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Changes in Hazardous Substances in Cotton after Mechanical and Chemical Treatments of Textiles

Abstract
ICP spectrometry was used to analyse the content of heavy metals in 23 samples of cotton of various origins which had been processed in the Polish domestic industry. Furthermore, the content of pesticides and pentachlorophenol (PCP) in 20 samples of cotton of various origins was determined by means of the high-performance liquid chromatography method (HPLC). Changes in hazardous substances in cotton after mechanical and chemical treatment during the production of cotton bed-cloth, starting from the raw materials in bales and ending with the finished product were monitored. The content of heavy metals extracted by means of artificial acid sweat, as well as of pesticides and PCP in the finished bed-cloth, was compared with the criteria of the 100 ÖKO TEX Standard. It was confirmed that the level of heavy metal and pesticide content in raw cotton samples and in the cotton bed-cloth after mechanical treatment (spinning, weaving) posed no serious risk to obtain products which met the human-ecological criteria defined by the 100 ÖKO TEX Standard. A much greater danger may be observed in the dyeing and printing processes, in which the contamination of dyestuffs and auxiliary materials increased the heavy metal content to a very great extent, exceeding the permitted values several times. On the other hand, the results confirmed that the heavy metals, pesticides and PCP amounts extracted from the finished textiles by artificial acid sweat did not exceed the permissible values allowed by the aforementioned criteria for textile products used in direct contact with the human body.

Key words: *cotton, heavy metals, pesticides, pentachlorophenol, mechanical treatment, chemical treatment, ICP spectrometry, HPLC, 100 ÖKO TEX Standard.*

Introduction

The basic requirements deciding whether textile products may be successfully commercialised are health & safety for the user, and harmlessness for the environment. Threats to health may be linked to the presence of harmful substances in a product, such as heavy metals (antimony, arsenic, lead, cadmium, cobalt, chromium, copper, nickel, mercury), pesticides and pentachlorophenol PCP [1-10].

The reasons for their presence in finished goods can be contamination of the textile raw materials, as well as chemical means and dyes applied in the chemical finishing treatment processes. The criteria defining permissible contents in a product (or their complete absence) of these and other harmful substances have been established at levels that should not cause adverse effects on users' health during the products' normal exploitation. Those most often applied are the human-ecological criteria for textile products, according to the 100 ÖKO TEX Standard [6].

When designing ecological textile products, the selection of raw materials, auxiliary chemical substances, dyes and applied technologies should match those criteria. In the technological process of manufacturing textile products, there exist opportunities in its various phases to increase or decrease the content of certain harmful substances through washing them out or bonding them with the fibre. Hence, it is crucial that the quantity of a harmful substance be as low as possible from the very beginning of the production process, i.e. from the input materials. Technological processes, chemical means and dyes should lead to the smallest possible increase in the content of such substances.

Cotton, as a natural textile raw material with perfect hygienic properties thanks to its hygroscopicity, sweat-absorbing capacities and usage comfort in direct contact with the body, is best for manufacturing ecological products.

This investigation project determined the level of contamination with heavy metals and pesticides in cotton, specifically those cottons processed in Polish industry. The changes in their content throughout the production process were examined, using cotton bed-cloth as an example.

Aims

The studies undertaken in this work comprised:

- an analysis of the metal content in 23 samples of cottons of various origins and processed in the Polish domestic industry, including heavy metals (cadmium Cd, cobalt Co, chromium Cr, copper Cu, nickel Ni, lead Pb, zinc Zn),
- analysis of the pesticide and pentachlorophenol (PCP) content in 20 samples of cotton of various origins (aldrin, atrazine, 2,4D, 4,4'-DDD, 4'-DDE, 4,4'-DDT, dieldrin, endosulfan I and II, endrin, α-HCH, β-HCH, γ-HCH, heptachlorine, hexachlorobenzene, carbanyl, parathion and simazine,
- testing and analysis of changes in the above-mentioned harmful substances during the process of producing cotton bed-cloth, beginning from the raw materials in bales, and ending with the finished product,
- analysis of the heavy metal (Cd, Co, Cr, Cu, Ni, Pb, Zn) content extracted by means of artificial acid sweat, as well as that of pesticides and PCP in the finished bed-cloth, as compared with the criteria of the 100 ÖKO TEX Standard.

Methods

Determination of heavy metal content

The plasmatic spectrometry method ICP (Inductively Coupled Plasma) was employed, which is currently among the most useful methods for analysing trace elements in biological and environmental materials.

The idea of the ICP method is based on the use of a rich emitted spectrum of the analysed sample which enters into inductively-coupled argon plasma. Analysis of the received spectrum makes it possible to identify the composition of a sample and simultaneously to determine the macro-, micro- and ultra-components.

An IRIS/AP spectrometer with a CID semi-conductor detector with axis plasma

observation (a product of Thermo Jarrel Ash, USA) was used. A CID camera controller controls all the spectrometer's functions, and the information is passed to a computer system. The readout system makes it possible to simultaneously register the full analytical spectrum received from the optical system of the Echelle type. The most important features of this type of optics are as follows: the capability of generating a two-dimensional picture, thanks to the use of the diffraction grating; the prism active for the perpendicular directions, and great resolving power and stability.

Samples of the textile products tested were mineralised with the MLS 1200 Mega microwave system (produced by Milestone), with an automatic pressure control of up to 25 bars and a temperature control of up to 240°C, for digesting and concentrating samples.

The results received were confirmed by the analysis of a certified comparative material, IAEA Cotton (V-9), as well as by testing the uniformity of samples and the repetitiveness of mineralisation. The precision of measurements was specified with a relative standard deviation within 0.2-2%. For the concentration of chemical elements close to the border of determinability, this value did not exceed 30%. It was stated that the received limits of determinability were sufficient to determine the level of content in the samples for the majority of elements [17]. It was found out that the As content in the finished cotton bed-cloth was below 1 ppm [11-13].

For the purpose of comparison with the 100 ÖKO TEX Standard, the content of heavy metals in finished fabrics was determined for the extracts by artificial acid sweat, according to the standard PN-EN-ISO 105-E04:1999.

Determination of pesticide content

The analysis of pesticide content with the high-performance liquid chromatography method (HPLC) was done in the Pharmacia LKB apparatus. Chromatographic separations were carried out on the Phurospher RP-18e (5µm, 4×250mm) column, made by Merck. Concentration of samples was carried out on the BAKER SPE column extraction system, a product of J. T. Baker. The extraction process was carried out on tiny columns with a volume of 6 ml.

The following certified materials were used for qualitative and quantitative analyses of pesticide content:

- standard of 99.8% pentachlorophenol (Analytical Department, Institute of Industrial Organic Chemistry, Warsaw),
- standard EPA 8270 Pesticides Matrix Spiking Mix (No. 47638-U, Supelco),
- standard EPA 608 Pesticides Matrix Spiking Mix (No. 48858-U, Supelco).

The purity of the organic solvents dichloromethane and acetonitrile was HPLC-grade. The remaining reagents applied in the analysis were of analytical grade.

The separations of the pesticide mixture were done in the gradient configuration at a temperature of 35°C. The use of two solvent solutions of created a linear profile of the gradient:

- solution A; 20% acetonitrile/0.01 mole/l phosphate buffer (pH=3.0),
- solution B; 80% acetonitrile/0.01 mole/l phosphate buffer (pH=3.0).

The elution of the marked components was conducted in the following phases: 0-3 min 100% A, 3-30 min 100% B. The flow velocity in the mobile phase was 0.5 ml/min. The analytical wavelengths of the UV-Vis detector were 220 nm and 240 nm.

Calibration for the method was effected for 6 series of standards within the range of concentrations from 10 to 1000 ng/g. The relative standard deviation for the pesticides determined was estimated from 3.24% for 2,4-D to 12% for parathion. The sensitivity of the method was defined at the level of 1 ng/g.

20 µl of the pesticide solution was introduced into the chromatographic apparatus. During the chromatographic analysis, the areas of peaks of the defined components were registered. The concentration of pesticides was settled from the calibration curve on the basis of measurements of three parallel determinations.

Results and Discussion

Metal content in cottons of various origins

The tests covered 23 samples of cotton processed in the Polish domestic industry, which originated from the 1997/98 crops in various growing regions. The content of heavy metals was determined for Cd, Co, Cr, Cu, Ni, Pb, and Zn. The heavy metal content was determined for 6 Uzbek samples, 5 Turkmen, 2 Kazakh, 3 Egyptian, and 1 Tajik, American, Greek, Turkish, Beninese, Burkinabe, and Chadian sample each [13-15].

Table 1 shows the results of tests for the presence of heavy metals in cotton from the various growing regions. The division into regions is as follows: Central Asia (Uzbekistan, Kazakhstan, Turkmenistan, and Tajikistan), South-West Asia (Turkey), Africa (Egypt, Benin, Chad, and Burkina Faso), Europe (Greece) and North America (USA). In the majority of samples tested, heavy metals were present.

Table 2 presents the number of samples in which the presence of heavy metals in cottons from the various regions was detected. The detailed results given in Figures 1-7 took the following assumptions into consideration:

- the highest concentration in the tested group of heavy metals was detected for Zn, which was present in all tested samples,
- 100% of the samples also contained trace quantities of Cu and Cr,

Table 1. *Results of tests for heavy metals presence in cotton from various growing regions (nf - not found, bold - the max. value obtained).*

Elements, ppm	Central Asia				South-West Asia	Africa		Europe	North America
	Uzbekistan	Kazakhstan	Turkmenistan	Tajikistan	Turkey	Egypt	remaining	Greece	USA
Cd	nf	nf-0.044	nf-**0.066**	nf	nf	nf	nf-0.042	nf	0.018
Co	nf-0.057	nf-0.009	nf-0.051	nf	nf	nf-0.117	nf-**0.123**	nf	nf
Cr	0.374-**0.926**	0.423-0.440	0.341-0.440	0.364	0.631	0.471-0.491	0.362-0.85	0.514	0.415
Cu	0.823-1.51	1.48-1.56	1.03-1.92	1.20	1.26	1.12-1.70	1.70-**2.08**	1.13	1.27
Ni	0.022-**5.87**	0.039-0.085	nf-5.87	0.045	0.297	0.046-0.348	nf-0.199	0.537	0.383
Pb	nf-0.299	0.502-0.612	nf-**0.796**	0.064	0.506	0.250-0.351	nf-0.666	0.261	0.063
Zn	3.70-21.0	15.4-15.8	5.28-14.0	10.1	8.81	6.59-13.1	15.3-**23.2**	9.22	3.14

- the remaining heavy metals considered in the tests, i.e. Ni, Pb, Co, and Cd, had different shares in the samples:
  Ni - 91.3%,
  Pb - 82.6%,
  Co - 26.0%,
  Cd - 21.7%,
  The defined contents of heavy metals were graded according to the decreasing share in the fibre mass and they appear as follows: Zn, Cu, Cr, Ni, Pb, Co, Cd.
- the content of some of the heavy metals presented a considerable dispersion of results, which is particularly visible for Ni, Zn and Pb; this is not clearly connected with the origin of the cotton. The level for the remaining metals tested is almost equal, independently of the origin of cotton.
- in the range of particular metals, the results are as follows:

Zn - a great variety of results, from 3.14 ppm for American cotton (and a similar level for two samples of Uzbek cotton) to 23.2 ppm for the Chadian one (the same level as one of the Uzbek samples). There is no clear connection of the Zn level with the cotton origin. For various samples of cottons with the same origin, the content of zinc varied by one grade. The situation was also true of Uzbek, Turkmen, and Egyptian cotton.

Cu - the received copper content is similar for all samples, remaining in the scope of 0.823 (Uzbek) to 2.08 (Beninese).

Cr - the trace quantity of chromium discovered in all samples remains on the level of tenth-fractions of ppm, with deviations from 0.34 to 0.93.

Ni - a considerable dispersion of results was obtained:
- in 8.7% - (2 samples) - none was found,
- in 53.0% - (10 samples) - the Ni level corresponds to hundredth-fractions of ppm,
- in 39.1% - (9 samples) - tenth-fractions of ppm,
- in 8.7% - (2 samples) - the Ni content is above 1 ppm.

Pb - trace values were encountered in the majority of samples (82.6%), within the scope of 0.06 ppm for American cotton to 0.79 ppm for one sample of Turkmen cotton. The results received indicate an almost equal level throughout the samples, in most cases corresponding to tenth-fractions of ppm. No lead was found in two Uzbek samples, one Turkmen and one Burkinabe.

Co - a trace quantity of cobalt was detected in only 26.1% of the samples, at the level of hundredth- or thousandth-fractions, or at the level of 0.1 ppm.

Cd - a cadmium presence was detected in 21.7% of the samples (5) with a uniform content of hundredth-fractions of ppm in Turkmen, Kazakh, American, Chadian and Beninese samples.

Table 2. Number of samples in which heavy metals were detected.

Origin of cotton	Number of samples tested	Number of samples in which heavy metals were detected						
		Cd	Co	Cr	Cu	Ni	Pb	Zn
Uzbekistan	6	0	1	6	6	6	4	6
Turkmenistan	5	1	1	5	5	4	4	5
Kazakhstan	2	1	1	2	2	2	2	2
Tajikistan	1	0	0	1	1	1	1	1
Egypt	3	0	1	3	3	3	3	3
Benin	1	1	1	1	1	0	1	1
Chad	1	1	1	1	1	1	1	1
Burkina Faso	1	0	0	1	1	1	0	1
Greece	1	0	0	1	1	1	1	1
USA	1	1	0	1	1	1	1	1
Turkey	1	0	0	1	1	1	1	1
Total	23	5	6	23	23	21	19	23
Share of samples with metals, %		21.7	26.1	100	100	91.3	82.6	100

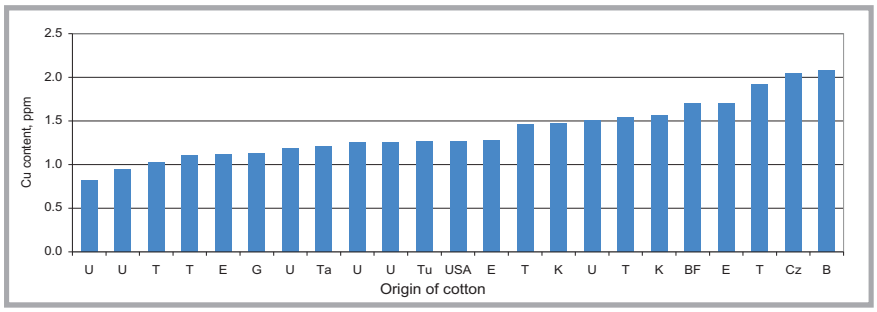

Figure 1. *Cu content in raw cotton. Symbols: B - Beninese, BF - Burkinese, Cz - Chadian, E - Egyptian, G - Greek, K - Kazakh, T - Turkmenian, Ta - Tajik, Tu - Turkish, U - Uzbek, USA - American*

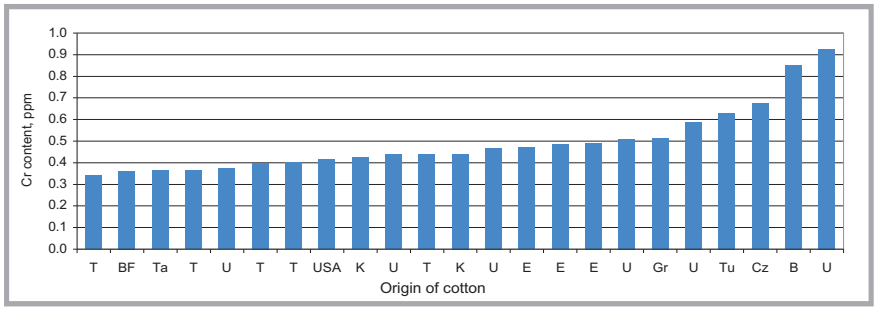

Figure 2. *Cr content in raw cotton. Symbols as in Figure 1.*

Pesticides and PCP content in cottons of various origins (bale raw material)

Table 3 presents the test results for pesticide content in ng/g in 20 samples of cotton of various origins. None of the analysed compounds was found in samples coming from Egypt, Burkina Faso, Chad, Benin, Greece and Turkey.

In cotton from Central Asia (Turkmenistan, Uzbekistan, Kazakhstan, Tajikistan) and from the USA, trace quantities of such compounds were detected.

Out of 19 analysed pesticides, no sample contained atrazine, endosulfan II, hexachlorobenzne or simazine. The trace quantities of pesticides which were detected amounted to between <10 ng/g (i.e. <0.01 ppm) and 266 ng/g (0.266 ppm). In several samples from Central Asia, trace values of such pesticides as DDT and Lindan (γ-HCH) were found, whose application had been forbidden many years ago.

Most pesticides were found in cotton samples coming from Uzbekistan and

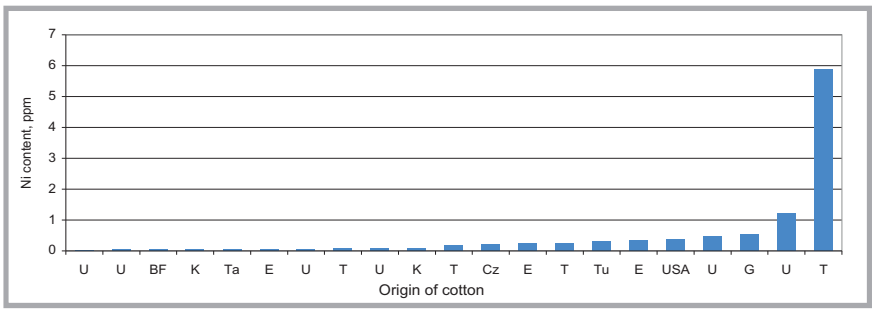

Figure 3. *Ni content in raw cotton. Symbols as in Figure 1.*

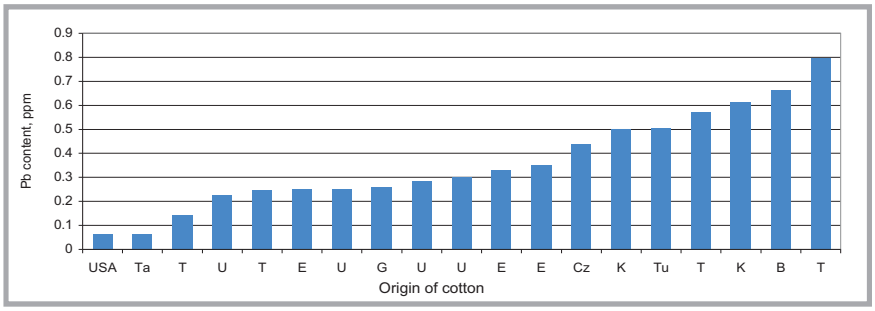

Figure 4. *Pb content in raw cotton. Symbols as in Figure 1.*

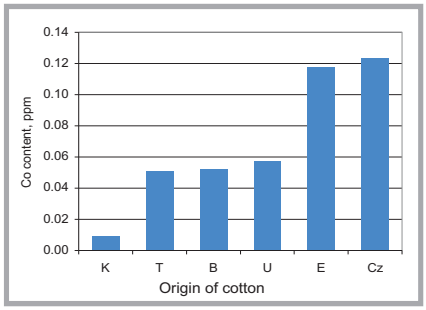

Figure 5. *Co content in raw cotton. Symbols as in Figure 1.*

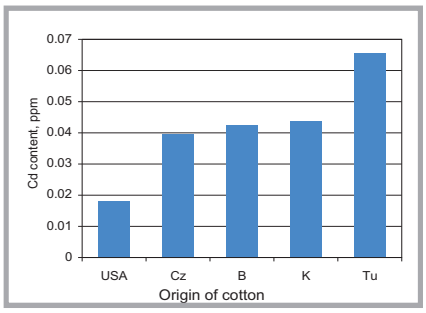

Figure 6. *Cd content in raw cotton. Symbols as in Figure 1.*

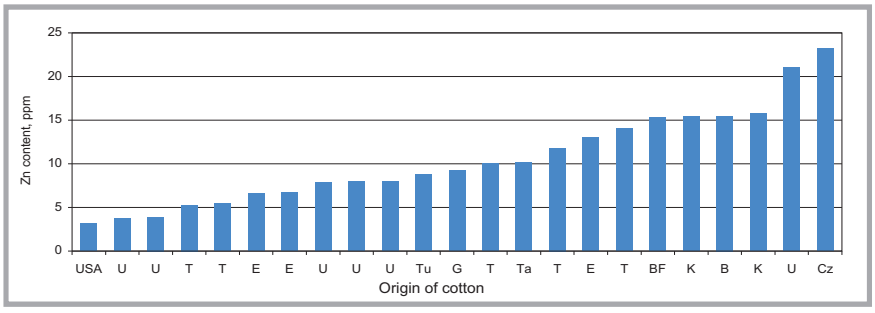

Figure 7. *Zn content in raw cotton. Symbols as in Figure 1.*

Kazakhstan. The global content of all pesticides analysed did not exceed 1 ppm in most adverse cases. This level has been accepted as safe for the user of a ready-made textile product in most situations, according to the 100 ÖKO TEX Standard. In relation to the requirements concerning pesticides in textile products (Attachment pos. Al. to the Decision of the Committee of the European Union of Feb. 17, 1999 establishing the ecological criteria for labelling textile products with the Union's eco-emblem 1999/178/EC), some samples did not fulfil the provisions. The requirements set the permissible border values for particular kinds of pesticides at the level of 0.05 ppm).

According to tests carried out according to the method described above, the level of such pesticides as aldrin, 4,4'-DDT, dieldrin, β-HCH and parathion was in many cases higher than 0.05 ppm. High contents of various pesticides were found in two Uzbek samples and in both samples from Kazakhstan. A considerable excess of the permissible level according to the established criteria was stated for aldrin, 4,4'-DDT, dieldrin, endrin (Uzbek cotton only), γ, β-HCH (Kazakh cotton only) and parathion.

Table 4 presents the percentage share of samples (and their origin) in which the presence of particular pesticides was detected. Out of 19 kinds of pesticides, 15 of them were found in samples from Kazakhstan, 12 from Uzbekistan, 10 from Turkmenistan, 6 from Tajikistan and 4 from the USA.

Most often detected were 4,4'-DDD (45% of samples) and endrin, aldrin and α-HCH (35%). The presence of 4,4'-DDT was stated in 25% of samples, and of γ-HCH in 15%. The usage of both of these is forbidden. None of the samples contained pentachlorophenol (PCP).

Summing up the results obtained, it is possible to state that:

- none of the tested 20 samples contained PCP, which is particularly harmful for the users' health,
- in cotton samples from Egypt, Burkina Faso, Chad, Benin, Turkey and Greece, none of the tested pesticides was found,
- in the majority of samples from Central Asia (cotton most often processed in the domestic industry), the presence of some of the pesticides was detected. Their global content in tested samples did not exceed the permissible level, according to the criteria of the 100 ÖKO TEX Standard,
- the most often detected pesticides were: 4,4'-DDD (in 45% of samples), aldrin, endrin, α-HCH (35%), parathion and dieldrin (30%),
- DDT and γ-HCH (Lindan), which are forbidden, were found respectively in 25% of samples (DDT) and in 15% of samples (Lindan). The cotton containing these pesticides was from Uzbekistan and Kazakhstan.

Summary of the content range of substances harmful to human health in cotton

Tests for the presence of substances harmful to human health such as heavy metals (Cd, Co, Cr, Cu, Ni, Pb, and Zn), pentachlorophenol (PCP) and 19 kinds of pesticides were carried out for 23 cotton

samples coming from various growing regions.

The presence of Cd, Co and Cr was only detected in several samples in trace quantities considerably lower than 1 ppm. Pb and Ni appeared in several more samples, in quantities also below 1 ppm. However, rare cases of Ni content above 1 ppm appeared, for which no explanation has been found.

Cu and Zn content was found in all tested samples within the interval of 1-2 ppm for Cu, and 3-23 ppm for Zn.

The defined content of heavy metals constitutes no serious threat to obtaining a product which matches the ecological requirements of the 100 ÖKO TEX Standard. None of the tested samples contained PCP.

Pesticides were detected in the majority of samples from Central Asia. In any case, their total content did not exceed the permissible level according to the 100 ÖKO TEX Standard.

Variations in heavy metal and pesticide content during the technological process of manufacturing cotton fabrics (from raw material to ready-made product)

Tests for heavy metals were done beginning from raw materials in bales in the spinning mill, through rotor grey yarn, the sized warp and weft used for manufacturing bed-cloth, grey cloth, cloth after cropping and finally the fabrics after consecutive phases of the technological process of finishing, i.e.:

- after preliminary treatment and bleaching,
- after dyeing,
- after printing,
- after finishing.

Hydrogen peroxide solution (H_2O_2) was used for bleaching. Dyeing was carried out on the Thermosol dyeing machine with reactive dyes of different makes. Printing was done on a rotary-screen printer with the use of pigment dyestuffs. The course of changes in the heavy metal content for mineralised samples from raw material to the finished product is presented in Table 5.

An analysis of the results in Table 5 indicated the changes in the heavy metal content as follows:

- at no stage of the examination were cadmium Cd and lead Pb detected, which means that the applied processing, auxiliaries and dyes did not add these substances to the product;
- in bale raw material, no cobalt Co was detected; this situation was maintained until after bleaching the fabric; the dyeing process with reactive dyes caused a visible increase in Co up to the level of 17.78 ppm, which continued until the end of the finishing process; the process of dyeing with pigments and finishing (classical finish) changed nothing;
- the chromium Cr content at the level of tenth-fractions of ppm was determined for the input raw material, and remained almost unchanged after

Table 3. *Results of analysis of pesticide content in cotton samples (nf - not found).*

Compound	Pesticide content in cotton according to origin, ng/g									
	Turkmenistan			Uzbekistan			Kazakhstan		Tajikistan	USA
	S1	S2	S3	S1	S2	S3	S1	S2	S1	S1
aldrin	12	nf	nf	143	136	68	<10	256	66	nf
atrazine	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
2,4-D	<10	<10	<10	nf	nf	nf	<10	nf	nf	43
4,4'-DDD	<10	nf	<10	36	<10	12	87	23	22	21
4,4'-DDE	nf	nf	nf	nf	<10	27	nf	77	nf	<10
4,4'-DDT	23	nf	nf	nf	49	112	nf	190	<10	nf
dieldrin	24	nf	nf	nf	124	266	175	<10	43	nf
endosulan I	nf	nf	nf	nf	<10	nf	<10	nf	nf	nf
endosulan II	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
endrin	<10	nf	<10	78	62	79	42	43	nf	nf
α-HCH	17	nf	nf	nf	34	12	34	<10	nf	<10
β-HCH	<10	nf	nf	nf	<10	nf	210	<10	nf	nf
γ-HCH	nf	nf	nf	nf	<21	nf	89	<10	nf	nf
heptachlorine	nf	nf	nf	nf	nf	nf	21	nf	nf	nf
hexachlorobenzene	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
carbanyl	nf	nf	nf	22	nf	nf	nf	<10	nf	nf
parathion	<10	nf	nf	nf	77	212	133	92	nf	<10
simazine	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
2,4,5-T	<10	nf	nf	18	nf	nf	<10	<10	<10	nf

Table 4. *Percentage share and origin of cotton samples in which pesticide presence was detected.*

Name of the compound (pesticide)	Number of samples containing pesticides	% of samples containing pesticides	Origin of cotton
Aldrin	7	35	Uzbekistan, Kazakhstan, Turkmenistan, Tajikistan
atrazine	0	0	-
2,4-D	5	25	Turkmenistan, Kazakhstan, USA
4,4`-DDD	9	45	Turkmenistan, Uzbekistan, Kazakhstan, Tajikistan, USA
4,4`-DDE	4	20	Uzbekistan, Kazakhstan, USA
4,4`-DDT	5	25	Turkmenistan, Uzbekistan, Kazakhstan, Tajikistan
dieldrin	6	30	Turkmenistan, Uzbekistan, Kazakhstan, Tajikistan
endosulfan I	2	10	Uzbekistan, Kazakhstan
endosulfan II	0	0	-
endrin	7	35	Turkmenistan, Uzbekistan, Kazakhstan,
α-HCH	7	35	Turkmenistan, Uzbekistan, Kazakhstan, Tajikistan, USA
β-HCH	4	20	Turkmenistan, Uzbekistan, Kazakhstan,
γ-HCH	3	15	Uzbekistan, Kazakhstan
heptachlorine	1	5	Kazakhstan
hexachlorobenzene	0	0	-
carbanyl	2	10	Uzbekistan, Kazakhstan
parathion	6	30	Turkmenistan, Uzbekistan, Kazakhstan, USA
simazine	0	0	-
2,4,5-T	5	25	Turkmenistan, Uzbekistan, Kazakhstan, Tajikistan

Table 5. Change in heavy metal contents in technological processes of production of cotton bed-cloth (nf - not found).

Metal	Content of heavy metals in cotton in particular stages of production, ppm									
	Bale raw material	Rotor yarn tex 30	Sized yarn (warp)	Yarn, warp weft	Grey cloth	Cloth after cropping	Cloth after preliminary treatment and bleaching	Cloth after dyeing	Cloth after printing	Finished cloth
Cd	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Co	nf	nf	nf	nf	nf	nf	nf	17.78	17.12	18.24
Cr	0.45	0.33	0.37	0.35	0.38	0.37	0.36	5.20	4.93	5.34
Cu	1.02	1.73	1.10	1.40	1.33	0.96	nf	280.2	263.8	279.7
Ni	0.28	0.09	nf	0.05	0.40	0.26	0.04	0.34	1.31	1.29
Pb	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Zn	8.86	6.40	7.68	7.06	8.30	7.84	2.24	4.30	7.14	11.35

the spinning, weaving and bleaching processes. The subsequent dyeing process increased the chromium content significantly, to 5.2 ppm, and it remained unchanged until the end of the finishing process. This means that Cr appeared in dyestuffs as their contamination;

- a content of 1 ppm of copper Cu was detected for input raw material; this remained true for grey yarn and yarn after sizing, for grey cloth from the loom and after cropping; the process of preliminary treatment and bleaching caused the content to be reduced to the limit of detection. After dyeing, a great increase in copper content was discovered, which continued until the end of the process;
- the results of nickel Ni detection show small interchangeable variations after particular phases of the process, from raw material up to dyeing. A significant increase in Ni content was determined after printing, which means that nickel contaminated the dyeing pigments; further finishing process did not cause any changes in the content of this metal;
- the zinc Zn content fluctuated a little in the process from raw material to the finished product within the interval of 6 to 11 ppm; lower Zn content was obtained only for fabric after preliminary treatment and bleaching, in comparison to the preceding and following processes.

Table 6. Heavy metal content in different dyestuffs (nf - not found; As and Hg were not detected in the dyestuffs studied; P - pigment dyestuff; R - reactive dyestuff).

Element, ppm	Pigmatex Navy RN (liquid) (P)	Pigmatex Black NG (liquid) (P)	Pigmatex Green B (liquid) (P)	Novoblanc A (paste) (P)	Sumifix Blau R (liquid) (R)	Czerń Helaktynowa DN (powder) (R)	Błękit Helaktynowy D5RF (powder) (R)	Ostazin Blau HBR (powder) (R)
Cd	0.3393	1.022	0.3929	nf	0.5122	nf	<0.1	<0.1
Co	nf	< 0.03	nf	237.2	nf	6088	nf	270.5
Cr	nf	nf	3.242	108.9	2.914	8818	3.672	429.4
Cu	45210	13.53	22770	37.31	2603	1247	26890	224.4
Ni	35.07	2.424	6.779	nf	11.02	13.12	34.06	0.8511
Pb	30.05	16.28	32.19	82.79	84.81	35.66	35.87	30.12
Zn	582.8	7.737	68.10	nf	45.35	28.41	97.89	43.41

Table 7. Test results of content of heavy metals, pesticides and pentachlorophenol (PCP) in finished cotton cloth, finished cotton cloth after extraction with artificial sweat as compared with requirements according to ÖKO TEX Standard.

Inventory		Finished cotton bed-cloth	Extractable heavy metals from finished cotton bed-cloth	Requirements according to ÖKO TEX Standard 100
Heavy metals, ppm	As	nf	<1.0	≤ 1.0
	Pb	nf	~0.269	≤1.0
	Cd	nf	nf	≤ 0.1
	Cr	5.34	~0.502	≤ 2.0
	Cr (VI)	undetectable	undetectable	undetectable
	Co	18.24	0.5518	≤4.0
	Cu	279.7	11.83	≤50.0
	Ni	1.29	0.9072	≤4.0
	Hg	nf	nf	≤0.02
Content of pentachlorophenol (PCP), ppm		nf	nf	≤ 0.5
Content of pesticides (including PCP), ppm		nf	nf	≤ 1.0

Changes in heavy metal content in dyestuffs used in the dyeing and printing of cotton bed-cloth

It has been shown that the heavy metal content was distinctly reduced after the preliminary treatment of textile and bleaching. A sudden increase in heavy metal content both after dyeing and printing was observed. The appearance of large quantities of Co, Cu and Cr, as well as the increase in the content of Ni and Zn observed, may have been caused by contamination from reactive and pigment dyestuffs used in the chemical treatment of cotton bed-cloth.

To confirm these assumptions, the change in heavy metal content in different dyestuffs used in the technological process was determined. Table 6 shows the changes in heavy metal content in the different reactive and pigment dyestuffs used. It can be seen that the dyestuffs studied contain very large amounts of Cu, Co and Cr, as well as a much smaller content of Ni, Pb and Zn. The results observed coincide very well with the changes monitored in heavy metal content after the chemical treatment of cotton bed-cloth.

Contents of heavy metals, pesticides and PCP extractable by the use of artificial acid sweat in a finished fabric

Table 7 presents the results of tests for the content in the finished fabric of the following heavy metals: As, Cd, Co, Cr, Cu,

Ni, Pb and Hg, extractable with artificial acid sweat. It also shows the contents of pesticides and PCP, when compared with the 100 ÖKO TEX Standard. The results do not exceed the permissible values allowed by the above criteria for textile products used in direct contact with the human body.

Summary

The tests for contents of harmful substances in cotton from various growing regions showed that it can contain small quantities of heavy metals, such as zinc Zn, copper Cu, chromium Cr, nickel Ni, lead Pb, cobalt Co and cadmium Cd. Zn, Cu, and Cr were detected in all analysed samples, Ni and Pb appeared in the majority of them, whereas Co and Cd in only some of them.

The amounts of Co and Cd were very small, on the level of hundredth-fractions of ppm, of Cu in the range of 1-2 ppm, and of Zn from 3 to 23 ppm. None of the analysed samples contained PCP. The presence of pesticides was detected in the majority of samples from Central Asia. Their global content as determined did not exceed the permissible level according to the 100 ÖKO TEX Standard.

The level of heavy metals and pesticides detected in the samples as input material does not constitute any serious threat to obtaining products which fall within the human-ecological criteria defined by the 100 ÖKO TEX Standard.

However, as far as the heavy metal content in a ready-made product is concerned, a greater danger may be posed by the dyeing and printing processes, in which the contamination of dyestuffs and auxiliary materials with Cu, Co, Ni, Cr and others can be added to the cotton product.

An analysis of the heavy metal content in various phases of the process of cotton-bed fabric production with the classical finish demonstrated that no important changes to their levels took place during spinning, sizing, weaving, cropping and finishing. A decrease in the content of some heavy metals was observed after the process of preliminary treatment and bleaching, but an increase was observed after dyeing and printing.

Some heavy metals (Co, Cu and Cr) were extracted by artificial acid sweat not exceeding 3-10%. In our opinion, nickel Ni may cause the greatest danger and potential risk for the human body. As can be seen, practically 70% of this element is extracted. The greater the amount of nickel Ni in dyestuffs and auxiliaries, the greater the potential risk of allergic reactions etc.

In spite of causing an increase in content of some heavy metals, the dyes and pigments used allowed the production of a commodity matching the required ecological criteria [16-17].

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Editorial notes

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2. *The problems concerned with the topic of this paper were partially presented at the 7th International Cotton Conference, Gdynia, Poland; 6-7 September, 2001.*

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