Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (PCDD/F) in Wool and Wool Products

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Abstracts

PCDD/F were detected in wool products and in hair of lamb skins at concentrations ranging from low pg/g to 10 ng/g ΣPCDD/F. The maximum I-TEQ value was 86 pg I-TEQ/g. Low levels of less than 0.2 ng/g ΣPCDD/F were found in most analysed samples and were attributed to the background contamination of wool fat. The homolog profiles of serveral samples with elevated PCDD/F concentrations point to a pentachlorophenol contamination. In other samples unusual homolog profiles were found which can not be attributed to known sources of PCDD/F.

Introduction

In recent investigations it was shown that new cotton clothing can contain significant quantities of PCDD/F up to 300 ng/g [1)] and that the compounds are transferred from textiles to human skin during wearing [2)]. Contaminated textiles are responsible for high concentrations of PCDD/F in washing machine effluents and contribute significantly to the contamination found in sewage sludge [3,4)]. To complete information on contamination of textiles, 30 articles made of wool fabric (knitting wool, diaper pants, socks) and hair of three lamb skins were analysed in this study. Four samples of untreated sheep wool and four lanoline samples were investigated for comparative purposes.

Samples and Experimental

Two samples of untreated wool were purchased from a sheepherd. To exclude pesticide contamination, two other samples were collected directly by cutting a three month old lamb, that definitely had not been treated with any desinfectants. Knitting wool, socks, diaper pants and lamb skins were purchased in various shops in South Germany. Lanoline samples were collected at manufacturers of cosmetics.
Samples (4 - 8 g) were first cut in small pieces and then extracted in a soxhlet apparatus with toluene for 24 hours. An internal standard mixture of eight $^{13}C_{12}$-labelled PCDD/F congeners was added directly before the extraction procedure. The extract was reduced to dryness and the lipoid content of the samples was determined. A clean-up procedure with three chromatographic steps (mixed acid-base-silica, florisil, charcoal) was carried out. Lanoline samples (1 g) were dissolved in n-hexane, the internal standard mixture was added and the clean-up procedure was performed.

The determination of PCDD/F was carried out by HRGC/HRMS on a Finnigan MAT 8230 mass spectrometer at a resolution of 4,000 in the selected ion mode. Additionally to a HP Ultra 2 capillary column a Supelco SP-2331 column was used for isomer specific separation of PCDD/F.

Results and Discussion

In table 1 ΣPCDD/F, ΣPCDD and ΣPCDF levels and I-TEQ values of all analysed samples are presented. Figure 1 shows the frequency distribution of ΣPCDD/F levels in different sample types. 25 samples had very low levels of less than 0.2 ng/g ΣPCDD/F. Five samples showed slightly increased ΣPCDD/F values ranging from 0.2 to 0.5 ng/g.
Elevated contamination was determined in three samples of socks (1.0 to 1.4 ng/g ΣPCDD/F) and in three samples of knitting wool (3.5 to 6.0 ng/g ΣPCDD/F). The highest PCDD/F level was found in a sample of socks with 10.6 ng/g ΣPCDD/F.
The average contamination of all analysed wool products, excluding untreated wool and lanoline samples, was 1.0 ng/g ΣPCDD/F. This value is similar to the mean concentration found in cotton clothing [1]. I-TEQ values ranged from less than 1.0 pg I-TEQ/g in low contaminated wool samples up to 86 pg I-TEQ/g in samples with increased PCDD/F contents.

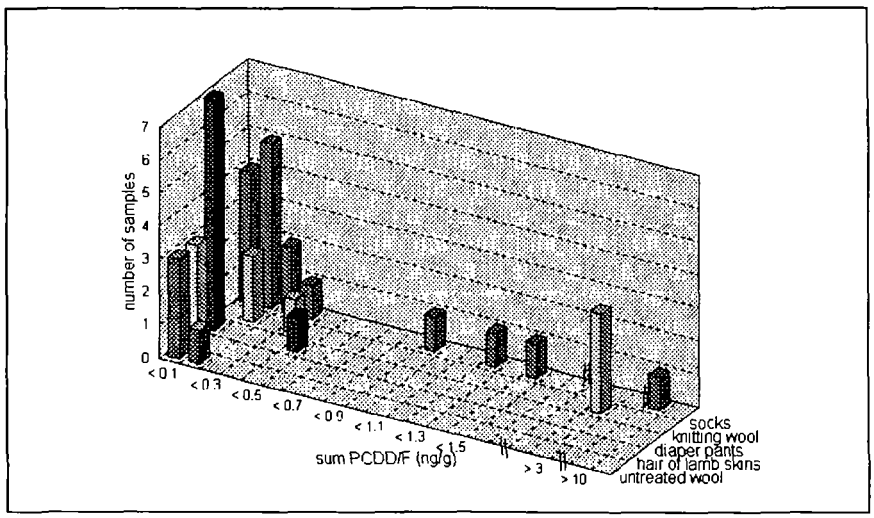

Figure 1: Σ PCDD/F levels in untreated wool and in wool products

Background contamination
In biological samples PCDD/F generally are accumulated in the lipid phase due to the lipophilic nature of these compounds. Since the amount of wool fat may differ in various samples of wool and wool products it might be assumed that PCDD/F levels are dependent on the lipoid contents of the samples. In table 1 lipoid contents and ΣPCDD/F values on a lipoid basis are presented. Actually the lipoid contents ranged from less than 1 % to about 20 %. ΣPCDD/F values on lipoid basis of most low contaminated wool products as well as ΣPCDD/F values of untreated wool were less than 10 ng/g lipoid and lay in the same order of magnitude as PCDD/F levels of lanoline samples, which contained pure wool fat. For this reason PCDD/F levels of low

contaminated wool products can be attributed to background contamination of wool fat. This assumption was supported by the fact that the PCDD/F homolog profiles of almost all low contaminated samples were nearly identical to the profiles found in untreated wool, as illustrated in figure 2, and were also found in lanoline.

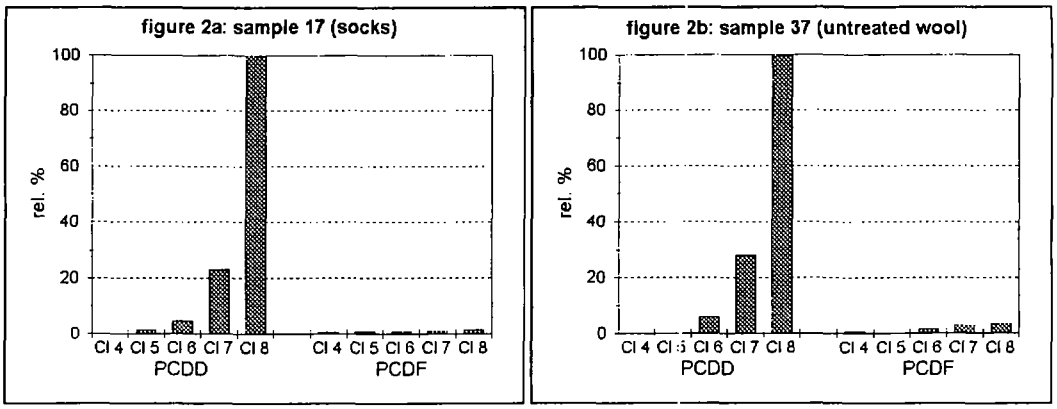

Figure 2: PCDD/F homolog profiles of background contaminated samples

In addition to the 2,3,7,8-substituted congeners, high concentrations of non-2,3,7,8-substituted congeners were present in all samples. Hence, the transfer of PCDD/F from the body of the animal to the wool fat can not be the only source of contamination, as it has to be expected that this route of exposure can only contribute to the amount of 2,3,7,8-substituted congeners. The accumulation of PCDD/F from the atmosphere on sheep wool is another possibility that has to be considered. However, it seems unlikely that atmospheric deposition is the main source of background contamination, since homolog profiles and isomer patterns of HpCDF homologs found in untreated wool and in most wool products are not typical of atmospheric particles [2,4]. On the other hand, considerable similarity was observed to the profile found in technical pentachlorphenol (PCP) [5,6], suggesting that this could be another source of background contamination of wool fat.

Increased contamination of wool products

Increased PCDD/F levels in high contaminated samples can not be attributed to high lipoid contents. Besides the background contamination of wool fat an additional contamination must have occurred in these samples during production or in the store. In consideration of the PCDD/F homolog profiles of various samples with elevated contamination, it is evident that increased PCDD/F levels of wool products can not be traced to a single source.

One sample of knitting wool and three samples of socks with increased contamination levels (samples 2, 19, 24 and 30 in table 1) showed PCDD/F homolog profiles that were very similar to the profiles found in technical PCP and were also observed in background contaminated samples (see figure 2). Moreover, typical PCP related isomer patterns of HxCDD and HpCDF homologs [5,6], namely high ratios of 1,2,3,6,7,8-HxCDD/1,2,3,4,7,8-HxCDD and 1,2,3,4,6,8,9-HpCDF/1,2,3,4,6,7,9-HpCDF were present in these samples. The homolog profiles together with the occurrance of the PCP fingerprints point to a PCP contamination.

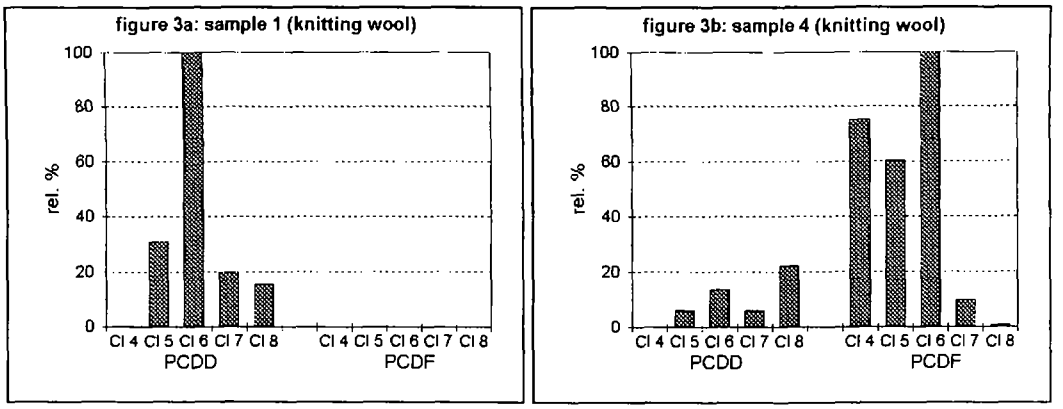

Figure 3: PCDD/F homolog profiles of high contaminated samples

In figure 3 two unusual homolog profiles are presented, which can not be attributed to a known source of PCDD/F. The profile of sample 1 (knitting wool) was clearly dominated by hexachlorinated dioxins (figure 3a). This sample showed the maximum I-TEQ value of all analysed samples (86 pg I-TEQ/g), due to high levels of 2,3,7,8-substituted HxCDD isomers. These congeners with TEFs of 0.1 contributed to over 90 % to the total I-TEQ value. In sample 15 (socks) the amount of HxCDD homologs was also increased but did not exceed the concentration of OCDD. Appart from these two samples with elevated ΣPCDD/F values, two low contaminated samples (samples 11 and 25) showed increased relative concentrations of PeCDD and HxCDD homologs, which were higher or comparable to the respective OCDD concentrations.

In sample 4 (knitting wool) tetra- to hexachlorinated furans were the dominating homologs (figure 3b). Concerning the I-TEQ value, the 2,3,7,8-substituted HxCDF isomers were the most important congeners in this sample. Besides this high contaminated sample, increased relative levels of PCDF were observed in sample 3 (TCDF and PeCDF) and in sample 18 (HpCDF and OCDF). In these samples the ΣPCDF levels were similar to the ΣPCDD levels.

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Table 1: PCDD/F concentrations in wool and wool products

no.	sample type	Σ PCDD/F (ng/g)	Σ PCDD (ng/g)	Σ PCDF (ng/g)	I-TEQ (pg/g)	lipoid (%)	Σ PCDD/F (ng/g lipoid)
1	knitting wool	6.007	5.990	0.017	86.1	0.3	2003
2	knitting wool	3.592	3.577	0.015	13.8	5.0	71.8
3	knitting wool	0.107	0.064	0.043	0.4	2.8	3.83
4	knitting wool, brown	4.360	0.710	3.650	37.0	1.6	272.4
5	knitting wool, brown	0.340	0.323	0.017	1.5	15.3	2.23
6	knitting wool, brown	0.193	0.182	0.011	0.7	14.7	1.31
7	diaper pants	0.031	0.030	0.001	0.2	0.6	5.18
8	diaper pants	0.026	0.024	0.002	0.06	1.1	2.39
9	diaper pants	0.016	0.015	0.001	0.03	1.3	1.23
10	diaper pants	0.018	0.018	-	0.03	1.2	1.53
11	diaper pants	0.488	0.466	0.022	3.7	1.0	48.8
12	diaper pants	0.015	0.0143	0.0004	0.07	1.3	1.13
13	diaper pants	0.026	0.0259	0.0005	0.1	1.0	2.64
14	diaper pants	0.018	0.018	-	0.04	1.4	1.30
15	socks	0.989	0.984	0.005	6.6	1.5	65.9
16	socks	0.063	0.062	0.001	0.2	1.2	5.27
17	socks	0.378	0.365	0.013	0.9	2.8	13.5
18	socks	0.054	0.025	0.029	0.15	0.9	6.08
19	socks	1.423	1.301	0.122	6.5	3.8	37.5
20	socks	0.252	0.252	-	1.3	3.2	7.86
21	socks	0.182	0.166	0.016	0.75	1.4	13.0
22	socks	0.256	0.243	0.013	1.4	2.4	10.7
23	socks	0.156	0.136	0.020	2.1	3.7	4.21
24	socks	10.951	10.922	0.029	23.2	0.9	1217
25	socks	0.173	0.172	0.001	1.1	0.9	19.2
26	socks	0.100	0.088	0.012	0.34	1.8	5.53
27	socks	0.096	0.078	0.018	1.8	1.5	6.37
28	socks	0.143	0.128	0.015	1.3	2.3	6.21
29	socks	0.196	0.186	0.010	0.63	2.1	9.36
30	socks	1.276	1.085	0.191	5.4	2.7	47.3
31	hair of lamb skin	0.003	0.003	0.0002	0.02	1.8	0.17
32	hair of lamb skin	0.020	0.0199	0.0003	0.08	8.2	0.25
33	hair of lamb skin	0.006	0.006	0.0001	0.01	8.6	0.07
34	untreated wool (sheep)	0.097	0.087	0.010	1.1	21.3	0.46
35	untreated wool (sheep)	0.050	0.041	0.009	0.7	6.8	0.74
36	untreated wool (lamb)	0.064	0.0617	0.0026	0.2	4.4	1.46
37	untreated wool (lamb)	0.159	0.150	0.009	0.7	10.1	1.58
38	lanoline	0.255	0.248	0.0065	1.3	-	-
39	lanoline	2.437	2.381	0.057	7.2	-	-
40	lanoline	0.402	0.393	0.009	1.0	-	-
41	lanoline	0.343	0.327	0.016	0.6	-	-