

PCDD/F mass balance of a recycling paper mill

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Introduction

The possibility of the formation of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) in the pulp industry is a well known fact. In spite of some very detailed studies in the field of pulp bleaching there is still no systematic investigation about the input, formation and fate of PCDD/F in paper mills. In a first step all parts of the production process from the raw material to the final product of a recycling paper mill were analysed.

Materials and Methods

The investigation was composed of two parts.

In order to gain a first survey about the input and the fate of PCDD/F in the paper mill, samples were taken during one week of production. Intending to register the whole production process with its inputs and outputs, 51 samples had to be taken, including sample mixtures from the main mass fluxes. In a first screening seven samples and one mixture of the deinking chemicals were analysed.

In the second part of the investigation random samples were collected in the chronological order of the production process. These samples especially were used to calculate the PCDD/F balance resulting from the deinking process and to verify the results of the first part of the investigation.

All samples were prepared according to a standard method. The samples were spiked with a mixture of fifteen carbon-13 labeled PCDD/F prior to extraction. Liquid-liquid partition with dichloromethane for the water samples and Soxhlet extraction with ethanol/water for solid samples were carried out. The extracts were purified by an extensive multistep cleanup procedure including superactive basic alumina, silica/sulfuric acid, silica/potassium hydroxide and a carbon/celite column. The analysis were carried out by HRGC/HRMS using a DB-5 fused-silica capillary column, coupled with a Finnigan MAT 90 mass spectrometer with electronic impact ionization. For each congener at least two isotope masses were measured.

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Results and Discussion

The final results of both samplings are summarized in Figure 1. As expected, the highest amounts of PCDD/F were found in the deinking sludge (44.37 ng I-Teq/kg dw and 24.82 ng I-Teq/kg dw) and in the sludge from the effluent treatment plant (11.01 ng I-Teq/kg dw). The levels of the waste water and the circulating water are very low, 0.055 and 0.013 ng I-Teq/l respectively. In both samplings significant lower PCDD/F concentrations were determined in the outgoing recycled paper (1.54 and 1.12 ng I-Teq/kg dw) compared to the input of the waste paper (4.44 and 2.96 ng I-Teq/kg dw). A reduction of the PCDD/F levels by a factor of about 2.7 to 2.9 has been observed.

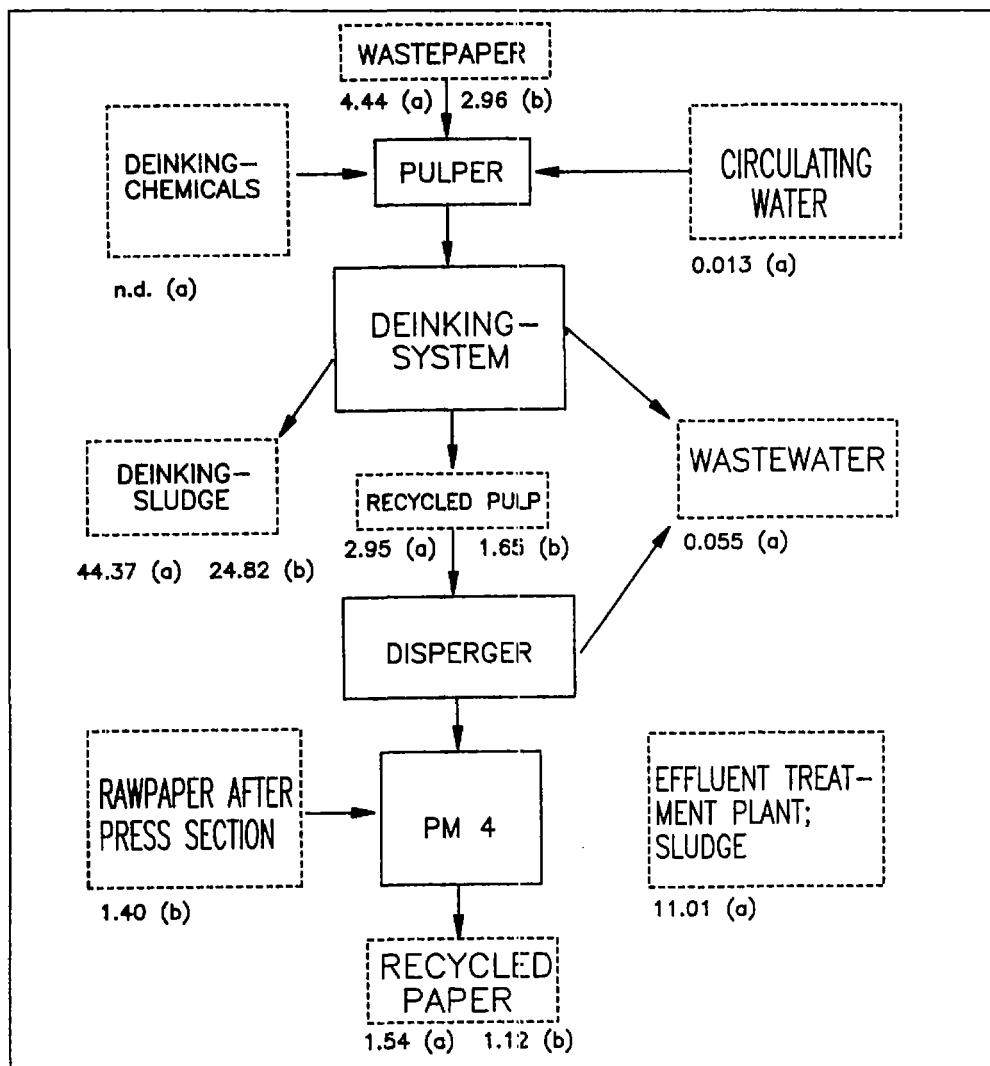


Figure 1: Scheme of the recycling paper mill

All results are given in ng I-Teq/kg.

a) Results from first sampling in July 91.

b) Results from second sampling in December 91.

The partition of the PCDD/F in the paper mill can be calculated including the mass fluxes. The waste paper had a 99.5% share in the PCDD/F-input. The main output comes from the deinking sludge (about 60%) and the recycled paper (about 30%). In this case the effluent treatment sludge had not been considered, because this output was already included in the effluents of the paper mill. A formation of PCDD/F could not be observed.

The typical PCDD/F pattern of some solid samples are presented in Figure 2. Mainly low concentrations of some TCDFs, some non-2378 substituted HxCDDs and higher levels of the HpCDDs and the OCDD could be found. The PCDD/F pattern of all samples correspond with one another, as well as the ratios between the main compounds are nearly constant in all solid samples. This confirmed the thesis, that no relevant amounts of PCDD/F are formed in the production process or introduced by process chemicals which have not been analysed in the first screening.

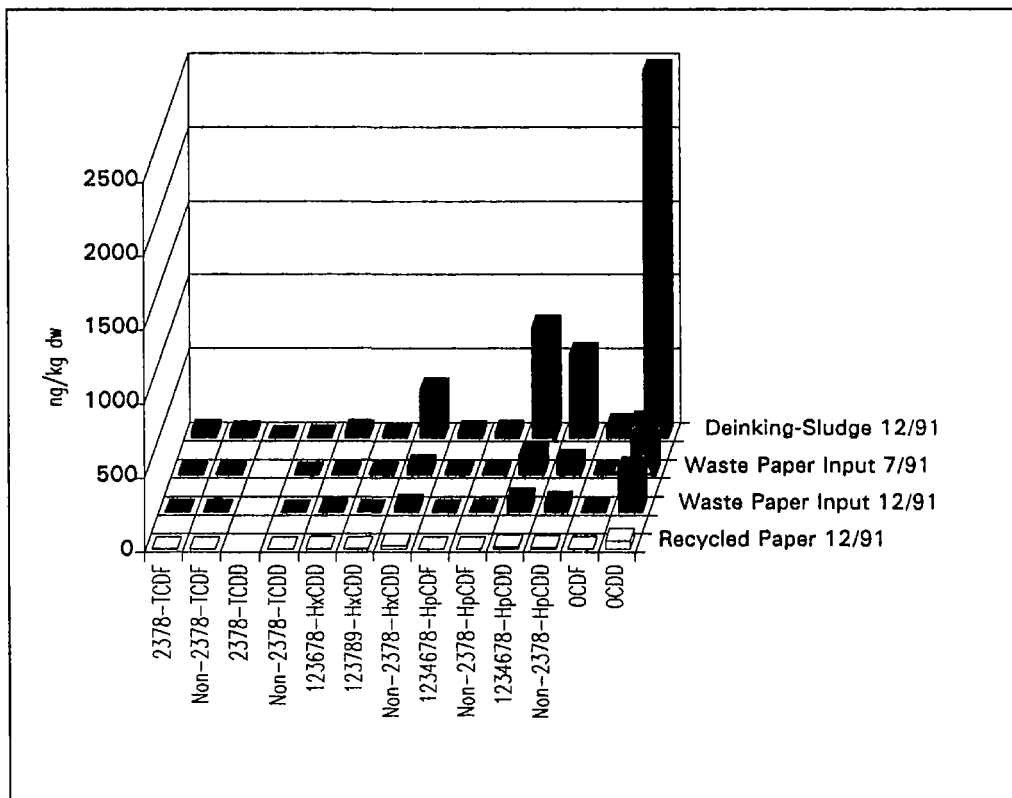


Figure 2: PCDD/F pattern of samples from a recycling paper mill

The results of the second sampling showed lower values of PCDD/F (Figure 1). However the results of the first sampling were verified, regarding the detected PCDD/F pattern (Figure 2) and the PCDD/F partition in the recycling paper mill. With these results a simplified PCDD/F balance of the deinking process was calculated. The PCDD/F-input in the deinking plant results from the waste paper in a share of 99.5%, according to the first results. 96% of the PCDD/F-output consisted of the deinking sludge and the recycled pulp. Therefore only this three samples were used for balancing. The results are shown in table 1. The PCDD/F mass balance is fulfilled very well.

	Input	Output		Mass balance
	waste paper ($\mu\text{g I-Teq/h}$)	recycled paper ($\mu\text{g I-Teq/h}$)	deinking sludge ($\mu\text{g I-Teq/h}$)	output/ input (%)
BGA-Teq	19.4	9.1	13.5	116
I-Teq	18.4	9.2	11.8	114

Table 1: PCDD/F balance of the deinking process

Referring to the results, the following conclusions can be drawn:

- The PCDD/F-input in a recycling paper mill comes from the waste paper. The main output is in the deinking sludge.
- The concentrations of PCDD/F in the recycled paper are about three times lower than the PCDD/F concentrations in the corresponding waste paper.
- No measurable amounts of PCDD/F are formed during the deinking or the papermaking process.

Acknowledgement

This study is part of the BMFT-project Nr.01ZV9004 'Investigation of the formation and fate of toxic organochlorine substances in the pulp and paper industry'. The authors would like to thank the Bundesministerium für Forschung und Technologie (BMFT) and the Verband Deutscher Papierfabriken (VDP) for their financial support.