

## Further Investigations of the Sources of PCDD/F in Municipal Sewage Sludge

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### **Abstract**

Wastewater from washing machines was found to be a major source of PCDD/F in household wastewater and sewage sludge. It was shown that this contamination originated in laundry. In further investigations a contamination of the laundry through textile production processes was ruled out.

### **Introduction**

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) are present in all municipal sewage sludges, even in rural areas where no industrial sources are present. In an effort to identify the non-industrial sources of PCDD/F in sewage sludge, we first investigated the contribution of surface runoff. It was estimated to contribute only 3-4% of the PCDD/F flux in the wastewater treatment plant in Bayreuth <sup>1</sup>. At last years conference we presented work indicating a significant contribution of domestic wastewater to the PCDD/F flux. At that time we had one sample and some circumstantial evidence suggesting that wastewater from washing machines was the principle source <sup>2</sup>.

In the past year we have focussed our efforts on the investigation of PCDD/F in washing machine wastewater. After initially confirming the results of the first sample presented at last years conference we proceeded to look for the source of the PCDD/F.

### **Analytical Methods**

Aqueous samples were extracted in a separatory funnel with toluene (20% of the sample volume). Each sample was extracted three times and the extracts were combined. The solid samples were Soxhlet extracted for 24 hours in toluene. The clean-up followed the method described previously <sup>3</sup>. The HRGC/HRMS analysis was performed on a HP 5890 gas chromatograph directly coupled to a VG autospec ultima mass spectrometer operating at a resolution of 10,000.

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## PCDD/F Levels in Wastewater from Washing Machines

Samples were collected from four different loads of wash from two different washing machines. The wastewater (85-90L) was collected for each wash in a basin at the outlet of the machine. The sample was mixed thoroughly and an aliquot of 2L was taken for analysis.

The concentrations ( $\Sigma$ PCDD/F) ranged from 3,900 to 7,100 pg/L (Mean 6,000 pg/L) and were similar to those found in the first analysis of washing machine wastewater. These data were used to conduct a crude mass balance for the Stuttgart-Büsnau treatment plant which receives only household wastewater. Assuming an average concentration of 6,000pg/L and every inhabitant in Stuttgart-Büsnau (Pop 8000) washes 1 time a week, a total of 4.3 mg of  $\Sigma$ PCDD/F would enter the sewer system from this source each week. Measurements at the wastewater treatment plant indicated that ca. 4.6 mg/wk of  $\Sigma$ PCDD/F leave the plant in sewage sludge. Thus washing machine wastewater would appear to be a major source of the PCDD/F in sewage sludge.

This conclusion is supported by the homologue profile. The average profile of the four wastewater samples together with the typical sludge profile are plotted in Figure 1. There is an obvious similarity between the two profiles.

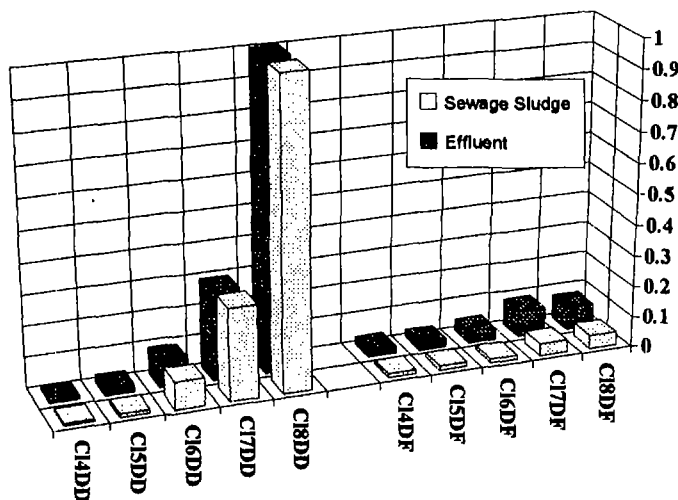


Figure 1: Relative PCDD/F-Pattern in Sewage Sludge and Washing Machine Effluent

The similar concentrations found in all 4 laundry samples led us to conclude that the presence of PCDD/F in washing machine wastewater is widespread and not restricted to a certain dye or a certain material.

## **The Washing Machine as a Source of PCDD/F**

The possibility that the washing machine was the source of the PCDD/F in the wastewater was examined by running the washing machine through its cycle with detergent but without laundry. The wastewater was collected and analysed. The concentrations were a factor of 100 lower than those present in the wastewater samples with laundry. Hence it was concluded that neither the detergent nor the machine itself was the source of the PCDD/F present in the wastewater.

## **Detergent as an Indirect Source of PCDD/F**

One possible explanation for the PCDD/F levels was a reaction of bleaching agents with substances in the laundry. A popular commercial detergent containing bleach had been used for the wastewater samples presented above. In order to test this hypothesis a load of laundry (6 kg white linen) was divided in 2 parts, one half was washed with the commercial detergent and the second half with a bleach free detergent. The wastewater with bleach contained 390 ng  $\Sigma$ PCDD/F per wash while the bleach free wastewater contained 460 ng.

## **New Textiles as a Source of PCDD/F**

At this point it appeared likely that the laundry itself was the source of the PCDD/F in the wastewater. We first looked to see if new textiles were the source, keeping in mind the observation above, namely, that both white wash and coloured wash released PCDD/F and that the concentrations were relatively uniform among the different loads of laundry analysed.

Five different synthetic textiles and eight different cotton materials were analysed. Cotton accounts for 50 % of the textiles sold in Germany. The concentrations were very low, with the  $\Sigma$ PCDD/F ranging between 7 and 30 pg/g textile. This is equivalent to about 21 - 90 ng per wash  $\Sigma$ PCDD/F if one assumes that 3 kg new clothes are washed and the PCDD/F in the new textiles are completely extracted during washing. From this result it is clear that the concentrations in the new textiles cannot explain the PCDD/F found in the washing machine effluent.

## **Used Textiles as a Source of PCDD/F**

Having ruled out new textiles as a PCDD/F source, we turned to used textiles. A new cotton undershirt was worn for 3 days. It was then cut in half. One half was analysed and the second half was washed (with other clothing) and then analysed. The  $\Sigma$ PCDD/F are plotted in Figure 2 along with the levels measured in an identical new undershirt that had not been worn. The concentrations increase by a factor of several hundred after the undershirt is worn. About 50% is removed through washing. Assuming that all laundry has the same concentration as the worn undershirt and that 50% is removed during washing, the expected concentration in the washing machine effluent would be 1800 ng/wash. This more than explains the concentrations that were measured in washing machine wastewater.

The homologue pattern present in the worn clothing reinforce this interpretation. In Figure 3 the homologue sums found in the worn undershirt and the average

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homologue sums found in washing machine effluent are plotted. The patterns are very similar.

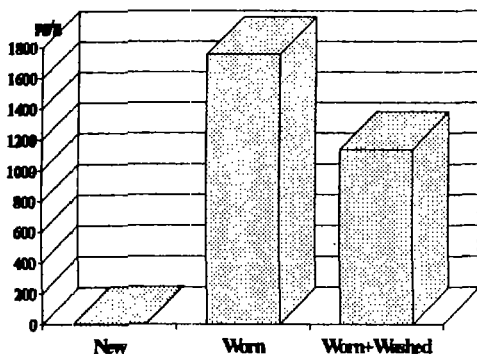


Figure 2:  $\Sigma$ PCDD/F in new, worn and worn+washed cotton undershirt

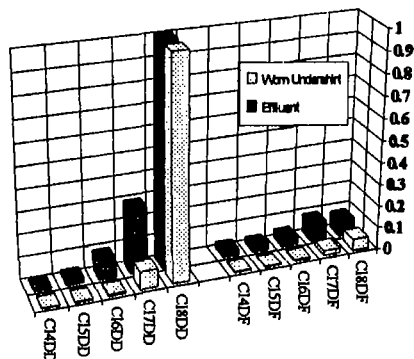


Figure 3: Relative PCDD/F-Pattern in a worn undershirt and washing machine effluent

Hence it was concluded that clothing is at some point during its use acquiring PCDD/F which is then the principle source of these compounds in household wastewater.

## Conclusions

Washing machine effluent is a major source of the PCDD/F present in household wastewater and in non-industrial sewage sludges. The PCDD/F in the washing machine wastewater originates in the laundry. PCDD/F accumulate in clothing when it is worn. The search for the PCDD/F source is continuing with an investigation of uptake from indoor and outdoor air.

## References

- 1.) Hutzinger O, McLachlan M S, Reissinger M, Horstmann M, Kaune A, Buresch H. Niederschlagsbedingte Einträge von PCDD/F in ein städtisches Einzugsgebiet. Bd. 8: *Niederschlagsbedingte Schmutzwasserbelastung der Gewässer aus städtischen befestigten Flächen*, Karlsruhe 1992
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- 3.) Horstmann M, Kaune A, McLachlan M S, Reissinger M, Hutzinger O. Temporal Variability of PCDD/F Concentrations in Sewage Sludge; *Chemosphere* 1992;25:1463-1468