

## Pentachlorophenol Mediated Contamination of Leather and Leather Goods with Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans

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### Introduction

For more than 20 years pentachlorophenol (PCP) was one of the most commonly used fungicides for preserving wood, leather and cotton material. In the last ten years legal action was taken to restrict PCP use in many countries. In Germany the production and use of pentachlorophenol was banned in 1989 and a regulatory limit of 5 mg/kg for the PCP content in leather and other matrices was established.<sup>1</sup> However, in many developing countries the compound is still in use and imported leather and leather goods often exceeded this limit.

Technical PCP formulations are known to be contaminated with various organochlorine by-products like phenoxyphenoles, chlorinated diphenylethers and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F). Thus, it can be expected that goods manufactured from PCP treated materials also contain residues of these contaminants. We have already demonstrated that cotton textiles can be contaminated with up to 300,000 pg/g  $\Sigma$ PCDD/F via this pathway.<sup>2,3</sup> It was also shown that PCDD/Fs in textiles can be partly transferred to the outmost layers of the human skin (*stratum corneum*) during wearing.<sup>4</sup>

Malisch (1994) investigated the PCDD/F contamination of 11 leather samples that had routinely been analysed for PCP.<sup>5</sup> He found a qualitative relationship between the PCP and PCDD/F concentrations of the samples and concluded that consumers in Germany are sufficiently protected by the regulatory PCP limit of 5 mg/kg. However, the maximum concentrations in leather products were more than one order of magnitude higher than those reported for cotton textiles. Thus, PCP mediated PCDD/F contamination of leather goods may be a more significant problem than the contamination of cotton textiles.

Although there are also regulatory limits for the PCDD/F concentrations in commercial goods sold in Germany,<sup>1</sup> leather goods have not been routinely surveyed for these compounds. Due to the limited number of samples analysed to date, we conducted a more detailed study of PCDD/F contamination in leather and examined the correlation with PCP levels.

### Experimental

A total of 49 different leather samples including 19 pairs of shoes, 6 pairs of insoles, 6 pairs of gloves, 4 bracelets and 14 leather material samples were analysed for PCDD/F as described below. 32 samples had been collected from 1991 to 1995 by the State Examination Offices for the Health

System Northern Bavaria (Erlangen) and Southern Bavaria (Munich), respectively. These samples had been routinely analysed for PCP and the PCP data were placed at our disposal along with the samples. The other 17 samples were purchased in 1996 in retail shops in Bayreuth and from a leather manufacturer in the vicinity of Bayreuth, respectively.

#### PCDD/F Analysis

The leather samples were cut into small pieces and subdivided into portions of 1 g for analysis. For extraction the aliquots were sonified two times (15 min) with 50 ml n-hexane/acetone (1:1, v/v). Twelve  $^{13}\text{C}_{12}$ -labeled internal standards representing all ten homologue groups were added prior to the extraction procedure. The extraction efficiencies were shown to be comparable with the standard soxhlet extraction procedure using toluene. The combined extracts were cleaned up using a conventional method, which is published in detail elsewhere.<sup>2</sup> The HRGC/HRMS analyses were performed on a VG Autospec Ultima at a resolution of 10,000.

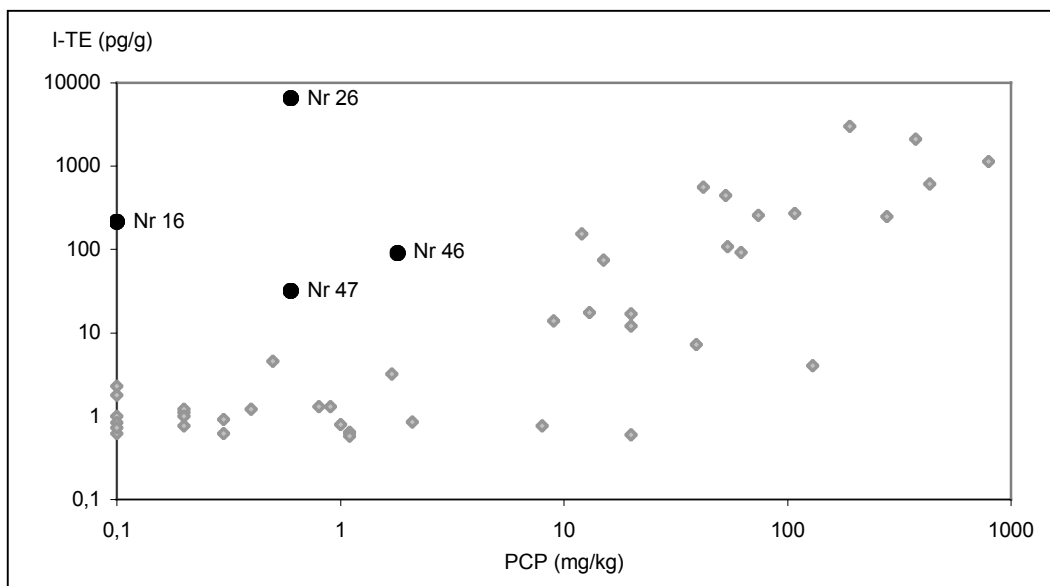
#### PCP Analysis

The PCP concentrations of the 17 newly bought samples were determined according to the routine method of the State Examination Office for the Health System Northern Bavaria using steam distillation with simultaneous extraction and GC/MS analysis of the methylated extract. As an internal standard  $^{13}\text{C}$ -labeled pentachlorophenol was added prior to extraction.

### **Results and discussion**

The PCDD/F concentrations of the samples ranged from 100 pg/g to 652,000 pg/g ( $\Sigma\text{PCDD/F}$ ). A total of 13 samples showed I-TE values of more than 100 pg/g with a maximum value of 6,500 pg/g for a shoe leather sample. The homologue patterns of the contaminated samples were in all cases but one (Nr 26) dominated by the highly chlorinated congeners with  $\text{Cl}_8\text{DD}$  contributing about 50-85% of the  $\Sigma\text{PCDD/F}$ . This is evidence that the PCDD/F contamination originated from PCP treatment of the leather material and is supported by the similarity between the isomer patterns observed in the leather and those reported for PCP in the literature, particularly for  $\text{Cl}_6\text{DD}$ .<sup>6,7</sup>

About 40% of the samples (21 of 49) exceeded the limit of 5 mg/kg PCP including 4 of 17 samples purchased during 1996. This result illustrates the need for further controls and PCP analyses of leather goods, even though the sample collection was not representative. **Figure 1** shows a plot of the measured PCDD/F concentration against the PCP concentration of the samples. Although there is no strict linear correlation, there is a trend of increasing PCDD/F levels with increasing PCP concentrations. However, some of the samples show a different behaviour. In this context, the four highlighted samples are of special interest. Although they are below the PCP regulatory limit of 5 mg/kg PCP, their PCDD/F concentrations are comparably high. The analytical results for these samples are given in **Table 1**.



**Figure 1:** Relationship between the PCP concentrations and I-TE values of the leather samples

**Table 1:** Analytical results of leather samples with high PCDD/F and low PCP levels

Nr / Year	Sort of leather	PCP (mg/kg)	$\Sigma$ PCDD/F (pg/g)	I-TE (pg/g)
26/95	Glove	0.6	604,000	6,500
16/92	Shoe leather	0.1	127,000	217
46/96	Bracelet	1.8	14,000	91
47/96	Bracelet	0.6	3,900	32

The high I-TE value of the glove sample (Nr 26) is due to unusually high concentrations of penta- and hexachlorinated dibenzofurans. Obviously, this particular sample was contaminated by another (unknown) PCDD/F source, which explains the low PCP concentration. In contrast, the PCDD/F pattern analysis of the other three samples indicated a PCP mediated contamination. The shoe leather (Nr 16) even exceeded the regulatory limit of 100 pg/g for the sum of all 2,3,7,8-substituted PCDD/F congeners, whereas the two bracelets (Nr 46, 47) were below the limits. Nevertheless, the I-TE values of these two samples were in the same range as reported for the highest contaminated cotton textiles<sup>2,3</sup> and may be of concern due to the intimate contact of these products with human skin.

In summary, as of 1996 a considerable fraction of leather goods sold in Germany was contaminated with PCDD/F most likely originating from PCP. Four samples showed high PCDD/F contamination, although their PCP concentrations were significantly lower than the German regulatory limit of 5 mg/kg (see Table 1). Thus, this regulatory limit is not in all cases a sufficient safeguard to protect against PCDD/F contamination in leather products.

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