

ANALYSES OF PCDDs AND PCDFs IN WASTEWATER FROM DISH WASHERS AND WASHING MACHINES

Rappe C, Andersson R

Institute of Environmental Chemistry, University of Umeå, S-901 87 Umeå, Sweden

INTRODUCTION

A series of PCDDs and PCDFs have been identified in sewage sludge. Unexpectedly, the contamination level was the same in two sludge samples from Sweden, one from the central Stockholm and the other from a rural area outside Uppsala, which only receives wastewater from households (1). For that reason the conclusion could be drawn that surface water contributes only marginally to this contamination as source of PCDDs and PCDFs in rural sewage. It has been suggested that household detergents could make a significant contribution to this contamination problem. Some of the detergents used in washing machines or dish washers are based on sodium hypochlorite or dichloroisocyanuric acid. These products could possibly generate PCDDs and PCDFs during the washing or dishing cycles (2). In order to test this hypothesis, a series of experiments have been performed using commercial detergents based on sodium hypochlorite.

EXPERIMENTAL

The washing machine experiments were performed at Statens Provningsanstalt, Borås, Sweden. To each laundry trial (4 kg) 2,2 dL of a powder detergent was added. Each washing generated 10 L of waste water. An aliquot of 2 L was sent to Umeå for analysis.

The dishwashing experiments were performed by Konsumentverket, Vällingby, Sweden. To each dishwashing trial 20 ml of a detergent was added, and the experiment generated 5 L of waste water. An aliquot of 2 L was sent to Umeå for analysis.

All experiments were performed in triplicates although the items for washing and dishing were not standardized. These items were collected in families. The following dishwashing experiments were performed

- D 1 Dirty dishes, without detergent
- D 2 Dirty dishes, with sodium hypochlorite based detergent
- D 3 Field blank, cleaned machine, clean dishes, no detergent (only one experiment)

The following cloth washing experiments were performed (in triplicates)

- W 1 Dirty items and water only
- W 2 Dirty items and non-chlorine detergent
- W 3 Clean items and hypochlorite based detergent
- W 4 Dirty items and hypochlorite based detergent
- W 5 Dirty items and non-chlorine detergent + hypochlorite based detergent
- W 6 Field blank, no items, water only, no detergent (only one experiment)

The waste water samples were spiked with relevant ¹³C-labelled compounds, filtered and extracted with dichloromethane. The particulate matter was mixed with NaCO₃ and packed on a column which was eluted with dichloromethane. The two extracts were combined,

concentrated and purified on a three column system (H_2SO_4 -silica column, Basic-alumina column, Carbowac C column). The extract was analyzed using HRGC/HRMS, a VG 70-250S system operating at a resolution of 8000.

RESULTS

A series of PCDDs and PCDFs were identified in all samples. A large variation could be seen in the triplicates as illustrated in Figure 1 (D 1, D 2, W 1, W 5). Please notify the difference in scales. The following mean values for the triplicates (counted as I-TEQ/89) were obtained

D 1	1.7 pg/g	W 1	1.14 pg/g	W 4	1.60 pg/g
D 2	3.3 pg/g	W 2	1.01 pg/g	W 5	1.34 pg/g
D 3	1.3 pg/g	W 3	0.83 pg/g	W 6	0.42 pg/g

DISCUSSION

1. Measurable amounts of PCDDs and PCDFs were found in the "field blanks".
2. The variation between triplicate samples was found to be larger than the variation between the mean values.
3. The variation found for the triplicate samples W 1 (dirty items and water only) indicates that this variation could be explained by the difference in dirt in the parallel samples.
4. No difference in congener patterns for tetra- and penta CDF and tetra- and penta CDDs could be found in experiments using chlorine-free and hypochlorite based detergents, see Figure 2.
5. This congener pattern is different from the congener pattern earlier reported for sewage sludge (1).
6. The large variation in triplicates makes comparison of mean values less meaningful.
7. If the mean values were used for the dishing experiments, the net increase is 1.6 pg TEQ/L, which corresponds to 8 pg TEQ/dishing cycle.
8. If the mean values were used to compare non-chlorine (W2) and hypochlorite based (W 4) detergents in the cloth washing, the corresponding figure is 6 pg TEQ/washing cycle.
9. Herring from the Baltic Sea contain 6 - 20 pg TEQ/g wet weight.
10. The total daily areal deposition in Sweden has been found to be 3 - 10 pg TEQ/m² (3).-
11. The levels of PCDDs and PCDFs in a few samples of human feces have been found to be 4 pg TEQ/g dry weight (4).
12. The contribution to the PCDD and PCDF levels in sewage sludge from chlorinated detergents is extremely low.

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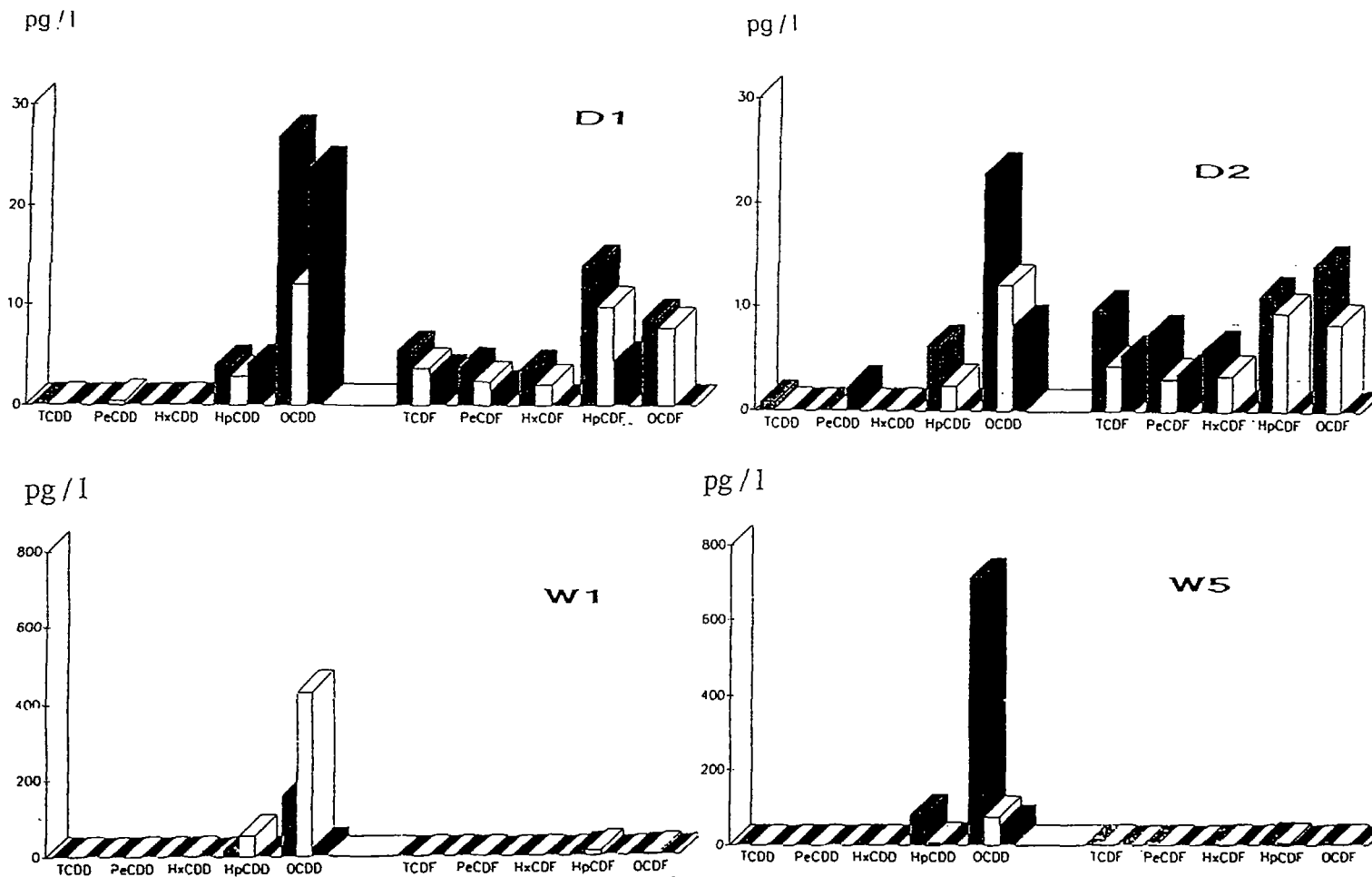


Figure 1. Levels of PCDDs and PCDFs in waste water from the triplicates of the dishing and cloth washing experiments. Please notify the difference in scales.

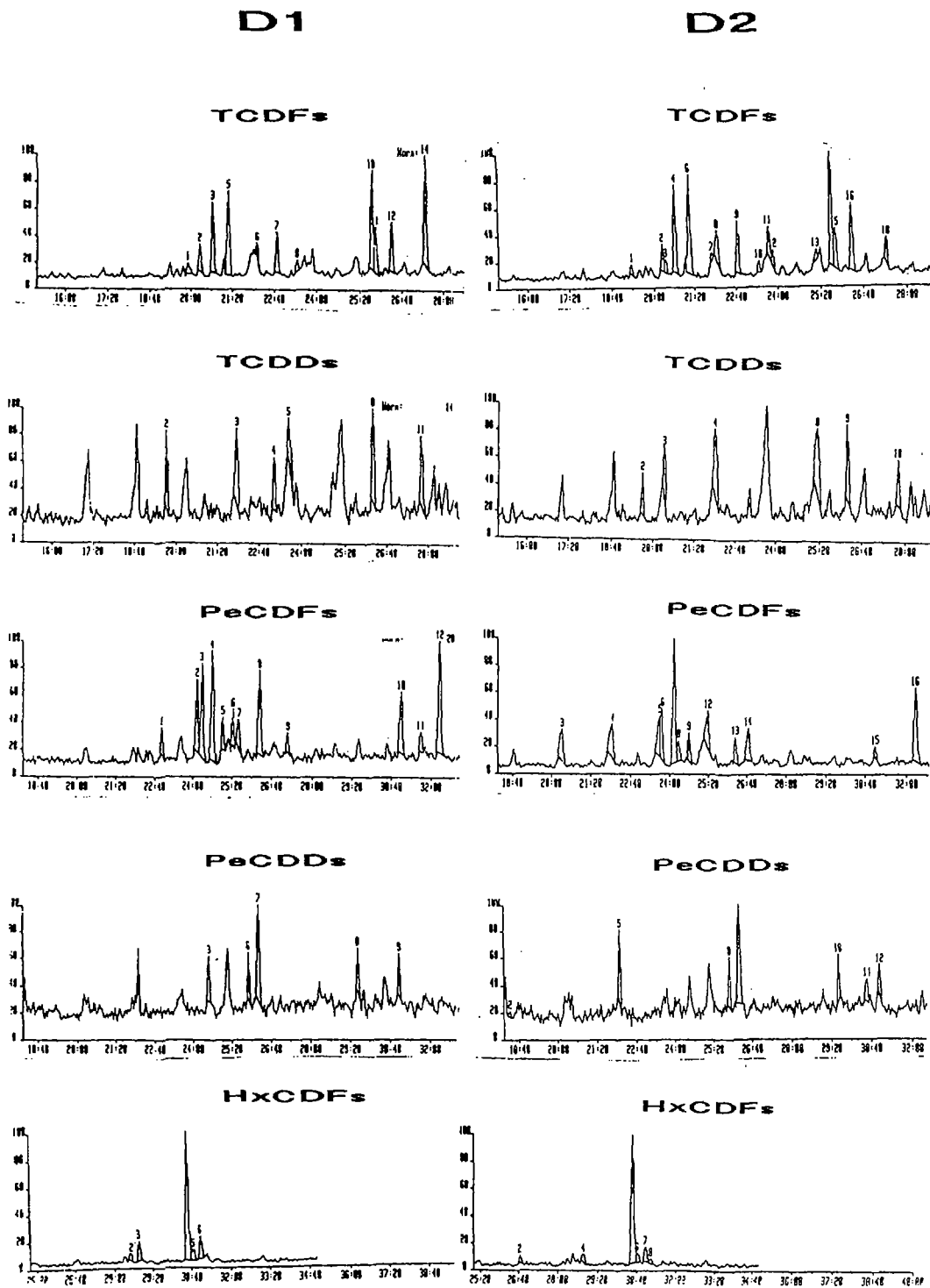


Figure 2. Mass fragmentograms from the dish washing experiments D 1 and D 2.