Scientific Paper

Presence of Dioxins in Textile Dyes and Their Fate During the Dyeing Processes

Boštjan Križanec,[a]* Alenka Majcen Le Marechal,[a] Ernest Vončina,[b] and Darinka Brodnjak-Vončina[c]

[a] *Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia*
[b] *Environmental Protection Institute, Prvomajska ul. 1, SI-2000 Maribor, Slovenia*
[c] *Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia*

Received 06-01-2005

Abstract

Considerable levels of highly toxic polychlorinated dibenzo-*p*-dioxins (PCCDs) and polychlorinated dibenzofurans (PCDFs) were determined in two among the six analysed disperse textile dyes. The dioxin homologue profile of these dyes was similar to that found in some environmental and industrial samples, connected with the textile industry. Dyes contaminated with dioxins were further used in industrial polyester dyeing processes at laboratory scale. We observed the changes in dioxin contents, dioxin transformations and their distribution during the textile dyeing process. After the dyeing and textile finishing processes the content of dioxins was up to fifteen times higher. More than 85% of the total dioxin content was found in dyed polyester. Other 15% was discharged with waste dye bath. Our results confirmed that the presence of dioxins in some textile dyes may be a significant source regarding human exposure and environmental contamination.

Key words: polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, textile dyes, formation

Introduction

Dioxin is a term for a group of poly-halogenated aromatic hydrocarbons including 75 polychlorinated dibenzo-*p*-dioxins (PCDDs) and 135 polychlorinated dibenzofurans (PCDFs).[1] Dioxins are persistent, toxic pollutants that accumulate in animal and human fats.[2] Exposure to even low doses of dioxins can lead to cancer, damage of the nervous system, immune system diseases and reproductive disorders.[3] Their structures are very similar, differing only in the number and spatial arrangement of chlorine atoms in the molecules (Figure 1).

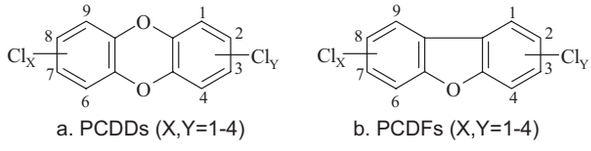

Figure 1. Molecular structure of the polychlorinated dibenzo-*p*-dioxins (a) and polychlorinated dibenzofurans (b).

Isomers with chlorine atoms at positions 2,3,7,8 are especially toxic and persistent. The so-called "dirty group" presents 17 isomers of PCDD/Fs. In the environment, PCDD/Fs can be transported over great distances through evaporation and condensation cycles.[4] As a result of global circulation patterns and low evaporation rates in cold climates, dioxins tend to accumulate in arctic regions where they bioaccumulate in living organisms.[5] PCDD/Fs, therefore, present a global environmental and health problems.

Thermal processes are the main source of dioxins. Dioxins are formed in the gas phase at temperatures above 600 °C and on the surface of solid phase in the temperature range between 225–400 °C.[6] Chemical industry is an important source of (PCDD/Fs) as by products.[7] PCDD/Fs can be formed during the synthesis of chlorophenols, chlorobenzenes, chlorobiphenyls, polyvinyl chloride, dyes, pigments, printing inks and halogenated pesticides.

PCDD/Fs were detected in sewage sludge tested in Germany.[8] Following a study of the potential sources of PCCD/Fs in sewage sludge, it was concluded that the contribution of several textile products could account for the source of PCDD/Fs in many municipal waste water treatment plants.[9] Furthermore, a logical category of products were tested to determine the sources of dioxins. The concentrations of PCDD/Fs were determined in different new garments, ranging from low pg/g to high 300 ng/g. The octachloro dibenzo-*p*-dioxin (OCDD) was the dominant homologue.[10] Dioxin homologue patterns that were found in more contaminated textile samples were annotated to PCDD/Fs patterns connected to pentachlorophenol and chloranil based dyes.

The contamination of textile fibres during production and finishing was also investigated.[11] Cotton cloth was subjected to a series of 16 typical finishing processes and analysed for PCDD/Fs at various stages of treatment. The maximum concentrations found in the raw textile products were 30 ng/kg in cotton and 45 ng/kg in synthetic materials. Concentration increases during treatment processes were attributed to an increase in OCDD. The contribution of textile production and finishing to the PCDD/Fs concentration increased with dyeing, and with wash and wear finishing processes resulted in a maximum concentration of 100 ng/kg. In this study only a few textile processes were investigated covering a small range of chemicals used in the textile industry. In addition, the concentrations of PCDD/Fs in the waste waters and the used chemicals were not determined.

A relatively small amount of data is available for PCDD/Fs contents in textile dyes and pigments. Considerable levels of PCDD/Fs were determined in some dioxazine dyes and pigments, phtalocyanine dyes and in printing inks. Dioxazine pigments were derived from chloranil, which was found to contain high levels of PCDD/Fs and has been suggested as the source of contamination.[12] In a sample of Ni-phthalocyanine dye higher congeners of PCDD/Fs were found in μg/kg concentration level.[13] Considerable levels of PCDD/Fs were also determined in some printing inks obtained from a supplier in Germany.[14] The identities of the dyes and pigments in these inks were not reported.

Synthesis of colorants represents a relatively large group of chemicals with complex synthesis processes. During synthesis of some colorants polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) can be formed.[12–14] Further formations of PCDD/Fs can occur via dyeing and textile finishing processes with conditions favourable for the generation of PCDD/Fs (high temperatures, alkaline conditions, UV radiations or other radical starters).

The main object of this work was to determine the presence and fate of dioxins, as well as the precursors´ compounds, in some selected textile dyes used by local industries. Emphasis was devoted on two black disperse dyes in which high levels of PCDD/Fs were determined.

Experimental

Textile disperse dyes were supplied by two different producers. The two black disperse dyes were a mixtures of anthraquinone disperse and azo-disperse dyes (Dye 1, Dye 2). The complete chemical composition of these dyes is unavailable. Commercial polyprene (polyester) fibres were used for the dyeing experiments. All the chemicals used were of analytical grade or dioxin analytical grade. Standards of PCDD/Fs were purchased from the Cambridge Isotope Laboratories (CIL, USA).

The analytical procedure for the determination of PCDD/Fs is quite complicated because concentrations of dioxins are low when compared to other chlorinated aromatic compounds like polychlorinated biphenyl ethers and polychlorinated biphenyls present in samples. High efficiency in the cleanup methods is necessary to make the analysis possible. Organic solvent extraction is used together with cleanup of the extract by multi-step column chromatography. The quantification of dioxins is based on an isotope dilution procedure using isotopically labelled $^{13}C_{12}$-PCDD/Fs.

Dye samples (1 g) were spiked with an internal standard mixture containing $^{13}C_{12}$-labelled isomers (100 pg) in 100 μL of nonane. The samples were then diluted in ethanol-water mixture and extracted with hexane. The solubility of all dyes was good in ethanol:water (1:1) mixture with an insignificant presence of emulsion by liquid-liquid extraction with hexane. Cleanup of organic (hexane) extract was performed on a mixed column (layers: silica gel/sulphuric acid, silica gel/KOH and silica gel) followed by additional cleaning using adsorption chromatography on a graphitised carbon column. Using adsorption chromatography on a graphitised carbon column, we separated the dioxin compounds that are planar, from other nonplanar interferences. The obtained dioxin fraction in toluene (60 mL) was concentrated to a final volume of 20 μL and analysed for PCDD/Fs content.

Two dyeing experiments were performed separately with 9 g of polyprene fibres. Disperse dyes (Dye 1 and Dye 2), which contain PCDD/Fs, were used in an industrial polyprene fibres dyeing process. Dyeing was carried out in a laboratory scaled dyeing machine MATHIS LABOMAT BFA-8 (Warner Mathis AG, Switzerland) equipped with infrared heating, in stainless steel dyepots of 200 cm^3 capacities. The dye-bath was maintained at 130 °C for 45 min. After dyeing, sample reduction clearing was carried out by heating in an aqueous solution containing sodium dithionite ($Na_2S_2O_4$) and sodium hydroxide at 70 °C. After the treatment, the samples were rinsed with distilled water and dried in the open air. Concentration of PCDD/Fs was determined in coloured polyprene fibres and in the waste dye-bath. A recovery test was performed by adding $^{37}Cl_{35}$-labelled 2,3,7,8-TCDD to the dye bath containing the fibres before the dyeing experiment. The complete process of dyeing and finishing is shown in Figure 2.

The final determination of PCDD/Fs in the sample extract was carried out using high resolution gas chromatographic separation on a HP 6890 GC (Hewlett-Packard, Palo Alto, CA, USA) coupled to a Finnigan MAT 95PL (Finnigan, Bremen, Germany) high resolution mass spectrometer. An aliquot (2 μL)

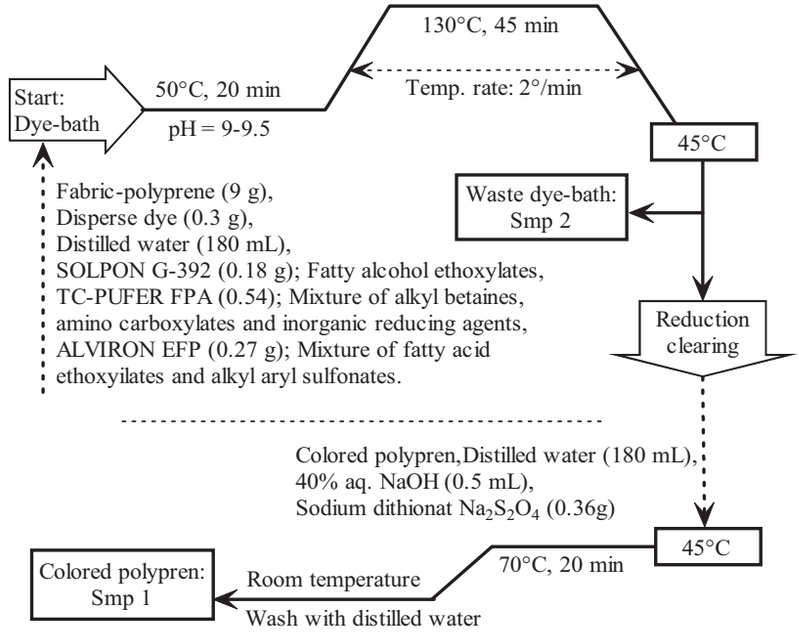

Figure 2. Dyeing method.

of sample was injected into the GC system, equipped with a JW-DB-5MS+DG capillary column (60m x 0.25 mm i.d., film thickness 0.25 μm) in splitless mode. The mass spectrometer operates in the electron impact ionization mode using selected ion monitoring (SIM), at a minimum resolution of 10,000. Samples were analyzed for the PCDD/Fs concentrations using the isotope dilution method based on US EPA 1613 protocol.[15] In addition to daily sensitivity and relative response factor (RRF) checks, the mean RRF was regularly re-evaluated for each congener. Quality control samples were included in the analysis scheme to ensure control of the analysis. Toxic equivalents (TEQs) were calculated using WHO toxic equivalency factors (TEFs).[16]

Results and discussion

All determinations of PCDD/F contents in the dye samples and the dyeing experiment samples were made in duplicate and the results given are the mean values of the two measurements. Among the six analysed samples of textile dyes, only in two disperse black dyes (Dye 1, Dye 2) was a considerable level of PCDD/Fs found (Table 1). OCDD was the dominant compound.

The PCDD/Fs homologue profile of the above mentioned dyes (Figure 3) is similar to that already found in laundry wastewater, domestic wastewater, sewage sludge, dry cleaning residues and some textile samples.[8–12] This profile was annotated to PCDD/Fs patterns connected to pentachlorophenol, suggesting that this could be the source of the PCDD/Fs in these samples. The homologue profile of Dye 1 and Dye 2 differ from homologue profiles found in chloranil-based dyes[12] and Ni-phthalocyanine dyes[13] but agree well with the profile found in some printing inks.[14]

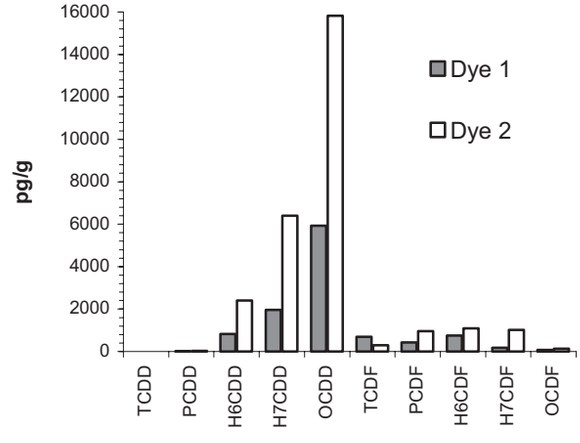

Figure 3. The PCDD/Fs homologue profile of Dye 1 and Dye 2.

The distribution of dioxins and their fate during textile dyeing processes were further investigated. A simple mass balance of PCDD/Fs in dyeing processes was performed, conducted using disperse dyes, Dye 1 and Dye 2. Several precautionary steps were taken to ensure the absence of PCDD/Fs contamination from other sources, as dyes. Prior to the dyeing experiments, all laboratory glassware was rinsed with a toluene-acetone mixture. Concentrations of PCDD/Fs were determined

Table 1. Concentrations of PCDD/Fs and TEQ in disperse dyes (pg/g).

	Concentration (pg/g)					
Congener/Group	Dye 1	Dye 2	Dye 3	Dye 4	Dye 5	Dye 6
2,3,7,8-TCDD	[a]	[a]	[a]	[a]	[a]	[a]
TCDD (tetra dioxins)	[a]	[a]	[a]	[a]	[a]	[a]
1,2,3,7,8-PCDD	[a]	[a]	[a]	[a]	[a]	[a]
PCDD (penta dioxins)	10	24	[a]	[a]	[a]	[a]
1,2,3,4,7,8-H6CDD	[a]	29	[a]	[a]	[a]	[a]
1,2,3,6,7,8-H6CDD	35	219	[a]	[a]	[a]	[a]
1,2,3,7,8,9-H6CDD	8	135	[a]	[a]	[a]	[a]
H6CDD (hexa dioxins)	824	2405	[a]	[a]	27	[a]
1,2,3,4,6,7,8-H7CDD	1131	4408	75	[a]	[a]	[a]
H7CDD (hepta dioxins)	1954	6396	128	[a]	[a]	[a]
1,2,3,4,6,7,8,9-OCDD	5928	15826	331	26	38	9
2,3,7,8-TCDF	[a]	49	[a]	[a]	[a]	[a]
TCDF (tetra furans)	700	301	38	[a]	[a]	[a]
1,2,3,7,8-PCDF	45	96	[a]	[a]	[a]	[a]
2,3,4,7,8-PCDF	12	37	[a]	[a]	[a]	[a]
PCDF (penta furans)	426	954	12	[a]	6	[a]
1,2,3,4,7,8-H6CDF	109	215	[a]	[a]	[a]	[a]
1,2,3,6,7,8-H6CDF	18	74	[a]	[a]	[a]	[a]
2,3,4,6,7,8-H6CDF	85	68	[a]	[a]	93	[a]
1,2,3,7,8,9-H6CDF	30	129	[a]	[a]	[a]	[a]
H6CDF (hexa furans)	759	1096	15	[a]	98	[a]
1,2,3,4,6,7,,-H7CDF	100	421	[a]	[a]	16	[a]
1,2,3,4,7,8,9-H7CDF	57	445	[a]	[a]	10	[a]
H7CDF (hepta furans)	181	1014	[a]	[a]	26	[a]
1,2,3,4,6,7,8,9-OCDF	80	127	[a]	27	25	[a]
Sum PCDD/Fs	**10862**	**28143**	**524**	**53**	**220**	**9**
Sum TEQ-WHO	**50**	**170**	**<5**	**<5**	**10**	**<5**
Sum 2,3,7,8 PCDD/Fs	**7638**	**22279**	**406**	**53**	**182**	**9**

[a] ND (<5) - not determined (<5).

Table 2. Mass balance of PCDD/Fs for the dyeing process with Dye 1.

Congener/Group	Input-Dye 1 (pg-abs)	Smp 1 (pg-abs)	Smp 2 (pg-abs)	Outlet-Sum[a] (pg-abs)
TCDD	[b]	[b]	[b]	[b]
PCDD	[b]	192	24	216
H6CDD	247	2497	345	2842
H7CDD	586	7765	869	8634
OCDD	1778	23812	2938	26750
TCDF	210	320	24	343
PCDF	128	343	57	400
H6CDF	228	329	25	354
H7CDF	54	57	10	67
OCDF	24	34	[b]	34
2,3,7,8-TCDD	[b]	[b]	[b]	[b]
1,2,3,7,8-PCDD	[b]	[b]	[b]	[b]
1,2,3,4,7,8-H6CDD	[b]	65	12	77
1,2,3,6,7,8-H6CDD	10	89	11	100
1,2,3,7,8,9-H6CDD	[b]	61	9	70
1,2,3,4,6,7,8-H7CDD	339	2971	347	3318
1,2,3,4,6,7,8,9-OCDD	1778	23812	2938	26750
2,3,7,8-TCDF	[b]	[b]	[b]	[b]
1,2,3,7,8-PCDF	13	17	[b]	17
2,3,4,7,8-PCDF	[b]	8	[b]	8
1,2,3,4,7,8-H6CDF	33	58	[b]	58
1,2,3,6,7,8-H6CDF	5	[b]	[b]	[b]
2,3,4,6,7,8-H6CDF	25	29	[b]	29
1,2,3,7,8,9-H6CDF	9	21	[b]	21
1,2,3,4,6,7,8-H7CDF	30	38	[b]	38
1,2,3,4,7,8,9-H7CDF	17	21	[b]	21
1,2,3,4,6,7,8,9-OCDF	24	34	[b]	34
Sum PCDD/Fs	**3255**	**35349**	**4292**	**39641**
Sum TEQ-WHO	**13**	**64**	**9**	**73**
Sum 2,3,7,8 PCDD/Fs	**2283**	**27224**	**3317**	**30541**

[a] Sum of absolute amounts of PCDD/Fs in coloured polyprene (Smp 1) and in waste dye-bath (Smp 2). [b] ND (<5) - not determined (<5).

in the raw polyprene fibres, and in the reagents. A blank experiment was performed without the addition of dye. The concentrations of PCDD/Fs in the blank samples were close to the detection limit. The input for mass balance, therefore, presents a content of PCDD/Fs in 0.3 g of dye. For the output, the content of PCDD/Fs was determined in coloured polyprene samples and waste dye-bath samples. The content of PCDD/Fs in the reduction clearing baths was under the detection limit. The mass balance of PCDD/Fs for the dyeing process with Dye 1 is shown in Table 2 and the mass balance of PCDD/Fs for the dyeing process with Dye 2 is shown in Table 3.

After the textile finishing processes with disperse dyes (Dye 1, Dye 2) the content of the PCDD/Fs was approximately tenfold higher. There is strong evidence that PCDD/Fs are formed from precursors´ compounds present in these dyes during the textile finishing processes. The PCDD/Fs homologue profile suggests that in this case chlorinated phenols are most probably precursors´ compounds. More than 85% of the total dioxin content was found in the dyed polyester samples. Other 15% was discharged with waste dye bath.

The aim of further experiments was to determine the point of PCDD/Fs formation in the dyeing experiment, and the influences of dyeing temperature and pH conditions on the formation of PCDD/Fs. The results in Table 4 present the mass balance for dyeing process with Dye 2 at 150 °C for 45 min. Other experimental conditions are the same as in previous experiments.

The results of this experiment are comparable with those results obtained with the described

Table 3. Mass balance of PCDD/Fs for the dyeing process with Dye 2.

Congener/Group	Input-Dye 2 (pg-abs)	Smp 1 (pg-abs)	Smp 2 (pg-abs)	Outlet-Sum[a] (pg-abs)
TCDD	[b]	[b]	[b]	[b]
PCDD	7	110	[b]	110
H6CDD	722	4119	125	4244
H7CDD	1919	7553	174	7727
OCDD	4748	28250	435	28685
TCDF	90	116	[b]	116
PCDF	286	284	[b]	284
H6CDF	329	290	10	300
H7CDF	304	259	6	265
OCDF	38	30	[b]	30
2,3,7,8-TCDD	[b]	[b]	[b]	[b]
1,2,3,7,8-PCDD	[b]	[b]	[b]	[b]
1,2,3,4,7,8-H6CDD	9	61	[b]	61
1,2,3,6,7,8-H6CDD	66	58	[b]	58
1,2,3,7,8,9-H6CDD	40	29	[b]	29
1,2,3,4,6,7,8-H7CDD	1322	3154	70	3224
1,2,3,4,6,7,8,9-OCDD	4748	28250	435	28685
2,3,7,8-TCDF	15	12	ND	12
1,2,3,7,8-PCDF	29	23	[b]	23
2,3,4,7,8-PCDF	11	10	ND	10
1,2,3,4,7,8-H6CDF	65	73	[b]	73
1,2,3,6,7,8-H6CDF	22	25	[b]	25
2,3,4,6,7,8-H6CDF	21	17	[b]	17
1,2,3,7,8,9-H6CDF	39	28	[b]	28
1,2,3,4,6,7,8-H7CDF	126	77	6	83
1,2,3,4,7,8,9-H7CDF	133	145	[b]	145
1,2,3,4,6,7,8,9-OCDF	38	30	[b]	30
Sum PCDD/Fs	**8443**	**41011**	**750**	**41761**
Sum TEQ-WHO	**51**	**73**	**1**	**74**
Sum 2,3,7,8 PCDD/Fs	**6684**	**31992**	**511**	**32503**

[a] Sum of absolute amounts of PCDD/Fs in coloured polyprene (Smp 1) and in waste dye-bath (Smp 2). [b] ND (<5) - not determined (<5).

Table 4. Mass balance of PCDD/Fs for the dyeing process with Dye 2 at higher temperature (150 °C).

Congener/Group	Input-Dye 2 (pg-abs)	Smp 1 (pg-abs)	Smp 2 (pg-abs)	Outlet-Sum[a] (pg-abs)
TCDD	[b]	13	[b]	13
PCDD	7	123	[b]	123
H6CDD	722	3390	58	3448
H7CDD	1919	5868	30	5898
OCDD	4748	21572	279	21851
TCDF	90	162	[b]	162
PCDF	286	233	[b]	233
H6CDF	329	232	[b]	232
H7CDF	304	225	5	230
OCDF	38	24	[b]	24
2,3,7,8-TCDD	[b]	[b]	[b]	[b]
1,2,3,7,8-PCDD	[b]	[b]	[b]	[b]
1,2,3,4,7,8-H6CDD	9	14	[b]	14
1,2,3,6,7,8-H6CDD	66	57	[b]	57
1,2,3,7,8,9-H6CDD	40	34	[b]	34
1,2,3,4,6,7,8-H7CDD	1322	2567	30	2597
1,2,3,4,6,7,8,9-OCDD	4748	21572	279	21851
2,3,7,8-TCDF	15	11	[b]	11
1,2,3,7,8-PCDF	29	15	[b]	15
2,3,4,7,8-PCDF	11	6	[b]	6
1,2,3,4,7,8-H6CDF	65	70	[b]	70
1,2,3,6,7,8-H6CDF	22	17	[b]	17
2,3,4,6,7,8-H6CDF	21	14	[b]	14
1,2,3,7,8,9-H6CDF	39	27	[b]	27
1,2,3,4,6,7,8-H7CDF	126	63	5	68
1,2,3,4,7,8,9-H7CDF	133	133	[b]	133
1,2,3,4,6,7,8,9-OCDF	38	25	[b]	25
Sum PCDD/Fs	**8443**	**31842**	**372**	**32214**
Sum TEQ-WHO	**51**	**58**	**1**	**59**
Sum 2,3,7,8 PCDD/Fs	**6684**	**24625**	**314**	**24939**

[a] Sum of absolute amounts of PCDD/Fs in coloured polyprene (Smp 1) and in waste dye-bath (Smp 2). [b] ND (<5) - not determined (<5).

dyeing conditions (Table 2). These results suggest that temperature has no significant influence on the formation of PCDD/Fs during the dyeing process.

Finally, the dyeing experiment was performed with Dye 1 as described in Figure 2, but without the reduction clearing finishing process. The PCDD/Fs content was determined in waste dye bath and in the dyed polyprene sample prior to reduction clearing (Table 5).

The results of the performed experiments suggest that formation of PCDD/Fs mainly occurs during dyeing (not reduction clearing), and that higher temperature (150 °C) has no significant influence on PCDD/F formation.

We also investigated the influence of pH-conditions on PCDD/Fs formation during analysis of the dye samples. PCDD/Fs are, according to literature, very stable under acid conditions. Acid wash sample treatment is often used for analytical sample treatment, especially for the cleanup of biological samples.[17–19] On the other hand, it was confirmed that dechlorination of PCDD/Fs occurs in the high alkaline solutions.[20] For this purpose three samples of Dye 1 analyses were separately treated under different pH-conditions (Table 6). The cleanup of organic (hexane) extract was the same for all samples as previous described. The results are shown in Table 7.

Table 5. Mass balance of PCDD/Fs for the dyeing process with Dye 1 without reduction clearing.

Congener/Group	Input-Dye 1 (pg-abs)	Smp 1 (pg-abs)	Smp 2 (pg-abs)	Outlet-Sum[a] (pg-abs)
TCDD	[b]	15	[b]	15
PCDD	[b]	77	5	82
H6CDD	247	1904	93	1997
H7CDD	586	4589	189	4778
OCDD	1778	19455	579	20034
TCDF	210	344	19	363
PCDF	128	271	23	294
H6CDF	228	204	11	215
H7CDF	54	99	14	113
OCDF	24	37	7	44
2,3,7,8-TCDD	[b]	[b]	[b]	[b]
1,2,3,7,8-PCDD	[b]	[b]	[b]	[b]
1,2,3,4,7,8-H6CDD	[b]	40	[b]	40
1,2,3,6,7,8-H6CDD	10	47	[b]	47
1,2,3,7,8,9-H6CDD	[b]	21	[b]	21
1,2,3,4,6,7,8-H7CDD	339	1739	70	1809
1,2,3,4,6,7,8,9-OCDD	1778	19455	579	20034
2,3,7,8-TCDF	[b]	[b]	[b]	[b]
1,2,3,7,8-PCDF	13	15	[b]	15
2,3,4,7,8-PCDF	[b]	7	[b]	7
1,2,3,4,7,8-H6CDF	33	43	[b]	43
1,2,3,6,7,8-H6CDF	5	[b]	[b]	[b]
2,3,4,6,7,8-H6CDF	25	29	[b]	29
1,2,3,7,8,9-H6CDF	9	19	[b]	19
1,2,3,4,6,7,8-H7CDF	30	46	11	57
1,2,3,4,7,8,9-H7CDF	17	24	[b]	24
1,2,3,4,6,7,8,9-OCDF	24	37	7	44
Sum PCDD/Fs	**3255**	**26995**	**940**	**27935**
Sum TEQ-WHO	**13**	**44**	**3**	**47**
Sum 2,3,7,8 PCDD/Fs	**2283**	**21522**	**667**	**22189**

[a] Sum of absolute amounts of PCDD/Fs in coloured polyprene (Smp 1) and in waste dye-bath (Smp 2). [b] ND (<5) - not determined (<5).

Table 7. Determined concentrations of PCDD/Fs in Dye 1 using different approaches in sample preparation.

Congener/Group	Dye 1 (pg/g)	Dye 1/KOH (pg/g)	Dye 1/H_2SO_4 (pg/g)
TCDD	[a]	25	24
PCDD	10	14	12
H6CDD	824	317	354
H7CDD	1954	403	394
OCDD	5928	1141	1145
TCDF	700	637	659
PCDF	426	319	284
H6CDF	759	300	289
H7CDF	181	75	79
OCDF	80	49	47
2,3,7,8-TCDD	[a]	25	24
1,2,3,7,8-PCDD	[a]	13	9
1,2,3,4,7,8-H6CDD	[a]	[a]	[a]
1,2,3,6,7,8-H6CDD	35	19	[a]
1,2,3,7,8,9-H6CDD	8	70	69
1,2,3,4,6,7,8-H7CDD	1131	210	210
1,2,3,4,6,7,8,9-OCDD	5928	1141	1145
2,3,7,8-TCDF	[a]	25	27
1,2,3,7,8-PCDF	45	34	21
2,3,4,7,8-PCDF	12	19	15
1,2,3,4,7,8-H6CDF	109	41	35
1,2,3,6,7,8-H6CDF	18	16	18
2,3,4,6,7,8-H6CDF	85	31	30
1,2,3,7,8,9-H6CDF	30	36	36
1,2,3,4,6,7,8-H7CDF	100	47	53
1,2,3,4,7,8,9-H7CDF	57	32	25
1,2,3,4,6,7,8,9-OCDF	80	49	47
Sum PCDD/Fs	**10862**	**3280**	**3287**
Sum TEQ-WHO	**50**	**76**	**66**
Sum 2,3,7,8 PCDD/Fs	**7638**	**1808**	**1764**

[a] ND (<5) - not determined (<5).

Table 6. Different approaches in sample preparation.

Sample:	**Dye 1**	**Dye 1/KOH**	**Dye 1/H_2SO_4**
Dissolving	EtOH: H_2O (150 mL)	2 M KOH/H_2O (150 mL)	2 M H_2SO_4/H_2O (150 mL)
Extraction/time	Hexane 50 mL/ 24 h	Hexane 50 mL/ 24 h	Hexane 50 mL/ 24 h

It is evident from the results that transformation reactions of PCDD/Fs occur during KOH and H_2SO_4 sample treatment (dechlorination, chlorination, molecule splitting…), resulting in higher concentrations of lower, and more toxic, congeners (TCDD) and in the decreasing of higher chlorinated compounds (OCDD). Our results are comparable with those obtained by catalytic transformation processes of PCDD/Fs in the presence of a metal catalyst (Pd,Pt,Zn),[21–25] and suggest that sample treatment conditions are very important for the formation/transformation of PCDD/Fs and, therefore, for accurate determination of PCDD/Fs in textile dye samples.

Conclusions

We analyzed six textile dyes for PCDD/Fs. In two disperse black dyes which were a mixture of anthraquinone disperse and azo-disperse dyes, considerable levels of PCDD/Fs were determined. The PCDD/Fs homolouge profile found in these dyes is similar to that found previously in textiles and samples connected with the textile industry.

Furthermore, dyes, Dye 1 and Dye 2, contaminated with dioxins were used in industrial polyester dyeing processes at laboratory scale and the distribution of dioxins and their fate during textile processes was investigated. After the textile finishing processes the content of the PCDD/Fs was approximately tenfold higher. There is strong evidence that PCDD/Fs are formed from precursors´ compounds in contaminated dyes under specific conditions during textile finishing processes.

Preliminary results, using different approaches for Dye 1 sample analysis, suggest that in the case of dye-sample preparation for PCDD/Fs analysis, the pH conditions are very important. Textile dyes are complex mixtures with additives which may act like a catalyst for the dechlorination and/or formation of PCDD/Fs under specific conditions.

Our future work will further investigate the presence of PCDD/Fs in textile dyes. The distribution of dioxins and their fate during textile processes will be investigated. Emphasis will be devoted to the photo transformation processes of dioxins in textile wastewaters and textiles, when coloured with contaminated dyes. The use of ultraviolet light for the degradation and elimination of organic pollutants in contaminated wastewaters is now one of the used processes. Textile wastewaters differentiate in quantities and types of suspended particles, as well as in dissolved organic materials that could either retard or enhance the photolysis of PCDD/Fs. Irradiation of waste waters with powerful (up to 300 kW) UV lamps with H_2O_2, NaOCl, Fenton's regent, etc. as catalysts could be the source of lower chlorinated and more toxic dioxin congeners.

The production of dyes and their use is a less investigated source of dioxins. Our results confirm that the presence of dioxins in some dyes may be a significant source regarding human exposure and environmental contamination. Regulation for dioxins in dyes and textiles is obsolete and indistinct in comparison with regulations for other matrices. Regulation for dioxins in substances, preparations and articles (apparel product) was amended in 1994 with the implementation, in 1996 of Germany jurisdiction.[26] This regulation is also valuable for dyes and textiles and is valid world-wide. However, information about the emissions of dioxins from the textile industry is limited, with a lack of complete and accurate emission data. The minimisation of environmental and human exposure will be difficult without a full knowledge of dioxins sources.

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Povzetek

Dioksine predstavljata skupini toksičnih obstojnih spojin polikloriranih dibenzo-*p*-dioksinov in polikloriranih dibenzofuranov. V okviru naših raziskav smo preverili prisotnost dioksinov v tekstilnih barvilih. Analizirali smo šest vzorcev tekstilnih barvil. V dveh vzorcih tekstilnih disperznih barvil smo določili znatne vsebnosti dioksinov. Porazdelitev dioksinov v teh vzorcih barvil je podobna porazdelitvi dioksinov določeni v nekaterih vzorcih povezanih s tekstilno industrijo. Barvila, ki vsebujejo dioksine smo uporabili v poizkusih barvanja in spremljali spremembe v porazdelitvi in koncentraciji dioksinov skozi postopek barvanja. Masna bilanca dioksinov v postopku barvanja pokaže povečanje vsebnosti dioksinov, medtem ko ostaja njihova porazdelitev nespremenjena. Pri barvanju pri visokih temperaturah in v alkalnem mediju nastajajo dioksini iz prekurzorskih (predhodnih) spojin. Več kot 85% celotne vsebnosti dioksinov smo določili v vzorcih obarvanega poliestra. Preostalih 15% smo določili v odpadni barvalni kopeli. Rezultati raziskav dokazujejo, da prisotnost dioksinov v nekaterih tekstilnih barvilih predstavlja znaten doprinos k vsebnosti teh spojin v širšem okolju.