Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Textiles and their Transfer to Human Skin, Sewage Sludge and other Matrices

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Abstract

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) were measured in new garments in concentrations ranging from low pg/g to high ng/g. Two different types of homologue patterns were found in the more contaminated textile samples, one which agreed well with the PCDD/F-pattern in pentachlorophenol (PCP), while the other closely resembled a pattern that has been reported for chloranil-based dyes. One of the highly contaminated textiles contained 2000 ng/g of PCP. A large fraction of the PCDD/F was readily washed out of new textiles during a normal laundry cycle. Extensive evidence was found indicating that the PCDD/F in new textiles are a major source of these compounds in sewage-sludge and dry cleaning residues. PCDD/F were also transferred from the garments to human skin during wearing and from there to other compartments.

Introduction

Following a study of the potential sources of PCDD/F in sewage sludge it was concluded that the contamination of laundry with PCDD/F could account for the main portion of PCDD/F-fluxes into many municipal waste water treatment plants (WWTP) [1,2]. Investigations of a number of textile finishing processes like bleaching or "Ease-of-Care" treatment yielded no evidence indicating that these were major sources of the contamination [3]. Furthermore, uptake of PCDD/F out of the atmosphere into clothing during wearing does not seem to be an important pathway for the higher chlorinated congeners that dominate the PCDD/F pattern in washing machine waste water [1]. We have continued our efforts to identify the main source(s) of PCDD/F in laundry and to study the fate of these compounds. Considerable attention was devoted to a compartment exposed to extensive contact with garments, human skin.

Experimental

Numerous samples from different matrices were analysed for PCDD/F. The dried samples were Soxhlet extracted in toluene or n-hexane/acetone mixtures for 16 hours and cleaned

up using modifications of published methods [4]. Twelve $^{13}C_{12}$ labelled internal standards representing all 10 homologue groups were employed. The HRGC/HRMS analyses were performed on a VG AUTOSPEC ULTIMA at a resolution of 10,000.

Results and Discussion

The PCDD/F-concentrations in 23 different garments were analysed. Common clothing items were selected, in most cases cotton or mixtures of cotton and synthetic. The PCDD/F contamination of these textiles ranged from <10 pg/g up to 300,000 pg/g ΣPCDD/F. Figure 1 shows the frequency distribution of the concentration of Cl_8DD, the dominant homologue in the analysed samples. While the early results of this study had indicated that there are insignificant quantities of PCDD/F in new textiles [5], it is apparent that a small fraction of new textiles has very high concentrations.

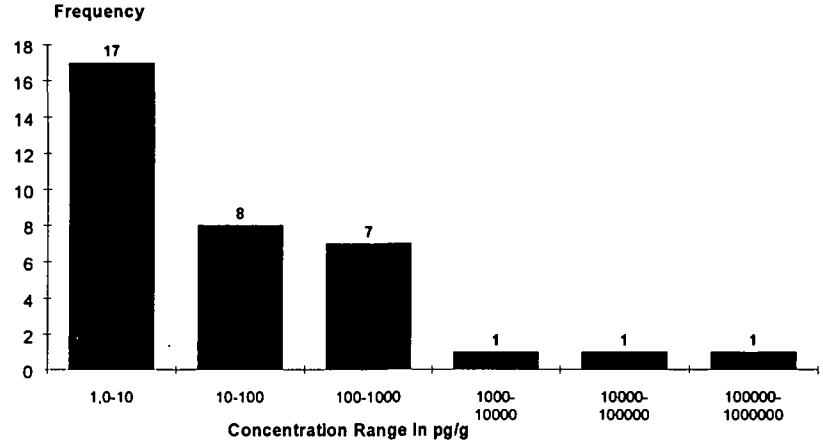

Fig. 1: Frequency distribution of the Cl_8DD concentrations found in 35 textile samples

The highest concentrations were found in coloured T-shirts from different producers. Two characteristic homologue patterns were found in the samples which were contaminated with more than 100 pg/g ΣPCDD/F.

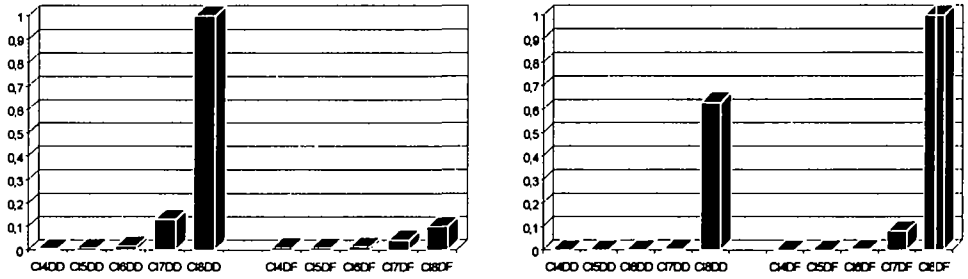

Fig. 2a+b: Two types of PCDD/F homologue patterns found in the textile samples

The pattern in Figure 2a was found with small variations in nine garments, while the pattern in Figure 2b was present in one sample. The similarity between the pattern in Figure 2a and the pattern in technical PCP samples [6] and the presence of high levels of other PCP signature congeners in the textiles (1,2,4,6,8,9-Cl_6DF, 1,2,3,4,6,8,9-Cl_7DF) implicates PCP

as a source of the dioxin and furan contamination. PCP has been widely employed as a preservative of cotton fabrics [7] and is probably still used for this purpose in the developing world. Three of the garments were analysed for PCP. One of the samples with the pattern in Figure 1 (ΣPCDD/F = 16,000 pg/g) contained 2,000 ng/g PCP, which supports the hypothesis that PCP is a source of the PCDD/F contamination. A second sample with high PCDD/F levels contained less than 10 ng/g of PCP. This need not contradict the hypothesis, however, as it is likely that PCP is effectively washed out of textiles during various finishing processes that involve alkaline baths, whereas the PCDD/F would be expected to be more strongly retained. Hence PCP is probably not a suitable tracer for PCDD/F in textiles, even when PCP was the original source of the PCDD/F.

The pattern in Figure 2b is distinct from that in Figure 2a and is characterised by high levels of Cl_7- and Cl_8DF. The absence of detectable amounts of Cl_7DD in Figure 2b indicates that PCP was not the source. The PCP concentration in the garment with this pattern was <10 ng/g. However, the pattern agrees well with the homologue pattern in chloranil-based dyes [8]. This garment with this pattern was a blue/green T-shirt. Dyestuffs may also be a second source of PCDD/F contamination in textiles.

Although the PCDD/F contamination is to some degree persistent during textile finishing, these compounds are readily transferred from the finished garments to other compartments. Figure 3 summarises the pathways which were identified in this study.

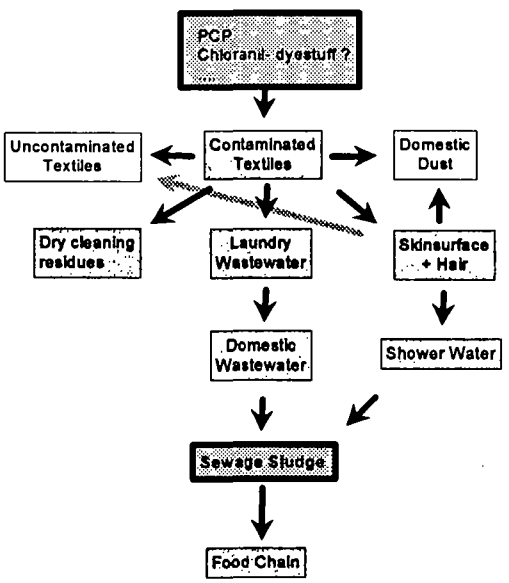

Fig. 3: Pathways of PCDD/F from textiles to other compartments

Transfer of PCDD/F was demonstrated between the following matrices: textiles and skin; textiles and laundry waste water; contaminated skin and uncontaminated textiles; skin and shower water; contaminated and uncontaminated textiles via laundry waste water or during wearing [1,5]. These transfer processes can explain previously reported observations, for instance the increase in PCDD/F concentration in an undershirt during wearing [5]. A large fraction of the PCDD/F in the textiles eventually is transferred to sewage sludge. The use of sewage sludge as an agricultural fertiliser leads to PCDD/F accumulation in soils and, when applied excessively, to a measurable accumulation in the agricultural food chain [9].

The PCDD/F in textiles can also explain the contamination of dry cleaning residues [10] and domestic dust, which appears to be a sink for PCDD/F from skin scale and shedded textile fibres [1]. PCDD/F-homologue patterns identical to those in Figure 2a were found in dry cleaning residues and domestic dust.

Conclusions

PCDD/F in clothing is a major source of the PCDD/F in domestic waste water. Sewage sludge is the principal sink for the PCDD/F in clothing. In view of the transfer of PCDD/F from clothing to human skin, dermal uptake is a possible route of exposure that needs to be further investigated.

Acknowledgement

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