

***Recycled wool raw materials:
Focus on parameters for chemical safety
assessment and PRSL Proposal***



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➤ Recycled textile material – woollen type:

- Material with high wool content ($WO > 70-80\%$)
- Material with low wool content blended with other fibers (e.g. «*Triblend WO/PC/PL*»)
- Material made up by luxury fibers (WS, WK, WP, etc)

➤ **Material with high wool content (WO > 70-80%)**

Origin:

POST-CONSUMER material (used clothes):

- From knitted apparel :
 - regenerated material called **«maglieria»**
- From Apparel made up by carded woven:
 - regenerated material called **«stame cardato»**
- From Apparel made up by combed woven:
 - regenerated material called **«stame pettinato»**

➤ Material with high wool content (WO > 70-80%)

Origin:

PRE-CONSUMER material (tailor trimmings):

- From combed woven:
 - regenerated material called «*tassello (pura lana)*»
- From carded woven:
 - regenerated material called «*lambswool*»
- From knitted fabrics:
 - regenerated material called «*tassello di maglia*»
- From spinning and twisting trimmings:
 - regenerated material called «*fila*»

➤ **Material with high wool content (WO > 70-80%)**

Quantitative data and origins:

POST-CONSUMER (used clothings): 70 – 80%

- **India:** (selection of used cloths by colors differences) – about 60-70% of post-consumer material.
- **Italy – Europe:** about 30-40% of post-consumer material.

PRE-CONSUMER (Tailor trimmings): 20 – 30%

- **Italy – Europe (est)**

OPERATIONAL PLAN

1 – Quantitative and qualitative assessment concerning recycled wollen-type raw material used by carded spinning companies in Prato textile district

2 – Sampling: more than 100 wollen-type recycled raw material selected by:

- Origin (pre-consume / post-consume)
- Type (*maglieria; stame; fila / tassello; lambswool*)

3 – Chemical analysis: priority groups of «concerned substances».

Chemical Analysis: priority groups of concerned substances

Parameter	
Aromatic amines from azo-colorants	Flame Retardant
Alkylphenols (AP / APEOS)	Chlorobenzenes and toluenes
Chlorophenols	Chlorinated paraffins (SCCP)
Perfluorinated Compounds (PFC)	Phthalates
Allergenic and Carcinogenic Dyes	Organotin compound
Heavy Metals (from perspiration solution)	Chlorinated solvents
Biocides / presevatives - Permethrins	Formaldehyde

Aromatic Amines derived from azo-colorants

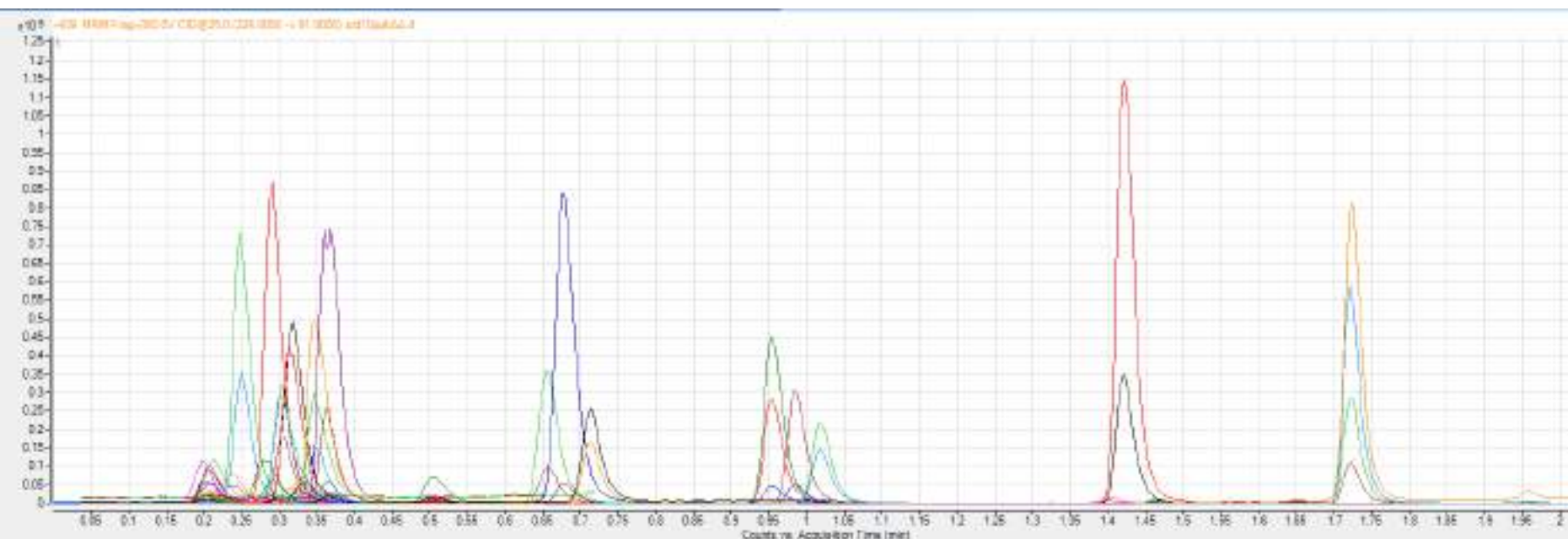
EN 14362-1 – GB/T 17592

Textiles: determination of certain aromatic amines derived from azo colorants

Technique: GC-MS/MS and LC-MS/MS

LOD: 1 mg/kg

10 ng/ml (ppb) standard of aromatic amines – about 0,05 mg/kg



Aromatic Amines derived from azo-colorants

EN 14362-1 – GB/T 17592

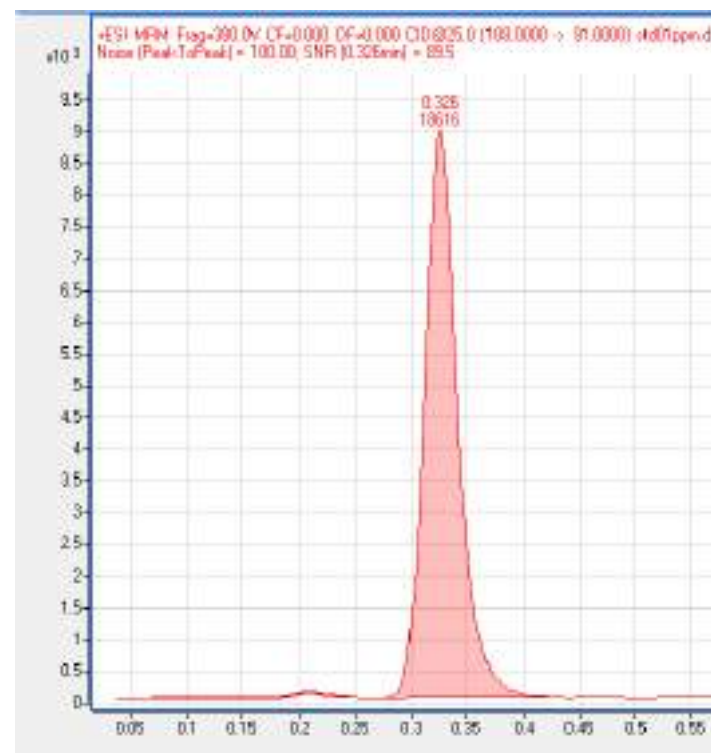
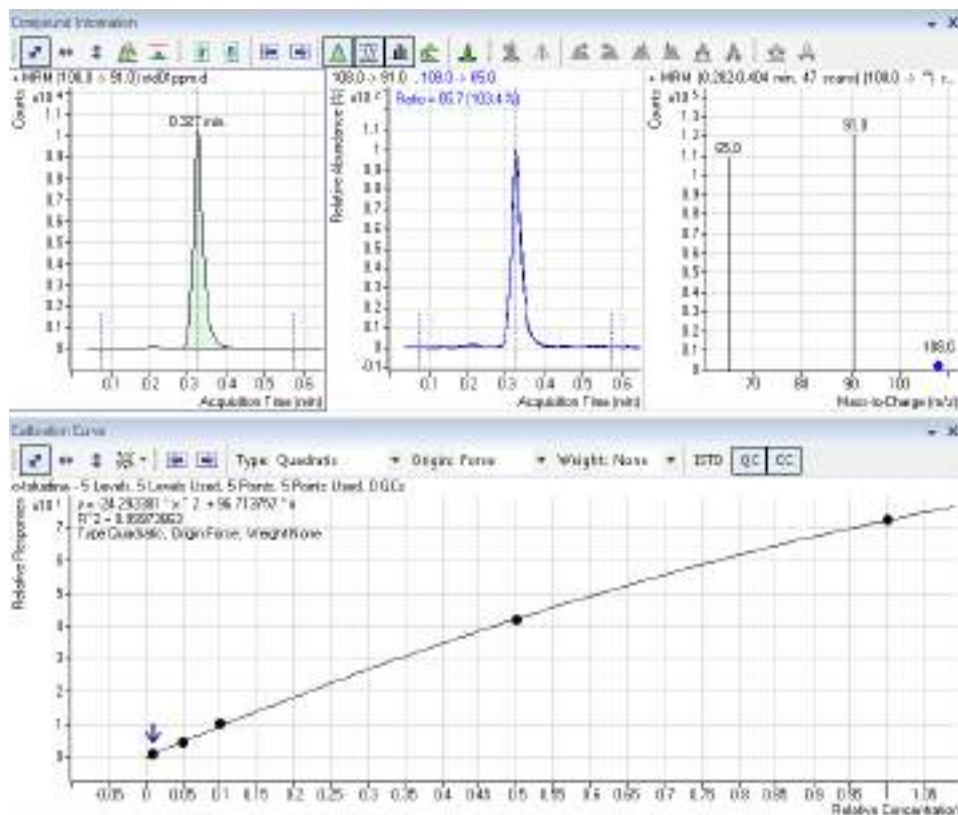
Textiles: determination of certain aromatic amines derived from azo colourants

Technique: GC-MS/MS e LC-MS/MS

LOD: 1 mg/kg

eg. Calibration Curve for o-toluidine

o-toluidine: quantitative analysis at 0,5 mg/kg



Ethoxylated Alkylphenols (APEOS)

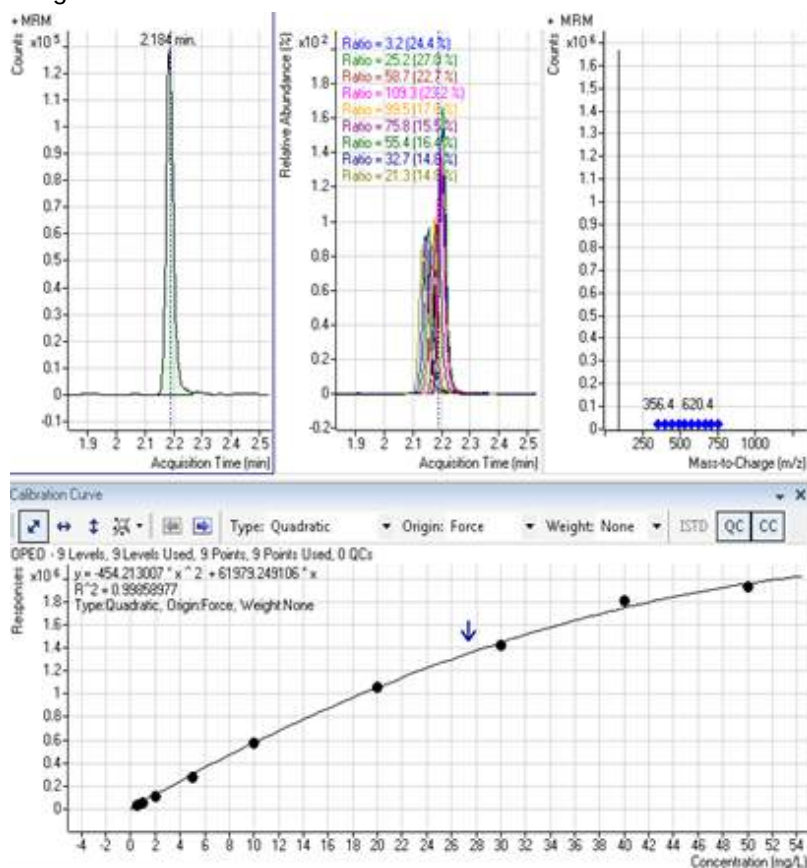
ISO 18254-1:2016

Textiles — Method for the detection and determination of ethoxylates alkylphenol (APEO) - Part 1: Method using HPLC-MS

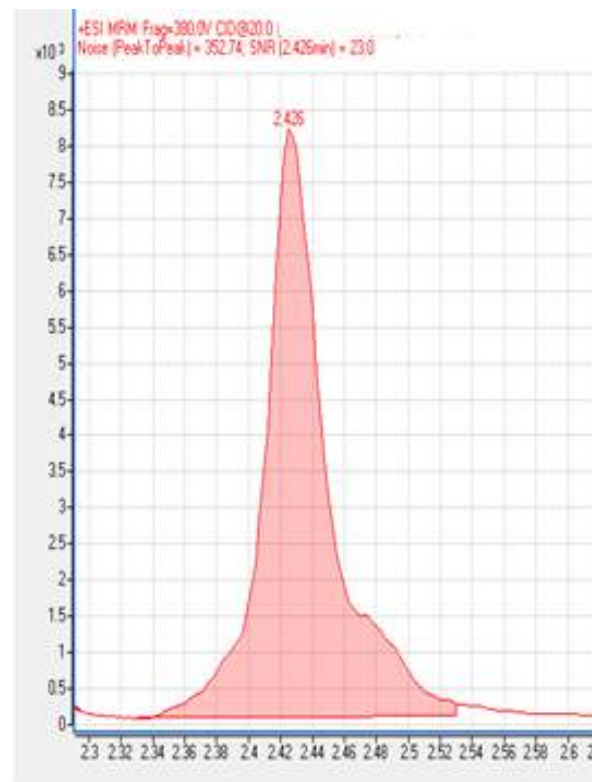
Technique: LC-MS/MS

LOD: 1 mg/kg

eg. Calibration Curve for OPEO



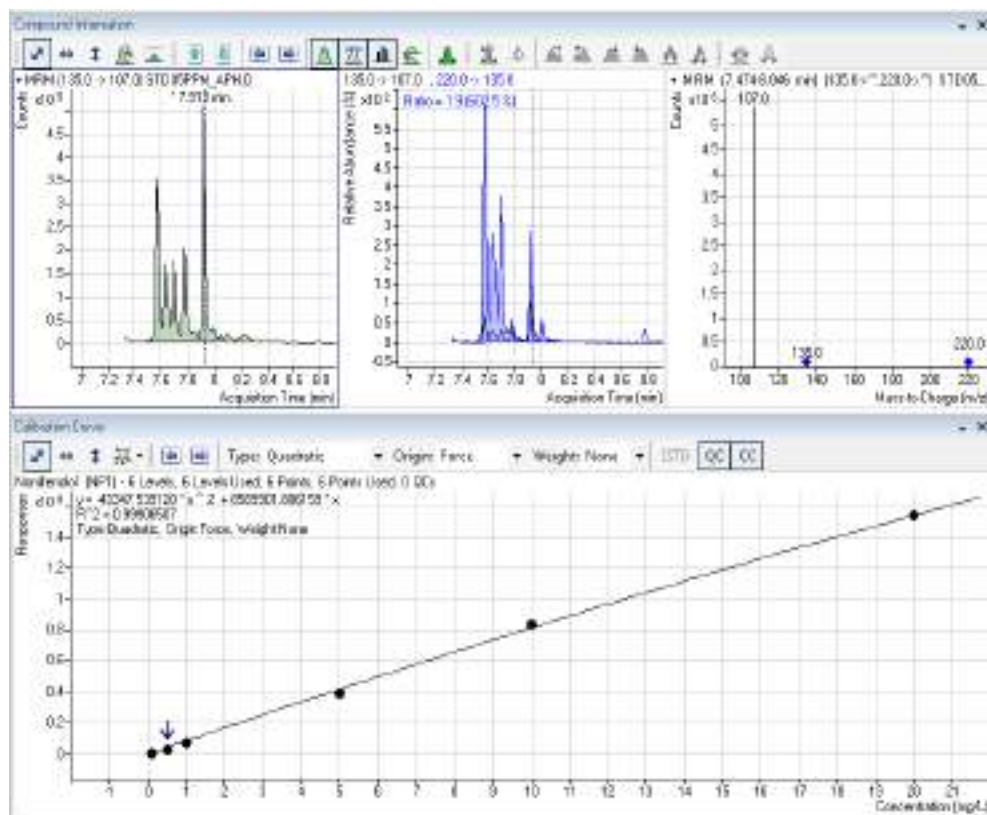
NPEO– quantitative analysis at 1 mg/kg



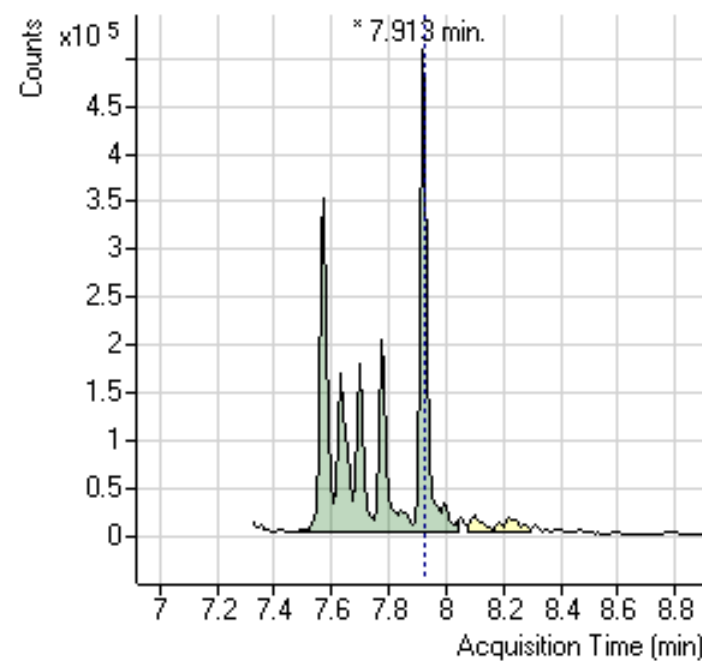
Alkylphenols - AP

In-house test method MIP_CE0124:2018 Ref ISO 18857-1	Technique: GC-MS/MS	LOD: 1 mg/kg
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eg. Calibration Curve for NP



NP– quantitative analysis at 1 mg/kg



Chlorophenols

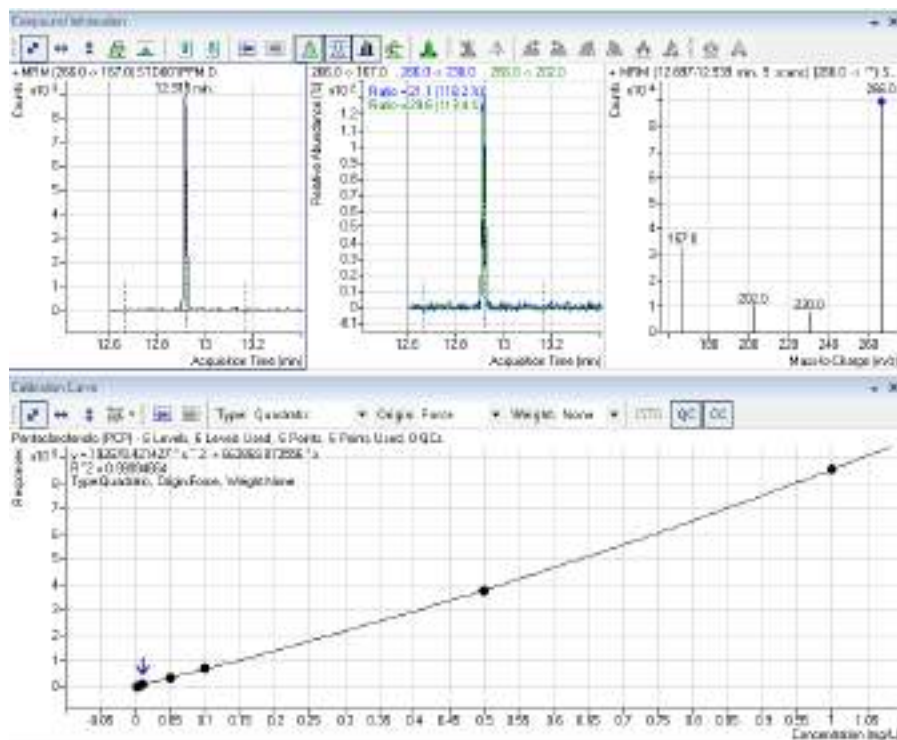
UNI 11057 – GB/T 18414.1

Textiles: Determination pentachlorophenol (PCP), tetrachlorophenols (TeCP) and relative salts

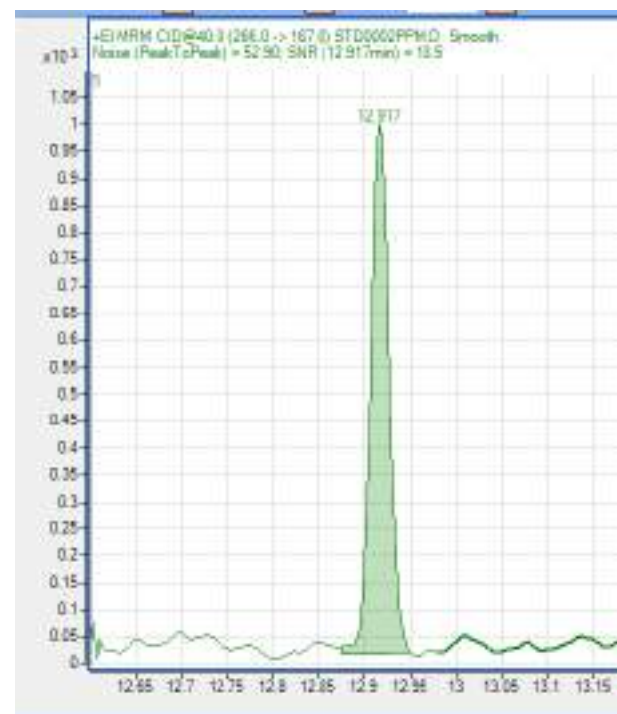
Technique: GC-MS/MS

LOD: 0,025 mg/kg

eg. Calibration curve for Pentachlorophenol



Pentachlorophenol – quantitative analysis at 0,01 mg/kg

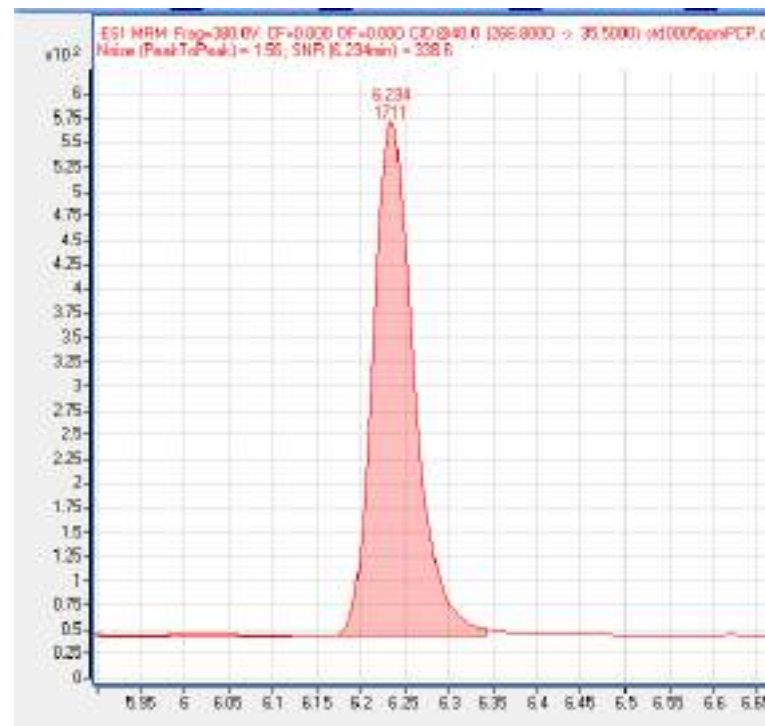
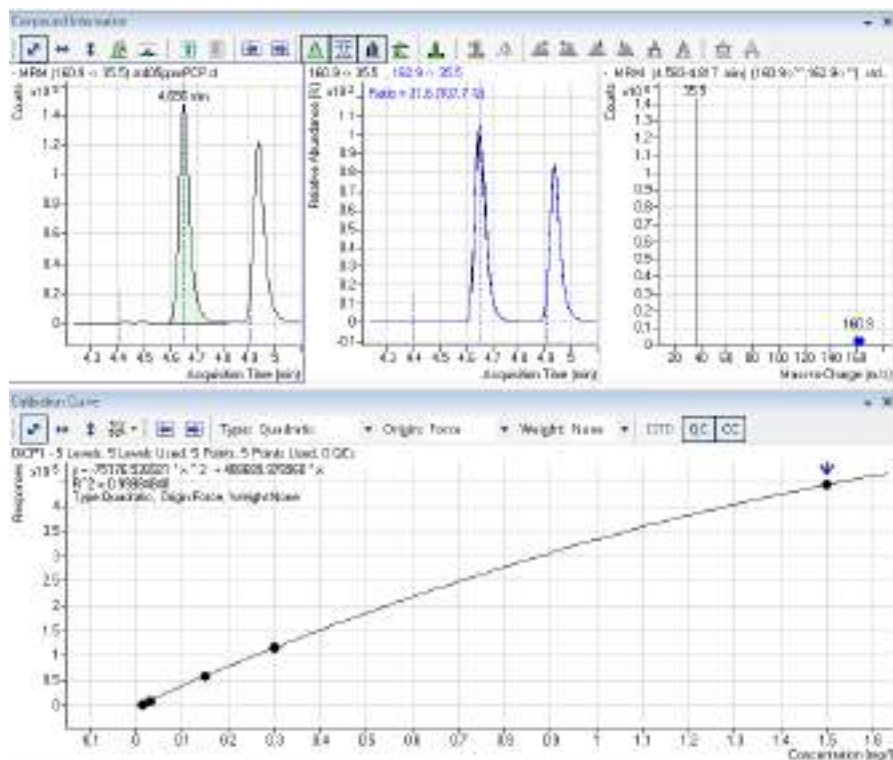


Chlorophenols

In-house Test Method Textiles: Determination chlorophenols	Technique: LC-MS/MS	LOD: 0,025 mg/kg
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Eg. Calibration curve for 2,4-Dichlorophenol

2,4-Dichlorophenol – quantitative analysis at 0,01 mg/kg

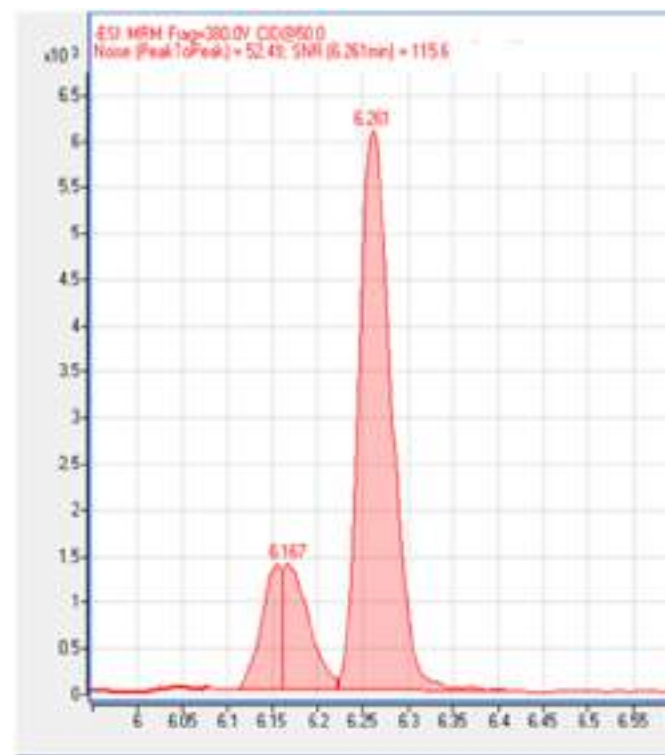
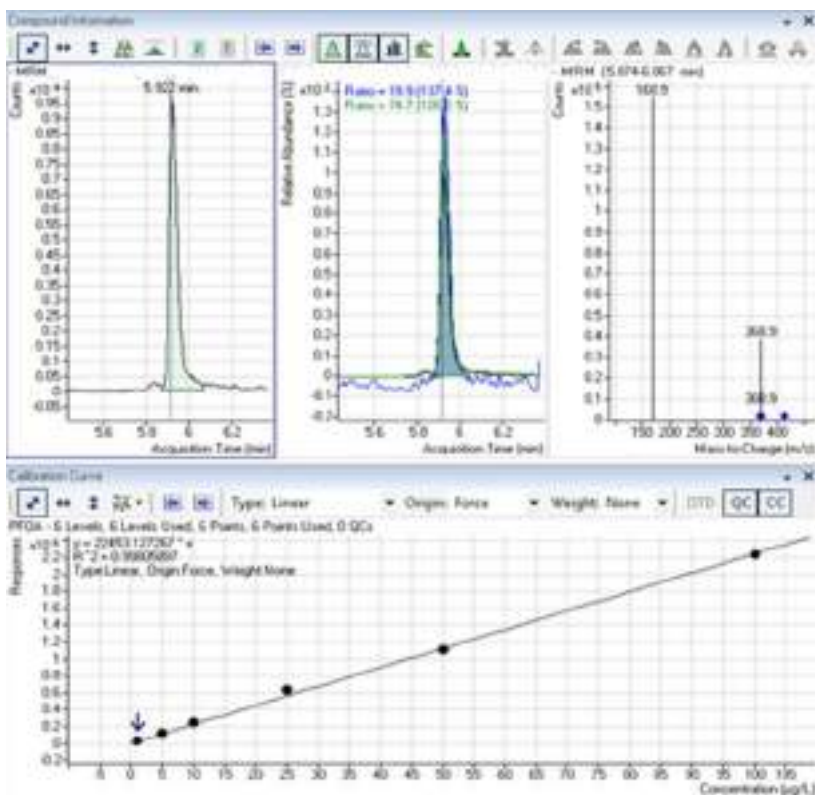


PFOS/PFOA and other Perfluorinate Compounds (PFC)

In-house test method MIP CE0084:2016 Ref UNI CEN/TS 15968:2010	Technique: GC-MS/MS (FTOH and FTA) LC-MS/MS (other PFC)	LOD: FTOH and FTA: 10 µg/m² - PFC: 1 µg/m² LOD (for fabric with 300 g/m² weight): FTOH and FTA: 0,033 mg/kg - PFC: 0,003 mg/kg
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Eg. Calibration curve for PFOA

PFOS – quantitative analysis at 1 µg/m²

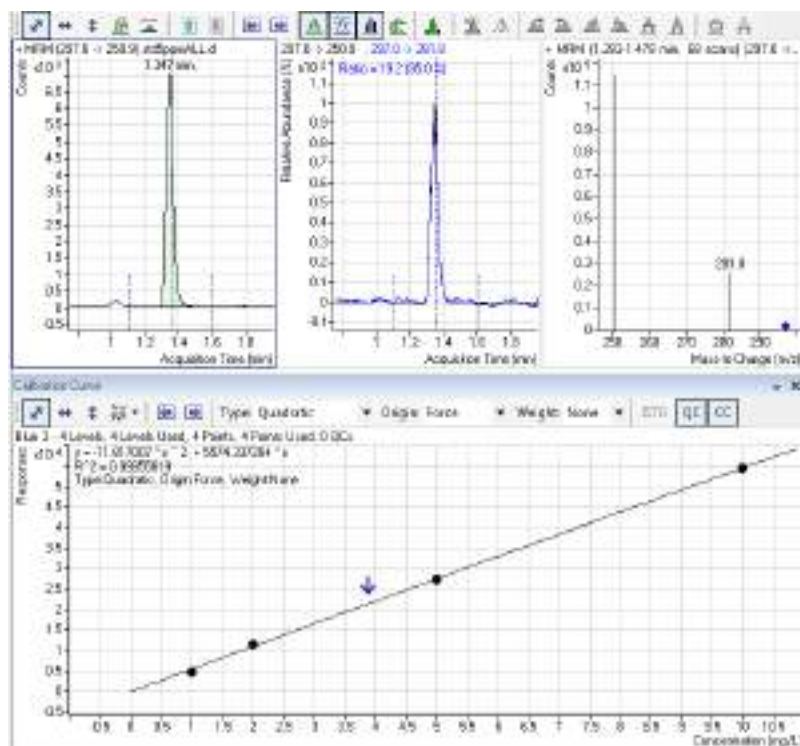


DISPERSE and CARCINOGENIC Dyes

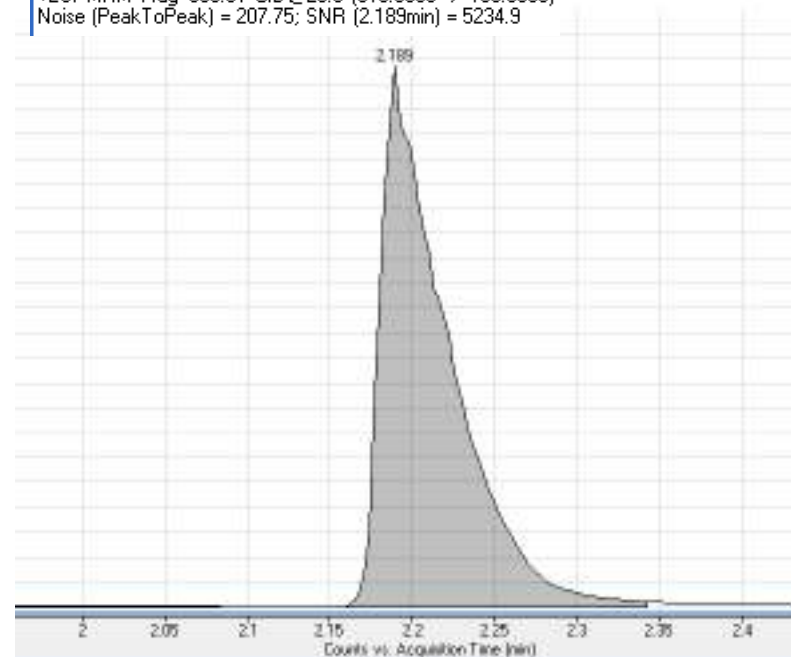
DIN 54231-2005(11) ISO 16373-2:2014 ISO 16373-3:2014	Technique: LC-MS/MS	LOD: 1mg/kg
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Eg. Calibration curve for DISPERSE BLUE 3

DISPERSE BLUE 3 – quantitative analysis at 1 mg/kg



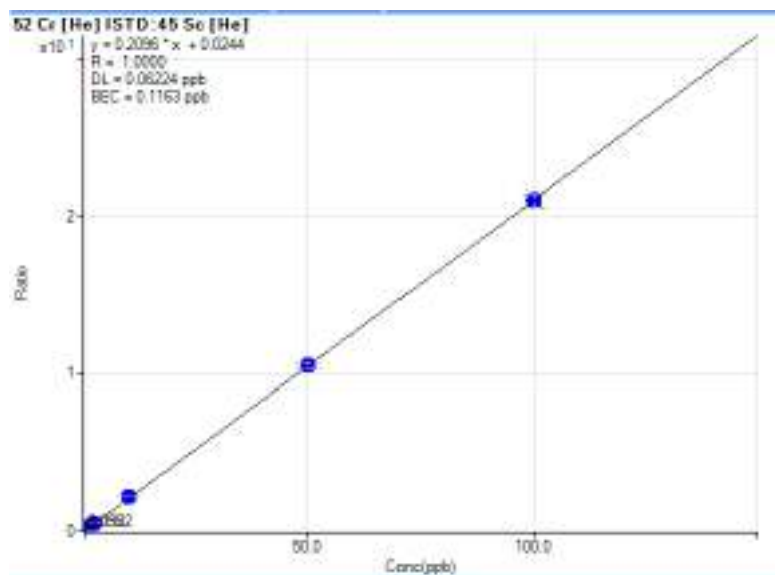
+ESI MRM Frag=380.0V CID@28.0 (319.0000 -> 168.9000)
Noise (PeakToPeak) = 207.75; SNR (2.189min) = 5234.9



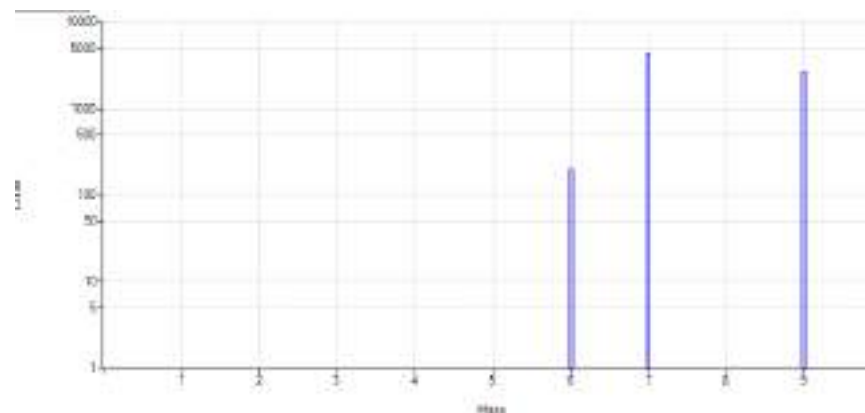
HEAVY METALS from perspiration solution

GB/T 17593-2 EN 16711-2:2015 (DIN 54233-3) ISO 17072-1:2011	Technique: ICP-MS (all metals except Cr (VI))	LOD: 0,1mg/kg
Hexavalent Chromium - Cr(VI) GB/T 17593-3	Technique: UV-VIS / LC-ICP-MS	LOD: 0,5mg/kg

Eg. Calibration curve for CHROMIUM



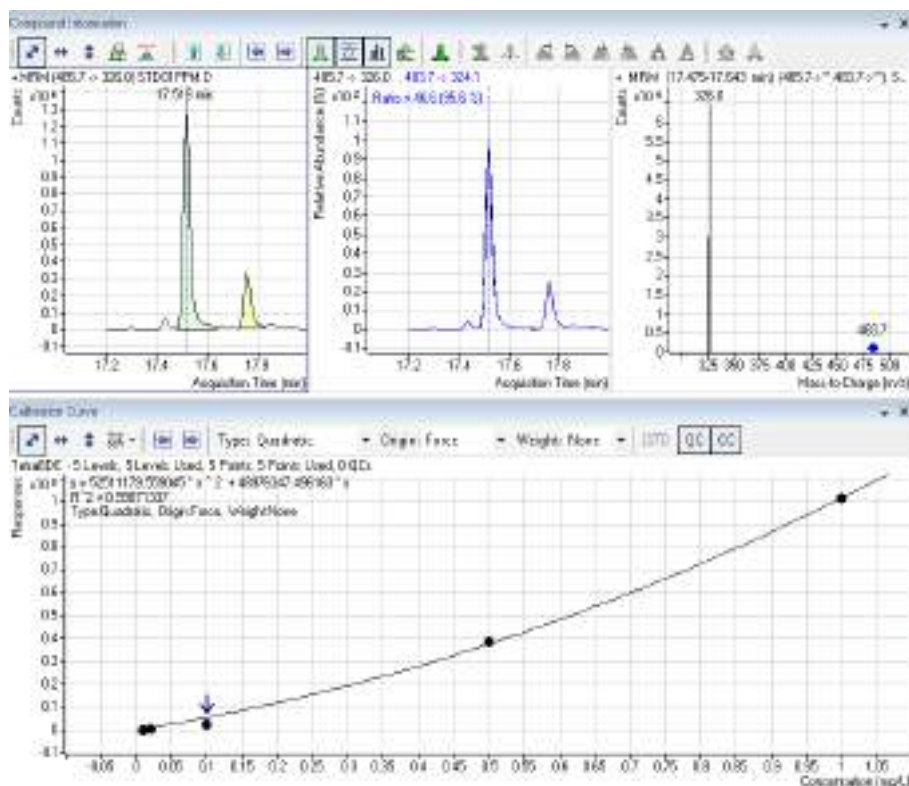
CHROMIUM – quantitative analysis at 0,5 mg/kg



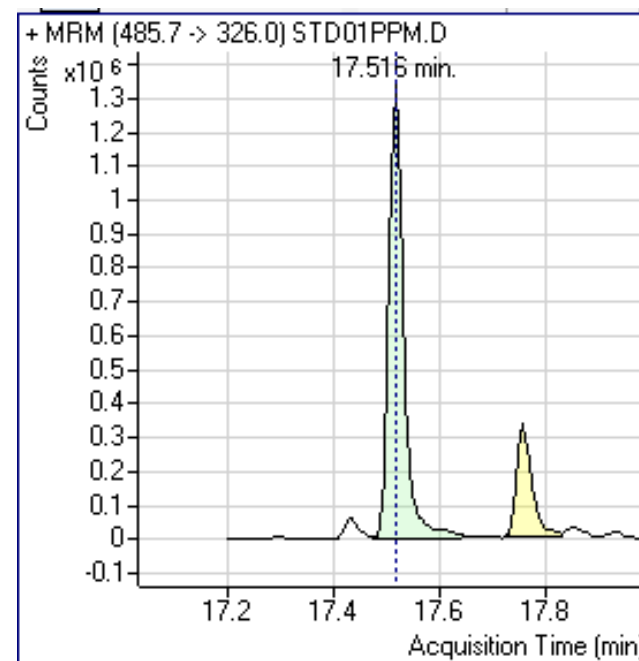
Flame retardant

GB/T 24279-2009 ISO 17881:2016	Technique: GC-MS/MS - LC-MSMS	LOD: 0,01 mg/kg
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Eg. Calibration curve for Tetra-DBE



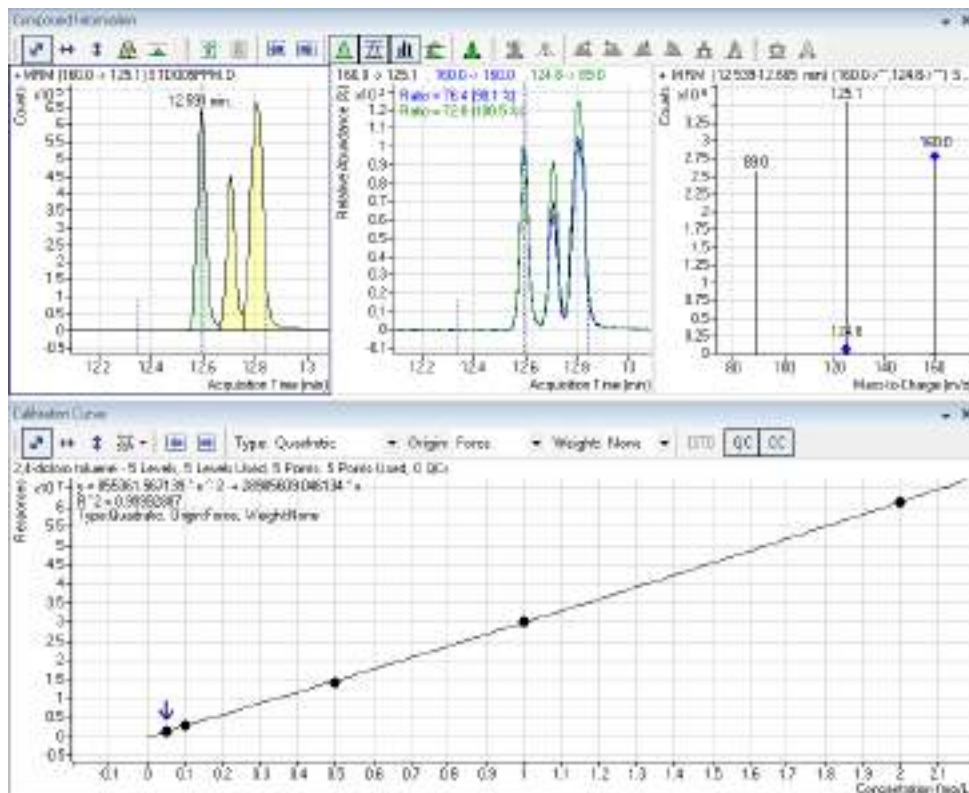
Tetra-BDE– quantitative analysis at 0,1 mg/kg



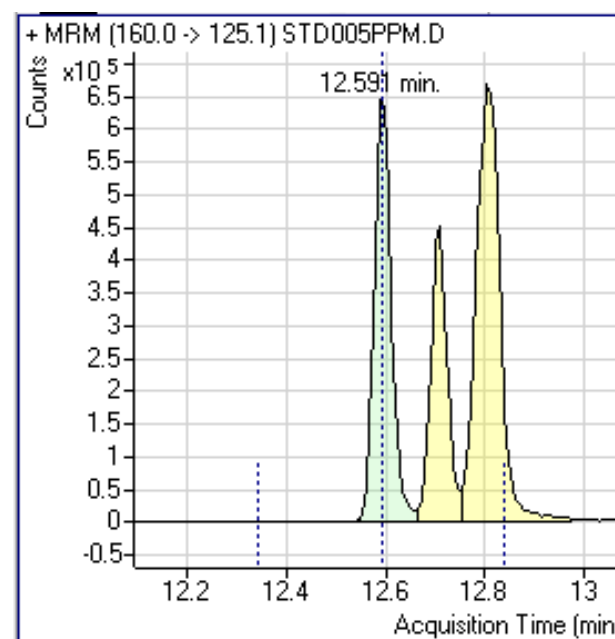
Chlorobenzenes and toluenes

DIN 54232:2010	Technique: GC-MS/MS	LOD: 0,05 mg/kg
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Eg. Calibration curve for 2,4-dichlorotoluene



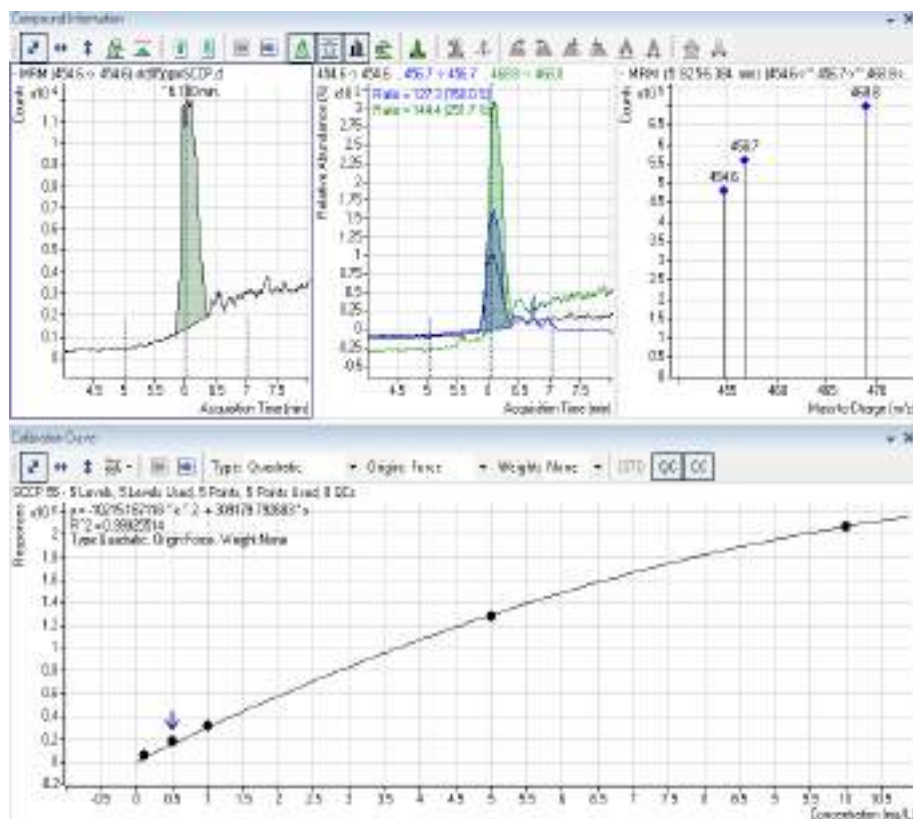
2,4-dichlorotoluene – quantitative analysis at 0,1 mg/kg



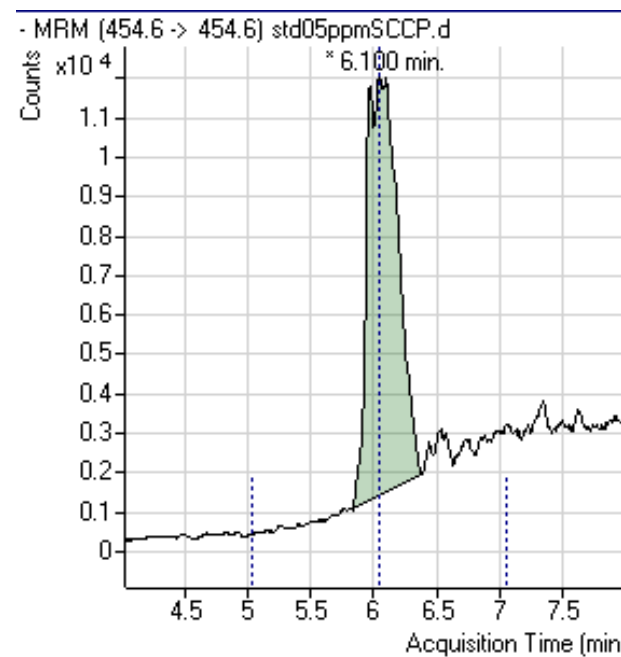
Chlorinated paraffins (SCCP)

ISO 18219:2015	Technique: LC-MS/MS	LOD: 0,5 mg/kg
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Eg. Calibration curve for SCCP



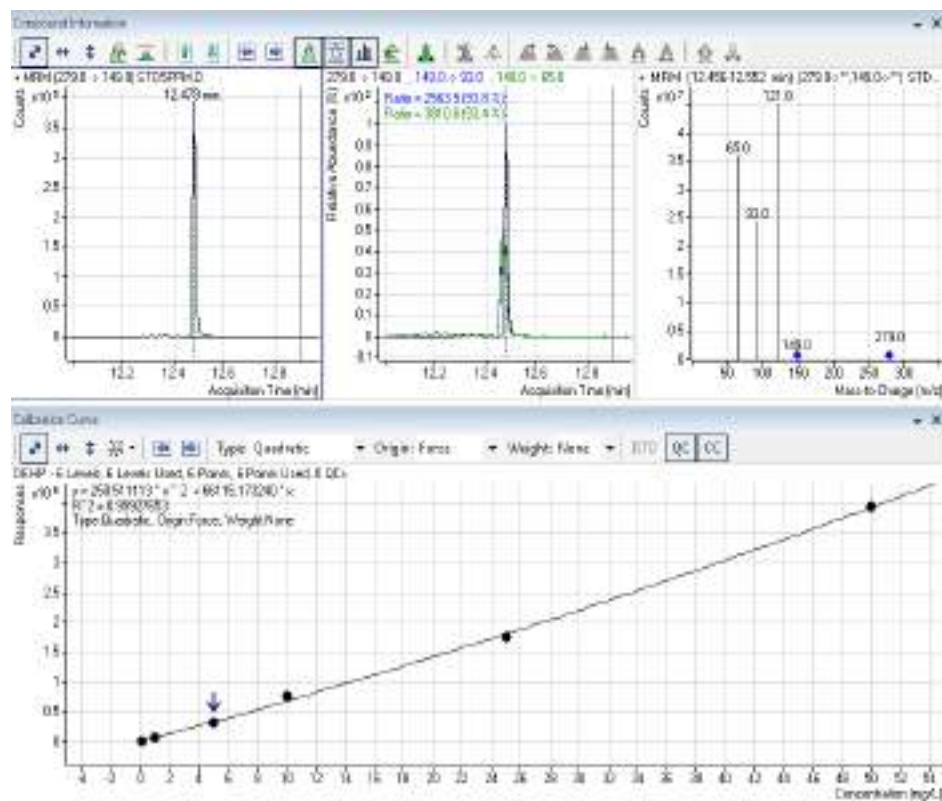
SCCP – quantitative analysis at 1 mg/kg



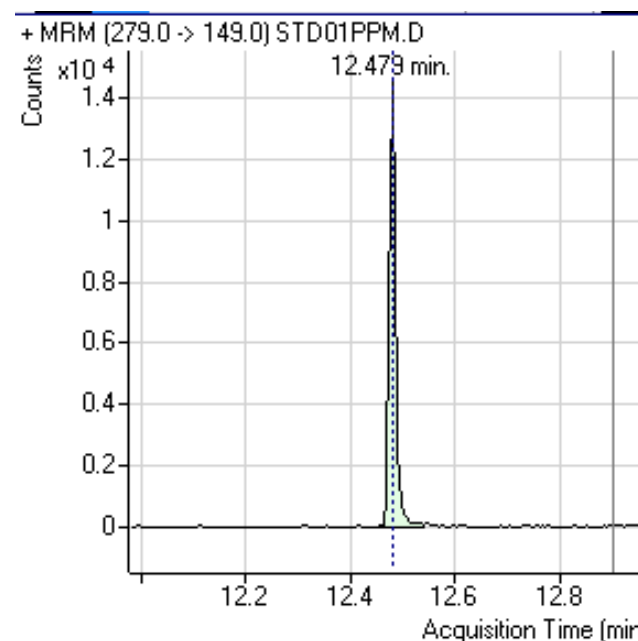
Phthalates

CPSC-CH-C1001-09.3:2010 GB/T 20388 UNI 14389 UNI 16181	Technique: GC-MS/MS	LOD: 5 mg/kg for DINP and DIDP – 1 mg/kg for other phthalates
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Eg. Calibration curve for DEHP



DEHP– quantitative analysis at 1 mg/kg

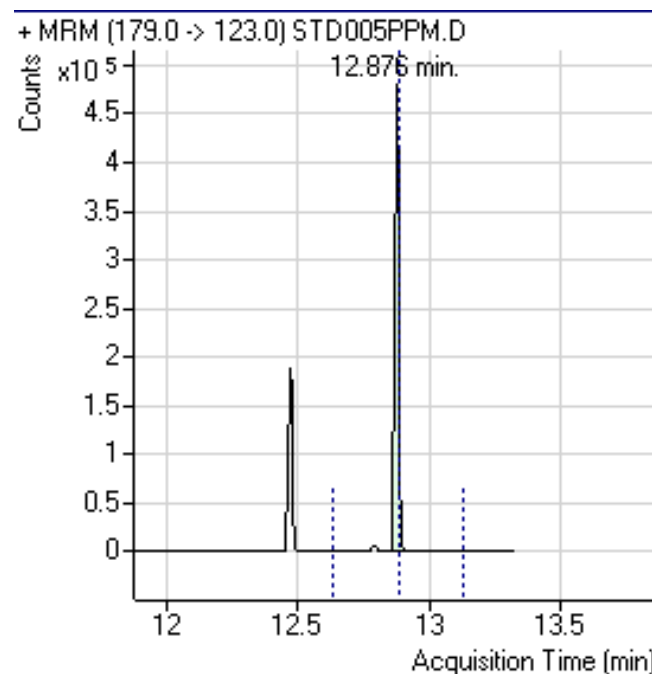
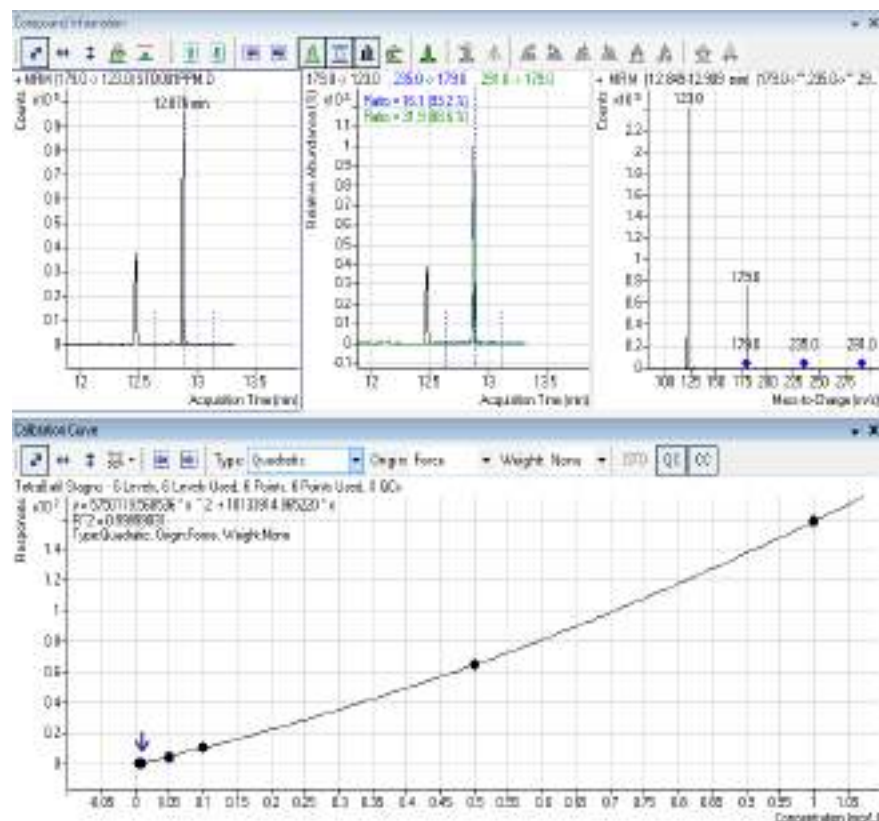


Organotin compounds

ISO/TS 16179:2012	Technique: GC-MS/MS	LOD: 0,01 mg/kg
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Eg. Calibration curve for Tributyl tin (TBT)

TBT – quantitative analysis at 0,1 mg/kg

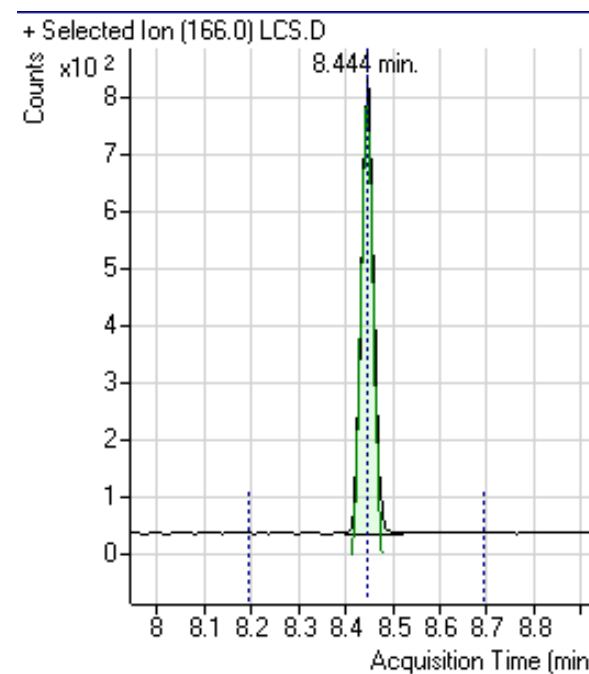
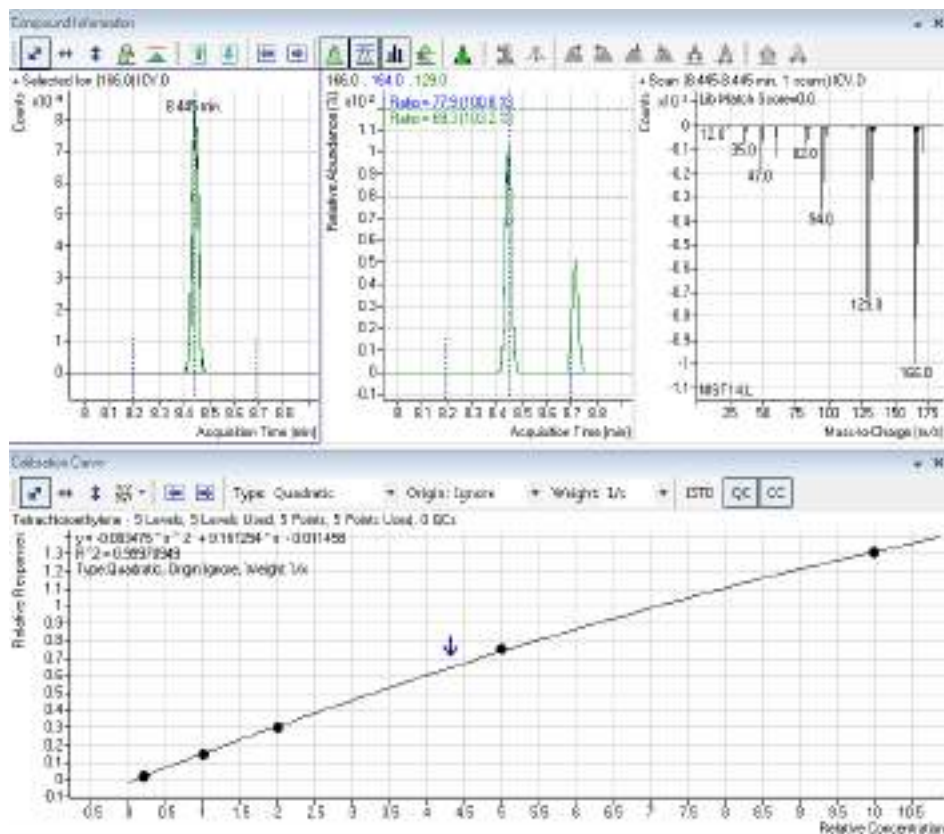


Chlorinated solvents

EPA 5021A + EPA 8260D	Technique: GC-MS/MS	LOD: 0,01 mg/kg
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Eg. Calibration curve for Tetrachloroethylene

Tetrachloroethylene – quantitative analysis at 0,1 mg/kg

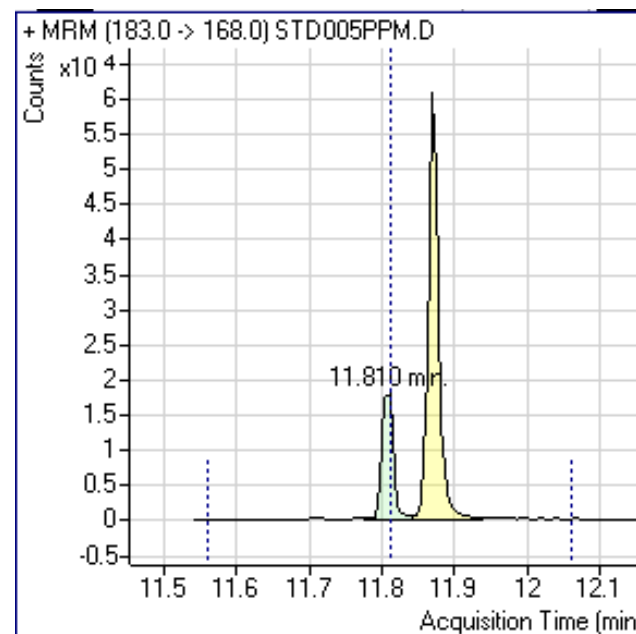
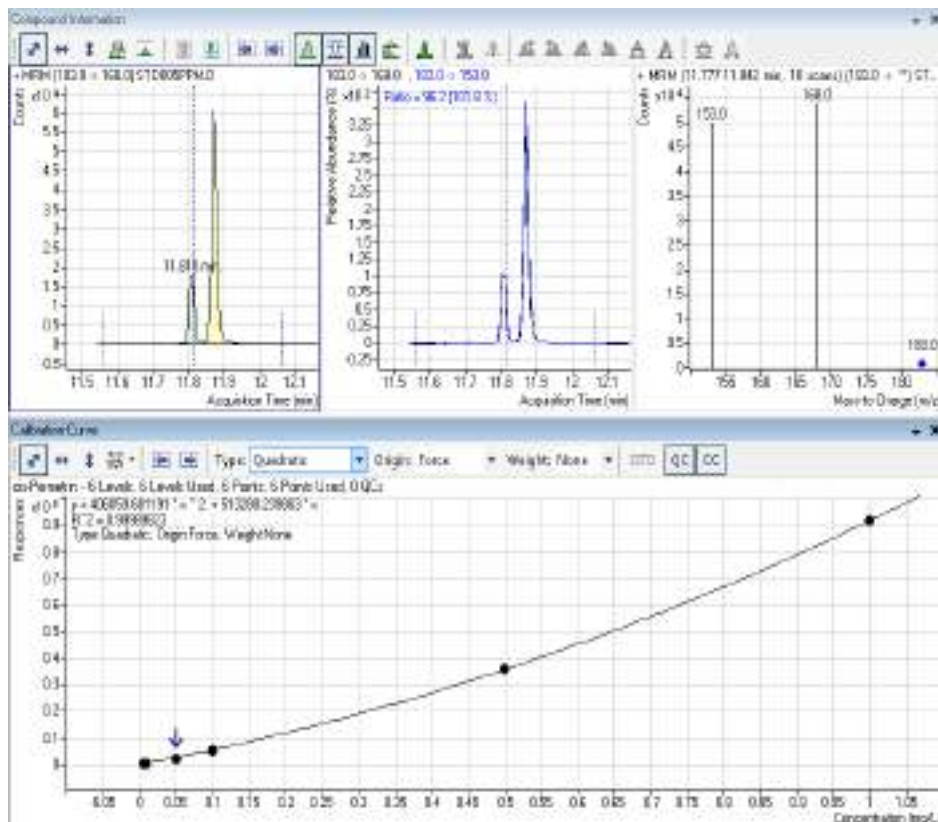


Biocides / preservatives and Permethrin

EPA 8081B + EPA 8141B + EPA 8270E	Technique: GC-MS/MS LC-MSMS	LOD: 0,01 mg/kg
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Eg. Calibration curve for cis-Permethrin

Permethrin – quantitative analysis at 0,05 mg/kg



RESULTS

Wollen-type regenerated material

Total: 108 samples

- From POST-CONSUMER: **64 samples**
- From PRE-CONSUMER: **44 samples**

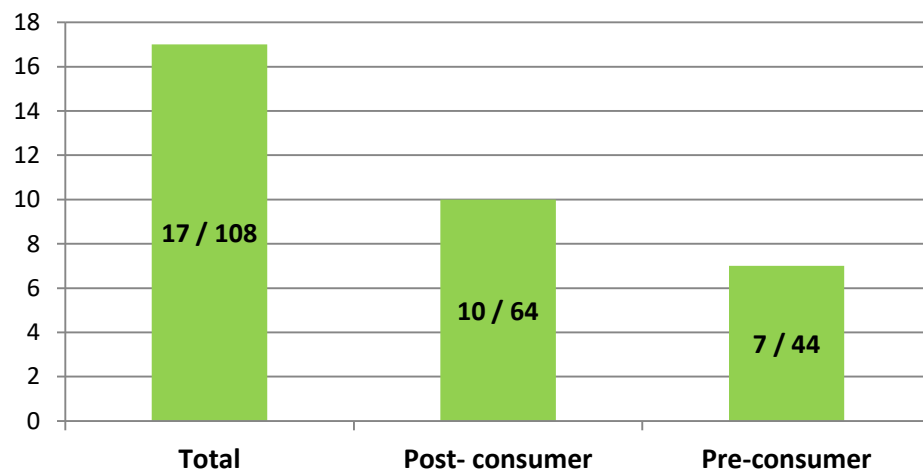
Levels of Contamination

Parameter	N° of contaminated samples	%
Aromatic amines from azo-colorants	17	16%
Alkylphenols (AP / APEOS)	108	100%
Chlorophenols	28	26%
Perfluorinated Compounds (PFC)	67	62%
Allergenic and Carcinogenic Dyes	89	82%
Heavy Metals (from perspiration solution)	7	6%
Formaldehyde	25/28	89%

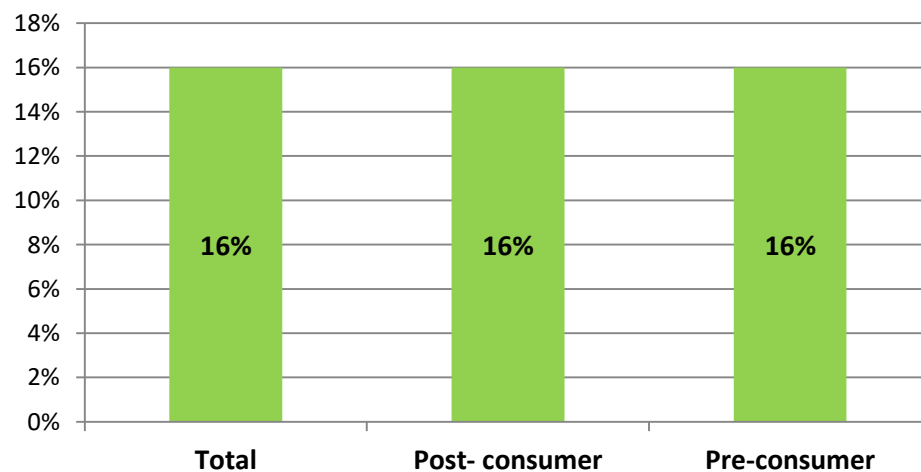
Levels of Contamination

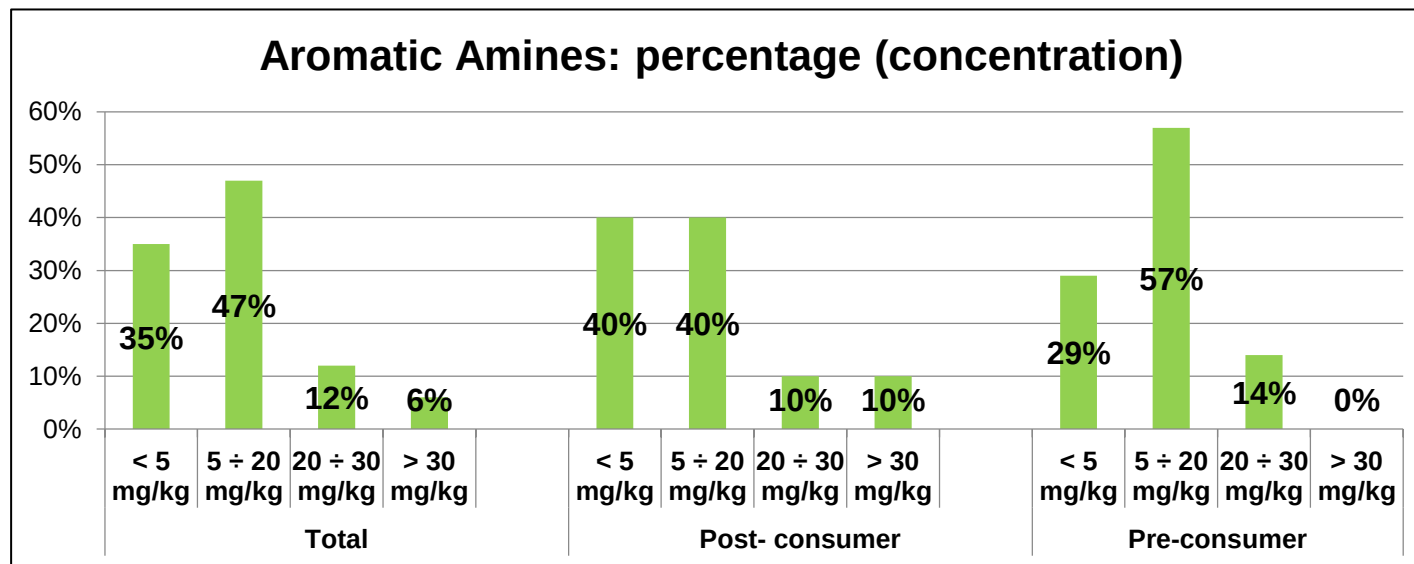
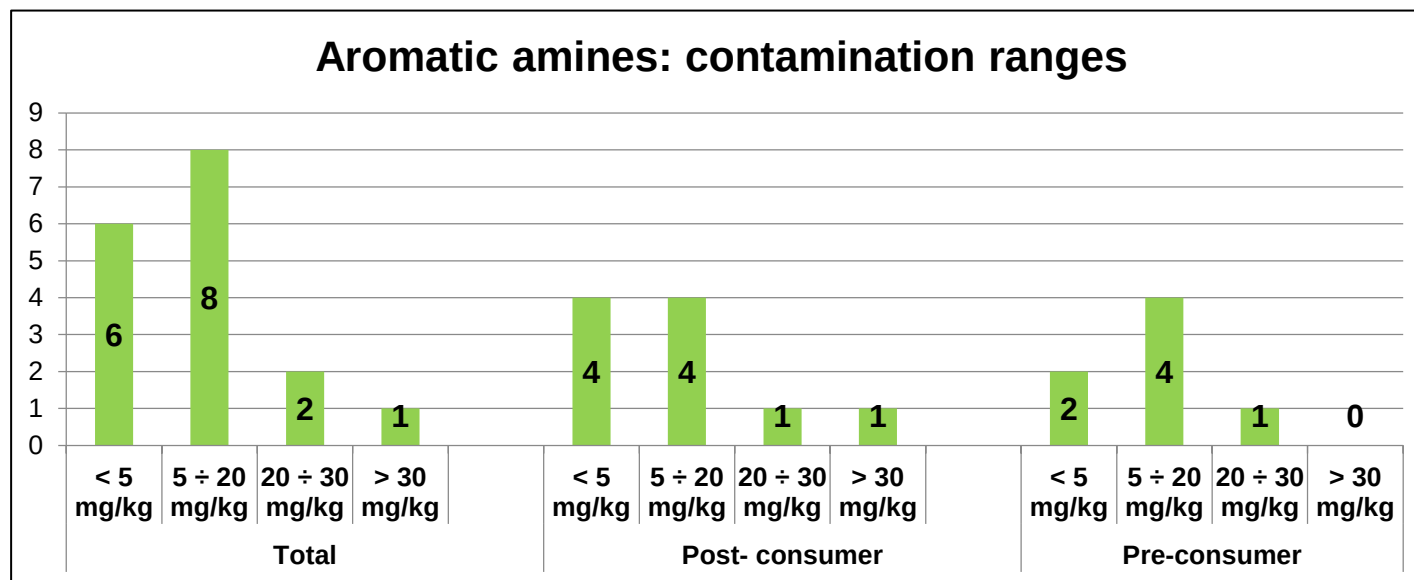
Parameter	N° of contaminated samples	%
Flame Retardant	0	0%
Chlorobenzenes and toluenes	2	2%
Chlorinated paraffins (SCCP)	0	0%
Phthalates	21	19%
Organotin compound	0	0%
Chlorinated solvents	18	17%
Biocides	10	9%
Permethrin	63	58%

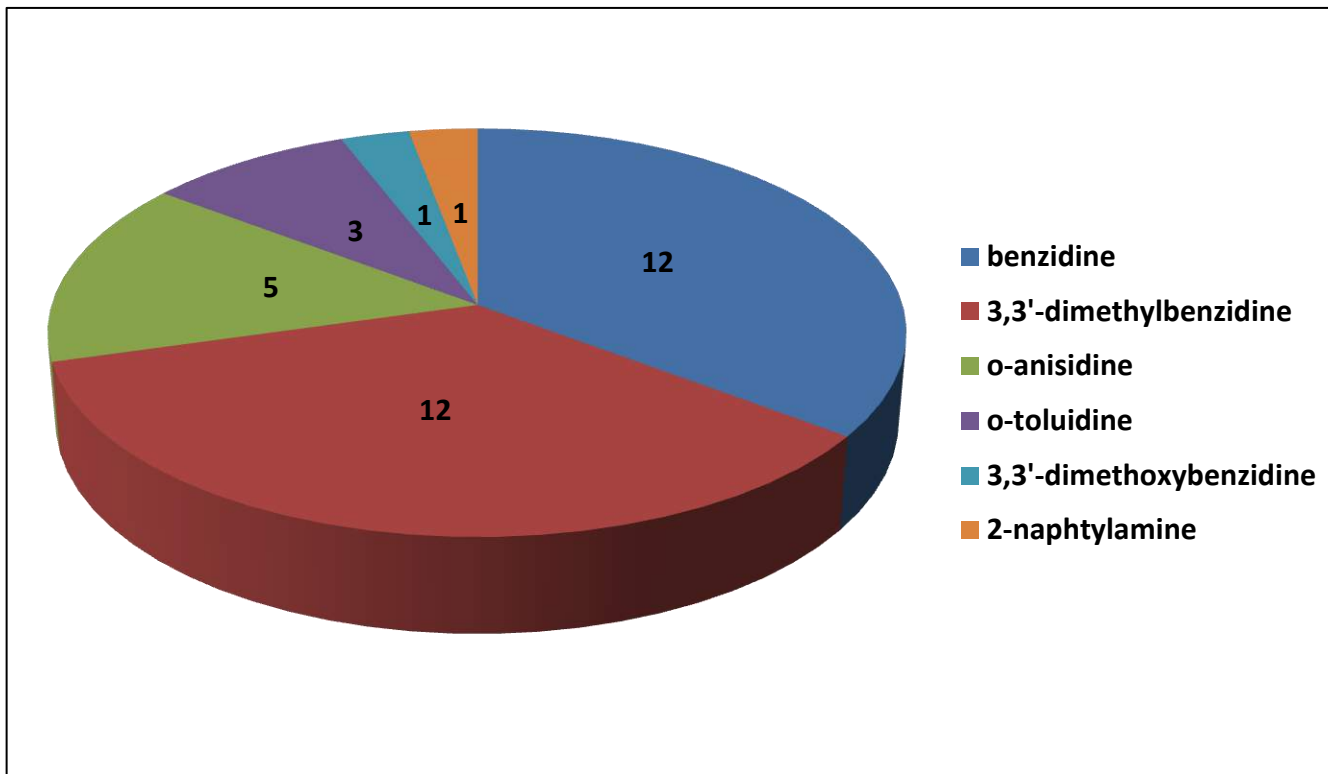
Aromatic Amines: contaminated samples



Aromatic amines: percentages





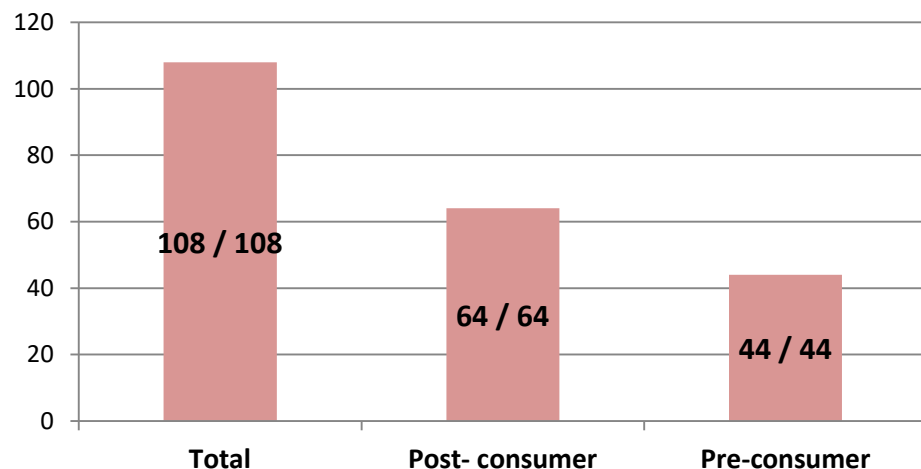


Frequencies by colors:

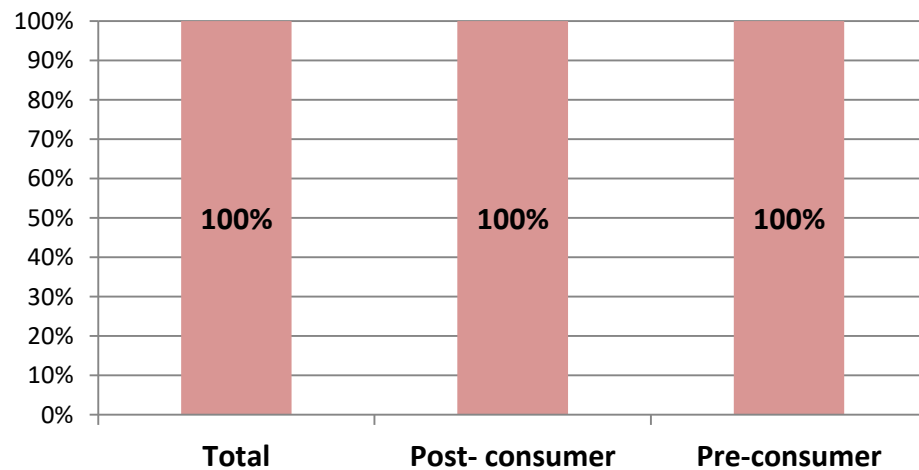
- Red shades (+++)
- Violet shades (++)
- Blue / Turquoise shades (+)
- Black / Charcoal shades (+)

Ethoxylated Alkylphenols (APEOS)

APEOS: contaminated samples

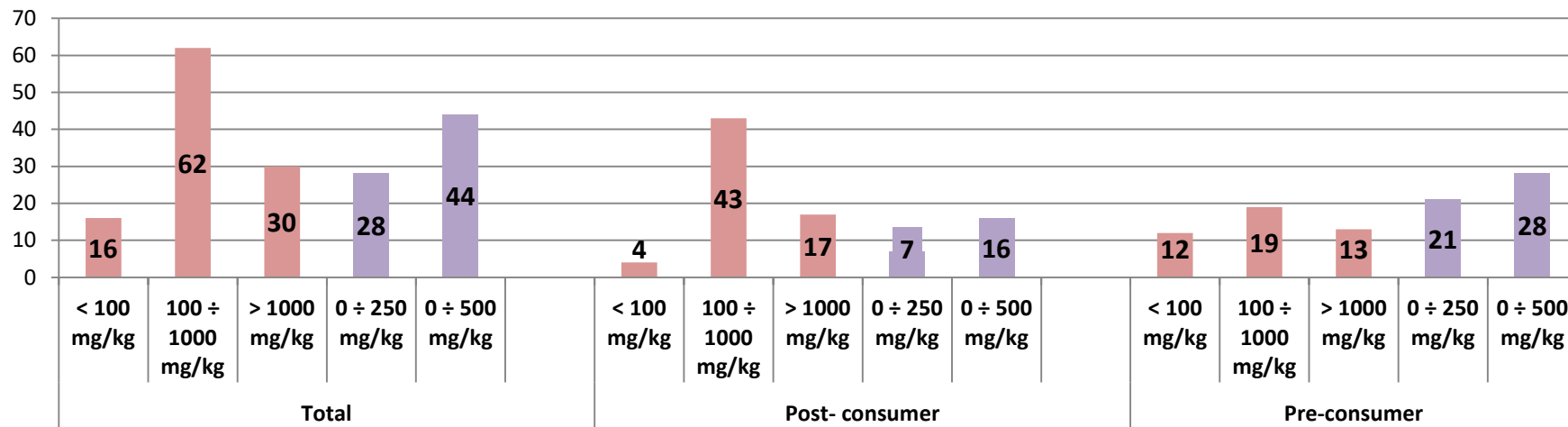


APEOS: percentages

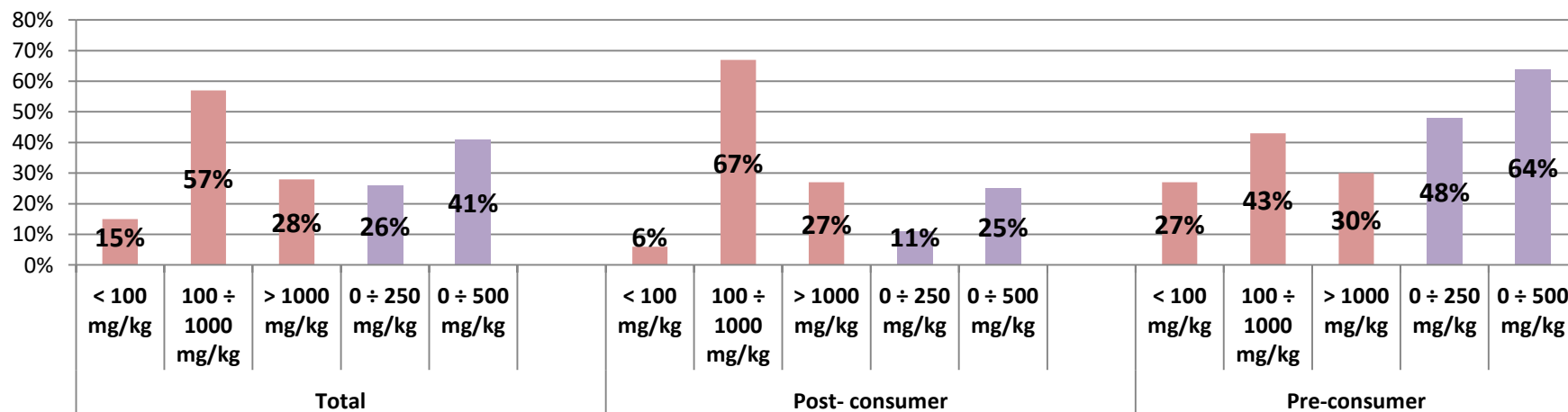


Ethoxylated Alkylphenols (APEOS)

APEOS: contamination ranges

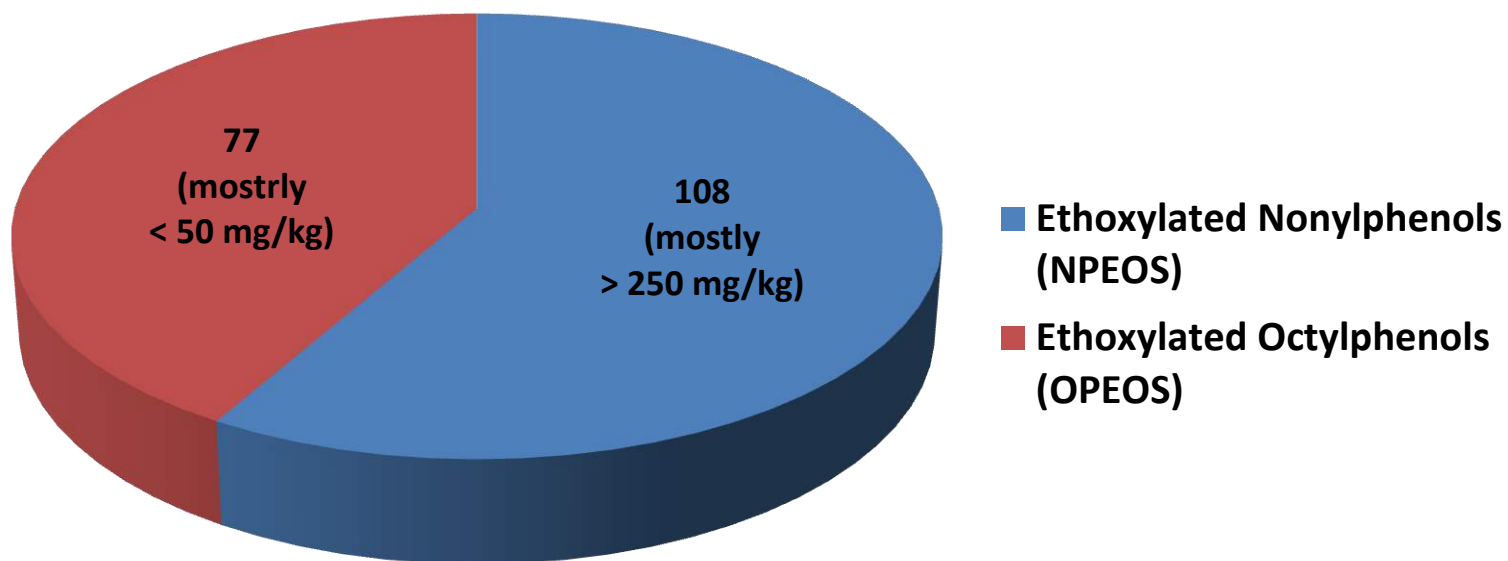


APEOS: contamination ranges (percentages)

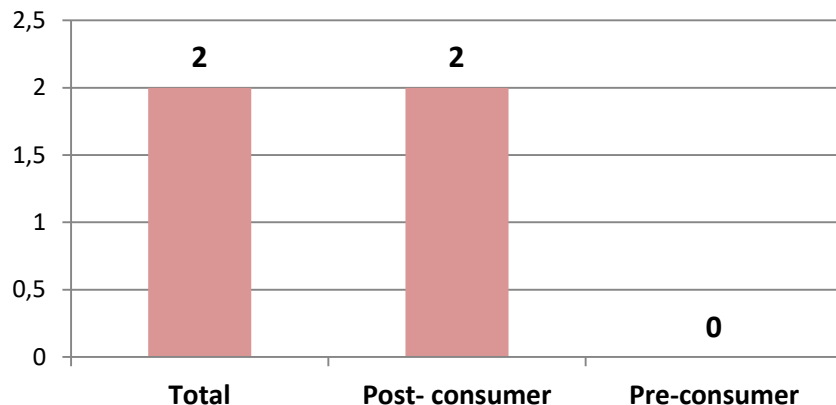


Ethoxylated Alkylphenols (APEOS)

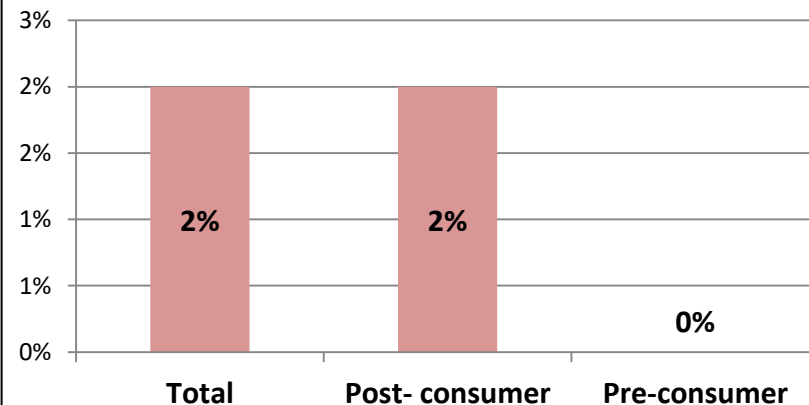
APEOS - frequency



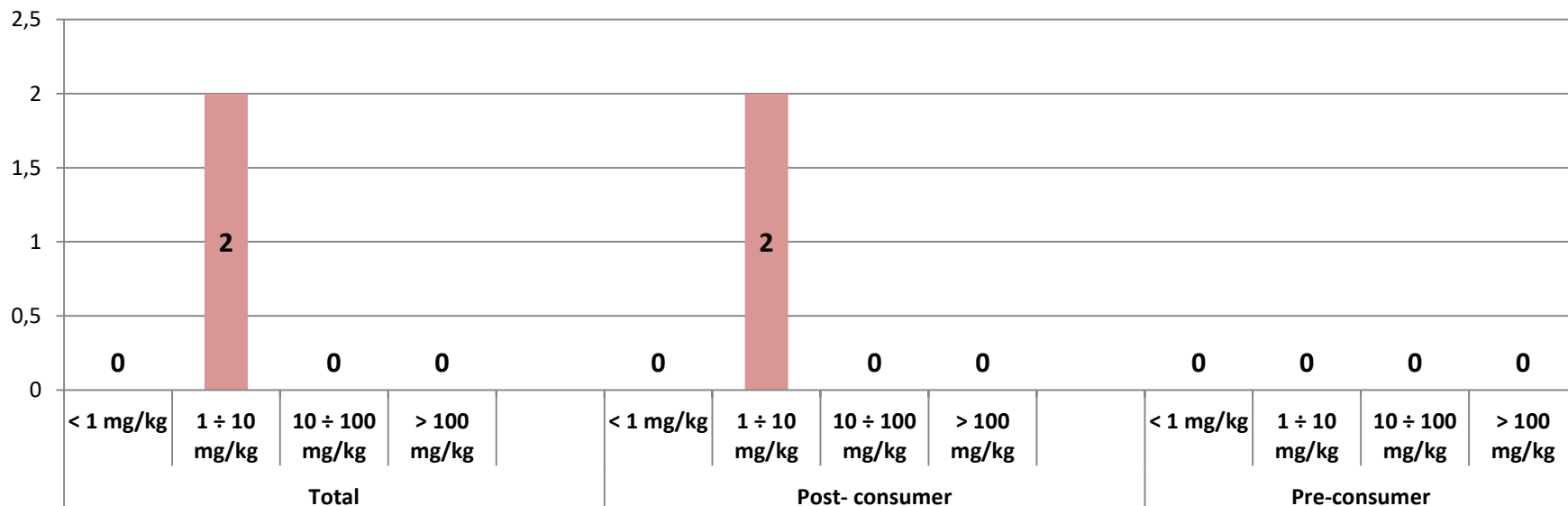
AP: contaminated samples

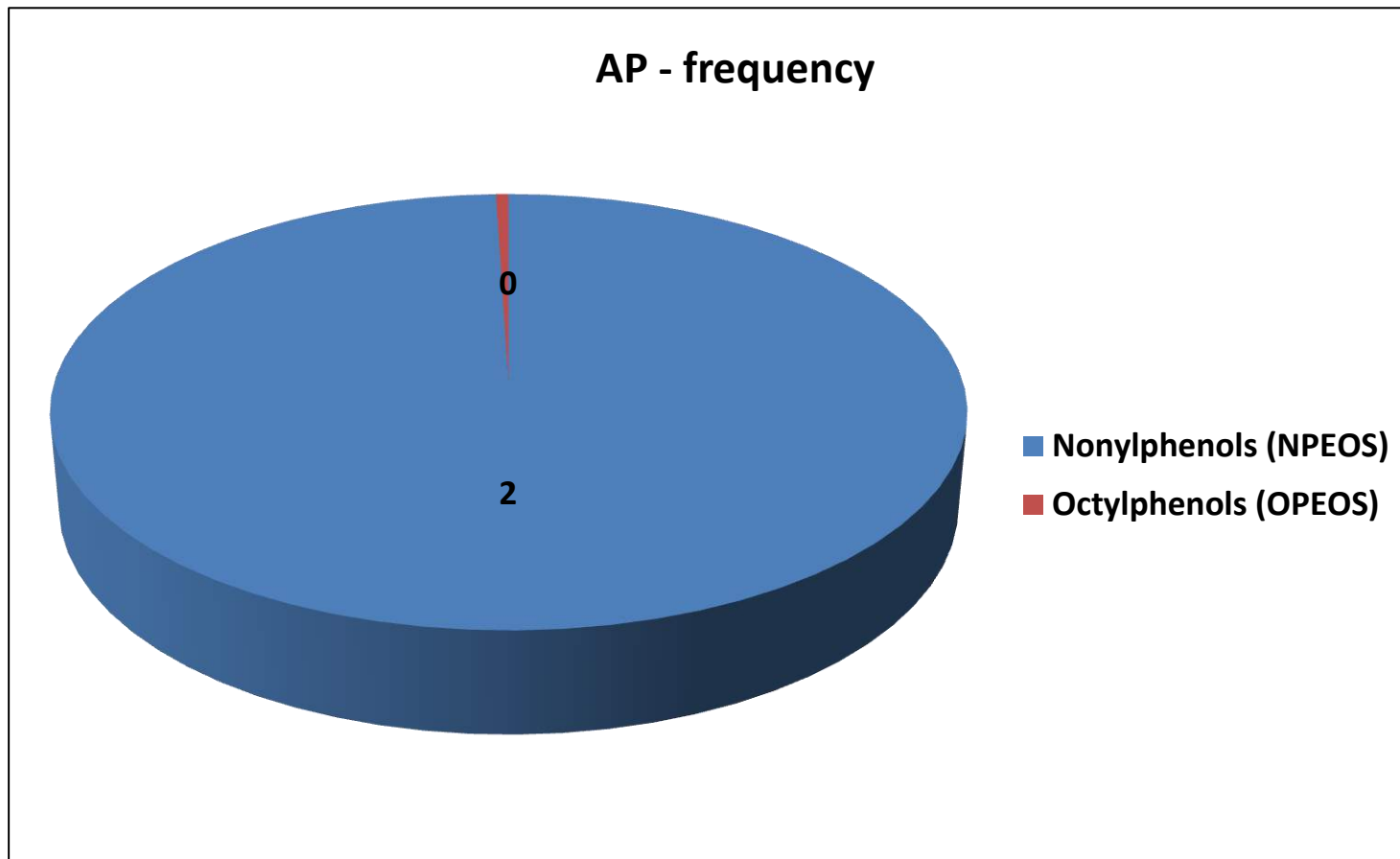


AP: percentages

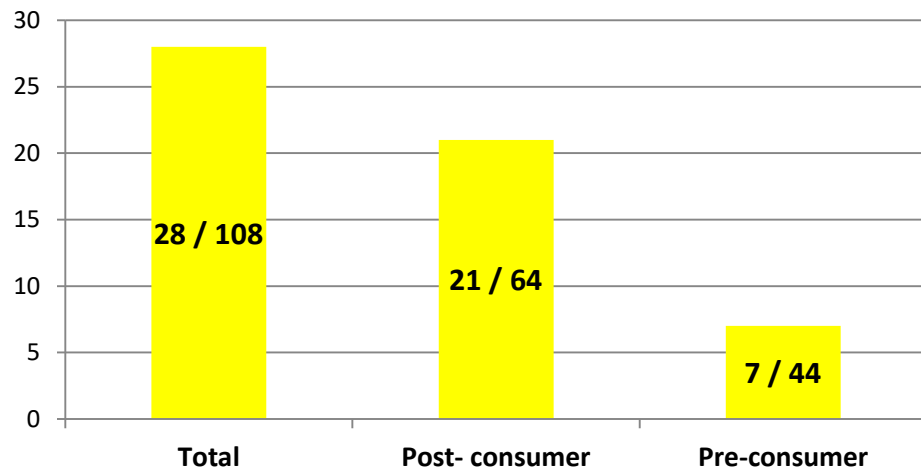


AP: contamination ranges

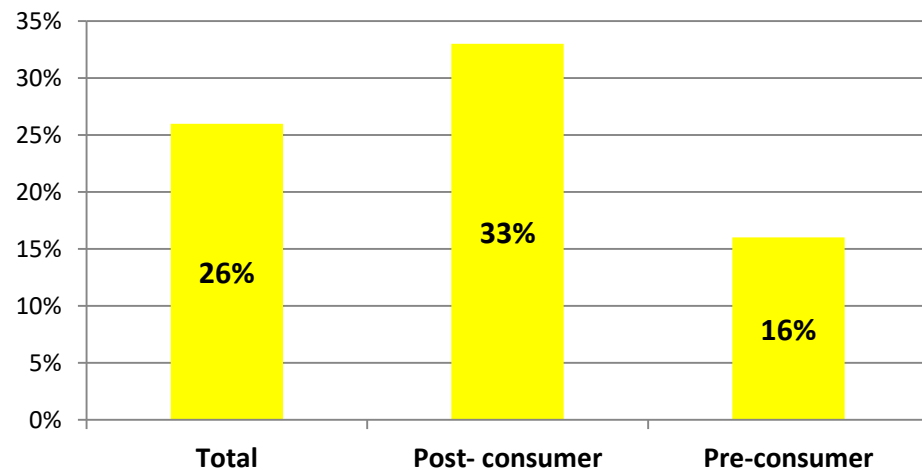




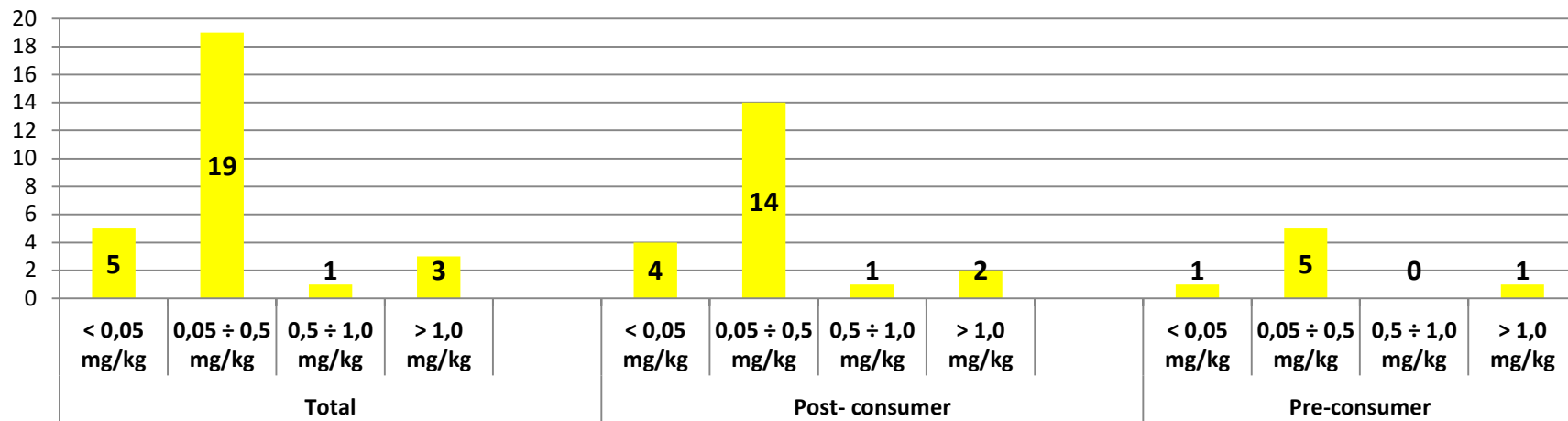
Chlorophenols: contaminated samples



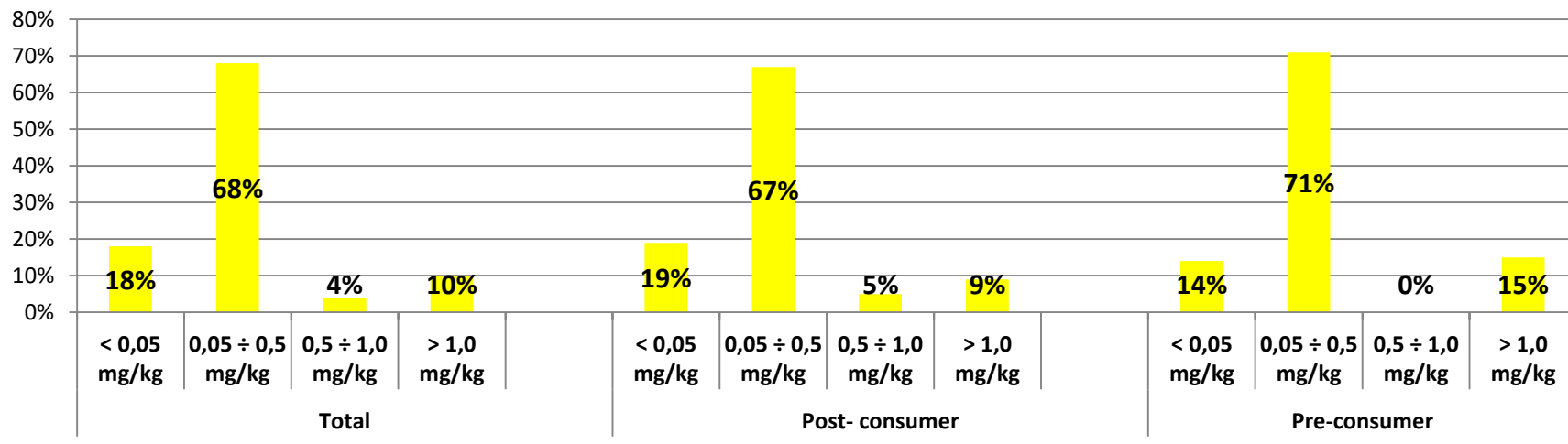
Chlorophenols: percentages



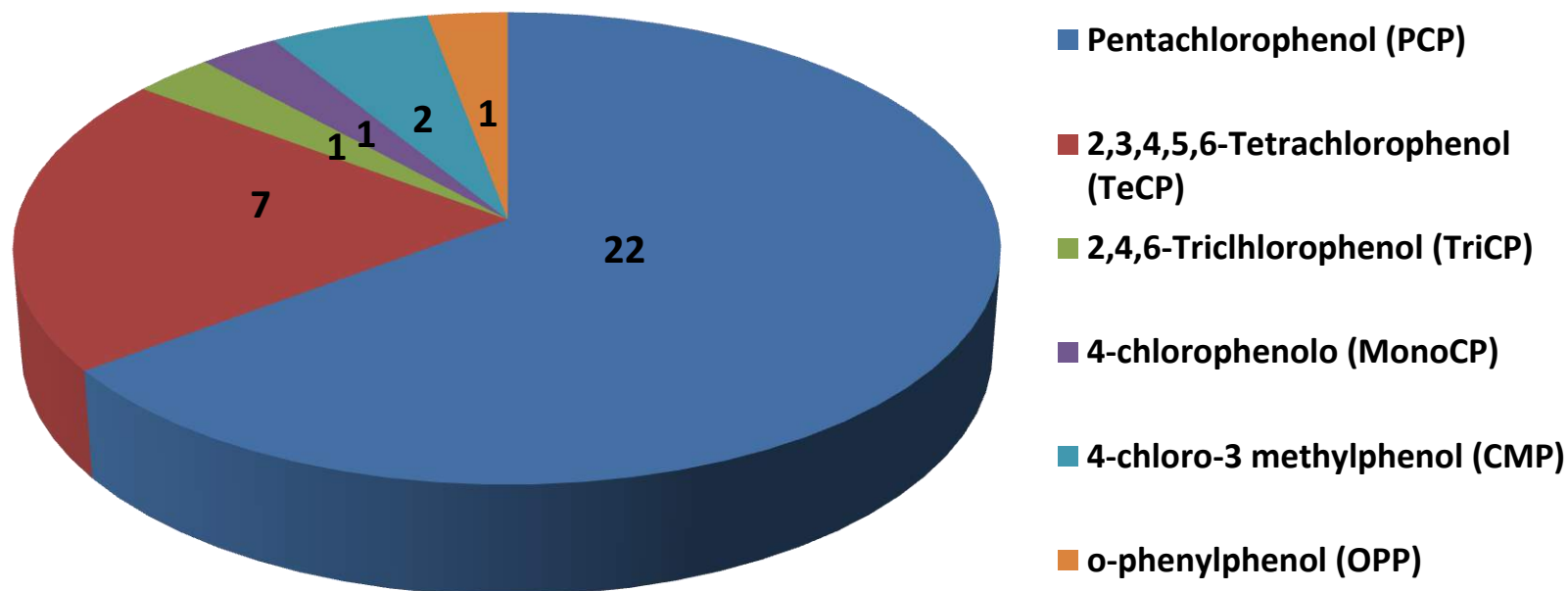
Chlorophenols: ranges

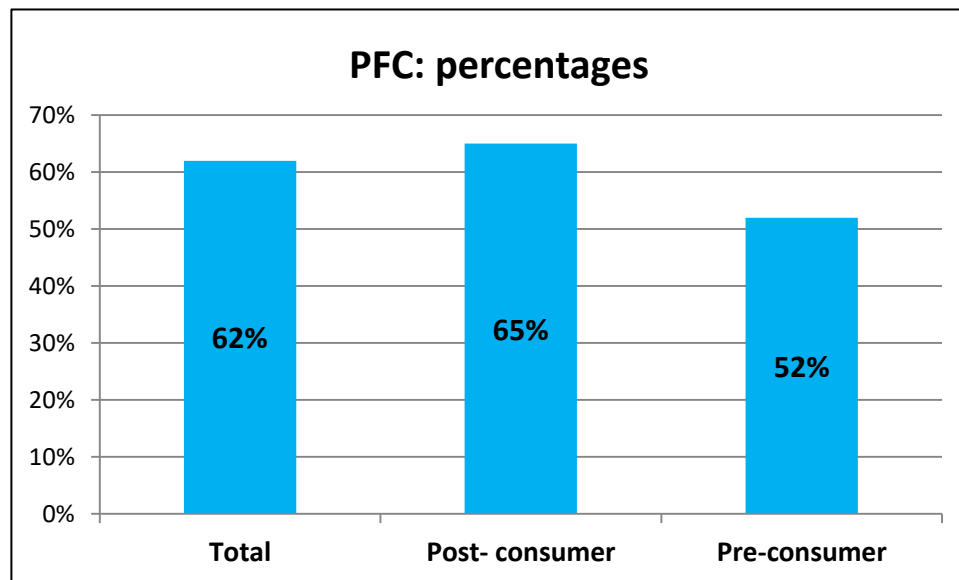
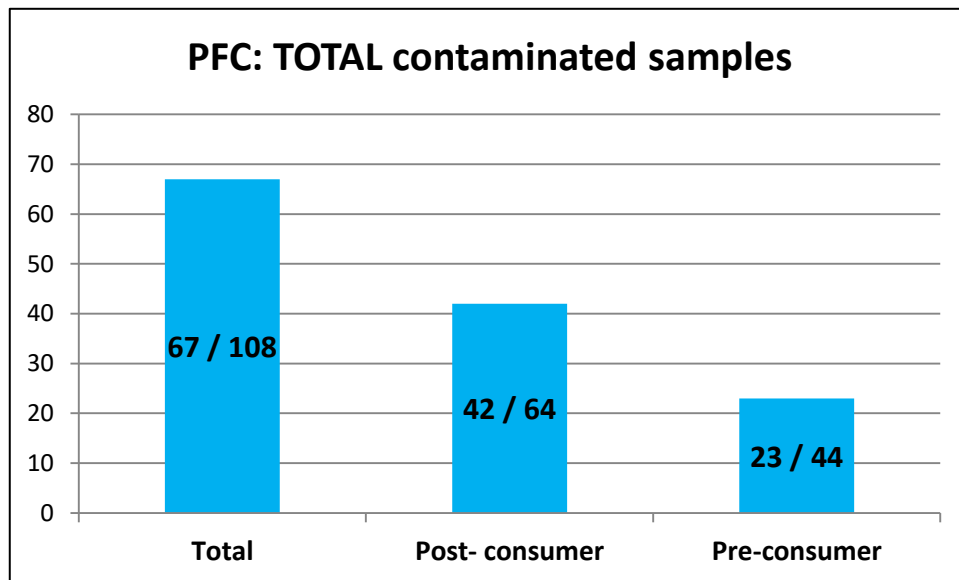


Chlorophenols: percentages

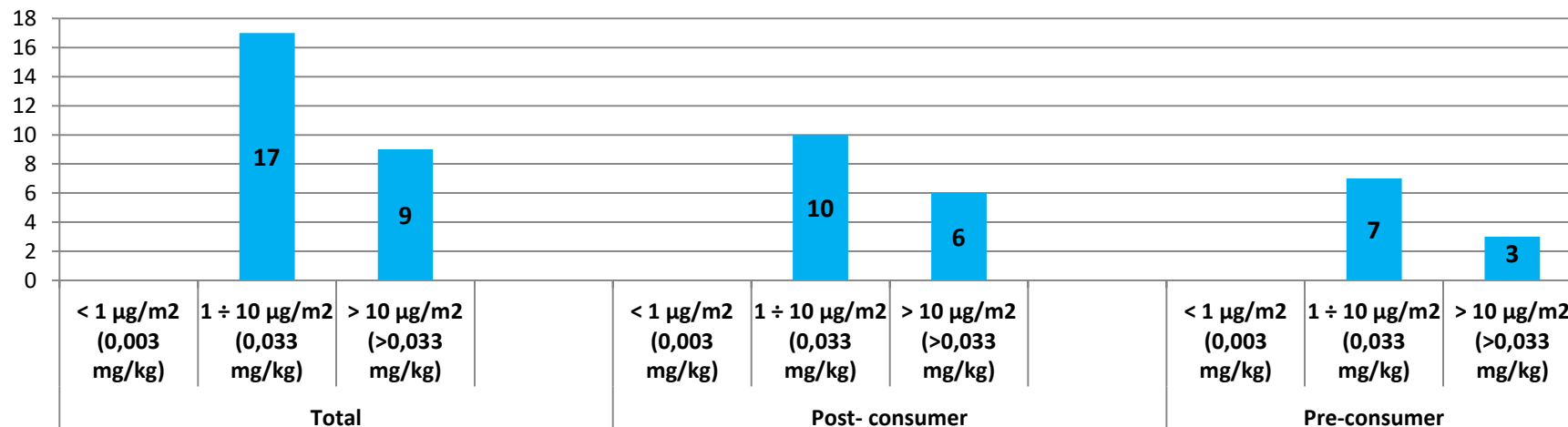


Chlorophenols: frequency

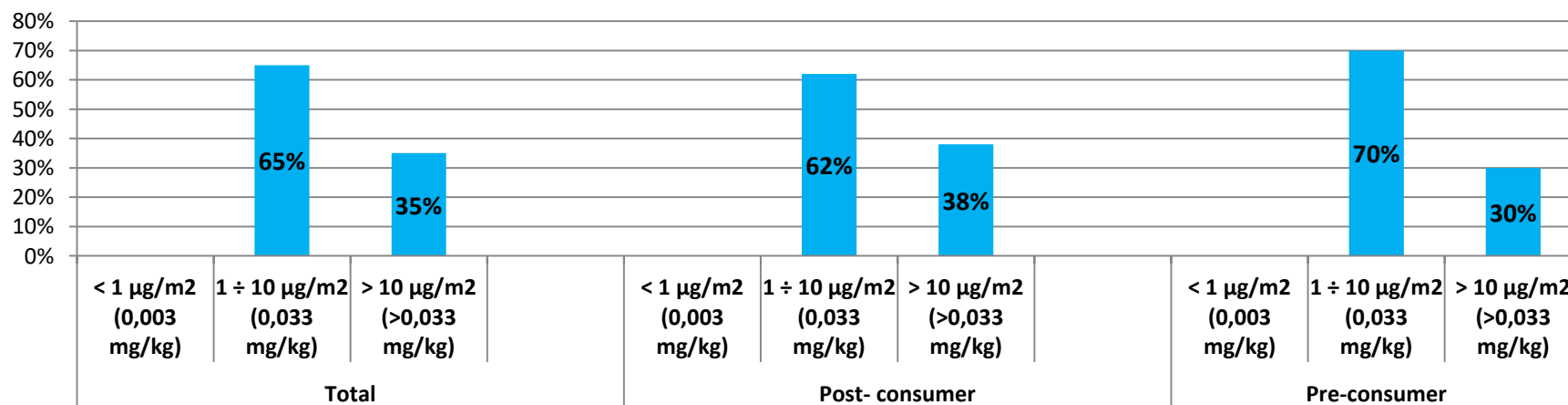




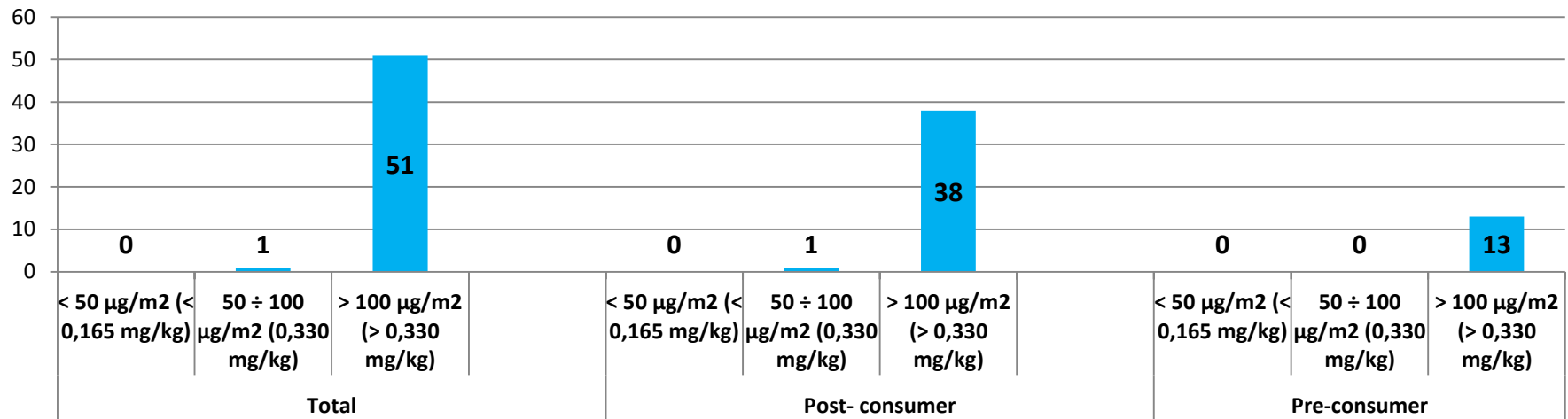
PFC: ranges



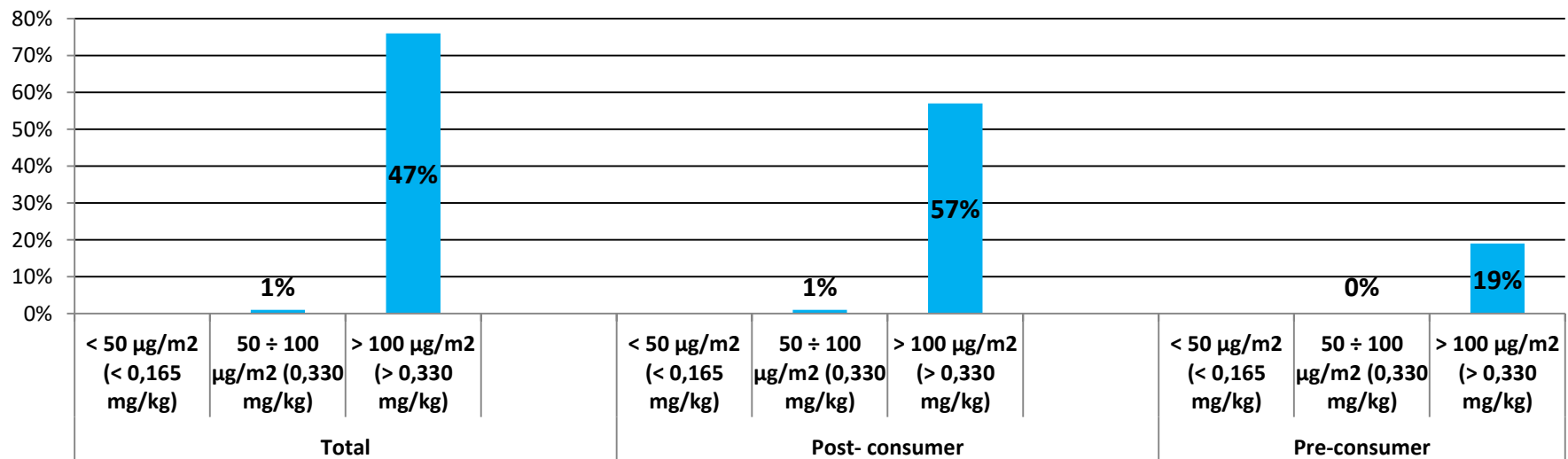
PFC: percentages

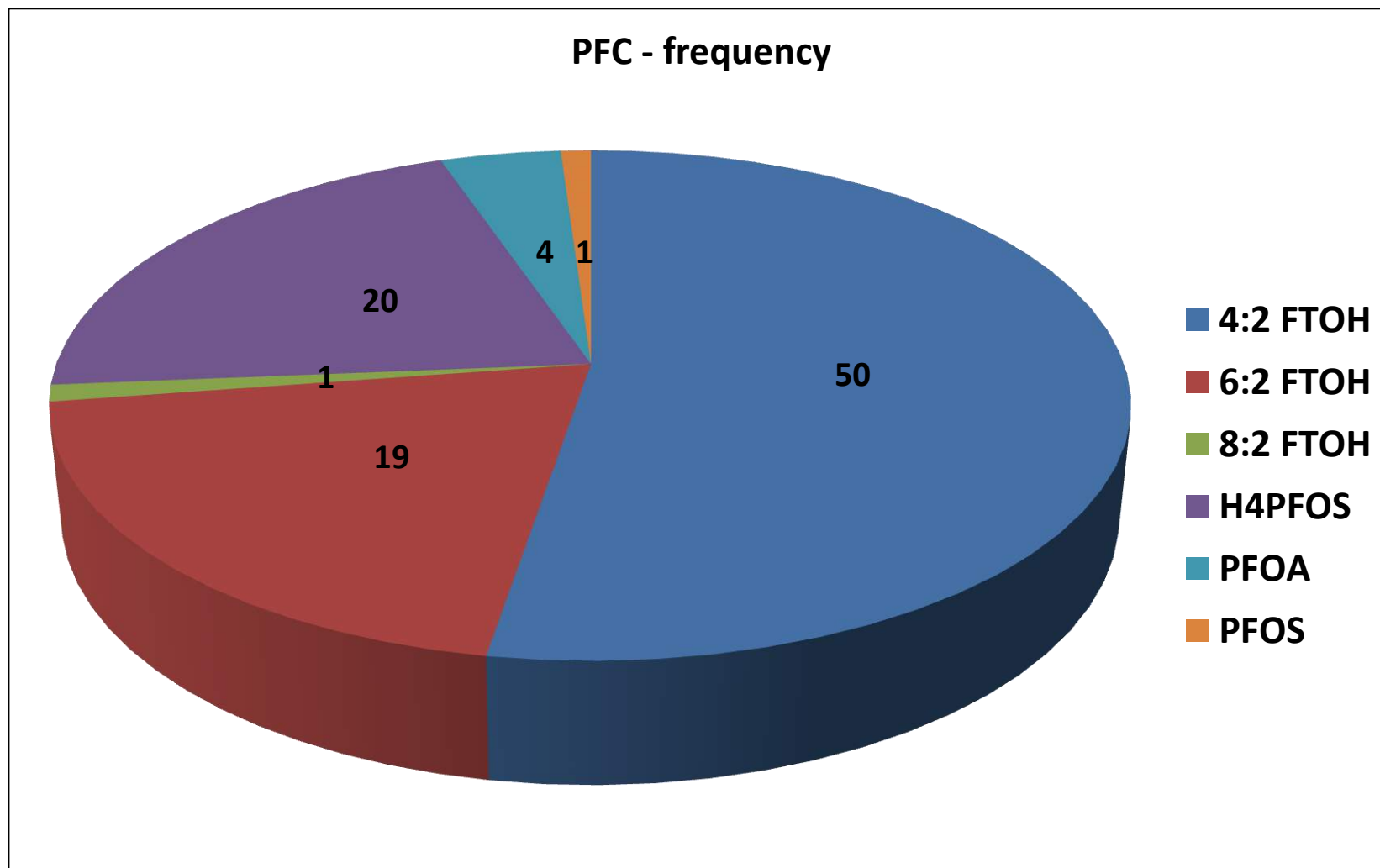


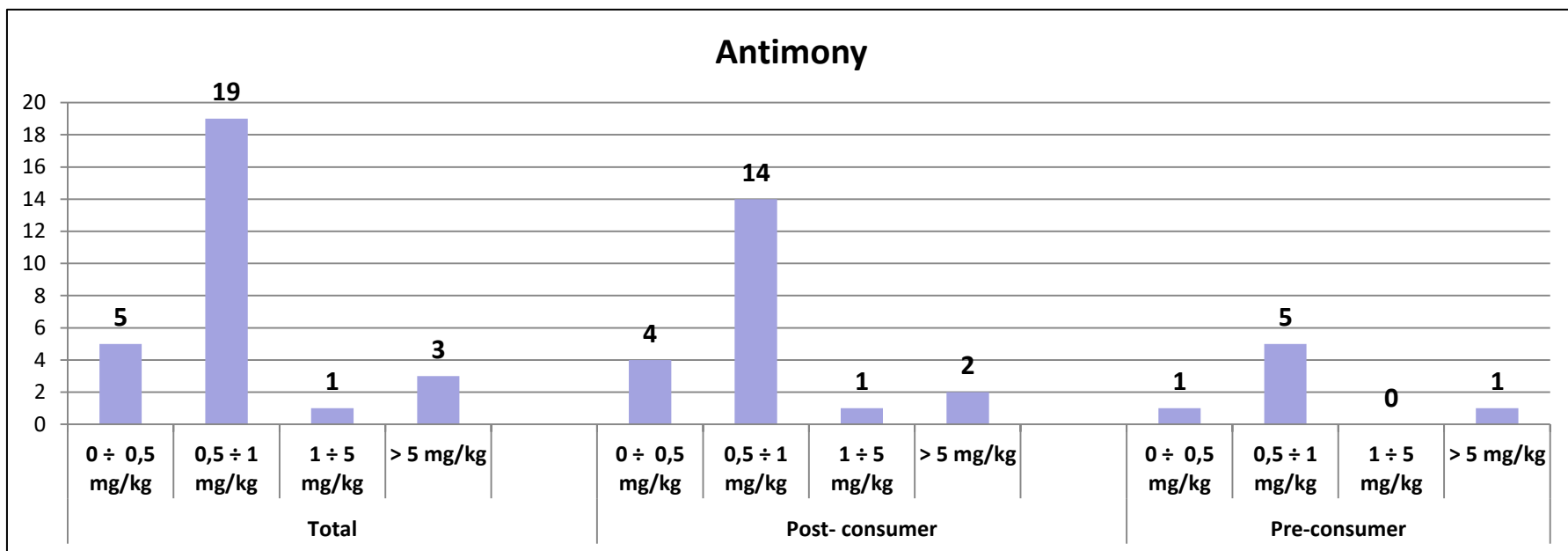
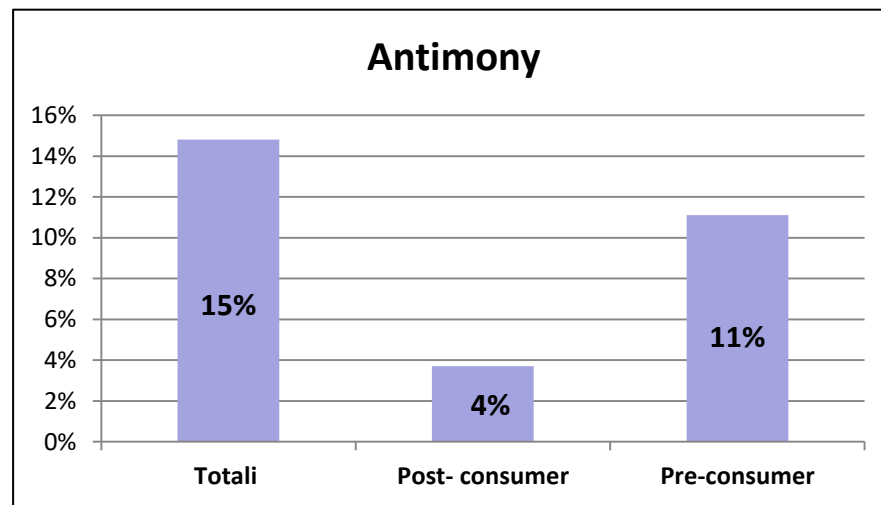
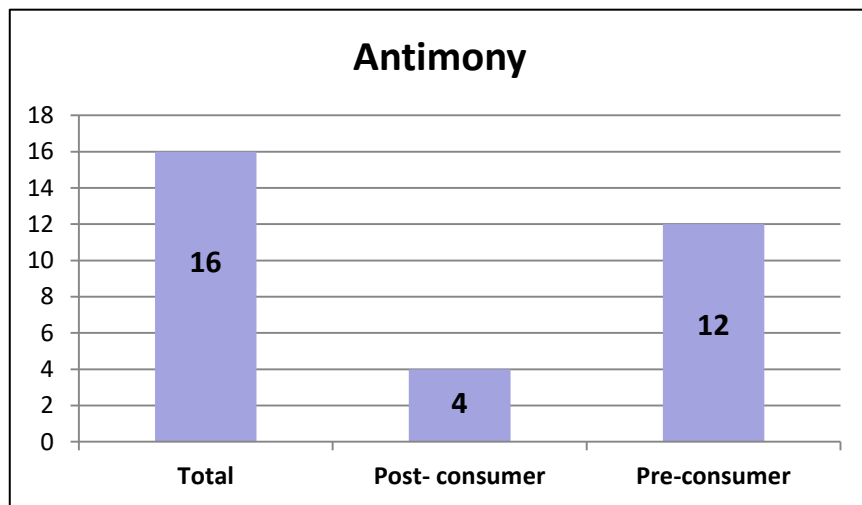
Telomers: ranges

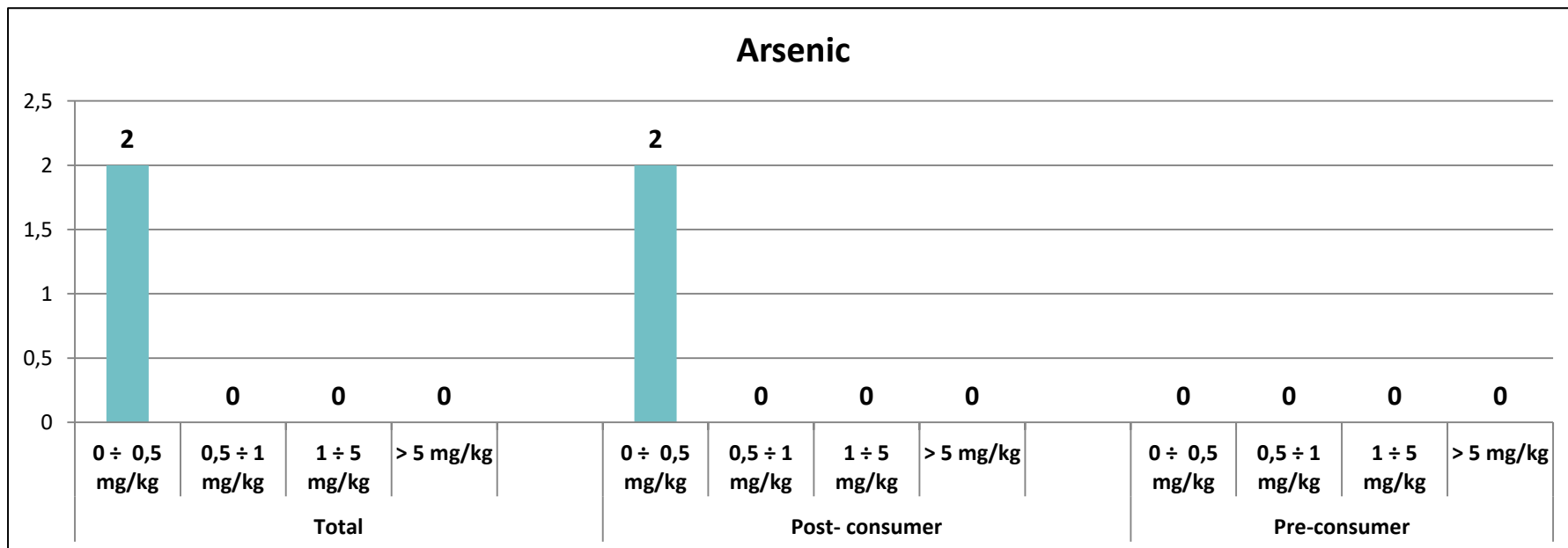
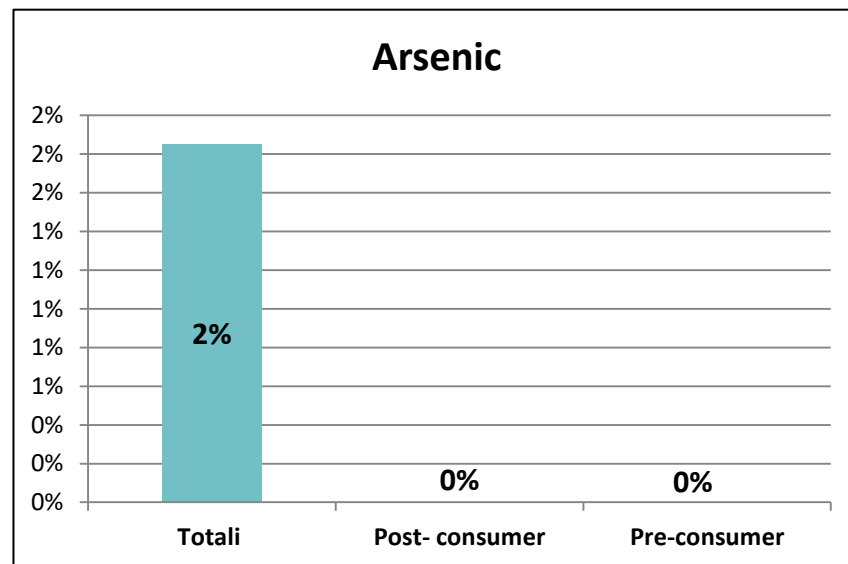
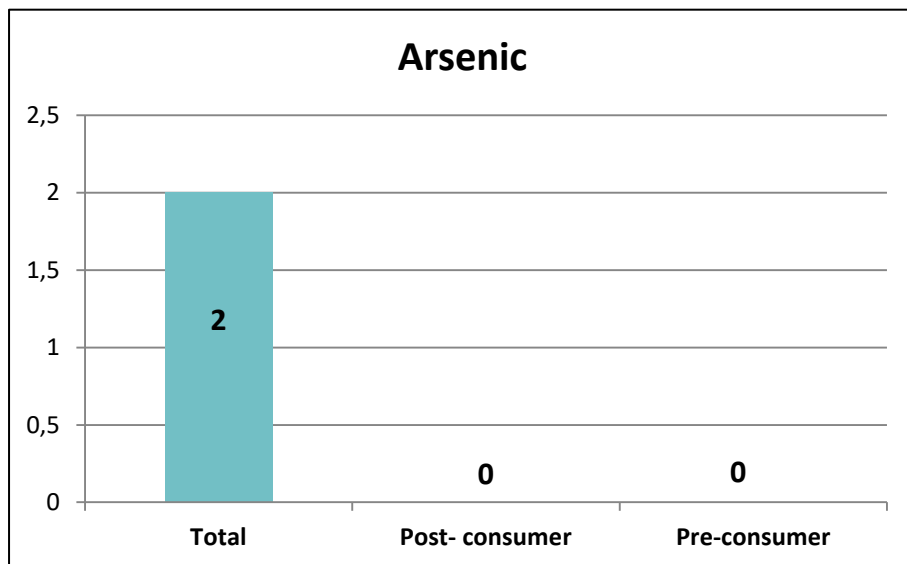


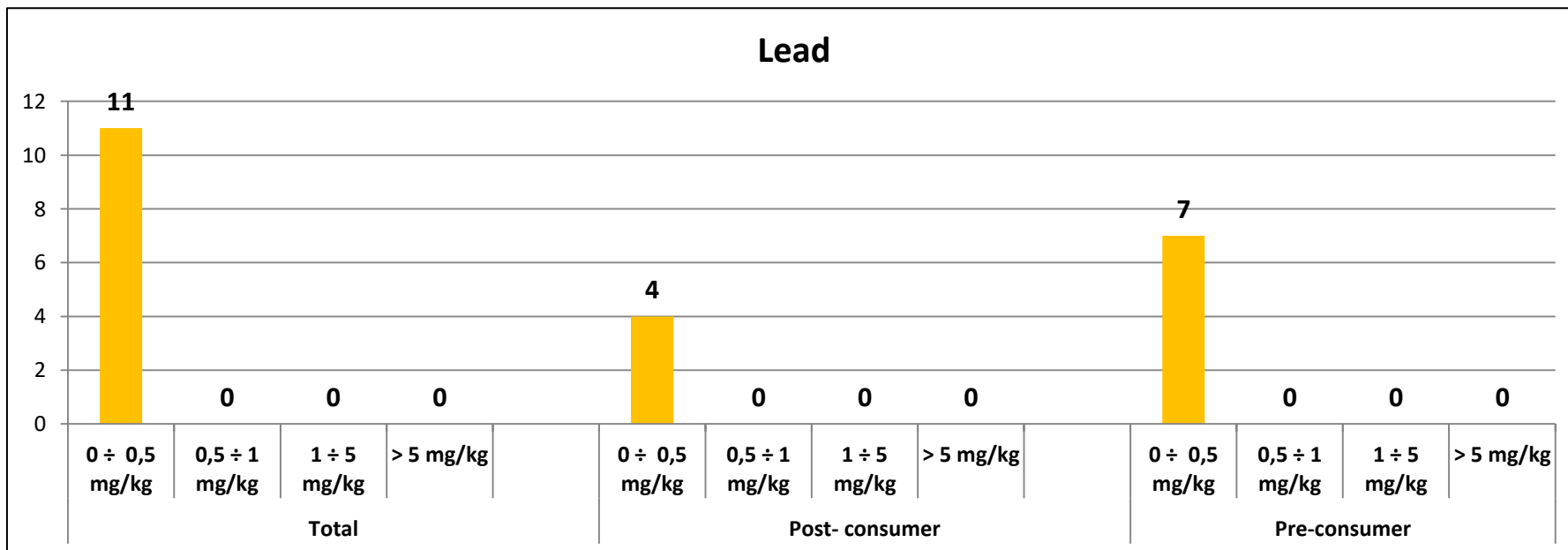
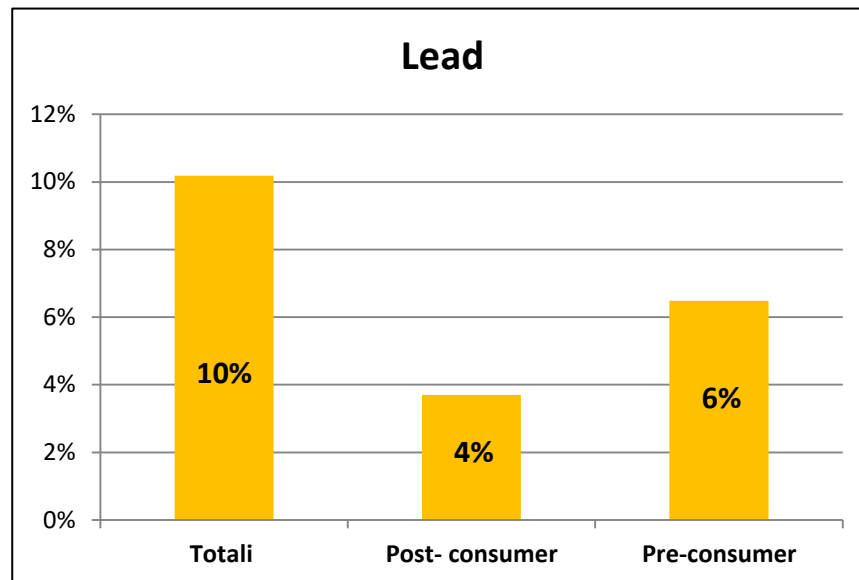
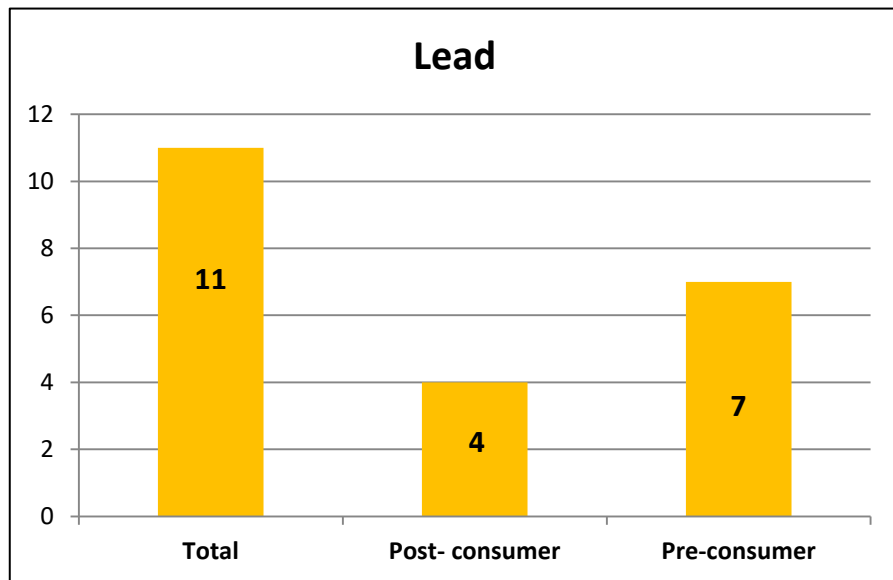
Telomers: percentages

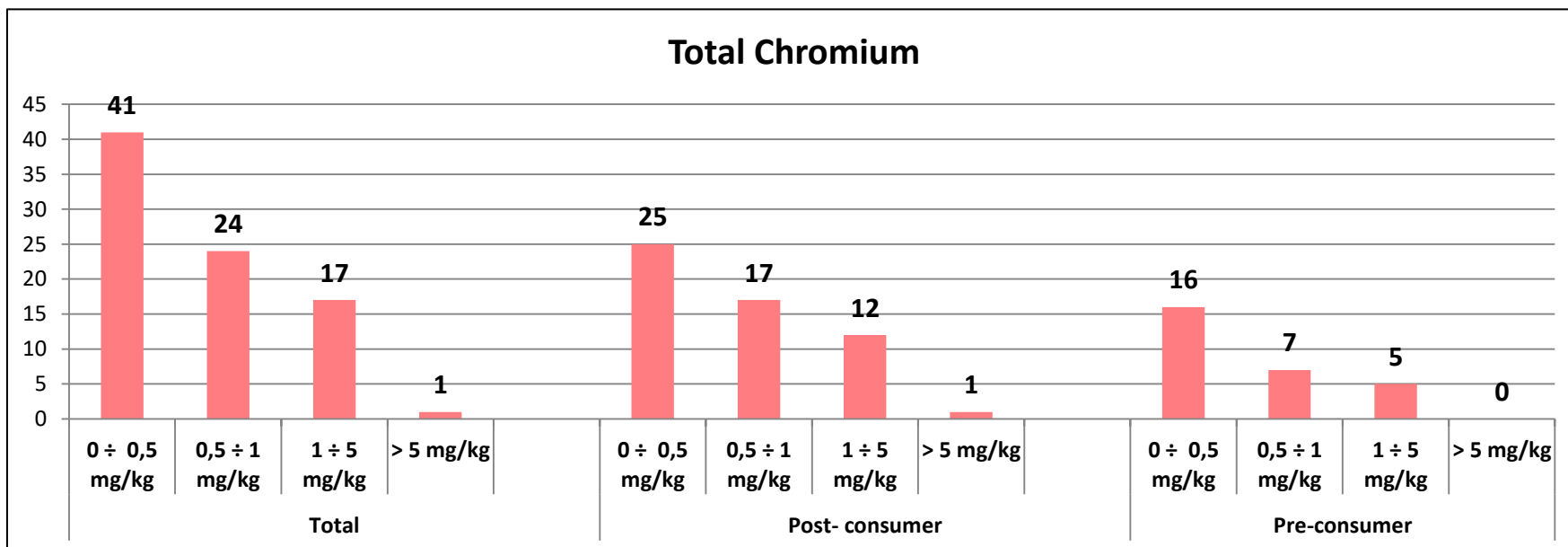
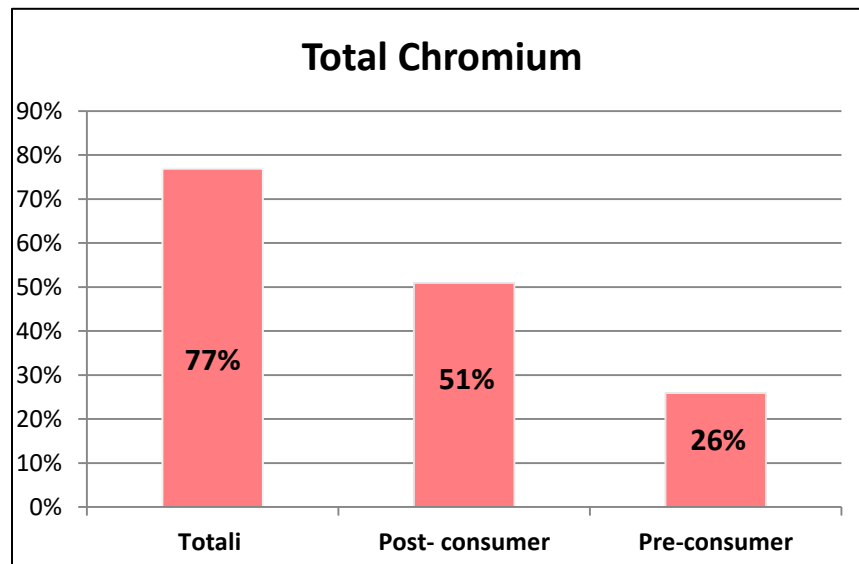
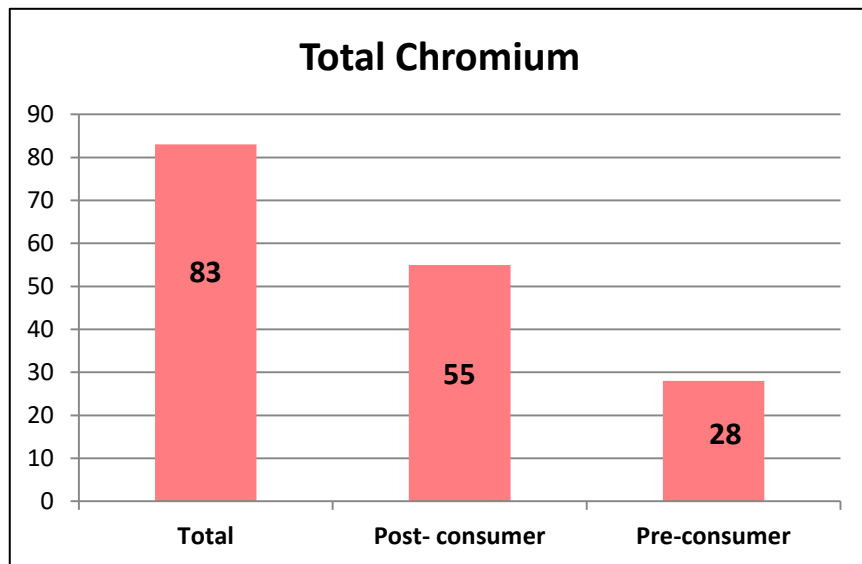


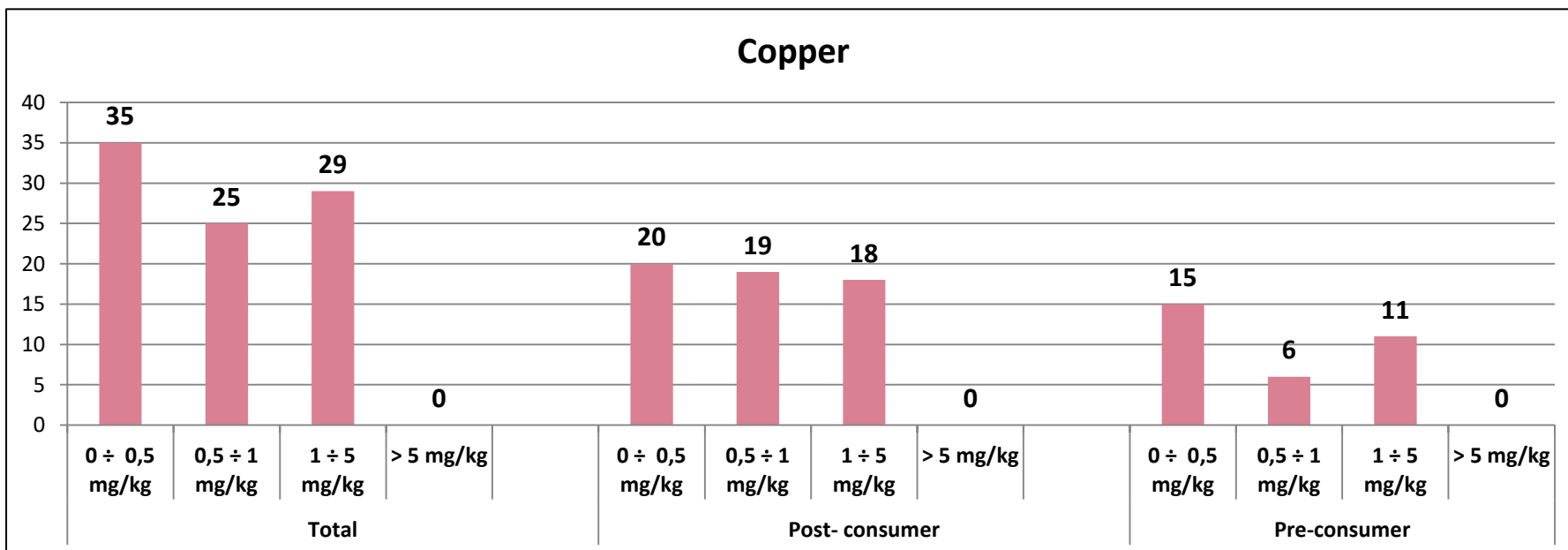
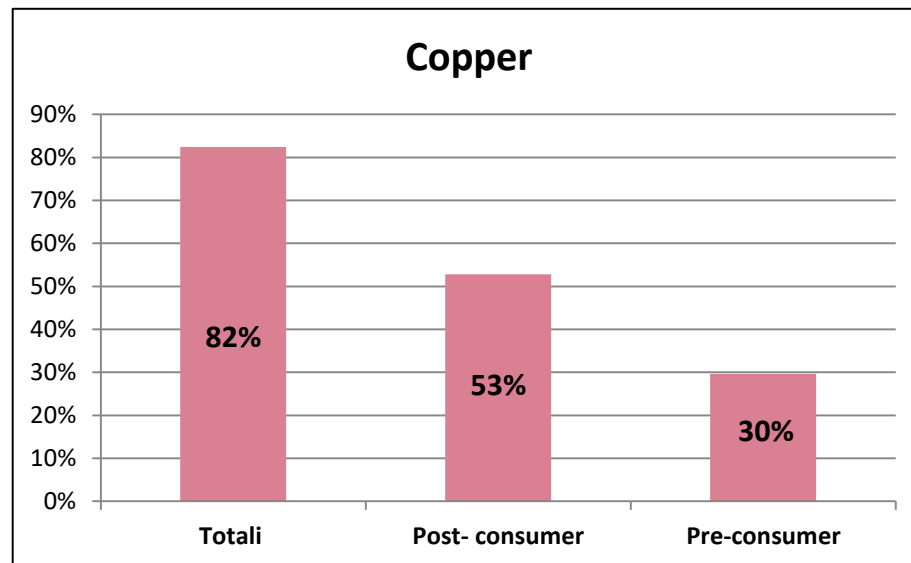
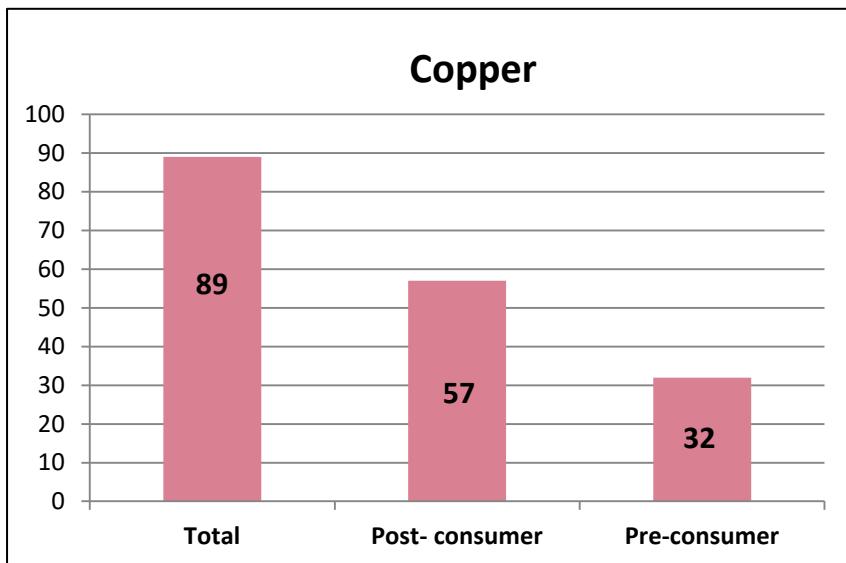


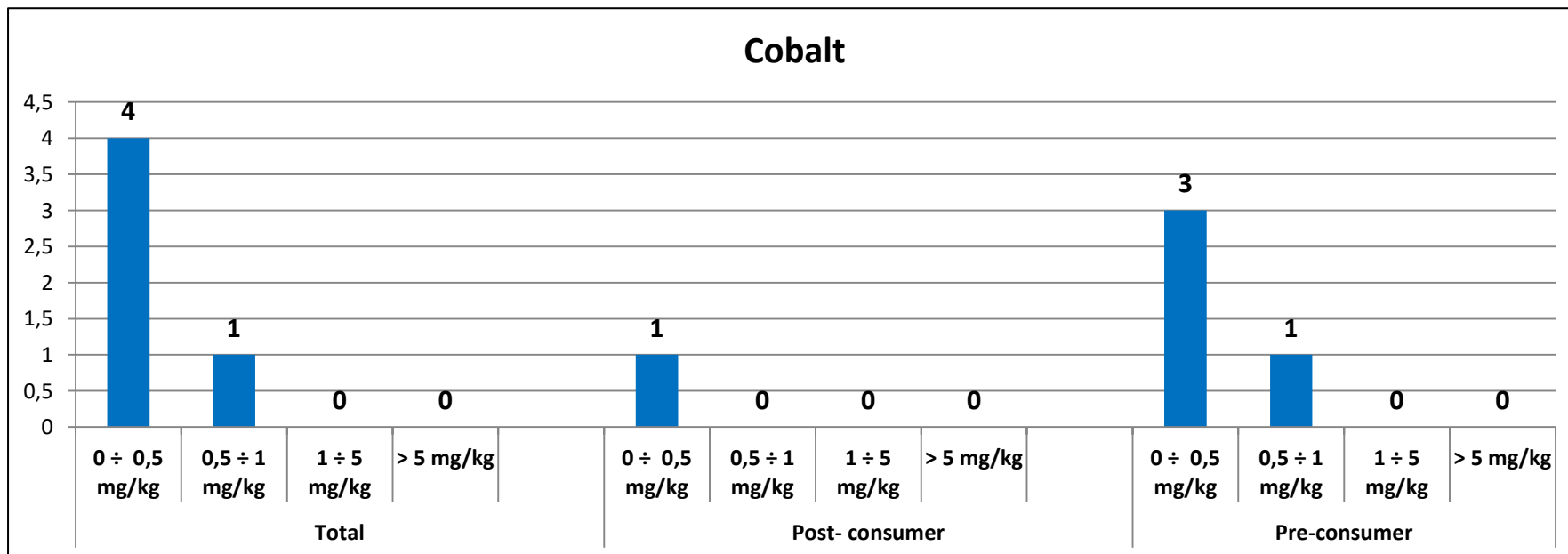
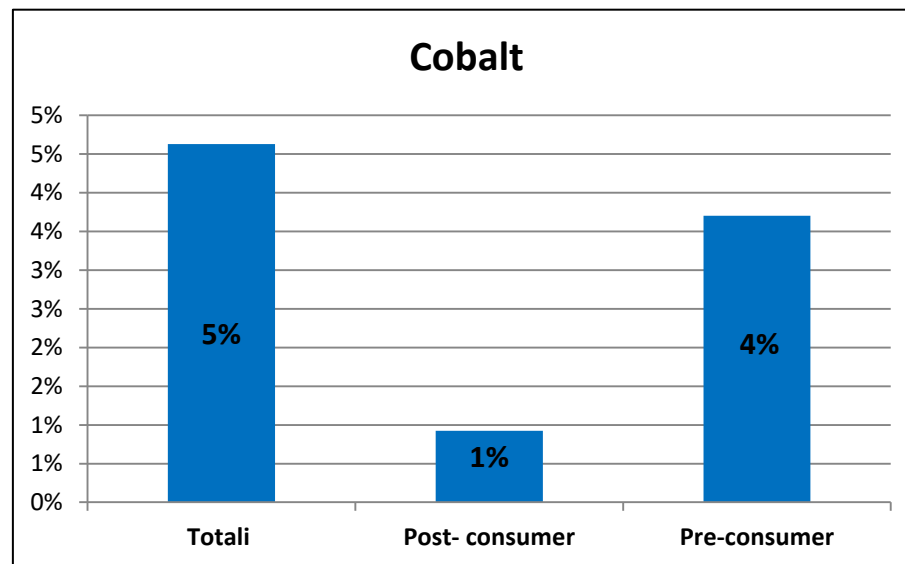
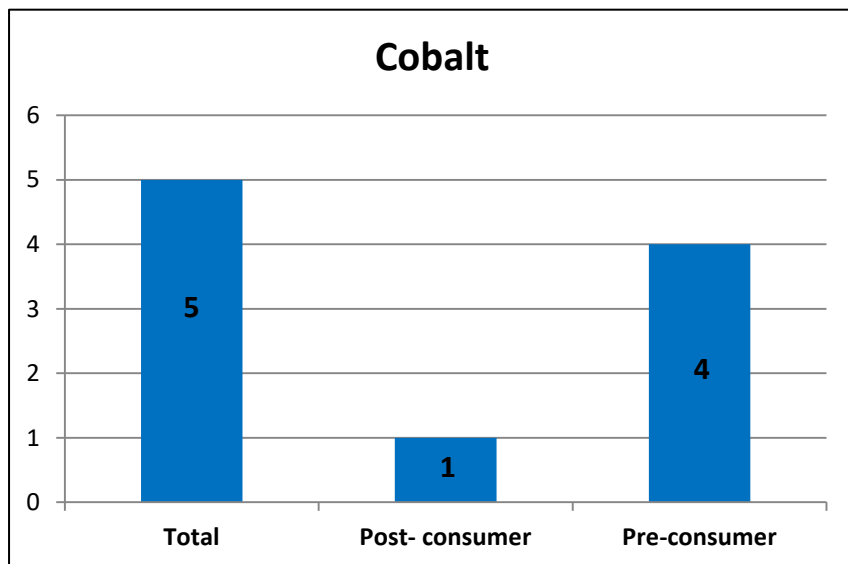


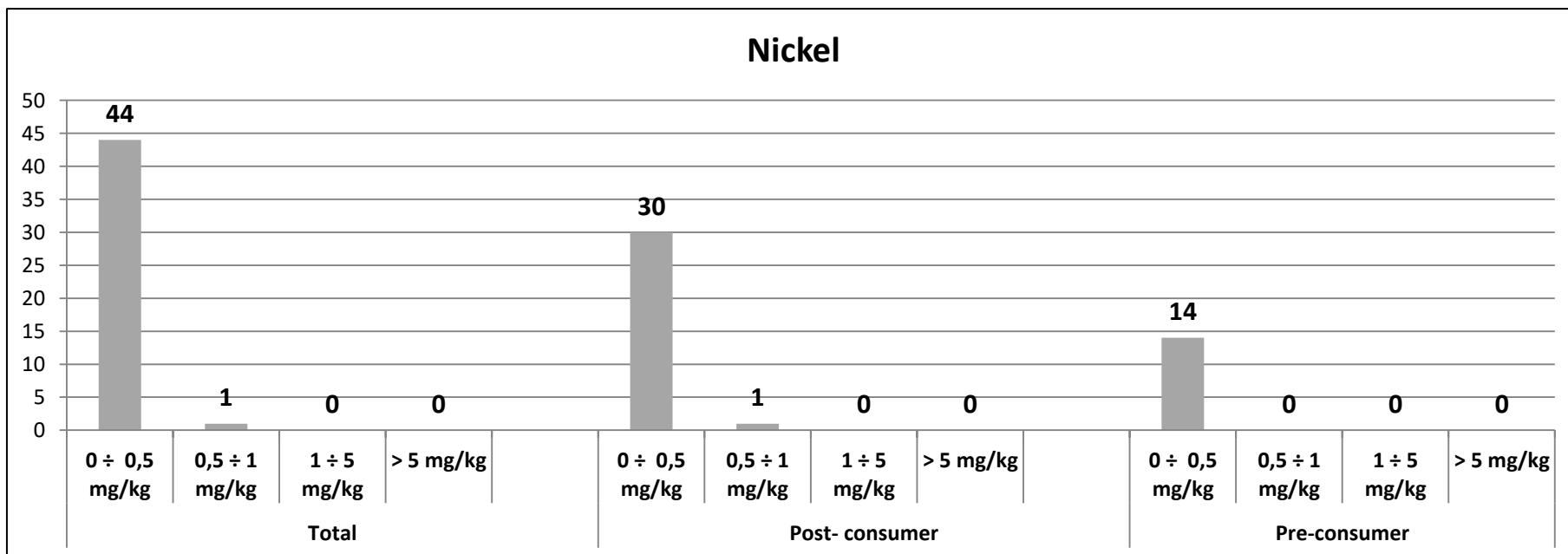
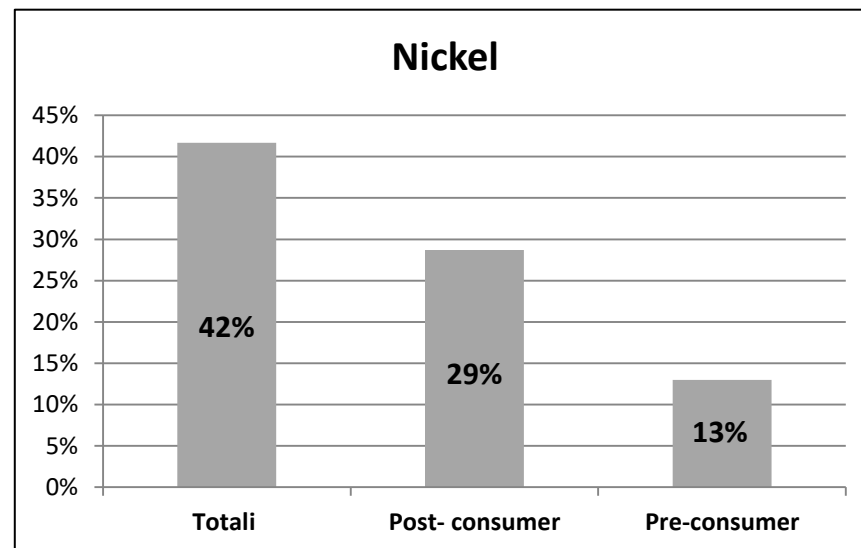
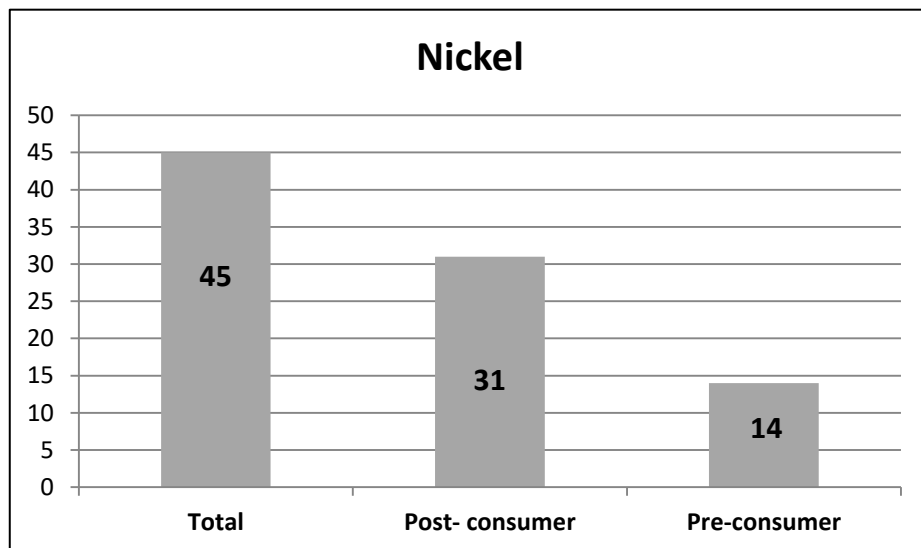


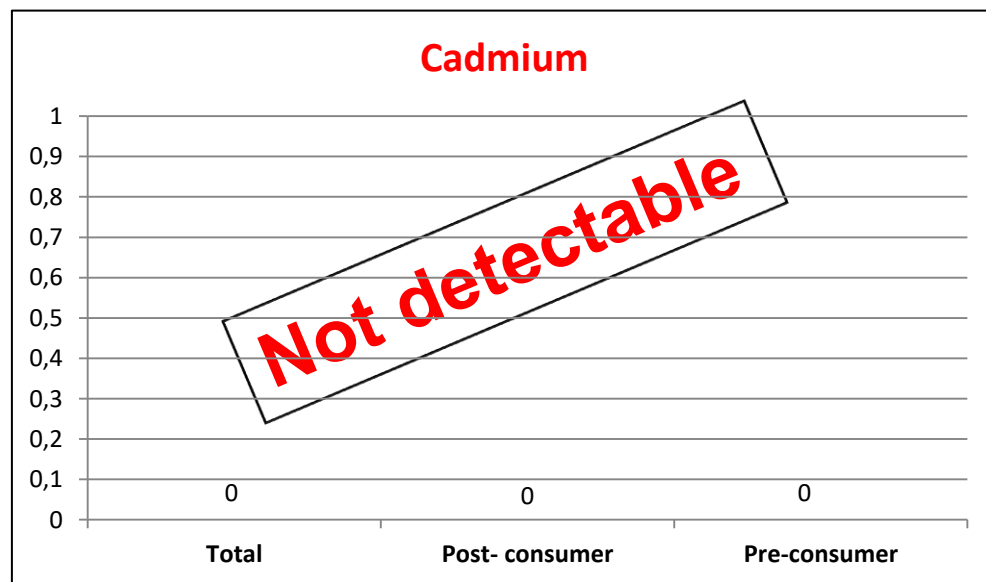
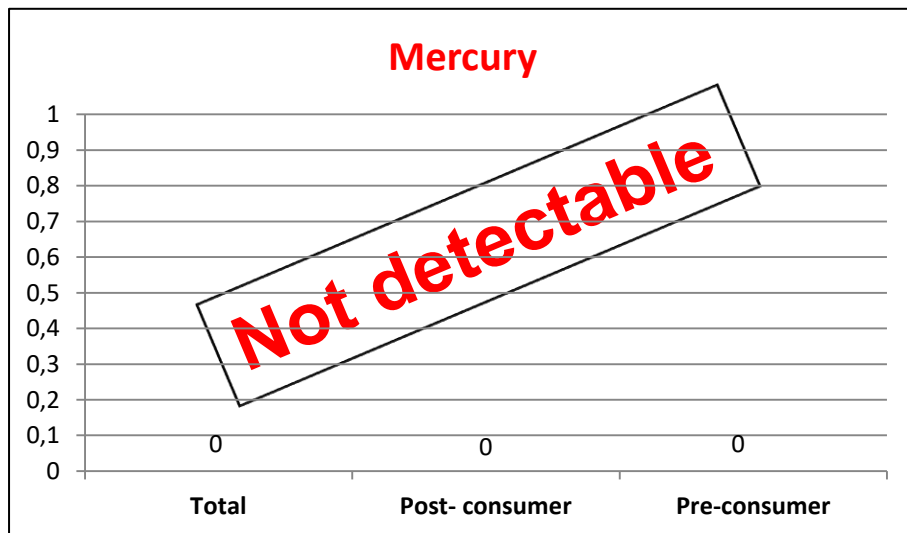




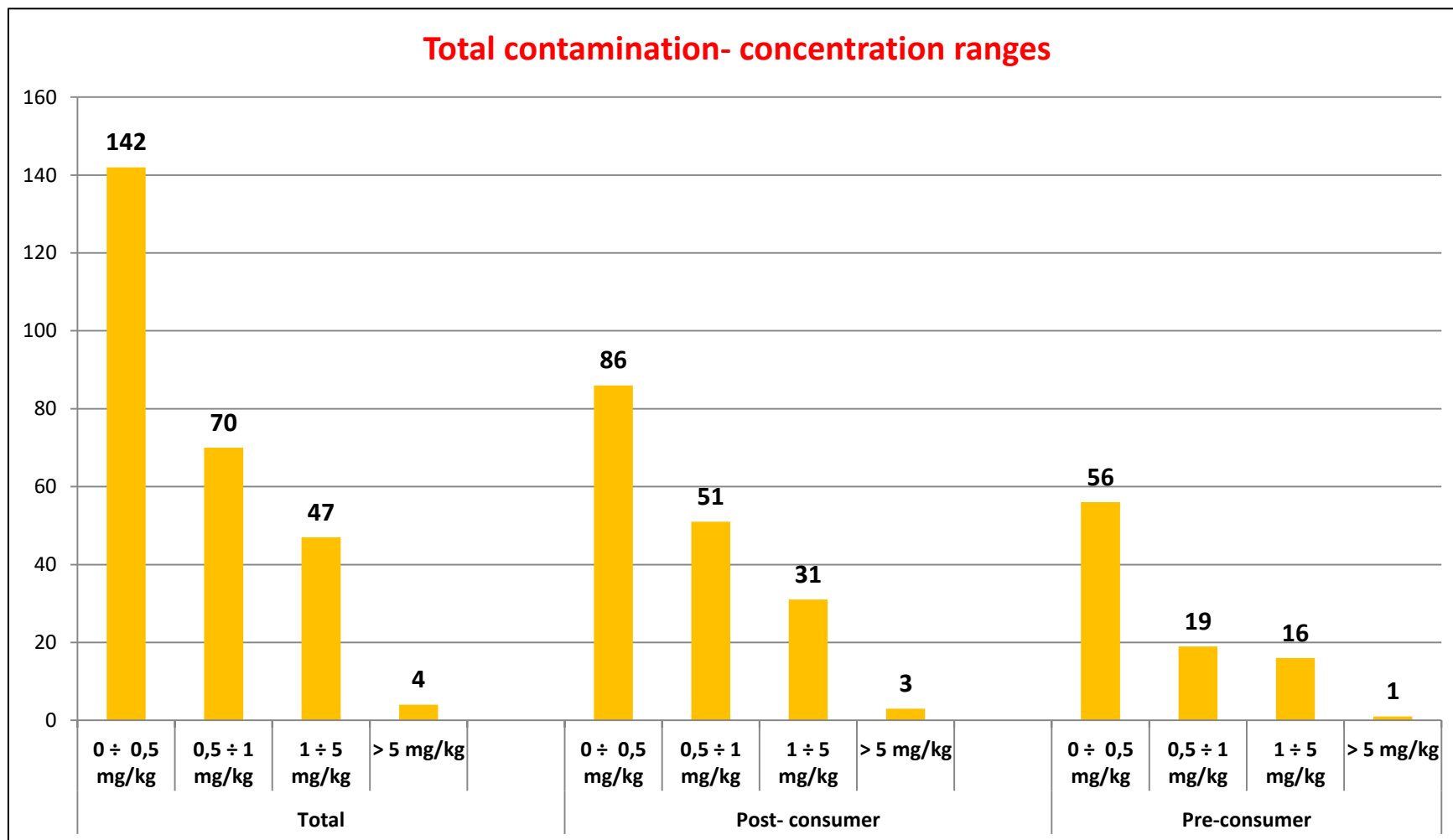


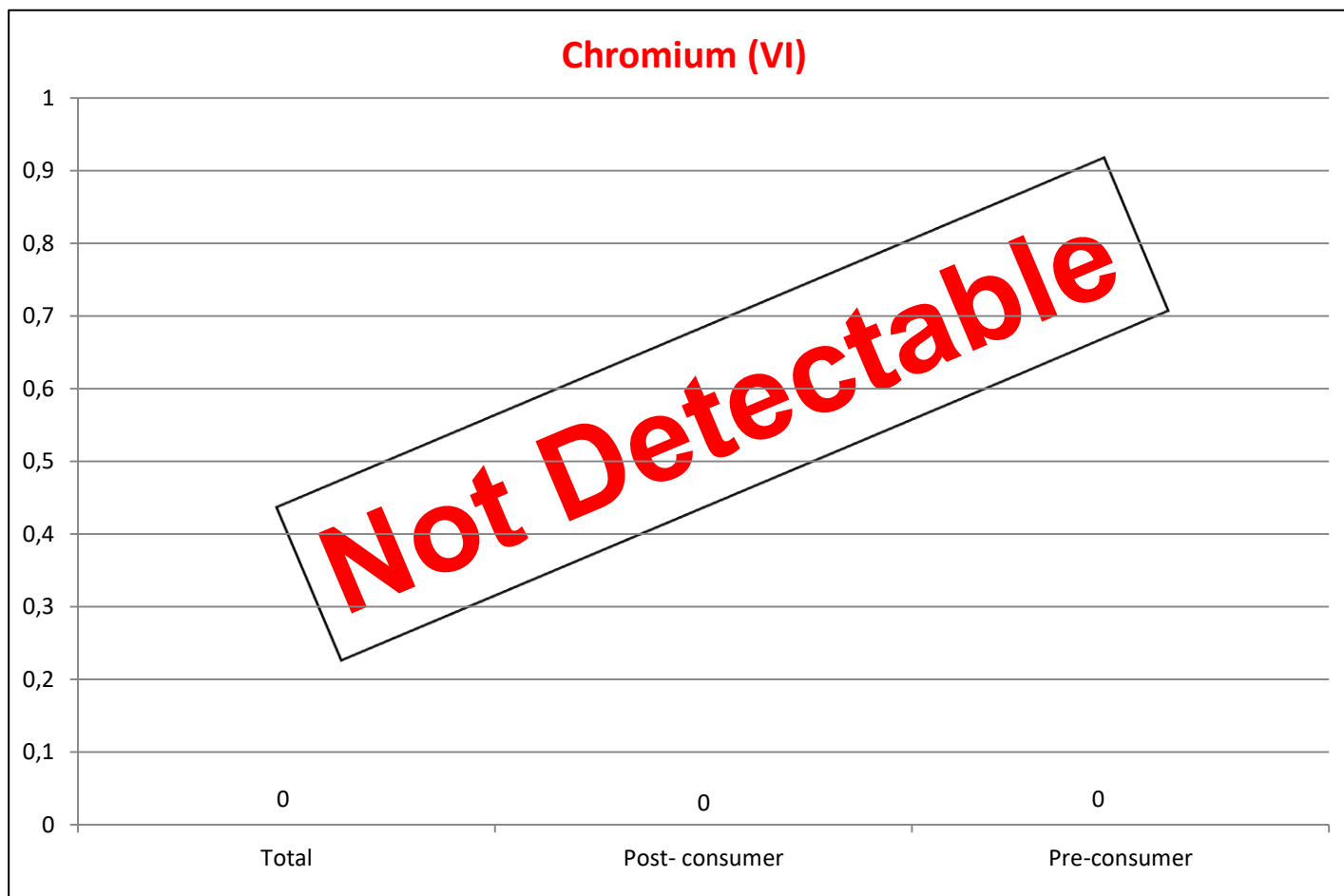




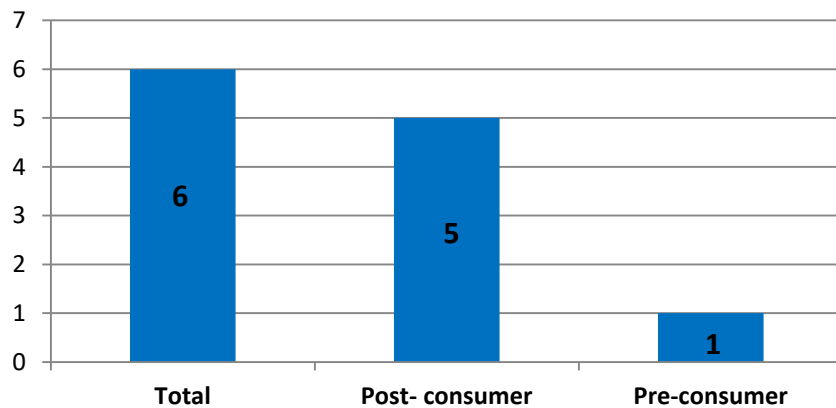


Total contamination- concentration ranges

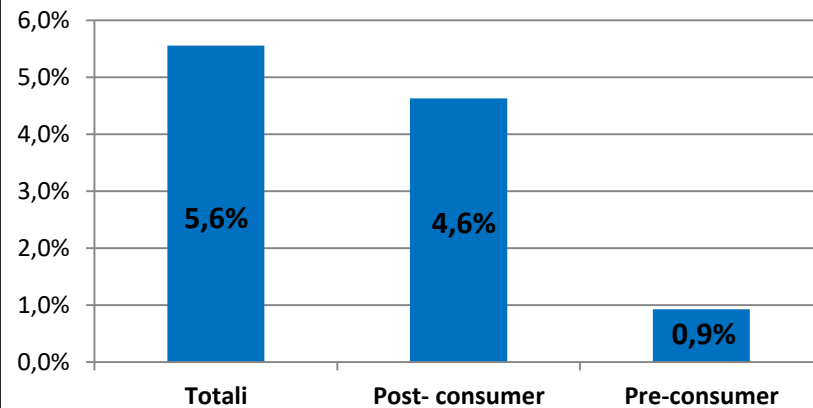


HEXAVALENT CHROMIUM

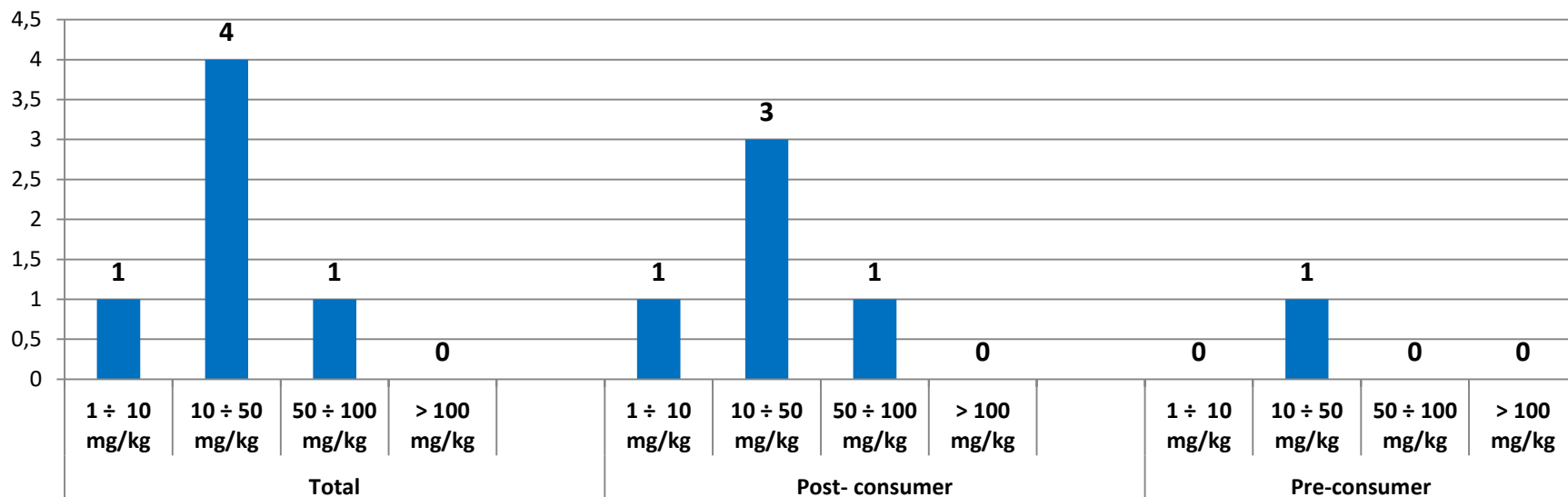
Disperse Blue 3 (ALLERGENIC)



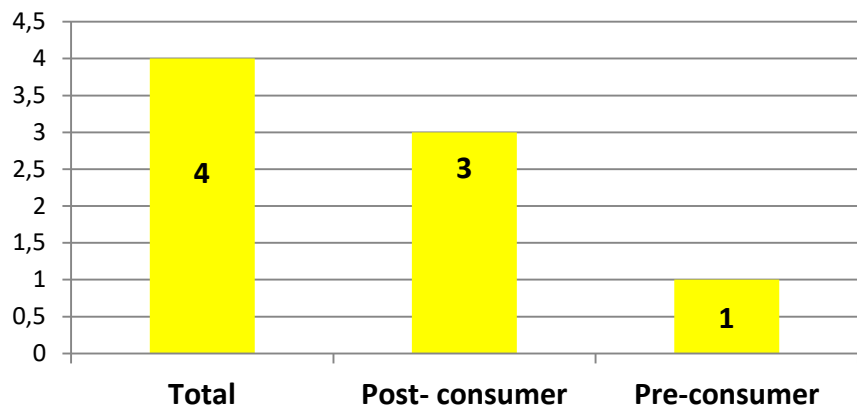
Disperse Blue 3



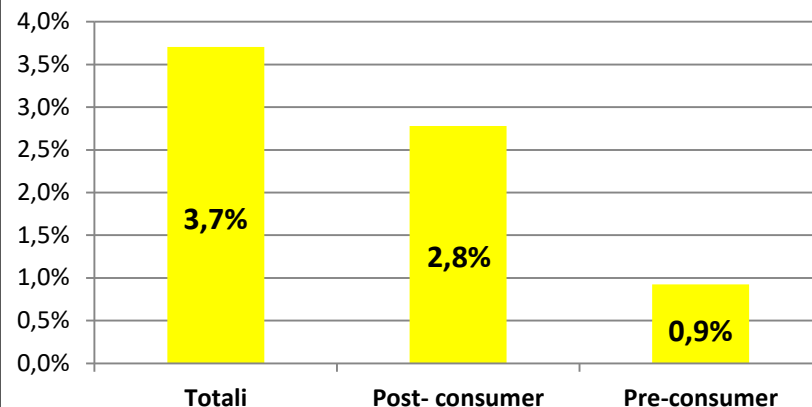
Disperse Blue 3



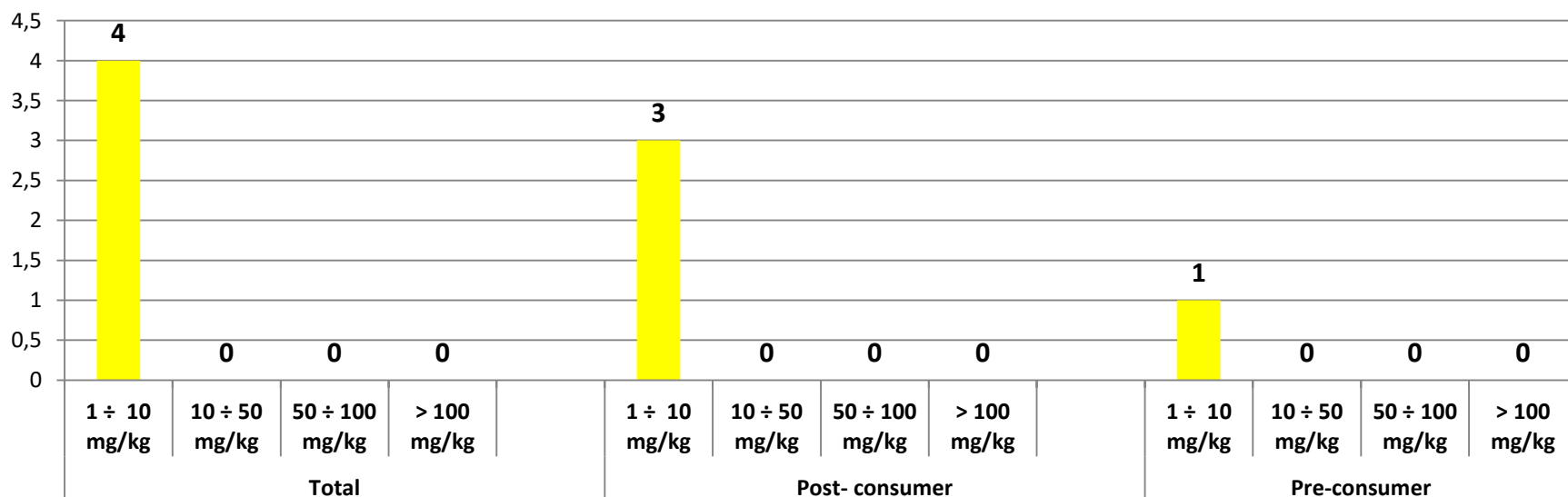
Disperse Yellow 3 (ALLERGENIC)



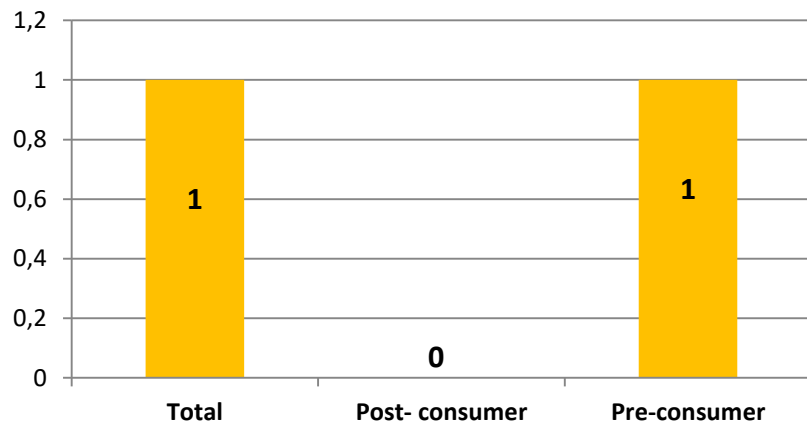
Disperse Yellow 3



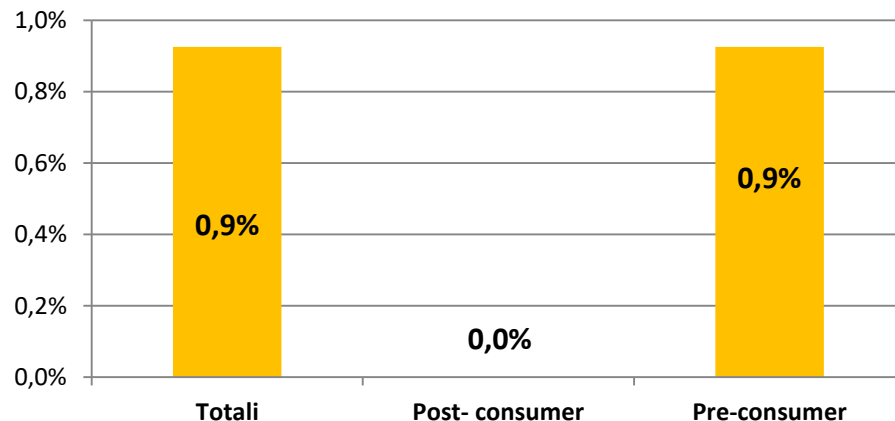
Disperse Yellow 3



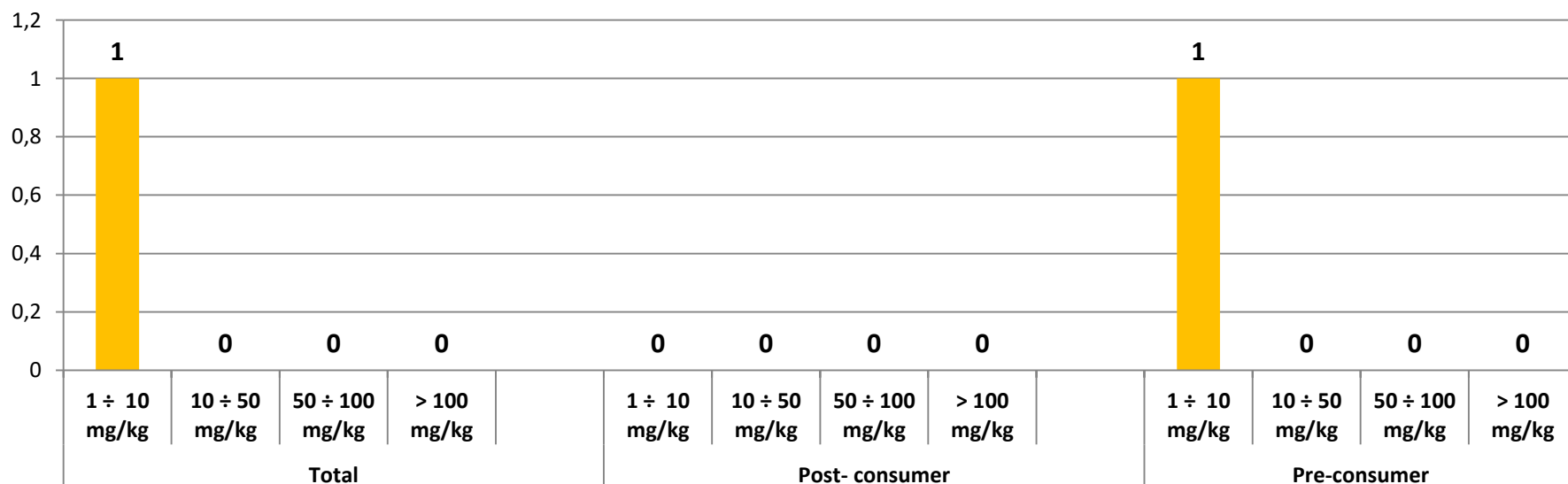
Disperse Yellow 23 (ALLERGENIC)



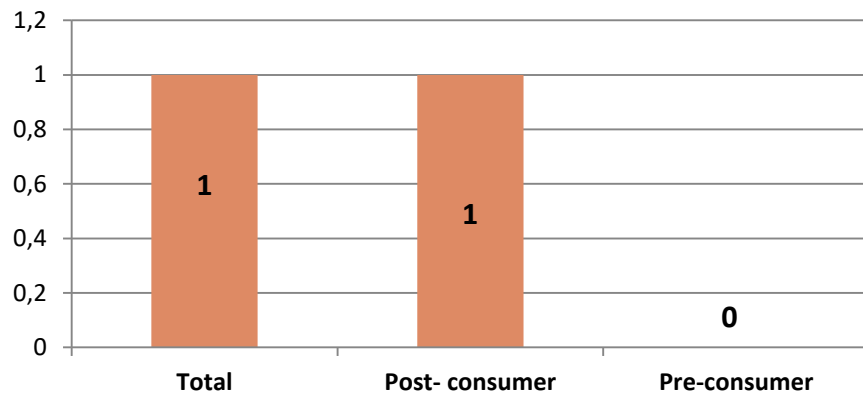
Disperse Yellow 23



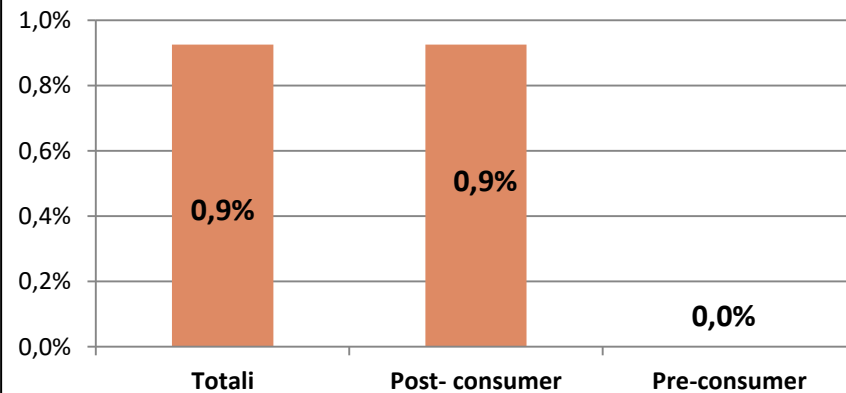
Disperse Yellow 23



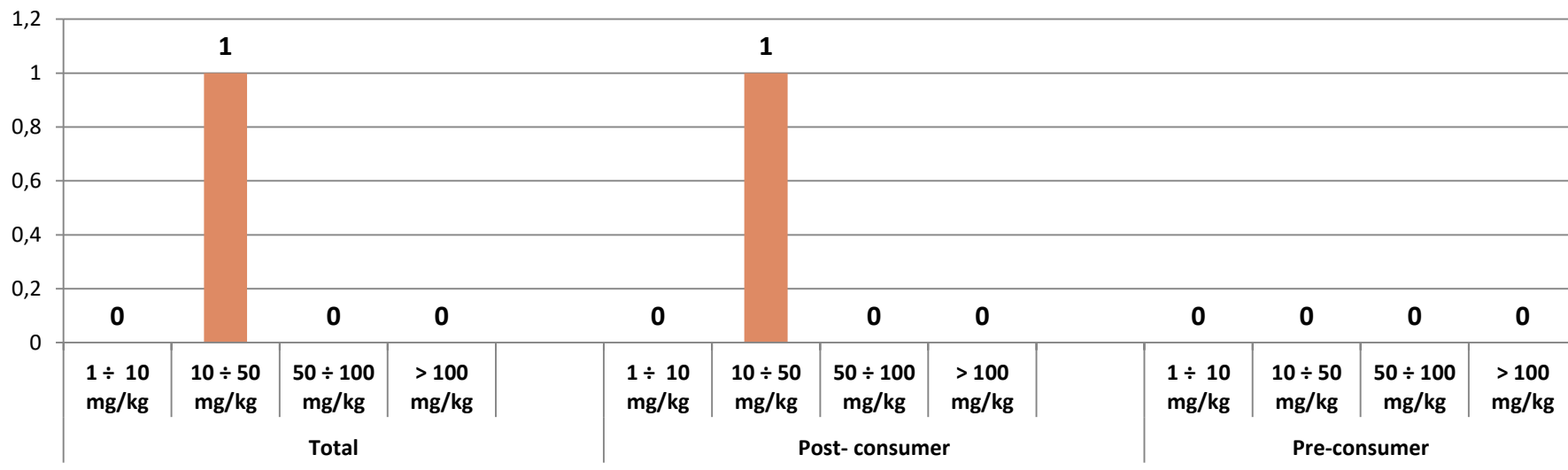
Disperse Orange 61 (ALLERGENIC)



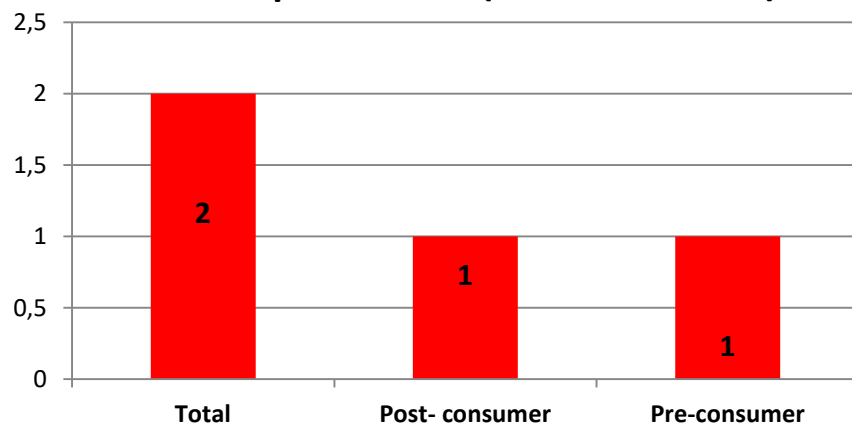
Disperse Orange 61



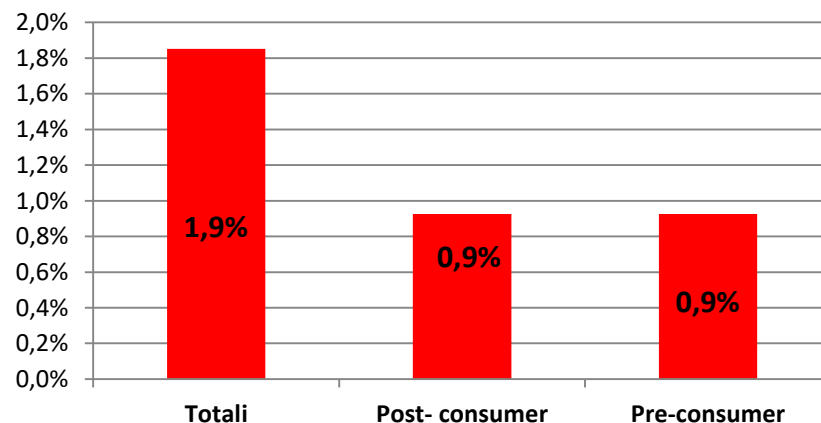
Disperse Orange 61



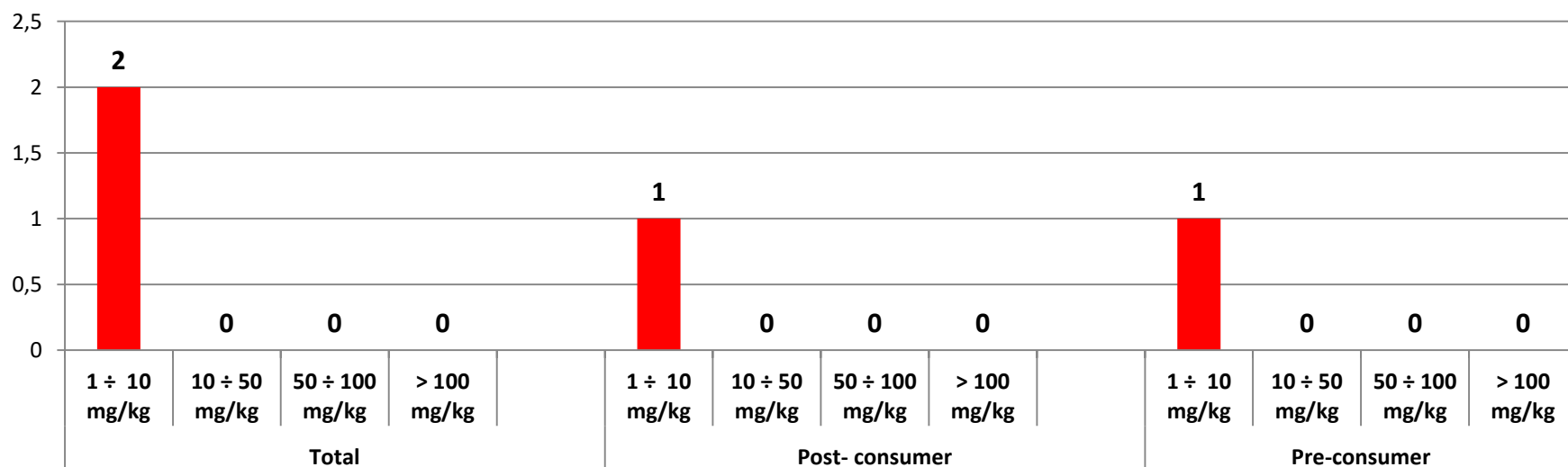
Disperse red 1 (CARCINOGENIC)



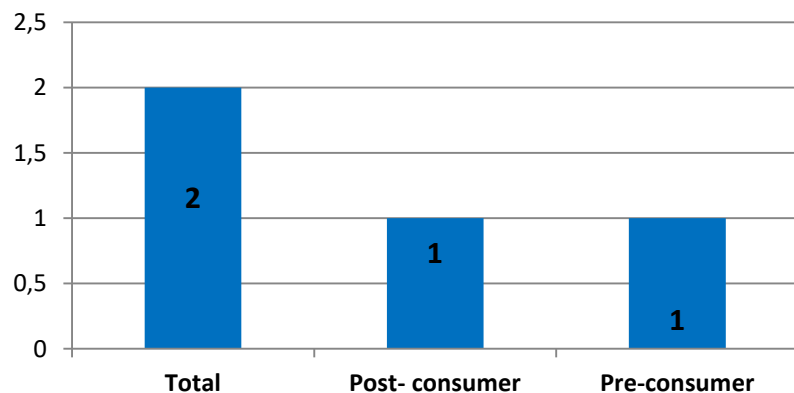
Disperse red 1



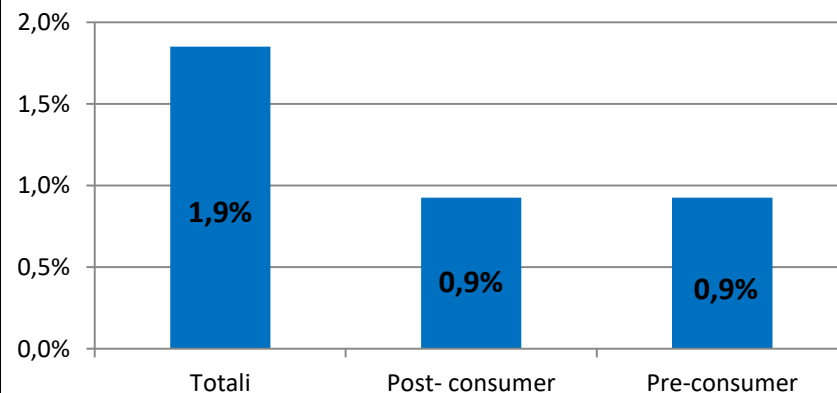
Disperse red 1



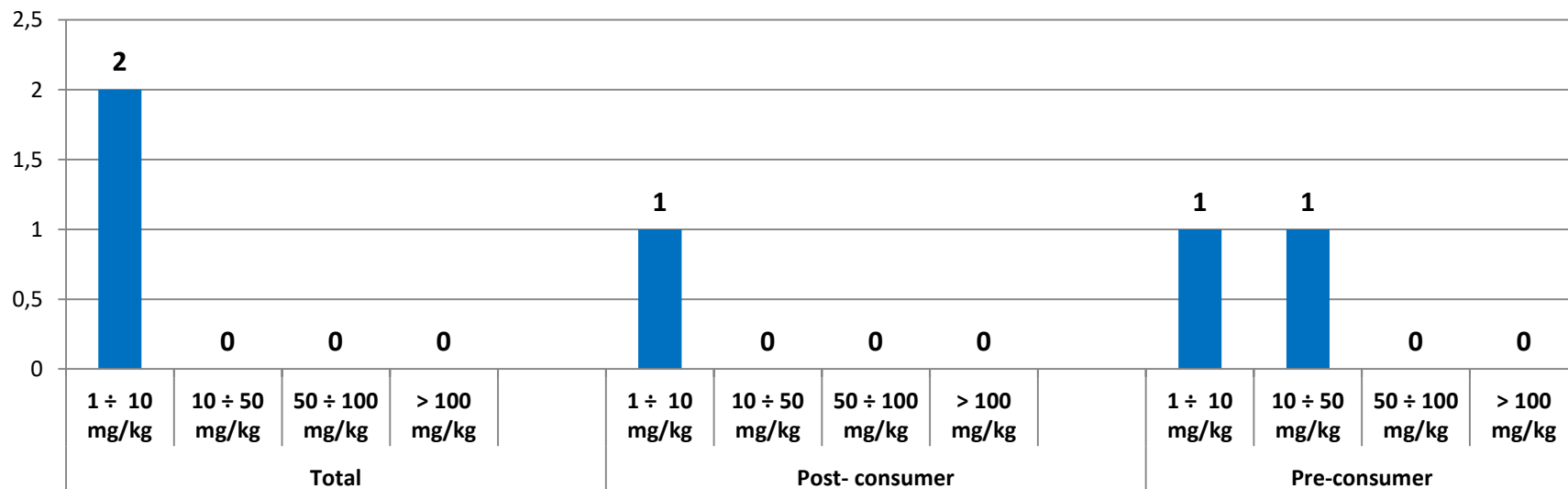
Direct Blue 6 (CARCINOGENIC)



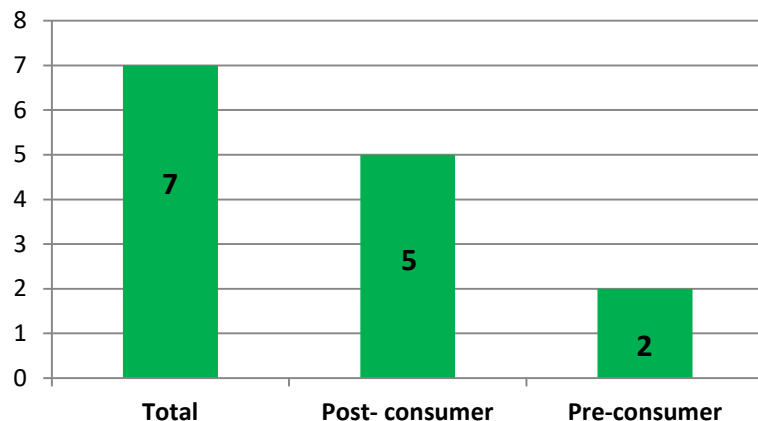
Direct Blue 6



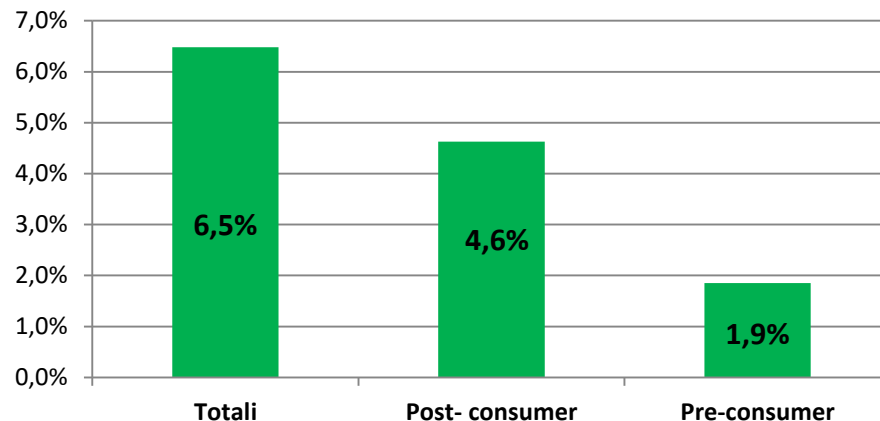
Direct Blue 6



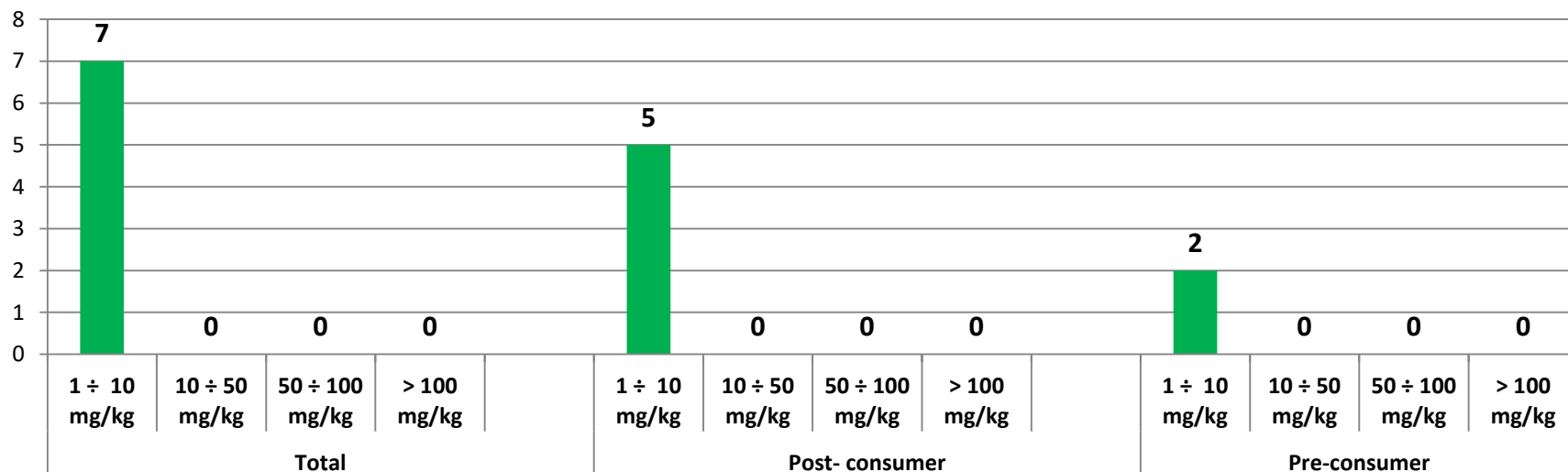
Basic Green 4 (CARCINOGENIC)



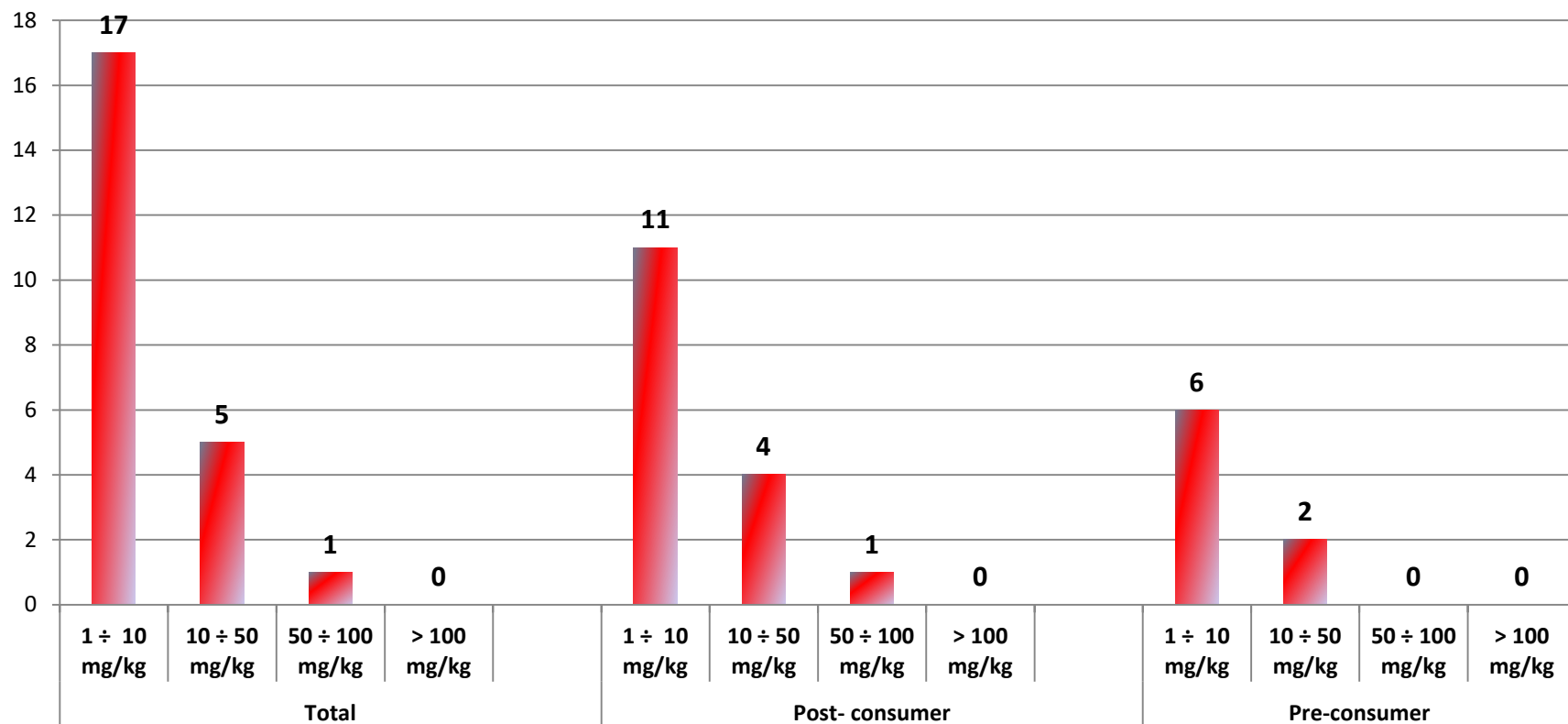
Basic Green 4



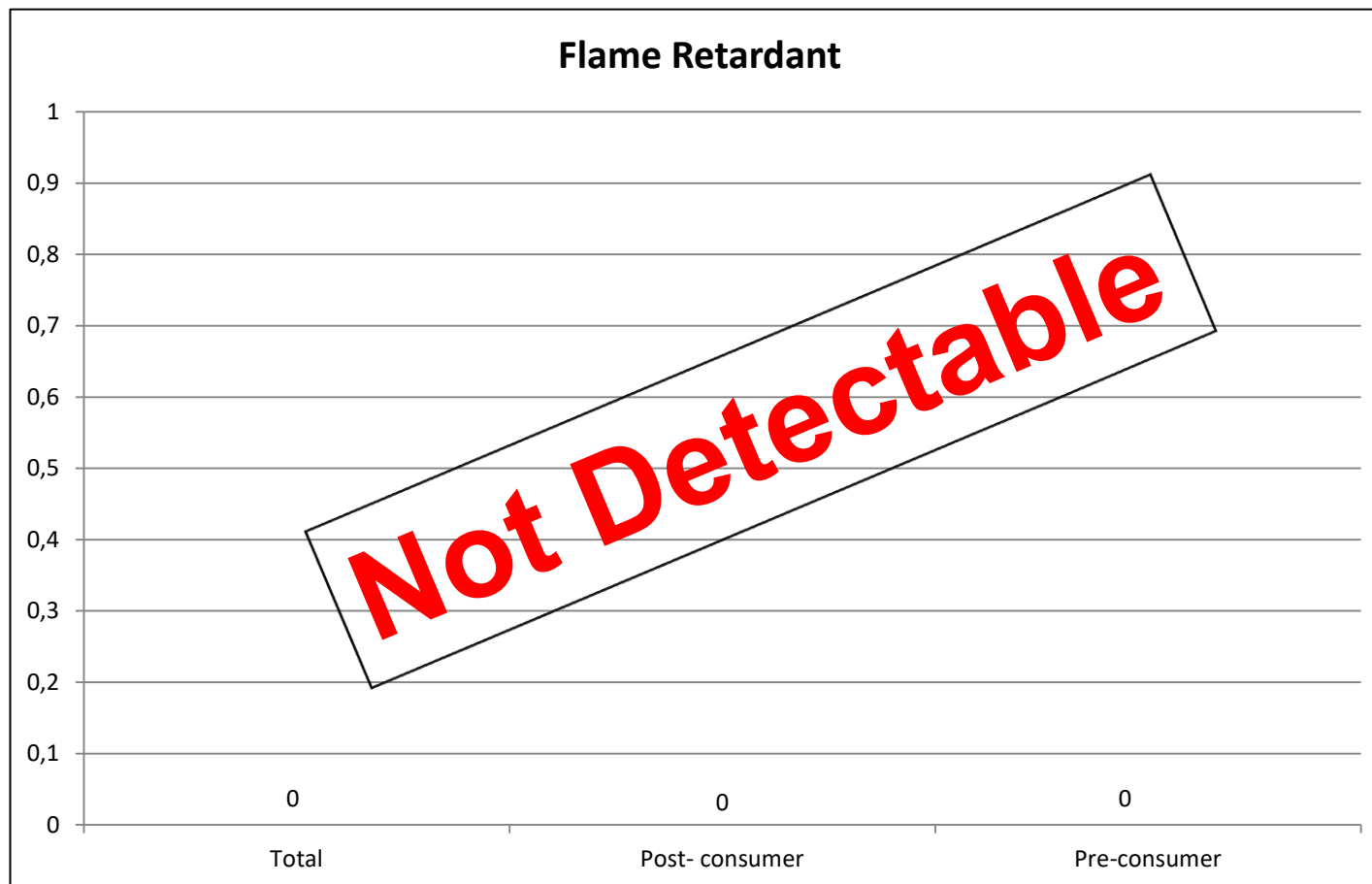
Basic Green 4



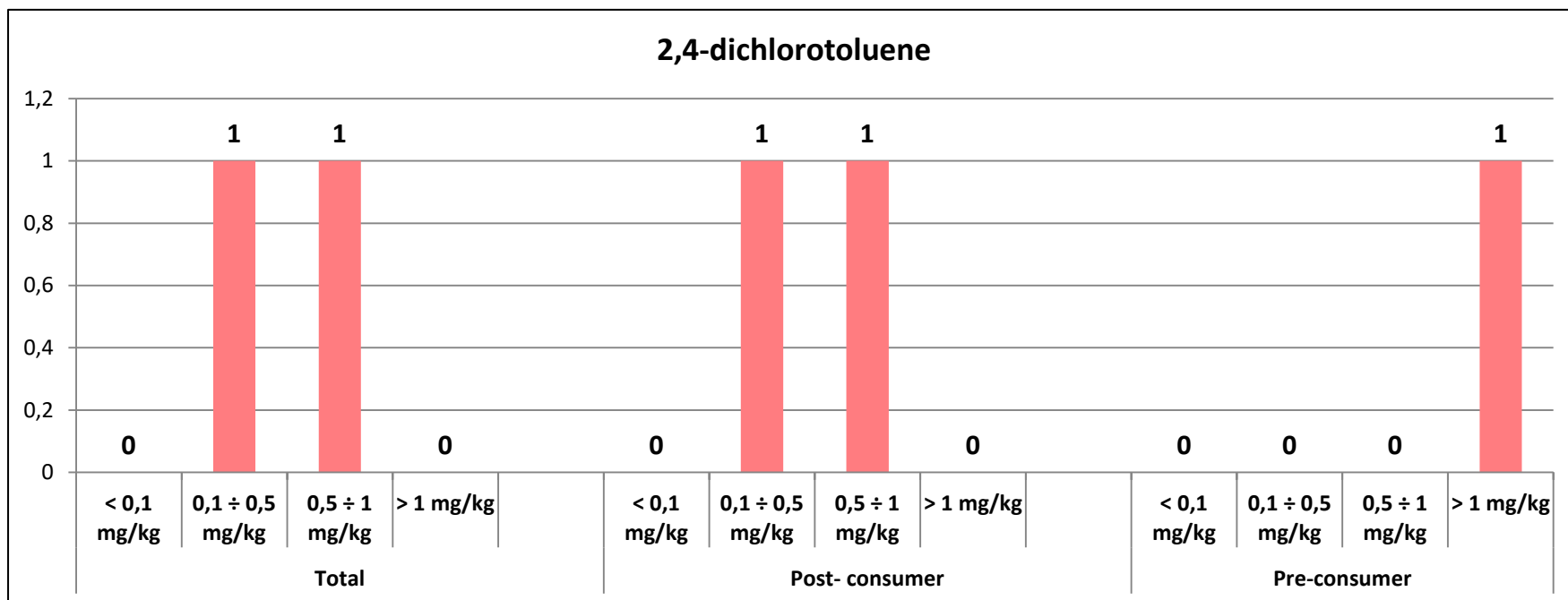
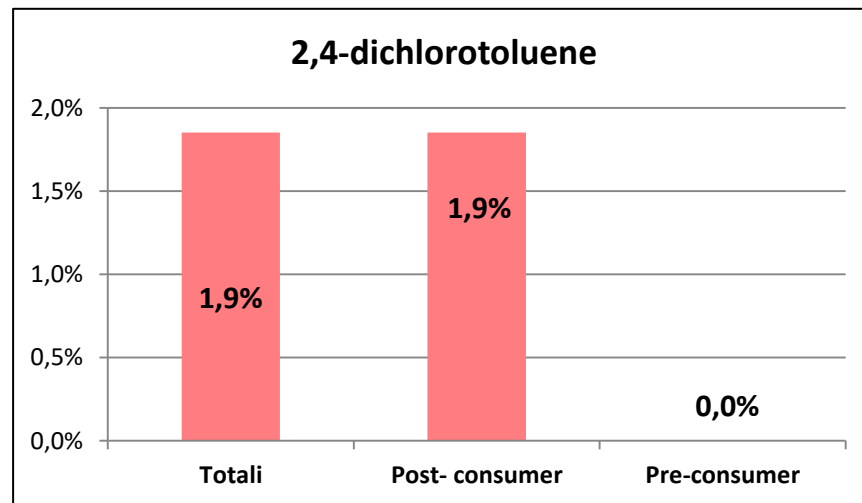
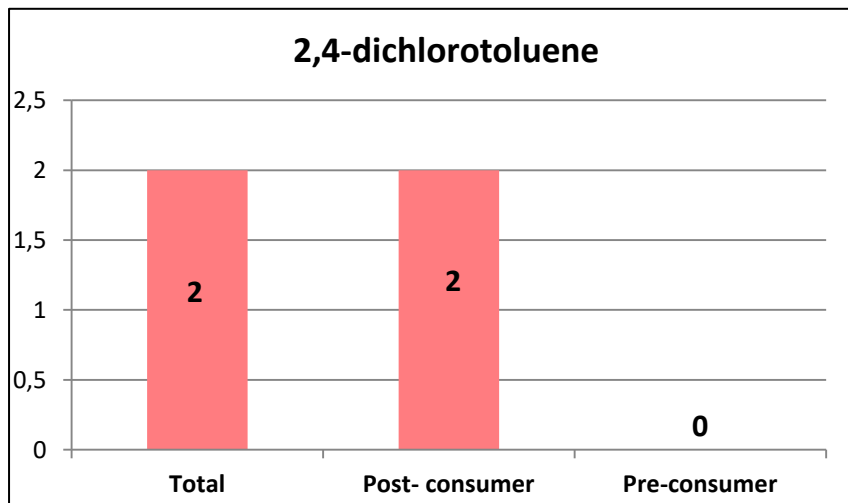
Total concentration ranges

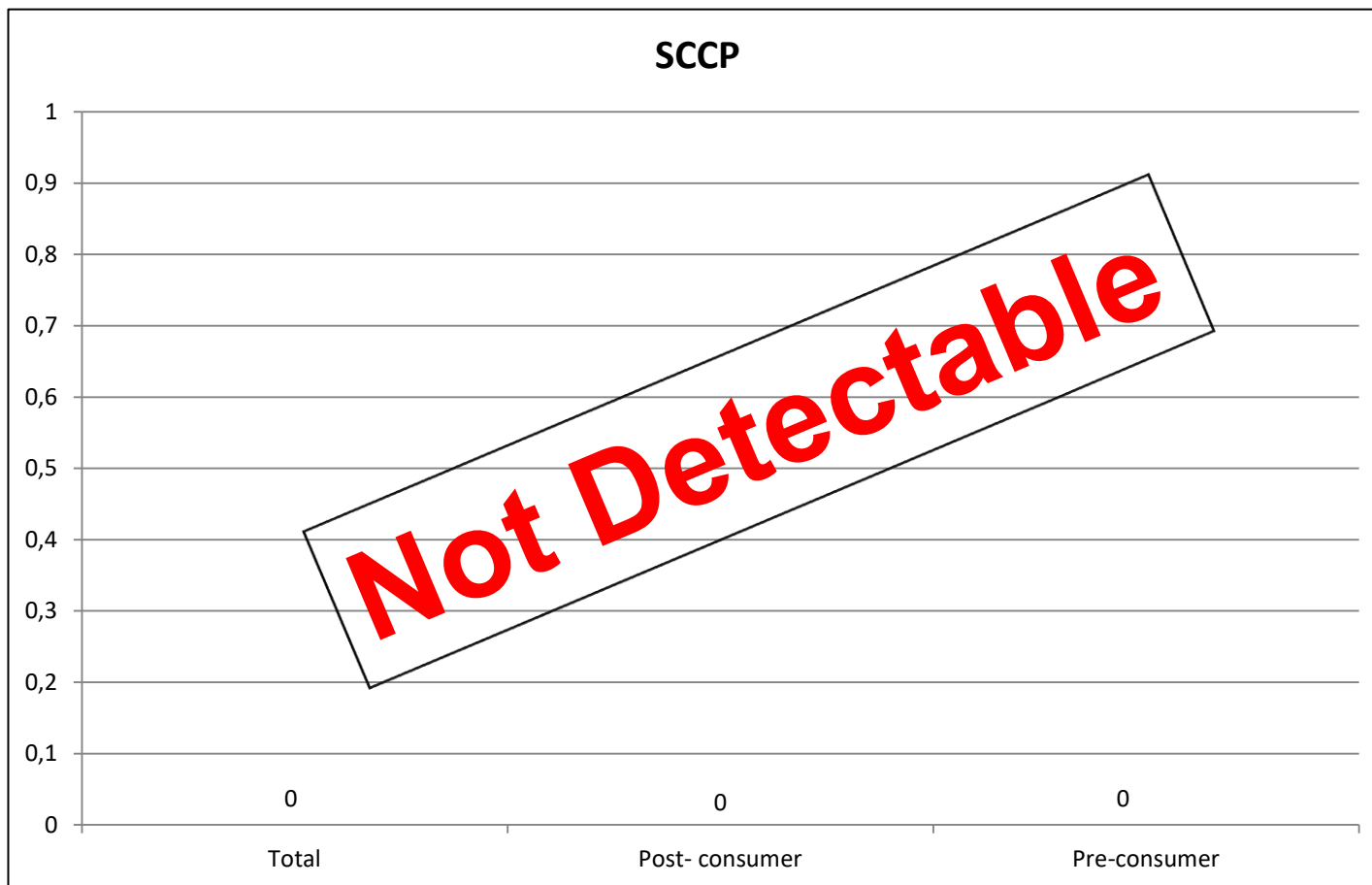


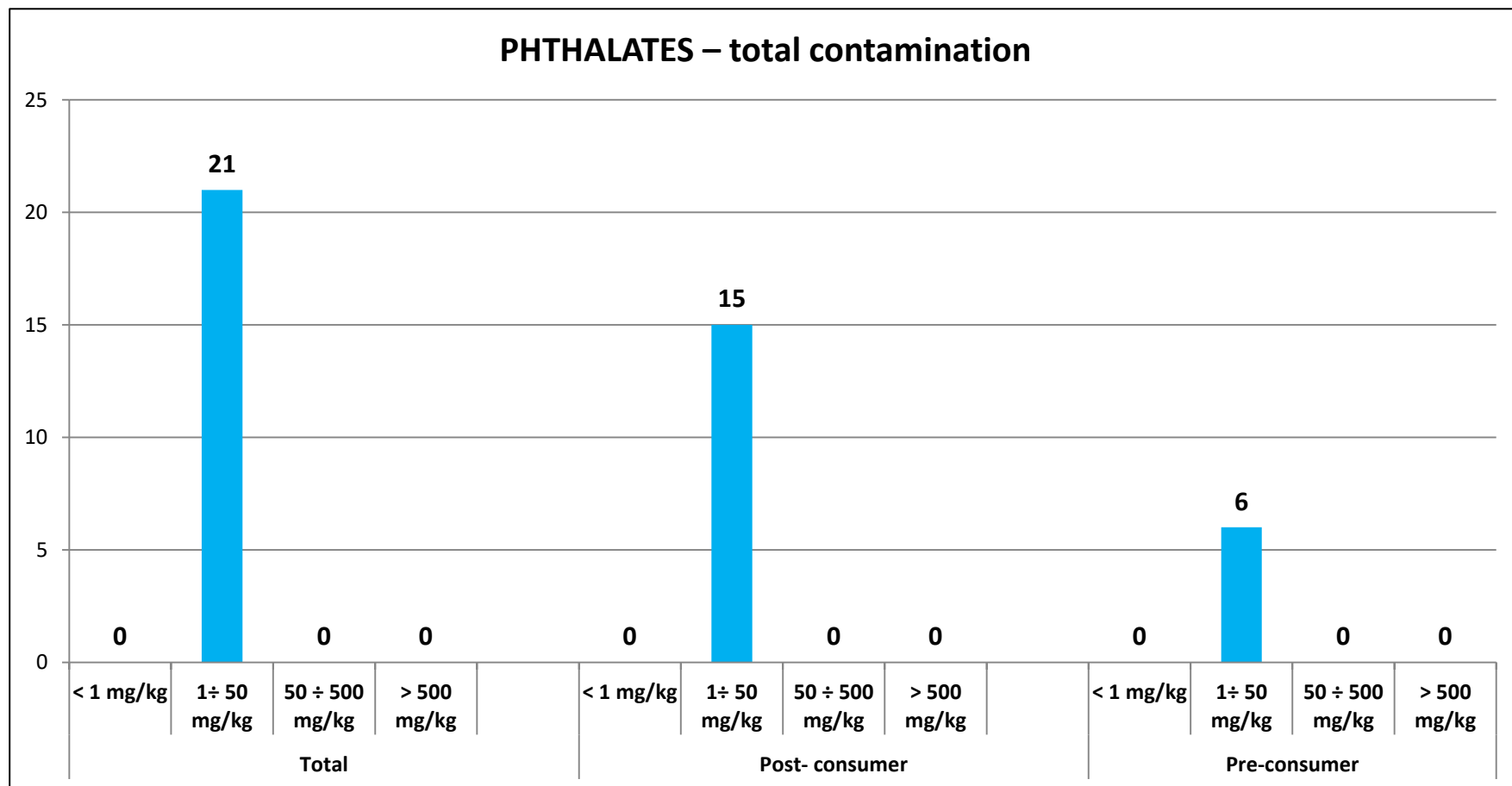
Brominated and Chlorinated FLAME RETARDANT

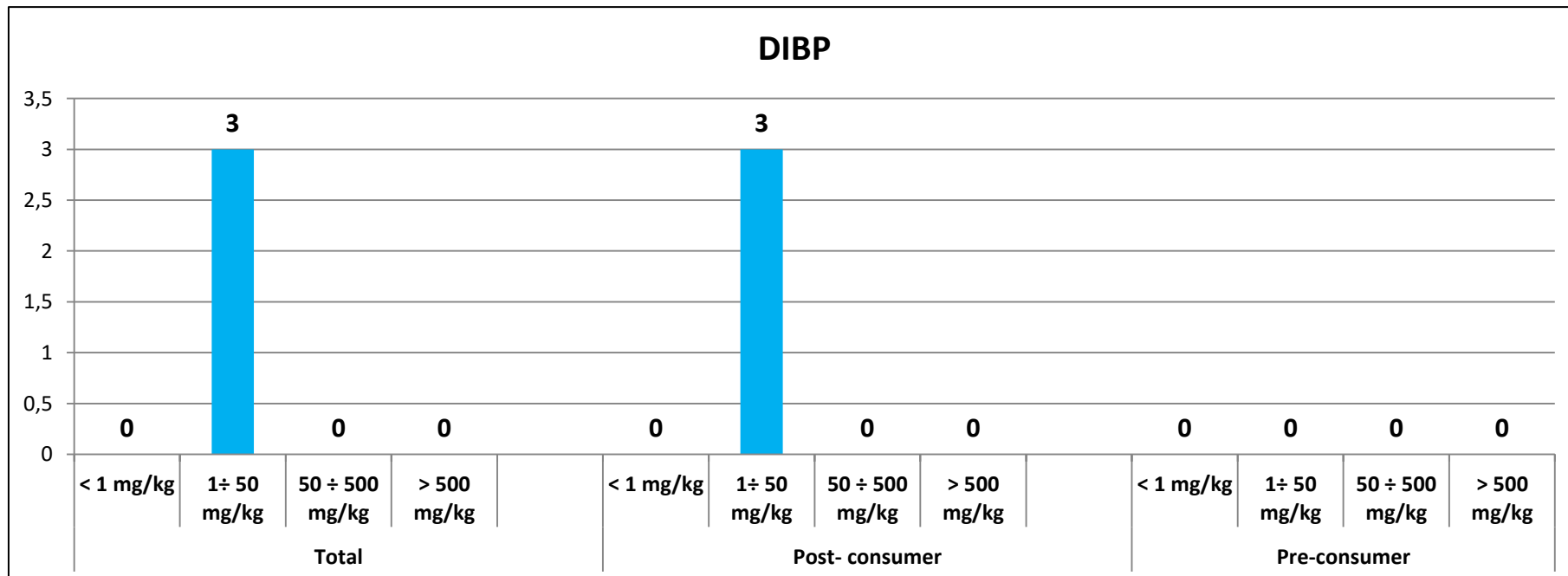
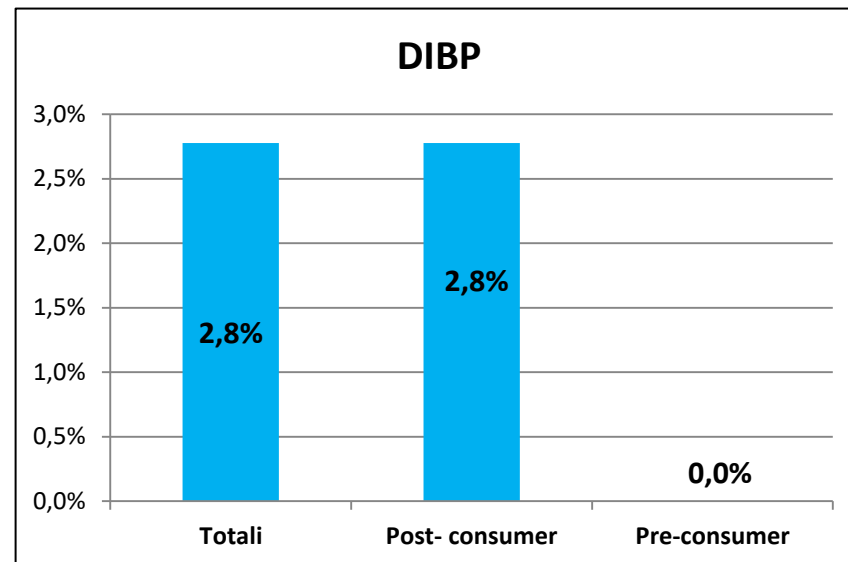
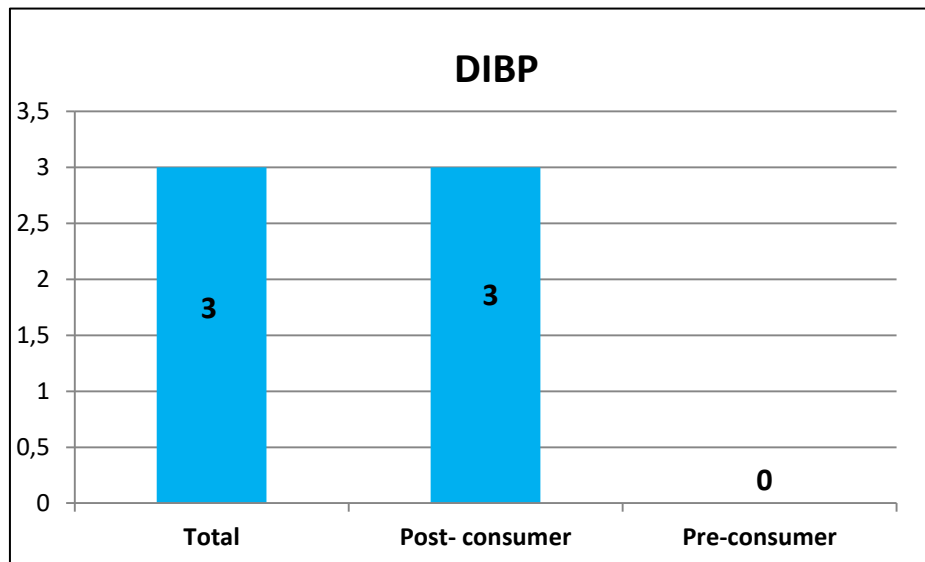


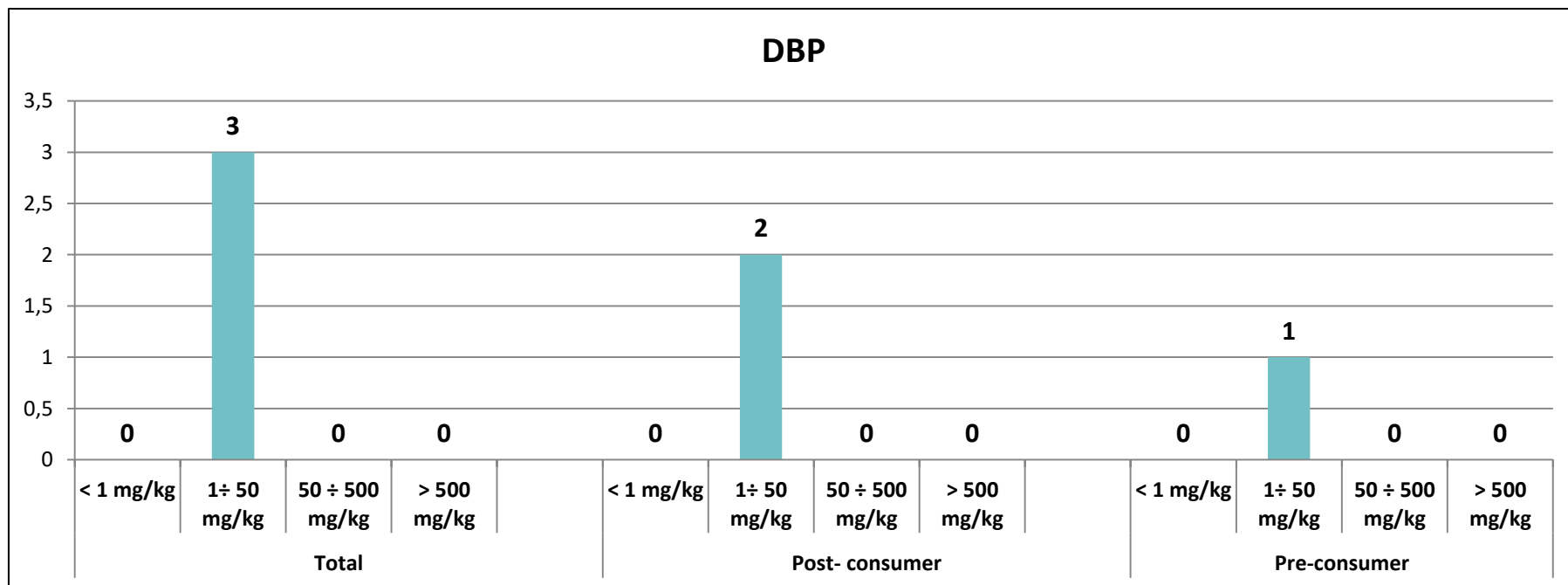
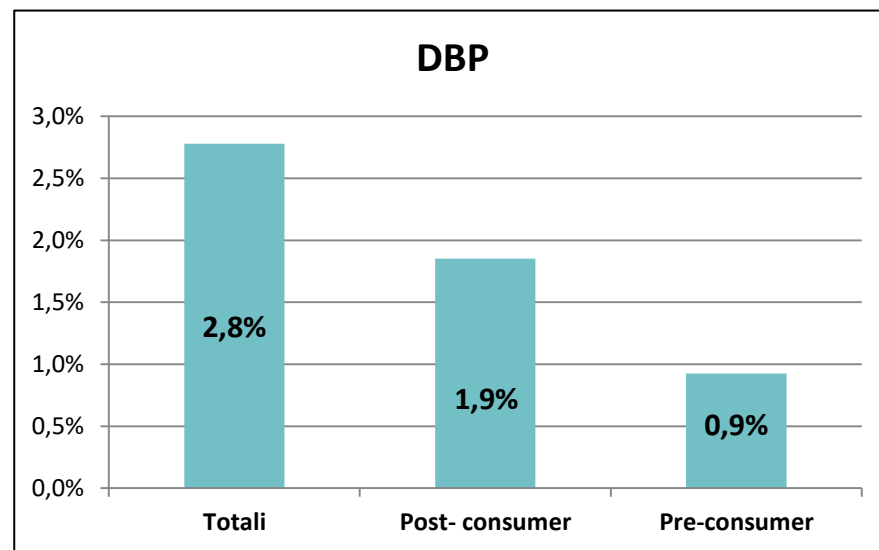
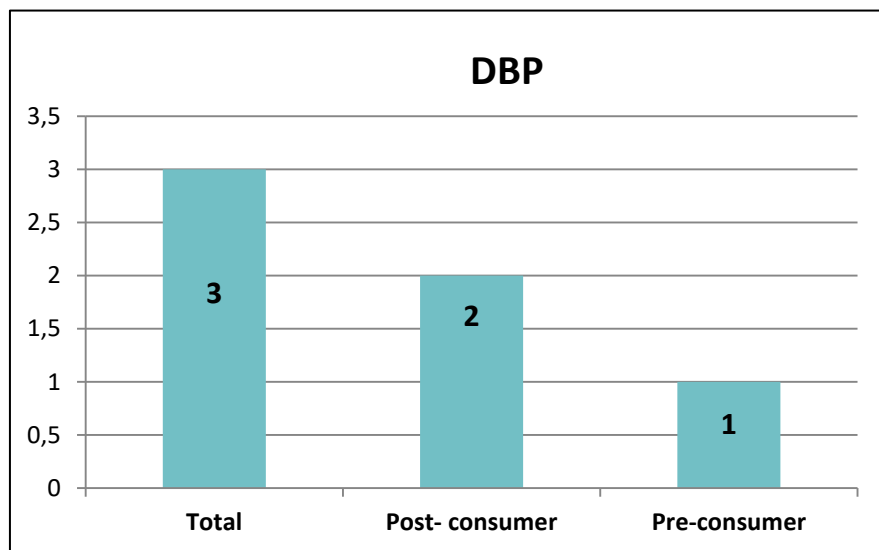
Chlorobenzenes and Toluenes (Carriers)

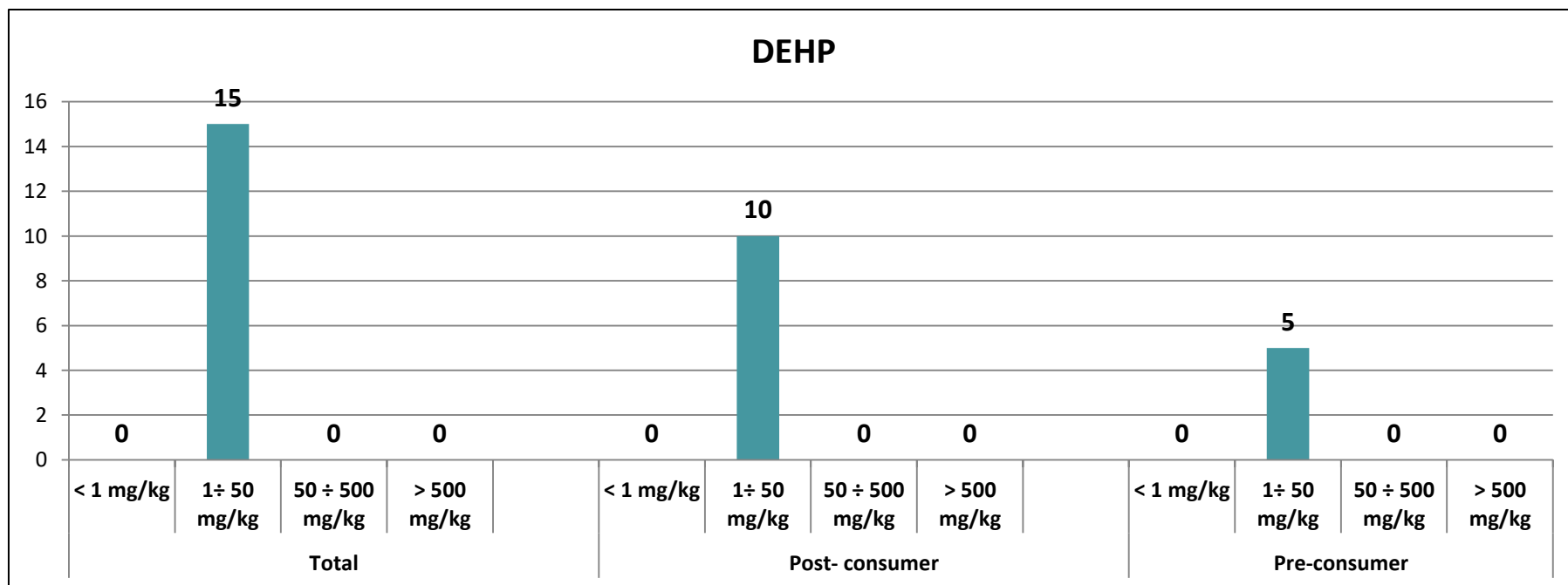
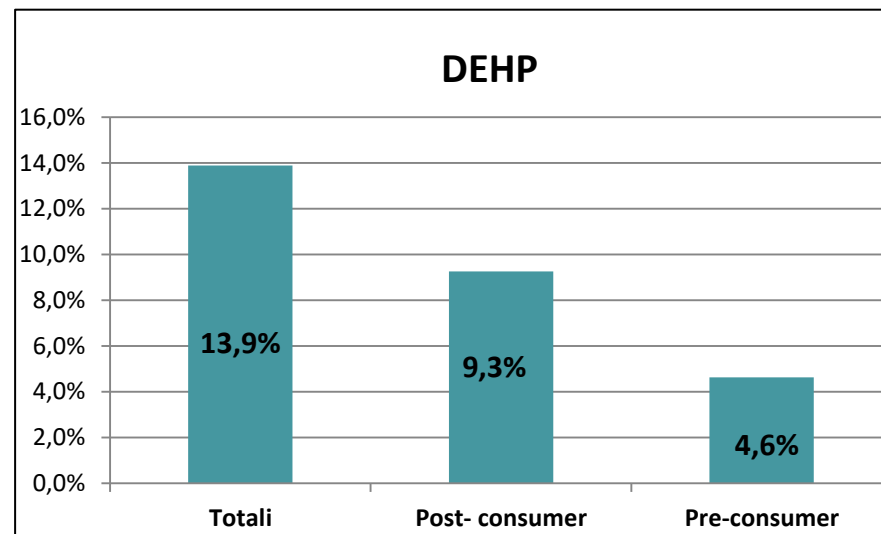
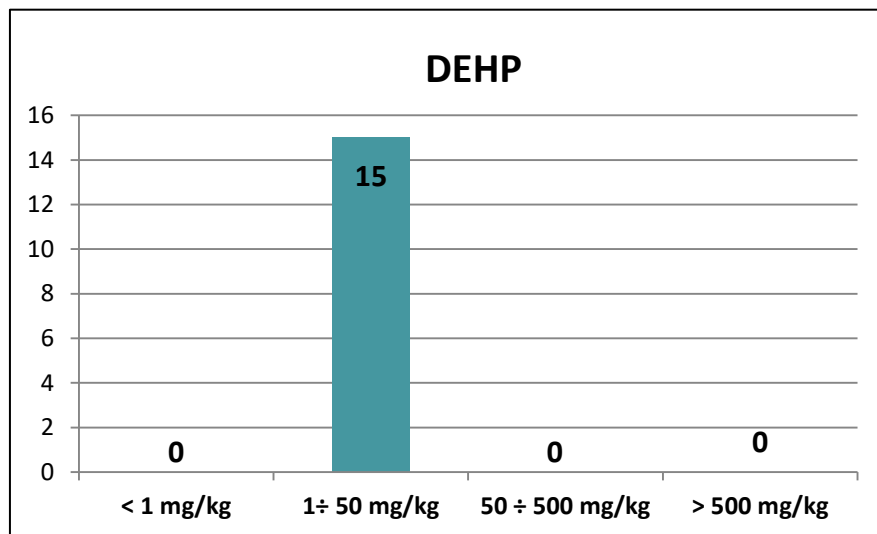


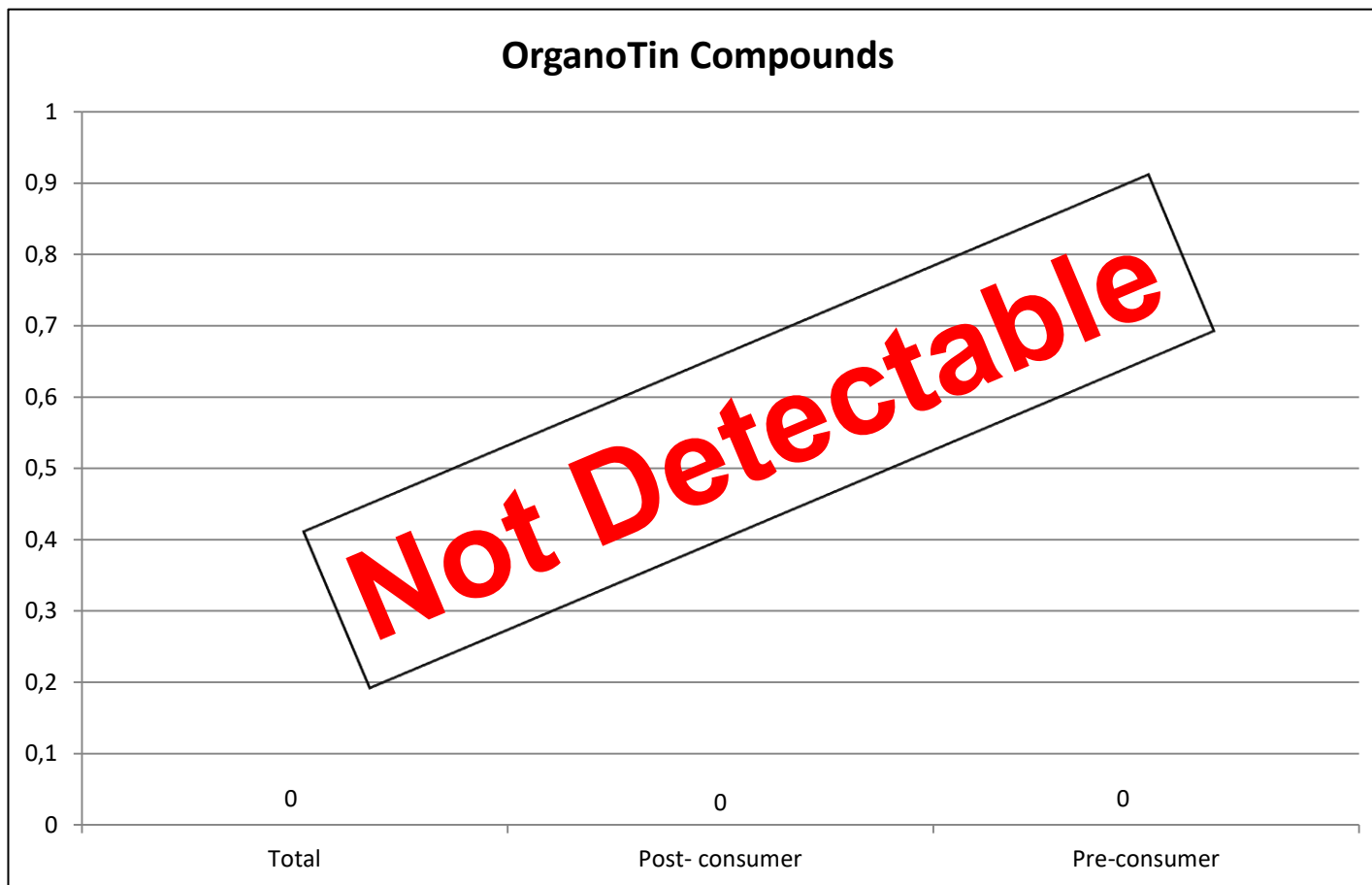


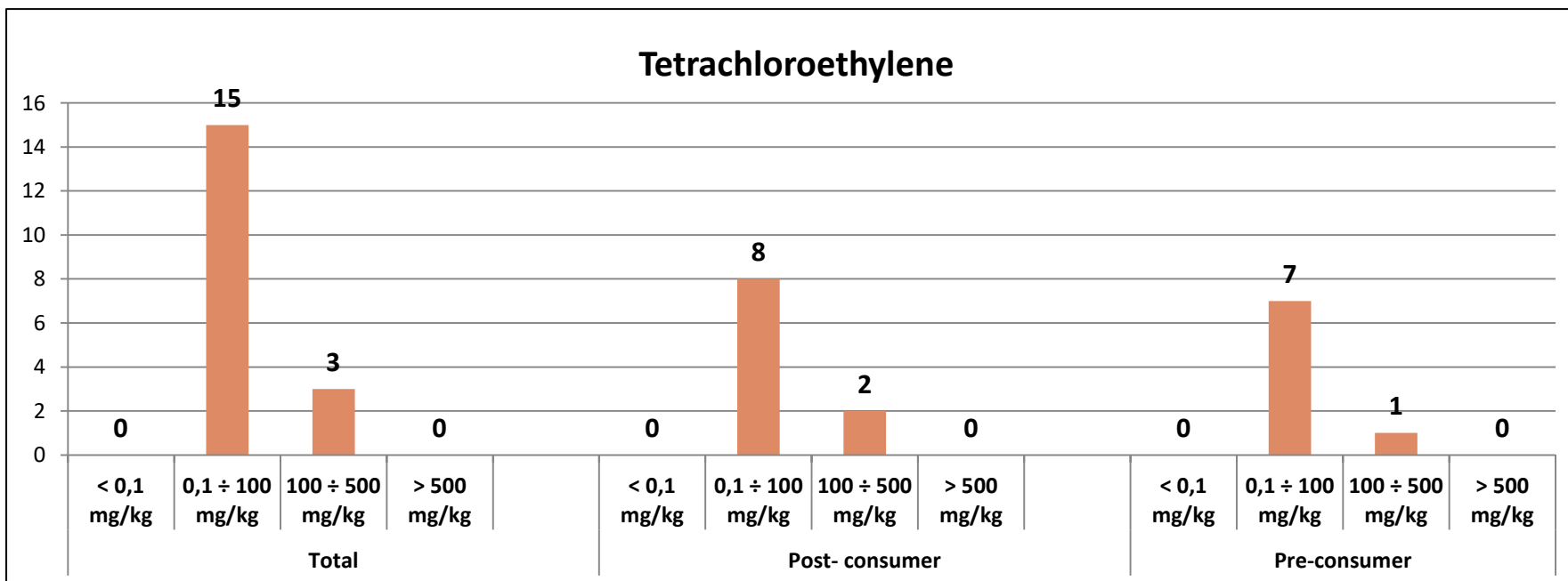
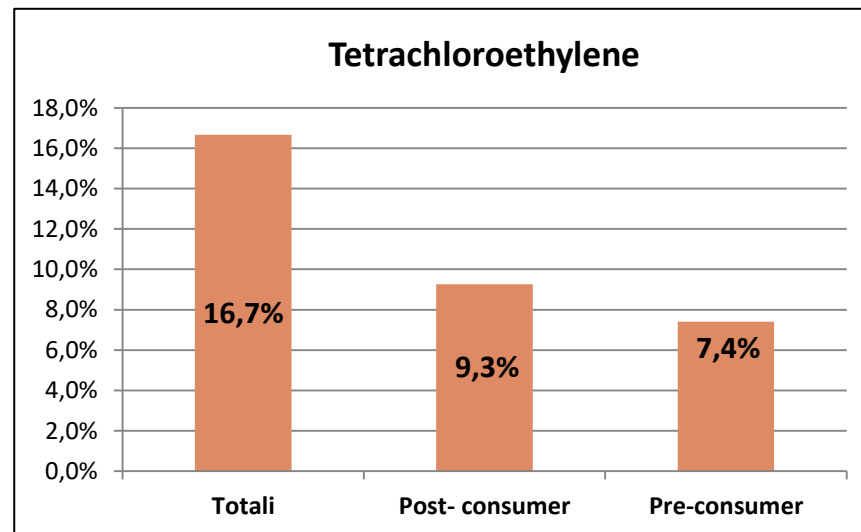
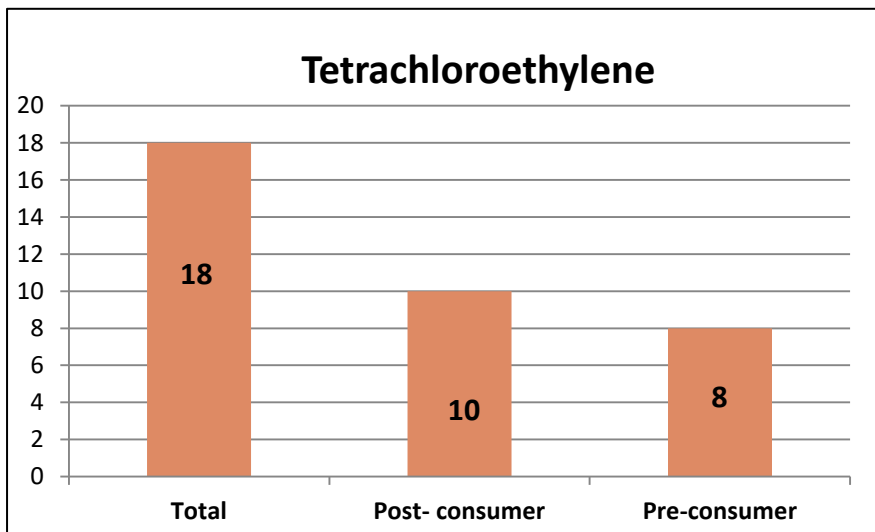


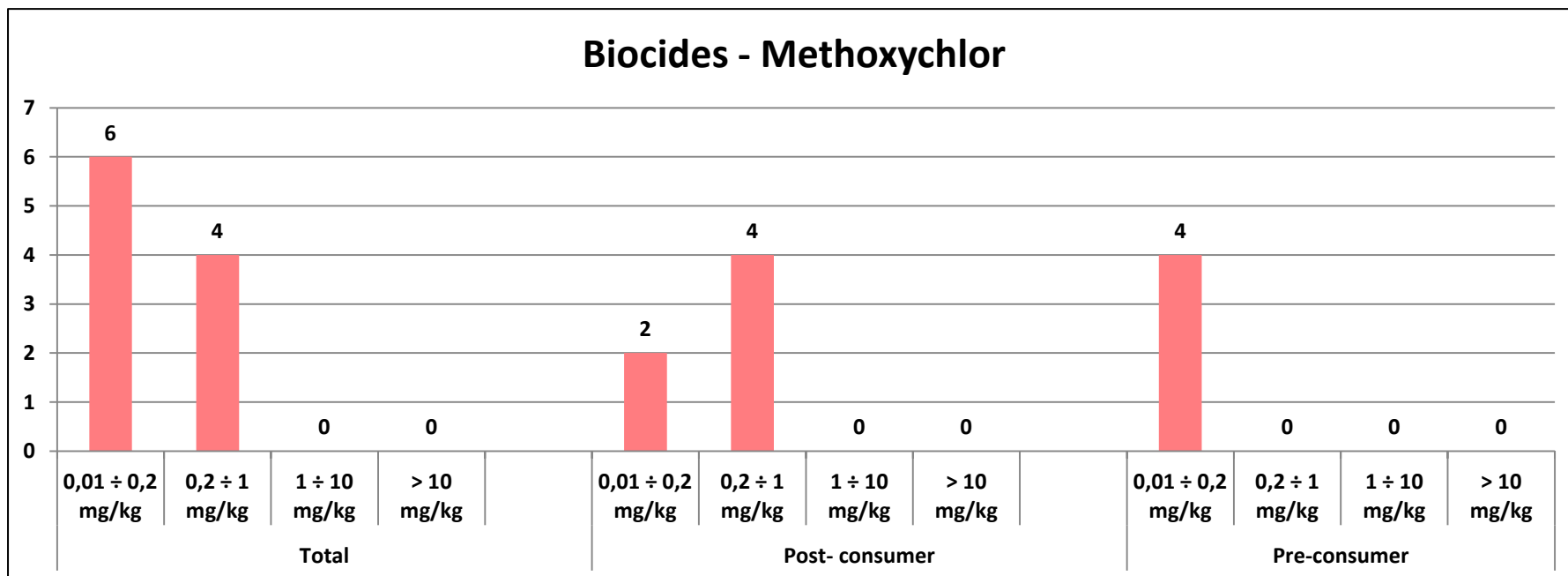
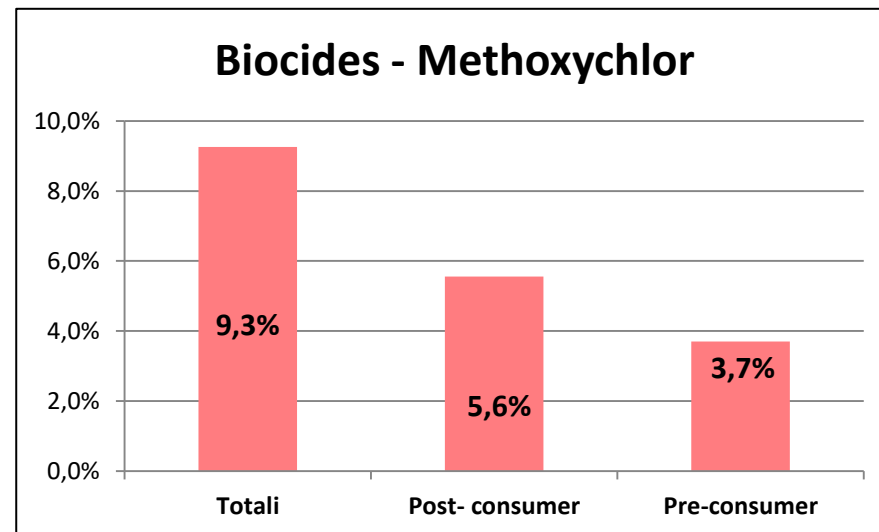
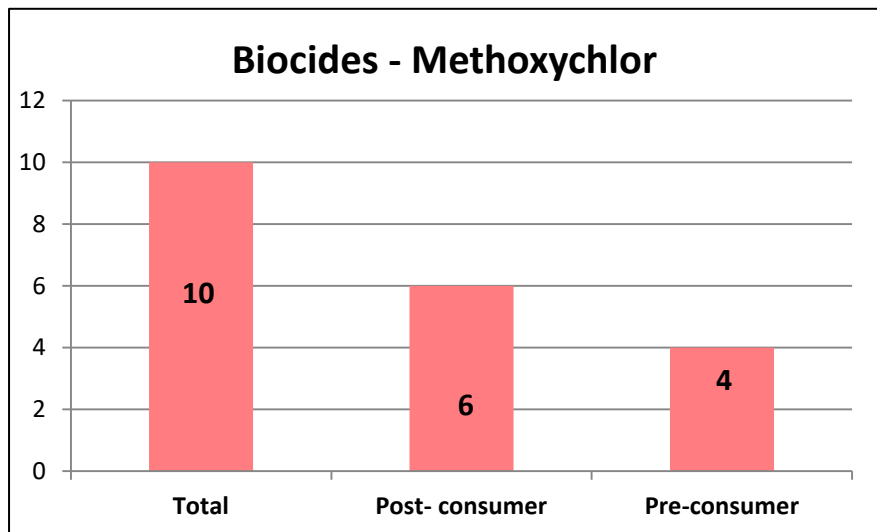


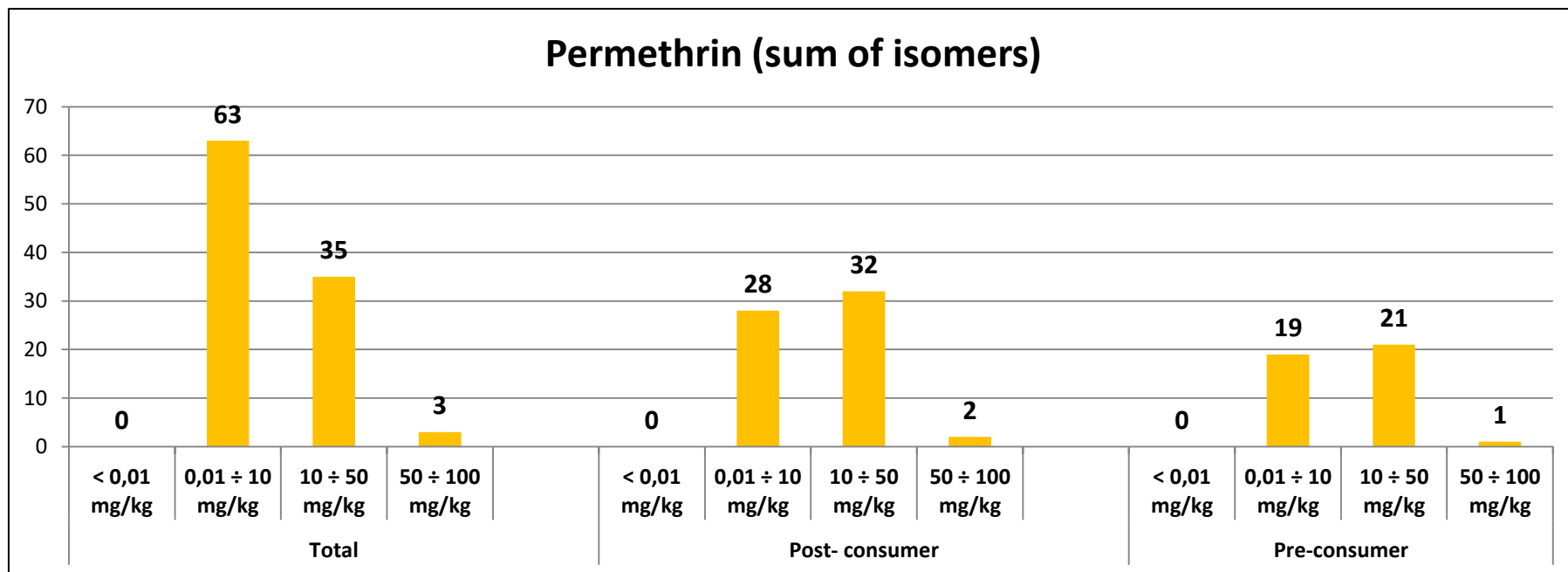
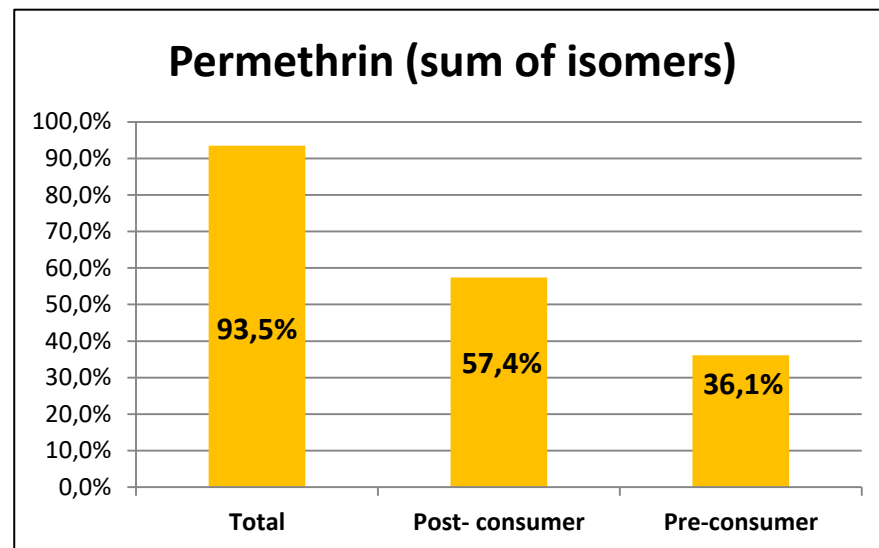
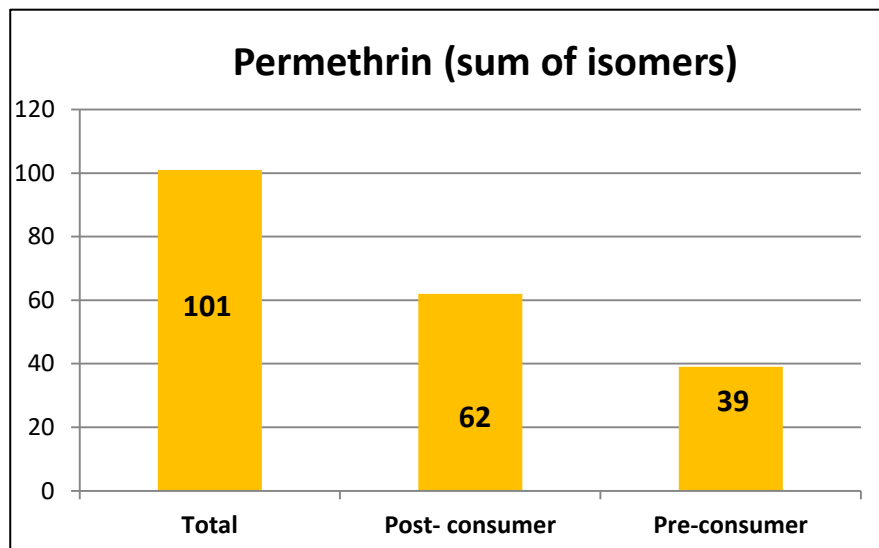








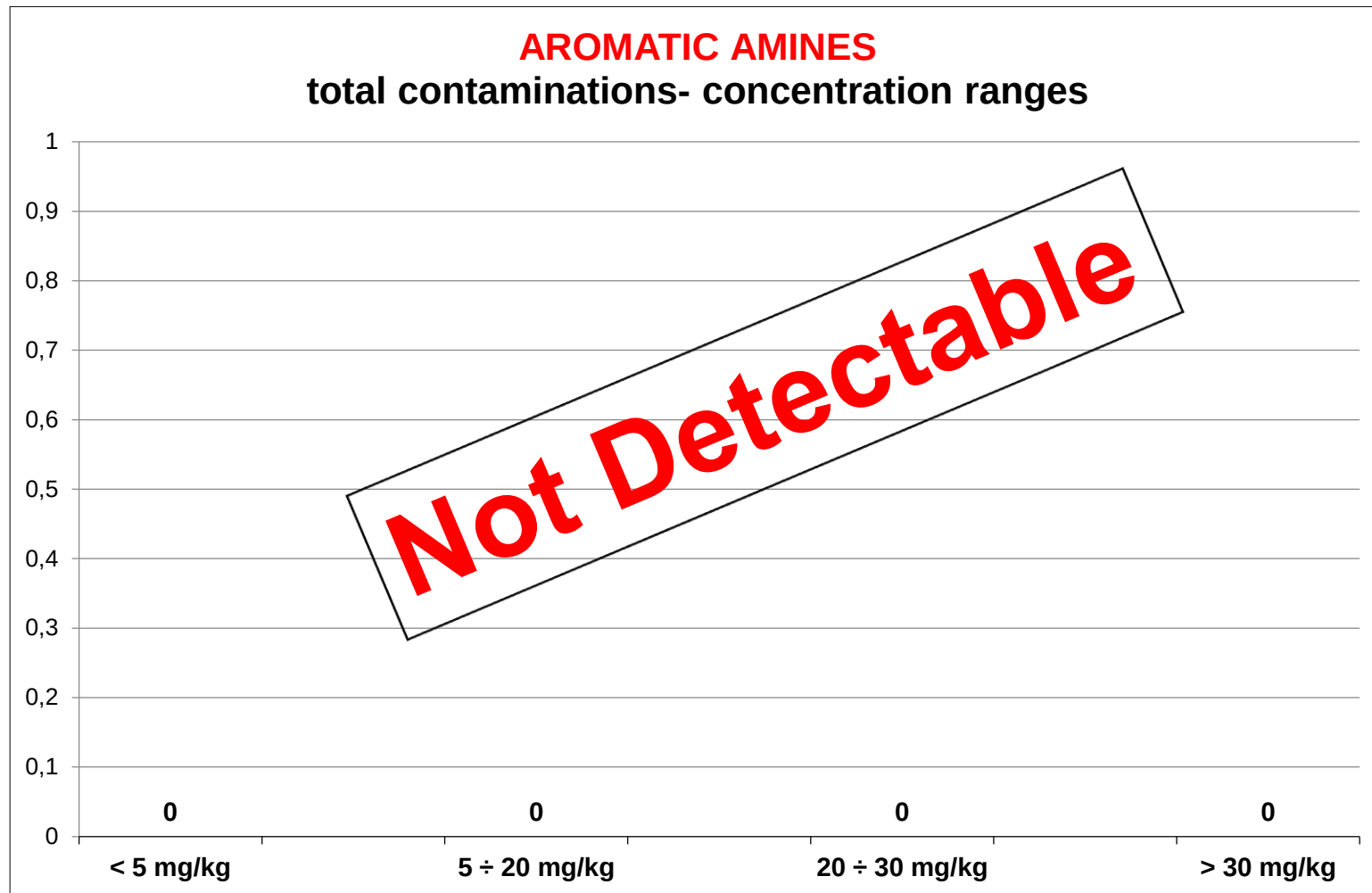


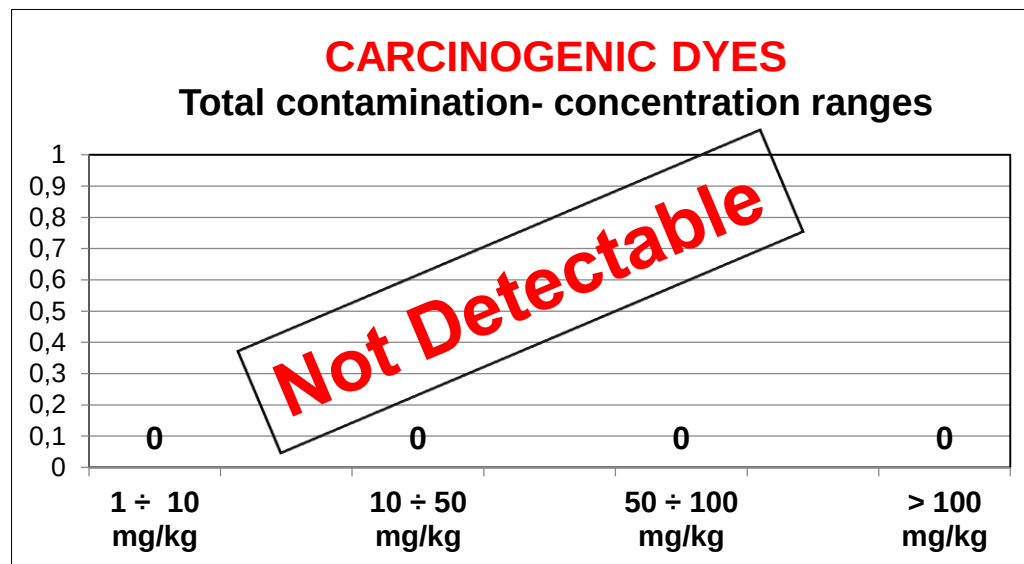
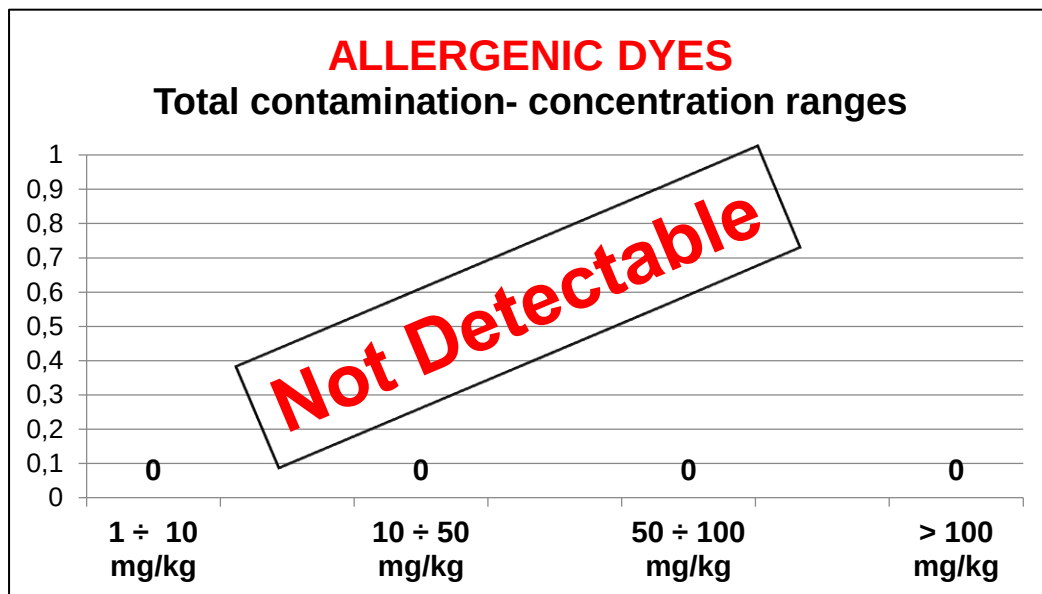


Regenerated Materials:

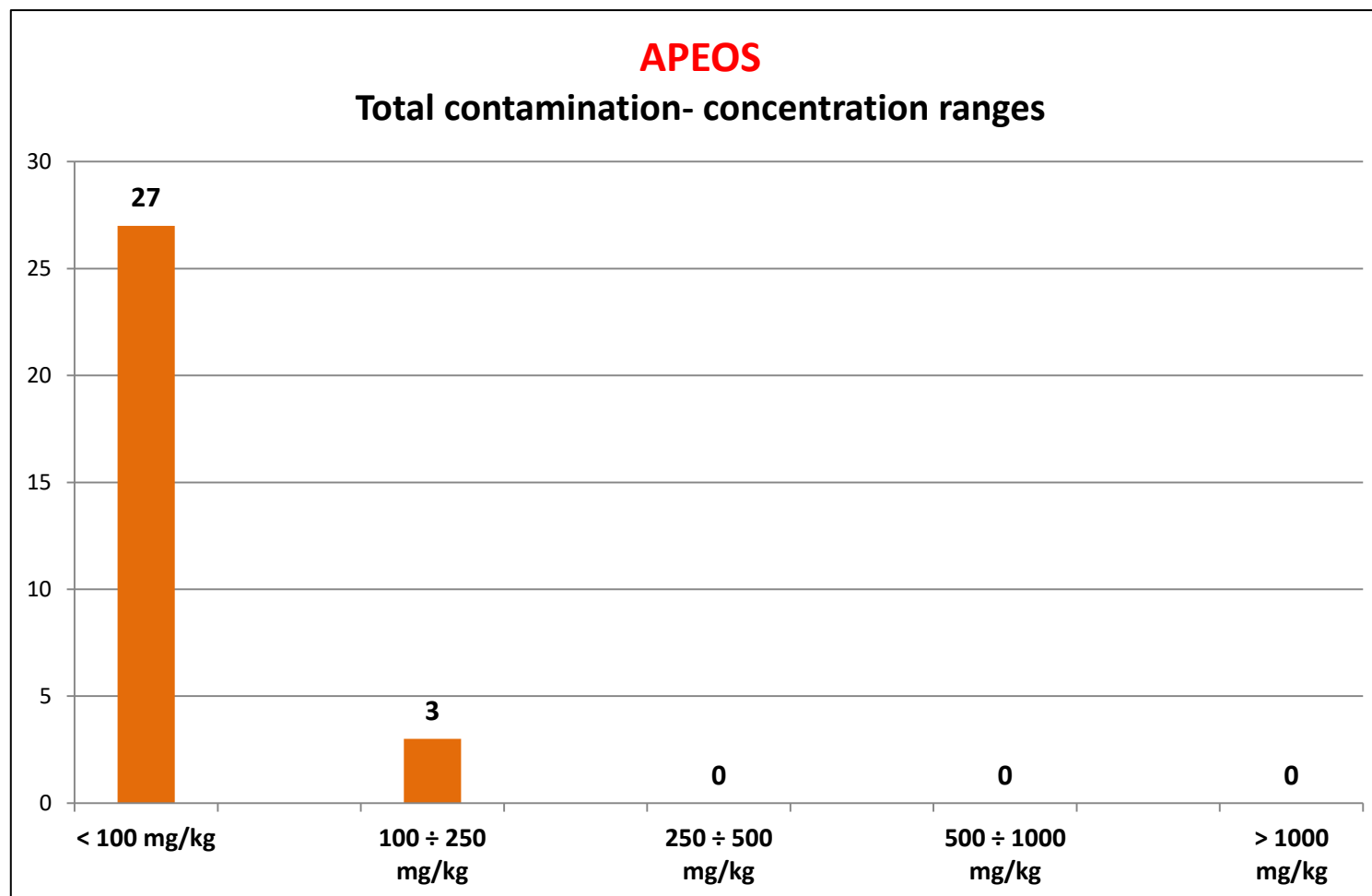
Cotton-Type textiles

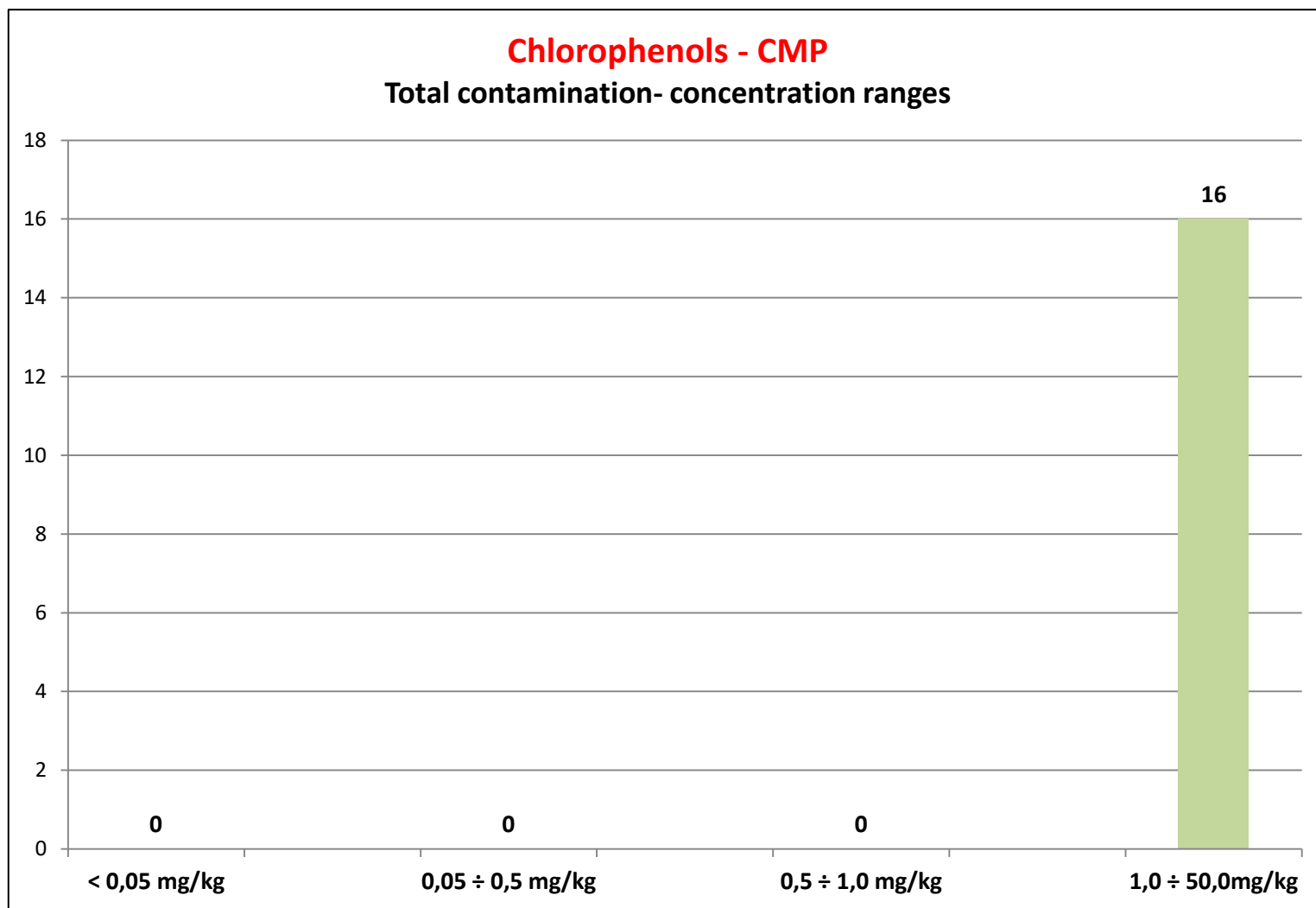
Regenerated cotton-type materials

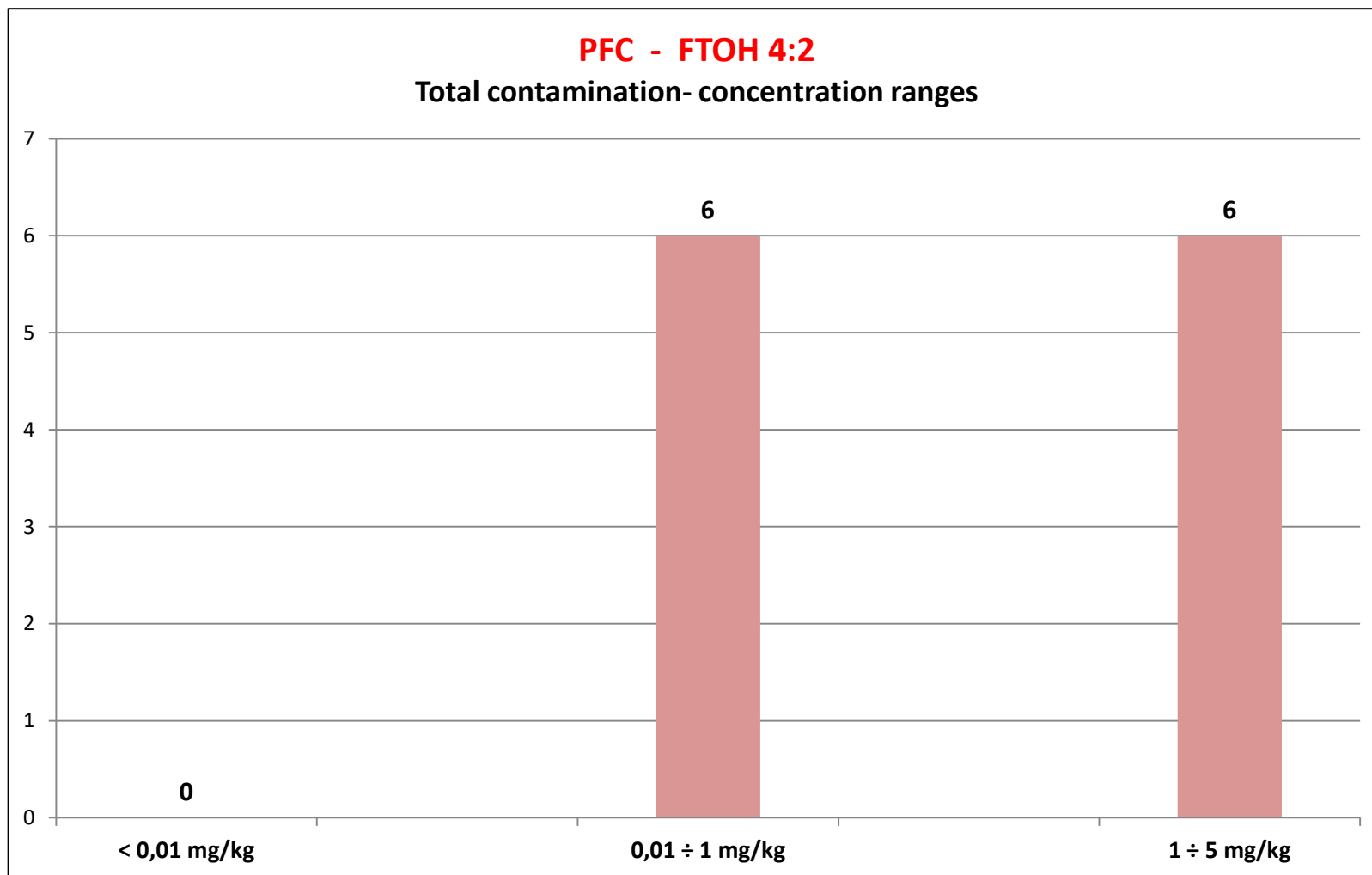


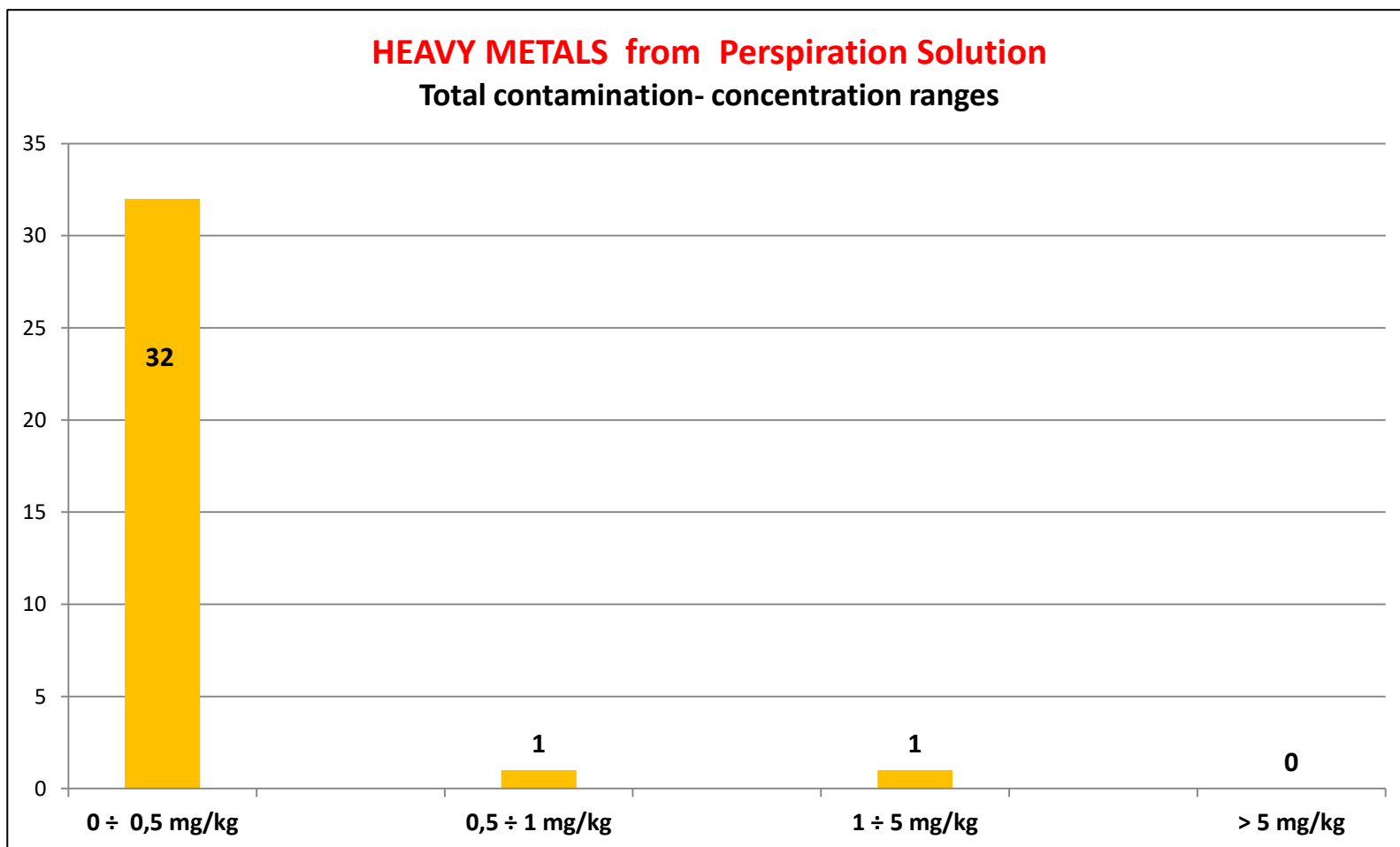


Regenerated cotton-type materials









MRS� proposal

for

Recycled Wool

raw materials

Parameter	CNMI – Guidelines 2016		DETOX	MRSL Proposal for Recycled Wool - Raw Material	% of lots PASS
	Proactive		Prato District Commitment		
	Baby (<36m)	Adult			
Aromatic amines from azo-colorants	≤ 20 mg/kg	≤ 20 mg/kg	≤ 1 mg/kg	≤ 20 mg/kg (each)	Pass 82%
Alkylphenols – (AP)	≤ 100 mg/kg	≤ 100 mg/kg	≤ 1 mg/kg	≤ 10 mg/kg (sum)	Pass 100%
Ethoxylated Alkylphenols – (APEOS)	≤ 100 mg/kg	≤ 100 mg/kg	≤ 1 mg/kg	≤ 500 mg/kg (sum) (until 2022/03)	Pass 41%
				≤ 250 mg/kg (sum) (until 2025/03)	Pass 26%
Chlorophenols	≤ 0,05 mg/kg	≤ 0,05 mg/kg	≤ 0,05 mg/kg	≤ 0,5 mg/kg - PCP, TeCP (each) ≤ 1,0mg/kg-MoCP,DiCP,TriCP (each)	Pass 86%
Perfluorinated Compounds - (PFC)	≤ 1 µg/m²	≤ 1 µg/m²	≤ 1 µg/m²	PFOS ≤ 1 µg/m² (= ca 4 µg/kg)	Pass 99%
	Telomers (FTOH): ≤ 10 µg/m²	Telomers (FTOH): ≤ 10 µg/m²	Telomers (FTOH): ≤ 10 µg/m²	PFOA - PFC (acid)≤10 µg/m² (sum) PFOA ≤25 µg/kg (2020/07/04)	Pass 65%
				Telomers (FTOH): ≤ 100 µg/m² (sum) (= ca 400 µg/kg)	Pass 53%
Allergenic Dyes	≤ 50 mg/kg	≤ 50 mg/kg	≤ 5 mg/kg	≤ 50 mg/kg (each) (until 2022/03)	Pass 95%
Carcinogenic Dyes	≤ 5 mg/kg	≤ 5 mg/kg	≤ 5 mg/kg	≤ 50 mg/kg (each) (until 2022/03)	Pass 100%

Parameter	CNMI – Guidelines 2016		DETOX	MRSL Proposal for Recycled Wool - Raw Material	% of lots PASS
	Proactive		Prato District Commitment		
	Baby (<36m)	Adult			
Formaldehyde	≤ 16 mg/kg	≤ 75 mg/kg	≤ 16 mg/kg	≤ 75 mg/kg	Pass 93%
Flame Retardant	≤ 5 mg/kg	≤ 5 mg/kg	≤ 5 mg/kg	≤ 5 mg/kg	Pass 100%
Chlorobenzenes and Chlorotoluenes	≤ 1 mg/kg	≤ 1 mg/kg	≤ 0,5 mg/kg	≤ 1 mg/kg	Pass 100%
Chlorinated paraffins (SCCP)	≤ 50 mg/kg	≤ 50 mg/kg	≤ 1 mg/kg	≤ 10 mg/kg	Pass 100%
Phthalates (BBP, DEHP, DIBP, DBP, DINP)	≤ 50 mg/kg	≤ 50 mg/kg	≤ 10 mg/kg	≤ 50 mg/kg (each)	Pass 100%
Phthalates (others)	≤ 500 mg/kg	≤ 500 mg/kg	≤ 5 mg/kg (≤ 10 DINP)	≤ 50 mg/kg (each)	Pass 100%
Organotin compound	≤ 0,5 mg/kg	≤ 1 mg/kg	≤ 1 mg/kg	≤ 1 mg/kg (each)	Pass 100%
Chlorinated solvents (TetraChloroEthylene)	≤ 500 mg/kg TCE: Not Req	≤ 500 mg/kg TCE: Not Req	≤ 0,5 mg/kg TCE:10 mg/kg	≤ 10 mg/kg (sum) Terachloroethylene: ≤ 200 mg/kg	Pass 97%
Biocides	≤ 20 mg/kg	≤ 20 mg/kg	≤ 1 mg/kg	≤ 5 mg/kg (each)	Pass 100%
Permethrin (case study)	//	//	//	≤ 50 mg/kg (sum)	Pass 97%

MRSL PROPOSAL - Heavy metals

Heavy Metal (from acid perspiration)		CNMI – Guidelines 2016		DETOX	MRSL Proposal for Recycled Wool - Raw Material	% of lots PASS
		Proactive		Prato District Commitment		
		Baby (<36m)	Adult			
Antimony		≤ 30 mg/kg	≤ 30 mg/kg	//	≤ 30 mg/kg	Pass 100%
Arsenic		≤ 0,2 mg/kg	≤ 1 mg/kg	//	≤ 1 mg/kg	Pass 100%
Cadmium		≤ 0,1 mg/kg	≤ 0,1 mg/kg	//	≤ 0,1 mg/kg	Pass 100%
Cobalt		≤ 1 mg/kg	≤ 4 mg/kg	//	≤ 4 mg/kg	Pass 100%
Chromium	(hexavalent)	≤ 0,5 mg/kg	≤ 0,5 mg/kg	//	≤ 0,5 mg/kg	Pass 100%
	(total)	≤ 1 mg/kg	≤ 2 mg/kg	≤ 1 mg/kg	≤ 2 mg/kg	Pass 90%
Copper		≤ 25 mg/kg	≤ 50 mg/kg	//	≤ 50 mg/kg	Pass 100%
Lead		≤ 0,2 mg/kg	≤ 1 mg/kg	//	≤ 1 mg/kg	Pass 100%
Nickel		≤ 1 mg/kg	≤ 4 mg/kg	//	≤ 4 mg/kg	Pass 100%
Mercury		≤ 0,02 mg/kg	≤ 0,02 mg/kg	//	≤ 0,02 mg/kg	Pass 100%

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