Recent Update on Organic Pollutants

Bruce Horak

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Edited by **Bruce Horak**

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Preface

This book aims to highlight the current researches and provides a platform to further the scope of innovations in this area. This book is a product of the combined efforts of many researchers and scientists, after going through thorough studies and analysis from different parts of the world. The objective of this book is to provide the readers with the latest information of the field.

Even a decade after the Stockholm Convention on Persistent Organic Pollutants (POPs) was signed, a large variety of organic chemicals still pose ecological hazards of top most priority. The expansion of information base on organic pollutants (OPs), environmental fate and effects, as well as the cleansing methods, is accompanied by a rise in importance of certain pollution sources, associated with possible generation of new hazards for humans and nature. This book provides an analytical and environmental update, and can be specifically important for engineers and experts.

I would like to express my sincere thanks to the authors for their dedicated efforts in the completion of this book. I acknowledge the efforts of the publisher for providing constant support. Lastly, I would like to thank my family for their support in all academic endeavors.

Editor

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Contents

Part 1

High Concern Sources of Organic Pollutants

1

Textile Finishing Industry as an Important Source of Organic Pollutants

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1. Introduction

The textile finishing industry is, among all industries in Europe, the greatest consumer of high quality fresh water per kg of treated material and with the natures of their production processes significantly contributing to pollution. Wastewater from the textile industry is also a significant environmental pollution source of persistent organic pollutants.

Not only textile wastewater but also textile products often contain chemicals such as formaldehyde, azo-dyes, dioxins, pesticides and 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 of dyes and auxiliary chemicals (the synthesis of dyes involves a large variety of chemicals with complex synthesis paths, during which toxic, carcinogenic and persistent organic compounds can be formed, such as dioxins, and traces can be found in commercial dyes), others are added to give certain characteristics to the products (colour, flame retardancy, anti wrinkling properties *etc.*) (Križanec & Majcen Le Marechal, 2006), or are already present in the raw textile material. The mentioned compounds have been found in wastewater after home washing, in organic solvent after dry-cleaning and also in the atmosphere after incineration. Possible sources of organic pollutants are also wastewater treatment methods and the incineration of textile materials.

The formation of dioxins can occur via dyeing and textile finishing processes with conditions favourable for their generation (high temperature, alkaline conditions, ultraviolet (UV) radiation, and other radical initiators). Textile dyes are designed to be resistant to microbial, chemical, thermal and photolytic degradation. After the dyeing process, a lot of non-bonded dyes are released into the wastewater, which can also be treated by Advanced Oxidation Processes (AOPs) in order to destroy the dye molecule and to decolourise the wastewater and reduce organic pollution. It is well-known that under the experimental conditions of such methods, which can be very useful because of the short-time of treatment, hazardous compounds can be formed due to very powerful oxidizing agents such as hydroxyl radicals ($OH^{\bullet}$).

In line with the improvement of people's living standard and the growing awareness and need to preserve the environment several regulations were introduced also in the textile industry in order to control the use of chemicals in textile processes. Under REACH regulation (REACH regulation controlled the quality of fabric, apparels, and shoes and other textile materials, so as to protect human health and the environment) the following main groups of compounds in textiles are under control: Azo Dyes, Phthalates, Formaldehyde, Flame-retardants, Pentachlorophenol, Carcinogenic dyes, Sensitizing disperse dyes, Hexavalent chromium, Polychlorinated biphenyls, Heavy metals, Nickel release, Total lead content, Organic tin compounds, Total cadmium content, Organic chlorine carrier, Nonylphenol, Octylphenol, and Nonyl phenol ethoxylate, and several established directives (e.g. Azo dyes - Directive 2002/61/EC, Pentachlorophenol (PCP)-Directive 94/783/EC)) regulated/banned the use of these substances throughout the textile production chain (www.cirs-reach.com/textile/).

Market pressure, on the other hand, leads to the introduction of an extensive range of new products, especially dyes, and for many of them environmental and health impact data are still lacking. The quantification of chemicals within the environment is leading to the development of sensitive analytical methods in order to effectively detect and control pollution by organic pollutants.

2. Textile raw material

2.1 Fibres

Two general categories of fibres are used in the textile industry: natural and chemical (man-made) fibres. Man-made fibres encompass both purely synthetic materials of petrochemical origin, and regenerated cellulose material from wood fibres. A detailed classification of fibres is presented in Table 1.

Natural fibre		
Animal origin	*Vegetable origin*	*Mineral*
Raw wool	Cotton	Asbetos
Silk fibres	Flax	Glass
Other hair fibres	Jute	Metalic
Alpaca	Linen	Copper
Camel	Ramie	Steel
Cashmere	Hemp	
Horse		
Llama		
Mohair		
Rabbit		
Vicuna		
Chemical (man-made) fibres		
Natural polymers fibres	*Synthetic polymer fibres*	
Viscose, Cupro, Lyocell	Inorganic polymer	
Cellulose Acetate	Glass for fibre glass	
Triacetate	Metal for metal fibre	
	Organic polymers	
	Polyester (PES)	
	Polyamide (PA)	
	Polyacrylonitrile (PAC)	
	Polypropylene (PP)	
	Elastane (EL)	

Table 1. Classification of fibres

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2.2 Organic pollutants in textile raw materials

Different kinds and amounts of organic pollutants (contaminants) can already be present in fibres before they arrive at the textile mill. The potential contaminants may be released from the raw materials into the water or air during processing, when the fabric is heated or scoured. Due to the large amount of the fibre used during textile manufacturing, even trace contaminants can produce large amounts of pollutants. Many textile operations lack an incoming quality-control system for fibres. Testing of the natural or chemical fibres for organic pollutants is very rarely done in textile mills.
Textile raw materials contain: natural impurities from cotton, wool, silk, etc., fibre solvents (when chemical fibres are produced by dry-spinning or solvent-spinning processes), monomers (caprolactam ex polyamide 6), catalysts (antimony trioxide in polyesters' fibres), sizing agents (woven textiles esp. cotton and cotton blends), and preparation agents (esp. woven and knitted textiles made of man-made fibres). (Lacasse & Baumann, 2004)

2.3 Natural fibres

Natural fibres are acquired from animal, mineral, and plant sources. Several types of organic pollutants are found in natural fibre and all have the potential to create significant pollution problems. For example, waxes, oils, fats, and grease from animal fibre can contribute to biochemical oxygen demand (BOD), and chemical oxygen demand (COD). Pesticide residues from plant fibre can contribute to aquatic toxicity. Metals can accumulate in sludge or during the treatment system itself, thus causing potential long-term problems.
Cotton is the most significant natural fibre. Cotton fibre contains 88-96 % of cellulose and the residue is pectin substances, wax, proteins, ash, and other organic components (less than 1%). Chemicals such as pesticides, herbicides, and defoliants can be used during the production of cotton. These chemicals may remain as a residue on raw cotton fibres that reach the textile mill. Tests of cotton samples from growing regions worldwide, performed from 1991 to 1993, reported levels of pesticides below the threshold limit value for foodstuffs (US EPA 1995).
Although the content of pesticides in raw cotton fibres was negligible, almost half of the insecticides used in agriculture were used in cotton production. For this reason the reduction of insecticides for economic, environmental, and human health reasons was necessary. Insect-resistant (Bt) cotton (GM IR) started being used in 1996. So, the production of Bt cotton during the first ten years (1996-2005) reduced the total volume of those active insecticide ingredients by 94.5 million kilograms, representing a 19 % reduction in insecticides (Naranjo, 2009).
In 2001 it was reported that cotton was contaminated by pentachlorophenol (PCP) when being used, not only as a defoliant, but also as a fungicide during transportation and storage. (UK, 2001).
Wool is another significant commercial natural fibre. It is an animal hair from the bodies of sheep, sheared once or sometimes twice a year, and its quality and quantity vary widely, depending on the breed of sheep and their environment. Raw wool contains natural impurities (wool grease, suint, dirt) and residues of pesticides. Pesticides are applied onto sheep in order to control external parasites such as lice, blowflies, mites etc.
The used pesticides generally fall into four main groups (BAT, 2003):

- **organochlorine insecticides (OCs):** γ-hexachlorocyclohexane (lindane), pentachlorophenol (PCP), dieldrin, DDT,
- **organophosphorous insecticides (OPs):** diazinon, propetamphos, chlorfenvinphos, chloryriphos, dichlorfenthion,

- **synthetic pyrethroids insecticides (SPs):** cypermethrin, deltamethrin, fenvalerate, flumethrin, cyhalothrin and
- **insect-growth regulators (IGRs):** cyromazine, dicyclanil, diflubenzuron, triflumuron.

Biocides, organohalogen and organophosphorus compounds are among the priority substances listed for emission-control in the IPPC Directive. Diazinon (OP), propetamphos (OP), cypermethrin (SP) and cyromazine (IGR) are the most commonly-used ectoparasiticides for treating sheep. Insect-growth regulators such as dicyclanil, diflubenzuron and triflumuron are registered only in Australia and New Zealand. Lindane, which is the most toxic of the hexachlorocyclohexane isomers and also the most active as a pesticide, is still found in wool coming from the former Soviet Union, the Middle East and some South American countries (BAT, 2003). Wools from South America exhibited the highest levels of organochlorine insecticides, whilst wools from Australia and New Zealand exhibited the lowest levels of OCs (Shaw, 1989).

Pesticides such as OCs, OPs, and SPs have a lipophilic nature, so they associate strongly with the natural oils within the wool and as removed using these oils during wool scouring operations. The chemical stability of organochlorine pesticides is reflected in their resistance to microbial degradation. The lipophilic nature, hydrophobicity, and low chemical and biological degradation rates of organochlorine pesticides have led to their accumulation in biological tissues, and subsequent magnification of concentrations in organisms progressing up the food-chain.

The fate of the Ectoparasiticides (antiparasitic drug) in the wool scouring process is following. 96 % of the pesticides are removed from the wool (4 % is retained on the fibre after scouring). Of this 96 % around 30 % or less is retained on-site in recovered grease and the remaining fraction is discharged into the effluent and submitted to wastewater treatment.

Levels of organochlorine insecticides pentachlorophenol (PCP) in textile products are usually too low to be quantified accurately by traditional methods. PCP has been found at levels as high as 100 ppm in consumer products such as wool carpets (Wimbush, 1989). Wimbush tested 140 wool carpets and found that 88 % of them had a PCP content below 5 ppm. Only 3 carpets contained more than 50 ppm of PCP (US EPA, 1996).

Silk accounts for only 0.2 % of total fibre production. It is a protein fibre like wool and derived from the silkworm. The silk fibre is composed of fibroin filaments wrapped with sericine (silk gum), which has to be removed during pretreatment. (BAT, 2003)

2.4 Chemical fibres

Synthetic fibres may contain several types of impurities existing in the fibres before they reach the textile mill. These kinds of impurities are imparted onto the fibres during fibre manufacturing and fall into the categories of finishes, polymer synthetic by-products, and additives. Impurities associated with synthetic fibres are:

- Finishes: antistatic, lubricant,
- Polymer synthesis by-products: non-reactive monomers, low-molecular-weight oligomers, residual catalyst, and
- Additives to facilitate processing: antistatic agents, lubricants, humectants, and others.

Table 2 presents those compounds typical of synthetic fibre extracts. The compounds in Table 2 were not only found in the process wastewater from synthetic fibre dyeing and finishing operations but were also detected in synthetic fibre extracts.

Fibre	Compounds
Polyester	*tetra* hydro-2,5-dimethyl *cis* furan, ketones (methyl isobutyl ketone, 3-methyl cycle pentanone, hexanone, diethyl ketone), dodecanol, alcohols (C_{14} and C_{18}), esters of carboxylic acids (C_{14}-C_{24}), hydrocarbons (C_{14}-C_{18}), carboxylic acids (C_{16}-C_{24}), phthalate esters
Acrylic	hydrocarbons (C_{15}-C_{18}), esters of carboxylic acids (C_{17}-C_{22}), alcohols, phthalate esters, *N, N*-dimethyl acetamide
Nylon 6	diphenyl ether, hydrocarbons (C_{16}-C_{20}), carboxylic acids (C_{14}-C_{18}) and dicarboxylic acids, esters of carboxylic acids (C_{10}-C_{18}), alcohols (C_{20}-C_{22})

Table 2. Compounds typical of synthetic fibre extracts

Some of these impurities are produced during the polymerization of synthetic fibres and some are added to control the surface and electrical properties of the fibre. These impurities can create pollution problems.

The above review of possible organic pollutants in textile raw materials indicates the necessity for quality control regarding incoming fibre. Some textile companies have endorsed standard testing methods for fibres and have actively worked to ensure that the fibre user and the producer exchange information about quality control. It is important to set up good incoming fibre quality-control based on performance-testing, statistical sampling, and the analysis of extractable materials, in order to identify potential pollution problems before they arise.

3. Finishing processes within the textile industry

3.1 Basic process within the textile industry

The textile chain begins with the production or harvesting of raw fibres. These basic processes are schematically presented in Fig. 1. Treatments that are broadly referred to as 'finishing processes' are pretreatment, printing, dyeing, finishing, and coating, including washing and drying.

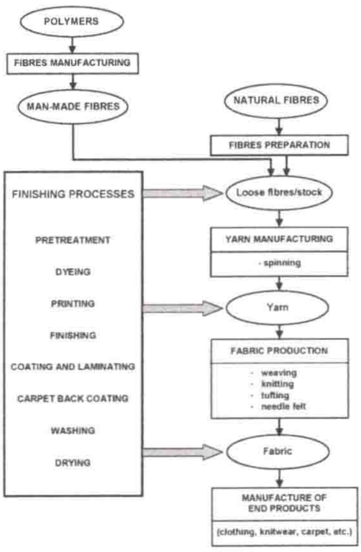

Fig. 1. Schematic presentation of textile processes

3.2 Possible organic pollutants in textile finishing processes

Most textile finishing operational units use chemical specialties. The major specialty consumption operations are pretreatment processes (desizing, scouring, bleaching), dyeing, printing, and finishing. (Mattioli, et al, 2002)

So, this chapter focuses on those textile finishing processes that might produce organic pollutants.

3.2.1 Pretreatment processes

Pretreatment processes depend on the kind and form of the treated fibre, as well as the amount of material to be treated. These processes should ensure the removal of foreign materials from the fibres in order to improve their uniformity, hydrophilic characteristics, and affinity for dyestuffs and finishing treatments. The pretreatment processes are desizing, scouring, bleaching, and mercerizing.

3.2.1.1 Desizing

Desizing is the process for removing size-chemicals from textiles. The possible organic pollutants in effluents after desizing, are presented in Table 3.

Fibres	Organic substances
Cotton	carboxymethyl cellulose, enzymes, fats, hemicelluloses, modified starches, non-ionic surfactants, oils, starch, waxes
Linen	
Viscose	
Silk	carboxymethyl cellulose, enzymes, fats, gelatine, oils, polymeric sizes, polyvinyl alcohol, starch, waxes
Acetates	
Synthetics	

Table 3. Possible organic pollutants in effluents after the desizing process

The washing water from desizing may contain up to 70 % of the total COD in the final effluent. Synthetic esters' oils are less problematic because they are emulsified or soluble in water and easily biodegraded. More problems are caused by compounds such as silicon oils, because they are difficult to emulsify, and poorly biodegradable. Silicon oils are found in elastane blends with cotton or polyamide.

3.2.1.2 Scouring

Scouring is the cleaning process for removing impurities from both natural and synthetic materials. In natural fibres, impurities can be present such as oils, fats, waxes, minerals, and plant-matter. Synthetic fibres can contain spinning, finishing, and knitting oils.

Scouring is performed in an alkali medium together with auxiliaries that include:

- non-ionic surfactants (alcohol ethoxylates, alkyl phenol ethoxylates) and anionic surfactants (alkyl sulphonates, phosphates, carboxylates),
- compounds for removing metal ions (nitrilotriacetic acid (NTA), ethylenediaminetetraacetate (EDTA), diethylene triamine pentaacetate (DTPA), gluconic acid, phosphonic acids as complexing agents),
- polyacrylates and phosphonates as special surfactant-free dispersing agents and
- sulphite and hydrosulphite as reducing agents (to avoid the risk of the formatting of oxycellulose when bleaching with hydrogen peroxide).

Table 4 presents those possible organic pollutants derived from scouring.

Fibers	Organic substances
Cotton	anionic surfactants, cotton waxes, fats, glycerol, hemicelluloses, non-ionic surfactants, peptic matter, sizes, soaps, starch
Viscose	anionic detergents, fats, non-ionic detergents, oils, sizes, soaps, waxes
Acetates	
Synthetics	anionic surfactants, anti static agents, fats, non-ionic surfactants, oils, petroleum spirit, sizes, soaps, waxes
Wool (yarn and fabric)	anionic detergents, glycol, mineral oils, non-ionic detergents, soaps
Wool (loose fiber)	acetate, anionic surfactants, formate, nitrogenous matter, soaps, suint, wool grease, wool wax

Table 4. Possible organic pollutants in waste-effluents after the scouring process

3.2.1.3 Bleaching

Bleaching is a chemical process for removing unwanted coloured matter from materials. Several different types of chemicals are used as bleaching agents and selection depends on the type of fibre. The most frequently used oxidizing agents for cellulose fibres are hydrogen peroxide (H_2O_2), sodium chlorate(I) (NaClO), sodium chlorate(III) ($NaClO_2$). Peracetic acid and optical brightening agents are also applicable.

Bleaching with H_2O_2 is connecting with the use of H_2O_2 stabilisers. During the bleaching process, hydroxyl radicals attack the cellulose fibre starting with oxidation of the hydroxyl groups, and eventually ending with cleavage of the cellulose molecules, thus decreasing the degree of polymerisation. Reaction is catalysed by heavy metals such as iron, copper, and cobalt. H_2O_2 stabilisers (EDTA, NTA, DTPA, gluconates, phosphonates and polyacrylates) inhibit these reactions. NTA, EDTA and DTPA form very stable metal complexes. EDTA and DTPA are also poorly eliminated compounds, and they could pass non-degraded through the common wastewater treatment system. Their ability to form a very stable complex with metal makes the problem even more serious because they can mobilise those heavy metals present in the effluent, and release them into the receiving water. Other auxiliaries used in hydrogen peroxide bleaching are surfactants with emulsifying, dispersing, and wetting properties.

Sodium chlorate(I) was, for a long time, one of the more widely-used bleaching agents throughout the textile finishing industry. Nowadays bleaching with sodium chlorate(I) is limited in Europe for ecological reason. NaClO leads to secondary reactions that form a number of organic halogen compounds, such as carcinogenic trichloromethane.

3.2.1.4 Mercerizing

Mercerizing is a chemical process that improves the strengths, lustres and affinities of dyes for cotton fabrics. Several organic pollutants can be used. Possible organic pollutants in mercerizing effluents are alcohol sulphates, anionic surfactants, and cyclohexanol.

3.2.2 Dyeing

Dyeing is used to add colour to textile materials. Textiles may be dyed at various stages of production.

Dyeing can be carried out in a batch or in a continuous mode. The choice between the two processes depends on the type of make-up, the chosen class of dye, the equipment available, and the cost involved. Both continuous and discontinuous dyeing involve preparation of the dye, dyeing, fixation, washing, and drying. Quite a large amount of the non-fixed dye leaves the dyeing units.

Besides dyes, other auxiliary substances can be added to the dyeing process, and may give rise to water pollution. Possible pollutants are: fatty amine ethoxylates (levelling agent), alkylphenol ethoxylates (levelling agent), quaternary ammonium compounds (retarders for cationic dyes), cyanamide-ammonia salt condensation products (auxiliaries for fastness improvement), acrylic acid-maleic acid copolymers (dispersing agent), ethylenediamine tetraacetate (EDTA), diethylenetriaminepentaacetate (DTPA), ethylenediaminetetra-(methylenephosphonic acid) (EDTMP), diethylenetriaminepenta(methylenphosphonic acid) (DTPMP).

All these are water soluble and non-biodegradable compounds, which can pass non-transformed or partially-degraded through a wastewater treatment system. Some of them are toxic (quaternary amines) or can give rise to metabolites that may affect the reproduction-chain within an aquatic environment (BAT, 2003).

Organic dyes are presented in Chapter 4.

3.2.3 Printing

Printing, like dyeing, is a process for applying colour to a substrate. The printing techniques are: rotary screen, direct, discharge, resist, flat screen, and roller printing. Pigments cover about 75-85 % of all printing operations, do not require washing steps and generate a small amount of waste. Compared to dyes, pigments are typically insoluble and have a high affinity for fibres. Printing paste residues, wastewater from wash-off and cleaning operations, and volatile organic compounds from drying and fixing, are typical emission sources from printing processes.

Printing process wastewater is small in volume, but the concentration of pollutants is higher than that in wastewater from dyeing. Wastewater after printing contains the following organic pollutants: urea, dyes or pigments, and organic solvents.

These pollutants are likely to be encountered in wastewater after printing, and are presented in Table 5 (BAT, 2003).

Additionally, organic pollutants after the finishing processes, such as aliphatic hydrocarbons (C_{10}-C_{20}) from binders, monomers (acrylates, vinylacetates, styrene, acrylonitrile, acrylamide, butadiene), methanol from fixation agents, other alcohols, esters, polyglycols from emulsifiers, formaldehyde from fixation agents, ammonia, *N*-methylpyrrolidone from emulsifiers, phosphoric acid esters, phenylcyclohexene from thickeners and binders, might also be distributed in the exhaust air.

3.2.4 Finishing

The term 'finishing' covers all those treatments that improve certain properties or the serviceability of the fibre. Finishing may involve those mechanical/physical and chemical treatments performed on fibre, yarn, or fabric, in order to improve appearance, texture, or performance.

Organic pollutants found during finishing processes are:

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