SURVEY OF METALS FOUND IN NON-DOMESTIC RAW COTTONS

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Abstract

Information about levels of metals in non-domestic raw cottons is limited or non-existent. Because of increased importation of these cottons for domestic consumption in recent years, interest in their metal content has increased for a number of reasons. High levels of certain metals may cause problems in yarn manufacturing, fabric production, dyeing and finishing, and considerations involving textile wastes in commercial fabric production.

A limited study of metals in raw cottons from Africa, China, Greece, Syria, and Russia was conducted. General comparisons of metals in these cottons and those found in four growing areas in the U.S. were made. In general, foreign cotton metals contents were much more variable than U. S. grown cottons. Calcium levels in three of these growing areas were determined to be 10 to 20% higher than domestic cottons. Iron content for the limited number of African and Greek cottons studied was also higher than U. S. cottons.

Introduction

Metals in cottons may contribute to problems in yarn manufacturing, fabric production and dying and finishing (Barnwell et. al. 1947, Cook, 1991, Brushwood and Perkins, 1992 and 1994, Rucker, et. al., 1992). High levels of abrasive materials such as silicon and other metals may cause frictional problems in rotor spinning and needle wear in the knitting process. During the dyeing and finishing process, complex salts formed from calcium and magnesium may affect dyeing quality (Cook, 1991). Other trace metals such as iron, copper, and aluminum contribute to yellowness of finished denim goods (Rucker, et. al., 1992). Metal residues from textile wastes in commercial fabric production have become an increasingly important consideration in recent years. Proper disposal of solid and liquid textile wastes containing residual metals in commercial fabric production can present problems to the textile industry (Perkins and Brushwood, 1993). Environmental limits on certain metals are strict and are expected to be even stricter in the future.

Naturally occurring metals such as potassium are important nutrients for normal cotton development (Dhindsa, et. al., 1975). Potassium in cottons is water soluble and highly related to field and weathering conditions (Domelsmith and Berni, 1984, Muller, 1982). Other metals such as aluminum, calcium, magnesium, sodium, iron, and silicon occur naturally in cottons. Trace amounts of copper, manganese, and zinc also are often found present (Guthrie, 1955, Heinzeman and O'Connor, 1950).

There is some information available on levels of metals from previous studies of a number of U. S. grown cottons covering four major growing areas (Brushwood and Perkins, 1994). This survey of primarily California, Texas, and Mississippi cottons indicated differences between growing areas. Some variations in metal content were also seen between growing seasons because of such factors as boll field weathering and harvest histories. However, variations in metal content for the more abundant naturally occurring metals such as potassium, sodium, calcium and magnesium were small compared to regional differences. Averages and ranges of potassium content ranged from highs averaging about 6000 ppm in California to lows about 3000 ppm in Texas cottons. In general, the levels of the light metals potassium, magnesium, and sodium were consistently higher in California cottons and calcium levels were higher in Texas cottons. Trace amounts of heavier metals such as iron, copper, manganese and zinc were also found in cottons from these growing areas.

With increased importing of more non-domestic foreign cottons by U. S. processors in the last few years, interest in the presence and quantity of metals in these cottons has intensified. Very little published information, however, is available. One might expect wide variations in metal content in cottons from non-domestic sources considering the diversity of varieties, cultural practices, and growing areas. Processors must be aware of any potential problems that may occur from the presence of certain metals in these cottons. Therefore, a brief survey of a variety of imported cottons in our inventory and general comparisons to levels found in U. S. cottons is presented in this paper.

Experimental

Cottons from our inventory were conditioned in the laboratory (ASTM standard D-1776) for at least two weeks before moisture contents were determined for each. Moisture contents (in triplicate) for all of these cottons averaged 6.89 ± 0.10%. Metal concentrations and ash contents were calculated on a dry fiber basis using 6.89% moisture content as a factor to adjust to dry fiber weight.

Ten gram (± 0.005 g) samples of raw cotton were ashed for 2.5 hours at 650°C in a muffle oven. After ashing, the residues were weighed and ash content was calculated for each sample. These ash residues were then dissolved in 5 ml. of concentrated hydrochloric acid (38%) and subsequently made up to 25 ml. with de-ionized water. Dilutions from this

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solution were made with de-ionized water depending upon the expected concentration of element in the sample and the linear absorbance operating range of the atomic absorption instrument.

Atomic absorption (AA) analysis for each metal was made on a Buck Scientific 200A Spectrophotometer reading in the absorbance mode using an air/acetylene flame. To overcome the possible ionization of the potassium or sodium in the air/gas flame, cesium at the concentration of 1000 µg/ml of sample and standard was added when determining these two elements. The cesium was supplied by dissolving 3.1675 g of cesium chloride (99.9%) in 5 ml. of de-ionized water. Additions of the cesium chloride to the samples and standards were at the rate of 2ul/ml. To overcome the possible depression of the sensitivity for calcium and magnesium by silicates, aluminum or phosphates, 1000ug/ml of lanthanum was added to the samples and standards for these two elements. The lanthanum was supplied by dissolving 6.6840g of lanthanum chloride in 5 ml. of de-ionized water. Two microliters of this solution per milliliter of sample were added.

Dilutions made to obtain appropriate absorbencies at the respective wavelengths for the metals were 1250x for potassium, 625x for magnesium, 200x for calcium, and 125x for the element sodium. The original 10 grams per ml. of solution (2.5x) was used to determine concentrations of the heavier metals, copper, manganese, iron and zinc. Two are more determinations were made on each sample and calculations were based on a calibration curve using four or more standard concentrations for each metal. A blank (no ash) was always included in each determination and used as a reference sample.

Twenty four (24) non-domestic cottons from Europe, Africa, and Asia from varying mills and CQRS inventories were analyzed for metals. Subsequent results were to be compared to metal contents determined for U.S. cottons at an earlier date.

Results and Discussion

Metals in U.S. Cottons

In a previous study (Brushwood and Perkins, 1994) metals in cotton from four major U. S. growing locations were determined. Results of this study that include variations in variety and season are listed in Table 1. Most of the variations for each growing area, as expected, were seasonal due to weather factors. Potassium levels in California grown cottons averaged 5900 ppm, 5250 ppm in the High Plains of Texas, 3420 ppm in Mississippi, and 3000 in Texas cottons. Average potassium levels were higher in California and Texas High Plains Areas. Calcium content averaged 680, 930, 830, and 850 ppm for California, Texas High Plains, Mississippi, and Texas cottons, respectively. Average magnesium contents ranged from a high of 700 ppm for Mississippi, 620 ppm for California, 530 ppm for Texas High plains, to a low of 405 ppm for Texas cottons. Sodium content averaged 180 ppm for California, 160 ppm for Texas High Plains, 150 ppm for Mississippi, and 140 ppm for Texas cottons. The only other metal determined to be present at levels greater than 10 ppm, iron, averaged 32 ppm in the Mississippi and California and slightly higher at 55 and 63 ppm in the Texas and Texas High Plains growing areas, respectively. Copper, manganese, and zinc were determined to be less than 10 ppm in all those cottons analyzed from all four growing areas.

Metals in Non-Domestic Cottons

African. Metal contents were determined on a total of four African cottons (Table 2). The specific African country of origin for 2 of these cottons was in doubt. We, however, have included them. Two samples identified as Sudan cottons were determined to have average iron contents above 100 ppm. The other 2 African cottons averaged 62 ppm iron. Most of these iron concentrations were higher than the overall average for the highest U. S. growing area of Texas. High levels of iron could contribute to yellownness in lint and perhaps problems in textile dyeing. Potassium levels ranged from a low of 4760 ppm to a high of 5810 ppm, averaging close to concentrations usually found in cottons from Texas High plains at 5260 ppm. Calcium averaged 845 ppm (near the average for Texas cottons) and magnesium averaged 608 ppm (about the average for California cottons) for these four African cottons. Sodium content averaged 206 ppm or about 15% higher than the highest average for a U. S. growing (California). Other light and heavy metal concentrations measured were not significantly different from those found in U. S. cottons. Copper, manganese, and zinc concentrations were all determined to be less than 5 ppm each.

Chinese. We recently received 8 new Chinese cottons from a mill. These samples were labeled PM 1 through 8. Results for these cottons are shown in Table 2. Potassium concentrations varied from 3510 to 4350 ppm with an overall average of 4065 ppm. Overall average potassium concentrations for these Chinese cottons were at least 20% lower than those observed for the African cottons. Average calcium, magnesium, and sodium contents were found to be 640 ppm (near the average for California cottons), 386 ppm (slightly lower than the average for Texas cottons), and 122 ppm (lower than any average U. S. cotton growing area), respectively. These numbers also are about 24, 20, and 40% lower than averages for the same corresponding metals found in raw cottons from Africa. The total sum of calcium and magnesium content averages was about 200 ppm less than the lowest U. S. cotton average. Iron contents averaged 21 ppm, or about 30% of the African cottons. The highest iron content measured on the Chinese cottons was 27 ppm (slightly less

than averages for Mississippi and California cottons) and the lowest was 11 ppm. Copper, manganese, and zinc concentrations were determined to all be less than 5 ppm each.

Greek. Three different bales from Greece were sampled and metal content on them were also determined (Table 3). Average potassium content (4170 ppm) was comparable to averages for the same metal on Chinese cottons. The average calcium content for these cottons was 967 ppm, or slightly (4%) above the highest average concentration for calcium (Texas High Plains) in U. S. cotton at 930 ppm. Magnesium content averaged 483 ppm and sodium content averaged 135 ppm. Iron contents ranged from 16 to 96 ppm with an overall average of 58 ppm. Using U. S. cottons as a reference, iron levels in Greek cottons were on the high side and comparable to average iron concentrations in Texas growing areas. Copper, manganese, and zinc concentrations were determined to all be less than 5 ppm each.

Syrian. The three Syrian cottons (Table 3) in our study averaged 5003 ppm potassium, comparable to average potassium content found in African and Texas High Plains cottons. Calcium contents were determined to be an average of 1177 ppm. Compared to U. S. cottons, these Syrian Cottons contained about 25% more calcium than the highest average found for the same metal in Texas High plains. Averages of the other light metals, magnesium (533 ppm) and sodium (150 ppm) were comparable to U. S. cottons. Iron concentrations averaged 37 ppm, or comparable to averages for the same metal in cottons from California or Mississippi growing areas. Copper, manganese, and zinc concentrations were determined to all be less than 5 ppm each.

Russian. Potassium content for 6 Russian cottons (Table 3) were all greater than 5200 ppm, averaging 5700 ppm. Calcium contents varied from a low of 630 to a high of 1260 ppm, averaging 1003 ppm. Magnesium, sodium and iron contents were determined to be 562, 183, and 33 ppm, respectively. With the exception of about 40% more calcium being present, the averages for all of these metals determined were comparable to their respective content found in California cottons. Copper, manganese, and zinc concentrations were all determined to be less than 5 ppm each.

Cotton Ash Content

Ash content of raw cotton can vary from below one percent to well above two percent depending upon factors including area of growth, environmental conditions, foreign matter content and others (Guthrie, 1955). Ash contents for these 24 non-domestic cottons were determined. Results are summarized in Table 4. Also listed in the table, for comparison purposes, are results of ash contents on a number of U. S. cottons that had previously been determined. Ash results followed the general pattern that might be expected. High ash contents were determined for cottons grown in areas where exposure of open bolls to rain is limited or rare. In general, places like California, Africa, Syria, and Russia may well have high levels of non-cellulosic materials on them.

The relationship between ash content and measured potassium content for the non-domestic cottons in this study was found to gave a simple coefficient of correlation of 0.94 (figure 1). A similar correlation for the magnesium content was determined to be 0.97 (figure 2). When the potassium and magnesium contents were combined, the coefficient of simple correlation was 0.95. Thus, the average potassium (31%), calcium (7%), magnesium (4%), and sodium (1%) contents for these foreign cottons account for approximately 43% of ash weight in the cottons.

Summary

Ash and metal contents for 24 non-domestic cottons were determined and compared to corresponding ashes and metal contents determined for four U. S. growing areas. The dominant metal in the cottons was potassium ranging from 3500 to 6600 ppm; followed by calcium and magnesium, (380 to 1260 ppm); sodium (100 to 320 ppm); iron (11 to 152 ppm) and copper, manganese and zinc; (less than 10 ppm). The cottons grown in areas where the possibility of exposure of open bolls to rain is limited or rare generally had higher ash contents than those grown in other areas. Also, these same cottons gave overall higher average contents for the four most abundant metals potassium, calcium, magnesium and sodium.

Potassium contents for African, Syrian, and Russian cottons were comparable to the average California cotton. Chinese and Greek cottons averaged 4100 to 4200 ppm potassium. Except for the Chinese cottons, calcium contents of these non-domestic cottons seemed to be much more variable and higher than U. S. cottons. Levels of calcium in the Greek, Syrian, and Russian cottons averaged 10 to 20% higher than the U. S. grown cottons. Russian, Greek, and Syrian cottons averaged calcium contents of 1003, 967, and 1177 ppm, respectively. The calcium content of African cottons was comparable to those from the Texas cottons. Chinese cottons, on the other hand, contained the lowest amount of calcium of all cottons studied. High calcium content, as previously mentioned, could potentially causes the formation of insoluble calcium salts in wet processing that may interfere with the dyeing of the finished yarn or fabric. The other light metals, magnesium and, sodium, averaged within the general range of concentrations found on U. S. cottons. African cottons averaged just over 200 ppm sodium, but should be of no major concern.

Iron, which in undesirable quantities may cause yellowness in cotton, ranged from 15 to 93 ppm in U. S. cottons with an overall average of 46 ppm. The same metal in the non-domestic cottons ranged from a low average of 21 ppm for Chinese cottons to a high average of 90 ppm for African cottons. In general, the African and Greek cottons had higher iron content and Chinese, Syrian, and Russian cottons iron contents were comparable to U. S. cottons.

Although this is not a complete analysis of all metals found on raw cottons, the cottons tested represented samples from at least five non-domestic locations and included the most common ones found in significant quantities in cotton with two notable exceptions. We did not measure silicon and aluminum concentrations. These results should provide general information to cotton processors who have concerns about the roles of metals in yarn manufacturing, dyeing, finishing, safety and health in the workplace and proper disposal of solid and liquid textile wastes containing metals.

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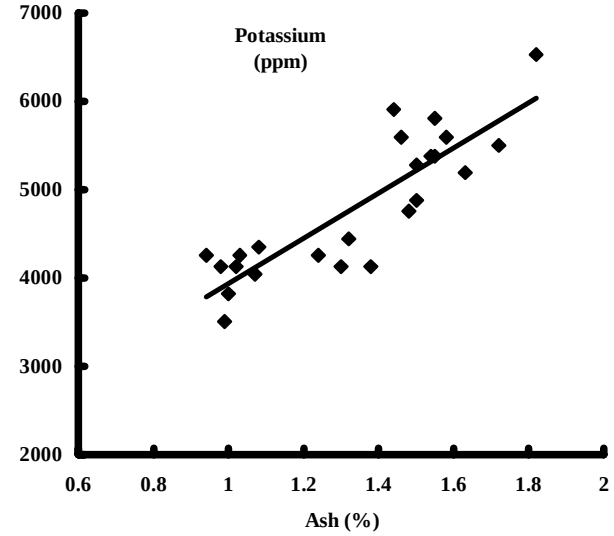

Figure 1. The relationship of potassium content and ash contents for non-domestic cottons.

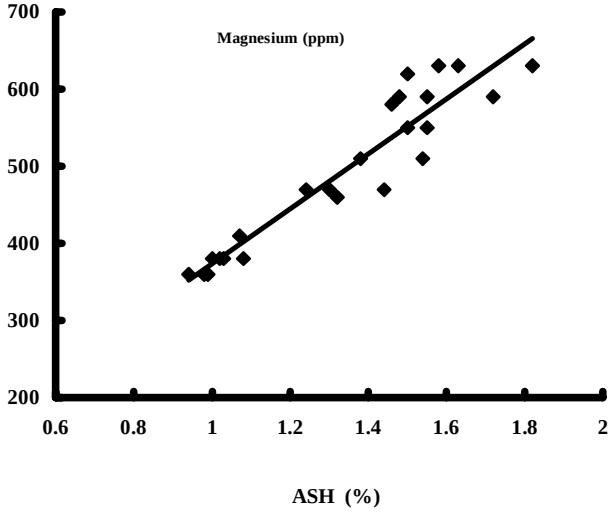

Figure 2. The relationship of magnesium content and ash contents for non-domestic cottons.

Table 1. The Effect of U. S. Growing Areas on Metal Content of Raw Cotton.

Growing Area	Metal Content (ppm)			
CALIE (N =13)	**k**	**CA**	**mg**	**NA**
Average	5900	680	620	180
Range	4800-6600	490-780	490-780	130-250
	Fe	**CU**	**MN**	**ZN**
Average	32	3	4	5
Range	15-66	2-3	3-4	4-7
Mississippi (N =10)				
	k	**CA**	**mg**	**NA**
Average	3420	830	700	150
Range	2100-4400	530-1250	340-1250	110-220
	Fe	**CU**	**MN**	**ZN**
Average	32	2	4	4
Range	26-40	2-3	3-4	3-4
Texas High Plains (N = 4)				
	k	**CA**	**mg**	**NA**
Average	5250	930	530	160
Range	3150-6130	750-1040	460-590	140-190
	Fe	**CU**	**MN**	**ZN**
Average	55	---	---	---
Range	50-60	---	---	---
Texas (N = 7)				
	k	**CA**	**mg**	**NA**
Average	3000	850	405	140
Range	2170-5170	760-1240	350-500	100-220
	Fe	**CU**	**MN**	**ZN**
Average	63	3	7	5
Range	21-93	2-3	6-8	4-6

Table 2. Metal Content of Raw Cottons Grown in Africa and China

Growing Area	Metal Content (ppm)							
ID Mark	**k**	**CA**	**mg**	**NA**	**Fe**	**CU**	**MN**	**ZN**
Africa								
#1	5590	1000	630	280	73	2	1	0
#2	5810	1080	590	240	50	2	0	2
Sudan 13782	4880	630	620	160	84	4	1	1
Sudan 13929	4760	670	590	145	152	2	0	1
China								
PM-1	4260	480	380	130	16	3	1	1
PM-2	4260	1260	360	180	27	2	1	1
PM-3	4130	370	360	120	23	1	1	1
PM-4	3820	520	380	110	16	1	1	0
PM-5	4130	630	380	115	27	1	1	0
PM-6	4350	480	460	110	27	1	0	0
PM-7	4040	780	410	110	18	1	0	0
PM-8	3510	600	360	100	11	2	1	0

Table 3. Metal Content of Raw Cottons Grown in Greece, Syria,and Russia.

Growing Area	Metal Content (ppm)							
ID Mark	**k**	**CA**	**mg**	**NA**	**Fe**	**CU**	**MN**	**ZN**
Greece								
65286	4260	890	470	115	16	1	1	1
65307	4130	890	470	160	91	2	2	1
65314	4130	1120	510	130	96	2	0	2
Syria								
60260	5190	1710	630	170	50	1	1	0
60274	5380	930	510	170	39	2	2	0
60284	4440	890	460	110	23	2	1	0
Russia								
#1	5590	820	580	220	46	1	1	0
#2	5380	1230	550	320	48	2	0	0
#3	5280	630	550	170	27	1	1	1
472456	5910	890	470	130	16	1	1	0
473533	6530	1190	630	115	39	2	0	0
473570	5500	1260	590	145	23	1	0	0

Table 4. Ash Content of Raw Cottons Grown Domestically and Internationally.

Location	Ash (%)	Range (%)
U.S.		
California (N=13)	1.80	1.61 - 2.07
Mississippi (N=10)	1.17	0.79 - 1.42
Texas (N=7)	1.07	0.91-1.71
Texas HP (N=4)	1.62	1.41-1.90
S.Carolina (N=1)	1.70	-----
Foreign		
African (N=4)	1.53	1.48 - 1.58
Chinese (N=8)	1.02	0.94 - 1.08
Greek (N=3)	1.31	1.24 - 1.38
Syrian (N=3)	1.50	1.32 - 1.63
Russian (N=6)	1.58	1.44 - 1.82