Textile dyes and pigments as a source of dioxins

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Introduction

Synthesis of colorants represents a relatively large group of chemicals with complex synthesis processes. Over $7x10^5$ ton of dyestuff is produced annually worldwide with more than 100,000 types of dyes and pigments. During synthesis of some colorants polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) can be formed. Dioxins are related to halogens, especially chlorine and bromine homologues are most toxic and persistent. About 40% of worldwide used colorants contain organically bounded chlorine. Further formations of PCDD/Fs can occur via dyeing and textile finishing processes with conditions favoured for the generation of PCDD/Fs (high temperatures, alkaline conditions, UV radiations or other radical starters).
Relative small number of data is available for PCDD/Fs presence and contents in textile dyes and pigments. Known sources of PCDD/Fs are dioxazine dyes and pigments, produced from chloranil[1]. Chloranil is produced from chlorinated phenols and during the synthesis PCDD/Fs as by products are formed. In a sample of Ni-phthalocyanine dye higher congeners of PCDD/Fs were found in µg/kg concentration level[2].
In our work six samples of disperse dyes were analysed for PCDD/Fs content. In two disperse black dyes, a mixture of anthraquinone and azo-disperse dye, considerable level (µg/kg) of PCDD/Fs was determined. The OCDD was the dominant compound. Distribution of dioxins and their fate during textile processes were further investigated.

Methods and Materials

Experiment 1: Dye samples were spiked with an internal standard mixture containing $^{13}C_{12}$-labeled isomers, diluted in ethanol-water mixture and extracted with hexane. Cleanup of extract was performed on a mixed column (layers: silica gel/sulphuric acid, silica gel/KOH and silica gel) followed by the additional cleaning using adsorption chromatography on graphitised carbon column. Quantification was performed using high resolution gas chromatography/high resolution mass spectrometry (Finnigan MAT 95PL) at resolution of 10,000. Results are presented in Table 1.

Experiment 2: A disperse dye which contains PCDD/Fs was used in industrial polypren fibrous dyeing process. Two dyeing experiments were separately performed with 9g of polypren fibrous. Dyeing was carried out in a laboratory scale dyeing machine equipped with infrared heating, in stainless steel dyepots of 200 cm^3 capacity. The dyeing method is shown in Figure 1. At the end of dyeing the dyed samples were reduction cleared using the method shown in Figure 2. After the treatment, the samples were rinsed with distilled water and dried in the open air. Concentration of PCDD/Fs was determined in coloured polypren and in dye-bath. Sample of polypren fibrous (Smp. 1) was Soxhlet extracted with toluene for 10 hours. Dyes bath was spiked with the internal standard mixture and extracted with hexane (Smp. 2). The sample cleaning and quantification was performed as described in Experiment 1.

Figure 1: Dyeing method

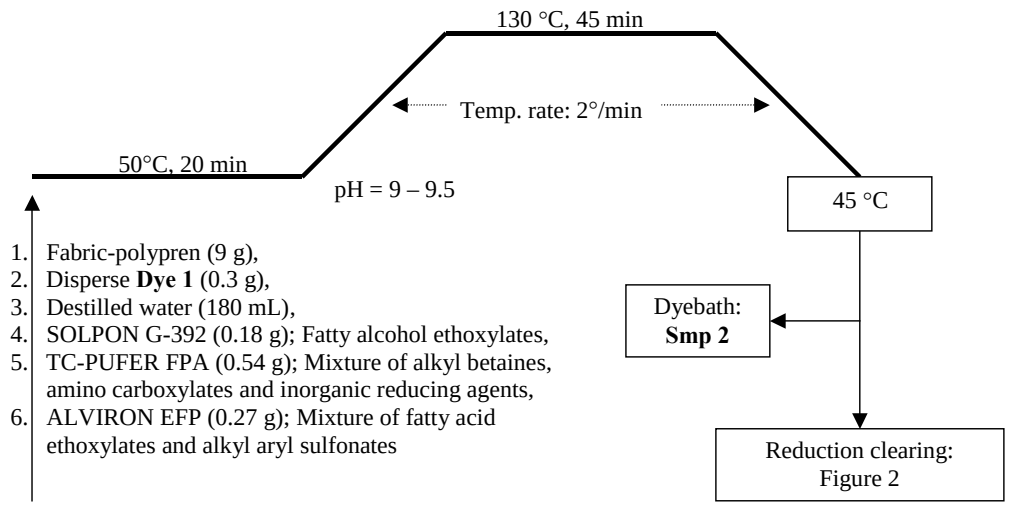
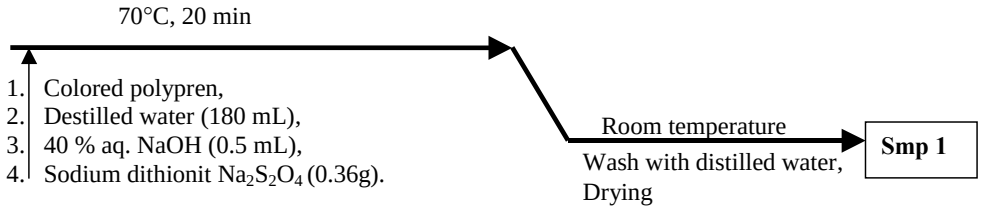


Figure 2: Reduction clearing



Blank samples: Prior dyeing experiments, all laboratory glassware was rinsed with toluene-acetone mixture. Concentrations of PCDD/Fs were determined in raw polypren fabrics and in reagents. The concentrations of PCDD/Fs in these samples were close to detection limit.

Results and Discussion

All the determinations were made in duplicate and the results given are the mean values of the two measurements.
In two disperse black dyes, a mixture of anthraquinone and azo-disperse dyes (Dye 1, Dye 2), a considerable level of PCDD/Fs was determined (Table 1). The OCDD was the dominant homologue. The homologue profile of these dyes is similar to that found in laundry wastewater, domestic wastewater, sewage sludge, dry cleaning residues and some textile samples [3,4]. 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 differs from homologue profiles found in chloranil-based dyes and Ni-phthalocyanine dyes but agrees well with the profile found in some printing inks[5].

Table 1: Results of experiment 1; concentrations of PCDD/Fs in dyes samples.

	Concentration (ng/kg)					
Congener/Group	**Dye 1**	**Dye 2**	**Dye 3**	**Dye 4**	**Dye 5**	**Dye 6**
2,3,7,8-TCDD	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
Σ TCDD	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
1,2,3,7,8-PCDD	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
Σ PCDD	10	24	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
1,2,3,4,7,8-H6CDD	ND (< 5)	29	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
1,2,3,6,7,8-H6CDD	35	219	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
1,2,3,7,8,9-H6CDD	8	135	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
Σ H6CDD	824	2405	ND (< 5)	ND (< 5)	27	ND (< 5)
1,2,3,4,6,7,8-H7CDD	1131	4408	75	ND (< 5)	ND (< 5)	ND (< 5)
Σ H7CDD	1954	6396	128	ND (< 5)	ND (< 5)	ND (< 5)
1,2,3,4,6,7,8,9-OCDD	5928	15826	331	26	38	9
2,3,7,8-TCDF	ND (< 5)	49	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
Σ TCDF	700	301	38	ND (< 5)	ND (< 5)	ND (< 5)
1,2,3,7,8-PCDF	45	96	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
2,3,4,7,8-PCDF	12	37	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
Σ PCDF	426	954	12	ND (< 5)	6	ND (< 5)
1,2,3,4,7,8-H6CDF	109	215	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
1,2,3,6,7,8-H6CDF	18	74	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
2,3,4,6,7,8-H6CDF	85	68	ND (< 5)	ND (< 5)	93	ND (< 5)
1,2,3,7,8,9-H6CDF	30	129	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
Σ H6CDF	759	1096	15	ND (< 5)	98	ND (< 5)
1,2,3,4,6,7,8,-H7CDF	100	421	ND (< 5)	ND (< 5)	16	ND (< 5)
1,2,3,4,7,8,9-H7CDF	57	445	ND (< 5)	ND (< 5)	10	ND (< 5)
Σ H7CDF	181	1014	ND (< 5)	ND (< 5)	26	ND (< 5)
OCDF	80	127	ND (< 5)	27	25	ND (< 5)
Sum PCDD/F	**14350**	**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**

Mass balance of PCDD/Fs in dyeing process shows increasing of PCDD/Fs. After textile dyeing in finishing processes the content of the dominant compound OCDD was approximately fifteen times higher. There is a strong evidence that PCDD/Fs are formed from precursors compounds in contaminated dyes during textile finishing processes. In our further work the chemistry of these dyes will be investigated. Distribution of dioxins and their fate during textile processes will still be investigated. Emphasis will be devoted to phototransformation processes of dioxins in textile wastewaters and textiles, coloured with contaminated dyes.

Table 2: Results of experiment 2; mass balance of PCDD/Fs.

Congener/Group	Input-Dye 1[a)] (pg-abs)	Smp 1 (pg-abs)	Smp 2 (pg-abs)	Outlet-Sum[b)] (pg-abs)
2,3,7,8-TCDD	ND	ND	ND	ND
Σ TCDD	ND	ND	ND	ND
1,2,3,7,8-PCDD	ND	ND	ND	ND
Σ PCDD	3	192	24	216
1,2,3,4,7,8-H6CDD	ND	65	12	77
1,2,3,6,7,8-H6CDD	10.5	89	11	100
1,2,3,7,8,9-H6CDD	2.4	61	9	70
Σ H6CDD	247	2497	345	2842
1,2,3,4,6,7,8-H7CDD	339	2971	347	3318
Σ H7CDD	586	7765	869	8634
1,2,3,4,6,7,8,9-OCDD	1778	23812	2938	26750
2,3,7,8-TCDF	ND	ND	ND	ND
Σ TCDF	210	320	24	343
1,2,3,7,8-PCDF	13.5	17	ND	17
2,3,4,7,8-PCDF	3.6	8	ND	8
Σ PCDF	128	343	57	400
1,2,3,4,7,8-H6CDF	33	58	ND	58
1,2,3,6,7,8-H6CDF	5.4	ND	ND	ND
2,3,4,6,7,8-H6CDF	25.5	29	ND	29
1,2,3,7,8,9-H6CDF	9	21	ND	21
Σ H6CDF	228	329	25	354
1,2,3,4,6,7,8,-H7CDF	30	38	ND	38
1,2,3,4,7,8,9-H7CDF	17.1	21	ND	21
Σ H7CDF	54.3	57	10	67
OCDF	24	34	ND	34
Sum PCDD/F	**4275**	**35414**	**4292**	**39706**
Sum TEQ-WHO	**15**	**64**	**9**	**73**
Sum 2,3,7,8 PCDD/Fs	**2291**	**27224**	**6634**	**33858**

a) Theoretic absolute amount of PCDD/Fs in input Dye 1 (0.3 g); b) Sum of absolute amounts of PCDD/Fs in Smp 1 and Smp 2.

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