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Some new sources of PCDD/F in recycled pulp products

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Introduction

Wastepaper is extensively used as raw material for paper and board production. In 1991 more than 6.6 million tons of wastepaper were utilized by the German paper industry. An extensive study about the input and fate of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the pulp and paper industry showed that in general the collected wastepaper contains higher amounts of PCDD/F than a comparable newly produced paper of the same type /1/. This could be referred to some different contaminations during former processing and use.

Results

The major PCDD/F-input in the paper and board production comes from the wastepaper /1/. In 1991 and 1992 twelve sample of wastepaper used for paper manufacturing and samples of untreated recycled pulp were analysed. The PCDD/F values ranged between 2.96 to 9.97 ng I-TE/kg dry matter. There were slight differences between the different wastepaper types. In general 'semi-industrial' and 'industrial' wastepaper types showed slightly higher levels of PCDD/F than 'collected' wastepaper, which mainly consists of newspapers and magazines.

For the production of carbon(less) copy papers chloroparaffins are sometimes used as dyeing solvent. The analysis of two carbonless copy papers showed only low amounts of PCDD/F, 0.88 and 7.27 ng I-TE/kg, respectively. Therefore, these paper types are not an important source of PCDD/F in the wastepapers.

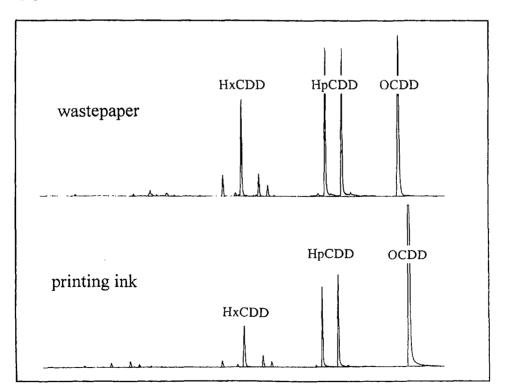
In the last years printing inks were suspected to be another source of PCDD/F in recycled paper products. Some studies about certain pigments and dyes were already made /2-4/. Mainly dioxazine pigments have been examinated, which are hardly used for rotogravure or offset printing inks. Therefore some analysis of common rotogravure and offset printing inks have been carried out. The investigated samples are application mixtures for two- and fourcolour printing. The results are summarized in Table 1.

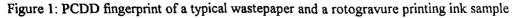
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sample type	concentration in ng I-TE (½ detection limit)/ kg (ppt)
rotogravure printing ink (two-colour)	90.1
rotogravure printing ink (four-colour)	62.4
offset printing ink (four-colour)	38.2
offset printing ink (four-colour)	17.5

Table 1: PCDD/F concentrations in application mixtures of printing inks

The PCDD/F amounts ranged between 17.5 to 90.1 ppt, whereby the rotogravure printing inks showed the higher values. Figure 1 illustrates the PCDD fingerprints of a typical wastepaper sample and a rotogravure printing ink. The agreement of the detected congeners is remarkable. These findings indicate that printing inks are an additional source of PCDD/F in wastepapers. In consideration of the small content of printing inks in the normal 'collected' wastepapers and the measured PCDD/F amounts the printing inks cannot cause the main PCDD/F input in the wastepapers.

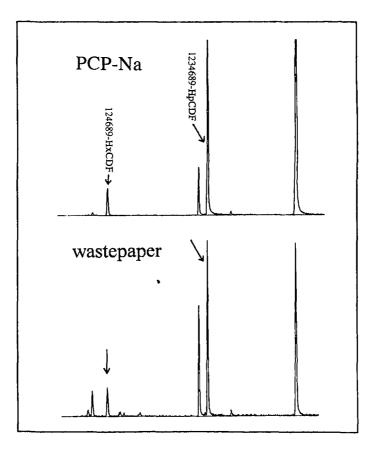


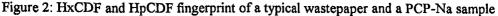


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In general pentachlorophenol (PCP) and sodium pentachlorophenate (PCP-Na) are a significant source of PCDD/F. Some earlier publications pointed out the very high PCDD/F contaminations of technical PCP and PCP-Na /5,6/. OCDD concentrations up to 1 000 mg/kg were often examinated. As these results were not up-to-date, a PCP-Na sample produced in 1992 in Europe has been analysed. The measured amout (3 374 μ g I-TE/kg) corresponded to the earlier results. Mainly the higher chlorinated dioxins were found in very high concentrations, e.g. 879 000 μ g I-TE/kg for OCDD and 260 200 μ g I-TE/kg for the HpCDDs. Therefore the use of PCP or PCP-Na as a fungicide in foreign countries can cause detectable PCDD contaminations in the wastepaper, especially in 'semi-industrial' and 'industrial' wastepaper types.

It is possible to draw some conclusions about the origin of PCDD/Fs in wastepaper samples with the help of some typical congeners - in case of PCP, the 124689-HxCDF and the 1234689-HpCDF /7/. Figure 2 showns, that these congeners are dominating in typical wastepaper samples as well. As a consequence PCP has still to be considered as a relevant PCDD input for wastepaper.







Conclusion

Summarzing the results, it could be clearly shown that the use of pentachlorophenol and printing inks cause an additonal PCDD/F input into the wastepaper and therefore in recycled pulp products, too. Investigating only a small number of samples, an estimation about the quantity referring to the corresponding sources cannot be made.

References

- /1/ Gruber, L., Stöhrer, E., Santl, H.; submitted for Dioxin'93, reported in this volume
- /2/ Williams, D.T., LeBel, G.L., Benoit, F.M.; Chemosphere Vol. 24, 169-180 (1992)
- /3/ Hutzinger, O., Towara, J., Fuchs, R., Hiller, B.; 'Vermeidung dioxinhaltiger Rückstände bei der industriellen Herstellung und Anwendung chlororganischer Produkte', BMFT-Research Report 14 505 308, Dezember 1991, S.2-13
- Remmers, J., Dupuy, A., McDaniel, D., Harless, R., Steele, D.; Dioxin'91, 23-27. Sept. 1991, Raleigh, USA, Poster Presentation P 110
- /5/ Hagenmaier, H., Brunner, H.; Chemosphere Vol. 16, 1759-1764 (1987)
- /6/ Cull, M.R., Dobbs, A.J., Goudot, M., Schultz, N.; Chemosphere Vol.13, 1157-1165 (1984)
- /7/ Hagenmaier, H; 'Untersuchungen der Gehalte an polychlorierten Dibenzodioxinen, polychlorierten Dibenzofuranen und ausgewählten Chlorkohlenwasserstoffen in Klärschlämmen', BMI-Research Report 103 03 305, Februar 1988

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