Recycled wool raw materials:

Focus on parameters for chemical safety assessment and PRSL Proposal

Bartolini Giuseppe, Franchi Andrea, Dall'Anese Riccardo, Zanobetti Stefano
(BuzziLab – Prato)

➢ **<u>Recycled textile material – woollen type</u>:**

- **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)**

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➢ 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»***

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➢ 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»***

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➢ 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)**

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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».

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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**

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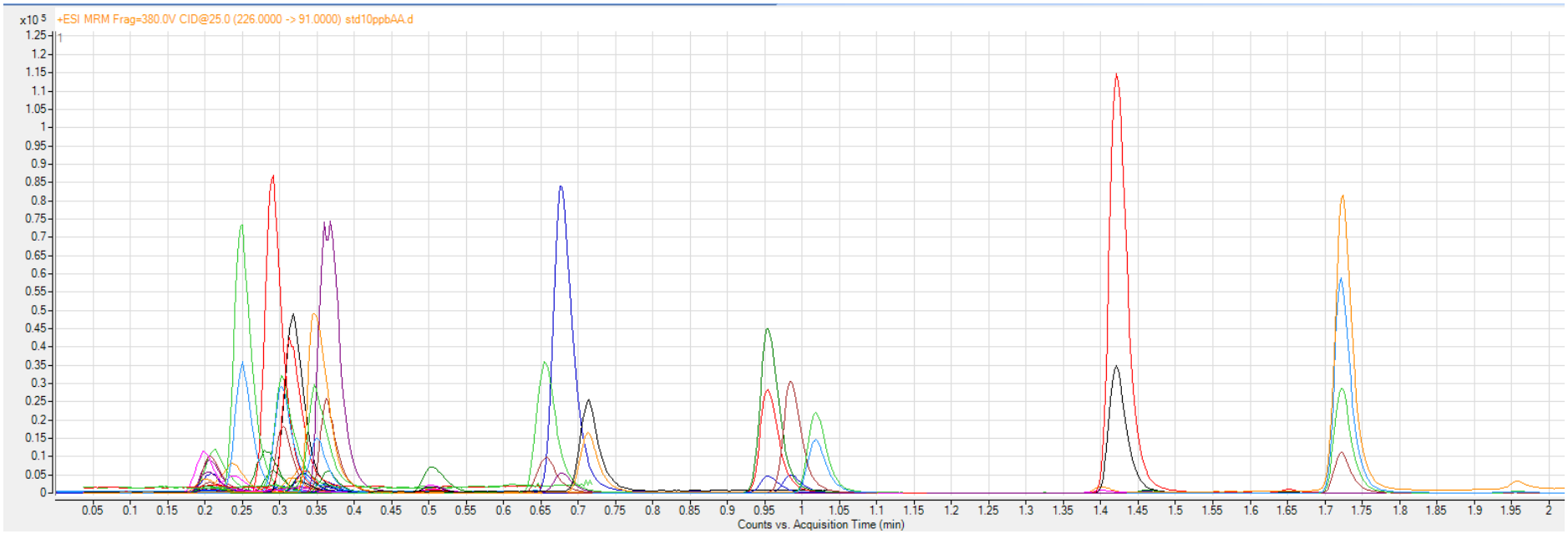
Aromatic Amines derived from azo-colorants

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



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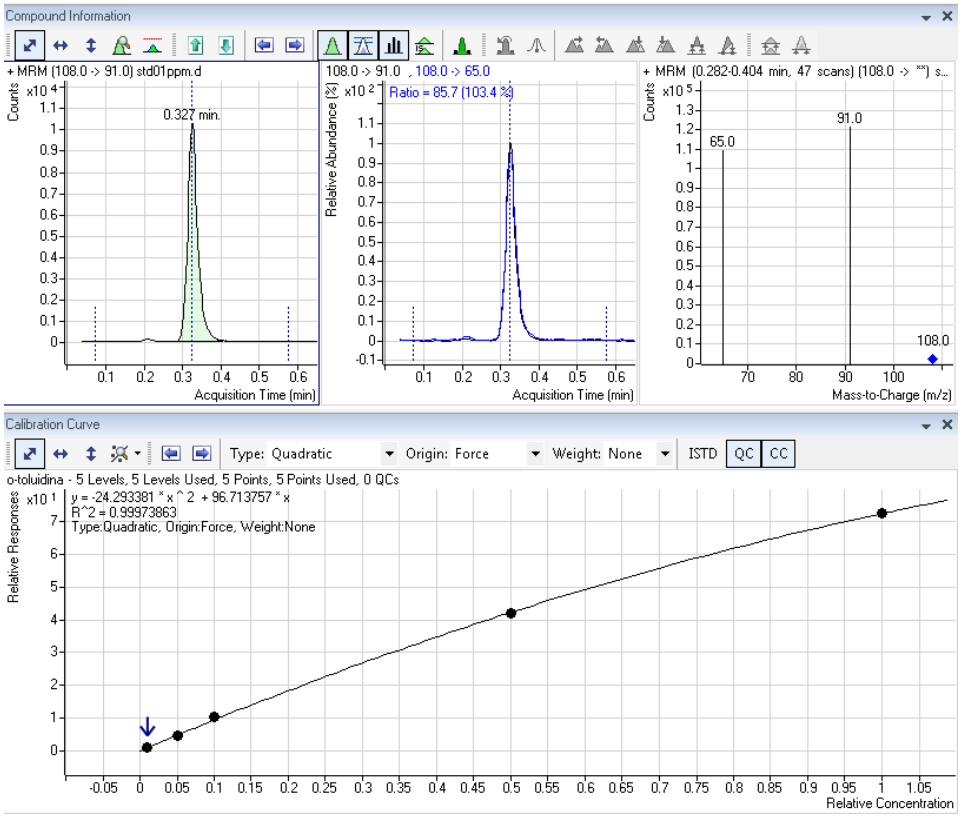
Analytical Procedure

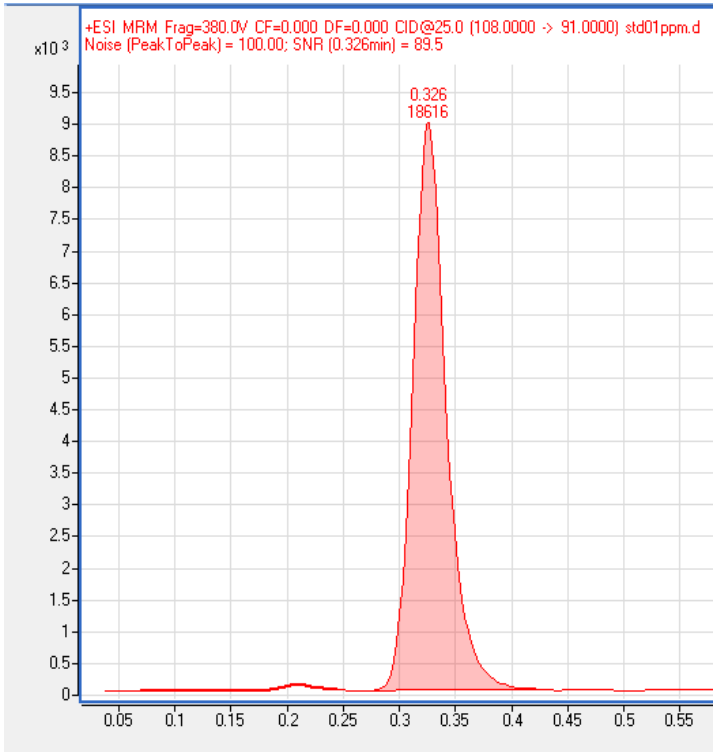
Aromatic Amines derived from azo-colorants

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

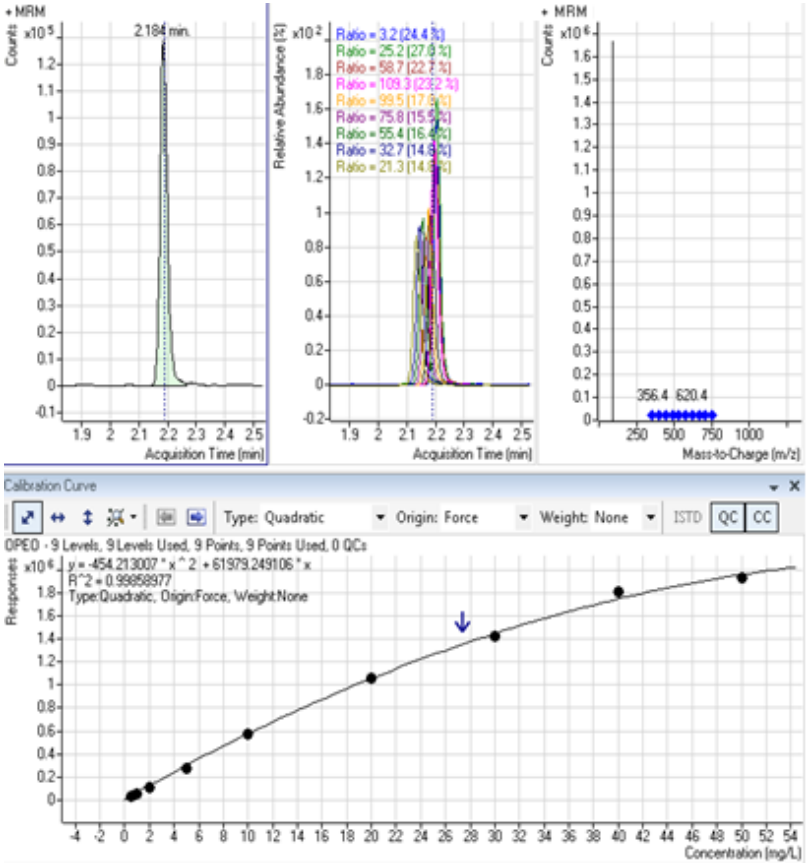


Analytical Procedure

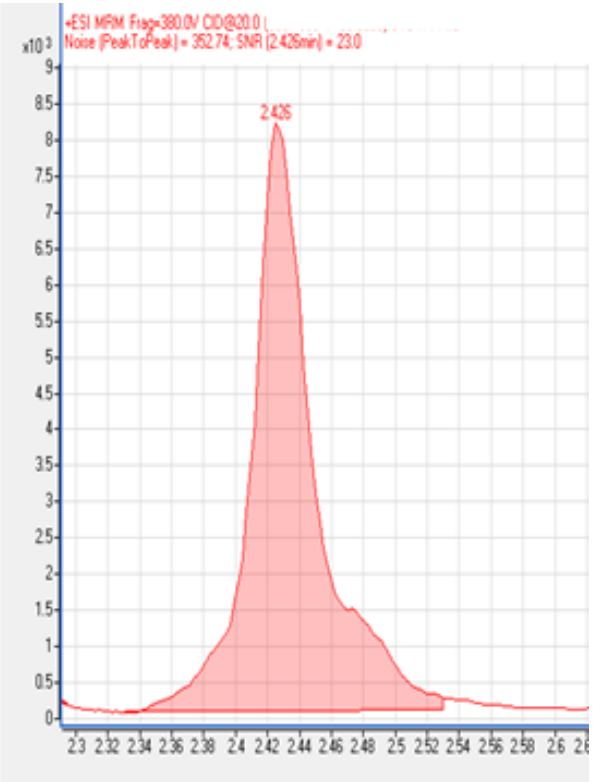
Ethoxylated Alkylphenols (APEOS)

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

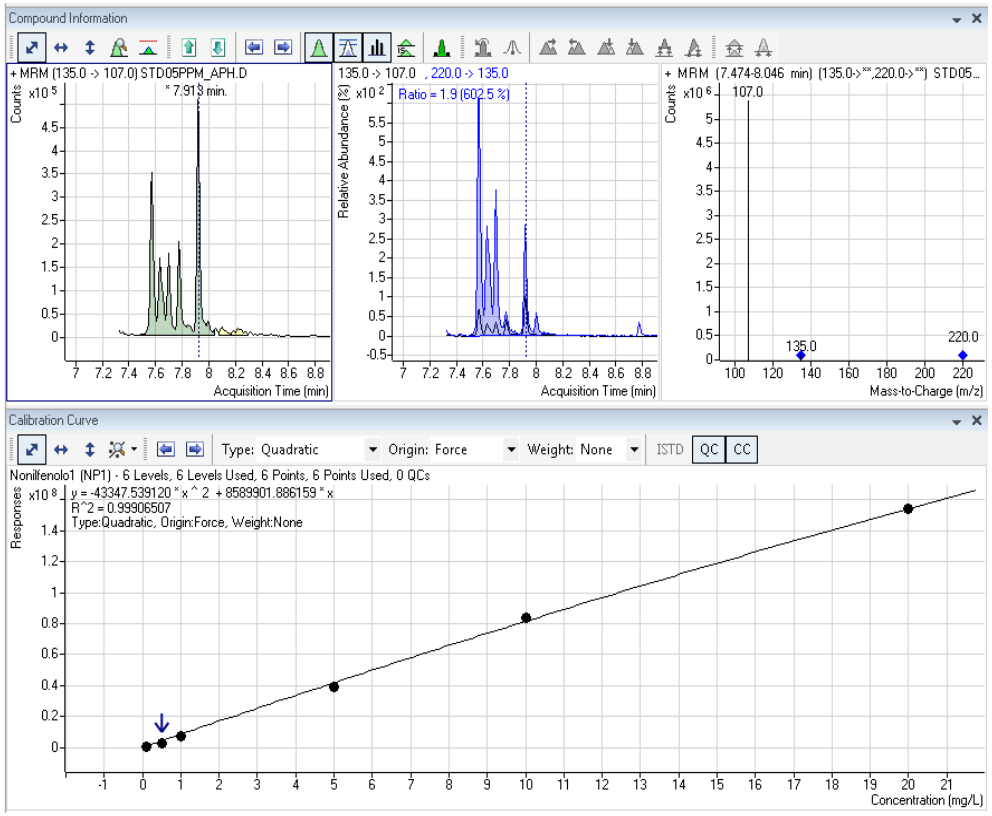


Analytical Procedure

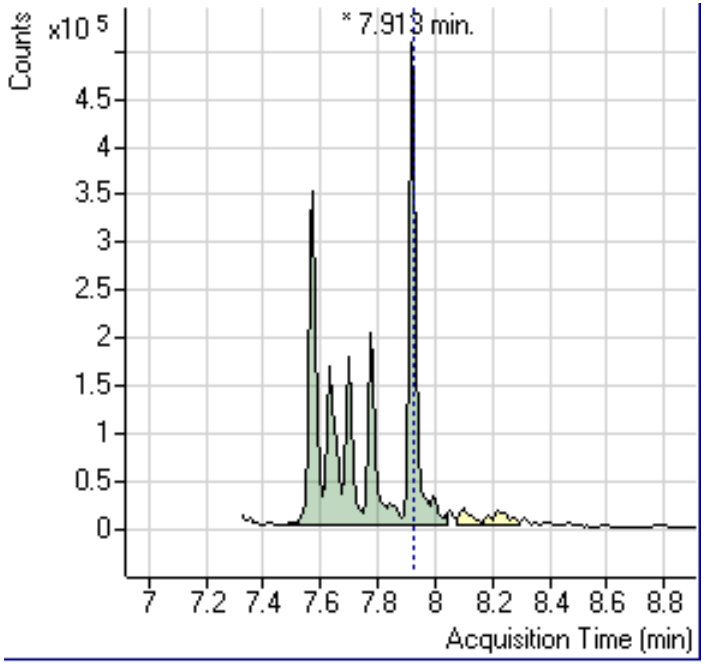
Alkylphenols - AP

In-house test method MIP_CE0124:2018 **Ref ISO 18857-1**	**Technique: GC-MS/MS**	**LOD: 1 mg/kg**

eg. Calibration Curve for NP



NP– quantitative analysis at 1 mg/kg



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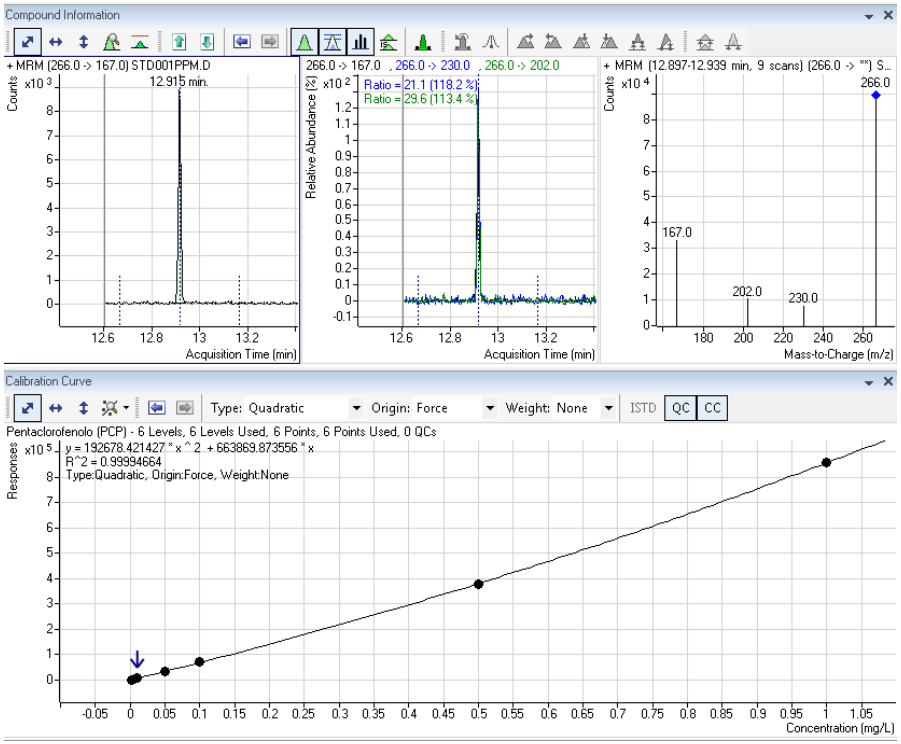
Analytical Procedure

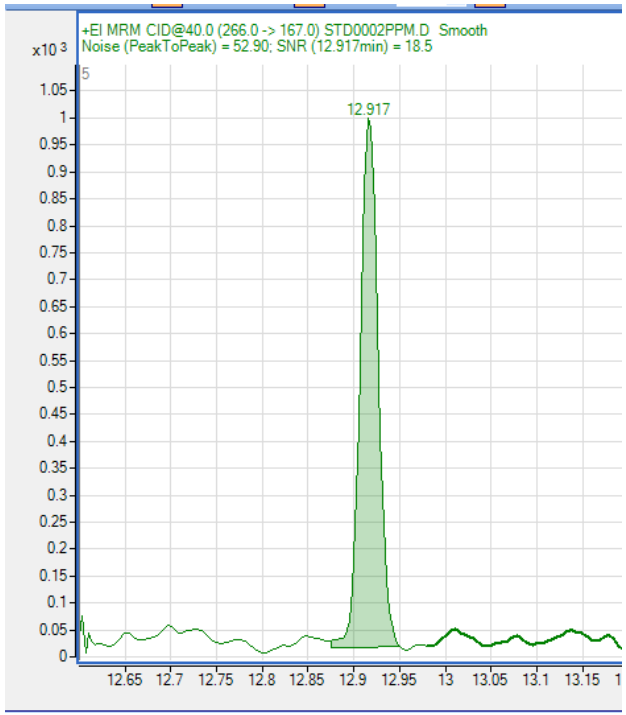
Chlorophenols

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

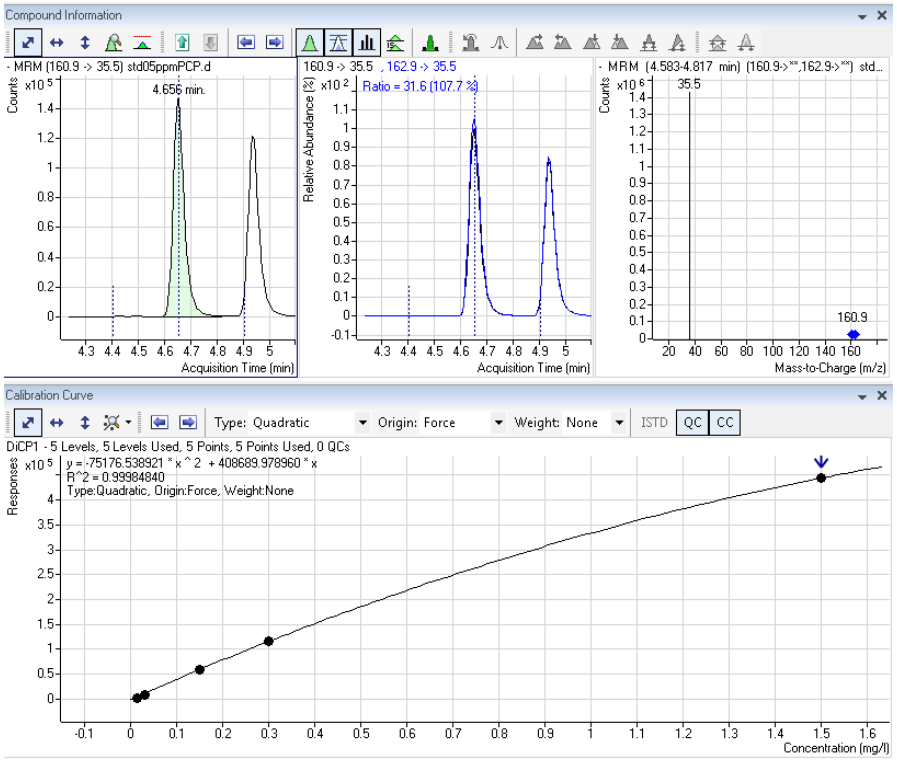


Analytical Procedure

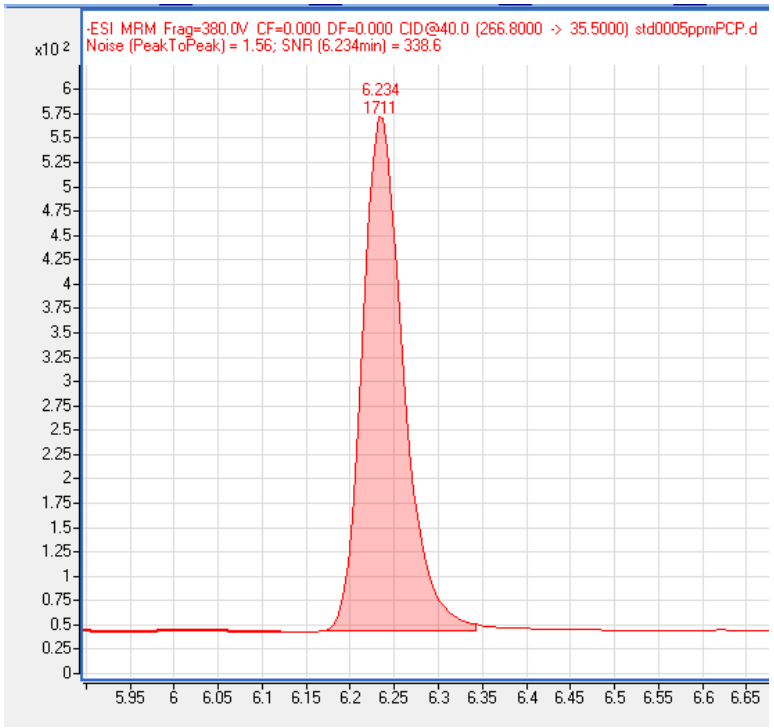
Chlorophenols

In-house Test Method **Textiles: Determination chlorophenols**	**Technique: LC-MS/MS**	**LOD: 0,025 mg/kg**

Eg. Calibration curve for 2,4-Dichlorophenol



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

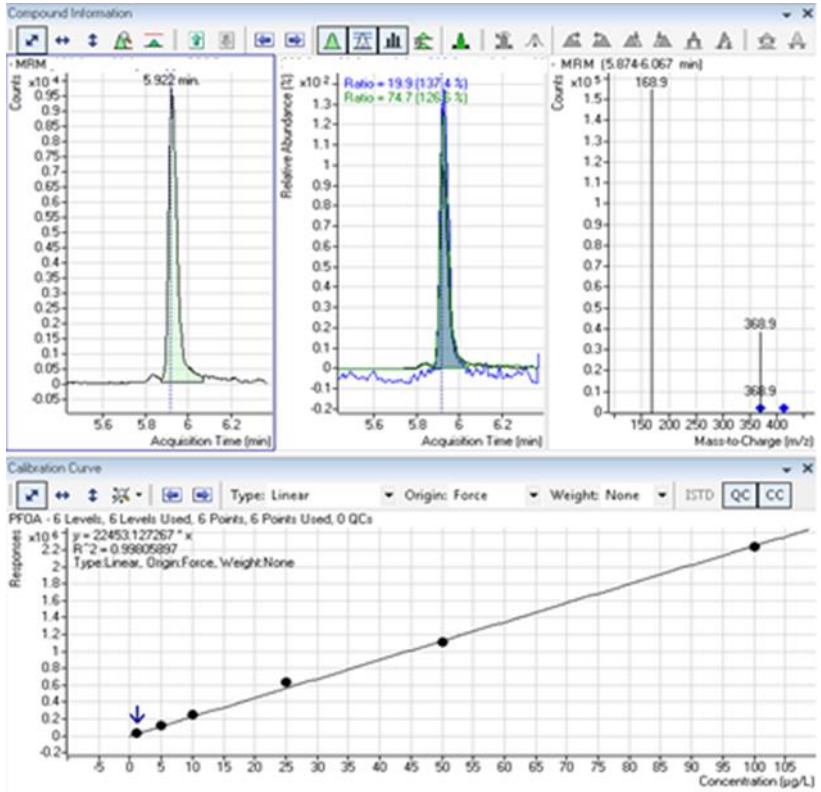


Analytical Procedure

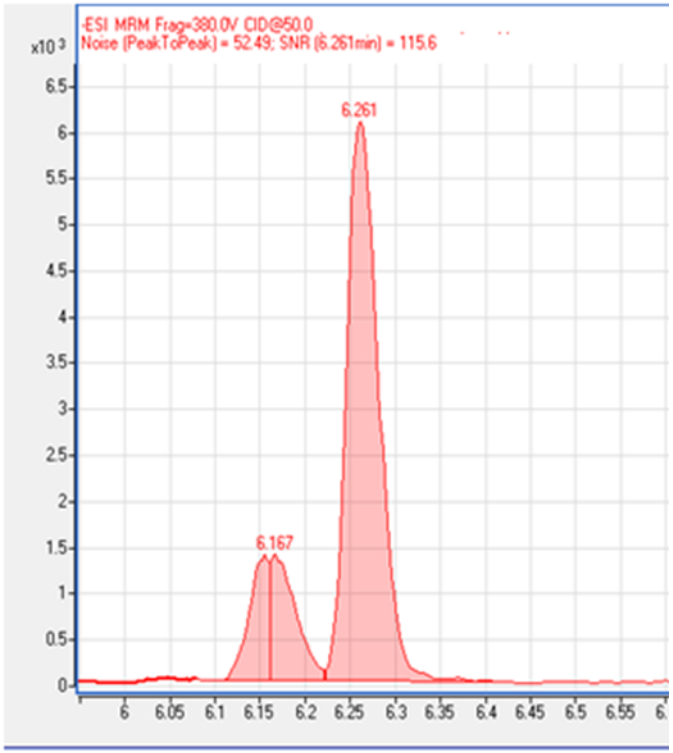
PFOS/PFOA and other Perfluorinate Compounds (PFC)

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**

Eg. Calibration curve for PFOA



PFOS – quantitative analysis at 1 µg/m2



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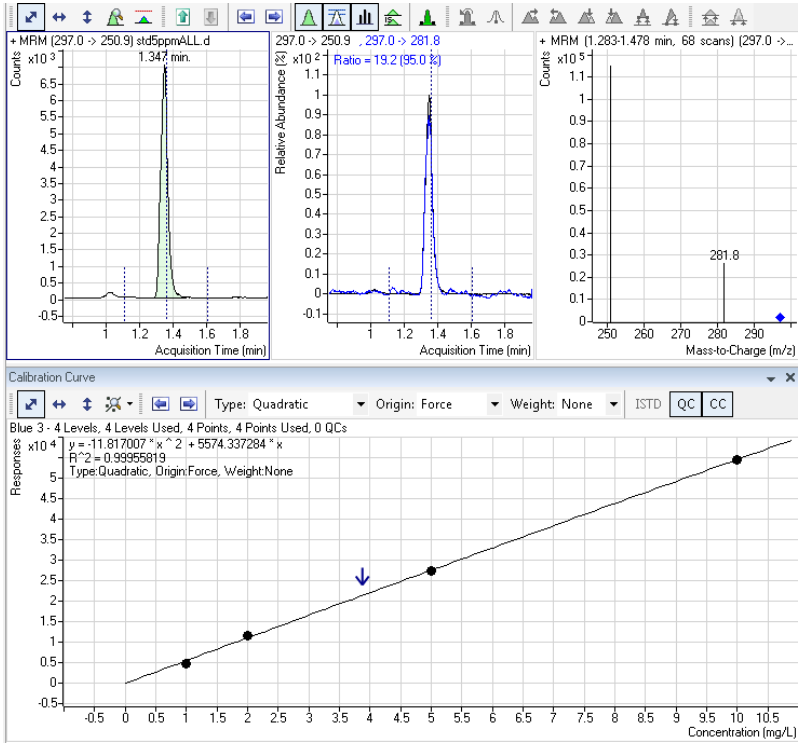
Analytical Procedure

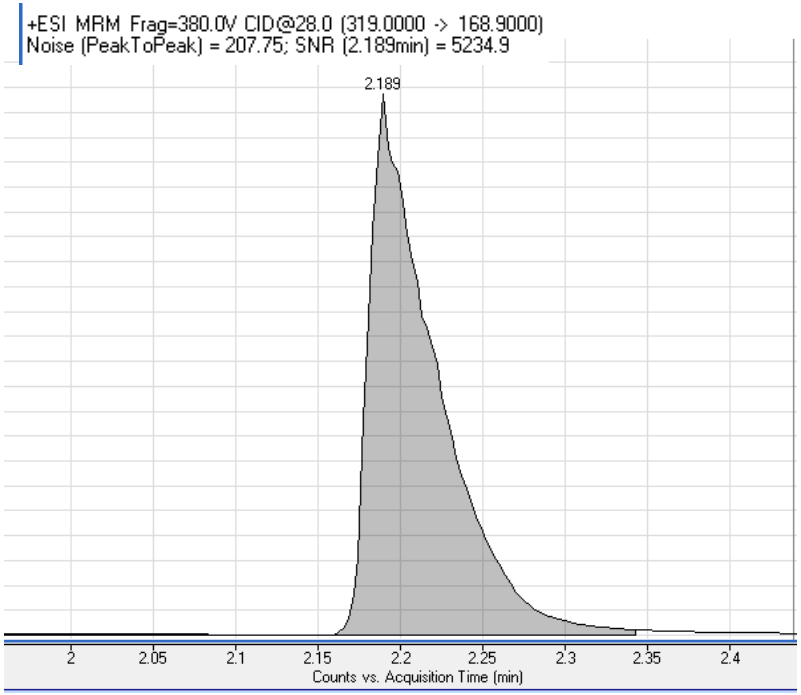
DISPERSE and CARCINOGENIC Dyes

DIN 54231-2005(11) **ISO 16373-2:2014** **ISO 16373-3:2014**	**Technique: LC-MS/MS**	**LOD: 1mg/kg**

Eg. Calibraton curve for DISPERSE BLUE 3



DISPERSE BLUE 3 – quantitative analysis at 1 mg/kg



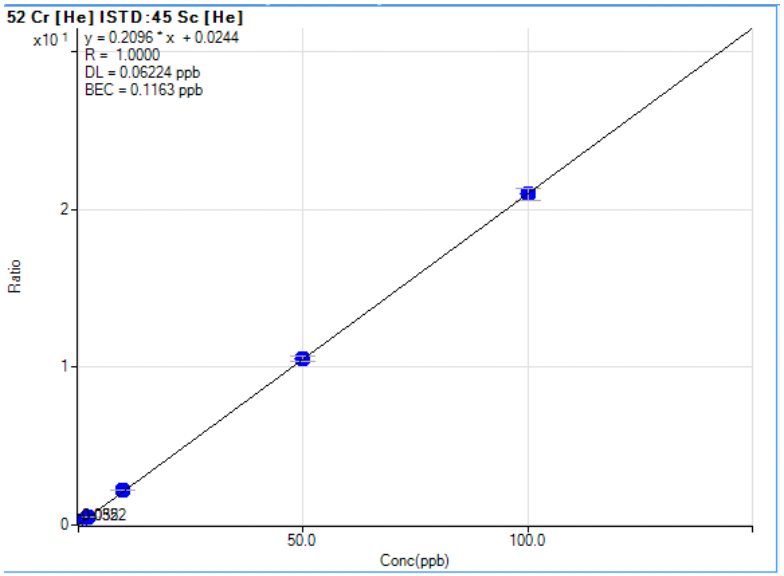
Analytical Procedure

HEAVY METALS from perspiration solution

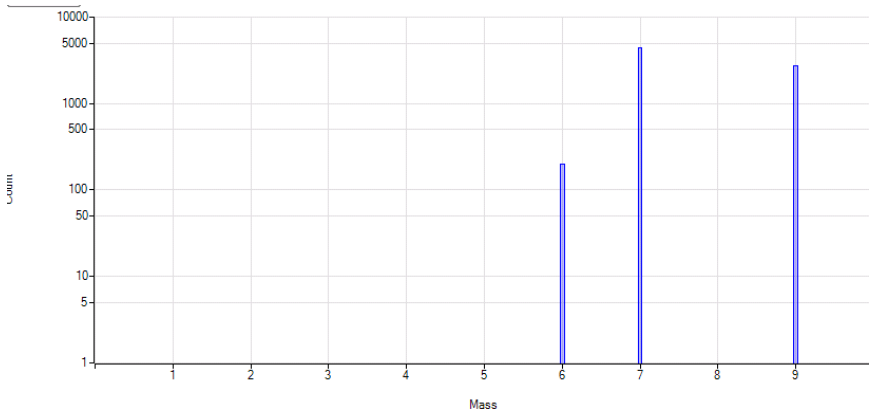
GB/T 17593-2 **EN 16711-2:2015 (DIN 54233-3)** **ISO 17072-1:2011**	**Technique: ICP-MS** **(all metals except Cr (VI)**	**LOD: 0,1mg/kg**

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



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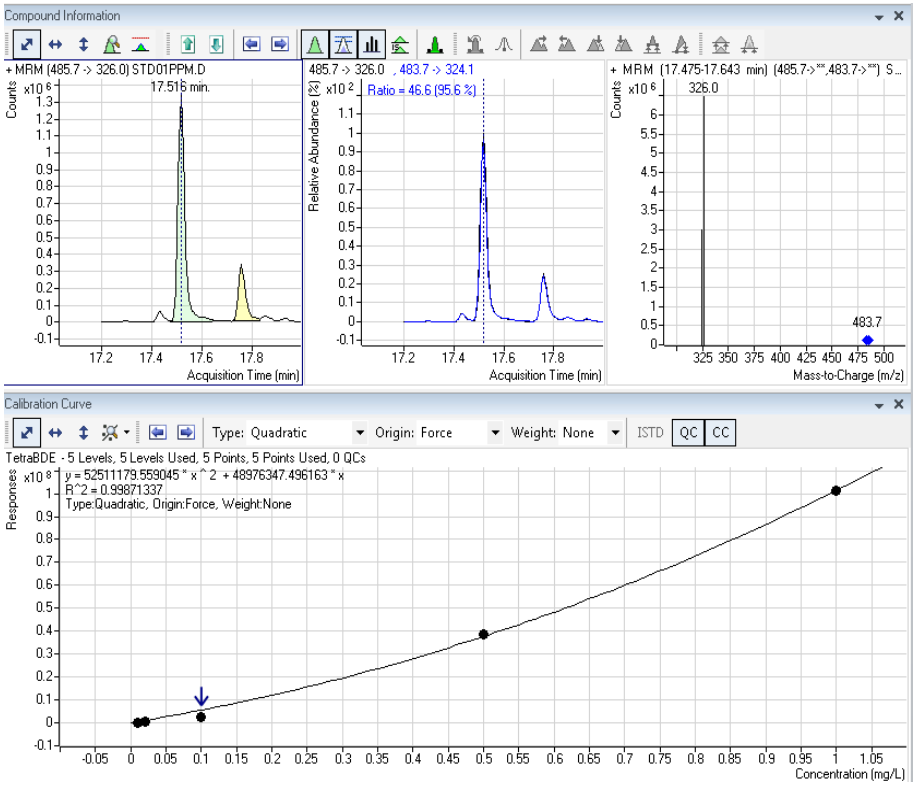
Analytical Procedure

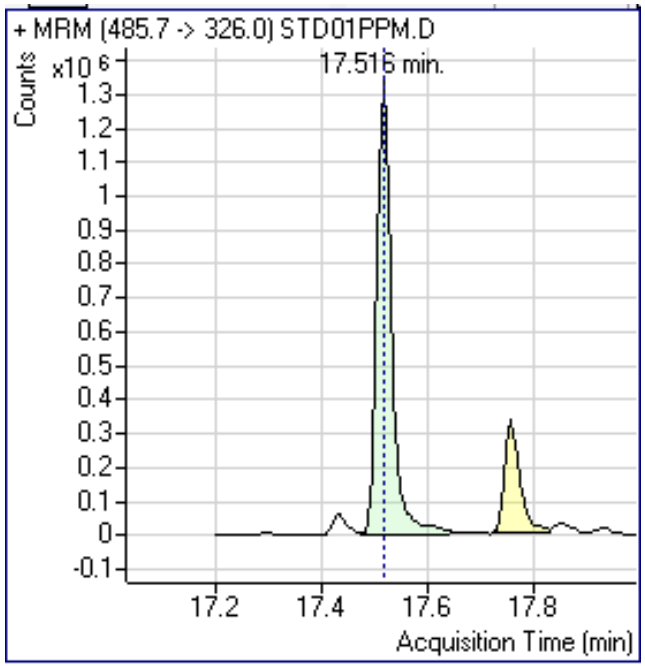
Flame retardant

GB/T 24279-2009 **ISO 17881:2016**	**Technique:** **GC-MS/MS - LC-MSMS**	**LOD: 0,01 mg/kg**

Eg. Calibration curve for Tetra-DBE



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

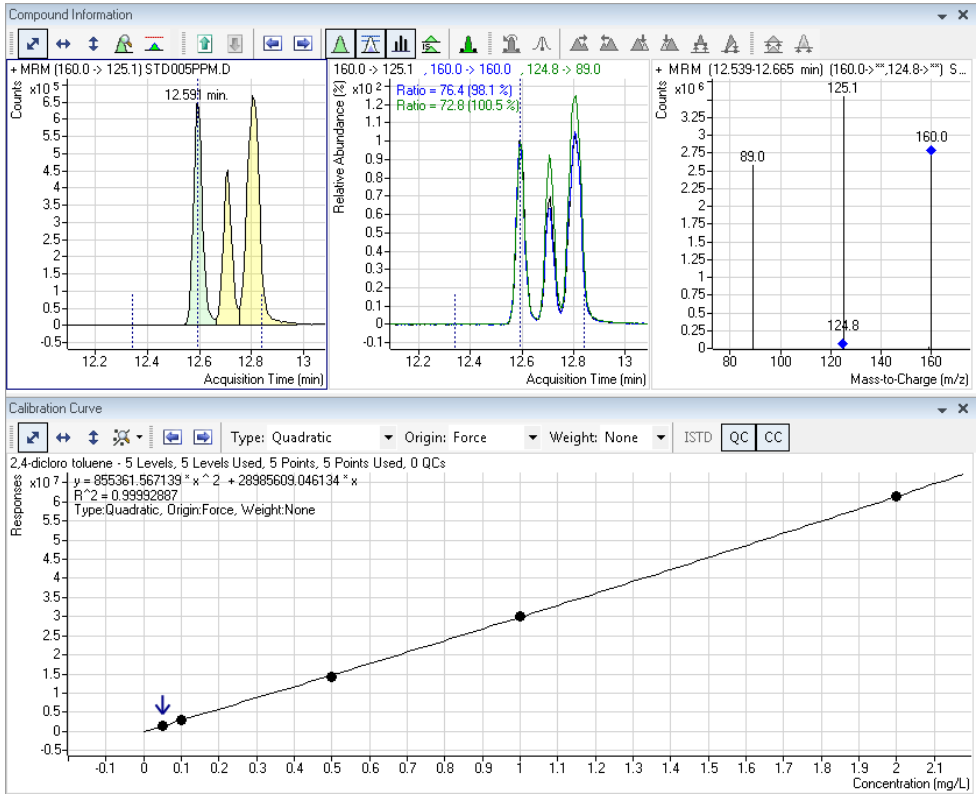


Analytical Procedure

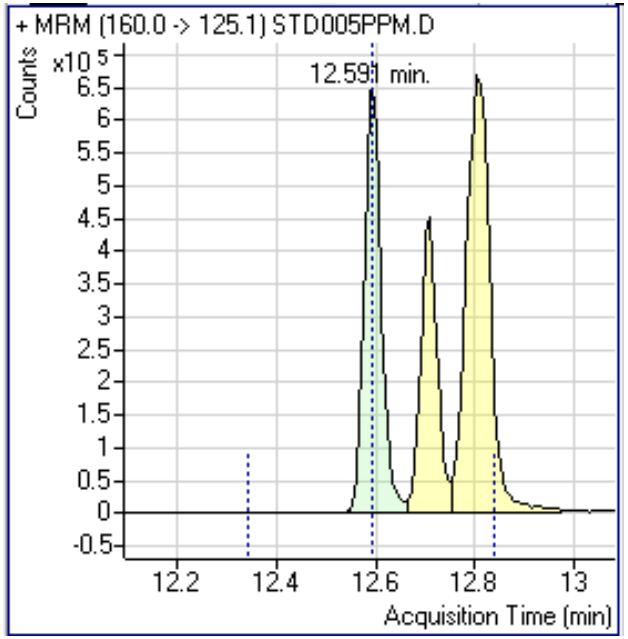
Chlorobenzenes and toluenes

DIN 54232:2010	**Technique:** **GC-MS/MS**	**LOD: 0,05 mg/kg**

Eg. Calibration curve for 2,4-dichlorotoluene



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

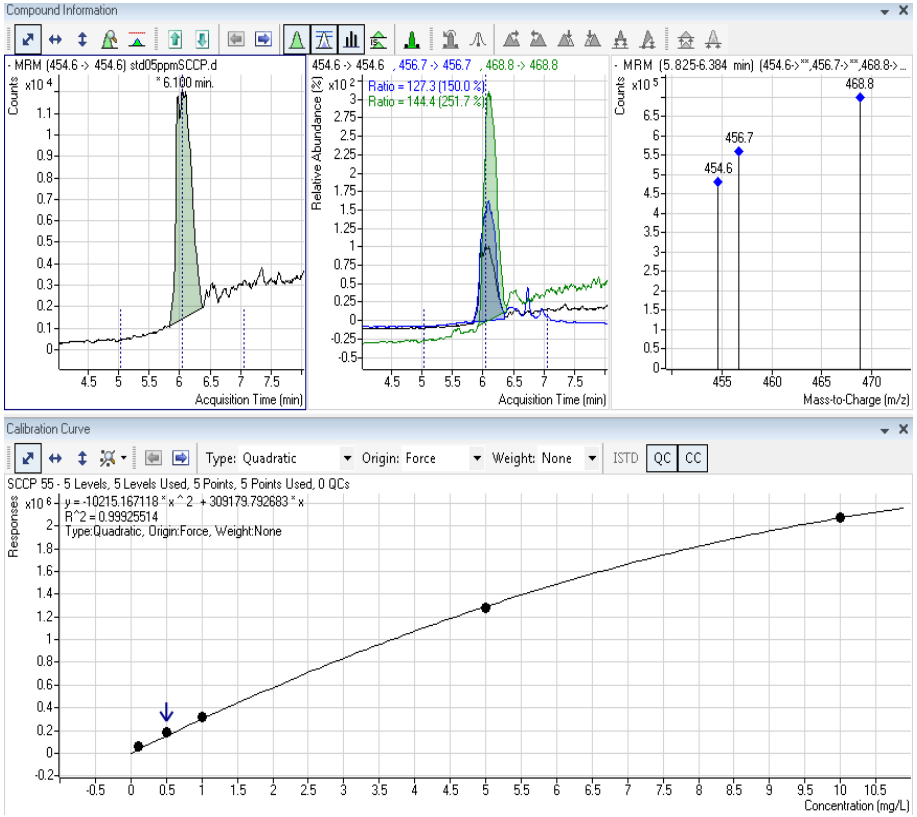


Analytical Procedure

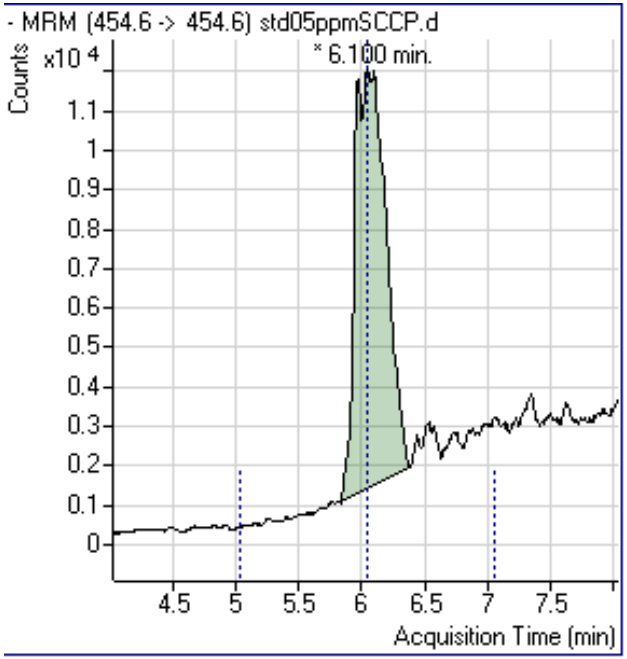
Chlorinated paraffins (SCCP)

ISO 18219:2015	**Technique: LC-MS/MS**	**LOD: 0,5 mg/kg**

Eg. Calibration curve for SCCP



SCCP – quantitative analysis at 1 mg/kg

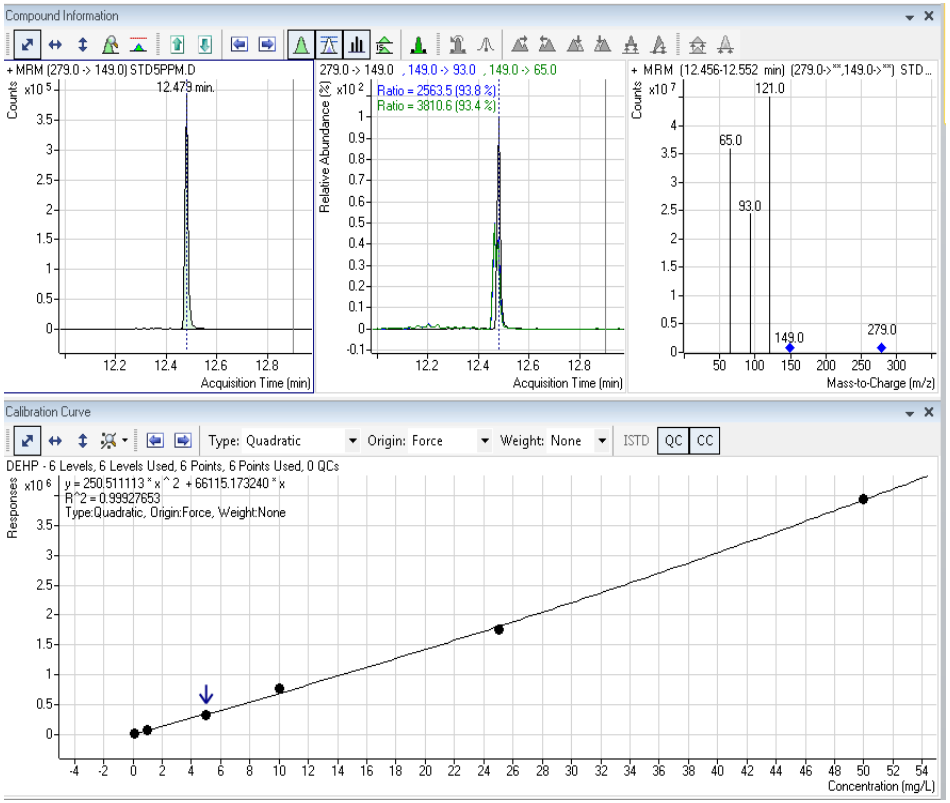


Analytical Procedure

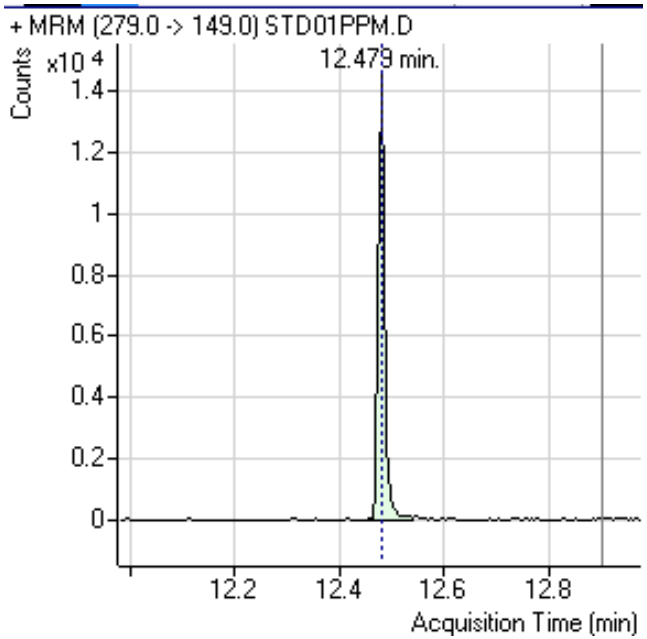
Phthalates

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**

Eg. Calibration curve for DEHP



DEHP– quantitative analysis at 1 mg/kg

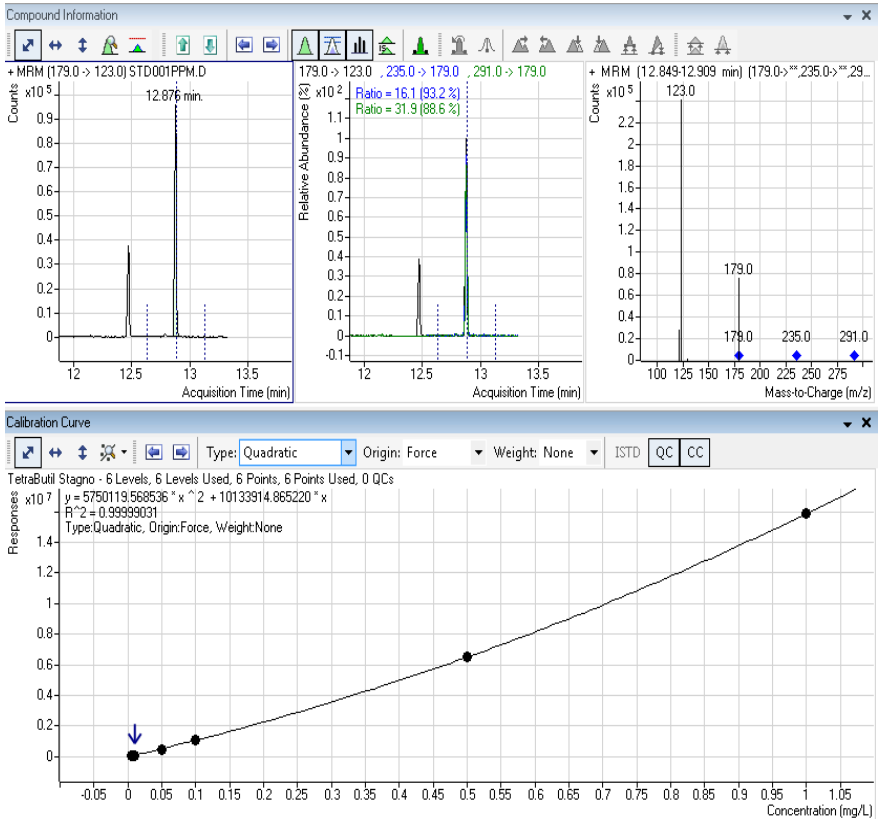


Analytical Procedure

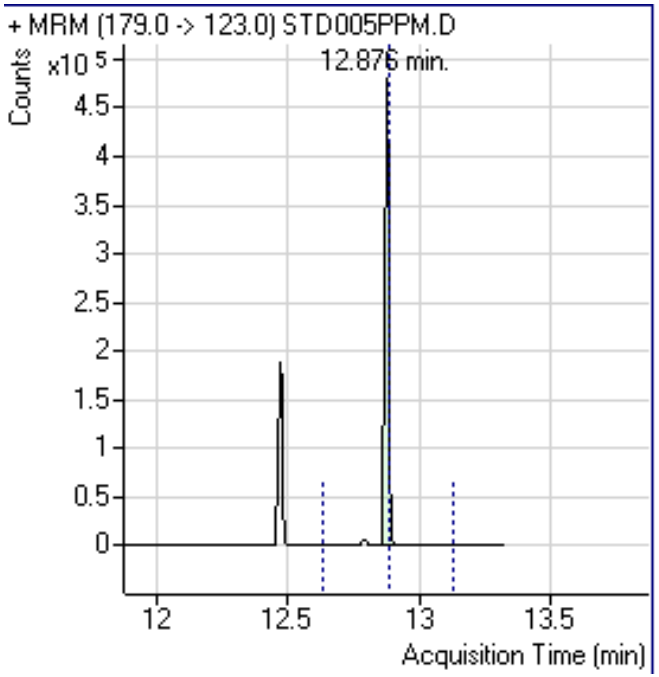
Organotin compounds

ISO/TS 16179:2012	**Technique: GC-MS/MS**	**LOD: 0,01 mg/kg**

Eg. Calibration curve for Tributyl tin (TBT)



TBT – quantitative analysis at 0,1 mg/kg

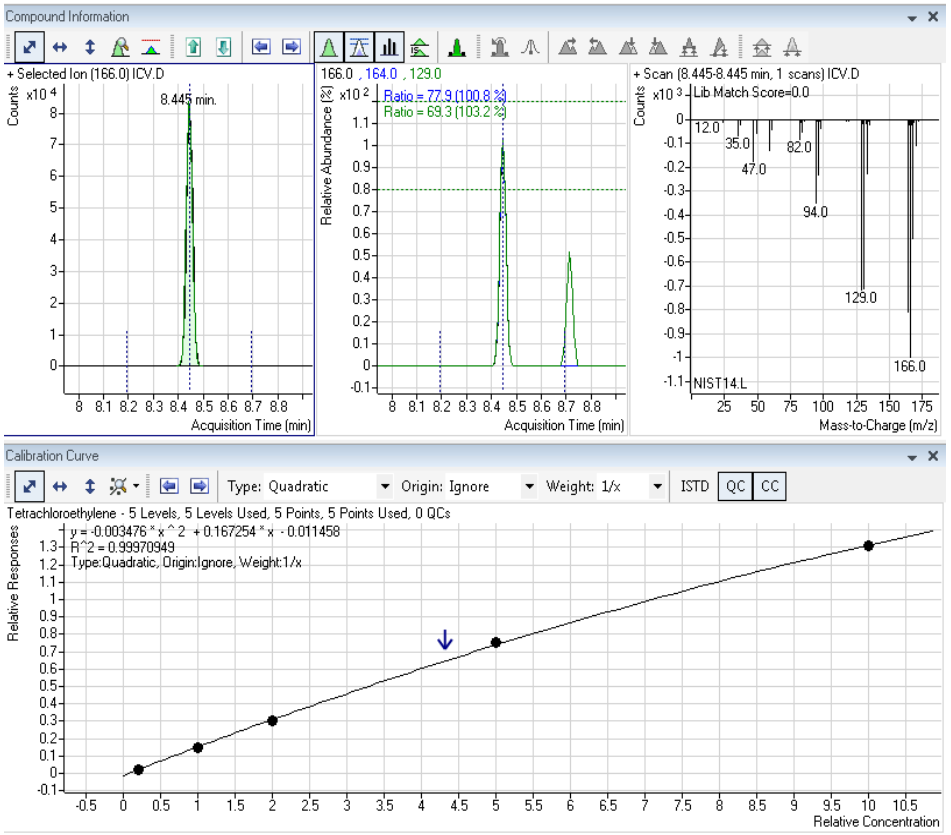


Analytical Procedure

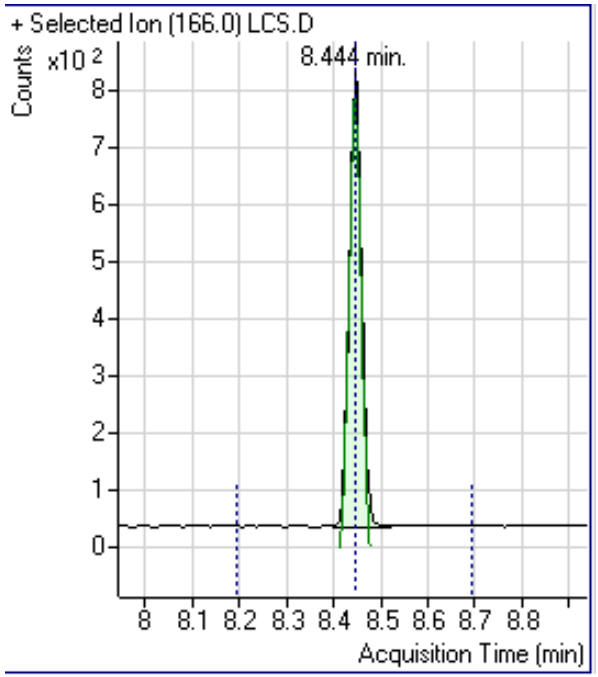
Chlorinated solvents

EPA 5021A + EPA 8260D	**Technique: GC-MS/MS**	**LOD: 0,01 mg/kg**

Eg. Calibration curve for Tetrachloroethylene



Tetrachloroethylene – quantitative analysis at 0,1 mg/kg

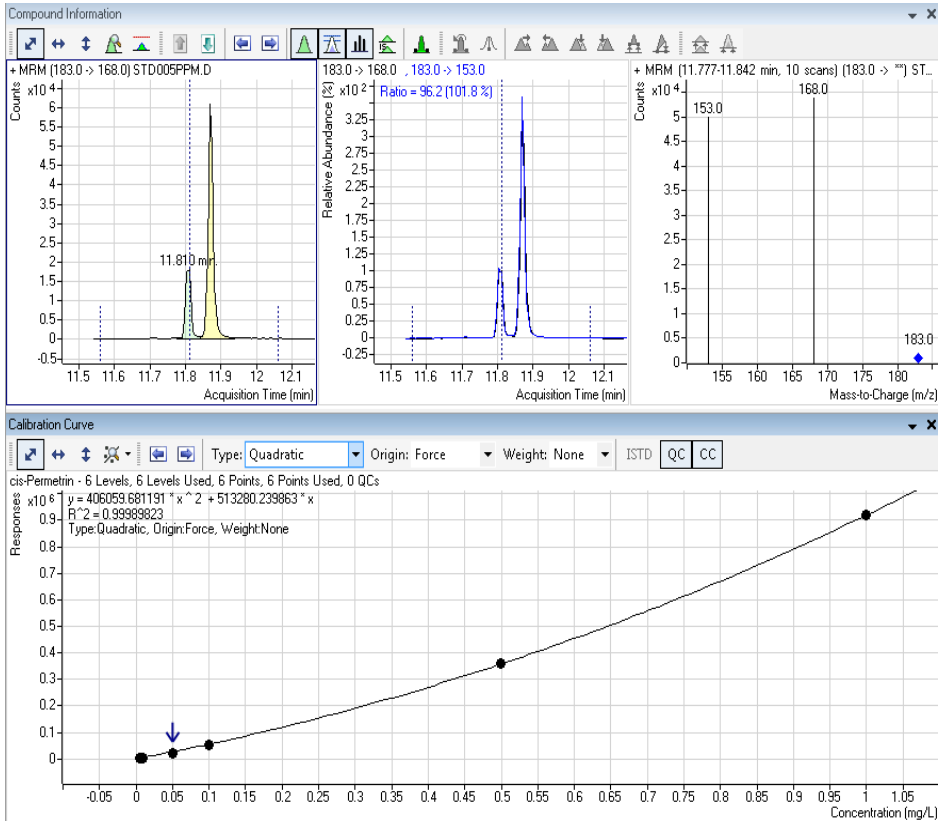


Analytical Procedure

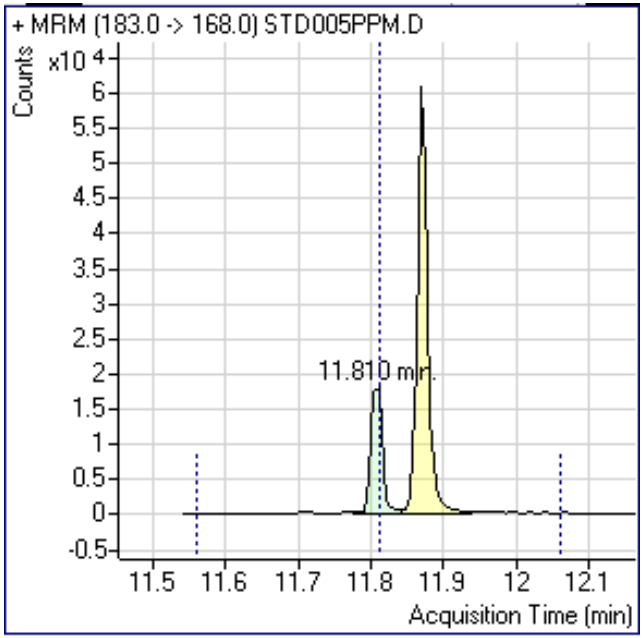
Biocides / preservatives and Permethrin

EPA 8081B + EPA 8141B + EPA 8270E	**Technique: GC-MS/MS LC-MSMS**	**LOD: 0,01 mg/kg**

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

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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%**

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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%

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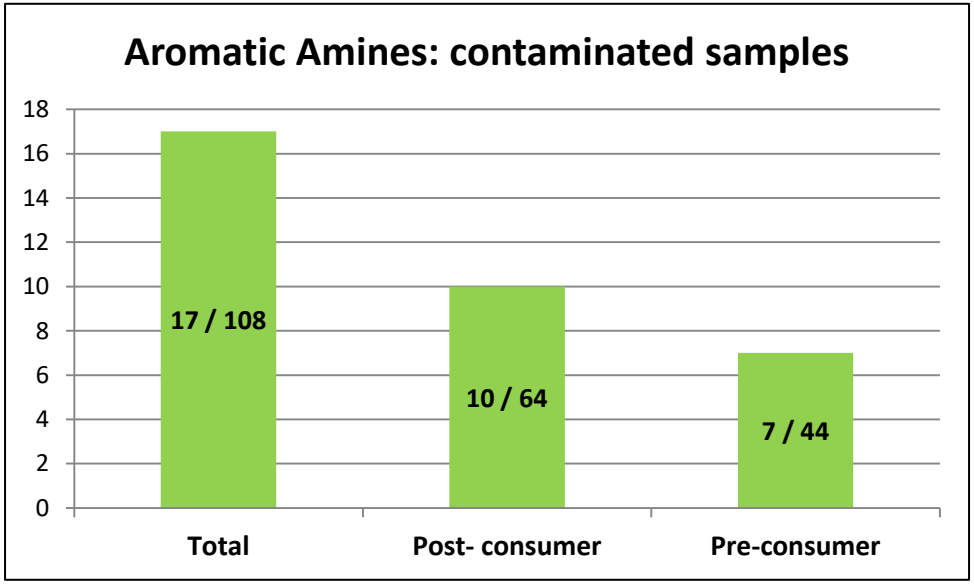
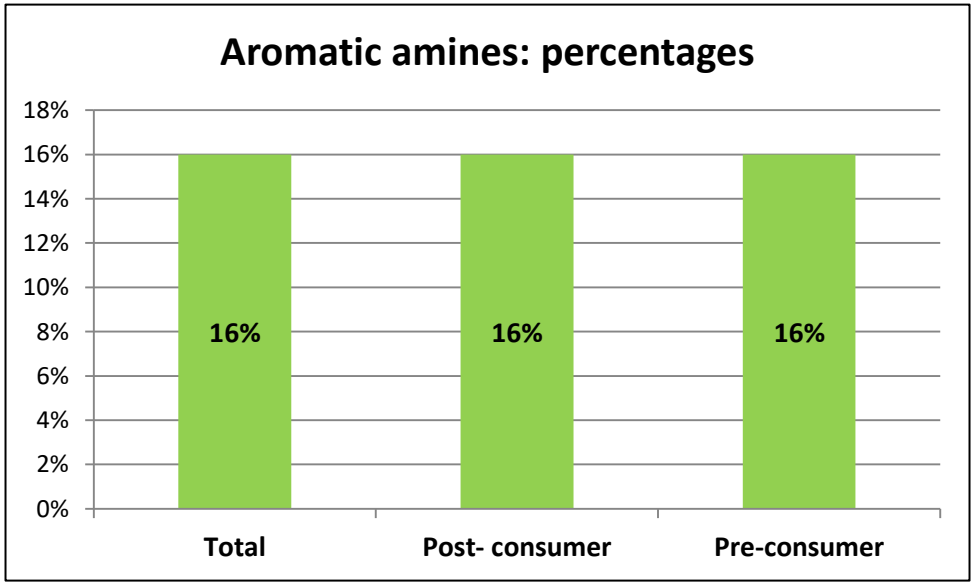
Aromatic Amines





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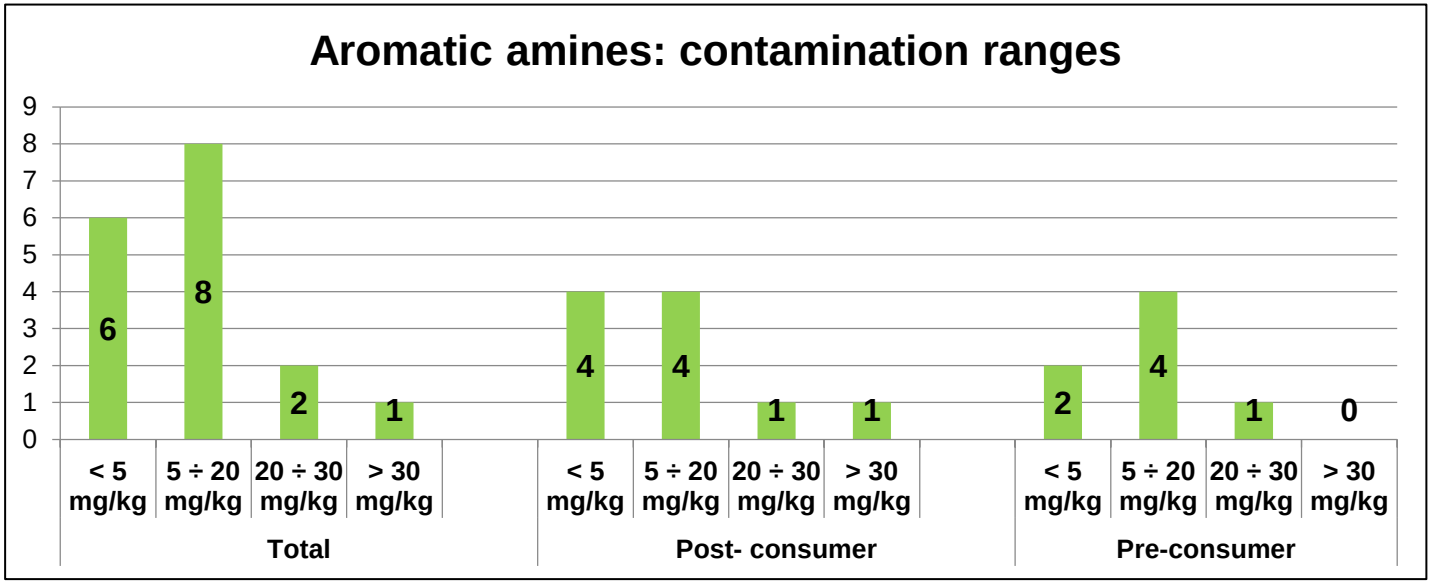
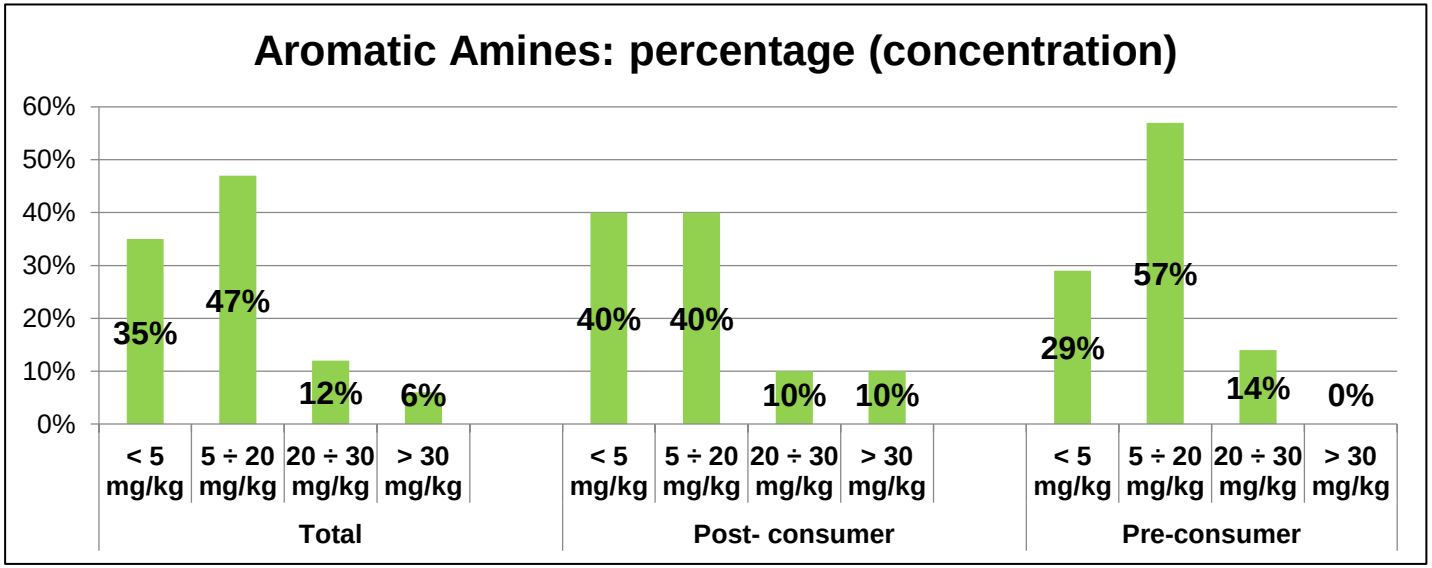
Aromatic Amines





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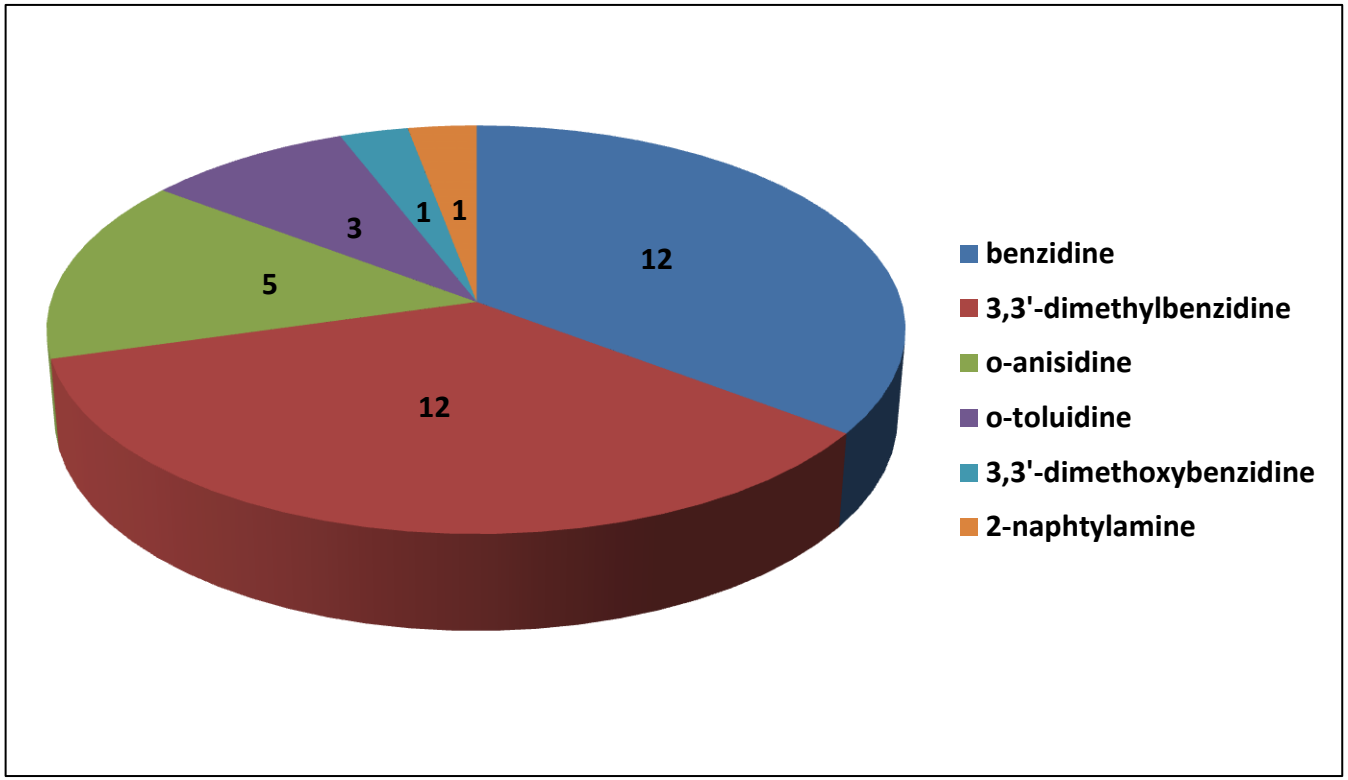
Aromatic Amines



Frequencies by colors:

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

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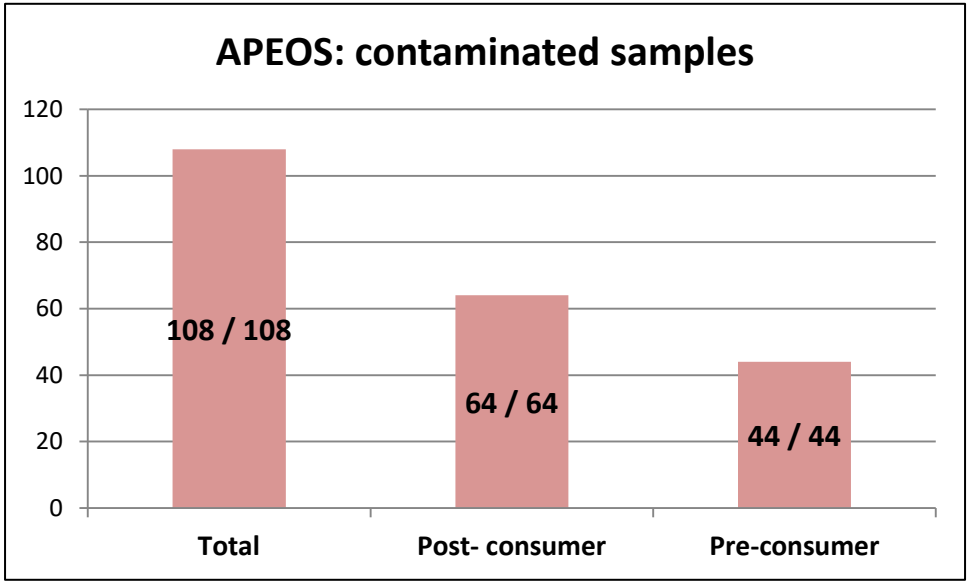
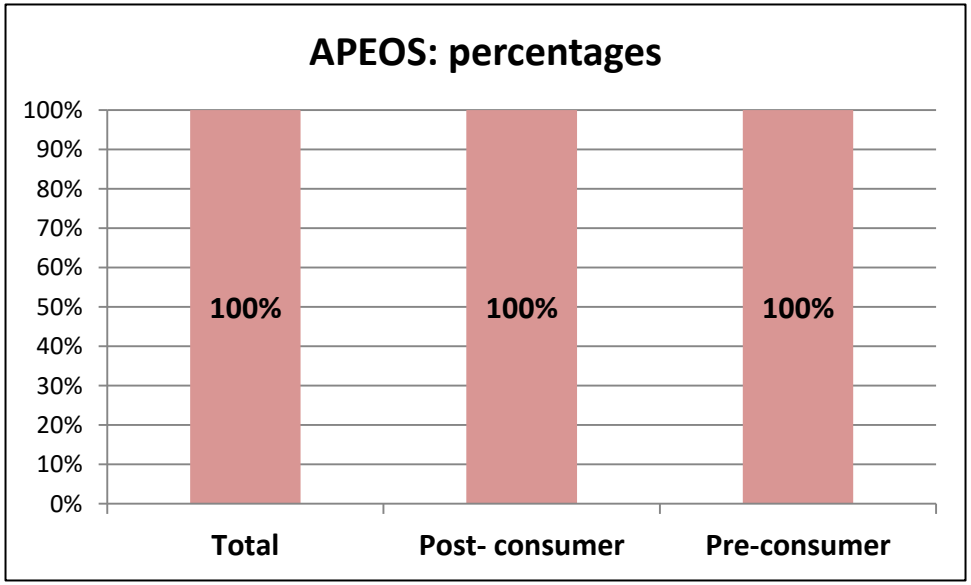
Ethoxylated Alkylphenols (APEOS)





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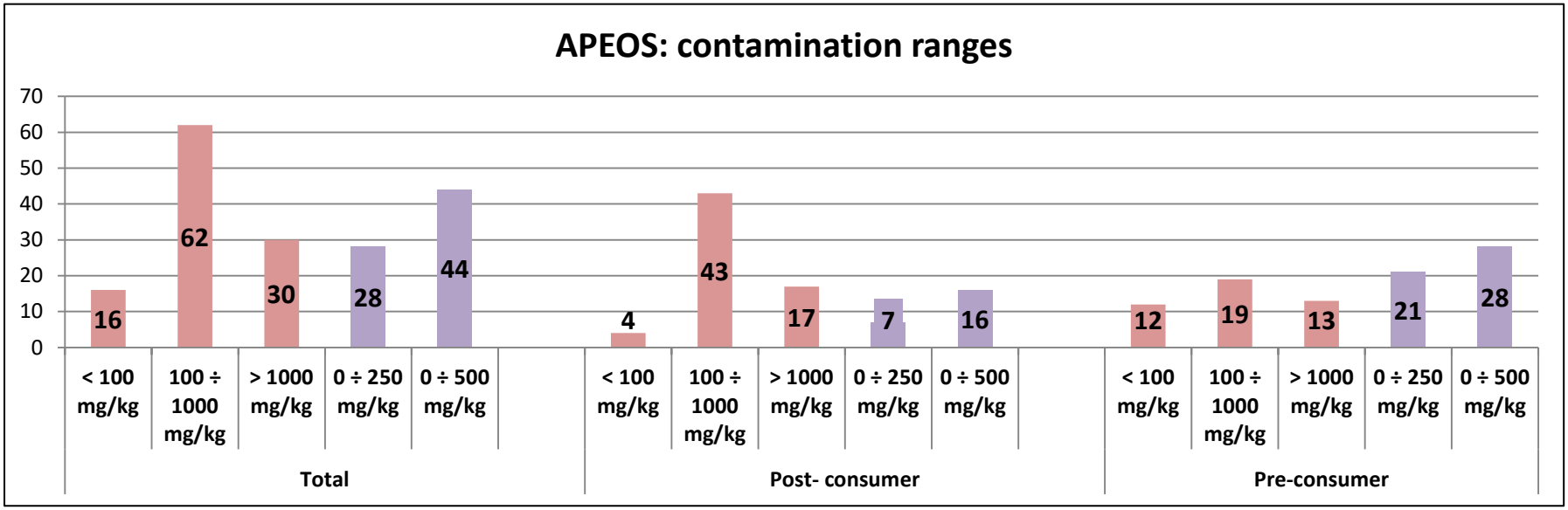
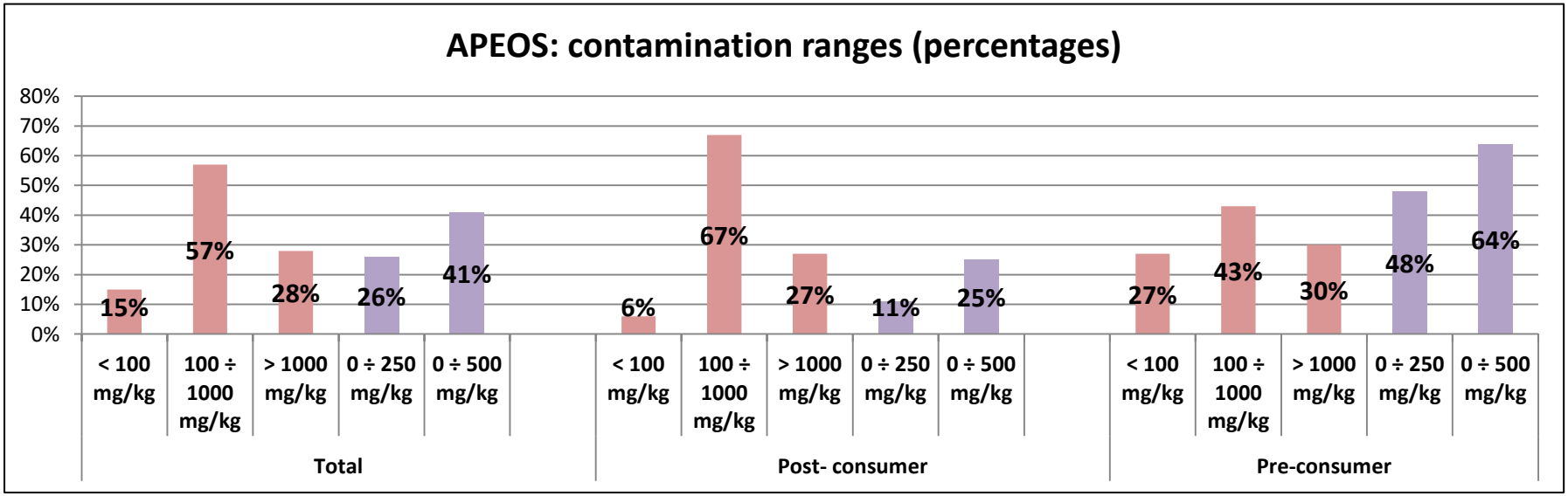
Ethoxylated Alkylphenols (APEOS)





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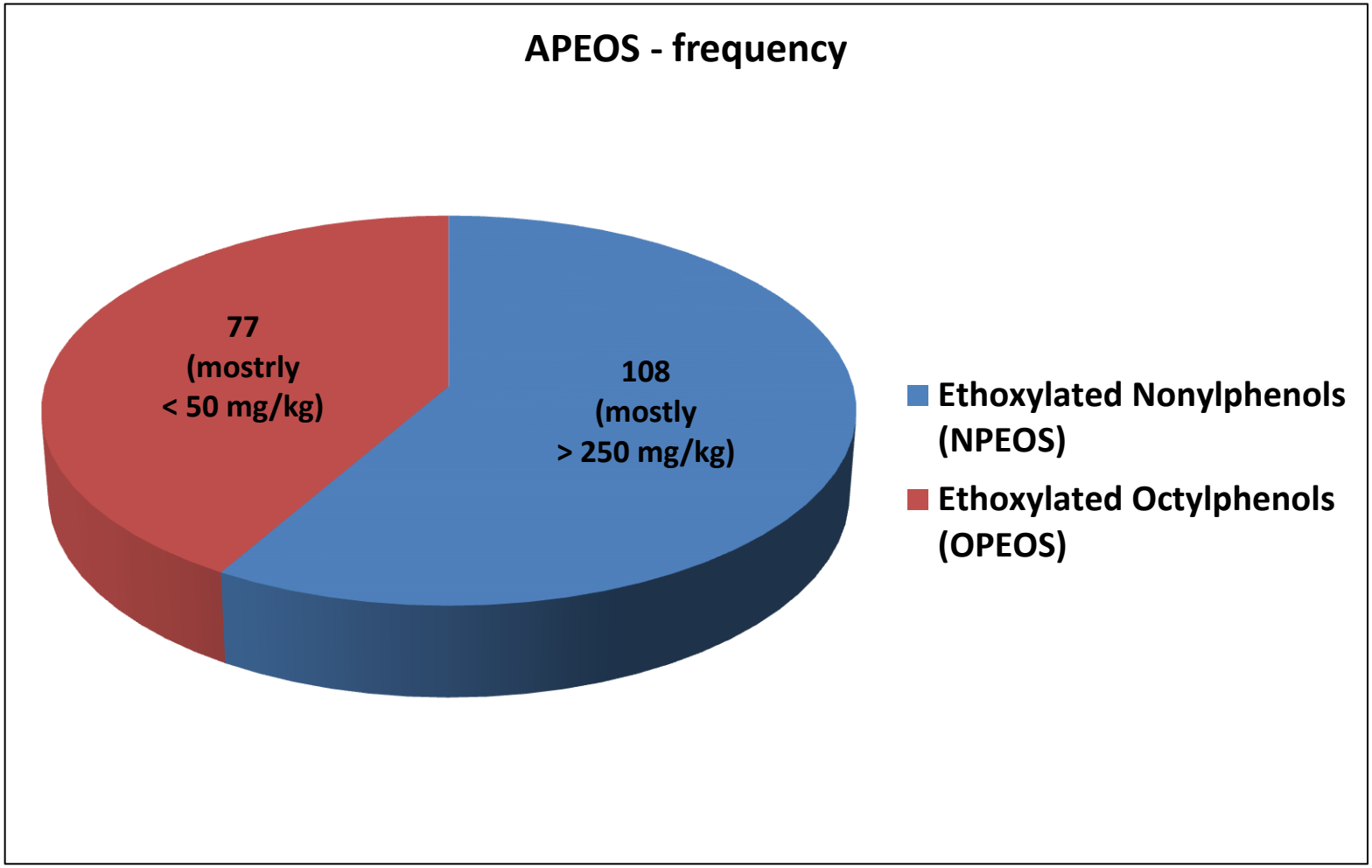

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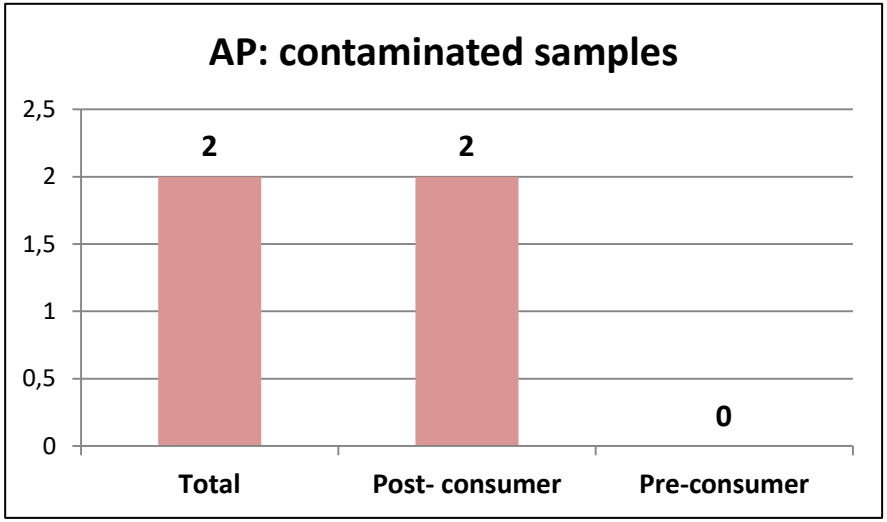

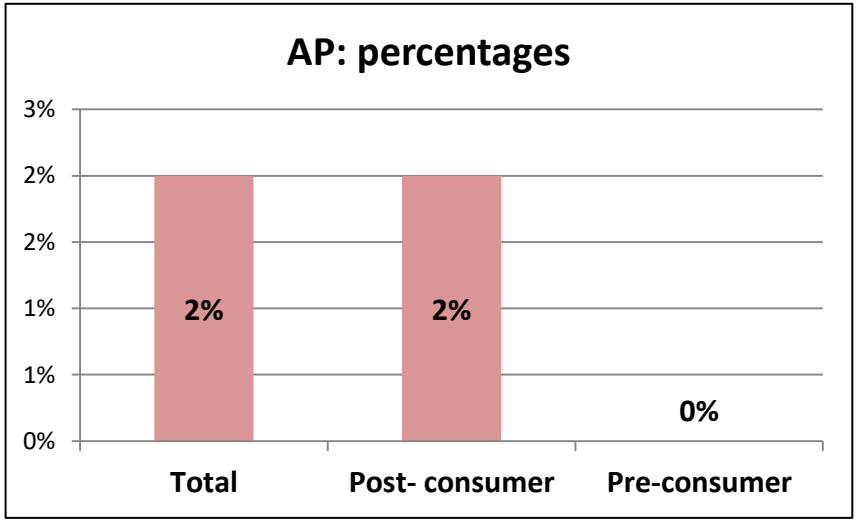

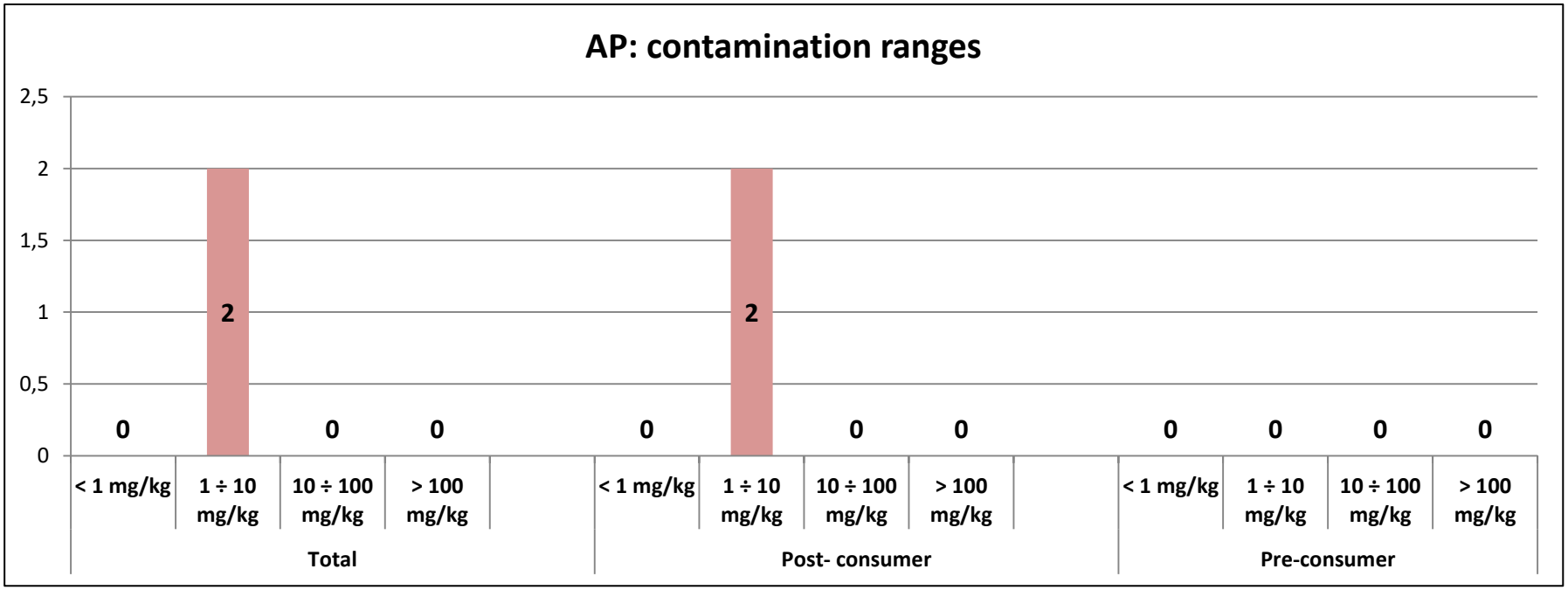

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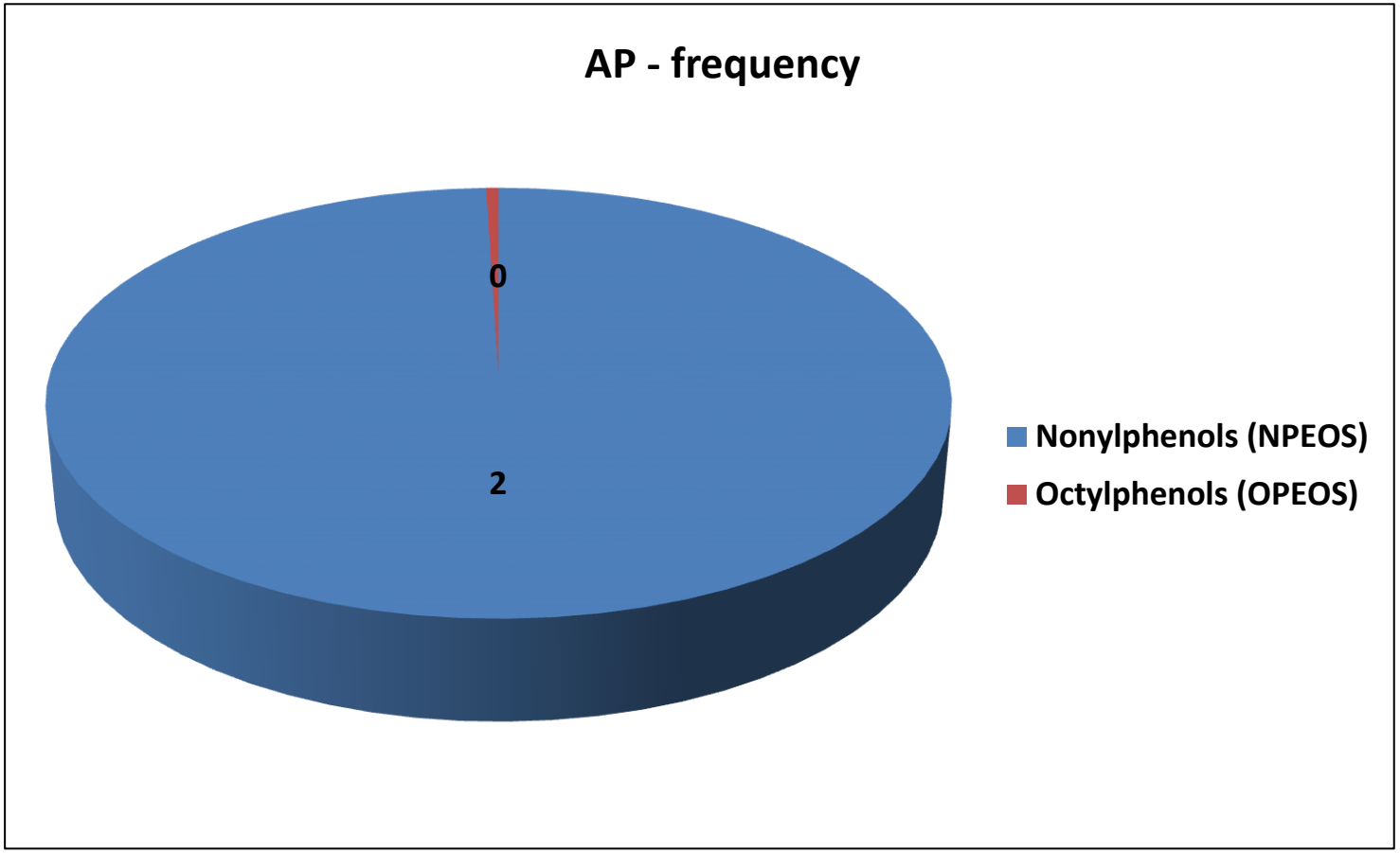
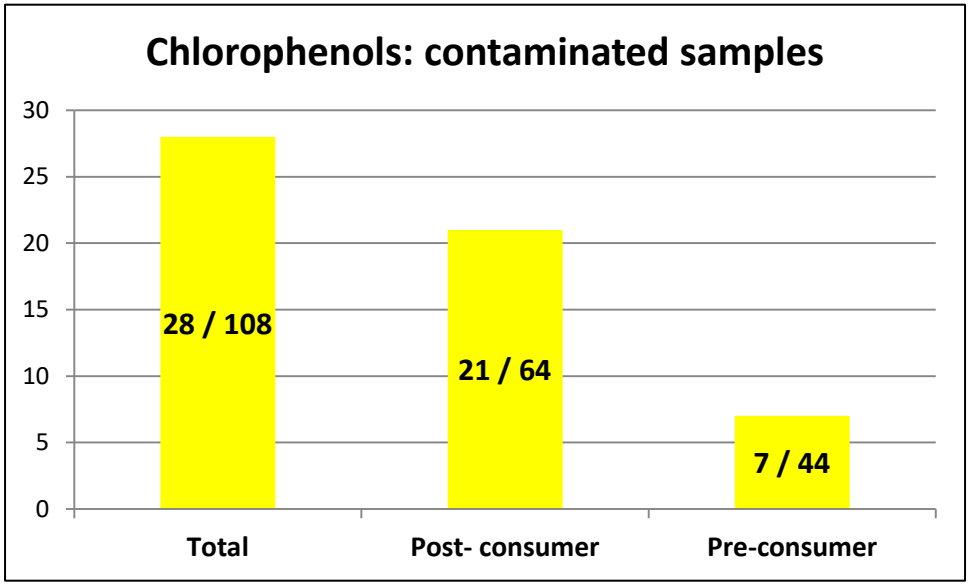
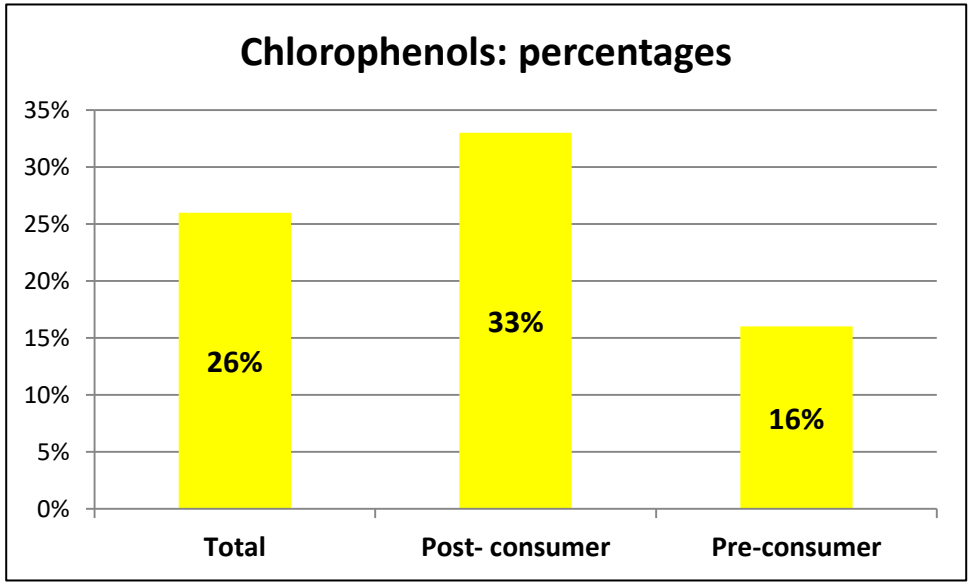


Chlorophenols





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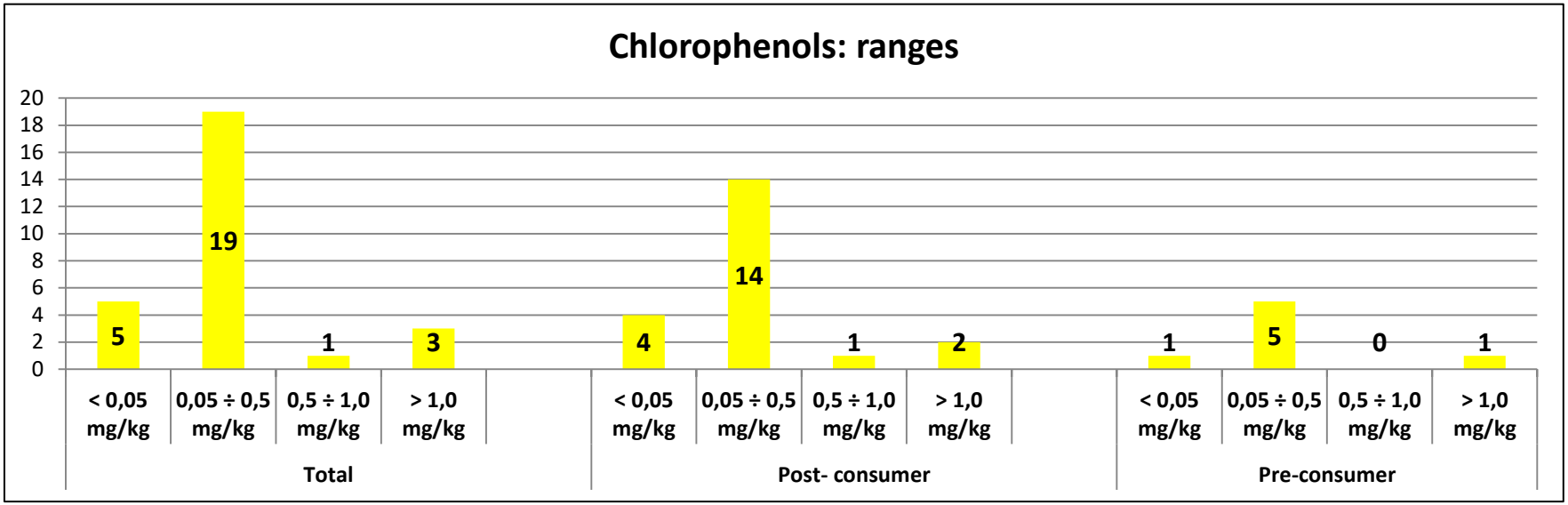
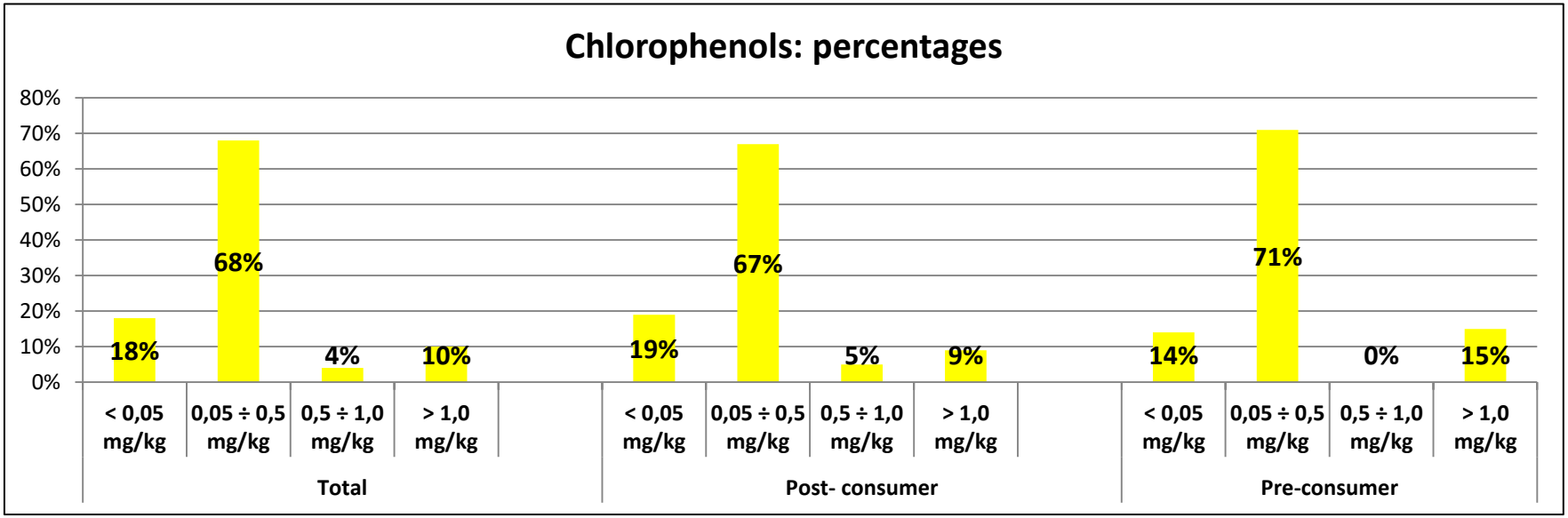
Chlorophenols





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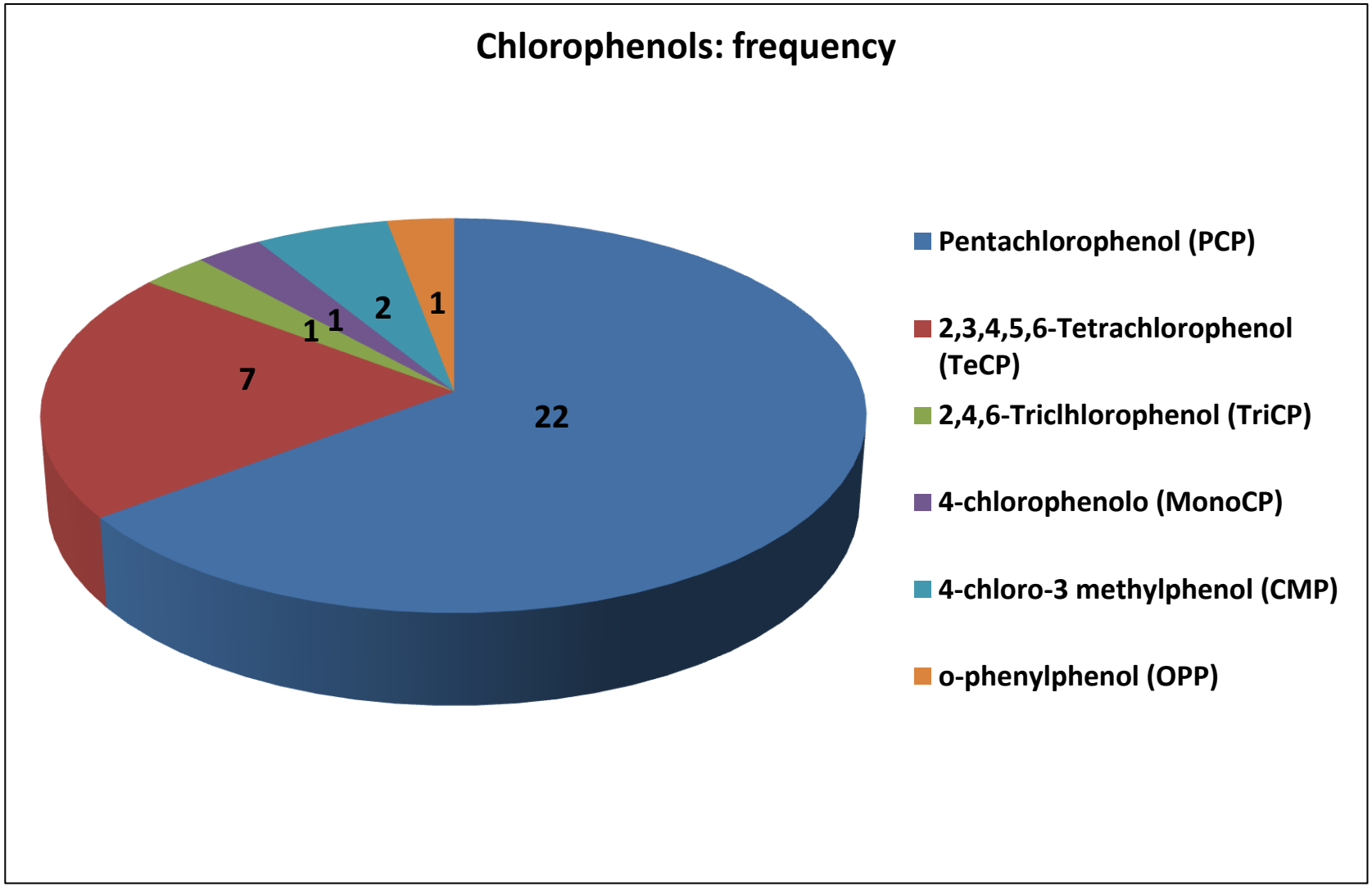
Chlorophenols



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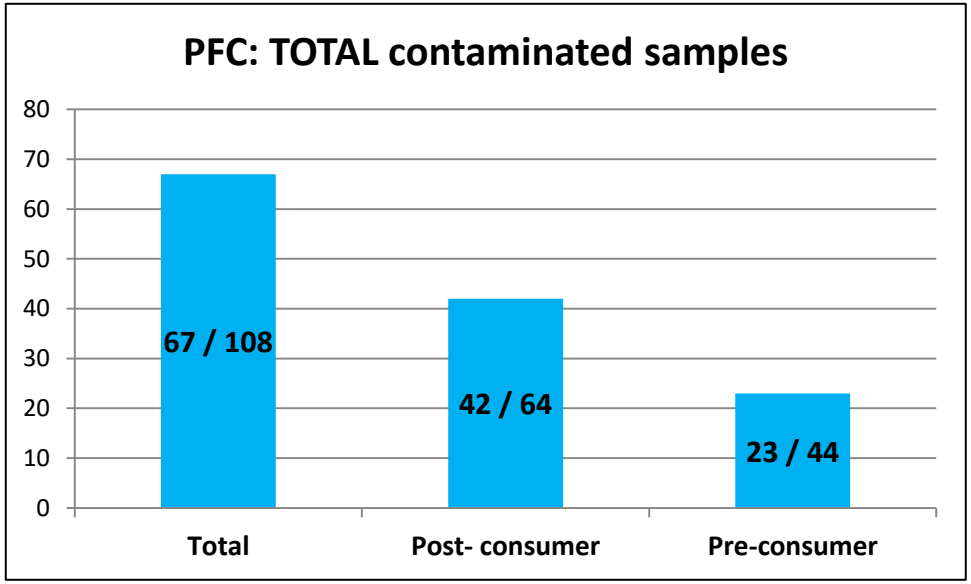

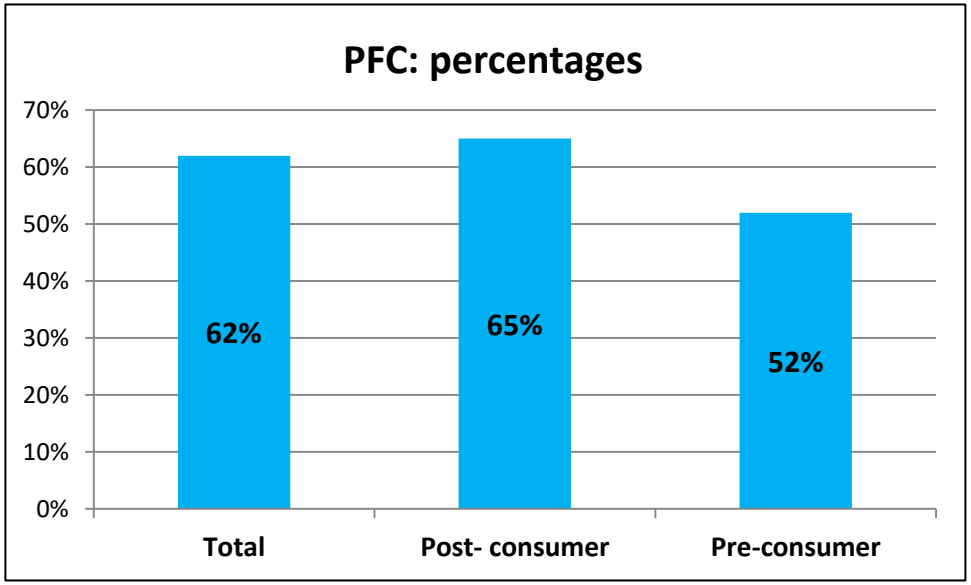

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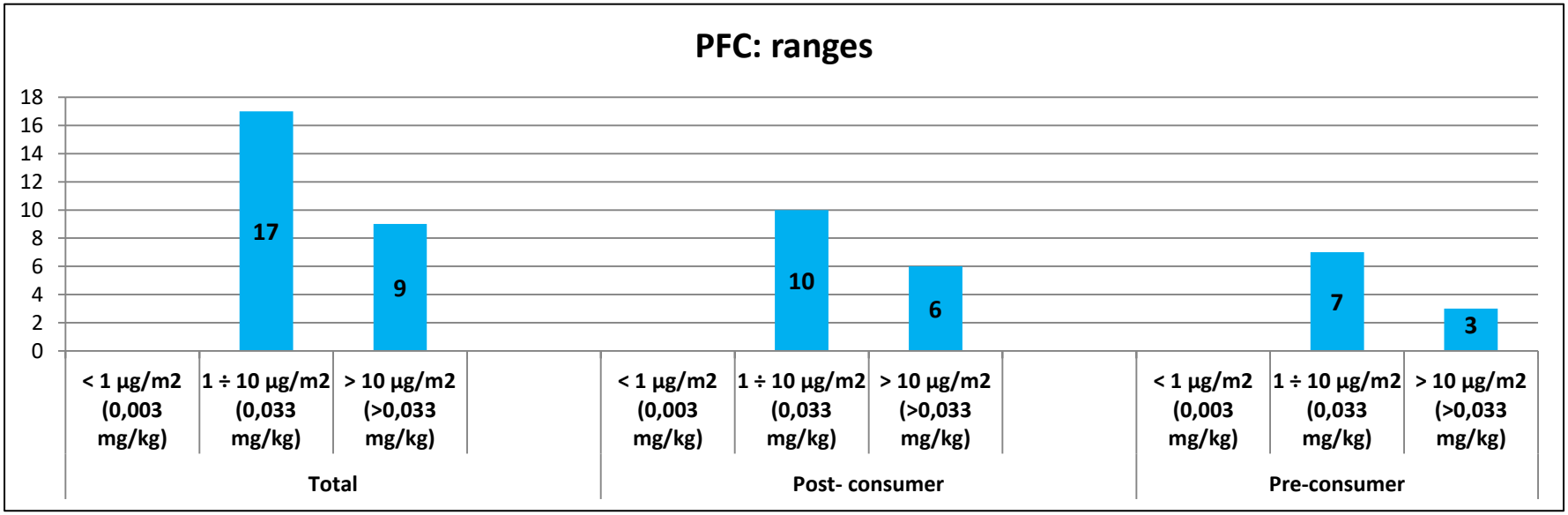

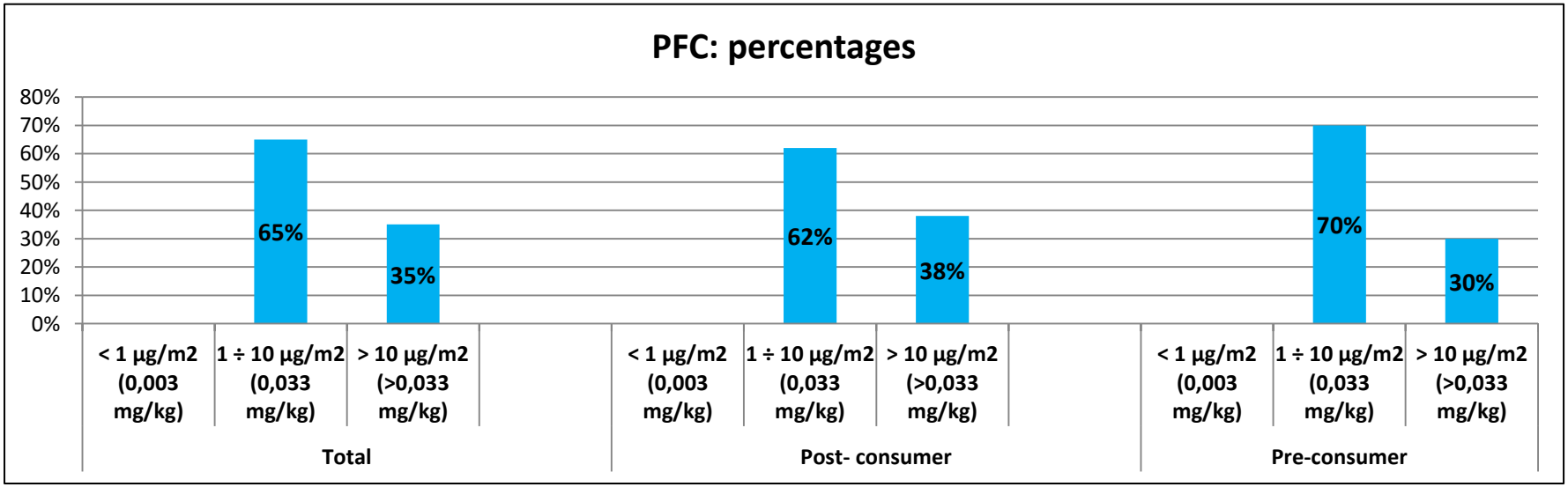

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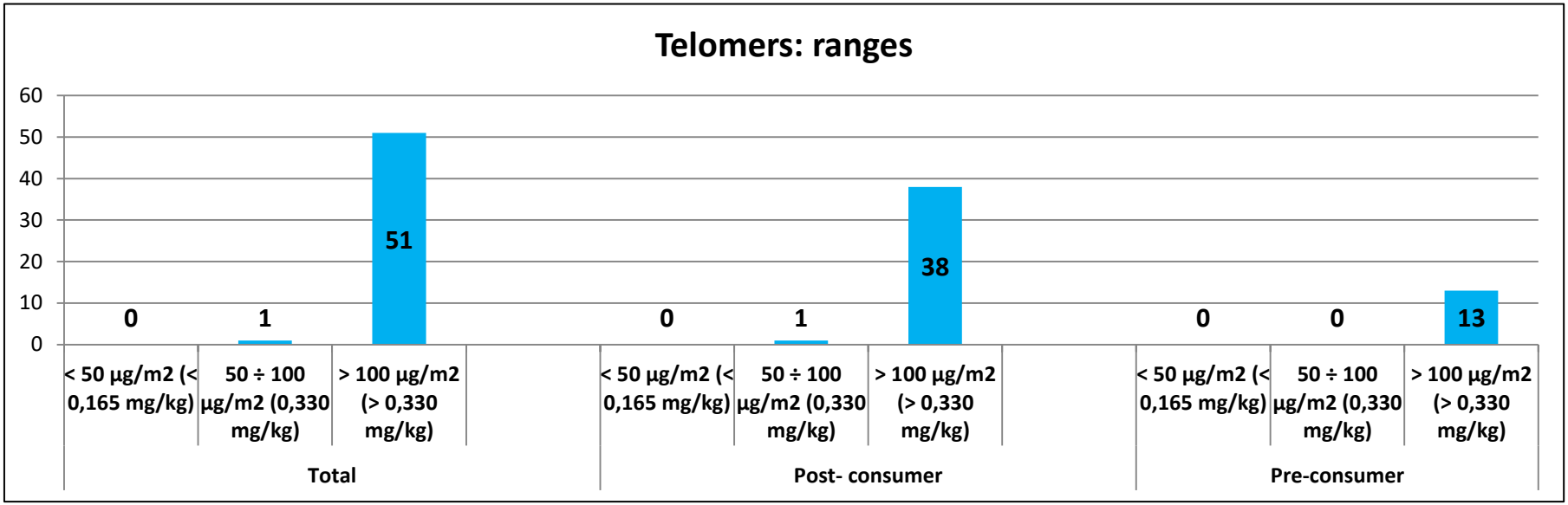

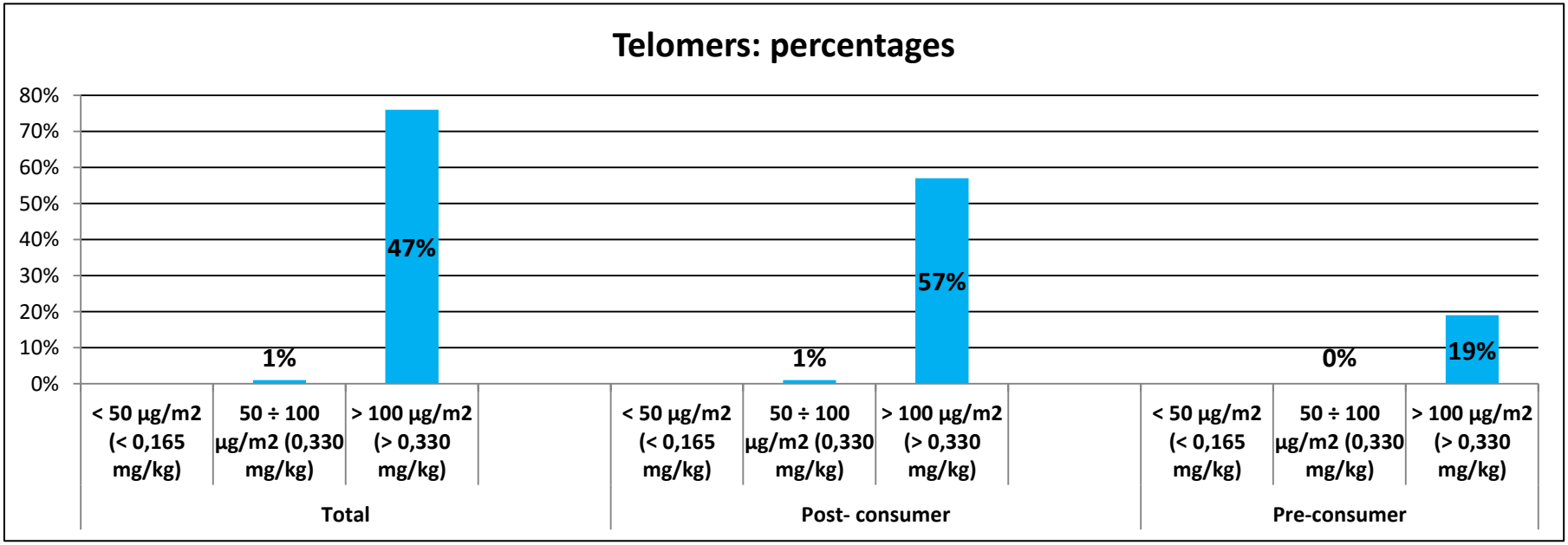

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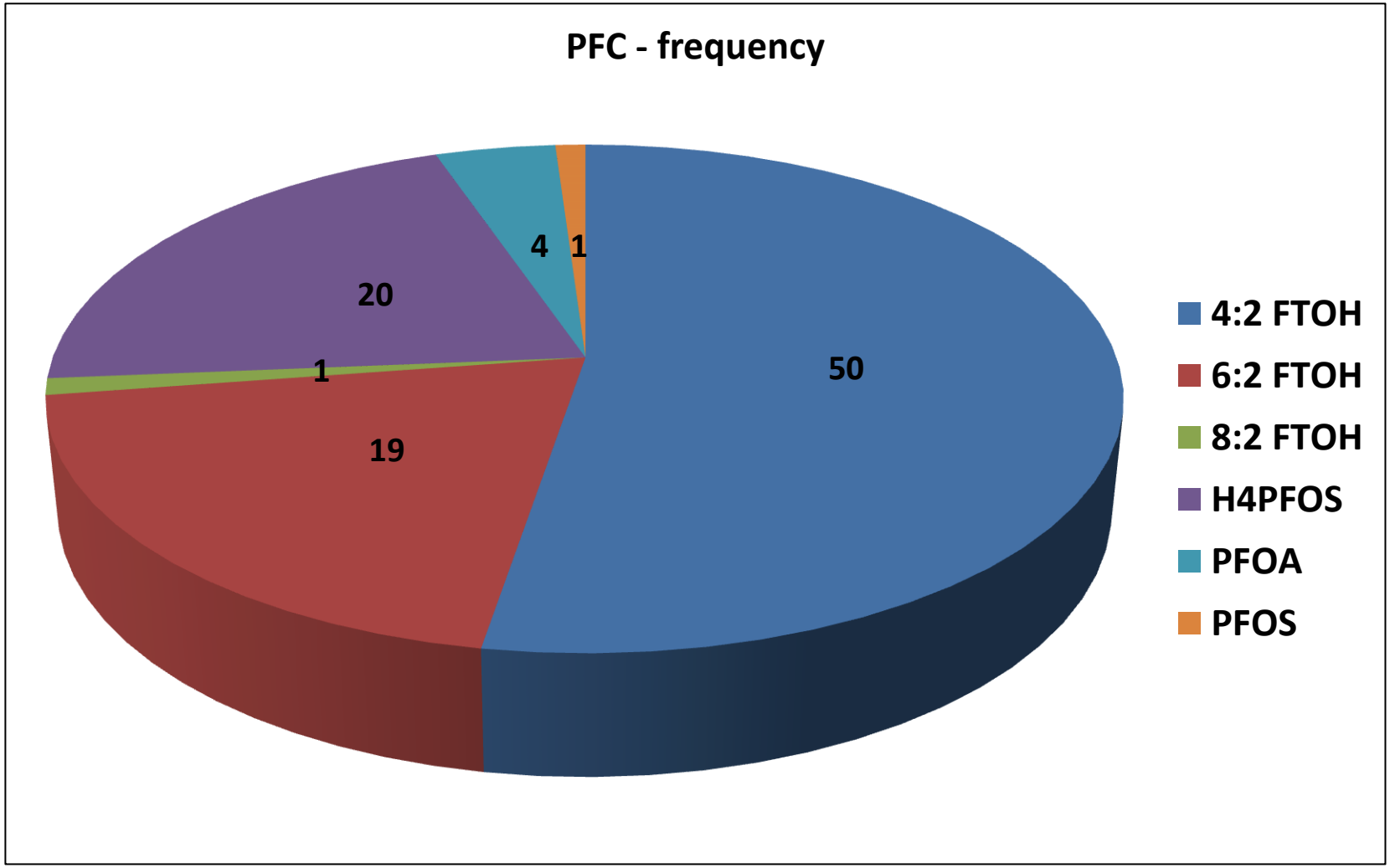

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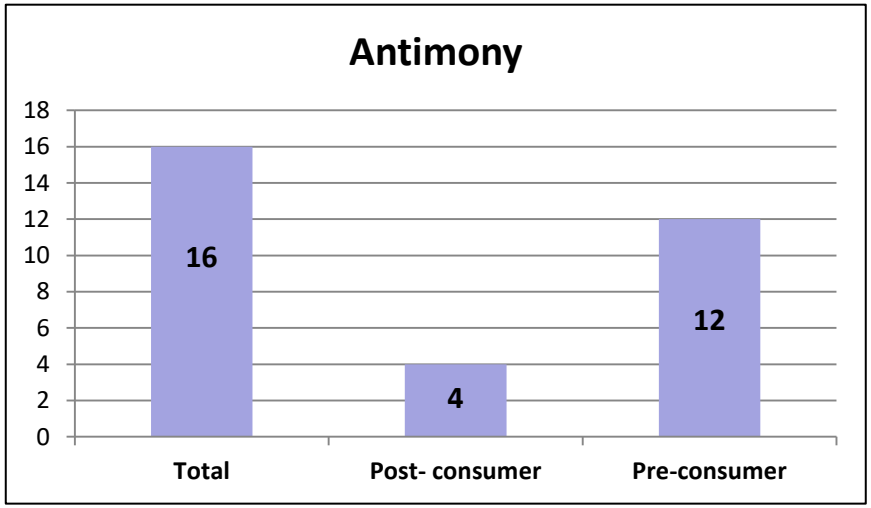

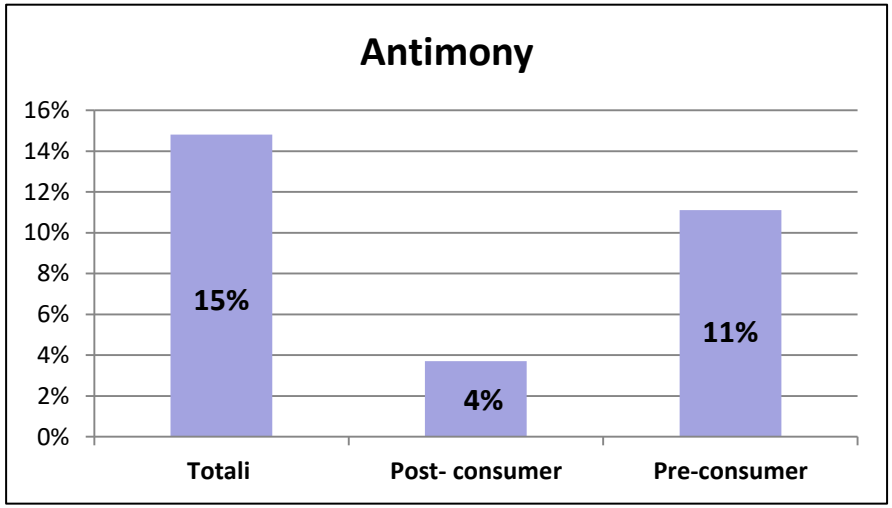

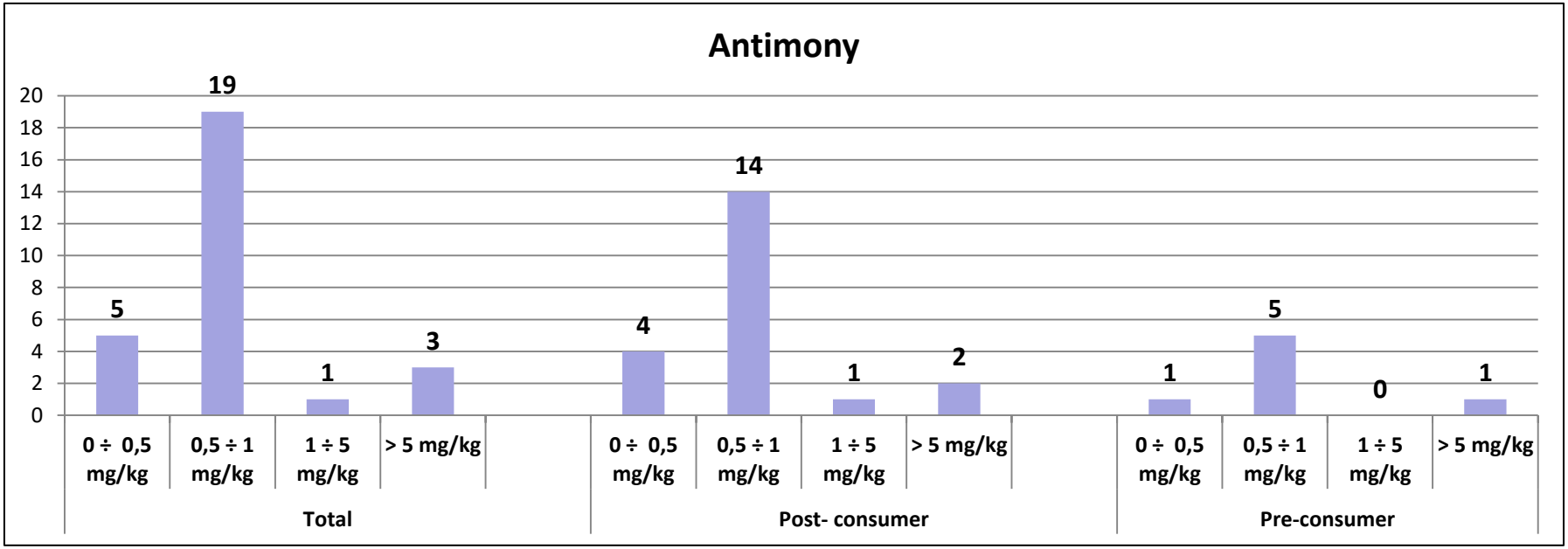

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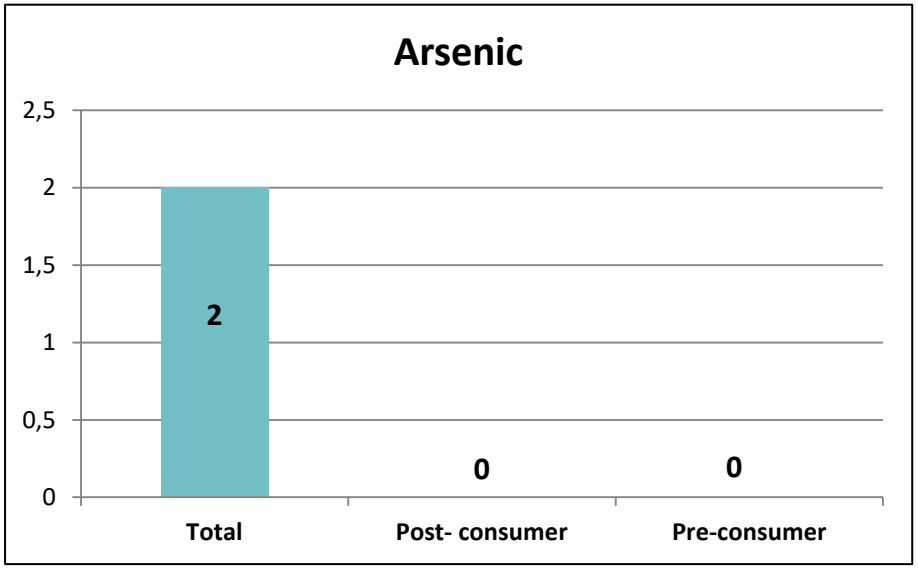

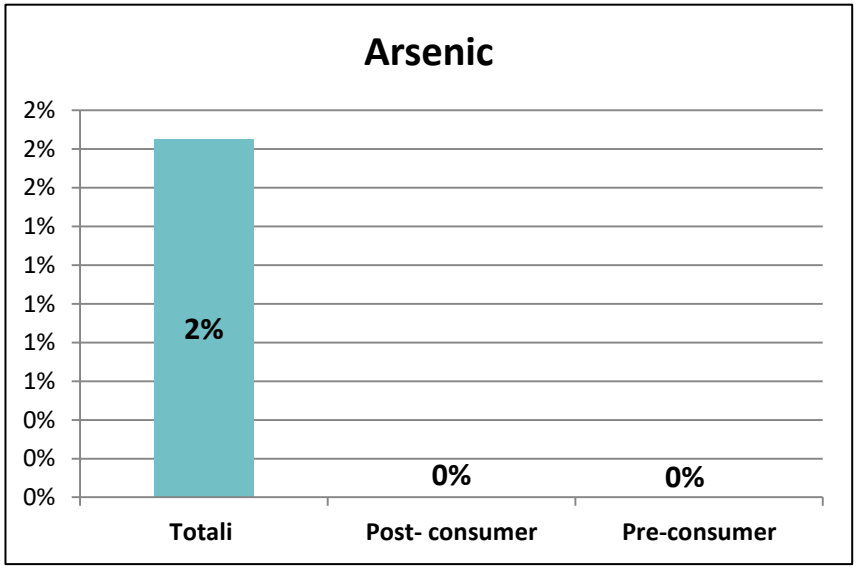

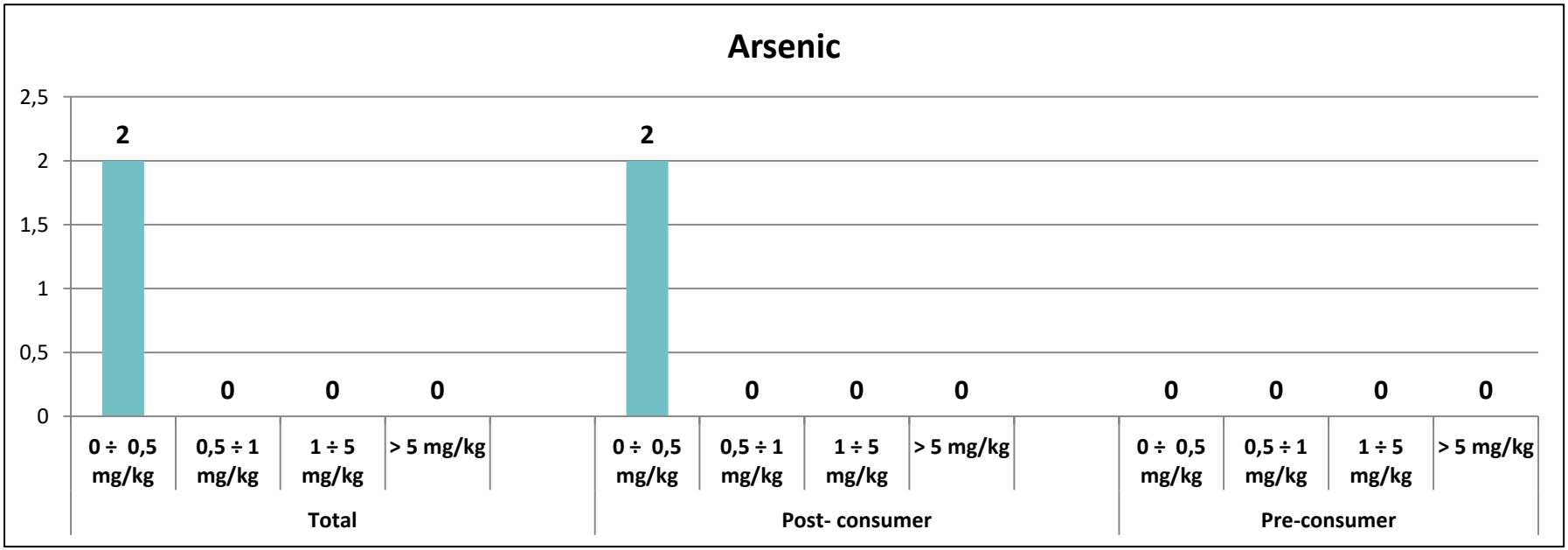

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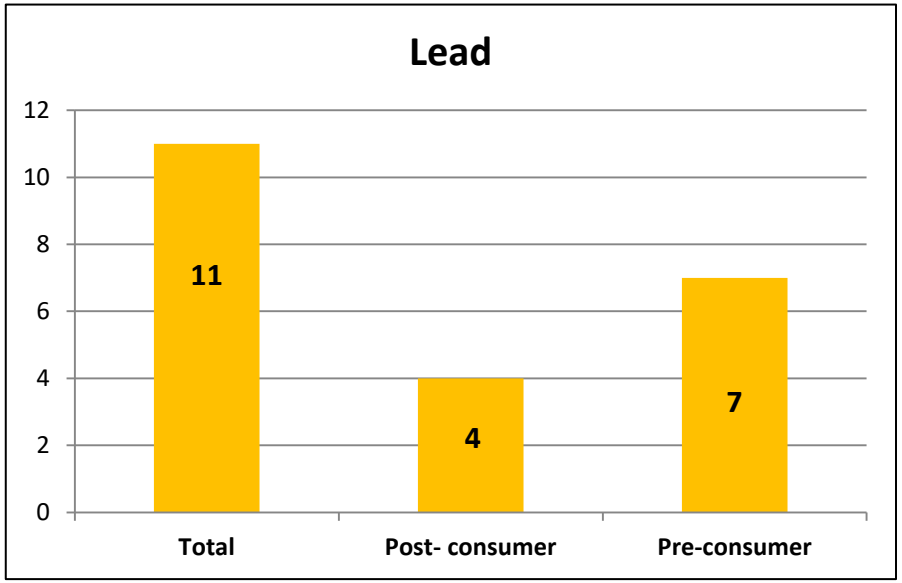

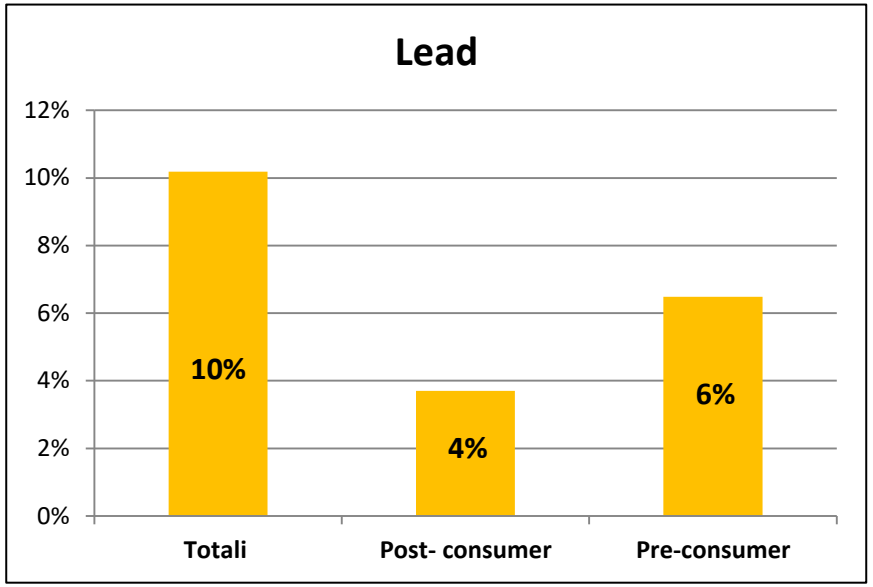

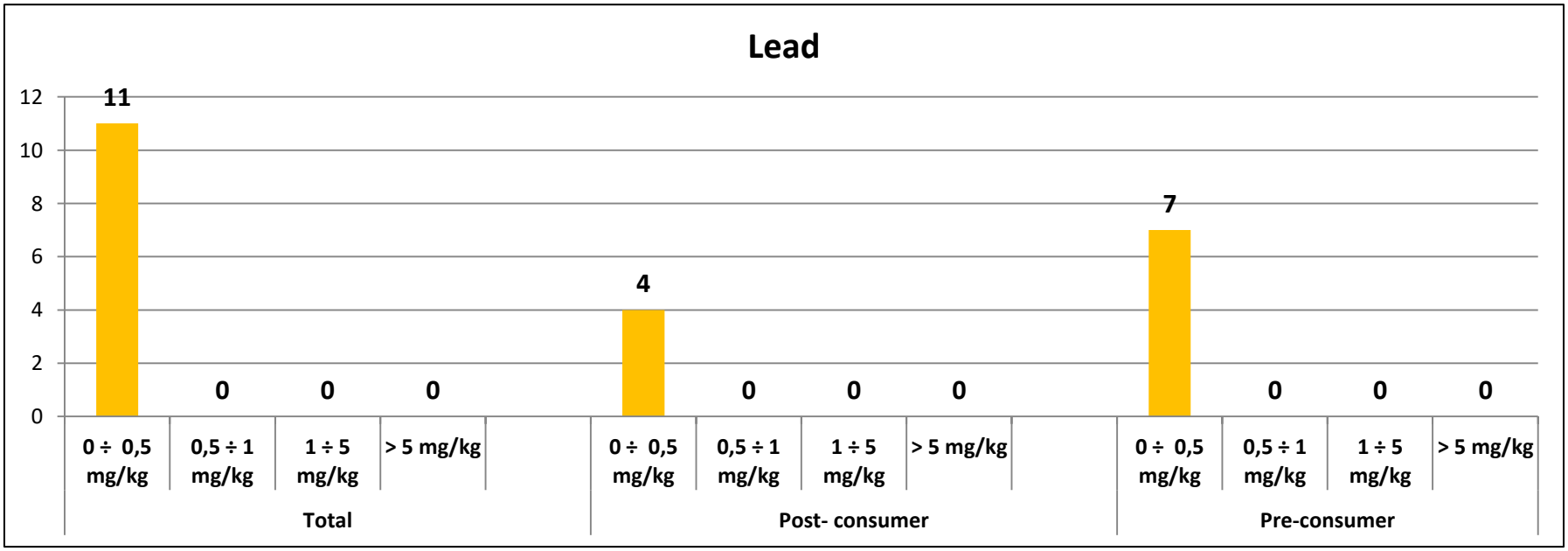

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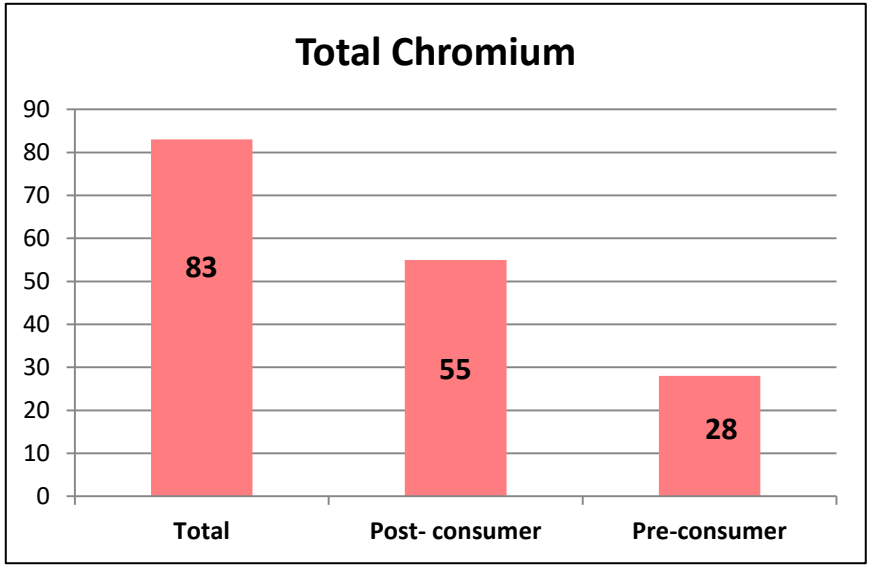

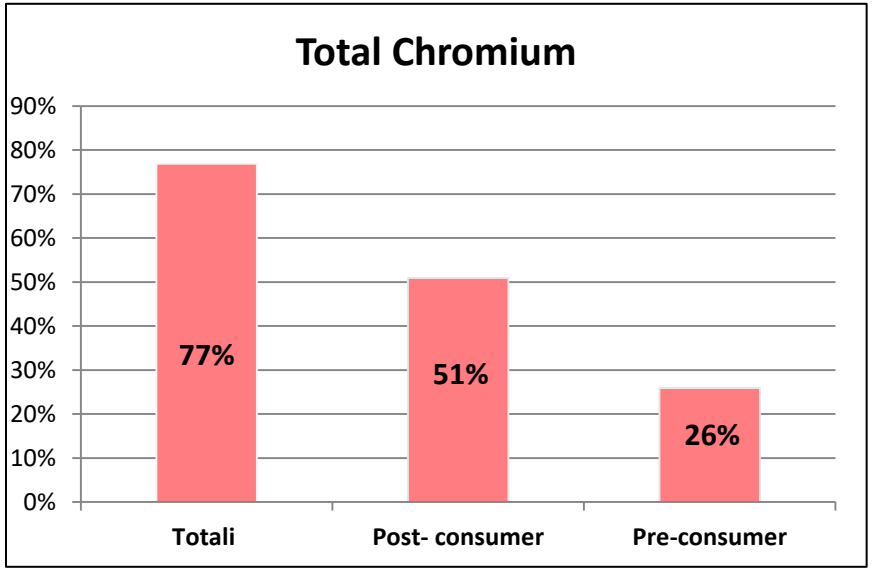

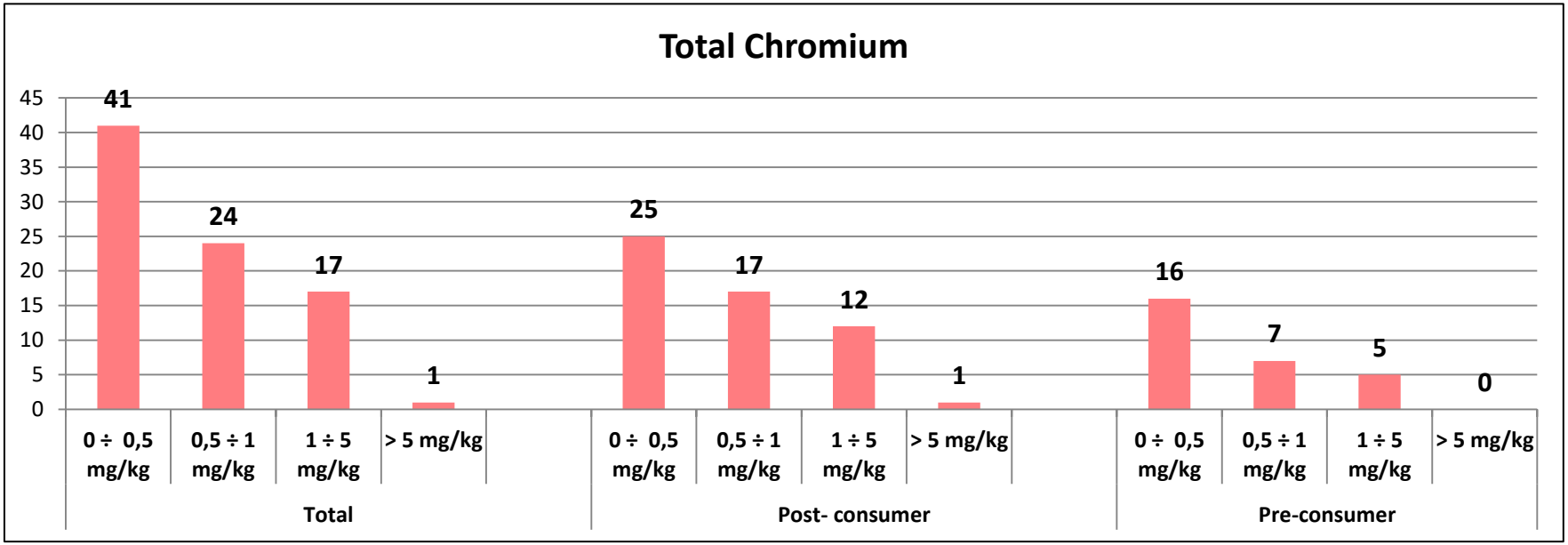

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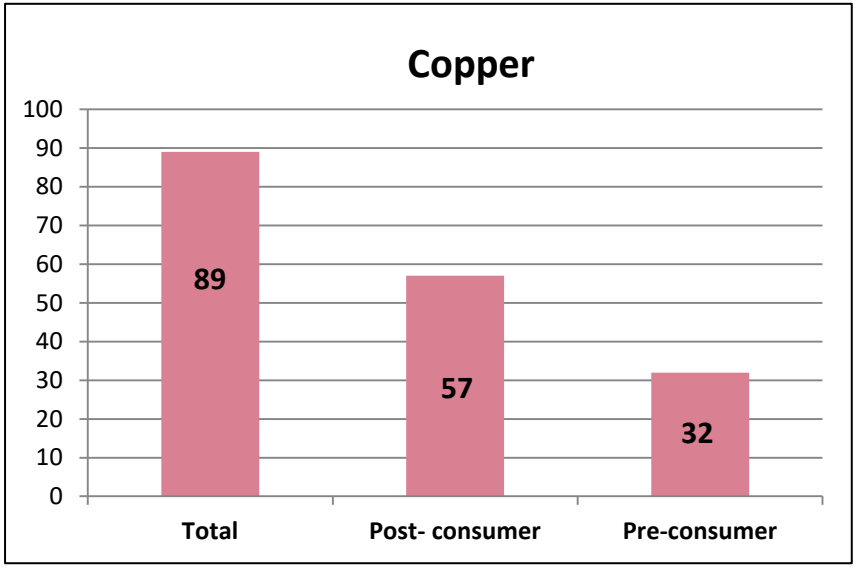

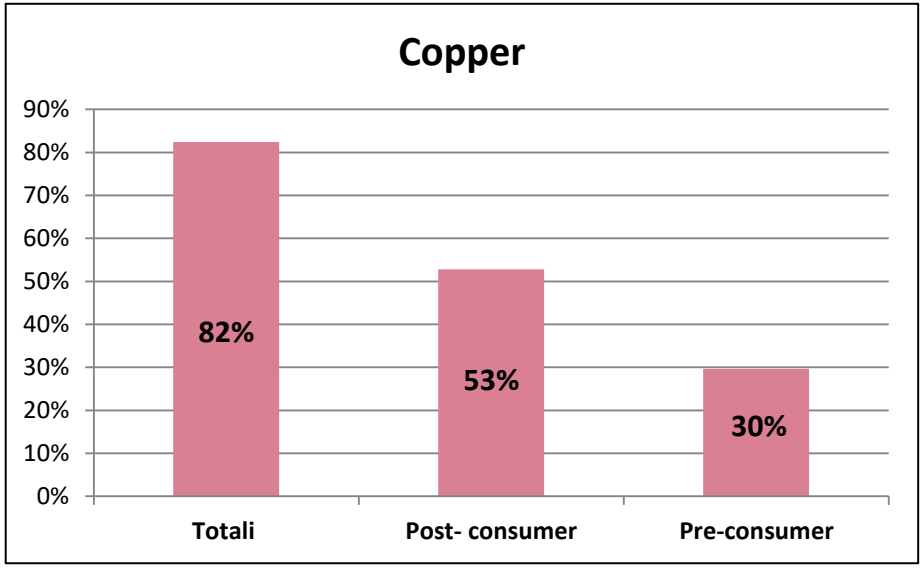

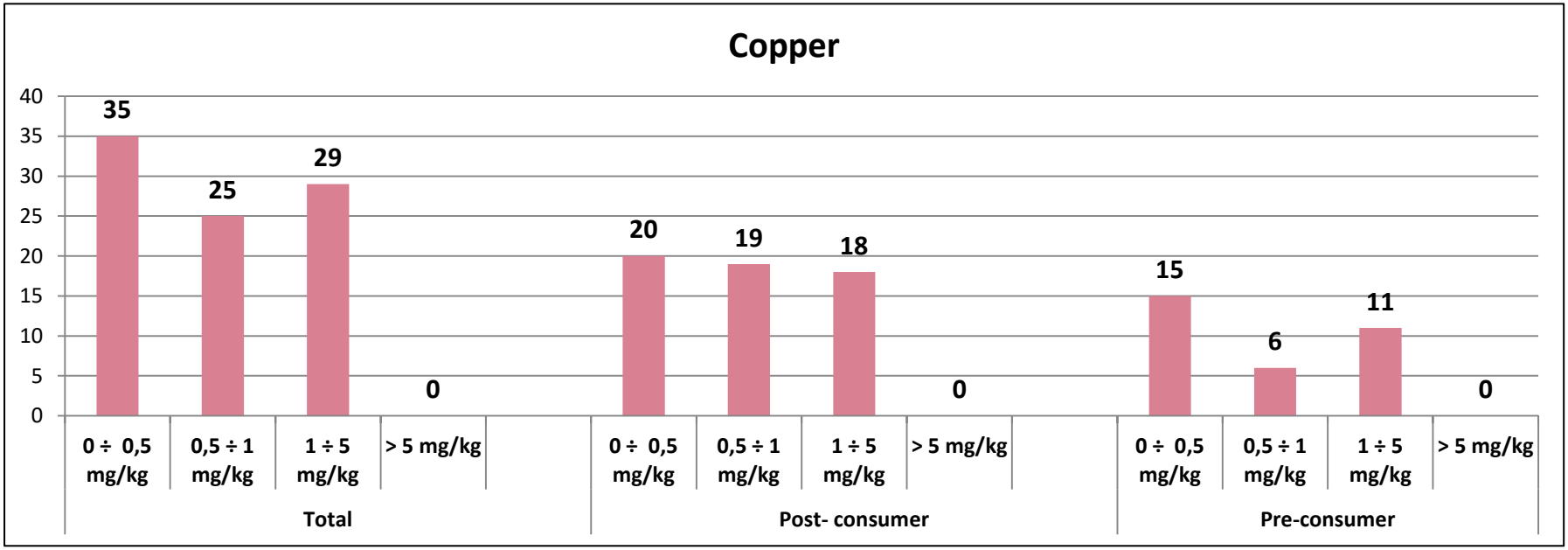

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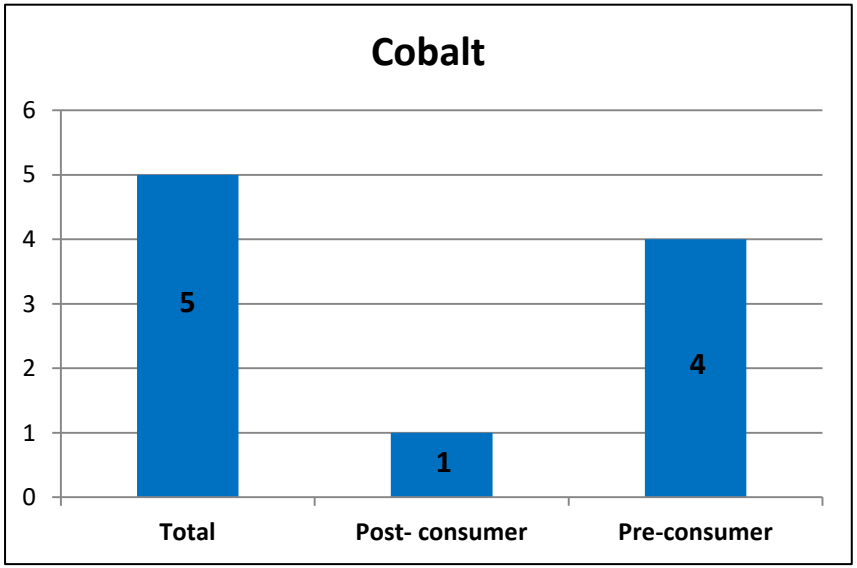

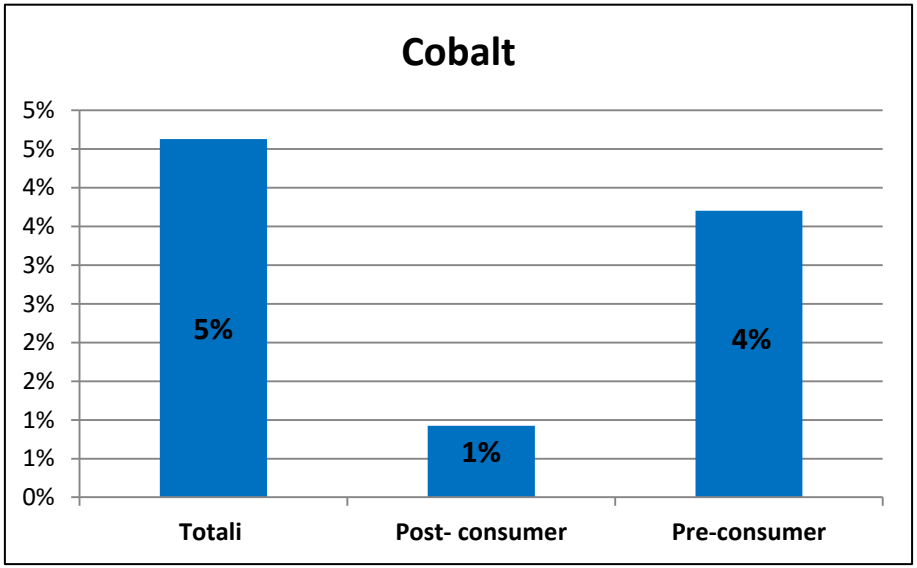

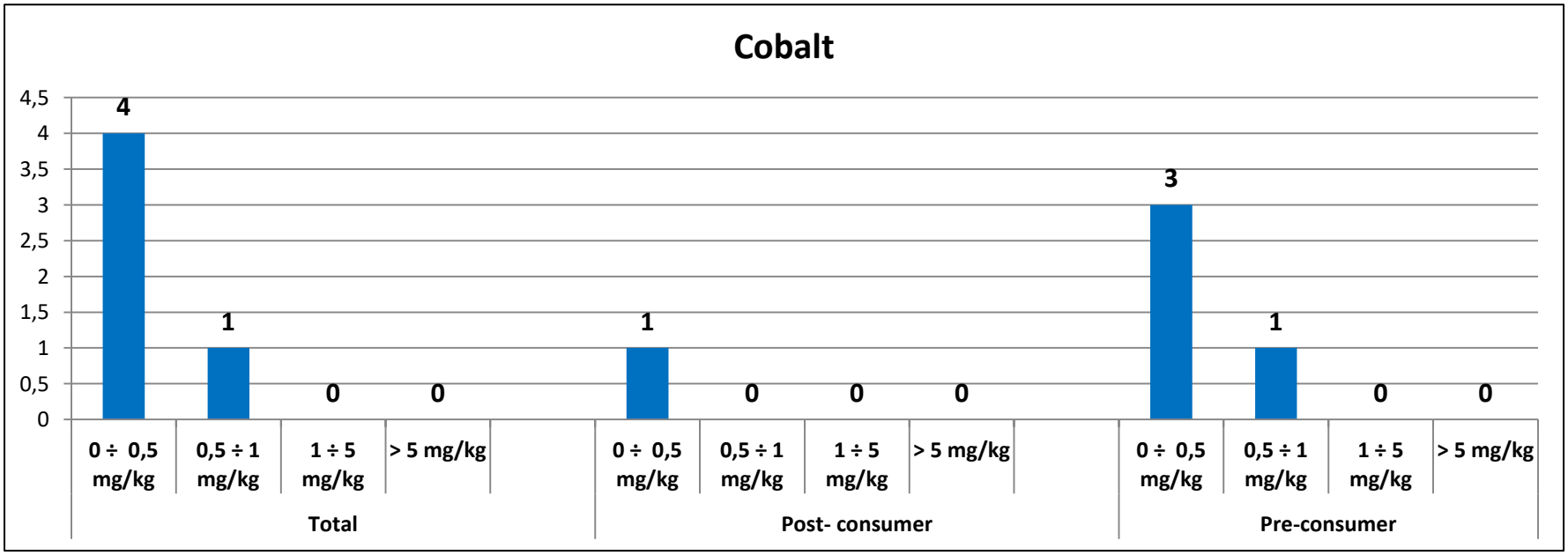

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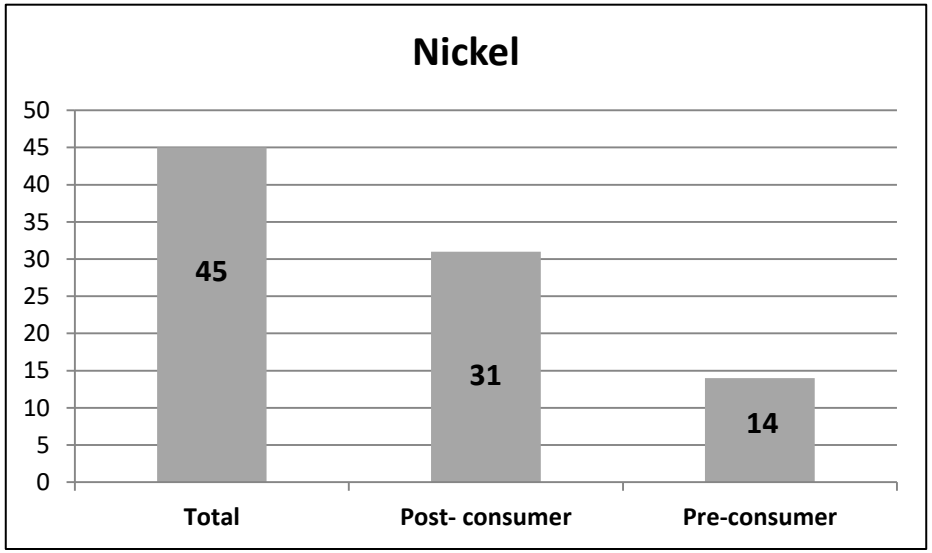

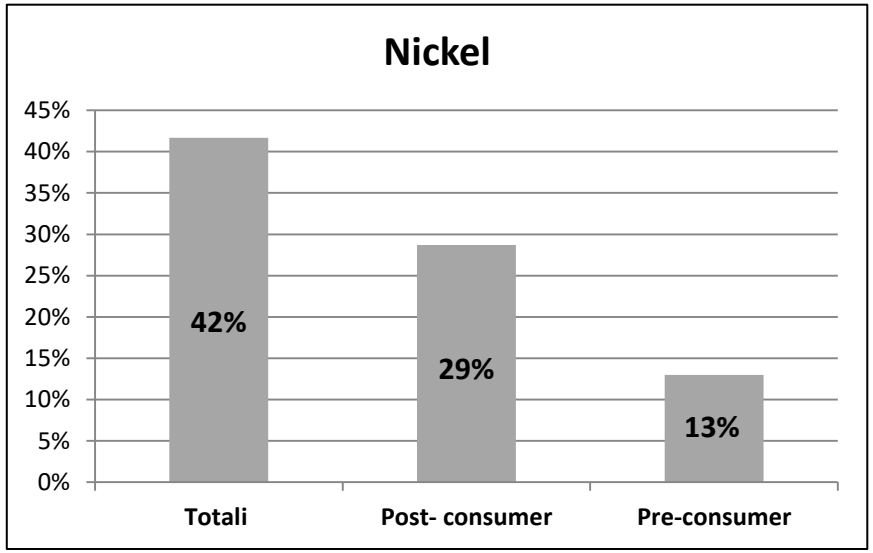

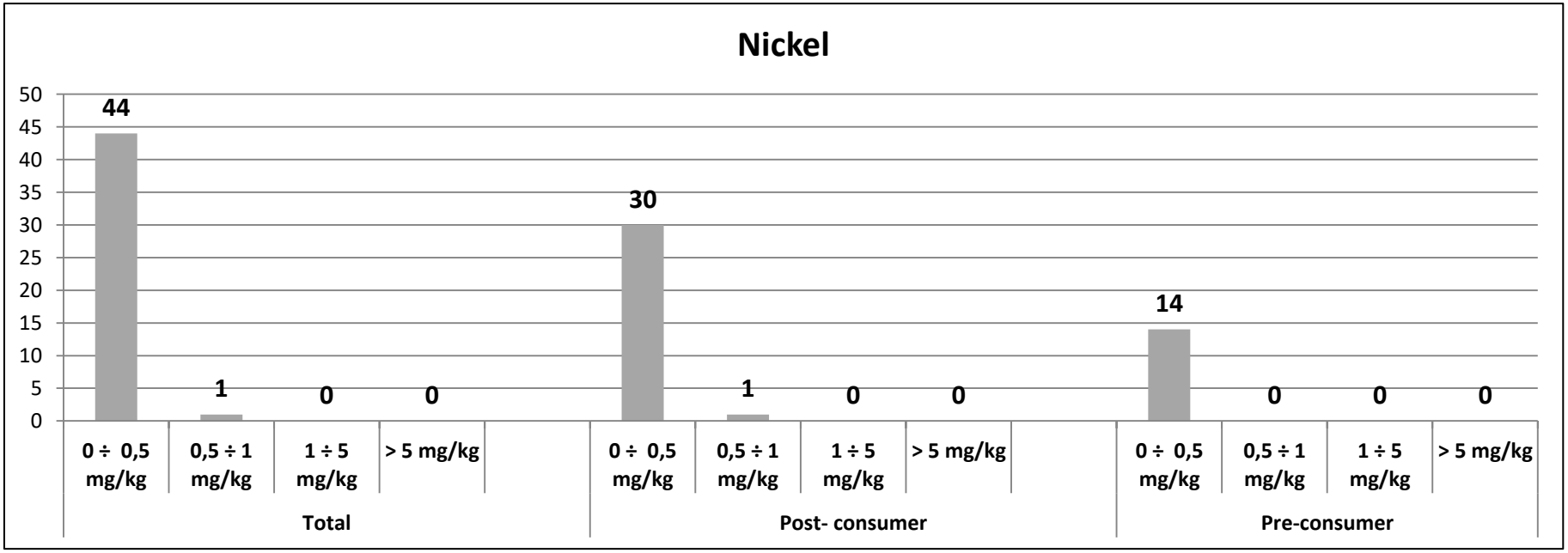

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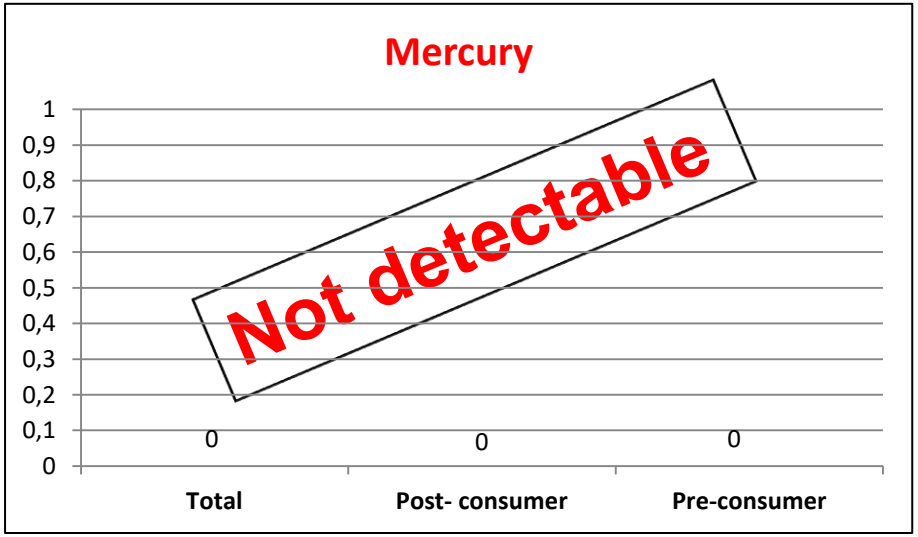

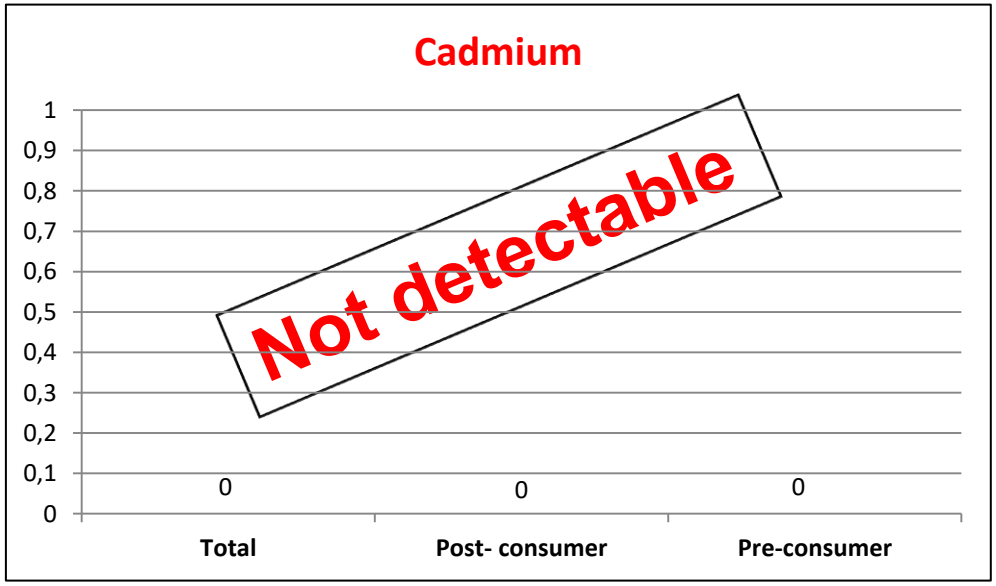

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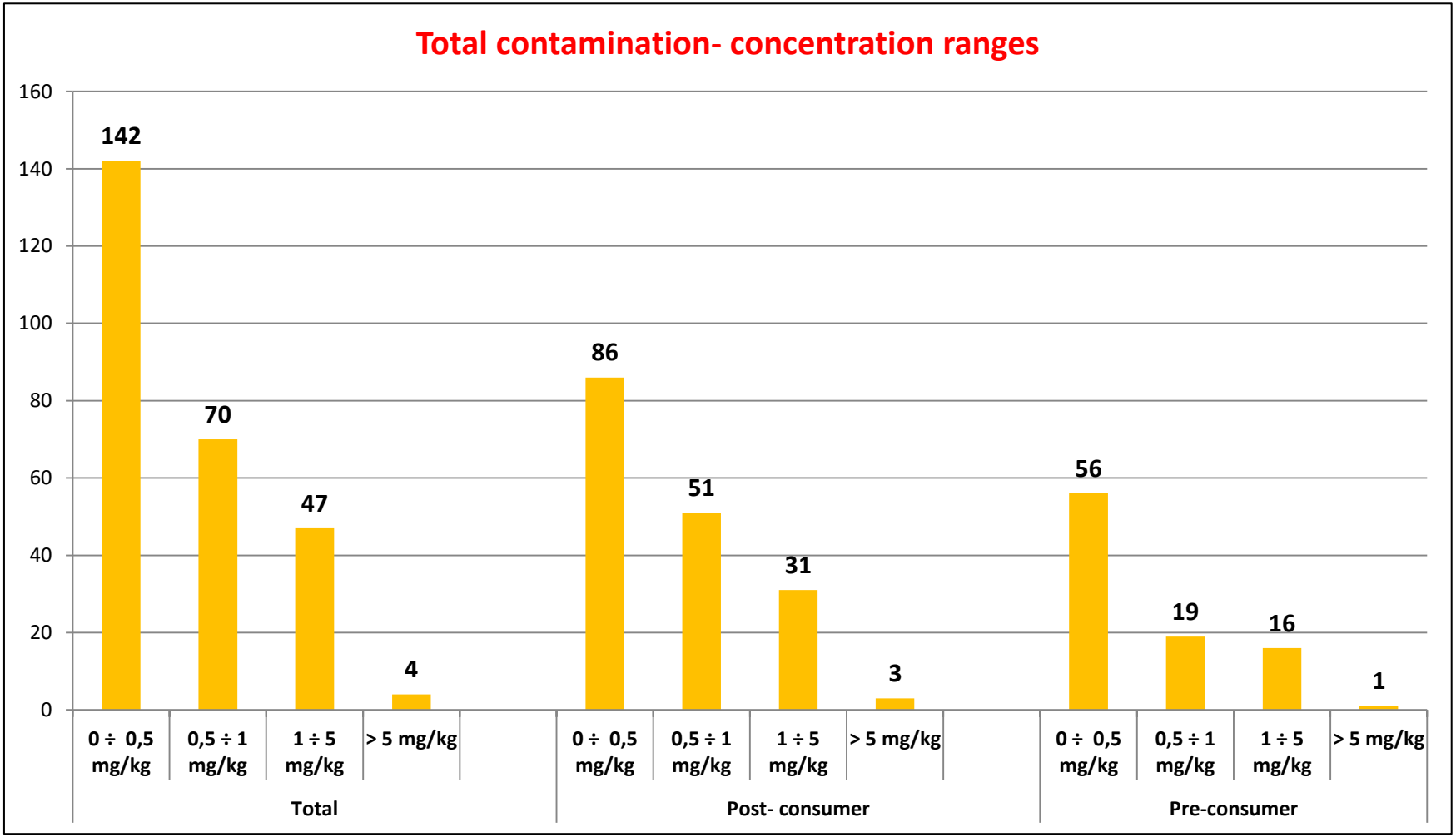

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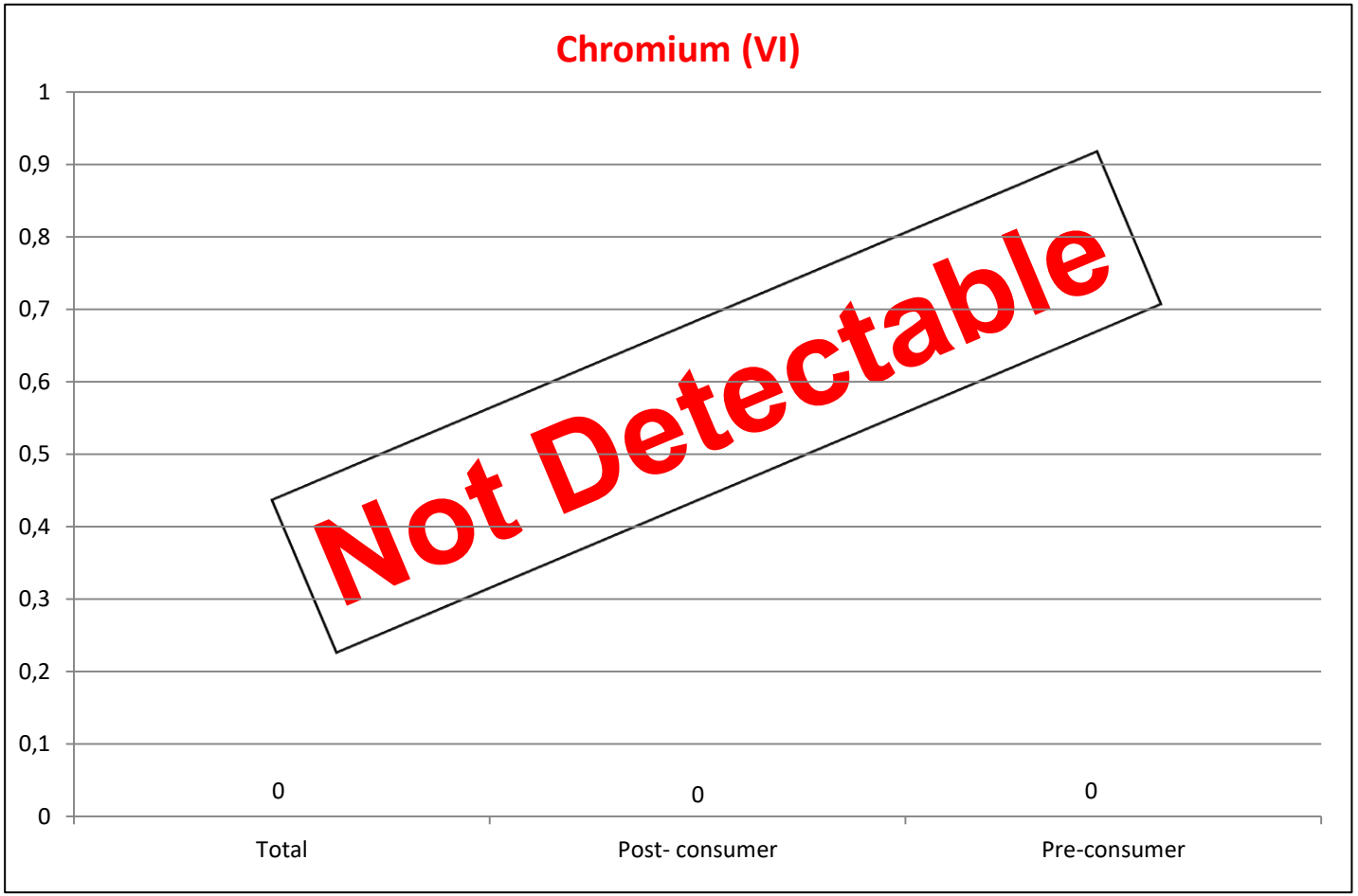
HEXAVALENT CHROMIUM



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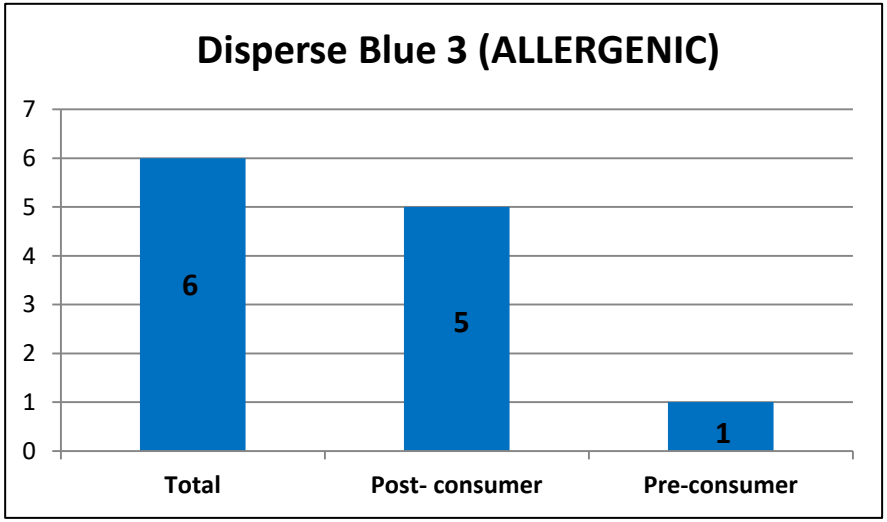
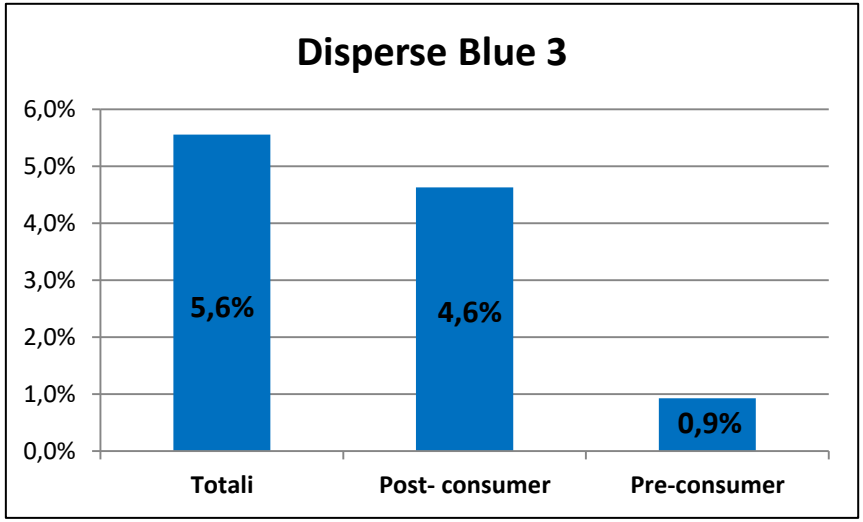
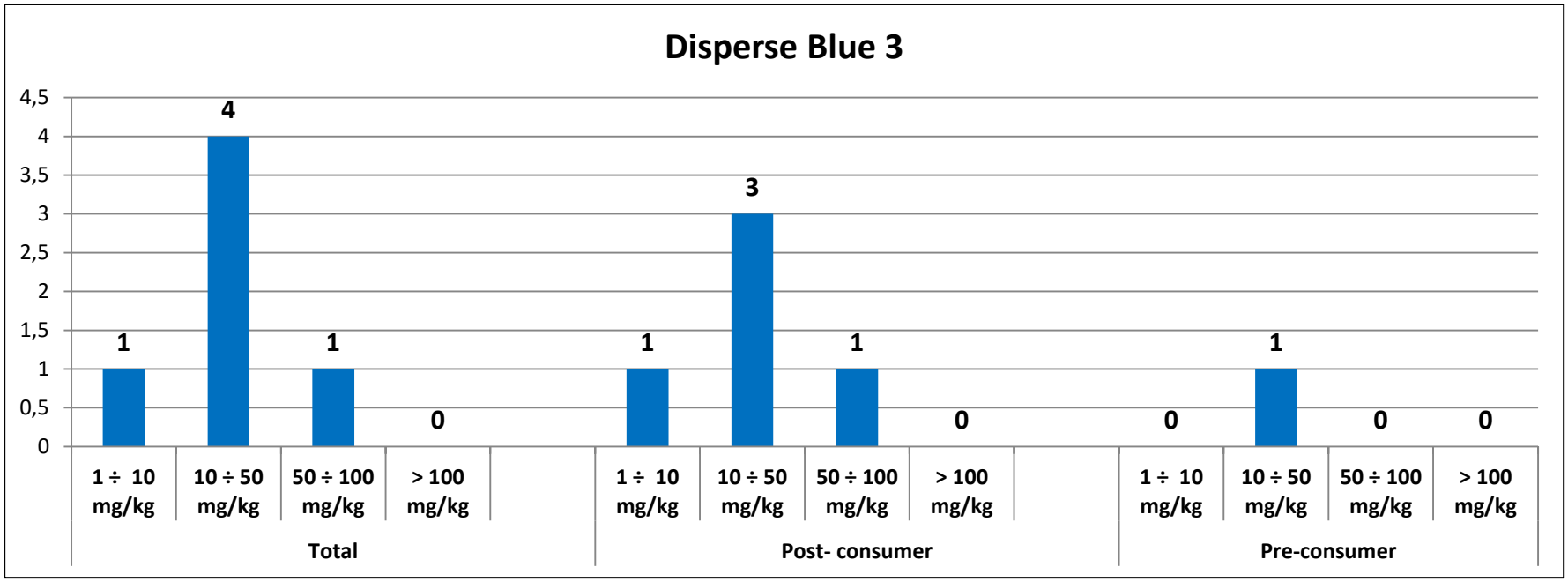
Allergenic – Carcinogenic Dyes







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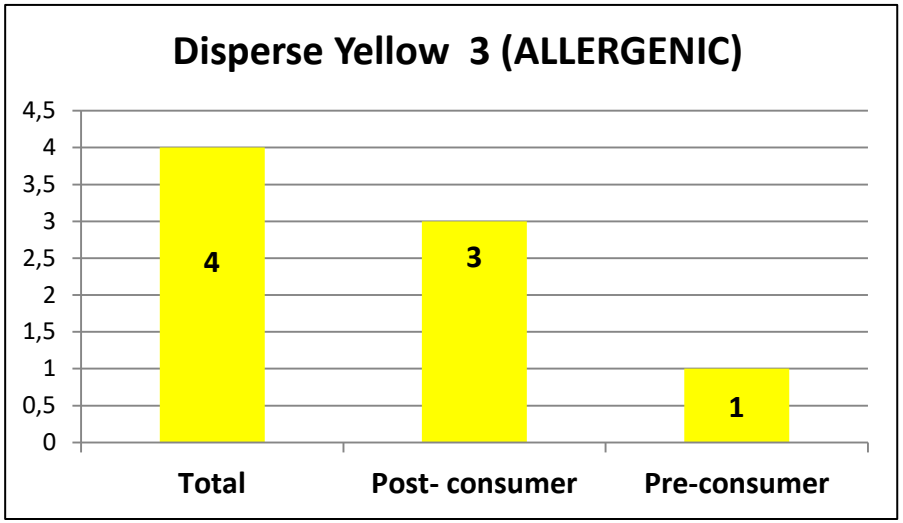
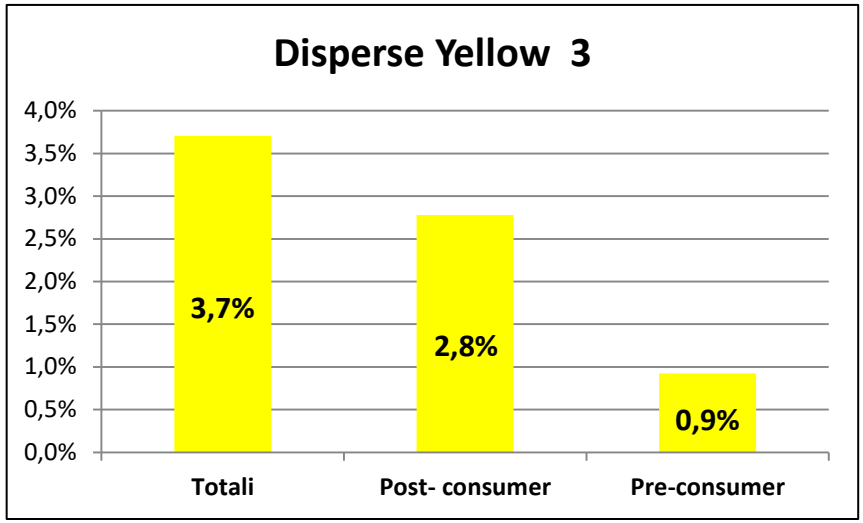
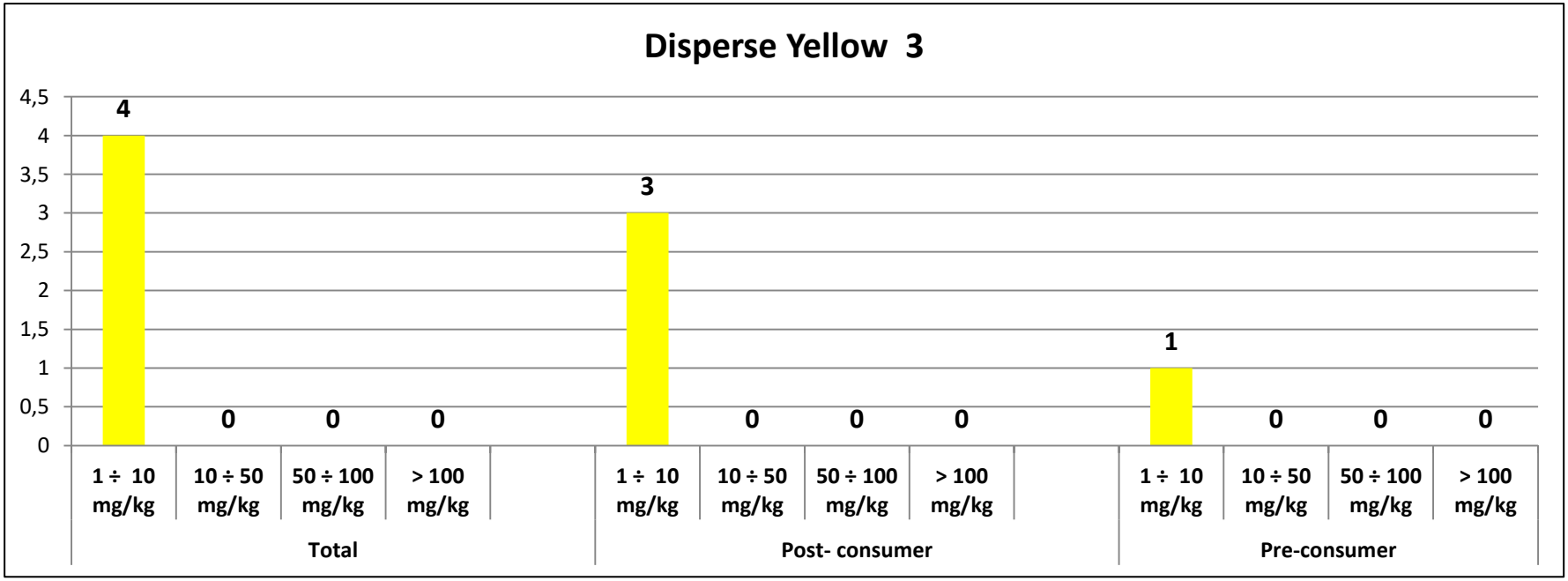
Allergenic – Carcinogenic Dyes







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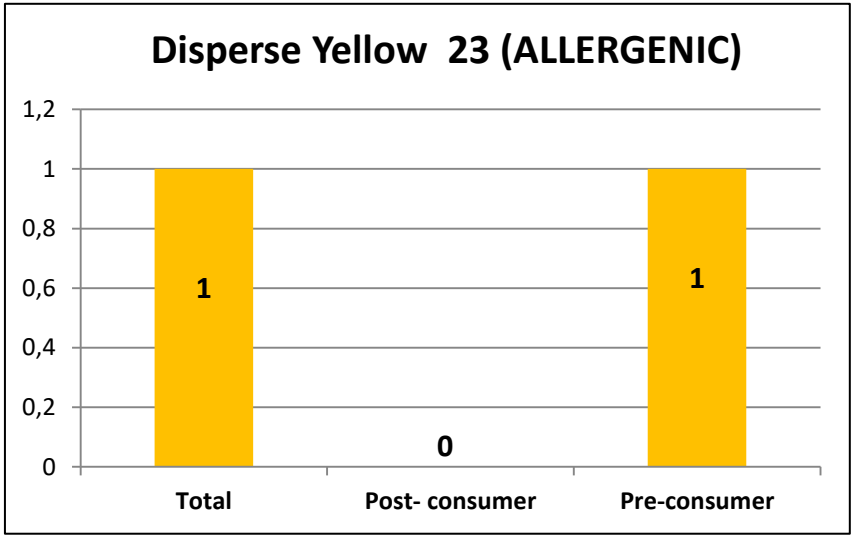
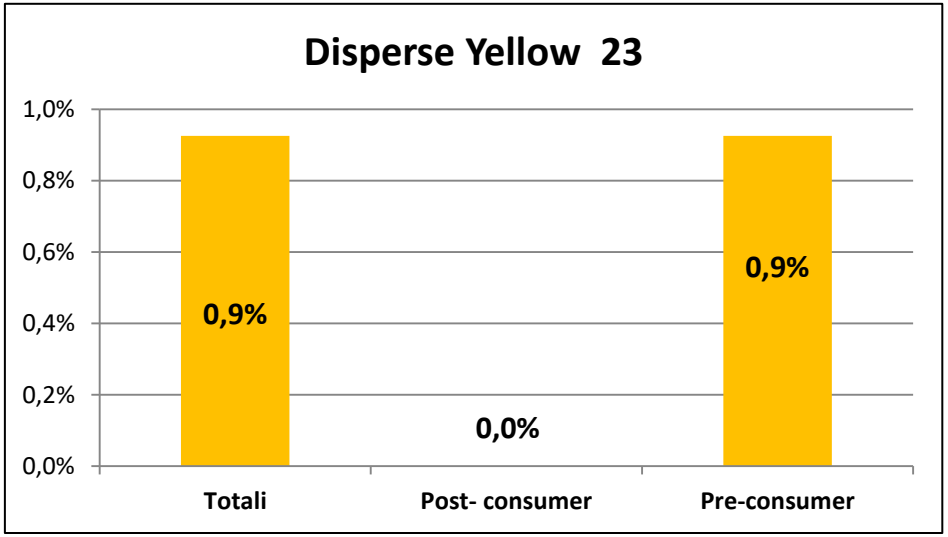
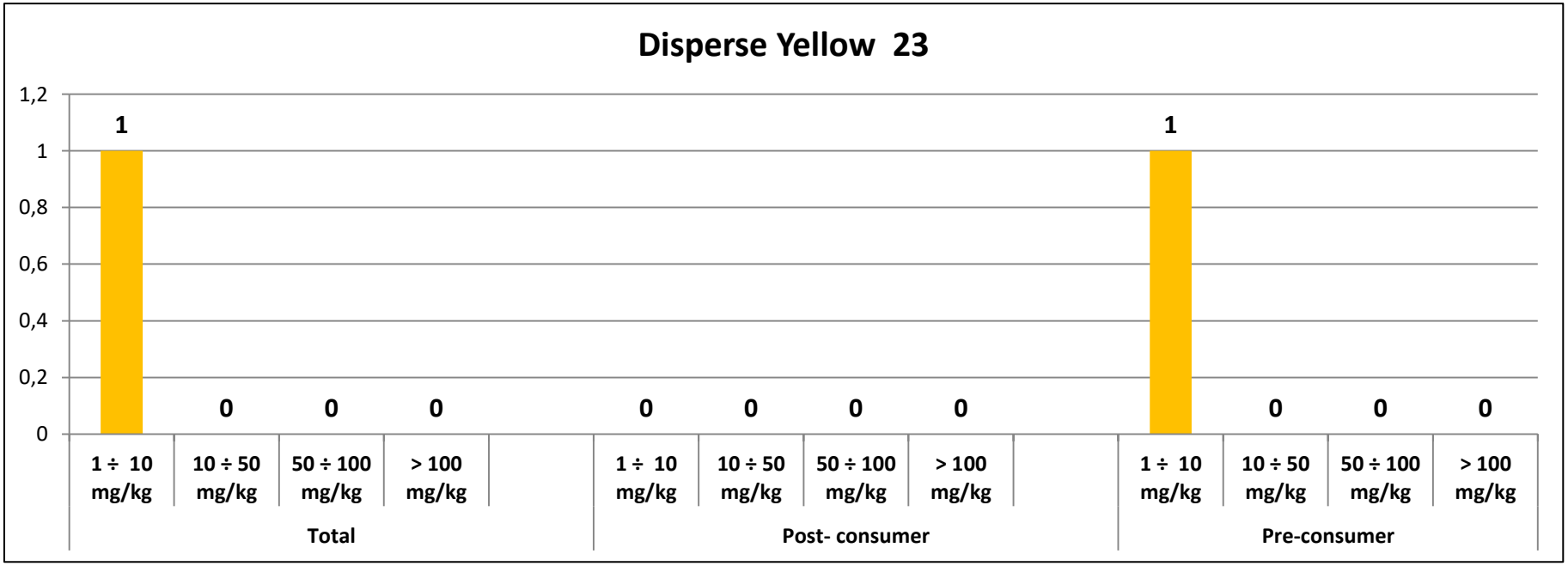
Allergenic – Carcinogenic Dyes







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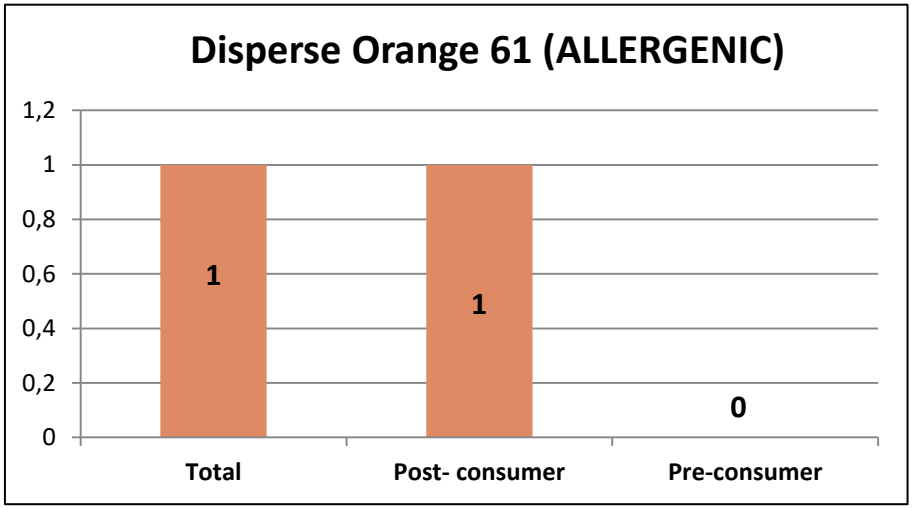
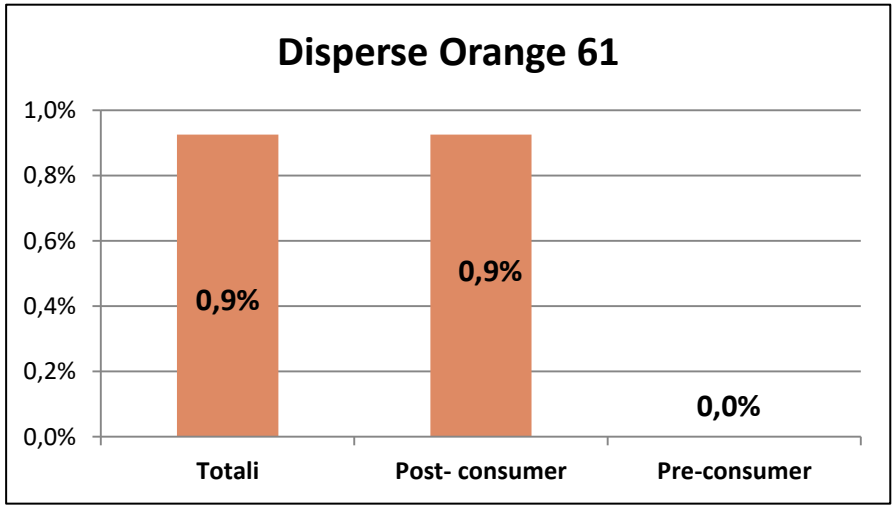
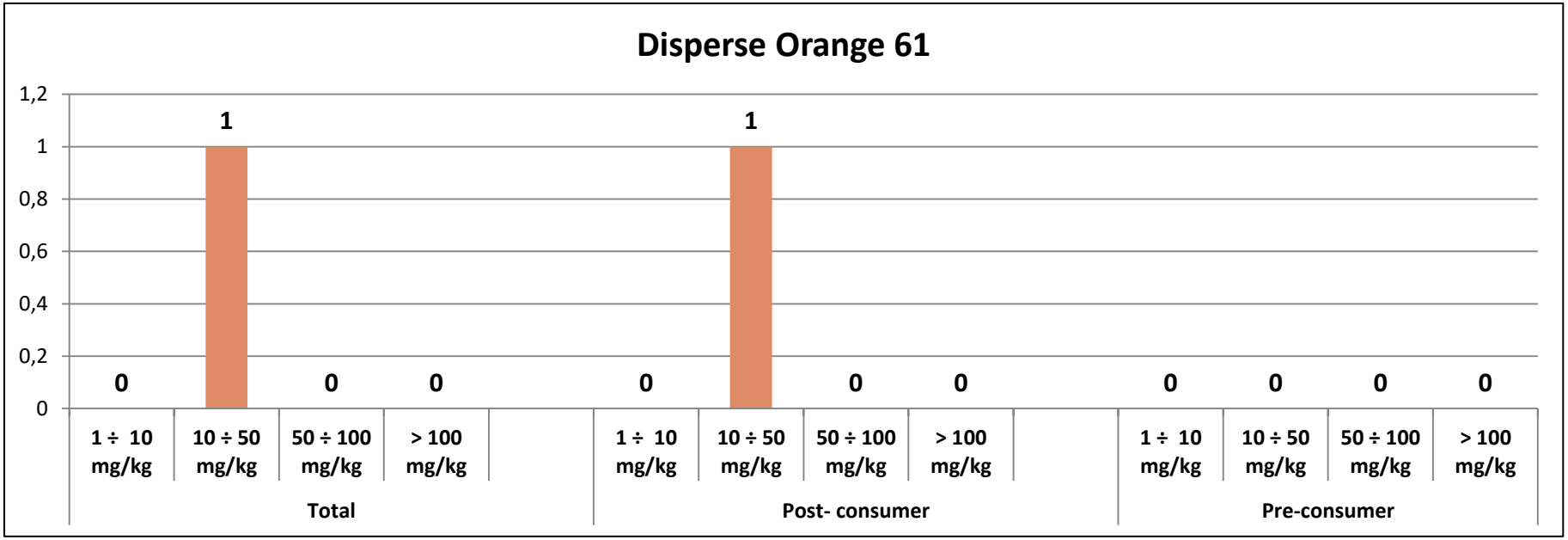
Allergenic – Carcinogenic Dyes







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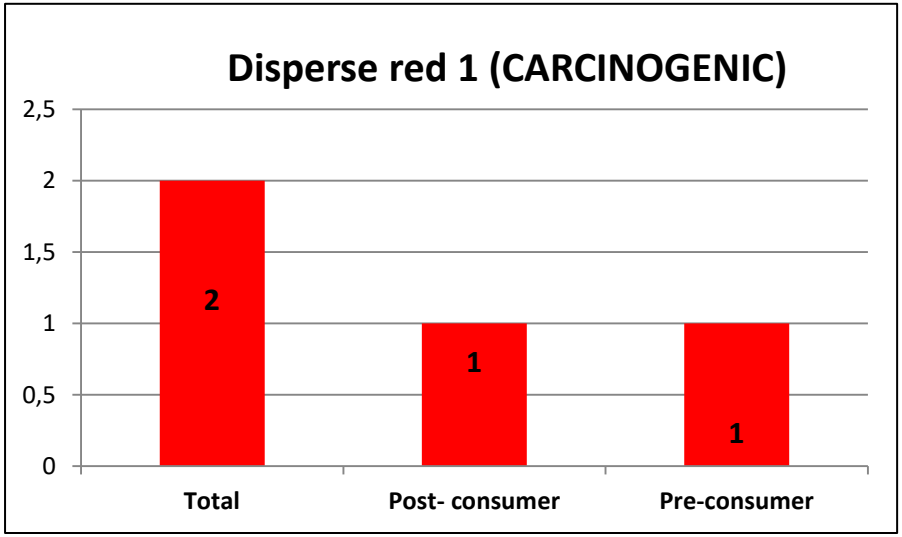
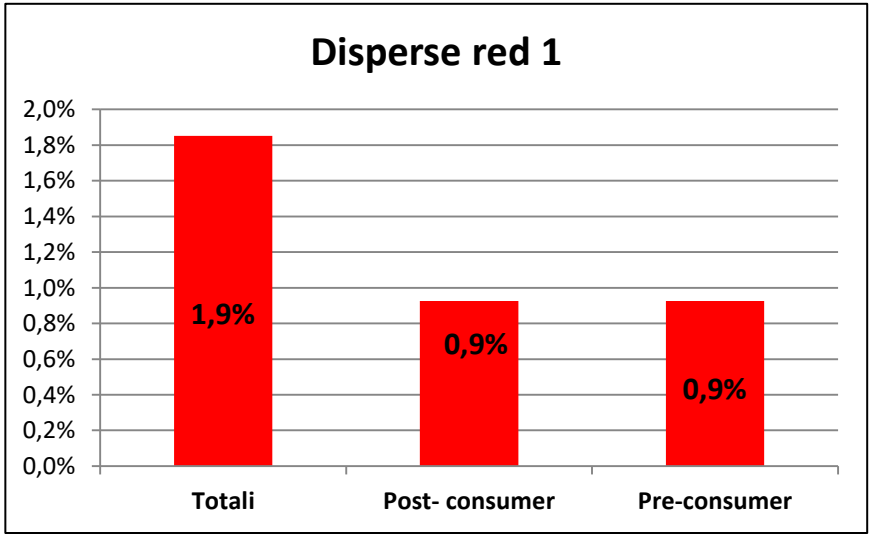
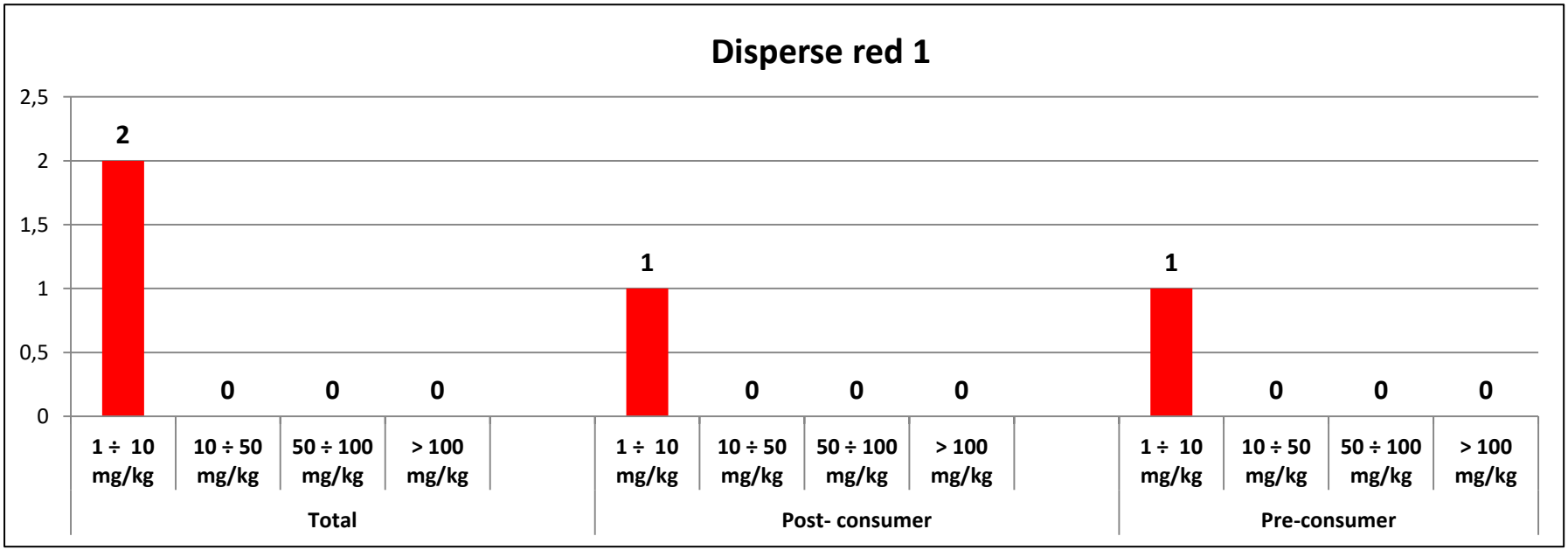
Allergenic – Carcinogenic Dyes







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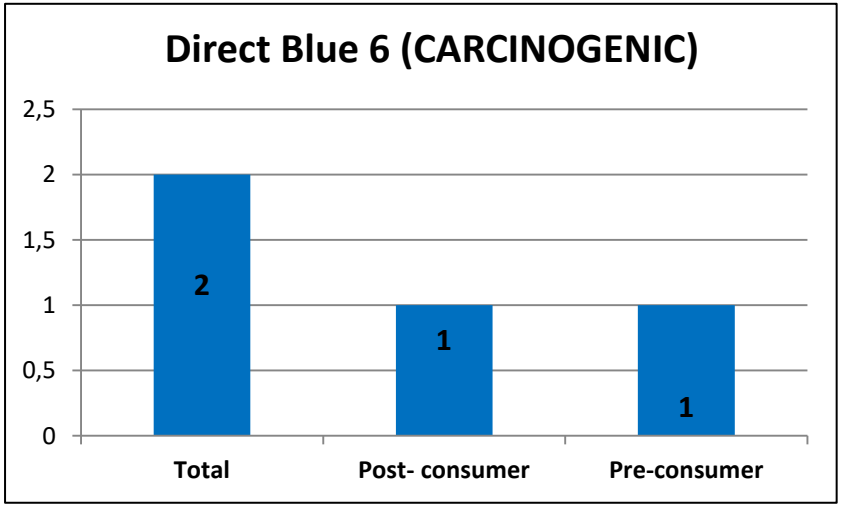
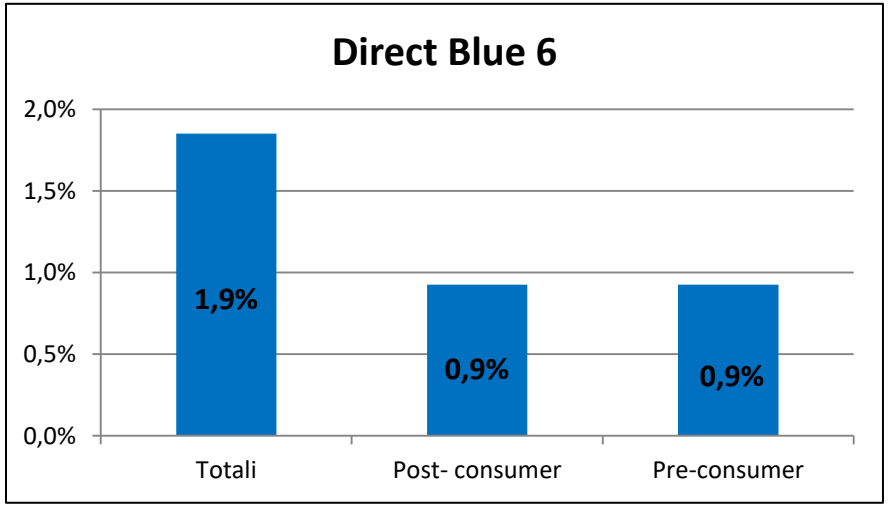
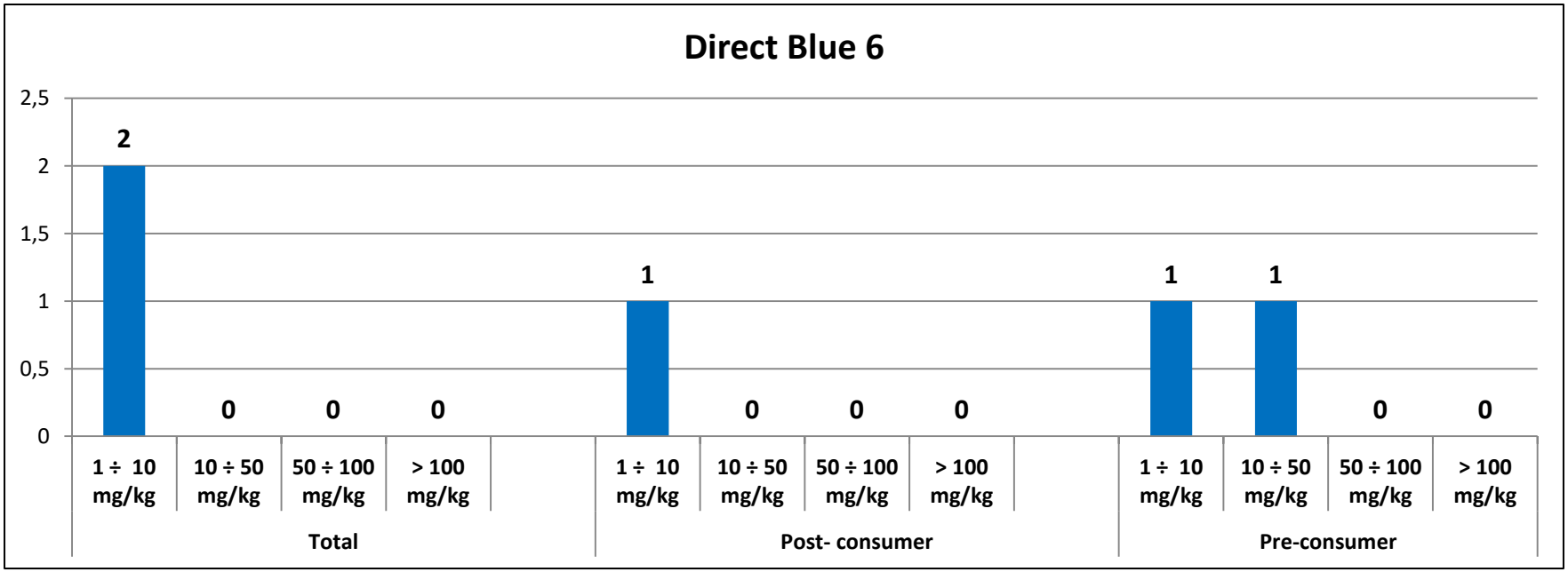
Allergenic – Carcinogenic Dyes







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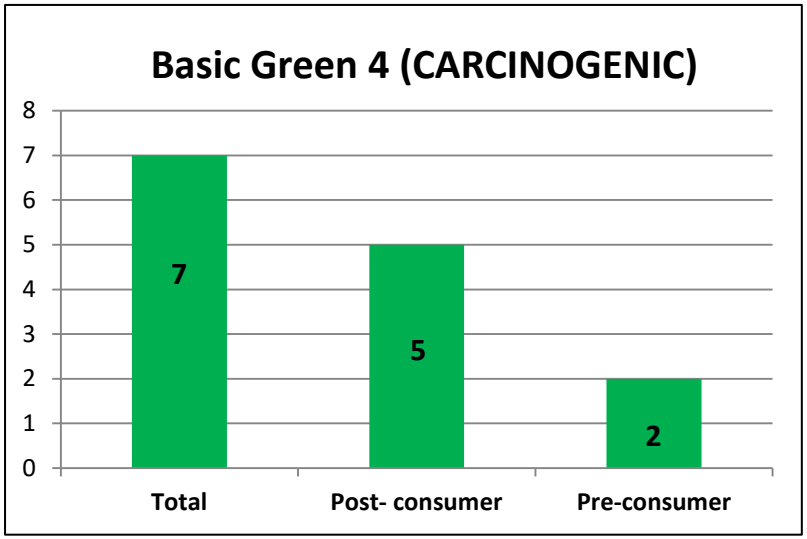
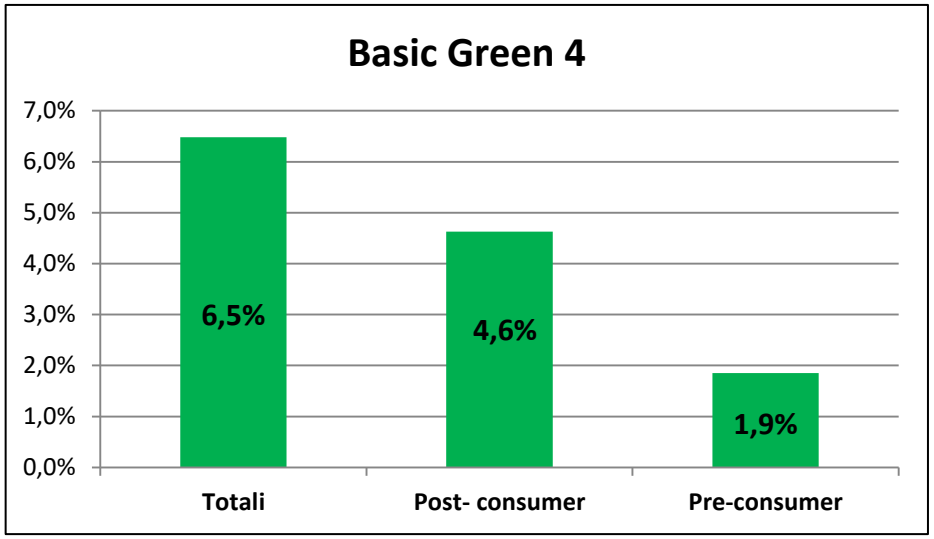
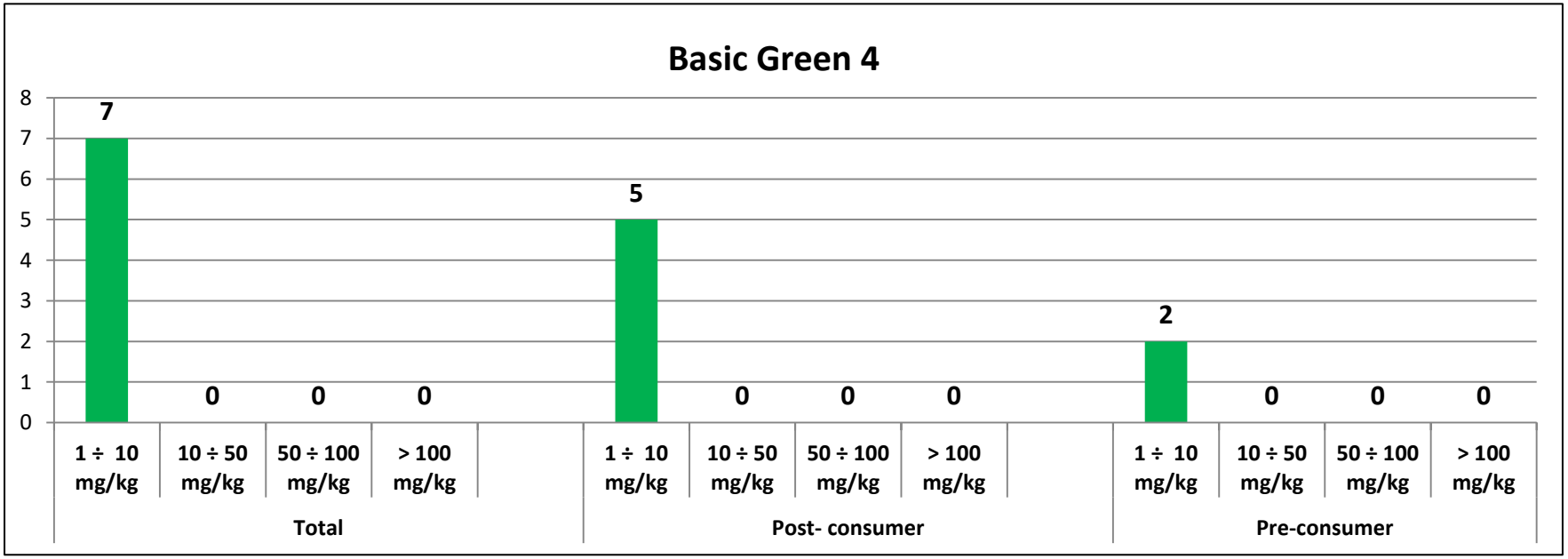
Allergenic – Carcinogenic Dyes







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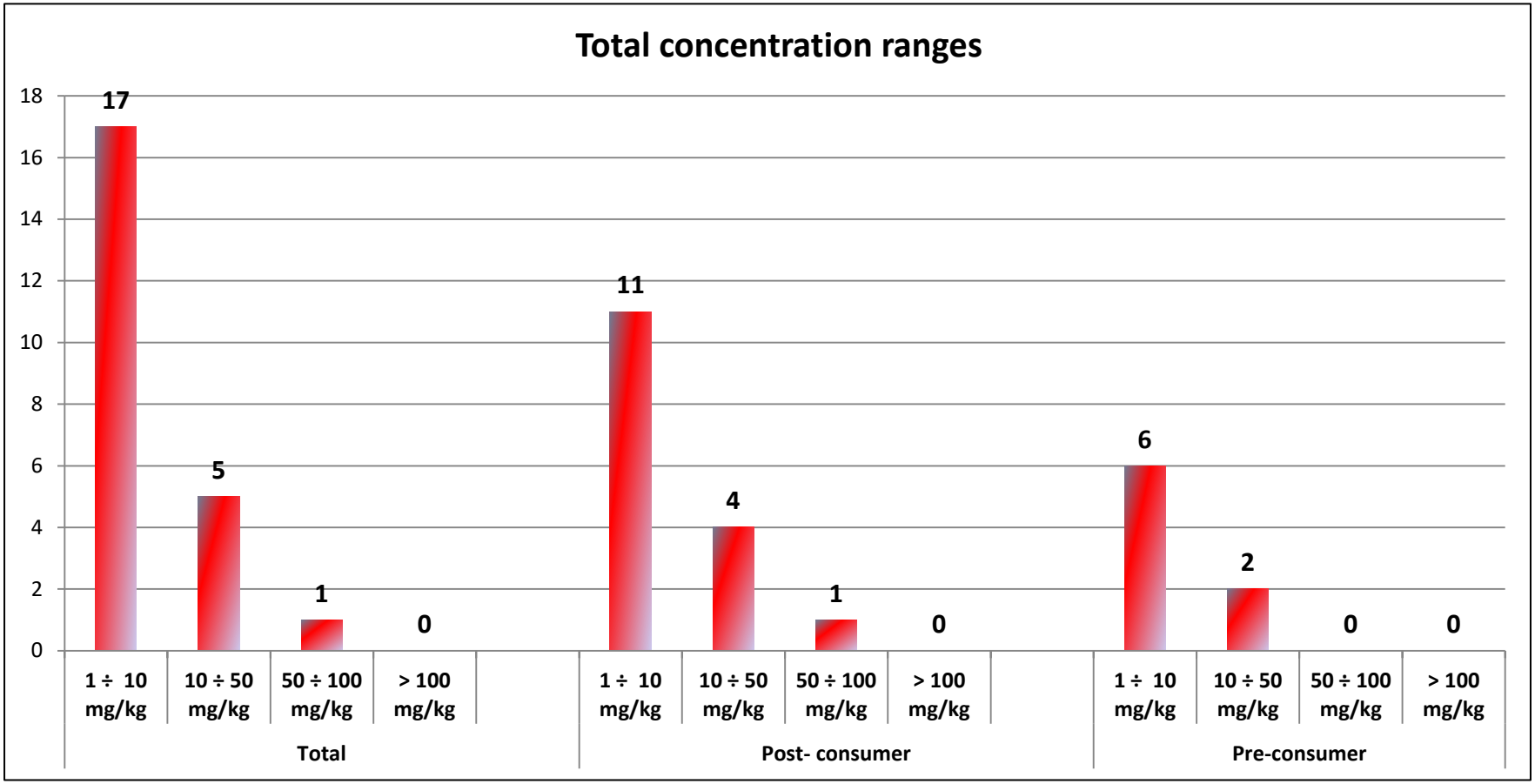
Allergenic – Carcinogenic Dyes



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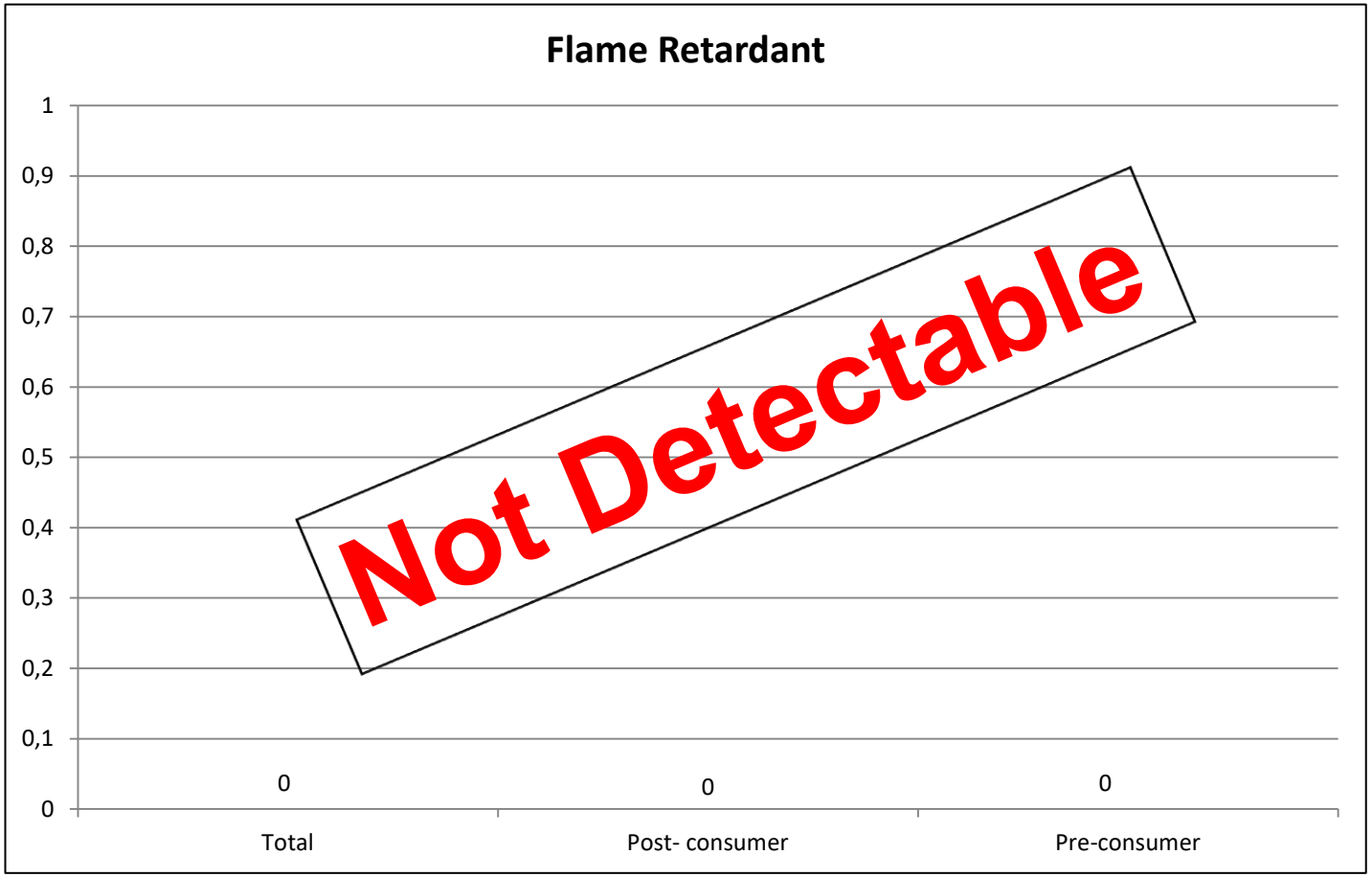
Brominated and Chlorinated FLAME RETARDANT



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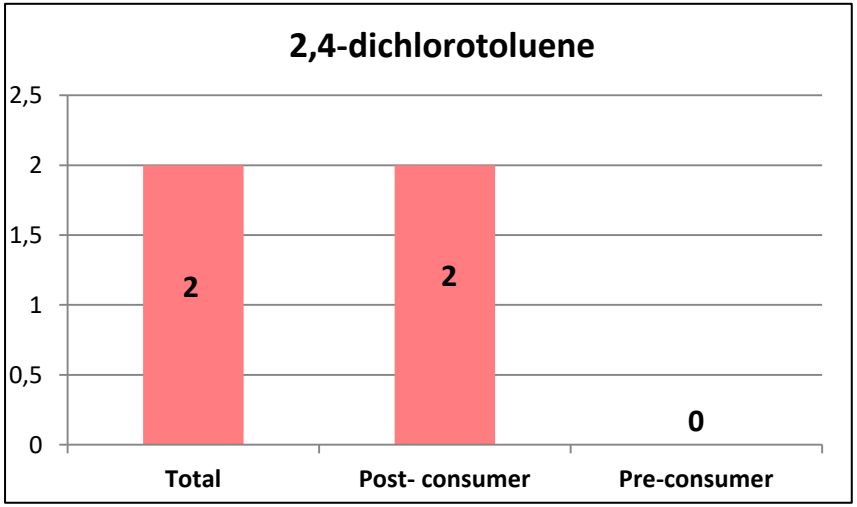
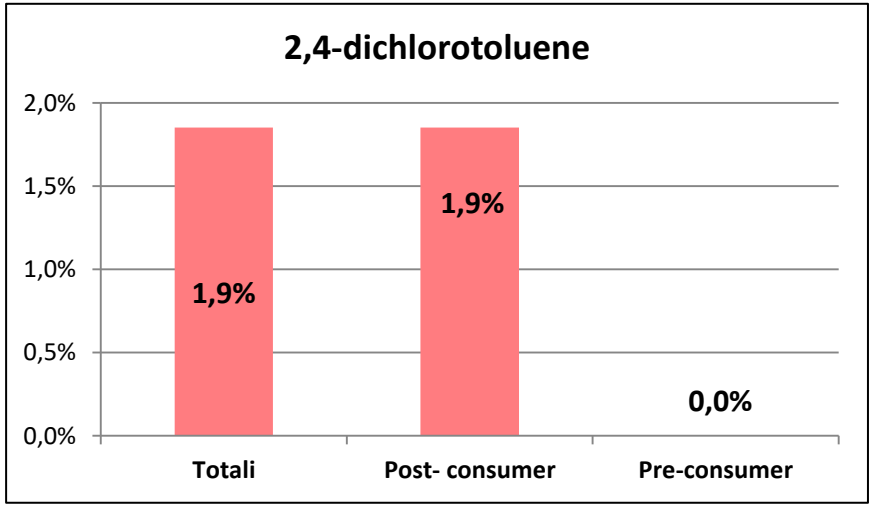
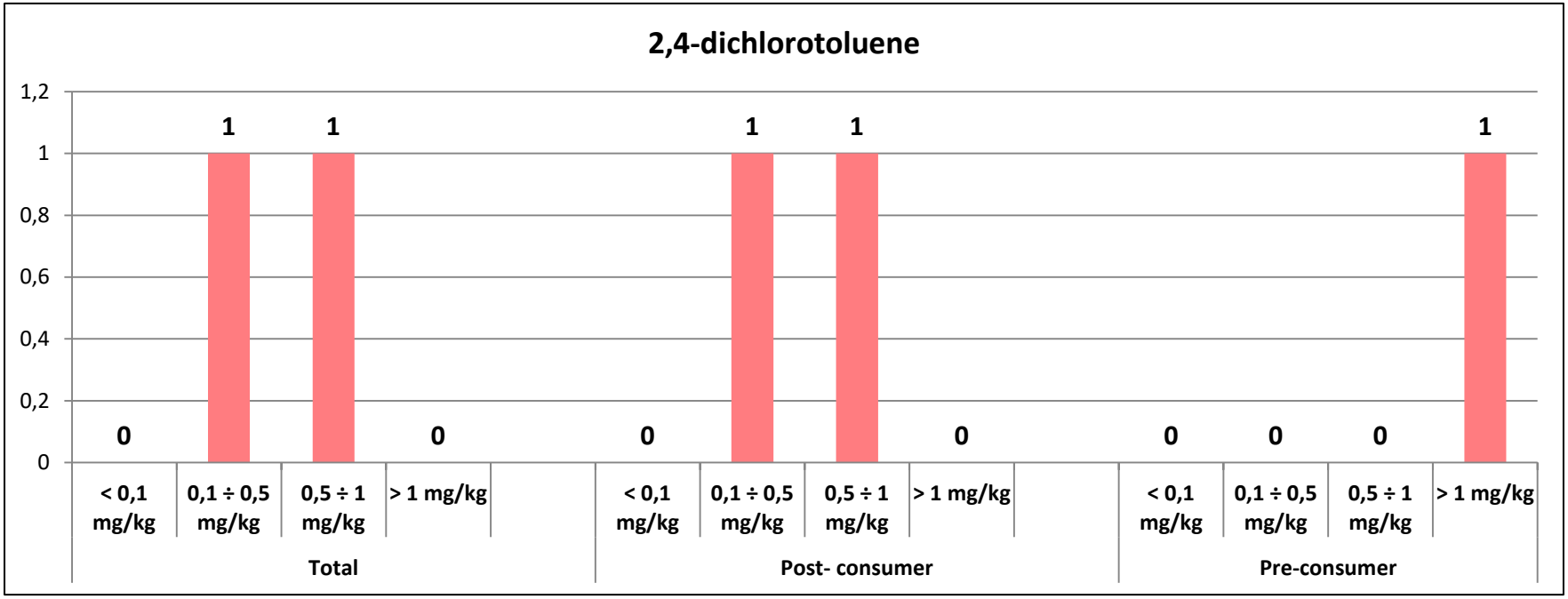
Chlorobenzenes and Toluenes (Carriers)







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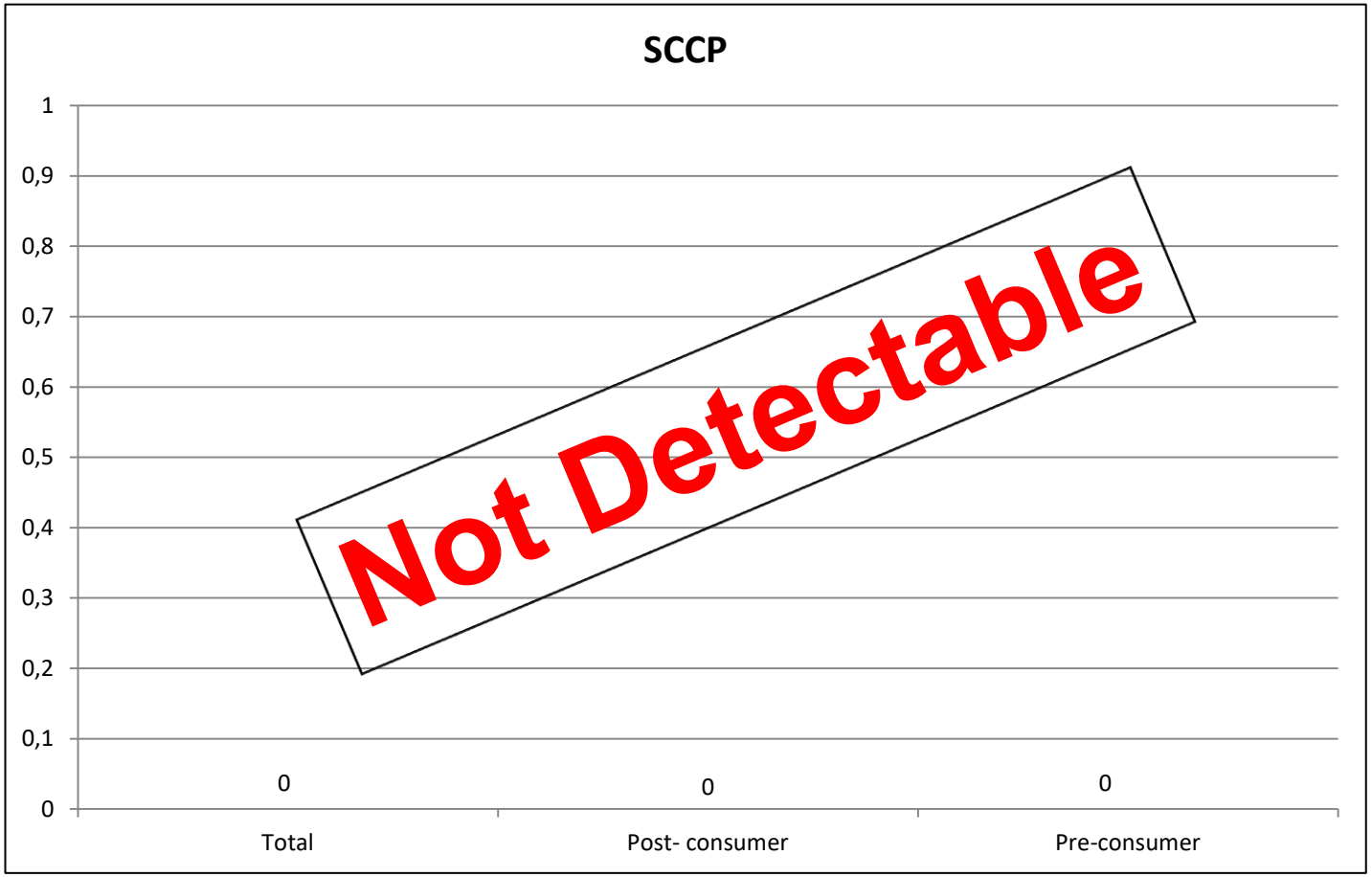
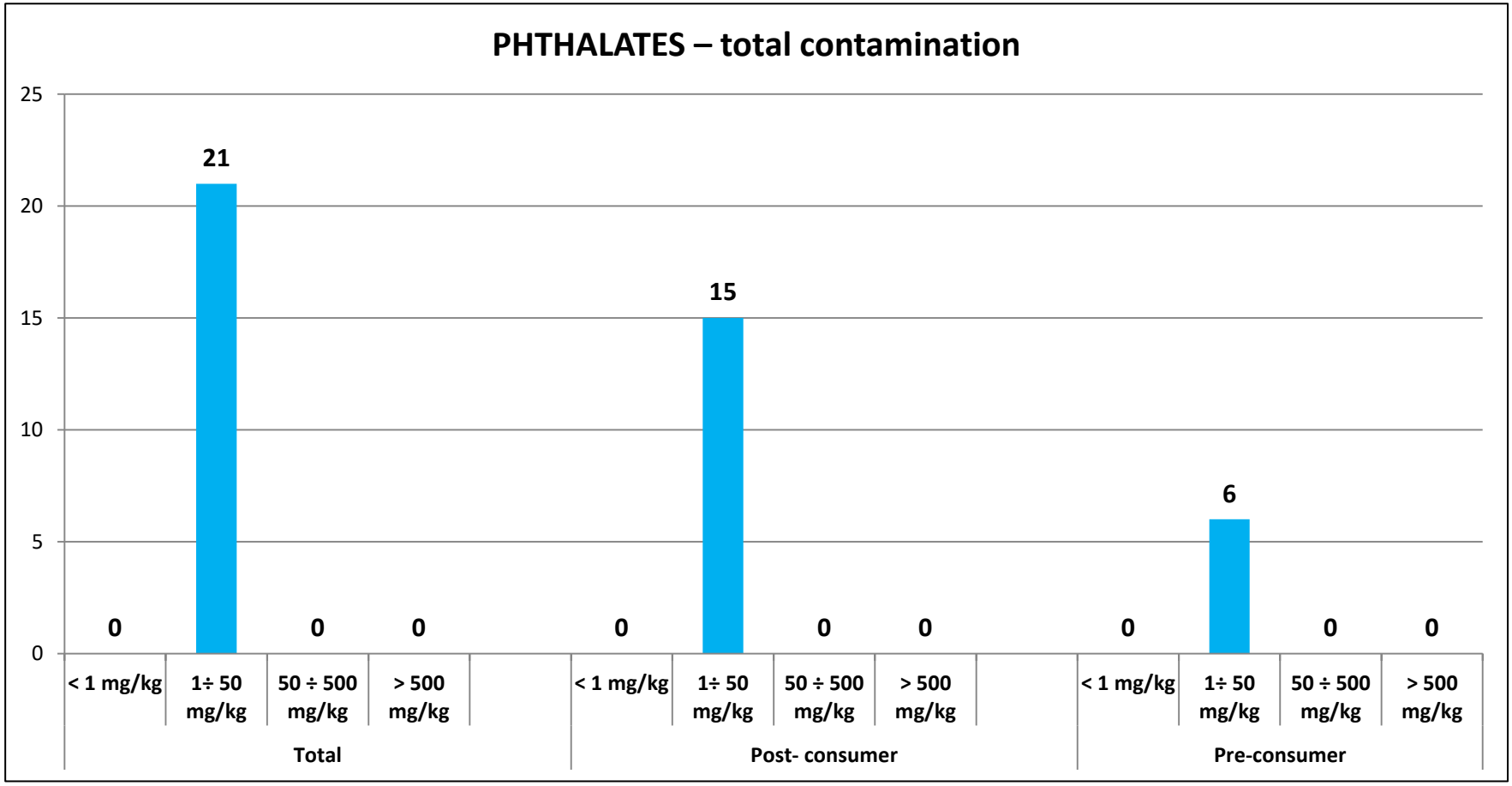
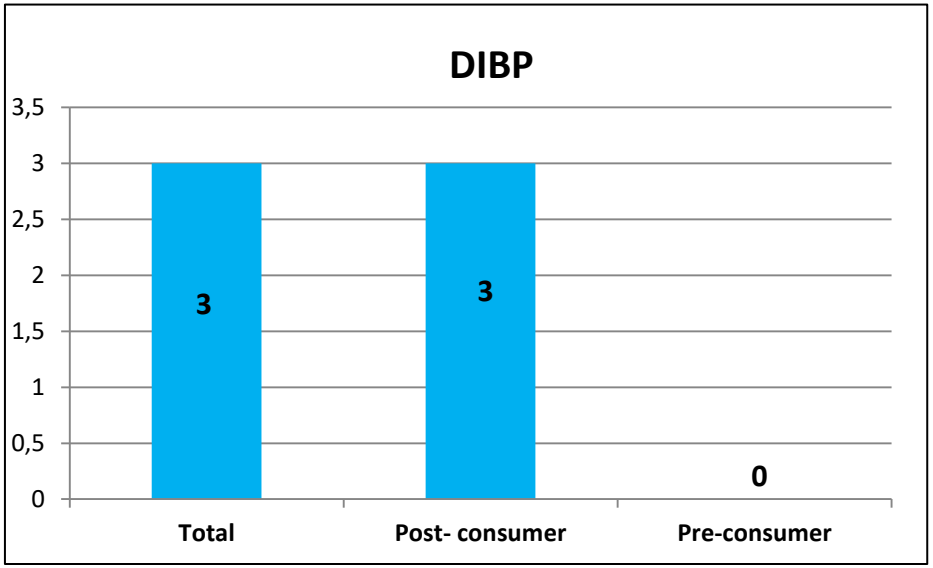
Chlorinated Paraffins (SCCP)

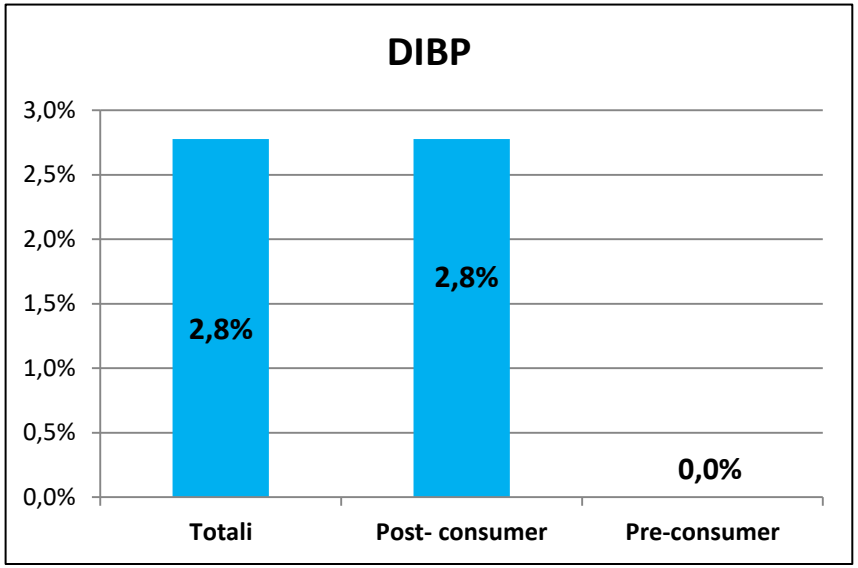


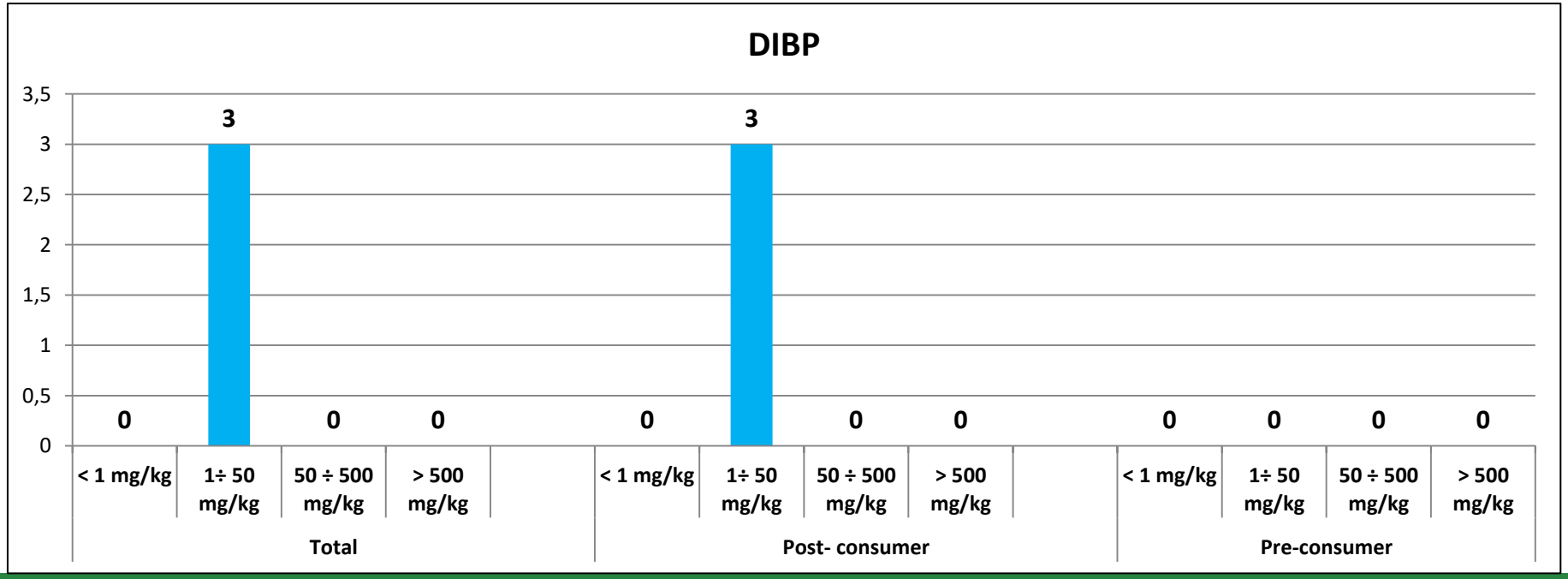
PHTHALATES


PHTHALATES – total contamination
25
20
15
10
5
0
21
15
6
0
0
0
0
0
0
0
0
0
< 1 mg/kg
1÷ 50 mg/kg
50 ÷ 500 mg/kg
> 500 mg/kg
Total
Post- consumer
Pre-consumer

PHTHALATES







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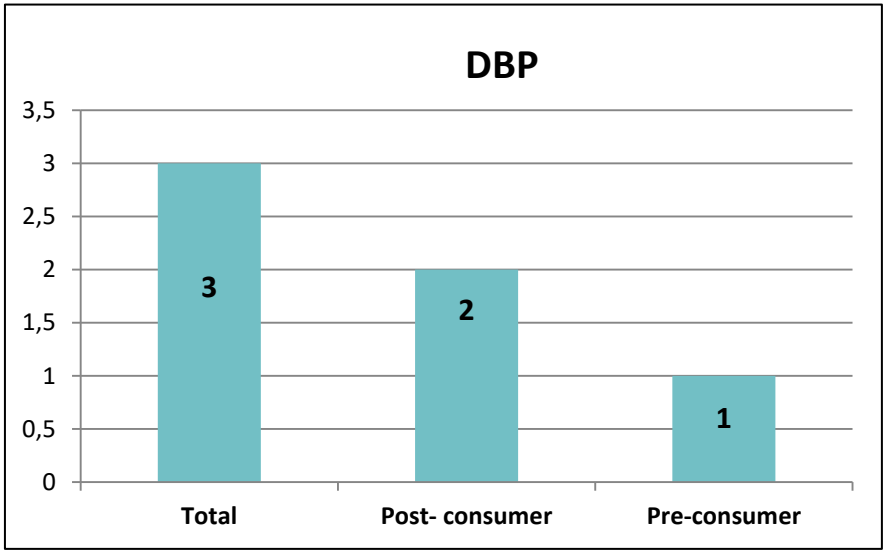

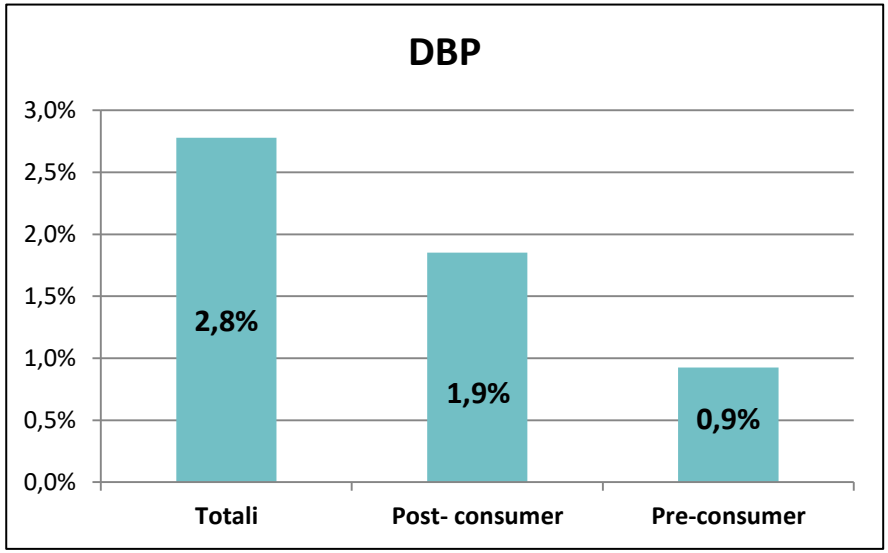

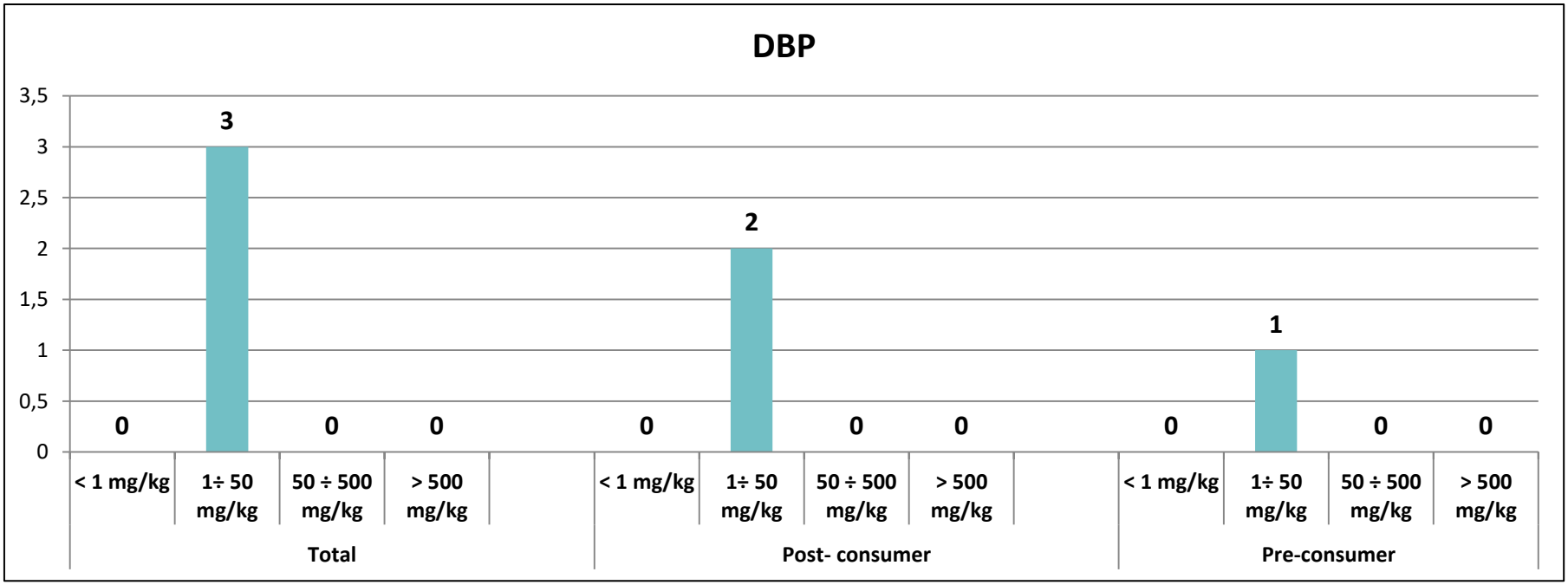

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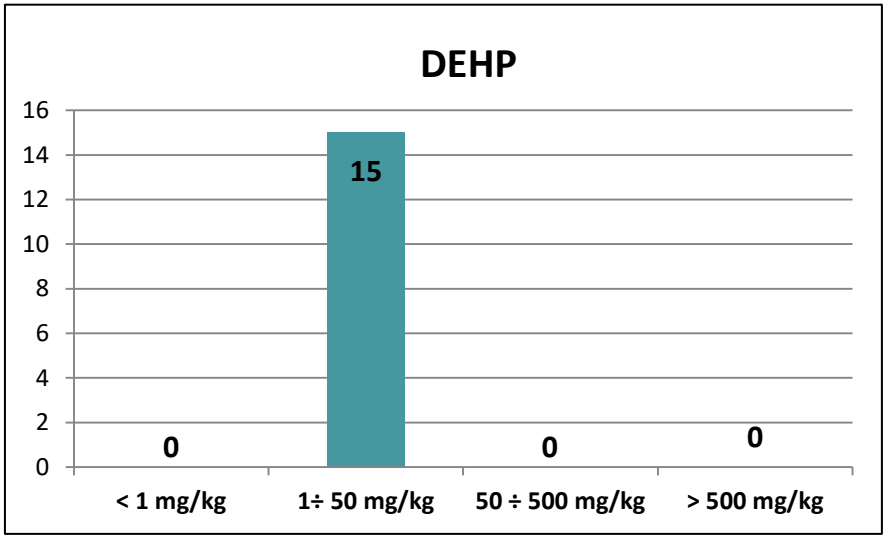
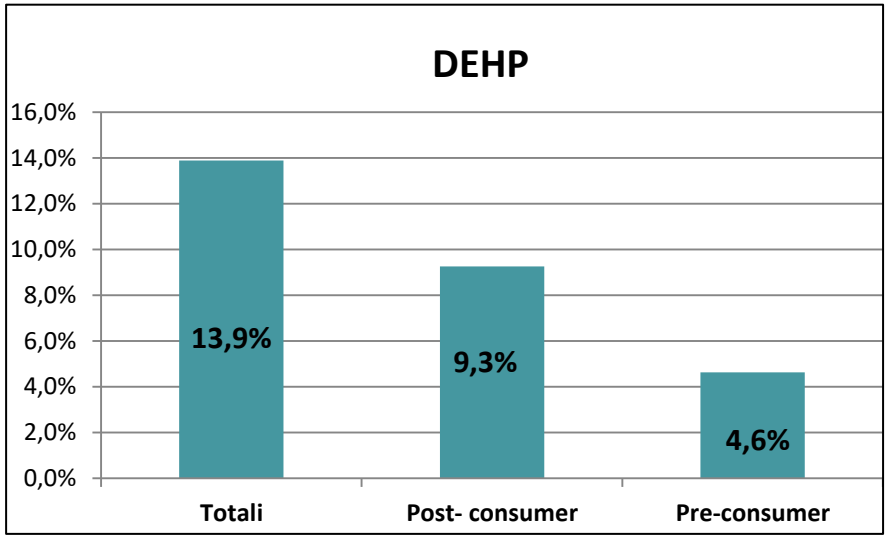
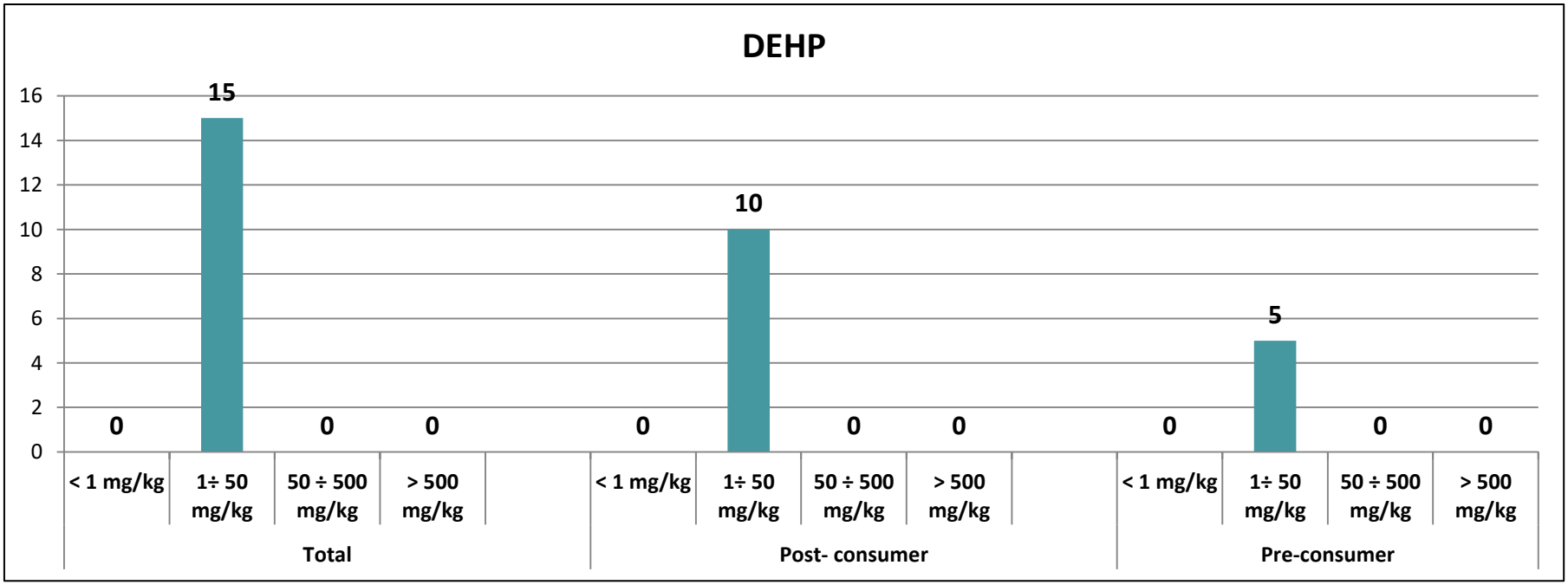
PHTHALATES







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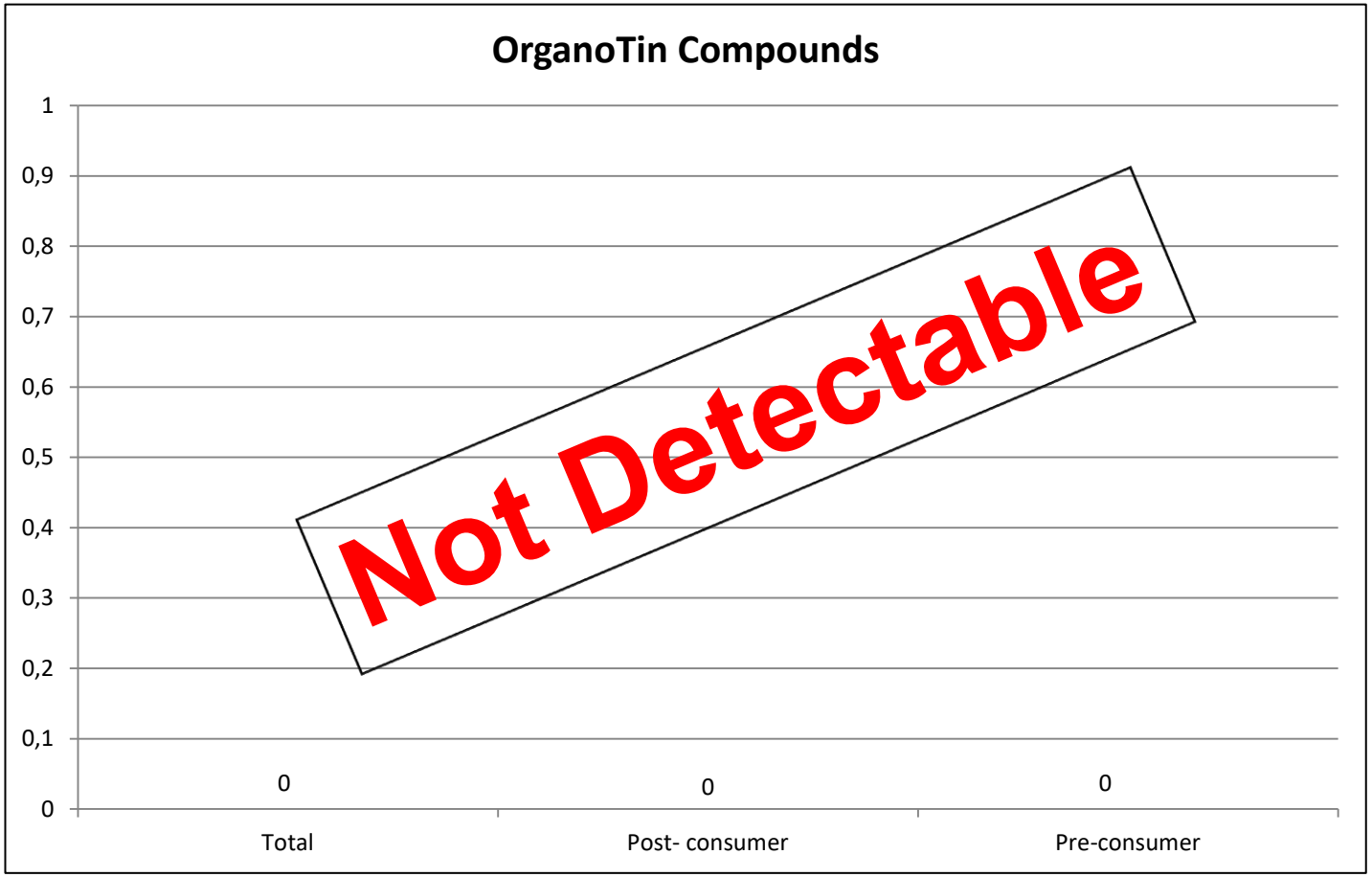
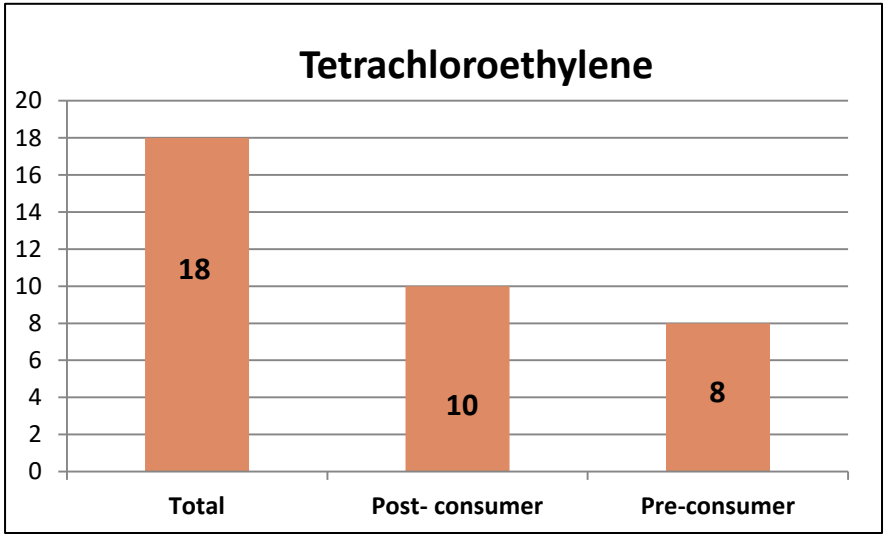
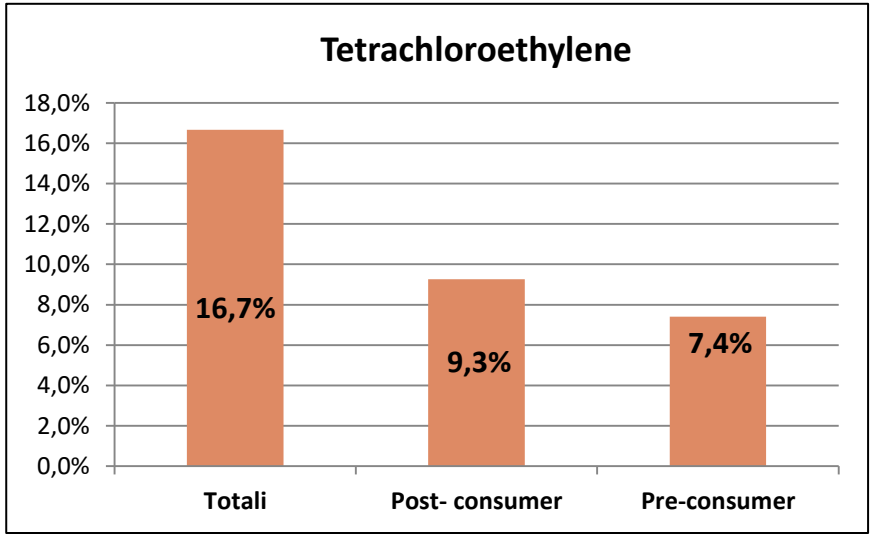
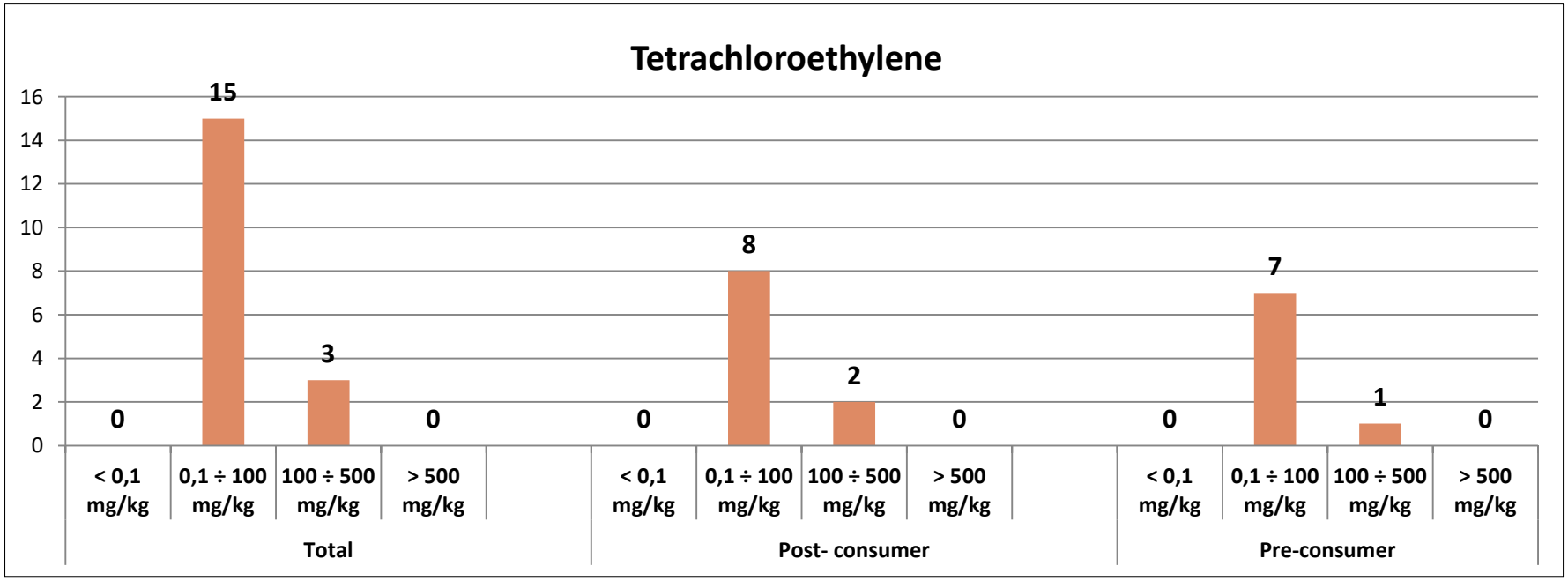
ORGANO TIN COMPOUNDS



CHLORINATED SOLVENTS







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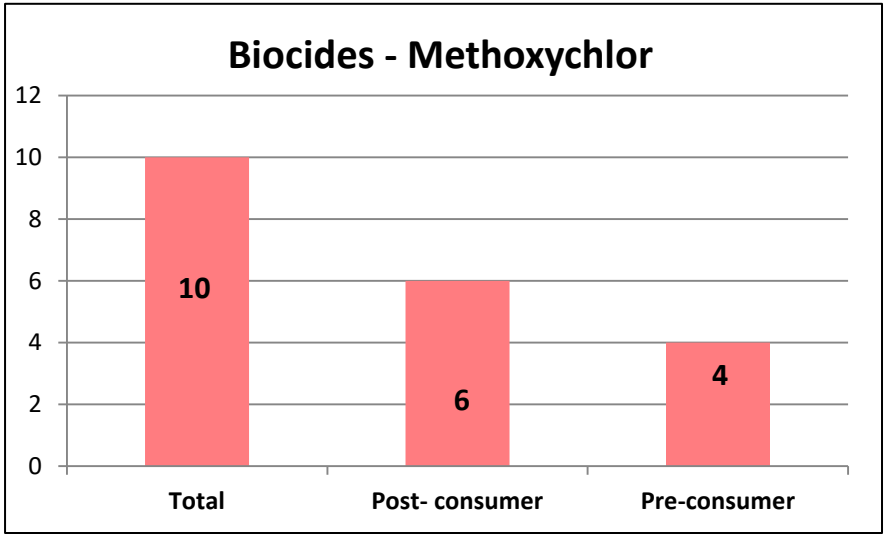
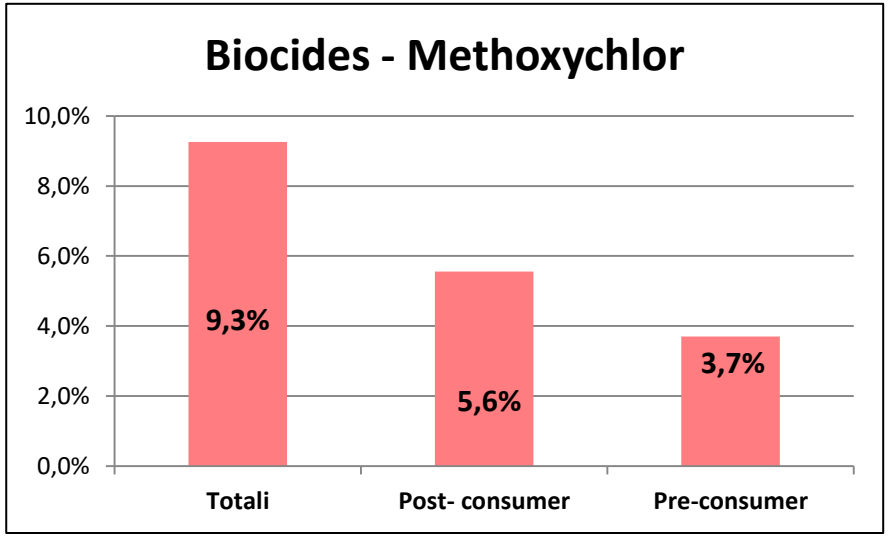
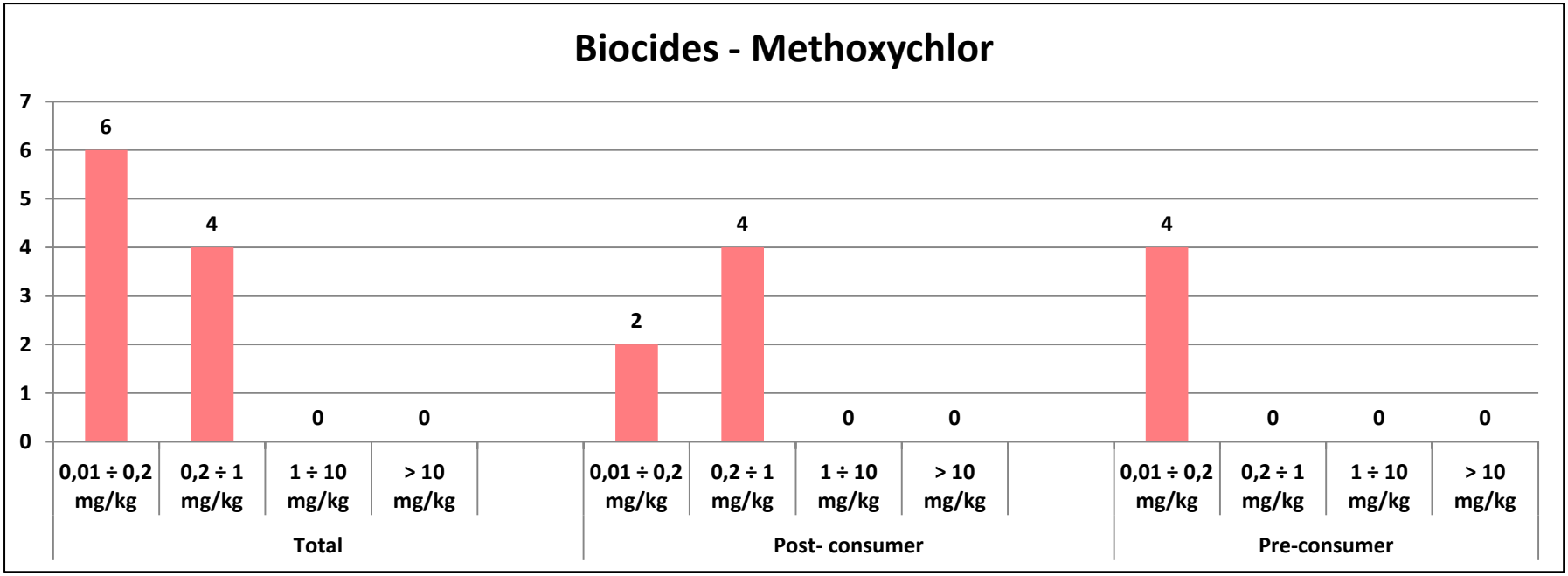
BIOCIDES / PRESERVATIVES







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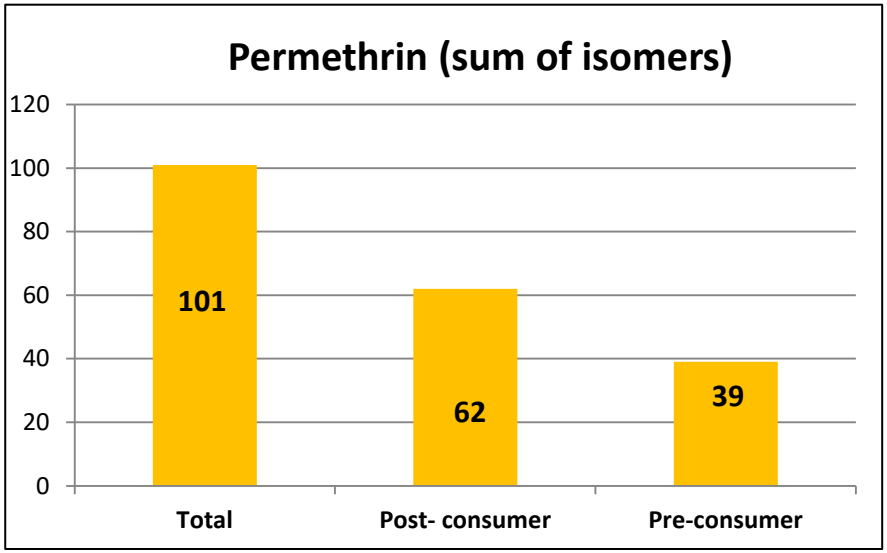

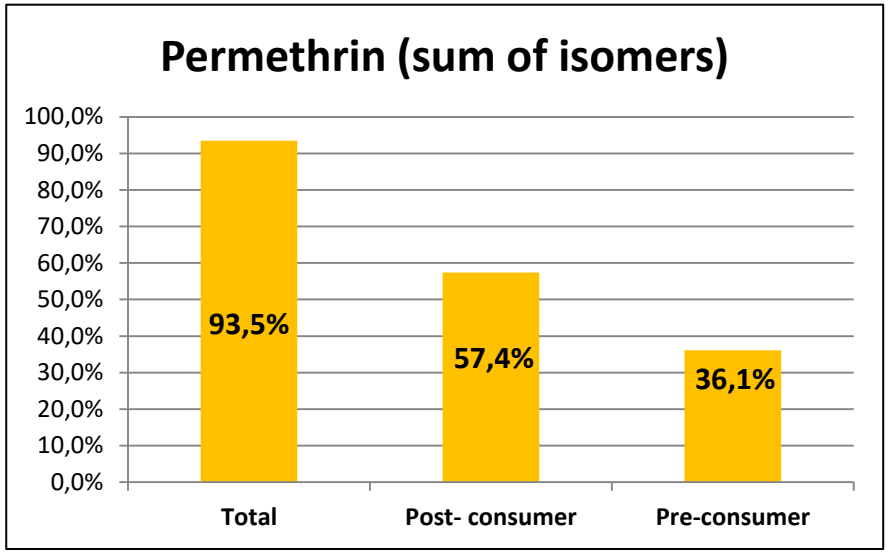

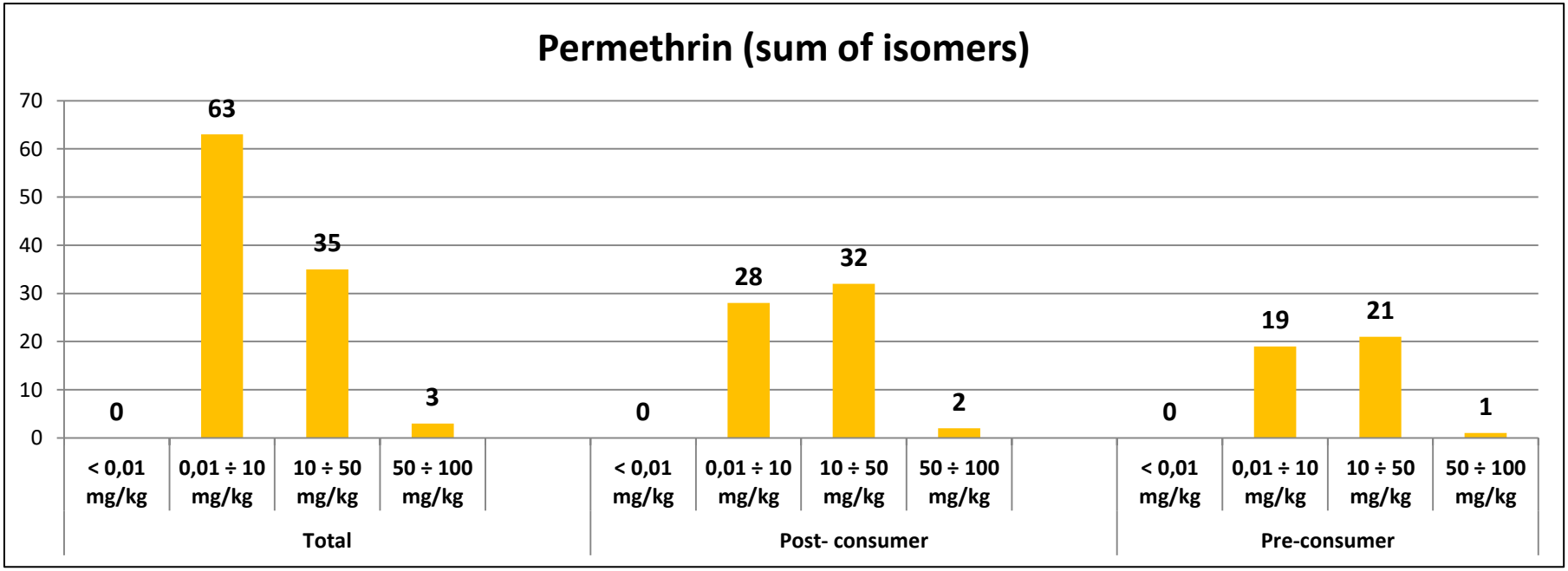

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Regenerated Materials:

Cotton-Type textiles

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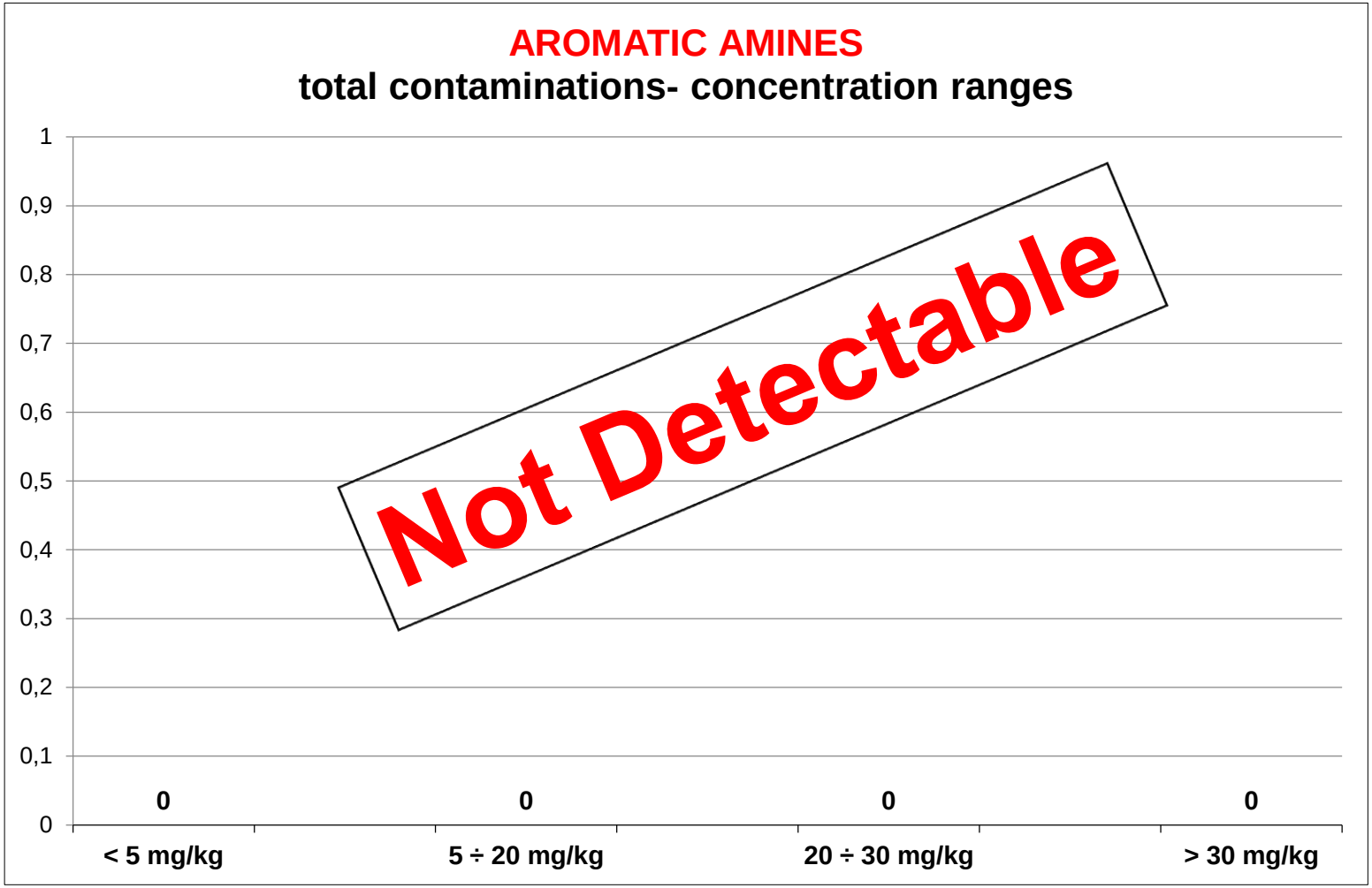
Regenerated cotton-type materials



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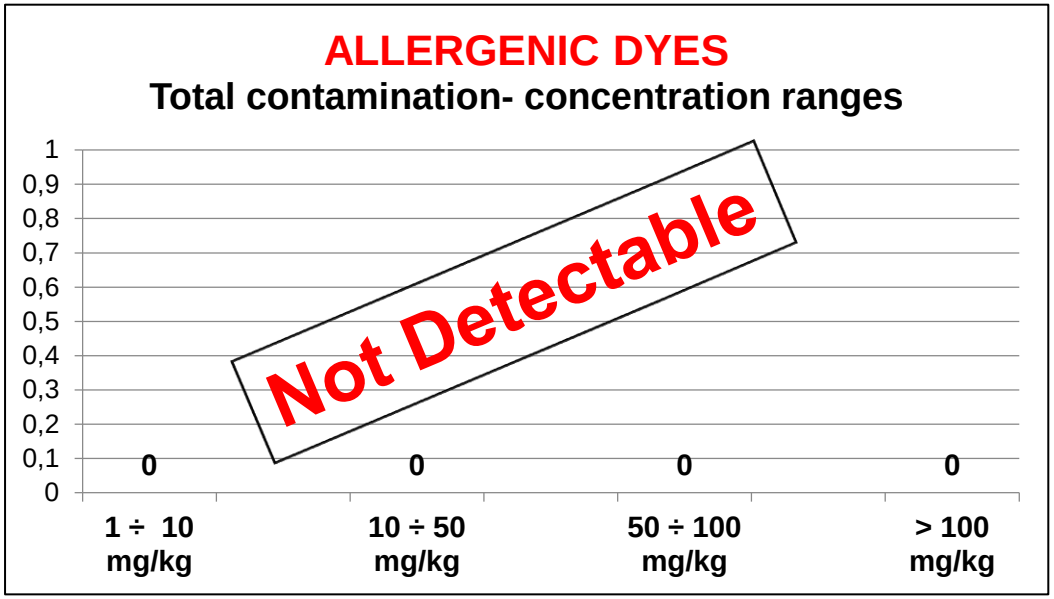
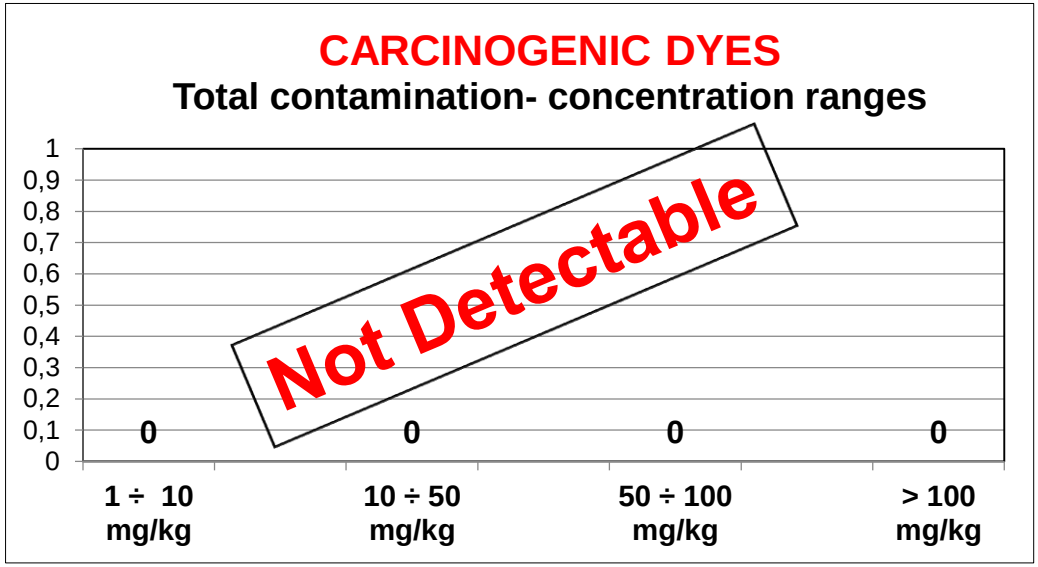
Regenerated cotton-type materials





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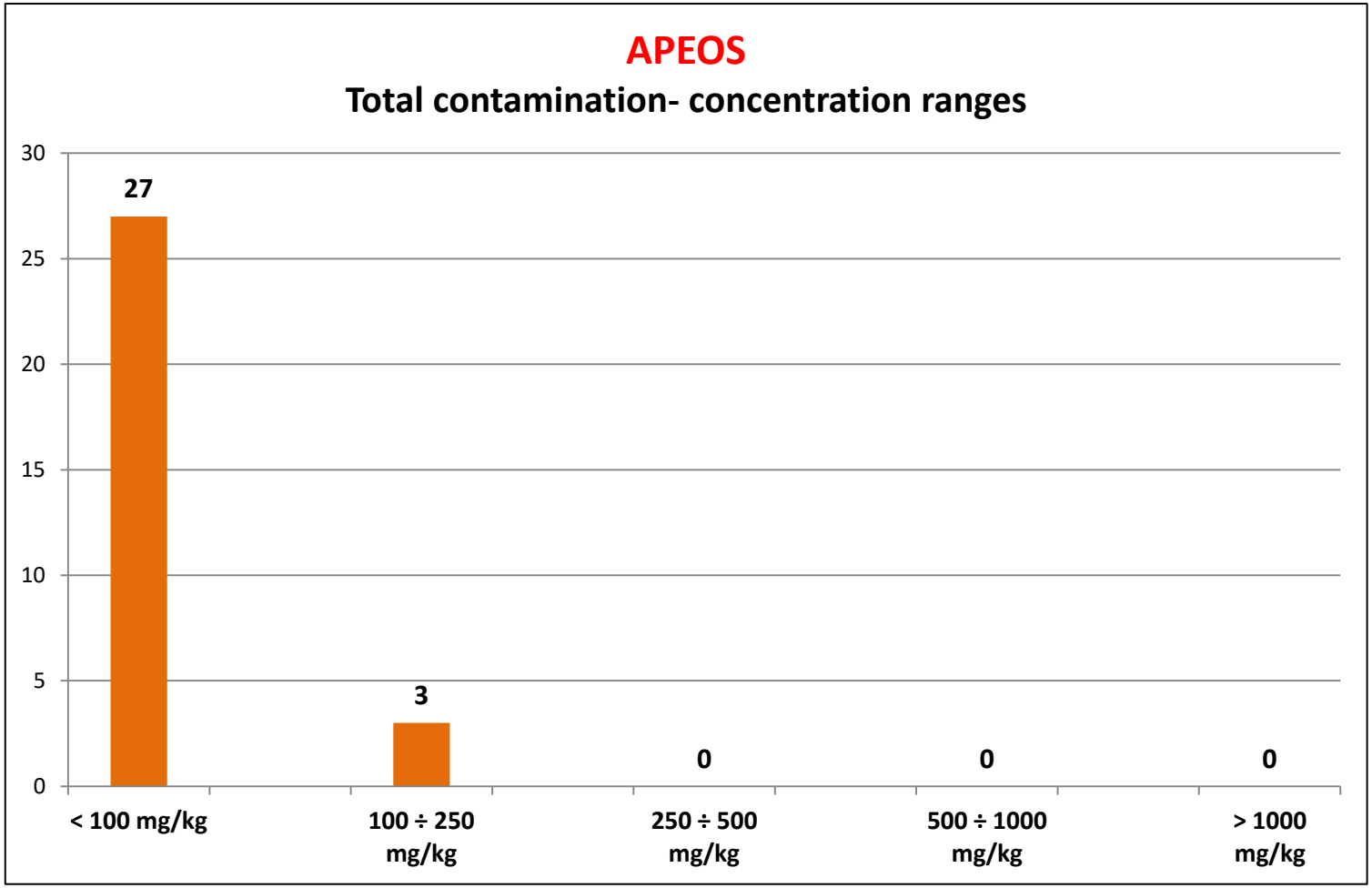
Regenerated cotton-type materials



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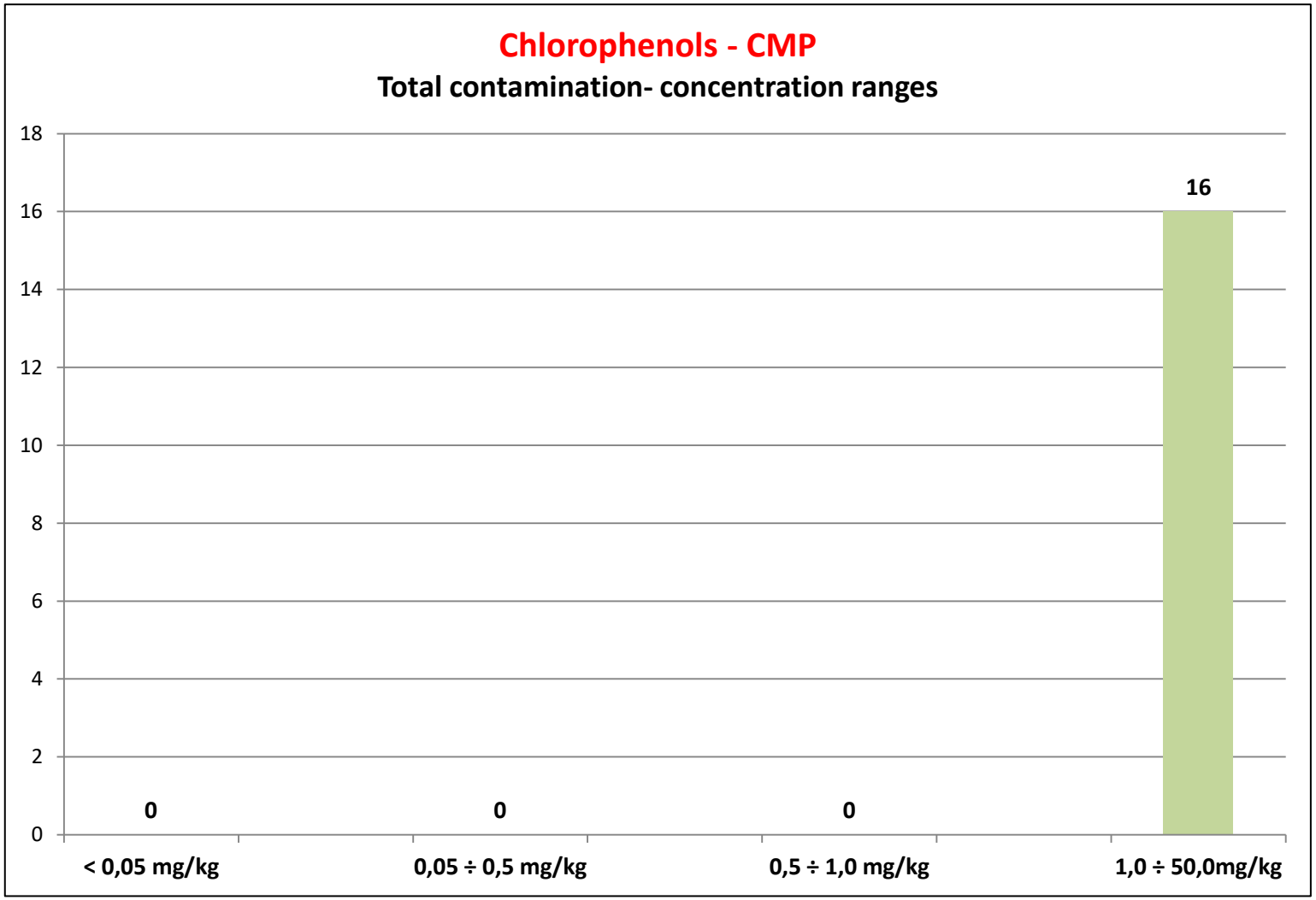
Regenerated cotton-type materials



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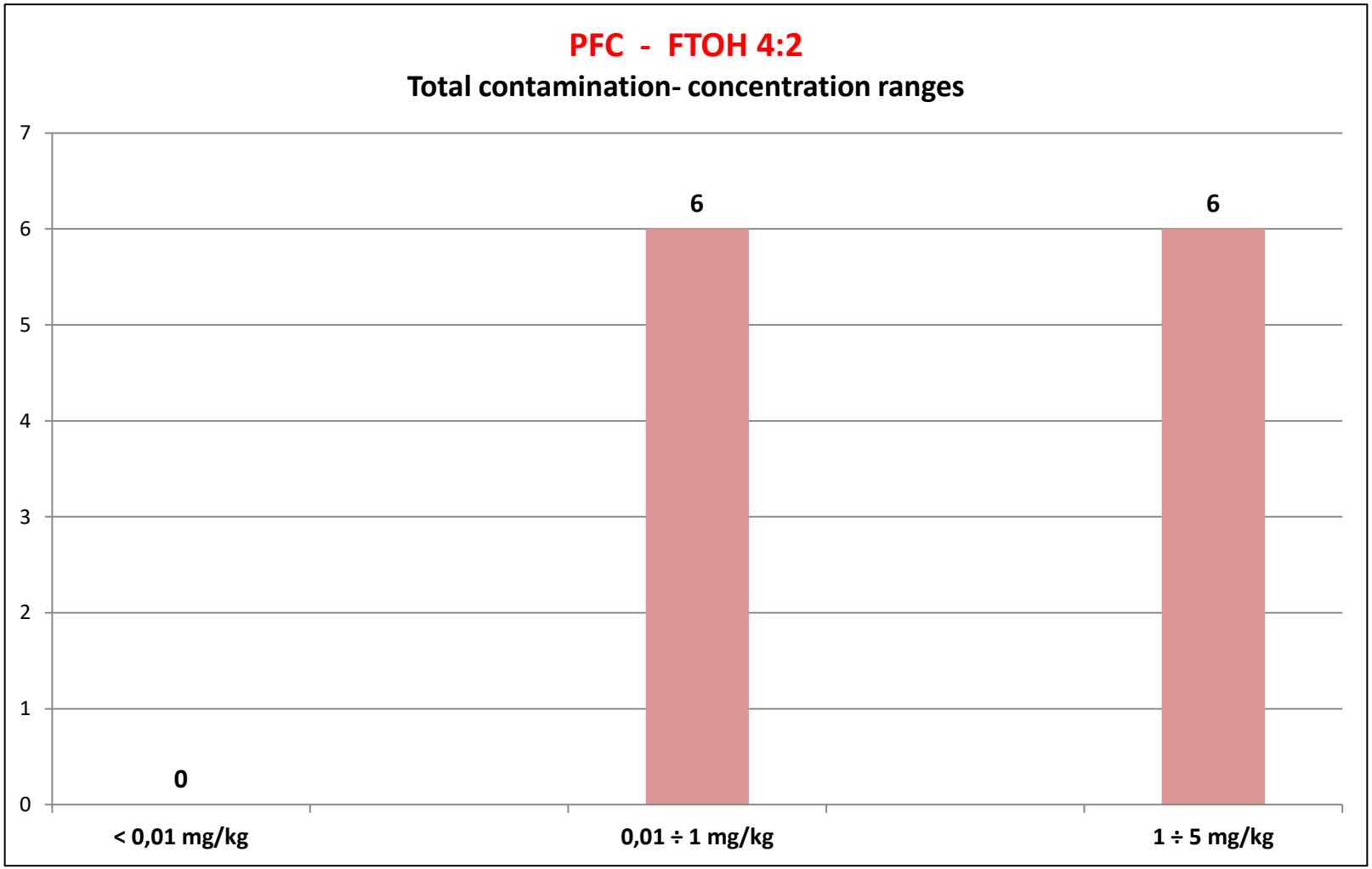
Regenerated cotton-type materials



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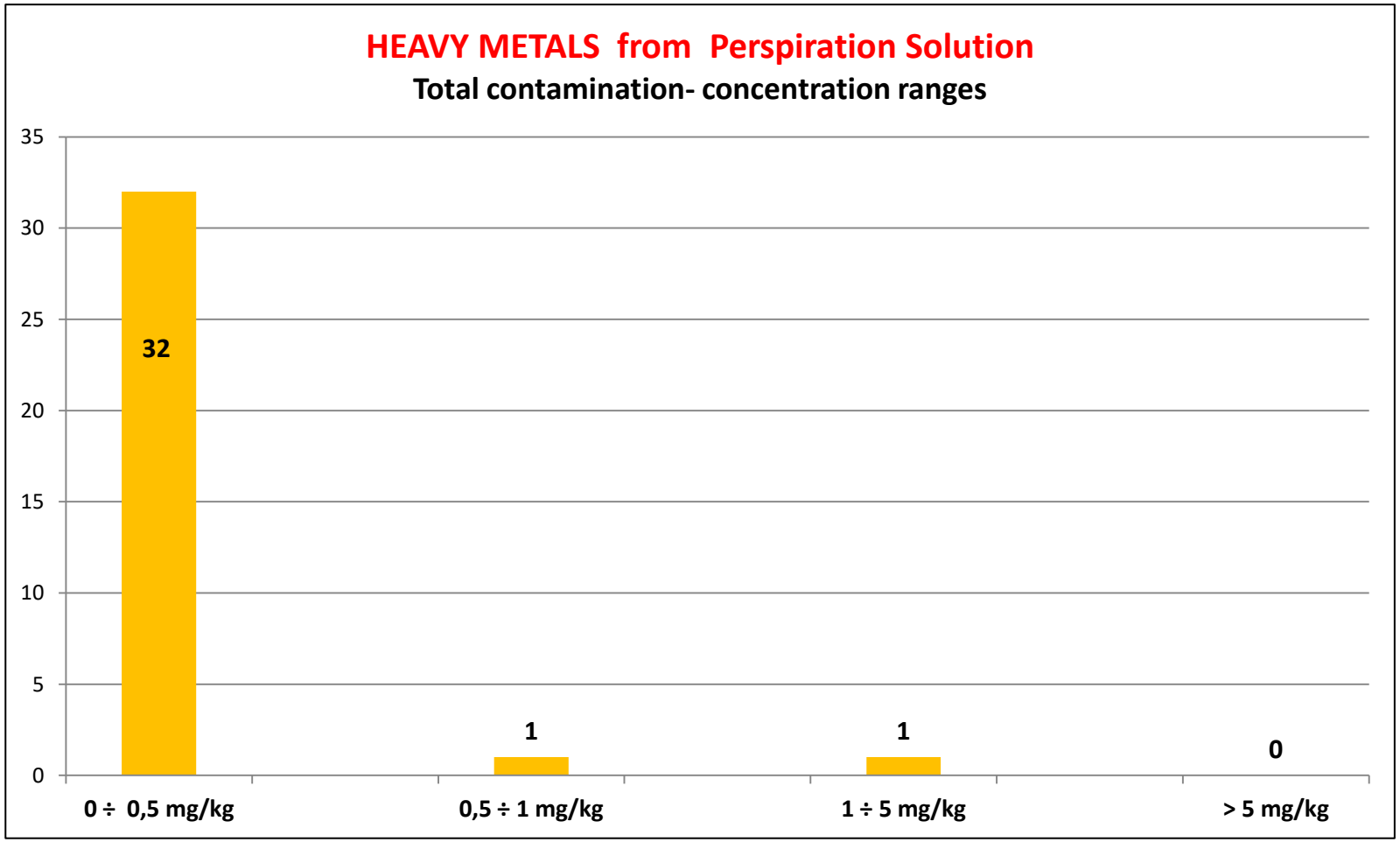
Regenerated cotton-type materials



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MRSL proposal

for

Recycled Wool

raw materials

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MRSL PROPOSAL

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) ≤ **1,0**mg/kg-**MoCP,DiCP,TriCP** (each)	Pass **86%**
Perfluorinated Compounds - (PFC)	≤ **1** µg/m² **Telomers (FTOH):** ≤ **10** µg/m²	≤ **1** µg/m² **Telomers (FTOH):** ≤ **10** µg/m²	≤ **1** µg/m² **Telomers (FTOH):** ≤ **10** µg/m²	**PFOS ≤ 1** µg/m² (= ca 4 µg/kg)	Pass **99%**
				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%**

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MRSL PROPOSAL

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%**

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MRSL PROPOSAL - Heavy metals

Heavy Metal (from acid perspiration)		CNMI – Guidelines 2016 Proactive		DETOX	MRSL Proposal for Recycled Wool - Raw Material	% of lots PASS
		Baby (<36m)	Adult	Prato District Commitment		
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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