EURL-SRM - Residue Observations Report

concerning the following…

- **Compound(s)**: 3-Hydroxycarbofuran, Abamectin, Amitrole, Cotinine, Diclofop, Diquat, Emamectin, Fentin, Gamma-Cyhalothrin, Haloxyfop, Nicotine, , PTU, Topramezone,
- **Additional compounds:** Chlorate, Cyanuric acid, Ethoxyquin dimer, Melamine, Paraquat, Perchlorate, Phosphonic acid Thiocyanate, Triazole acetic acid, Triazole lactic acid, Triazole alanine and Trifluoroacetic acid
- **Commodities**: Infant formulae of various types and milk
- **Extraction Method(s)**: Citrate buffered QuEChERS (EN 15662), QuPPe
- **Instrumental analysis**: LC-MS/MS

Analysis of Toxicologically Critical Pesticides and some Additional SRM Compounds in Infant Formulae and Milk - Part 2: Residue findings

Version 1 (last update: 26.04.2021)

1. Background information:

In a scientific opinion in March 2018 EFSA concluded that for infant food for children up to 16 weeks of age, the default MRL of 0.01 mg/kg currently applying for infant formulae (Reg. 141/2006/EC)[1] may not be sufficiently protective in the case of pesticides having ADI values that are lower than a health-based guidance value (HBGV) of 0.0026 mg/kg bw per day.

Thereafter, DG-SANTE compiled a list of compounds with ADI values < 0.0026 mg/kg bw per day and potential MRLs were calculated that would be considered safe for infants up to 16 weeks of age. The EURLs were asked to comment on the technical feasibility of the analysis of these compounds in infant formulae. Moreover, the EURLs were asked to develop and validate methods for a number of compounds and to conduct a pilot monitoring in infant formulae with LOQs equal or lower than the as safe considered levels. It was, furthermore, decided to run an additional pilot monitoring on milk samples, as milk is a key ingredient in most infant formulae.

[1] Regulation 2006/141/EC referring to infant formulae and follow-on formulae repealed by Regulation 609/2013/EU

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It was decided that the pilot monitoring project should entail different types of Infant food formulae (for infants up to 16 weeks age) and to include both organic and conventional products. The following 6 main infant formula categories were identified:

a) 'Normal' infant formula
b) Lactose-free infant formula (containing whey, in which lactose was hydrolysed to glucose and galactose)
c) Hypoallergenic infant formula (containing extensively hydrolysed milk proteins)
d) Anti-reflux infant formula (containing thickening agents)
e) "Comfort formula" for Infants with digestive problems such as colic and constipation (contains partly hydrolysed proteins)
f) Plant-based infant formula (based on e.g. soy or rice).

The selected, toxicologically critical compounds were divided into the following groups in collaboration with the EURL-AO: a) MRM (amenable to multiresidue methods), b) MRM/SRM (requiring modified MRM methods or where markers can be first screened by an MRM-method triggering re-analysis by a SRM in case of positive findings); c) SRM (compounds not amenable to multiresidue methods).

At a meeting with DG-SANTE and MSs in Brussels it was agreed to skip certain of the initially selected compounds and to start with the analysis of the collected milk samples and then continue with the infant formulae.

The calculated "safe MRLs" refer to infant food as it is consumed. For storage stability and microbiological safety reasons, however, infant formulae are usually produced and sold to consumers as powders. Residue levels determined in powdered infant formulae need to be converted into the levels in the ready to use product by applying a conversion factor that can be derived from the preparation instructions (recipe) of the manufacturer. The conversion factors of the products received varied between 7.52 and 7.98 (7.87 on average). Validation experiments were conducted by spiking the dry products with the spiking level referring to the dry infant formula. As a conservative measure for ensuring that the "safe MRL" in the dry product is not overestimated the lowest conversion factor of 7.5 rather than the average factor of 7.87 was used.

The present project was run in 2019 and 2020 starting with method development for the agreed compounds of toxicological concern. Thereafter validation experiments on infant formula powder mainly on category a) were conducted. Sampling took place in mid/end 2019 in cooperation with the EURL-AO and with the help of the NRLs. Afterwards, it was decided to add some additional toxicologically non-critical compounds to the scope, that are more likely to be detected in infant food. The milk samples were analysed in early 2020 and the infant formulae in mid-2020. During the process additional validation experiments were conducted on products of categories b) to f).

Table 1 gives an overview of the final scope in infant food powder and milk.

__Table 1:__ Final scope of SRM- and MRM/SRM-substances for the monitoring of infant food formulae and milk including the maximum MRL that is considered safe for infant food powder and for reconstituted products.

Compound	Initial Scope agreed with DG-SANTE / Additional scope	SRM/ MRM compound	Monitored in		ADI (mg/kg bw per day	Max. MRL/LOQ for reconst. products (mg/kg)	Max. LOQ for infant formula powder [2] mg/kg)	Extraction
			Infant food	Milk				
Abamectin	Initial	SRM	✓	✓	0.0025	0.0096	0.072	A-QuChERS
Emamectin	Initial	SRM	✓	✓	0.005	0.0019	0.0143	A-QuChERS
Fentin	Initial	SRM	✓	✓	0.0004	0.0015	0.0113	A-QuChERS
3-Hydroxycarbofuran	Initial	MRM/SRM	✓	✓	3-OH-CF 0.00015 Related comp. CF: 0.00015 BF: 0.0035 FT: 0.0035 CS: 0.005	0.0006	0.0045	A-QuChERS
Gamma-Cyhalothrin	Initial	MRM/SRM	✓	✓	Gamma 0.0012 Lamda 0.0025	Gamma 0.0046, Lambda 0,0095	Gamma 0.035 Lambda 0.071	A-QuChERS
Diclofop	Initial	MRM/SRM	✓	✓	0.001	0.0038	0.0285	A-QuChERS
Haloxyfop	Initial	MRM/SRM	✓	✓	0.00065	0.0025	0.01875	A-QuChERS
Amitrole	Initial	SRM	✓	✓	0.001	0.0038	0.0285	QuPPe AO
Nicotine	Initial	SRM	✓	✓	0.0008	0.0031	0.0233	QuPPe AO
Cotinine	Initial	SRM	✓	✓	0.0008	0.0031	0.0233	QuPPe AO
PTU	Initial	SRM	✓	✓	0.0003	0.0012	0.015	QuPPe AO
Diquat	Initial	SRM	✓	✓	0.002	0.0076	0.057	QuPPe AO
Topramezone	Initial	SRM	✓	✓	0.001	0.0038	0.0285	QuPPe AO
Trifluoroacetic acid (TFA)	Additional	SRM	✓	✓	0.05	-	-	QuPPe AO
Chlorate	Additional	SRM	✓	✓	0.01	-	-	QuPPe AO
Perchlorate	Additional	SRM	✓	✓	0.0003 (TDI)	-	-	QuPPe AO
Phosphonic acid	Additional	SRM	✓	✓	2.25	-	-	QuPPe AO
Triazole derivative metabolites: 1,2,4-Triazole-acetic acid (TAA) 1,2,4-Triazole-lactic acid (TLA) 1,2,4-Triazol-1-yl-alanine (TA)	Additional	SRM	**X**	✓	TAA: 1 TLA: 0.3 TA: 0.3	-	-	QuPPe AO
Thiocyanate	Additional	SRM	✓	**X**	?	-	-	QuPPe AO
Paraquat	Additional	SRM	✓	✓	0.004	-	-	QuPPe AO
Melamine	Additional	SRM	✓	✓	0.2	-	-	QuPPe AO
Cyanuric acid	Additional	SRM	**X**	✓	1.5 (TDI by WHO 2008)	-	-	QuPPe AO
Ethoxyquin-Dimer	Additional	SRM	✓	**X**	0.001	-	-	A-QuChERS

[2] Based on a conversion factor of 7.5

2. Sampling:

Aiming to analyse infant formulae and milk samples from a broad geographic area within the EU, the EURLs agreed on asking the NRLs to contribute infant formulae and milk samples. The instructions were that infant formula samples should belong to one of the above mentioned special groups and must be suitable for infants up to 16 weeks of age. As regards the milk samples the preference was put on full-fat heat treated milk samples (UHT). The samples were either brought personally by the NRL-colleagues to the Joint Workshop in Denmark or shipped via postal service. The collected samples are listed in the tables below. In addition several samples were samples by the EURL-staff in supermarkets in Germany and several other countries including Belgium, Cyprus, Czech Republic, Denmark, Greece, Latvia, Norway, Spain and Switzerland. Several milk samples were officially sampled in southern Germany and were non-homogenized.

Overall, 80 samples of infant food formulae purchased in 23 countries were collected, including 6 ready-to-use products (see Table 2 and Table 3). Table 2 gives an overview on the numbers of collected samples in each group and introduces abbreviations for the groups. Group b) to f) cover infant food for special demands and specific food intolerances and are thus less represented than 'normal' infant formulae, thus roughly reflecting the market situation. The largest number of samples collected was from group a) 'normal' (51% of all) followed by group c) 'hypoallergenic' (23% of all).

Most of the collected infant formula products were powders, which had to be made up with water. Few were liquid formulations, which were already prepared; so called ready-to-use formulae. Two infant formulae samples were based on goat´s milk and one on soy milk. Both, the milk and the infant formula samples were shared among the EURL-AO and –SRM to cover the whole agreed scope of MRM and SRM compounds.

Table 4 gives additional information on the countries in which the products were produced. The samples were collected from 23 countries overall and produced in 10 known countries. For 13 of the samples the country of production could not be identified based on the labelling. Most of the collected infant formulae products were produced in Germany including many of those samples in other countries. Many of the leading brands market their products under different brand names in different countries, with some of these brands being originally independent but eventually taken over by one of the leading brands. An overview on milk samples and their origin is given in Table 5.

Figure 1 and Figure 2 show the share of samples by sample group, manufacturer and production status (organic/conventional).

***Table 2**: Overview and numbers of collected infant formulae samples*

Category	Abbr.	Conventional	Organic	SUM	No. of Countries Production*	No. of Countries Sampling
Normal infant formula	Normal	30	11	41	9	17
Lactose-free infant formula	L-Free	8	-	8	5	7
Hypoallergenic infant formula	HA	18	-	18	5	12
Anti-reflux infant formula	AR	6	2	8	6	7
Infant formula for digestive problems	Comf.	3	-	3	1	2
Soy/rice based infant formula	Non-Milk	1	1	2	2	2
Total		66	14	80	10	23

* Where country was named

Table 3: Origin and type of infant food samples from 23 countries (21 EU and 2 EFTA).

Country	Normal	L-free	HA	AR	Comf.	Non-Milk	Sum
DE	7	5		2	2	1	17
CZ	4	1					5
ES	3		1		1		5
BE	4					1	5
LV	2	2		1			5
FR		1	2	1			4
PT	2	1	1				4
CY	3						3
DK	1	2					3
AT	1	1					2
HR	1	1					2
RO	1		1				2
HU		1	1				2
NL	1			1			2
SE	1	1					2
GR			1	1			2
BG	2						2
IE			1	1			2
IT	2						2
SI				1			1
FI		1					1
NO	3	1					4
CH	3						3
SUM	**41**	**18**	**8**	**8**	**3**	**2**	**80**

Table 4: Producing country and type of infant food samples from 10 known producing countries (9 EU and 2 EFTA) and additional 13 samples with non-stated origin.

Country	Normal	L-free	HA	AR	Comf.	Non-Milk	Sum
DE	10	8	2	4	2	1	27
EU/non stated	7	2	1	2	1		13
NL	4	5	2				11
IE	3	1	1	2			7
PL	4	1	1				6
SE	5						5
FR	3					1	4
ES	2	1					3
GR			1				1
PT	1						1
CH	2						2
SUM	**41**	**18**	**8**	**8**	**3**	**2**	**80**

Table 5: Overview of collected milk samples

Category	Conventional	Organic	SUM	No. of Countries (EU/EFTA) from which samples originated
	Number of samples			
Heat treated milk	42	2	44	20
Raw milk	9	1	10	1 (all DE)
Total	51	3	54	-

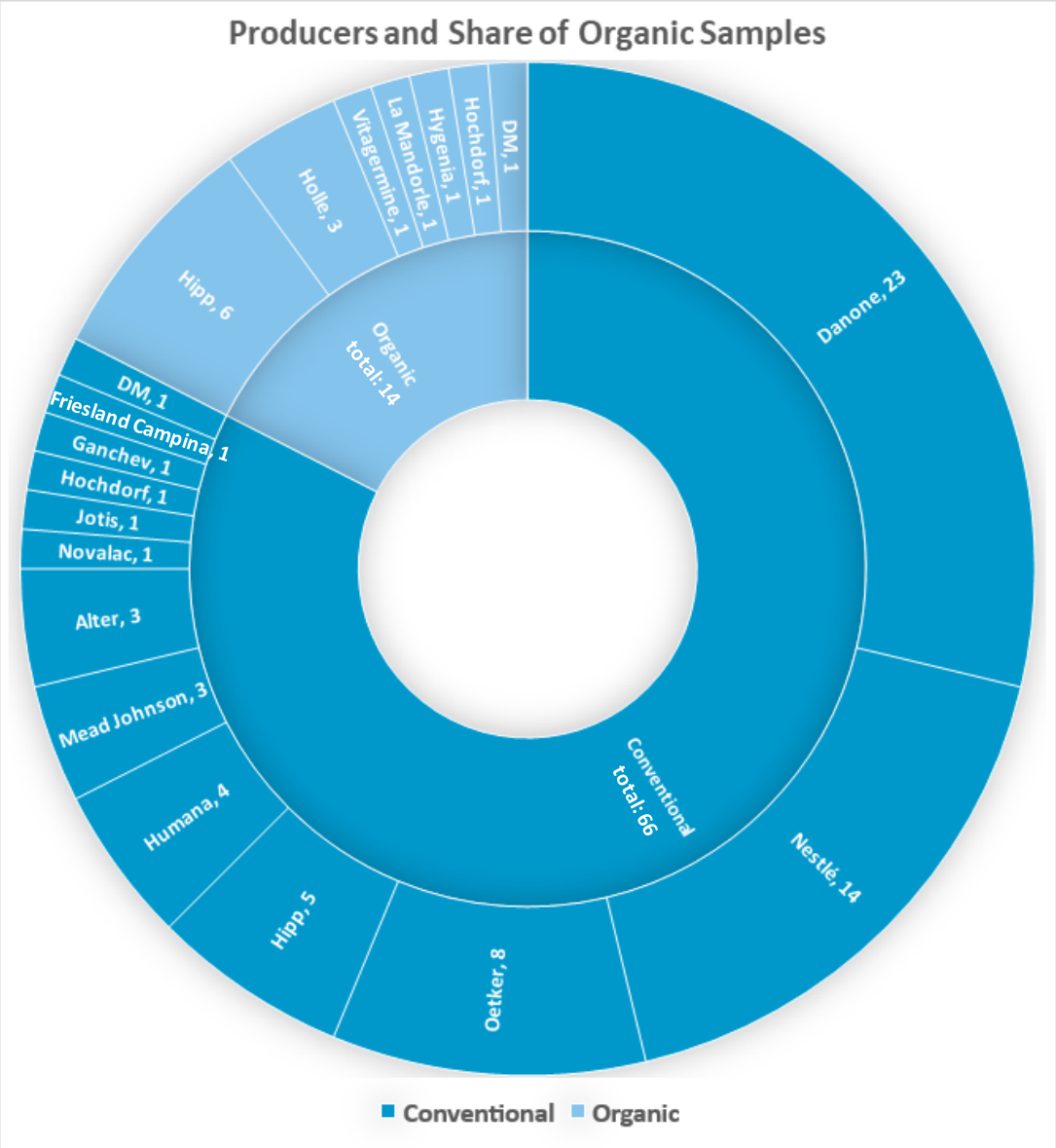

Figure 1: Infant formulae producers and share of organic samples among the analysed samples

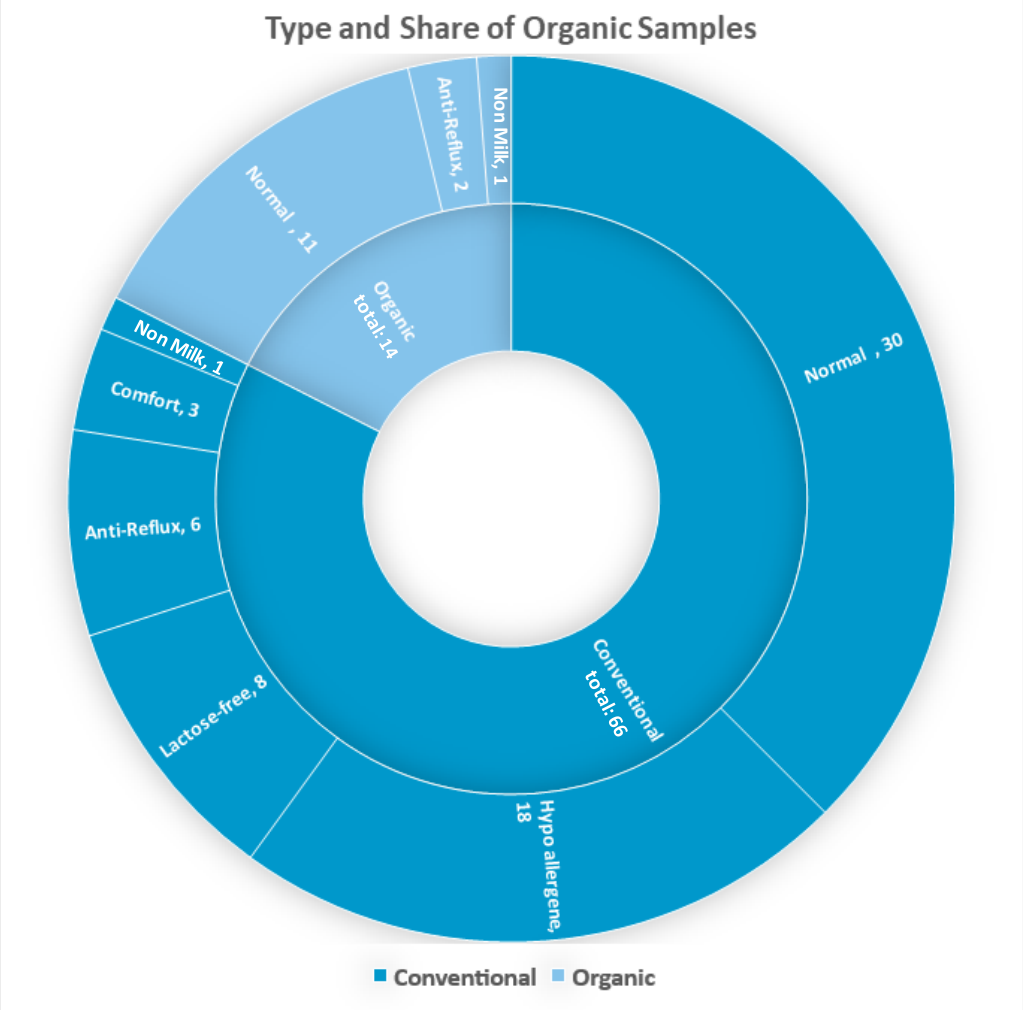

Figure 2: Infant formulae categories and share of organic samples among the analysed samples

3. Analysis

Detailed information on method development, conditions of extraction and measurement as well as details on validation experiments are given in the EURL-SRM analytical observation report 'Analysis of Toxicologically Critical SRM Compounds in Infant Formulae and Milk – Part1: Analytical Aspects'.

In method validation the lowest spiking levels were chosen below the maximum safe MRLs (between 7% - 92% of the max. MRL; see Observation Part 1). To check the transferability of the validation data generated on a group a) commodity to the commodities of group b) to f), an additional LOW-level validation study was conducted (see Observation Part 1).

Infant formulae and milk samples were extracted by A-QuEChERS and QuPPe AO employing 2 g and 10 g sample portions respectively. In case of ready-to-use infant formulae also 10 g sample was employed. Each sample was extracted once by each method. In case of positive findings no repeated extraction or additional verification was performed.

As internal standards, chlorpyrifos D_{10}, propyzamide D_3 as well as several isotopically labelled analogues of target analytes (ILISs) were used. Matrix-matched calibrations at 60% and 120% of the respective lowest validated level (LOW) were prepared using extracts of heat-treated and raw milk. Separate matrix-matched calibration standards were prepared for ready-to-use products.

Some of the additionally analysed compounds are ubiquitous contaminants (e.g. chlorate, perchlorate, phosphonic acid and TFA) with blank extracts containing high background levels thus making it difficult to prepare proper matrix-matched standards. In such cases calibration standards were prepared at 100%; 200% and 400% of the lowest validated level. In such cases the slope of the linear calibration curve was used for calculation rather than the calibration function with the high intercept.

4. Results

4.1. Infant formulae samples

The following tables show the results of the targeted analytes in infant formulae. The results are grouped according to production type (organic/conventional) as well as according to the product type (see abbreviations in Table 2).

Illustrated is the number of analysed samples, the number of positive samples, the share of results below LOQ and the median of the positive results in mg/kg. All results refer to the reconstituted products. In case of two numerical results, the mean is shown. Values < LOQ were rounded to 1 significant figure and have to be regarded as semi-quantitative. These low values are merely given to gain insight on the occurrence of these contaminants in infant food formula at trace levels.

Also given in the tables are the maximum safe MRLs, calculated with the highly toxic compounds respective ADI values, which would be still considered safe for children up to 16 weeks of age.

4.1.1. Polar compounds ("QuPPe-Compounds")

Table 6 presents results for highly toxic polar compounds respectively to the Work-Programme, whereas additionally analysed polar compounds are shown in Table 7 and Table 8.

Table 6: Overview of results for highly toxic polar compounds in infant formulae (included in Work-programme)

Compound	Max. safe MRL	LOQ*	Normal (N=41)		L-Free (N=8)	HA (N=18)	AR (N=8)		Comf. (N=3)	Non-Milk (N=2)	
			Conv. (n=30)	Org. (n=11)	Conv. (n=8)	Conv. (n=18)	Conv. (n=6)	Org. (n=2)	Conv. (n=3)	Conv. (n=1)	Org. (n=1)
	In mg/kg of reconst. product		# of positive samples (Median of detected levels – M – in mg/kg reconstituted product)								
Amitrole	0.0038	0.0027	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nicotine	0.0031	0.0027	30 [All < LOQ] (M 0.0005)	11 [All< LOQ] (M 0.0004)	n.d.	3 [All < LOQ] (M 0.0002)	3 [All < LOQ] (M 0.0002)	1 [< LOQ] (0.0003)	n.d.	n.d.	n.d.
Cotinine	0.0031	0.00067	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PTU	0.0012	0.00067	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diquat	0.0076	0.0067	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*LOQ = LSVL (Lowest Successfully Validated Level) – Validation at lower levels was not attempted
n.d. = not detected

Table 7: Overview of results for additionally analysed polar compounds in infant formulae samples

Compound	LOQ* for reconst. products [mg/kg]	Normal (N=41)		L-Free (N=8)	HA (N=18)	AR (N=8)		Comf. (N=3)	Non-Milk (N=2)	
		Conv. (n=30)	Org. (n=11)	Conv. (n=8)	Conv. (n=18)	Conv. (n=6)	Org. (n=2)	Conv. (n=3)	Conv. (n=1)	Org. (n=1)
		# of positive samples (Median of detected levels – M – in mg/kg reconstituted product)								
Paraquat	0.0067	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TFA	0.0067	28 [All < LOQ] (M 0.0007)	10 [All< LOQ] (M 0.001)	4 [All < LOQ] (M 0.0004)	8 [All < LOQ] (M 0.0009)	6 [All < LOQ] (M 0.0007)	2 [All < LOQ] (0.001)	n.d.	1 [< LOQ] (0.003)	n.d.
Melamine	0.0027	7 [All < LOQ] (M 0.0006)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*LOQ = LSVL (Lowest Successfully Validated Level) – Validation at lower levels was not attempted
n.d. = not detected
TFA = Trifluoroacetic acid

Table 8: Overview of results for additionally analysed polar compounds in infant formulae samples

Compound	Data	LOQ * for reconst. products [mg/kg]	Normal (N=41)		L-Free (N=8)	HA (N=18)	AR (N=8)		Comf. (N=3)	Non-Milk (N=2)	
			Conv. (n=30)	Org. (n=11)	Conv. (n=8)	Conv. (n=18)	Conv. (n=6)	Org. (n=2)	Conv. (n=3)	Conv. (n=1)	Org. (n=1)
			# of positive samples (Median of detected levels – M – in mg/kg reconstituted product)								
Chlorate	Positives	0.0027	30 (M 0.0092)	11 (M 0.0049)	8 (M 0.0025)	18 (M 0.0042)	6 (M 0.0074)	2 (0.0050)	3 (M 0.0057)	1 (0.014)	1 (0.0046)
	Pos. ≥ LOQ		30 (M 0.0092)	11 (M 0.0049)	3 (M 0.0047)	14 (M 0.0045)	6 (M 0.0074)	2 (0.0050)	3 (M 0.0057)	1 (0.014)	1 (0.0046)
Perchlorate	Positives	0.0027	22 (M 0.0006)	10 (M 0.0015)	8 (M 0.0017)	4 (M 0.0043)	6 (M 0.0019)	2 (0.0022)	n.d.	n.d.	1 (0.0058)
	Pos. ≥ LOQ		2 (0.0019)	7 (M 0.0019)	7 (M 0.0017)	2 (0.011)	4 (M 0.0030)	2 (0.0022)	-	-	1 (0.0058)
Phosphonic acid	Positives	0.0067	30 (M 0.0029)	11 (M 0.0026)	8 (M 0.0062)	18 (M 0.0041)	6 (M 0.003)	2 (0.003)	3 (0.0061)	1 (0.0085)	1 (0.016)
	Pos. ≥ LOQ		2 (0.015)	1 (0.013)	3 (M 0.0085)	3 (M 0.0072)	-	-	1 (0.0069)	1 (0.0085)	1 (0.016)
Thiocyanate	Positives	0.067	30 (M 0.55)	11 (M 0.45)	8 (M 0.088)	18 (M 0.067)	6 (M 0.60)	2 (0.38)	3 (M 0.25)	n.d.	1 (0.02)
	Pos. ≥ LOQ		30 (M 0.55)	10 (M 0.46)	6 (M 0.092)	11 (M 0.086)	5 (M 0.63)	2 (0.38)	2 (0.36)	-	-

*LOQ = LSVL (Lowest Successfully Validated Level) – Validation at lower levels was not attempted
n.d. = no detections or detections at negligible levels

4.1.2. Non-polar compounds ("QuEChERS-Compounds")

Table 9 presents results for highly toxic non-polar compounds that are amenable to the QuEChERS multuiresidue method. Ethoxyquin dimer was additionally tested as many infant formulae had fish oil as an ingredient.

Table 9: *Overview of results for highly toxic non-polar compounds in infant formulae samples*

Compound	Max. safe MRL	LOQ*	Normal (N=41)		L-Free (N=8)	HA (N=18)	AR (N=8)		Comf. (N=3)	Non-Milk (N=2)	
			Conv. (n=30)	Org. (n=11)	Conv. (n=8)	Conv. (n=18)	Conv. (n=6)	Org. (n=2)	Conv. (n=3)	Conv. (n=1)	Org. (n=1)
	In mg/kg of reconst. product		# of positive samples (Median of detected levels – M – in mg/kg reconstituted product)								
Abamectin	0.0096	0.0067	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Emamectin	0.0019	0.0013	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-OH-Carbofuran	0.0006	0.00053	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
γ-Cyhalothrin	0.0048	0.0043	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fentin	0.0015	0.0013	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Haloxyfop	0.0025	0.0020	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diclofop	0.0038	0.0033	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Topramezone	0.0038	0.00067	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethoxyquin-Dimer	-	0.00067	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*LOQ = LSVL (Lowest Successfully Validated Level) – Validation at lower levels was not attempted
n.d. = no detections or detections at negligible levels

4.2. Milk samples

Following tables show the results of the target analytes in the analysed heat-treated and raw milk samples. Illustrated is the number of analysed samples, the number of positive samples, the share of results below LOQ and the median of the positive results in mg/kg. In case of two numerical results, the mean is shown. Values < LOQ were rounded to 1 significant figure and have to be regarded as semi-quantitative.

4.2.1. Polar compounds ("QuPPe-Compounds")

Table 10 presents results for highly toxic polar compounds analysed as required by the EURL Work-Programme, whereas additionally analysed polar compounds are shown in Table 11 and Table 12.

Table 10: *Overview of results for highly toxic polar compounds in milk samples (included in Work-programme)*

Compound	LOQ* [mg/kg]	Heat treated Milk		Raw Milk	
		Conventional (n=42)	Organic (n=2)	Conventional (n=9)	Organic (n=1)
		# of positive samples (Median of detected levels in mg/kg)			
Amitrole	0.01	n.d.	n.d.	n.d.	n.d.
Nicotine	0.01	36 [all < LOQ] (Median 0.001)	2 [all < LOQ] (Mean 0.0008)	6 [all < LOQ] (Median 0.001)	1 [< LOQ] (0.0009)
Cotinine	0.01	n.d.	n.d.	n.d.	n.d.
PTU	0.01	n.d.	n.d.	n.d.	n.d.
Diquat	0.01	n.d.	n.d.	n.d.	n.d.

*LOQ = LSVL (Lowest Successfully Validated Level) – Validation at lower levels was not attempted
n.d. = no detections or detections at negligible levels

Table 11: *Overview of Results for Additionally Analysed Polar Compounds in Milk Samples*

Compound	LOQ* [mg/kg]	Heat treated Milk		Raw Milk	
		Conventional (n=42)	Organic (n=2)	Conventional (n=9)	Organic (n=1)
		# of positive samples (Median of detected levels in mg/kg)			
Paraquat	0.01	n.d.	n.d.	n.d.	n.d.
TFA (Trifluoroacetic acid)	0.01	42 [all < LOQ] (Median 0.005)	2 [all < LOQ] (Mean 0.004)	9 [all < LOQ] (Median 0.006)	1 [< LOQ] (0.006)
TAA (1,2,4-Triazole-acetic acid)	0.05	n.d.	n.d.	n.d.	n.d.
TLA (1,2,4-Triazole-lactic acid)	0.05	n.d.	n.d.	n.d.	n.d.
TA (1,2,4-Triazole-alanine)	0.05	n.d.	n.d.	n.d.	n.d.
Melamine	0.005	4 [< LOQ] (Median 0.0013)	n.d.	2 [< LOQ] (Mean 0.0031)	n.d.
Cyanuric acid	0.00	3 [all > LOQ] (Median 0.0081)	n.d.	n.d.	n.d.

*LOQ = LSVL (Lowest Successfully Validated Level) – Validation at lower levels was not attempted
n.d. = no detections or detections at negligible levels

Table 12: Overview of Results for Additionally Analysed Polar Compounds in Milk Samples

Compound	LOQ* [mg/kg]	Heat treated Milk		Raw Milk	
		Conventional (n=42)	Organic (n=2)	Conventional (n=9)	Organic (n=1)
		# of positive samples (Median of detected levels in mg/kg)			
Chlorate	0.01	32 [14 ≥ LOQ; 18 < LOQ] (Median 0.005)	2 [all < LOQ] (Mean 0.004)	9 [all < LOQ] (Median 0.001)	1 [<LOQ] (0.001)
Perchlorate	0.01	23 [all <LOQ] (Median 0.001)	1 [<LOQ] (0.0004)	4 [all < LOQ] (Median 0.001)	1 [<LOQ] (0.003)
Phosphonic acid	0.05	39 [all < LOQ] (Median 0.007)	2 [all < LOQ] (Mean 0.006)	n.d.	n.d.

*LOQ = LSVL (Lowest Successfully Validated Level) – Validation at lower levels was not attempted
n.d. = no detections or detections at negligible levels

Table 13: Distribution of Residues in Conventional Heat Treated Milk Samples

Compound	LOQ* [mg/kg]	Heat treated Milk Conventional (N=42)				
		# of positive samples				
		< 0.005 mg/kg	0.005 – 0.01 mg/kg	0.01 – 0.05 mg/kg	0.05 – 0.1 mg/kg	> 0.1 mg/kg
Chlorate	0.01	14	6	8	2	2
Perchlorate	0.01	23	-	-	-	-
Phosphonic acid	0.05	5	26	8	-	-

*LOQ = LSVL (Lowest Successfully Validated Level) – Validation at lower levels was not attempted

4.2.2. Non-polar compounds ("QuEChERS-Compounds")

Table 14: Overview of Results for Highly Toxic Non-polar Compounds in Milk Samples

Compound	LOQ* [mg/kg]	Heat treated Milk		Raw Milk	
		Conventional (n=42)	Organic (n=2)	Conventional (n=9)	Organic (n=1)
Abamectin	0.002	n.d.	n.d.	n.d.	n.d.
Emamectin	0.002	n.d.	n.d.	n.d.	n.d.
3-OH-Carbofuran	0.002	n.d.	n.d.	n.d.	n.d.
γ-Cyhalothrin	0.002	n.d.	n.d.	n.d.	n.d.
Fentin	0.002	n.d.	n.d.	n.d.	n.d.
Haloxyfop	0.002	n.d.	n.d.	n.d.	n.d.
Diclofop	0.002	n.d.	n.d.	n.d.	n.d.
Topramezone	0.002	n.d.	n.d.	n.d.	n.d.

*LOQ = LSVL (Lowest Successfully Validated Level) – Validation at lower levels was not attempted
n.d. = not detected

Document History

Action	When	Document Version
Initial Experiments	May – December 2019	
Further Validation Experiments	November 2019 – January 2020	
Analysis of samples	Within 2020	
Observation document placed on-line	April 2021	V1