PCDDs AND PCDFs IN SEDIMENTS IN A RIVER SYSTEM IN SOUTHERN MISSISSIPPI, USA

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ABSTRACT

We have analyzed 61 sediment samples from southern Mississippi. Most Cl_4-Cl_8 PCDDs and PCDFs were found in all samples. The congener profiles were dominated by octa CDD. The concentration of octa CDD was found to exceed 10 000 pg/g d.w. even in samples from apparently pristine areas. The concentrations of 2,3,7,8-tetra CDD and 2,3,7,8-tetra CDF were not influenced by a pulp mill adjacent to the Leaf River.

INTRODUCTION

The 61 samples were collected from rivers, creeks and other tributaries within the drainage area of the Leaf River, the Chickasawhay River and the Pascagoula River in southern Mississippi, USA. One purpose of this study was to characterize the concentrations, homologue group distribution (profiles) and isomeric patterns of PCDDs and PCDFs.

In 1992, the Mississippi Department of Environmental Quality (DEQ) reported PCDD and PCDF concentrations (dry weight) of sediment samples collected in the Leaf River and Pascagoula River (1). These samples were taken upstream and downstream from a modern pulp mill now using 100% chlorine dioxide substitution for bleaching. All samples showed a dominance of hepta- and octa CDD. Concentrations up to 5 000 pg octa CDD/ g d.w. were reported (1). Using multivariate data analyses (MDA) and hierarchical cluster analyses, no differences in concentrations and profiles could be found for samples taken above and below the pulp mill (2,3).

SAMPLING

We collected the samples with either a Ponar or spoon. The sediments were mixed and proportioned into sampling jars. The sediments were coded, packaged and shipped to the analytical laboratory.

The sampling sites in the Leaf, Chickasawhay and Pascagoula River drainage areas are shown in Figure 1. Samples were taken from Leaf River (N=11), Bowie River (N=4), Weldy Creek (N=1), Tallahala Creek (N=9), Bogue Homa Creek (N=6), Thompson Creek (N=5), Chickasawhay River (N=8), Pascagoula River (N=7), Black Creek (N=7), Big Creek (N=1), and Big Cedar Creek (N=2).

ANALYTICAL

We followed the extraction and clean-up procedures described by Kjeller et al. (4). The final extracts were analyzed by HRGC/HRMS using a polar 60 m Rtx-2330 for all 2,3,7,8-substituted PCDDs and PCDFs and a non-polar DB-5 column for all homologues and the hepta-and octa CDDs and CDFs. The GC columns were interfaced to a VG 70-250S double focusing mass spectrometer operating at a resolution of 8 000 - 10 000. The instrument was operated in a selected ion monitoring (SIM) mode. A blank sample was analyzed for every batch of 4-6 samples.

The dry weight (d.w.) determination was done by heating the sample at 130° C overnight. The loss of ignition (LOI) determination was done by heating the sample at 500° C for 2 hours.

Most sediment data in the literature have been reported on a dry weight basis. Where, however, the compounds of interest, like PCDDs and PCDFs, are highly lipophilic and probably formed on or bound to organic particles, the results can be reported based on the content of organic compounds as determined by the LOI. This was the case for a study of the sediments of Dala River in Sweden (5). Our results here are reported both on a dry weight and LOI basis.

RESULTS

Most PCDDs and PCDFs were detected in all the sediments from southern Mississippi. With limited exceptions, there was minimal variation in congener profiles, isomeric patterns and concentrations among sediments from apparently pristine areas and more populated and potentially polluted areas. In all samples we found a pronounced dominance of octa CDD and the two hepta CDDs, see Figure 2. Our findings are in agreement with the 1992 Mississippi DEQ data (1).

Comparison of the concentrations of octa CDD, based on both dry weight and on LOI, illustrate that, generally, no significant trends in the rivers could be observed. Black Creek is the only river where a significant trend was observed, where the concentrations of octa CDD were much higher at the lower part of the creek after passage through the De Soto National Forest.

The high concentrations of octa CDD found in the samples from Bogue Homa Lake (26 000 pg octa CDD/g d.w.) and Tallahala Creek (13 000 pg octa CDD/g d.w.) were unexpected because these appear to be pristine areas. In the Pascagoula River upstream and immediately downstream from the confluence with Black Creek, the concentrations are 16 000 and 17 000 pg octa CDD/g d.w., respectively.

On a LOI-basis, the highest values were found in the Pascagoula River in the area of Black Creek and throughout the Chickasawhay River and in Tallahala Creek near Laurel (350 000 - 400 000 pg octa CDD/g LOI). Values as low as 20 000 pg octa CDD/g LOI were found in the upper part of Black Creek.

A kraft pulp mill is located on the Leaf River between sampling points 505 and 506. From 1984-1989 this mill used elemental chlorine in its bleaching process. Since 1989, the mill has operated using complete chlorine dioxide substitution. Pulp bleaching with elemental chlorine has been associated with 2,3,7,8-

tetra CDF and 2,3,7,8-tetra CDD (2,3). In Figure 3 we report the results for the 2,3,7,8-tetra CDD and 2,3,7,8-tetra CDF for the sampling points along the Leaf River and Pascagoula River on a LOI basis. The figure shows that the highest concentrations were found in the Pascagoula River below the confluence with the Chickasawhay River. Moreover, the concentrations downstream from the pulp mill were not higher than upstream from the mill. Consequently, the mill is not a point source into the Leaf River. This confirms our prior conclusions from the statistical analyses of the Mississippi DEQ data, the mill's effluent data, and other relevant data (2,3).

The ΣPCDDs/ΣPCDFs (D/F) ratio can be a useful parameter for source identification of PCDDs and PCDFs (7). This ratio has been calculated for all the sediment samples in this study. With the exception of two sites from the Chickasawhay River, six sites from Tallahala Creek and one site from Thompson Creek, the D/F ratio was in the range of 43 - 1200, the majority of which were above 100. This is notable because, with the exception of sewage sludge, no environmentally significant source has been identified with such a dominance of PCDDs (8,9). In the commercial pentachlorophenols this ratio is normally 1 - 14 (10).

In the Chickasawhay River, two of the three most northern sampling points have the D/F-ratio of 26 and 35, and the most northern site in Thompson Creek had the D/F-ratio of 18. This latter site is located inside the De Soto National Forest, and the octa CDF value for this site was 150 pg/g d.w. or 2 800 pg/g LOI, the second highest octa CDF value in the whole study.

The two locations in Tallahala Creek had D/F ratios of 1.4 and 13. The location with the 1.4 ratio was near a junkyard. The pattern of the PCDFs found at these two locations indicates a potential source of PCBs in the junkyard leaking into the creek, possibly from electrical equipment (11).

The isomeric patterns in most of the sediment samples are very similar. These patterns have more similarities with the patterns earlier reported for sewage sludge from the U.S.A., Sweden, Germany and the U.K. (8,9) than the typical incineration patterns as described by Rappe (7).

CONCLUSIONS

Deep-sea sediments are major sinks or reservoirs for PCDDs and PCDFs. The presence of these compounds in river sediments will reflect multiple inputs by local sources, transport via water, and air deposition after long range transport. Analyses of dated sediment cores show that PCDDs and PCDFs are quite stable. Kjeller et al. recently identified PCDDs and PCDFs in a 100 year old sediment core from the Baltic Sea (12). Schramm et al. have analyzed sediment cores from two lakes in the rural Black Forest in Germany (13). In both studies an increase of PCDDs and PCDFs was found in the post 1960 layers. PCDDs and PCDFs adsorbed to sediments retain their original homologue group profiles and isomeric patterns and can be used as markers of various sources of PCDDs and PCDFs in old and new sediments (7, 12).

An illustration of the use of sediment analysis from the Dala River in Sweden was presented at DIOXIN '89 by Kjeller et al. (5). The patterns and concentrations were quite different in the pristine upper parts of the river compared to the more industrialized lower part (5, 14).

Several possible sources can be identified from the sediment samples from southern Mississippi. Increased levels of PCDFs were found in Tallahala Creek, possibly caused by PCBs leaking from a nearby junkyard. For all other samples there was a remarkable dominance of PCDDs over PCDFs and the isomeric patterns

and homologue profiles were almost identical. Octa- and hepta CDDs are dominant in all samples; this pattern has been found in other sediment samples (5, 9), in sewage sludge from the U.S.A., Sweden, Germany and the U.K. (8,9) and in some technical pentachlorophenol formulations (9, 10, 11). Moreover, a *de novo*, enzymatic or photochemical formation of octa CDD from chlorophenols, reactions which have been described by Öberg et al. (15) and Vollmuth et al. (16) and typical household effluents, described by Horstmann and McLachlan (17) and de Wit et al. (18), as well as unknown sources and pathways must be considered.

The octa CDD values from southern Mississippi are 10 times higher than the octa CDD concentrations from the lower part of the Dala River, which runs through an industrialized part of Sweden. If the comparison is made with the pristine upper part of the Dala River, the concentrations of octa CDD in southern Mississippi are up to 1 000 times higher.

On a dry weight basis, the values for octa CDD in the upper part of Bogue Homa Creek are 35-70 times higher than the octa CDD values found in the upper part of Black Creek. On a LOI-basis, this difference was found to be between 7-10 times. In Black Creek, the octa CDD concentrations based on dry weight increased by a factor of 37 after passage through the De Soto National Forest. On a LOI-basis this increase was 11 times. In the De Soto National Forest, no specific source(s) could be expected for octa- and hepta CDDs or octa CDF. Earlier spraying of 2,4,5-T and 2,4-D in this area cannot be associated with octa-and hepta CDDs or octa CDF (11).

Further investigations are planned to identify the specific source or sources causing the unexpected situation in this part of the US, where unusually high concentrations of the higher chlorinated PCDDs were found in relatively pristine areas.

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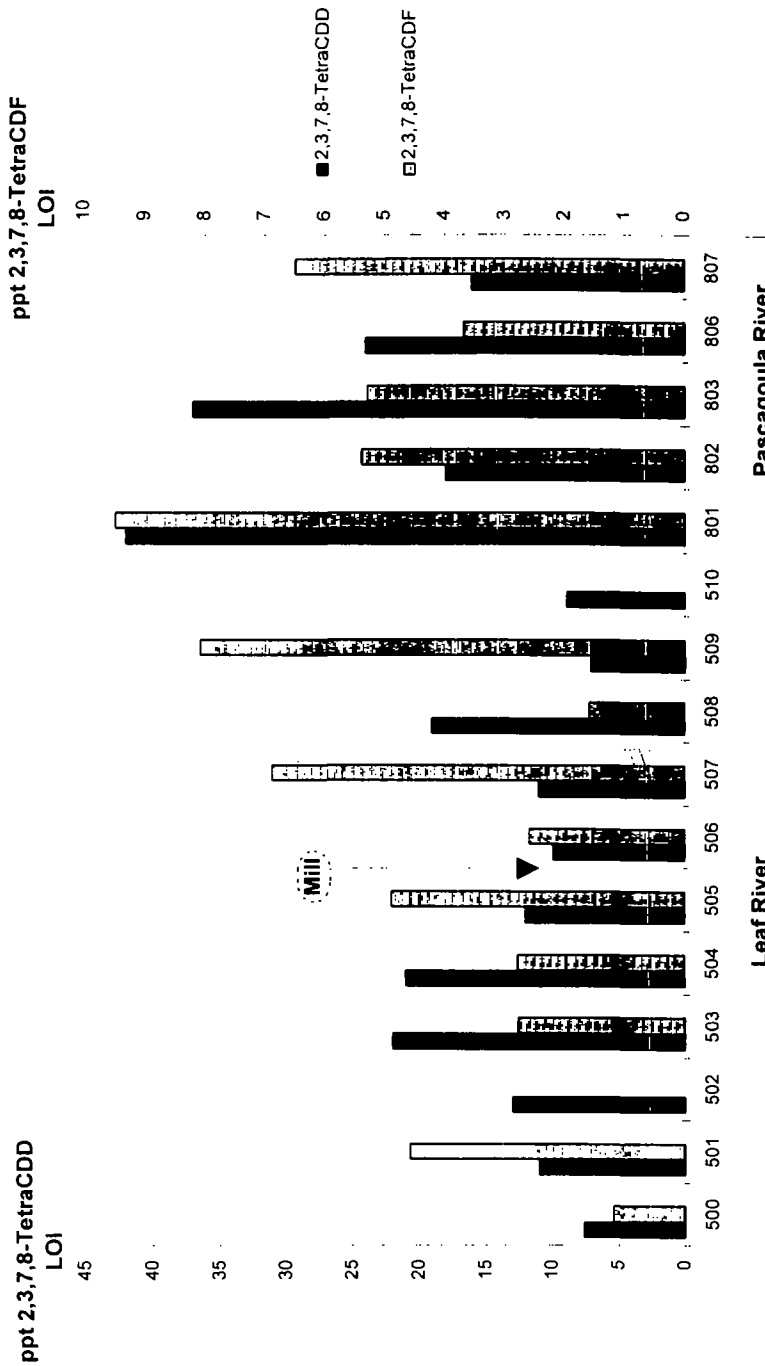

Figure 3: Concentrations of 2,3,7,8-tetraCDD and 2,3,7,8-tetraCDF in Leaf River and Pascagoula River sediment

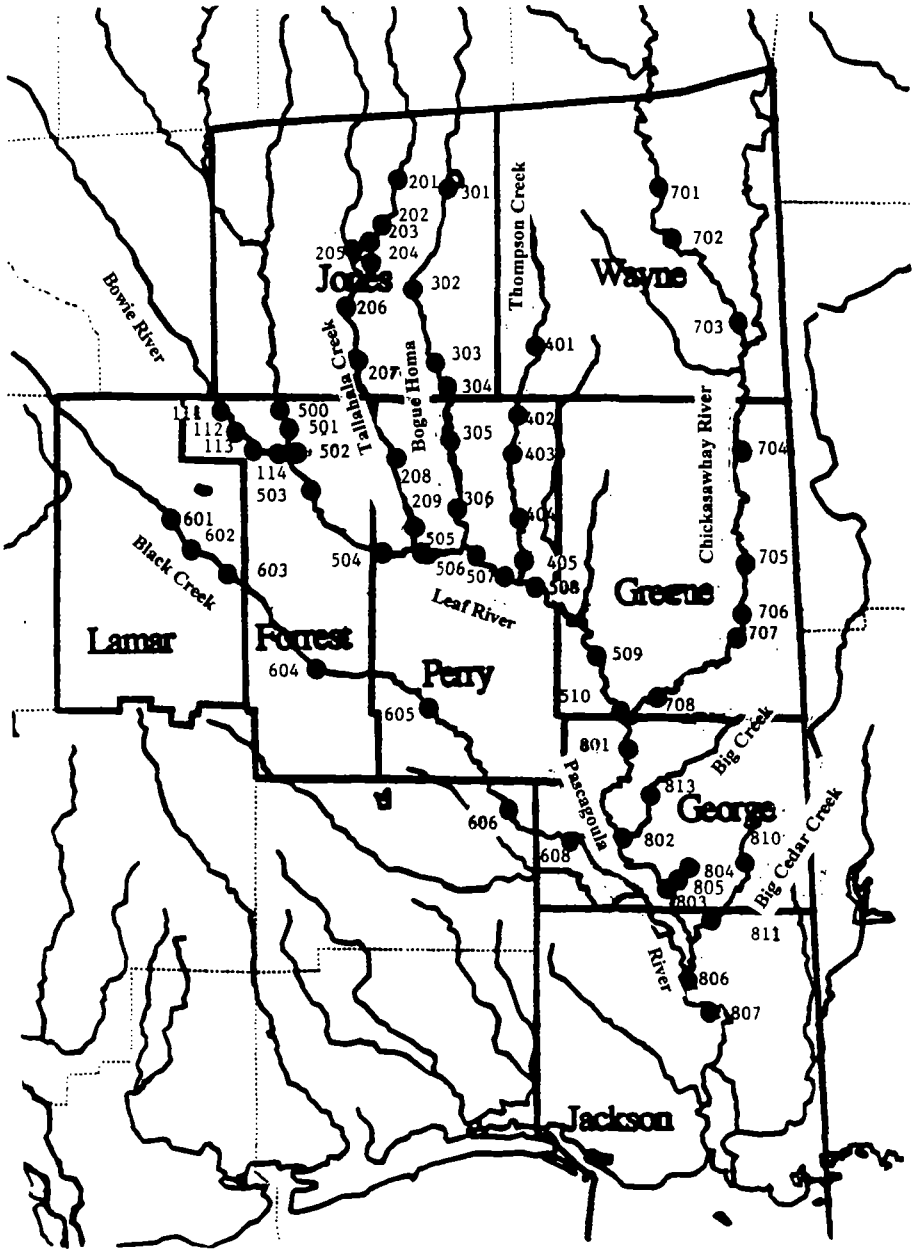

Figure 1: Sediment sampling sites in the Leaf, Pascagoula and Chickasawhay River drainage areas

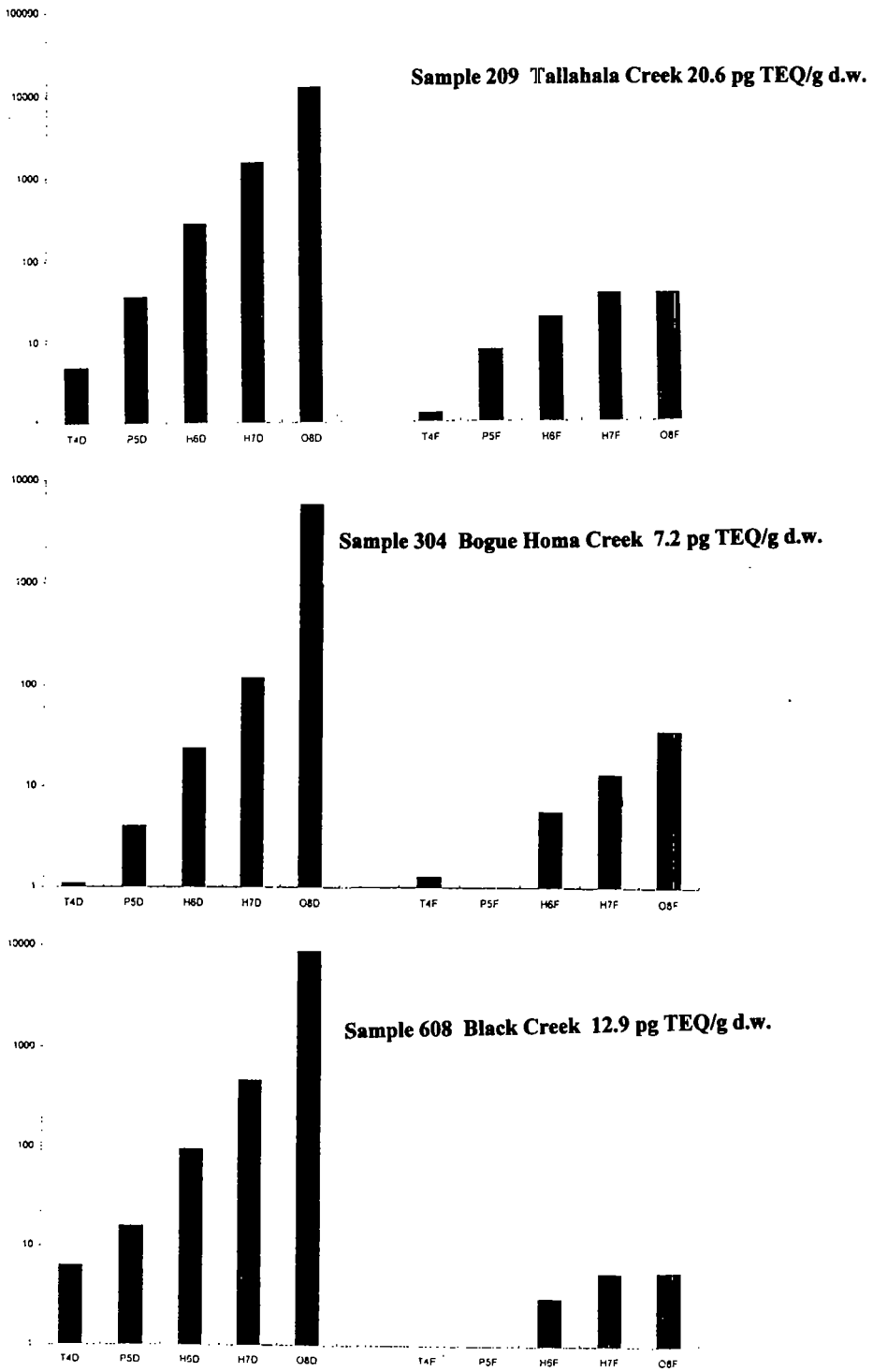

Figure 2: Congener group profiles for sediment samples in a logarithmic scale