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Review

Dioxins and Dioxin-like Persistent Organic Pollutants in Textiles and Chemicals in the Textile Sector

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Over 7×10^5 tons of dye-stuff is produced annually with more than 100,000 commercially available dyes. Synthesis of colorants involves a relatively large group of chemicals with complex syntheses. During the synthesis of colorants, highly toxic, carcinogenic and persistent organic compounds, such as dioxins, can be formed. Dioxins are related to halogens, chlorine and bromine homologues being the most toxic and persistent. About 40 % of globally used colorants contain organically bound chlorine. The use of colorants in the textile industry, with their wide applications and complex chemistry could be a significant source of dioxins and/or precursor compounds for the formation of dioxins and other persistent organic pollutants (POPs). The aim of the paper is to give an overview of the dioxin-like compounds in chemicals, with an emphasis on colorants, textiles and their fate in the environment.

INTRODUCTION

Persistent organic pollutants (POPs) are widespread organic compounds, mostly from an anthropogenic source. These persistent, semi volatile, bio-accumulative and toxic compounds are causing increasing concern. Some POPs are produced deliberately (pesticides), others are formed as by-products or accidentally (PCDD/Fs). Groups of POPs are mostly chlorine related. More than 60 % of products of the European chemical industry either contain chlorine or are produced with the aid of chlorine.[1]

The UN Environmental Programme (UNEP) global protocol has proposed a list of 12 POPs (Table I) with 3 broad categories of POPs: pesticides, industrially-produced chemicals and by-products and contaminants. A Convention for the control of POPs is currently being developed along with a mechanism by which additional chemicals may be added to the list of POPs.[2]

The most toxic among POPs are the commonly named dioxins and dioxin-like compounds. Dioxin is the term for a group of chemical compounds with 75 polychlorinated dibenzo-*p*-dioxins (PCDDs) and 135 polychlorinated dibenzofurans (PCDFs).[3] They are very similar in structure, differing only in the number and spatial arrangement of chlorine atoms in the molecule. In this group, isomers with chlorine atoms at positions 2,3,7,8 are especially toxic. The so-called "dirty group" comprises 17 isomers of PCDD/Fs, among which 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) is the most toxic (Figure 1). There are also brominated dioxins (PBDD/Fs), fluoro dioxins and mixed dioxins PXDD/Fs (X = Cl, Br, F). PBDD/Fs are contaminants with properties similar to polychlorinated

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TABLE I. List of UNEP-POPs

[a]Pesticides	[b]Industrial Chemicals		[c]By products
Aldrine[a]	Dieldrin[a]	Mirex[a]	Hexachlorobenzene[a,b,c]
Chlordane[a]	Dioxins (PCDDs)[c]	Furans (PCDFs)[c]	Heptachlor[a]
DDT[a]	Endrin[a]	PCBs[b,c]	Toxaphene[a]

$X + Y = 1–8$ (75 congeners)

Polychlorinated dibenzo-*p*-dioxins

$X + Y = 1–8$ (135 congeners)

Polychlorinated dibenzofurans

Figure 1. Molecular structure of the polychlorinated dibenzo-*p*-dioxins and dibenzofurans.

dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs), together with their persistence and toxicity.[4,5] Fluorinated congeners of dioxins are taken to be less dangerous to humans and the environment due to their short half-life and low toxicity.[6]

Dioxins are present in traces in all matrices in the environment. They tend to bind to organic matter in sediments and soils, accumulate in fatty tissues, and they can be transported over long distances from the source of emission. In the environment, they can be quickly transported to great distances through evaporation and condensation cycles.[7] As a result of global circulation patterns and low evaporation rates in cold climates, dioxins tend to accumulate in arctic regions where they bio-accumulate in living organisms.[8] They pass to humans through the food chain. In humans, dioxins have a half-life time of 7–15 years. Exposure to even low doses of dioxins can lead to cancer, damage to the nervous system, immune system diseases and reproductive disorders.[9] Dioxins appear to act like extremely persistent synthetic hormones. They bind effectively to specific aryl hydrocarbon receptors (AhR) in living cells and trigger a chain of reactions resulting in biochemical and cellular changes.[10]

Over recent decades, a great deal of emphasis has been placed on evaluating the dioxin-like toxicity.[11] Risk assessment of dioxins is based on the concept of a toxic equivalency factor (TEF). The use of TEFs provides a simple, single number toxic equivalent (TEQ), which is an indicator of the overall toxicity of a sample. Within the TEQ method, TEF is assigned to each PCDD/F.[12] With the strongest affinity to AhR receptors, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) is the most toxic and has a TEF equal to one. Several other compounds, which have similar structures, do not bind as strongly to the AhR as TCDD and, therefore, larger doses are required to achieve a comparable effect.

Many organizations and research institutes from different countries are involved in the process of defining hazardous substances and reviewing strategies in order to control pollution by POPs. The main goal is to reduce pollution to levels that will be harmless to man and/or nature.

SOURCES AND PROPERTIES OF PCDD/Fs

Many studies have been reported on the emission sources of dioxins.[13] PCDD/Fs have been found in a series of historical sediment cores samples, the primary sources being incineration and combustion processes.[14] Concentrations found in the oldest samples are around 10–20 % of the concentrations found in samples from the 1990s. About 80–90 % of the present contribution relates to the chlorine based industry. High contamination of hepta and octa PCDD occurred in the post-1940 decade because of a commercial pentachlorophenol introduced at that time. The major sources of lower chlorinated PCDD/Fs are combustion and incineration processes in pre- and post-1940 samples. Environmental concentrations peaked in the 1960s and early 1970s and are now decreasing.

According to the European Dioxin Air Emission Inventory Project stage I,[15] which reflected the emission situation in the period 1993–1995, emissions from municipal solid waste incinerators are still the largest contributors to overall dioxin emission. Dioxin sources from iron-ore sintering plants are of similar emission importance. Further, emissions from hospital waste incineration and secondary non-ferrous metal production were identified as considerable contributors. Non-industrial processes such as domestic wood and coal combustion, accidental fires, traffic emissions, dioxin release from pentachlorophenol (PCP) treated wood were found to be significant, but with less quantifiable emission sources. A number of potential and relevant dioxin emission sources and pathways have not been investigated, especially non-atmospheric emission pathways. In the near future emissions from non-industrial sources are likely to exceed those from industrial installations. 90 % emission reduction will be achieved for some main industrial source types.

Chemical Manufacturing and Processing Sources

The chemical industry is an important source of dioxins (PCDD/Fs) as by-products[16] (Table II). PCDD/Fs can be formed during the synthesis of chlorophenols, chlorobenzenes, chlorobiphenyls, polyvinyl chloride, dyes, pigments, printing inks and halogenated pesticides. Generation of PCDD/Fs for chemical manufacturing processes is favoured if one or several conditions below apply:[17]

- High temperatures (>150 °C);
- Alkaline conditions;
- UV radiations or other radical starters;
- Presence of chlorinated organic compounds;
- Presence of metal catalysts.

TABLE II. Source of PCDD/Fs in the chemical industry

Chemical Industry	Products with the potential for formation and/or release of PCDD/Fs
Bleached chemical wood pulp and paper mills	bleached pulp wastewater sludge wastewater effluent
Manufacture of chlorine, chlorine derivates, and metal chlorides	chlorine, chlorine dioxide, metal chlorides
Manufacture of halogenated organic chemicals	chlorophenols, chlorobenzens, chlorobiphenyls, polyvinyl chloride, aliphatic chlorine compounds, dyes, pigments, printing inks, halogenated pesticides

Maximum emission levels have been set for the main industrial sources. Also, decreasing or constant emissions can be presumed for the majority of the other industrial sources considered. Neither the industrial nor the non-industrial sector, taken as a whole, is likely to achieve an emission reduction of 90 % in 2005 compared to the 1985 situation.

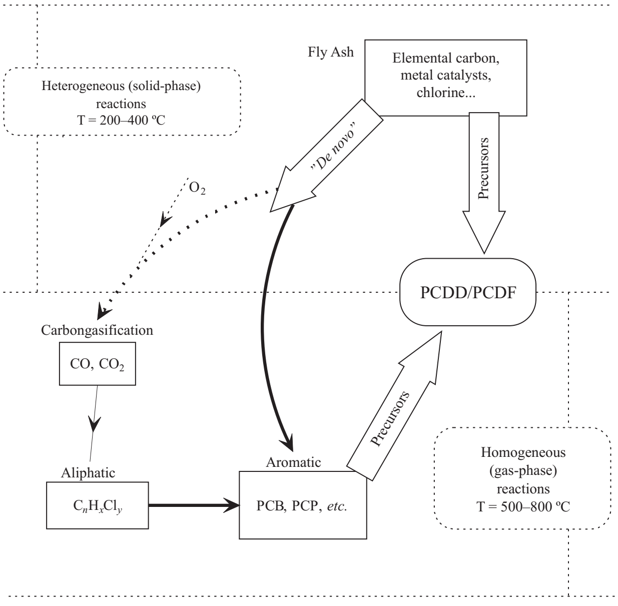

Figure 2. Shematic representation of the pathaways for PCDD/Fs formation.

Formation of PCDD/Fs

Thermal processes are the main source of dioxins. They are formed in the gas phase at temperatures above 500 °C and on the surface of the solid phase in the temperature range 200–400 °C[18] (Figure 2). Several theories have been put forward to explain the dioxin formation (Table III). Dioxins could be formed through the coupling of polychlorinated phenols, polychlorinated benzenes (precursors) or *via* a "*de novo*" mechanism from different sources of chlorine and oxygen on the carbon surface, with metal ions as the catalyst.

The Precursor Concept: A catalytic surface reaction on the fly ash from adsorbed precursors seems to be the major formation mechanism.[19] The precursor concept allows any number of possible organic precursor compounds to be the starting point.

De novo *Mechanism:* Organic particulate carbon is the starting precursor; dioxins are produced through a series of reactions (transfer of chlorine to carbonaceous particulate material with the formation of a carbon-chlorine bond and oxidation degradation of the macromolecular structure to carbon dioxide, along with the release of chloroaromatics like dioxins and furans).

Fly ash is a very complex matrix of numerous adsorbed compounds. Particle size distribution differs from one incineration process to another, and elemental composition also varies. Some metals and metal oxides incorporated into the fly ash surface suppress the formation of dioxins (Cu, Fe, Al) while others, such as Pb, retard it. Dioxin patterns are typical of specific processes.

Well known and investigated formations are photochemical formation processes of PCDD/Fs from chlorophenols, especially from pentachlorophenol (PCP)[20] (Figure 3). Photolytic formation of OCDD occurs when PCP is irradiated with natural or artificial light sources. Hexa and hepta chloro isomers of PCDDs are generated through the photo degradation of OCDD.

Environmental Behaviour of Dioxins

Atmospheric transport is the main long-range transport pathway for POPs, especially for PCDDs/Fs, which are more volatile. The levels, behaviour and processes in the

TABLE III. Theories of thermal formation of PCDD/Fs.

Theories	Mechanism	Catalyst	Reference
Precursor concept	Coupling of polychlorinated phenols, polychlorinated benzenes and other organohalogen compounds	Catalytic surface reaction on the fly-ash	[18,59,60]
"De novo"	Formation from organic particulate carbon, chlorine and oxygen through series of reactions	Metals and metals oxides incorporated into fly-ash surface (Cu, Fe, Al)	[18,59,58]

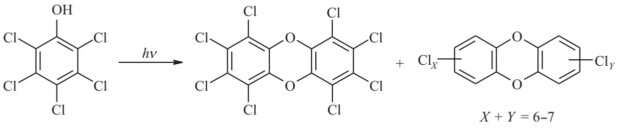

Figure 3: Photochemical formation of PCDDs from pentachlorphenol.

air and deposition have been comprehensively reviewed by Jones *et al.*[21] It has been often reported that there is quite a consistent homologue pattern of PCDD/Fs in the air, except for important local sources. After emission from primary sources, dioxins' fate and partition are determined in a competition of gaseous air-water exchange, particle-bound deposition and degradation. Potentially, the mixture of dioxins in the vapour phase can be selectively time/congener degraded by photolysis and reaction with OH-radicals. Dioxins, bounded by particles, are thought to be protected from atmospheric degradation reactions.

In general, dioxins are hardly water soluble with high octanol-water coefficients (K_{ow}). In environmental systems, they tend to bind to soil/sediments and other particles. Transport pathways and a number of aspects of dioxin behaviour in an aquatic environment have been reviewed by Fletcher and McKay.[22] Sorption to sediments, soils and dissolved organic matter strongly controls their environmental transport, fate and uptake by organisms. Equilibrium partitioning for several organohalogen compounds, including PCDD/Fs, between contaminated sediments and water was observed and described by Evers *et al.*[23] Equilibrium partitioning between the solid and aqueous phases, and the kinetics of the adsorption and desorption processes are influenced by numerous potential factors such as the amount and characteristics of the sediment, presence of dissolved organic matter in the aqueous phase, temperature, *etc.* The main pathway for the movement of dioxins in an aquatic environment is through the aquatic food chain.

Photolysis appears to be one of the most significant degradation mechanisms for PCDD/Fs in the environment. PCDD/Fs adsorb electromagnetic radiation at wavelengths higher than 290 nm and, therefore, can be degraded and/or transformed by sunlight.[24] Following the first order kinetics, PCDD/Fs undergo rapid photolysis in a variety of organic solvents and at much slower rates in water.[25]

A major photolytic pathway appears to be photodechlorination, resulting in the formation of lower chlorinated PCDD/Fs. A more important pathway for lower chlorinated PCDD/Fs is carbon-oxygen cleavage. Photolytic degradation products from the irradiation of PCDD/Fs in solvents may be significantly different from those observed when particulate-adsorbed and gas phase PCDD/Fs are irradiated.

Photolysis of PCDD/Fs in pure water is slow but increases dramatically when organic solvents are present as hydrogen donors. Solution studies report a preferential loss of chlorines from the lateral position (chlorines at positions 2,3,7,8) rather than from the peri position (chlorines at positions 1,4,6,9,). The opposite trend is observed when particulate-adsorbed and gas phase PCDD/Fs are irradiated. Natural and waste waters differ in quantities and types of suspended particulates and dissolved organic materials that could either retard or enhance the photolysis of PCDD/Fs.

DIOXINS AND DIOXIN-LIKE COMPOUNDS IN THE TEXTILE SECTOR

Textile products often contain chemicals such as formaldehyde, azo-dyes, dioxin and pesticides as well as heavy metals that might pose a risk to humans and the environment. Some of these chemicals found in finished products are there as residues from the production, others are added to give certain characteristics to the products (colour, flame retardancy, *etc.*).

The textile industry is a potential source of PCDD/Fs:[26]

– Pesticides such as pentachlorophenol, known to be contaminated with PCDD/Fs. Pentachlorophenol is used as a biocide for cotton and other materials;

– Dyestuffs contaminated by PCDD/Fs;

– Textile processes may utilize chlorinated chemicals contaminated by PCDD/Fs;

– Washing processes in alkaline media are part of the textile finishing processes;

– Large volumes of effluent water are released into the environment.

PCDD/Fs were detected in nearly all sewage sludges tested in Germany.[27] It was discovered that household wastewaters could be a great source of contamination.[28] 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 wastewater treatment plants.[29] Furthermore, a logical category of products were tested to determine the sources of dioxins.

PCDD/Fs were determined in different new garments in concentrations ranging from low pg/g to high 300 ng/g, with the OCDD as the dominant homologue.[30,31] Dioxin homologue patterns that were found in more contaminated textile samples were annotated to PCDD/F patterns connected with pentachlorophenol and chloranil based dyes.

Contamination of textile fibres during the production and finishing was investigated by Horstman *et al.*[32] Cotton cloth was subjected to a series of 16 typical finishing processes and analyzed for PCDD/Fs at various stages of treatment. Their concentration was very low in all samples. Maximum concentrations found in raw textile products were 30 ng/kg in cotton and 45 ng/kg in synthetic materials. Concentration increases during treatment processes

TABLE IV. Maximum concentration of PCDD/Fs determined in dyes, pigments and printing inks

	Maximum concentration found in dyes and pigments / ng kg^{-1}				
Congener/Group	Blue 106	Blue 108	Violet 23	Rotogravure-ink	Offset-ink
Σ TCDD	ND (0.3)	ND (0.3)	ND (0.3)	4	77
Σ PCDD	ND (0.3)	ND (0.3)	ND (0.3)	58	35
Σ H6CDD	ND (0.3)	1	21	2679	660
Σ H7CDD	34	ND (0.3)	30	5630	1100
OCDD	41953	23	7180	5810	890
Σ TCDF	ND (0.3)	ND (0.3)	ND (0.3)	5.5	90
Σ PCDF	ND (0.3)	ND (0.3)	0.5	13	340
Σ H6CDF	12	ND (0.3)	76	29	95
Σ H7CDF	71	12	26	64	566
OCDF	12463	11	941	129	960
Sum PCDD/F	54533	47	8275	14422	4813
Sum TEQ-WHO	7.45	0.1	8.7	87.2	41.2
Sum 2,3,7,8 PCDD	41984	23	7189	9087	1585
Sum 2,3,7,8 PCDF	12525	20	1031	175.5	1320

were attributable to an increase in OCDD. The contribution of textile production and finishing to the PCDD/Fs concentration increase in dyeing and in 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. Concentrations in wastewaters and used chemicals were not determined.

DIOXINS IN DYES, PIGMENTS, AND PRINTING INKS

The main source of dioxins in the textile industry are dioxazine and antraquinone dyes and pigments, produced from chloranil as intermediate product, and chloranil itself used as a catalyst in the production of dyes and pigments. PCDD/Fs are formed during the synthesis of *o*-chloranil from chlorinated phenols. Chloranil is formed as the final product of the chlorate-HCl oxidation of many aromatic compounds because of its great resistance to further oxidation.[33] Chloranil is also used in tyre manufacture and it has been used as a fungicide.

In Canada and Germany, various dyes and pigments were analyzed for the presence of PCDD/Fs. Considerable levels of PCDD/Fs were determined in some dioxazine dyes and pigments, phtalocyanine dyes and in printing inks (Table IV). Concentrations found in Direct Blue 106 dye, Direct Blue 108 dye and Violet 23 pigment were in the µg/kg range with OCDD and OCDF as dominant homologues.[34] 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. Hutzinger and Fidler[35] found µg/kg range levels of PCDD/Fs for higher chlorinated congeners in a sample of Ni-phthalocyanine dye. No PCDD/Fs were detected in two samples of Cu-phthalocyanine dyes and in one Co-phthalocyanine dye. Results of the analyses of PCDD/Fs were reported for four printing inks obtained from a supplier in Germany.[36] In the two inks used for rotogravure printing and two used for offset printing, the content of PCDD/Fs ranged from 17.7 to 87.2 ng TEQ/kg. Identities of the dyes and pigments in these inks were not reported. The homologue profile found for rotogravure printing inks is different from those found in offset

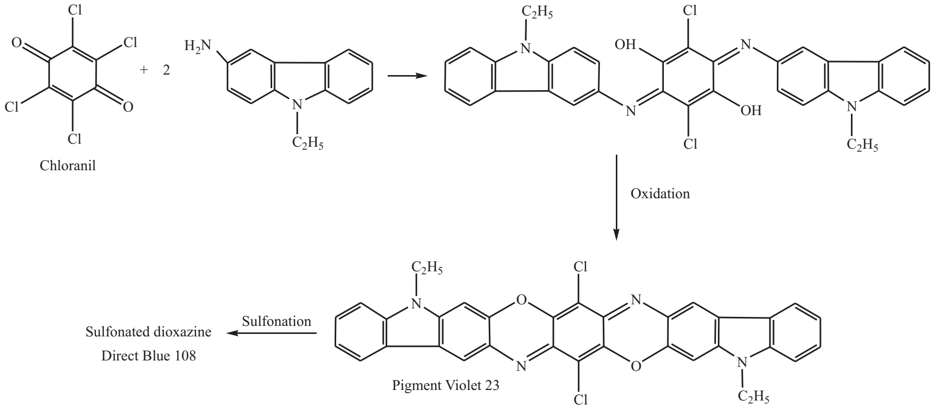

Figure 4. Formation of Direct Blue 108 from chloranil.

printing inks; therefore, the source of PCDD/Fs is different. Recently, six samples of disperse dyes were analyzed for PCDD/Fs content.[37] In two black disperse dyes (mixtures of antraquinone and azo substances), concentrations of 50 and 170 ng TEQ/kg were determined. OCDD was the dominant compound. A third dyestuff had 10 ng TEQ/kg whereas the PCDD/Fs concentrations of the remaining three samples were below the limit of quantification (5 ng/kg per congener). Distribution of dioxins and their fate during textile processes were further investigated.[38] Two dyeing experiments were conducted at laboratory scale utilizing disperse dye contaminated with PCDD/Fs. After the dyeing and finishing process, the PCDD/Fs and especially OCDD were increased compared to the input. The authors conclude that PCDD/Fs are formed in the textile process, most probably from precursors present in dyestuffs.

CHEMISTRY OF DYES AND PIGMENTS IN WHICH PCDD/Fs WERE DETERMINED

Dioxazine Dyes and Pigments

These are obtained by a reaction of tetrachlorobenzoquinone (chloranil) with aromatic amines in the presence of a base.[39] The 2,5-diaryl-amino-3,6-dichloro-1,4-benzoquinones formed are cyclized in inert solvents in the presence of aromatic sulfonyl chlorides at high temperatures (*e.g., o*-dichlorobenzene at 170–180 °C). An example of dioxazine dye is C.I. Direct Blue 108 derived from chloranil and 3-amino-*N*-ethylcarbazol (Figure 4). The unsulfonated dioxazine can be used as a pigment (C.I. Pigment Violet 23). Occurrence of PCDD/Fs in these colorants was attributed to chloranil, which contains PCDD/Fs. *o*-Dichlorobenzene could also be the source of PCDD/Fs if used in the synthesis of these colorants. PCDD/Fs can be formed during the synthesis of chlorobenzenes. A possible formation route is the formation during the synthesis of dioxazine colorants at 170–180 °C in the presence of aromatic sulfonyl chlorides.

Anthraquinone Dyes and Pigments

In colour chemistry, anthraquinone dyes and pigments are obtained by the substitution reactions of anthraquinone, rather than by electrophilic substitutions of benzene and naphthalene, or by nucleophilic and homolytic replacements of substituents in primary aromatic products.[40] Several isomeric quinones based on anthracene are known. Only 9,10-anthraquinone is used for dyestuff synthesis. There are several ways of 9,10-anthraquinone production:

– Anthraquinone is produced industrially from phthalic anhydride and benzene in the presence of aluminium chloride by the Friedel-Crafts reaction;[41]

– From anthracene with vanadium pentoxide, sodium chlorate, glacial acetic and sulphuric acids;[42]

– Anthraquinone is derived from anthracene. Condensed aromatic systems can be directly oxidized to quinones by various oxidizing agents.[42]

There is a possibility of anthraquinone produced by the Friedel-Crafts reaction containing PCDD/Fs.

Phthalocyanine Colorants

Phthalocyanine dyes have complex structures with the general formula presented in Figure 5. Substituted phthalocyanines are obtained either by direct substitution in an existing molecule or by synthesis with substituted starting materials. In large scale production, phthalic anhydride, urea, metal chloride and ammonium molybdate (as catalyst) are heated in a mixture of isomeric trichlorobenzene to 200 °C.[43] Contamination with PCDF/Fs probably occurs during the synthesis of phthalocyanines from chlorinated organic solvents (trichlorobenzene) in the presence of metal chlorides as catalysts for formation of PCDD/Fs at a high temperature (200 °C). Another possible source is the diazotization process in some phthalocyanines.

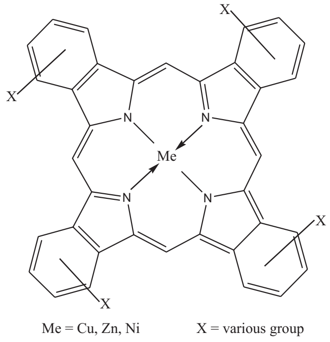

Figure 5. General structure of phthalocyanine colourants.

OTHER POPS RELATED TO THE TEXTILE INDUSTRY

Environmental problems regarding brominated flame retardants (BFRs) have recently become a matter of greater concern than ever before because of high levels of polybrominated diphyenyl ethers (PBDEs) and other BFRs found in human milk.[44,45] The levels of PBDE will continue to increase, causing toxic effects on humans. The most obvious sources of BFRs are effluents from factories producing BFRs, flame-retarded polymers and plastic products, such as electrical appliances.[44] Furthermore, emissions from the textile industry and BFRs from electronic equipment are sources of emissions as well.[45] The environment and the general human population are also exposed to the thermal-breakdown products of PBDEs, such as polybrominated and mixed brominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans (PBDDs/Fs and mixed PXDDs/Fs).[46]

There are few data on PCDD/Fs concentrations in dyes, pigments and textile products and almost no data on concentrations of other dioxin-like compounds in such samples.

It was estimated that during the textile finishing processes the concentration of PCDD/Fs could reach their maximum concentration, 100 ng/kg of the textile. In most cases, concentrations of PCDD/Fs before and after finishing processes show only small differences.[30,31,47] Similar results were obtained for the concentrations of brominated PBDD/Fs in products and in the exhaust air of textile facilities.[47] On the other hand, a high concentration of mixed PBCDD/Fs was detected after some flame retardant finishing textile processes.[47] A flame-retardant finish on upholstery material on the basis of PVC, Sb_2O_3, hexabromocyclododecane results in the final products concentrations of up to 19 μg/kg PBCDD/Fs.

FATE OF DIOXINS AND DIOXIN-LIKE COMPOUNDS IN THE ENVIRONMENT *VIA* TEXTILE DYES AND PIGMENTS

The main pathway for the release of dioxins from the dyes and pigment sectors is through textile dyeing processes *via* wastewater and final products. No data is available for the release of dioxins from dye manufactures.

Textile Wastewaters

The large volume of waste in the textile industry includes washing water from the preparation and continuous dyeing, alkaline waste from the preparation, and batch dye waste containing large amounts of salts, acids, or alkali. While there are few data on PCDD/Fs concentrations in final products (textiles),[30–32] there are no data on residues and wastewaters. When German textile finishing processes were investigated, no quantifiable concentrations were found. Releases into water depend on the materials and chemicals applied to raw materials, used in the processes and in water treatment. There is a risk of potential releases where the control of discharges of large quantities of certain chemicals is poor.

Photochemical Transformation and/or Formation of Dioxins in Textiles and Textile Wastewaters

Textile industry wastewaters are complex matrices, polluted with a wide range of chemicals that must be treated prior to disposal.

Use of ultraviolet (UV) light to degrade and destroy organic pollutants in contaminated waters is one of the advanced oxidation process (AOP) methods.[48] Irradiation of wastewaters with powerful (up to 300 kW) UV lamps with accelerating agents (H_2O_2, NaOCl, Fenton's regent, *etc.*) could be a source of several toxic compounds, including dioxins. Textile wastewaters may contain the well-known dioxin precursors such as pentachlorophenol and chloranil. Several analyses have confirmed that there is no correlation between PCP and PCDD/Fs in textiles although dioxin patterns gave strong indications that PCP should be the source.[29] Three new garments were analyzed for PCP. One of the samples with the PCP dioxin pattern contained 2 μg/g PCP. Another sample with high PCDD/Fs contained less than 10 ng/g of PCP. These findings make sense, since PCP is water soluble and will be removed in the finishing processes and final washing processes, whereas the PCDD/Fs adsorb to the fibre and will remain in the textile.

There is evidence that PCP is still present in textiles, despite being banned in 1989. Therefore, PCP and other chlorophenols can be the source of PCDD/Fs in wastewaters and textiles being worn. A generation of dioxins was reported from the direct photolysis of pentachlorophenol-containing water.[49] Formation of dioxins by the UV photolysis of pentachlorophenol with or without addition of hydrogen peroxide was investigated by Waddell *et al.*[50] Their study shows high levels of dioxins formed by UV degradation of PCP in both cases. Higher levels of PCDD, especially OCDD, were recorded.

Textile Products

Several studies of Horstman and McLachlen indicate that a small fraction of new textiles have very high concentrations of PCDD/Fs.[29–32] Dioxins from this source can be transferred to other compartments *via* several pathways. The transfer of PCDD/Fs between several matrices and pathways was demonstrated by Horstman and McLachlen[29] (Figure 6). A large part of PCDD/Fs in textiles are transferred during washing into sewage sludge, which is often used as an agricultural fertilizer and can be the source of dioxins in the food chain.

PCDD/Fs have been detected in the distillation residues from dry cleaning (cleaning of textiles with solvents).[51] Dioxins are extracted from the textiles into the solvent during the dry cleaning process. Dioxins are concentrated in the distillation residues during distillation of the solvent for recovery and reuse. A significant input of dioxins with solvents or additives has been excluded. The dry cleaning process itself does not generate any PCDD/Fs. According to this study, it was estimated that the uptake of PCDD/Fs from the atmosphere into clothing during wearing is a less important pathway for higher chlorinated congeners that prevail in the washing machine wastewaters.

Incineration of Textile Products

A dioxin mass balance was made in the Spanish municipal waste incinerator (MWI).[52] Analysis of different in-

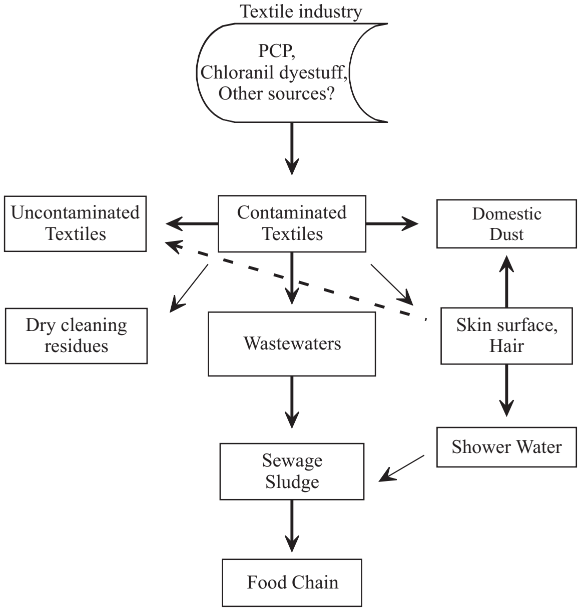

Figure 6. PCDD/Fs transfer pathaways.

cineration input waste materials shows the highest dioxin levels for textile samples. In two analyzed textile samples, dioxin concentrations varied between 140 and 170 pg I-TEQ/g with textile-known homologue profiles, which are dominated by HpCDD and OCDD (up to 54 and 60 µg/g). In this study, the output contribution of textile material was not estimated for the total emission of PCDD/Fs into the environment. Textile products with their wide applications and complex chemistry could be a significant source of dioxins and/or precursor compounds for the formation of dioxins and other POPs. However, modern MWI are under sophisticated control and the emission of PCDD/Fs into the air is very low. The limit value for PCDD/Fs emission from waste incinerator plants is 0.1 ng I-TEQ/Nm^3, as established by the European Union (EU).[53]

REGULATIONS ADDRESSING PCDD/Fs EMISSION IN INDUSTRY

Dioxins have never been produced intentionally on an industrial scale. To reduce new emissions of PCDD/Fs into the environment, indirect measures are needed. Despite many years of measuring their levels in numerous environmental samples, information on the emissions of dioxins and other POPs remains limited by a lack of complete and accurate emission data.[54]

The first regulation addressed the banned chemicals contaminated with PCDD/Fs in ppb to ppm-range I-TEQ (Ban of Polychlorinated Biphenyls and Pentachlorophenol in 1989). Regulation for dioxins in substances, preparations and articles (apparel product) was amended in 1994 with the implementation in 1996 of German jurisdiction[55] (Table V). This regulation applies also to dyes, pigments and textiles and is valid worldwide. With the EU directive[53] for all incineration plants, a limit value of 0.1 ng I-TEQ/Nm^3 was set for air emissions and 0.3 ng I-TEQ/dm^3 for releases into water.

TABLE V. Restricted limits for dioxins and furans in apparel products

Substance	Restricted limit
Group 1:	
2,3,7,8-TCDD	Sum of Group 1:
1,2,3,7,8-PCDD	1 µg kg^{-1}
2,3,7,8-TCDF	
2,3,4,7,8-PCDF	
Group 2:	
1,2,3,4,7,8-H6CDD	Sum of Group 1and 2:
1,2,3,6,7,8-H6CDD	5 µg kg^{-1}
1,2,3,7,8,9-H6CDD	
1,2,3,7,8-PCDF	
1,2,3,4,7,8-H6CDF	
1,2,3,6,7,8-H6CDF	
2,3,4,6,7,8-H6CDF	
1,2,3,7,8,9-H6CDF	
Group 3:	
1,2,3,4,6,7,8-H7CDD	Sum of Group 1,2 and 3:
1,2,3,4,6,7,8,9-OCDD	100 µg kg^{-1}'
1,2,3,4,6,7,8,-H7CDF	
1,2,3,4,7,8,9-H7CDF	
1,2,3,4,6,7,8,9-OCDF	
Group 4:	
2,3,7,8-TBDD	Sum of Group 4:
1,2,3,7,8-PBDD	1 µg kg^{-1}
2,3,7,8-TBDF	
Group 5:	
1,2,3,4,7,8-H6BDD	Sum of Group 4 and 5:
1,2,3,6,7,8-H6BDD	5 µg kg^{-1}
1,2,3,7,8,9-H6BDD	
1,2,3,7,8-PBDF	

CONCLUSIONS

Chemical industry is a negligible source compared to the air emission of dioxins from incineration and combustion sources. There are many data on air emission sources; according to the European Dioxin Air Emission Inventory Project, an air emission reduction of 90 % was supposed to have been achieved by 2005 compared to the 1985 situation.

Much less is known about dioxin emissions through chemical products, wastewaters, process residues and wastes. Production of dyes and pigments is a less investigated source of dioxins. Regulations for dioxins in dyes and pigments are obsolete compared to regulations for other matrices. Several studies have confirmed that colorants can contain considerable levels of dioxins. Dioxins from textiles can be transferred during washing into sewage sludge, which is often used as an agricultural fertilizer and can be the source of dioxins in the food chain.[56] A small part can also be transferred directly through human skin.[57] Textiles could be a significant source of dioxins and/or precursor compounds for the formation of dioxins and other POPs by incineration. However, information on the emissions of dioxins and other POPs from textile dyes and the pigment sector is limited due to a lack of complete and accurate emission data. Without a full knowledge of dioxin sources, we will go on struggling to minimize environmental and human exposure.

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SAŽETAK

Dioksini i slična postojana organska zagađivala u području tekstila i kemikalija za tekstile

Boštjan Križanec i Alenka Majcen Le Marechal

Godišnje se proizvodi preko 7 × 10^5 tona supstancija za bojenje s više od 100 000 komercijalnih boja. Sinteza boja uključuje veliku skupinu kemikalija i složene kemijske procese. Utvrđeno je da se tijekom sinteze bojila mogu stvoriti visoko toksične, karcinogene i postojane organske supstancije poput dioksina. Posebno su toksični i postojani klor- i brom- homolozi. Oko 40 % bojila u svijetu sadrže organski vezani klor. Uporaba bojila u tekstilnoj industriji, njihova široka primjena kao i složeni kemijski procesi proizvodnje mogu biti značajan izvor dioksina i njihovih prekursora kao i drugih postojanih organskih zagađivala (POP). Svrha ovog rada je dati pregled supstancija na bazi dioksina u području tekstila i bojenja, te procijeniti sudbinu tih supstancija u okolišu.