

PCDD/F in the paper industry: new results and mass balances

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Introduction

An extensive investigation about the input, formation and fate of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the pulp and paper industry has been carried out. A great number of samples have been taken in 13 pulp and paper mills and about 200 PCDD/F analysis of raw materials, intermediates, final products as well as stock additives, waste waters and sludges were made.

Results and Discussion

In order to gain an actual survey about the occurrence of PCDD/F in important types of paper and paperboard produced between 1991 and 1992 56 samples were analysed. The results are summarized in Table 1.

The values ranged between 0.83 to 11.53 ng I-TE/kg for papers and boards containing high amounts of recycled fiber and between 0.12 to 1.65 ng I-TE/kg for papers and boards containing only primary fibers. Products, which are completely produced out of recycled pulp, like solid fibre board and corrugated papers, showed the highest levels of PCDD/F. In general a decrease of the PCDD/F values could be observed, compared to earlier studies /1-4/.

An important change in the congener pattern has been figured out. The higher chlorinated dioxins, especially some HxCDD, both HpCDD and the OCDD, are the typical congeners which can be determined in recycled fiber products (see Figure 1). The chlorine bleaching pattern is only of minor importance in these samples.

In addition to about 150 samples of raw materials, intermediates, stock additives, waste waters and sludges from the pulp and paper mills were analysed. In combination with the quantity required and the stock flows, respectively, the PCDD/F mass balances of the pulp or paper mills were calculated. The formulation of PCDD/F mass balances in connection with the comparison of the congener patterns have been found to be an excellent method to determine the input, formation and fate of PCDD/F in large-scale units.

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Table 1: PCDD/F concentrations in papers and paperboards (produced in 1991/92)

| Type of paper or paperboard | Number of samples | ng I-TE/kg* (ppt) |
|--------------------------------|-------------------|-------------------|
| SC(supercalendered)-paper | 2 | 0.24 - 0.28 |
| LWC(light weight coated)-paper | 8 | 0.27 - 1.25 |
| Wood-Free Printing Paper | 3 | 0.17 - 1.00 |
| Hygienic Paper | 8 | 0.19 - 2.57 |
| Newsprint | 5 | 0.12 - 2.73 |
| Recycling Paper | 5 | 1.12 - 3.24 |
| Sulfite Wrapping Paper | 2 | 1.65 - 9.13 |
| Folding Box Board | 6 | 0.27 - 10.15 |
| Solid Fiber Board | 4 | 5.27 - 11.42 |
| Corrugated Paper | 13 | 0.17 - 11.53 |

* incl. all non-detectable congeners at half of their detection limits

The PCDD/F mass balance of a recycled paper mill has already been presented at DIOXIN 92 /5/, in the meantime mass balances of paper mills producing folding box board, solid fiber board, corrugated paper and some others have been carried out. The results correspond with the earlier one. The main PCDD/F-input in the production of recycled fiber products comes from the wastepaper.

It is remarkable that in general the waste paper contains higher amounts of PCDD/F than a corresponding newly produced paper of the same sort. This is due to some different contaminations during further processing and using. Some reasons of PCDD/F contamination will be presented in another paper.

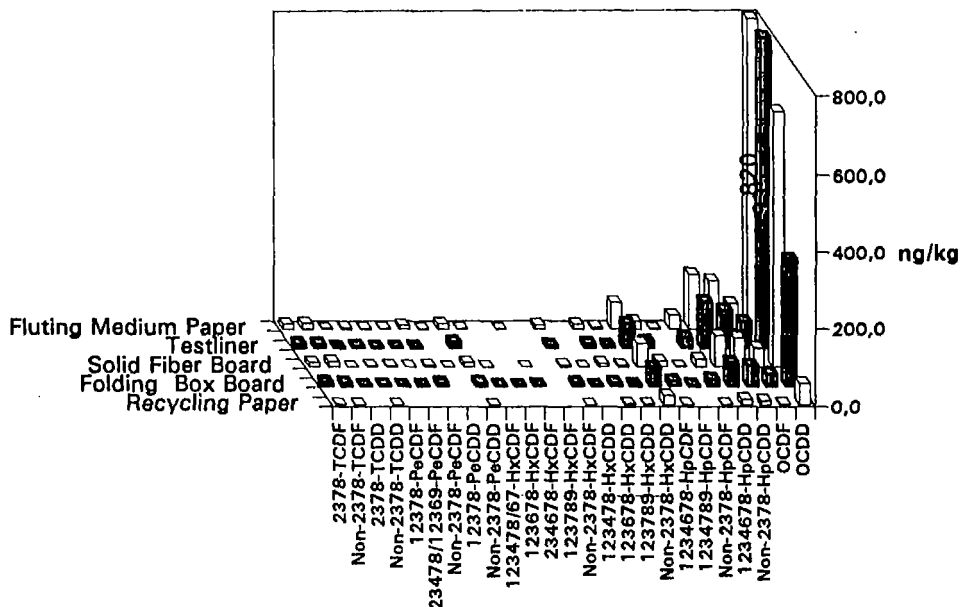


Figure 1: Typical PCDD/F pattern of some papers and boards containing high amounts of recycled fiber

Conclusion

In the paper and board manufacturing process no formation of PCDD/F has been found, this statement is also valid for the deinking process of wastepapers. No evaporation of PCDD/F could be observed in the dryer section of the paper machine.

The main input of PCDD/F in the production of papers containing only primary fibers is the imported chlorine bleached kraft pulp. PCDD/F mass balances for paper mills producing wastepaper-containing papers and cardboards showed the wastepaper as the main input. In some cases special stock additives (rosin sizing agents) are another small source of PCDD/F-input. The higher levels of PCDD/F in the waste paper may result partly from printing ink and pentachlorophenol. All results are summarized in Table 2.

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Table 2: Sources of PCDD/F in paper products

| | |
|---|----------------------------|
| Imported pulp (ECF, bleached with ClO ₂) | 0.2 - 1.3 ng I-TE/kg dw |
| Waste paper | 3 - 10 ng I-TE/kg dw |
| Printing ink (application mixtures) | up to 100 ng I-TE/kg |
| PCP (technical product) | up to 3·500·000 ng I-TE/kg |
| Special stock additives (application mixtures) | up to 55 ng I-TE/kg |

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