCDFs in the State of Mississippi, USA was conducted. One part of that study found extraordinarily high octa- and heptaCDDs concentrations in sediments from the Leaf - Pascagoula river system, especially where the rivers and tributaries passed through a national forest (7). In other parts of the study, very high octa- and hepta CDDs concentrations were found in man-made and naturally-formed lakes with no known anthropogenic sources in the same region (8,9,10). This study included both top sediment and sediment cores. In another part of this study, Rappe *et al.* (11) reported extraordinarily high dioxin levels in the soybean meal component of catfish feed. It was determined later by others that a ball clay added to the soybean meal was the source of the dioxin and that it also was used in chicken feed. This ball clay is very old, up to thousands or millions of years, and it is unlikely that anthropogenic activity could be the source of PCDDs to the ball clay. The hexa CDDs found in the soybean meal and the ball clay were almost identical to the hexa CDDs found in sediment samples from other parts of this study of the same area.

EXPERIMENTAL

We reanalyzed two of the samples analyzed by Öberg *et al.* (4). The $^{13}\text{C}_6$ -PCP treated sewage sludge samples were collected, treated and clean-up as previously described (4). The reaction time was 2.5 weeks and the final concentration of $^{13}\text{C}_6$ -PCP was 10 μM or 3 ppm. The instrumental analysis in the present study followed the $\text{M}+2^+$ and $\text{M}+4^+$ channels for the $^{13}\text{C}_{12}$ -labelled compounds. No $^{13}\text{C}_{12}$ PCDDs were added in this reaction, only the $^{13}\text{C}_{12}$ -labelled PCDFs. In Table 1 and in Figure 1 we give the results of the study and the chromatograms of the $^{13}\text{C}_{12}$ -channels for the hexa- and hepta CDD from the samples ACT-CP and SED22-CP. Some changes can be seen between the samples, but generally the

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trend is similar. In both samples we observed the lower chlorinated congeners only when $^{13}\text{C}_6$ -PCP had been used. In our earlier study we reported that no $^{13}\text{C}_{12}$ -PCDDs could be found in the control sample (4).

Table 1. Amount of $^{13}\text{C}_{12}$ -hexa-, hepta- and octa CDD (total pg) found in sludge samples fortified with $^{13}\text{C}_6$ -PCP.

| Sample | © Hexa CDDs | © Hepta CDDs | © Octa CDD |
|----------|-------------|--------------|------------|
| ACT-CP | 400 | 4000 | 2200 |
| SED22-CP | 150 | 1700 | 2600 |

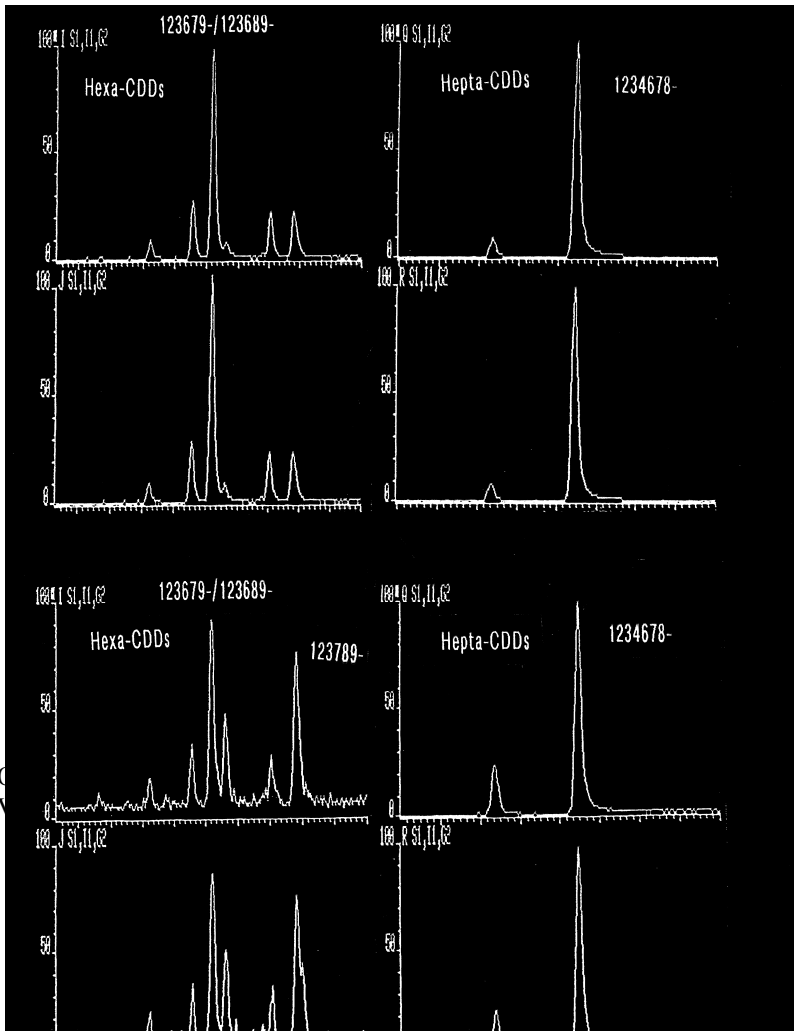
CONCLUSIONS

In this study, we used a reaction time of 2.5 weeks. The degradation of $^{13}\text{C}_6$ -PCP yielded lower chlorinated dioxins but the distribution was different for the different reactions. The formation of $^{13}\text{C}_{12}$ -hepta and $^{13}\text{C}_{12}$ -hexa CDDs from a reaction where $^{13}\text{C}_6$ -PCP was used shows the dimerization reaction leads to the formation of octa CDD and to certain lower chlorinated PCDDs. The penta- and tetra CDDs are below the detection limit and generally the $^{13}\text{C}_{12}$ -labelled compounds are found in decreasing concentrations with the number of chlorine present.

In both samples, 1234678-hepta CDD dominated to 1234679-hepta CDD. The hexa CDDs were dominated by the 123679-/123689-peak, and to a lesser extent 123789-hexa CDD, see Figure 1.

It is difficult to compare this with the ball clay study, where the reaction time could be as long as thousands or millions of years. However, we have proven that the formation and degradation of dioxins can occur from PCP, and further studies of this type of reaction should be conducted.

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ACKNOWLEDGMENT

This study was sponsored by Georgia-Pacific Corporation, Atlanta, USA.

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