Residue Findings of QuPPe-Compounds in Samples of Plant Origin from the German Market in 2019

Reported by: EURL-SRM

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The aim of this compilation is to give an overview as to which QuPPe-related compounds are currently encountered in food products of plant origin. This should help other institutions when it comes to taking decisions on how to expand the scope of analytes, on how to plan the sampling and on which types of samples QuPPe-compounds should be targeted.
At the CVUA Stuttgart 34 QuPPe-compounds were routinely monitored in 2019 (see Table 1).

Table 1: Scope of QuPPe-compounds that were routinely monitored by the CVUA Stuttgart in 2019

Compound	Notes on legal limits	General notes
Amitrole		Herbicide
Bialaphos	Not specifically regulated, MRL of 0.01 mg/kg applies	Herbicide (transforms to glufosinate)
Bromide		Metabolite of fumigant methylbromide, but also originating from irrigation water and soil
Chlorate	Currently new MRLs under discussion	Formerly used as herbicide, but nowadays mainly from irrigation water or cleaning of products and processing/storage equipment with chlorinated water
Chloridazon-desphenyl		Metabolite of chloridazon
Chlormequat		Growth regulator
Cyanuric acid	Regulated together with melamine as a contaminant	This compound can have various sources, e.g. **Triazine pesticides** (including the herbicides terbuthylazine, atrazine, cyanazine, the fungicide; anilazine and the insecticide cyromazine). From the above only terbuthylazine and cyromazine are currently being used within the EU, but degradants thereof are still found in the environment. Other possible sources include the following: **Cyanamide-based fertilizers.** Cyanamide contained in fertilizers may convert to melamine through trimerization, which can further hydrolyze to cyanuric acid. **Mono-, Di- and Trichloroisocyanurates:** These compounds are used as disinfectants, algaecides and bactericides. Their main use is in swimming pools (pool-tabs) where they retard the loss of chlorine in chlorinated water. They are also used in sanitation liquids and bleaching agents. In water they gradually convert to cyanuric acid. **Natural formation** of cyanuric acid has been reported (e.g. in humus).
Cyromazine		Fungicide (EU-approval expired in Dec. 2019). Also used as an ectoparasiticide (e.g. on sheep, but not on lactating sheep) and as a biocide on manure against fly larvae
Difenzoquat	Not specifically regulated, MRL of 0.01 mg/kg applies	Herbicide
Ethephon		Growth regulator

Compound	Notes on legal limits	General notes
HEPA	Non-regulated metabolite	Metabolite of ethephon. Natural formation by bacteria under anaerobic conditions was reported. Detected by the EURL-SRM in all analyzed samples of bovine liver (levels around 0.5 mg/kg)
ETU	Non-regulated degradant	Degradant of ethylen-bis dithiocarbamates. Mainly formed during processing.
Fosetyl		Fungicide (converts to phosphonic acid, which is the active component)
Phosphonic acid	Regulated with its parent compound fosetyl	Fungicide, used as such and also formed as a metabolite of fosetyl
Glufosinate		Herbicide, approval expired in mid-2018 and not renewed
MPP (MPPA)	Included in residue definition of glufosinate	Metabolite of glufosinate
N-Acetyl Glufosinate	Included in residue definition of glufosinate	Metabolite of glufosinate
Glyphosate		Herbicide
AMPA	Non-regulated metabolite. Planned inclusion in RD of glyphosate	Metabolite of glyphosate
N-Acetyl-Glyphosate	Non-regulated metabolite. Planned inclusion in RD of glyphosate	Metabolite of glyphosate
N-Acetyl-AMPA	Non-regulated metabolite.	Metabolite of glyphosate
Maleic hydrazide		Sprouting inhibitor
Melamine	Regulated as a contaminant	Metabolite of Cyromazine, but residues mainly from other sources such as triazine pesticides (see cyanuric acid) and cyanamide fertilizers. Melamine hydrolyzes to cyanuric acid
Mepiquat		Growth regulator
Mepiquat, 4-Hydroxy	Non-regulated metabolite	Metabolite of Mepiquat, mainly relevant for food of animal origin
Nereistoxin	Non-regulated metabolite	Transformation product of various members of the nereistoxin pesticides family, such as bensultap, cartap and thiocyclam
Nicotine*	MRLs set for rose hips, herbs and edible flowers, wild fungi, teas, herbal infusions and spices	Insecticide, contaminant from tobacco through air, soil and human contact.
Perchlorate	Regulated as a contaminant	Contaminant, e.g. from fertilizer
Propamocarb		Fungicide
Propamocarb N-desmethyl	Non regulated metabolite	Metabolite of propamocarb
Propamocarb-N-oxide	Non regulated metabolite	Metabolite of propamocarb
PTU	Regulated in infant- and baby food Reg. EC 125/2006 and 141/2006	Degradant of propineb. Mainly formed during processing.
Pymetrozine, 6-hydroxymethyl	Non-regulated metabolite	Metabolite of pymetrozine
Trimesium		Counter-ion of glyphosate, also naturally formed during the drying process of food

Residue Findings:

In 2019 a total of 2498 samples, mainly fruit and vegetables, but also cereals, pulses, processed goods, tea and others, were analyzed for QuPPe-amenable compounds at the CVUA Stuttgart. 1857 samples (74 %) contained quantifiable residues of one or more of the tested QuPPe compounds. Table 2 shows a compilation of the results.
Cyanuric acid, phosphonic acid, perchlorate, nicotine, chlorate and *melamine* exceeded the respective reporting limits in **> 10 % of the samples**. *Bromide, propamocarb, chlormequat, trimesium, propamocarb-N-oxide, chloridazon-desphenyl, HEPA, propamocarb N-desmethyl, mepiquat* and *ethephon* exceeded the respective reporting limits in **1 - 10 % of the samples**. *Chloridazon-desphenyl, maleic hydrazide, cyromazine, glyphosate, fosetyl, ETU, MPP, 4-hydroxy-mepiquat* and *nereistoxin* exceeded the respective reporting limits in **0.1 -1% of the samples.**
The following compounds did not exceed the reporting limits: *Bialaphos, daminozide, difenzoquat, N-acetyl-AMPA, glufosinate, N-acetyl-glyphosate, PTU* and *pymetrozine-6-hydroxymethyl*.

Table 2: Residue findings of QuPPe-compounds (CVUA Stuttgart 2019)

Compound	# samples	# pos.	% pos.	Max (mg/kg)	Mean[1)] (mg/kg)	Median[1)] (mg/kg)	# >MRL[2)]	% >MRL	RL[3)]
Cyanuric acid	2498	935	37	11.3	0.076	0.012	1[4)]	0.04	0.005
Phosphonic acid	2497	668	27	46.4	3.3	0.94	14	0.6	0.05
Chlorate	2498	491	20	15.6	0.142	0.010	235	9.4	0.005
Perchlorate	2498	471	19	2.1	0.068	0.016		0	0.005
Melamine	2497	262	10	12.4	0.216	0.039	2[4)]	0.08	0.005
Propamocarb	2497	101	4	3.6	0.159	0.025		0	0.005
Propamocarb-N-oxide	2497	81	3.2	0.6	0.052	0.015		0	0.005
Nicotine[5)]	206	69	33	0.34	0.051	0.028	15	7.3	0.005
Trimesium	2498	57	2.3	1.9	0.104	0.025	12	0.5	0.005
Chlormequat, sum	2497	56	2.2	4.5	0.494	0.057	19	0.8	0.005
HEPA	2497	51	2	2.8	0.249	0.10		0	0.005
Propamocarb-N-desmethyl	2497	47	1.9	0.23	0.023	0.011		0	0.005
Bromid	2498	43	1.7	71	23.7	17.1	1	0.04	5
Ethephon	2497	41	1.6	1.3	0.176	0.10	1	0.04	0.02
Mepiquat	2497	34	1.4	0.18	0.045	0.031		0	0.005
Chloridazon-desphenyl	2497	18	0.7	0.048	0.012	0.006		0	0.01
Maleic hydrazide	2497	13	0.5	10.8	4.9	4.1		0	0.01
Cyromazine	2497	12	0.5	0.61	0.117	0.036	1	0.04	0.01
Glyphosate	2497	11	0.4	2.2	0.408	0.12			0.02
Fosetyl	2497	10	0.4	26.4	2.7	0.12			0.01
ETU	2497	9	0.4	0.55	0.128	0.033			0.02
MPP (glufosinate metab.)	2497	8	0.3	0.1	0.053	0.052			0.01
Mepiquat, 4-Hydroxy	2497	4	0.2	0.065	0.044	0.050			0.005
Nereistoxin	2497	3	0.1	0.01	0.007	0.006			0.005
Amitrole	2497	2	0.08	0.01	0.009	0.009			0.005
N-Acetyl-Glufosinate	2497	2	0.08	0.12	0.090	0.090			0.005

[1)] Mean and median of positives
[2)] Numerical MRL-exceedances
[3)] RL= Reporting Limit (exemplary for fruits and vegetables)
[4)] Exceeding the Maximum Limit (ML) of 2.5 mg/kg (for Melamine and its structural analogues: Cyanuric acid, Ammeline, and Ammelide); see contaminant regulation 1881/2006/EC
[5)] Re-analysis with alkaline QuEChERS after screening

MRL exceedances

In 61 samples MRLs for different compounds were exceeded (see Table 3) and in additional 235 samples (not shown), the default MRL for chlorate was exceeded (which is not enforced, pending the establishment of agreed MRLs).

Table 3: Samples with QuPPe-compounds exceeding existing MRLs* (CVUA Stuttgart 2019)

Compound	Commodity	Country of Origin	Conc. (mg/kg)	>MRL*	>2x MRL**	Note
Bromide	Chestnut	Turkey	71	X		
Chlormequat	Oyster muschrooms	Poland	4.3	X		
	Paprika powder	unknown	0.25	X	X	
	Paprika powder	unknown	0.52	X	X	
	Paprika powder	unknown	0.57	X	X	
	Paprika powder	unknown	0.58	X	X	
	Paprika powder	unknown	0.62	X	X	
	Paprika powder	unknown	0.70	X	X	
	Paprika powder	unknown	0.77	X	X	
	Paprika powder	Unknown	0.95	X	X	
	Paprika powder	Unknown	1.2	X	X	
	Paprika powder	Unknown	1.3	X	X	
	Paprika powder	Unknown	1.5	X	X	
	Paprika powder	Unknown	1.6	X	X	
	Paprika powder	Unknown	1.8	X	X	
	Paprika powder	Unknown	2.1	X	X	
	Paprika powder	Unknown	4.5	X	X	
	Peeled tomatoes, preserved	Unknown	0.084	X	X	
	Cucumber	Turkey	0.22	X	X	
	Lemon grass	Thailand	0.019	X		
Cyanuric acid*	Avocado	Chile	3.6	X		
Cyromazine	Wild mushrooms, dried	Unknown	0.61	X		
Ethephon	Paprika powder	Unknown	0.61	X		
Melamine*	Potato	Germany	6.3	X	X	
	Coriander	Germany	12.4	X	X	
Nicotine	Grapes	Unknown	0.014	X		
	Mango	Unknown	0.014	X		
	Strawberries	Germany	0.015	X		
	Oyster muschrooms	Poland	0.016	X		
	Paprika powder	Hungary	0.16	X		
	Asparagus	Germany	0.016	X		
	Borecole	Germany	0.021	X	X	
	Celeriac	Unknown	0.014	X		
	Ginger	China	0.025	X	X	
	Iceberg lettuce	Germany	0.016	X		
	Lamb‘s lettuce	Germany	0.023	X	X	
	Lamb‘s lettuce	Italy	0.016	X		
	Leek	Germany	0.013	X		
	Spinach	Germany	0.013	X		
	Wine grapes	Germany	0.014	X		
Phosphonic acid	Baby and infant foods	Unknown	0.03	X	X	Fruit-based (apple)
	Baby and infant foods	Unknown	0.16	X	X	Cereal
	Rice	Unknown	8	X	X	
	Mango	South Africa	4.8	X	X	
	Passion fruits	Colombia	12.3	X	X	
	Sour cherries, preserved	Unknown	2.2	X		
	Wild muschrooms, dried	Unknown	24	X		
	Wild muschrooms, dried	Unknown	43.3	X	X	

Compound	Commodity	Country of Origin	Conc. (mg/kg)	>MRL*	>2x MRL**	Note
	Beetroots	Germany	6.2	X	X	
	Green beans	Kenia	2.4	X		
	Parsnip	Germany	2.7	X		
	Green beans	Morocco	2.8	X		
	Mushroom mixtures, dried	Unknown	18.6	X		
	Green beans	Morocco	2.9	X		
Trimesium	Moringa, dried	Unknown	0.15	X	X	Food supplement
	Moringa, dried	Unknown	0.24	X	X	Food supplement
	Dill, dried	Unknown	0.49	X		
	Black tea	Unknown	0.27	X	X	
	Hibiscus tea	Unknown	0.14	X	X	
	Hibiscus tea	Unknown	0.27	X	X	
	Hibiscus tea	Unknown	0.43	X	X	
	Jasmine tea	Unknown	0.16	X	X	
	Rosehip tea	Unknown	0.55	X		
	Rosehip tea	Unknown	1.9	X	X	
	Moringa, dried	Unknown	0.06	X		
	Moringa, dried	Unknown	0.061	X		

* In case of Melamine and Cyanuric acid MLs according Commission Regulation (EC) No 1881/2006

** >2xMRL means that the sample exceeded MRL even after deducting measurement uncertainty of 50%

Table 4: Top 15 residue levels of most frequently found QuPPe-compounds (with > 50 findings in total)

Compound	Commodity	Country of origin	Residue level (mg/kg)
Cyanuric acid	Wild muschrooms, dried	Unknown	11.3
	Avocado	Chile	3.6
	Paprika powder	Unknown	2.3
	Mushroom mixtures, dried	Unknown	1.5
	Paprika powder	Unknown	1.3
	Paprika powder	Unknown	1.1
	Shiitake, dried	China	0.98
	Pineapple	Costa Rica	0.97
	Food supplement, Moringa	Unknown	0.96
	Paprika powder	Unknown	0.9
	Pineapple	Costa Rica	0.86
	Pineapple	Costa Rica	0.84
	Paprika powder	Unknown	0.81
	Jasmine tea	Unknown	0.8
	Pineapple	Costa Rica	0.73
Phosphonic acid	Hops	Germany	174.6
	Wild muschrooms, dried	Unknown	138
	Rucola	Italy	64.5
	Blackberries	Unknown	52.7
	Blackberries	Germany	48.9
	Strawberries	Germany	46.4
	Grapes	Italy	43.9
	Strawberries	Germany	35.5
	Blackberries	Germany	34.9
	Blackberries	Germany	32.9
	Cucumber	Germany	32.8
	Wine grapes	Germany	31.4
	Basil	Germany	30.3
	Rucola	Italy	30.1

Compound	Commodity	Country of origin	Residue level (mg/kg)
	Wild muschrooms, dried	Unknown	29.5
Chlorate	Paprika powder	Unknown	15.6
	Paprika powder	Unknown	5.5
	Chives, frozen	Unknown	4.8
	Paprika powder	Unknown	4
	Paprika powder	Unknown	3.9
	Paprika powder	Hungary	3.3
	Paprika powder	Unknown	3.2
	Moringa, dried	Unknown	2.6
	Paprika powder	Unknown	2.4
	Paprika powder	Unknown	2.2
	Paprika powder	Unknown	1.7
	Paprika powder	Unknown	1.6
	Paprika powder	Unknown	1.4
	Paprika powder	Unknown	1.3
	Paprika powder	Unknown	1.2
Perchlorate	Herbal tea	Germany	2.1
	Basil	Germany	2.1
	Moringa, dried	Unknown	1.5
	Moringa, dried	Unknown	1.4
	Teas and tea-like products	Tansania	0.82
	Moringa, dried	Unknown	0.73
	Teas and tea-like products	Germany	0.7
	Moringa, dried	India	0.7
	Moringa, dried	Unknown	0.6
	Moringa, dried (food supplement)	Unknown	0.49
	Rucola	Germany	0.45
	Moringa, dried (food supplement)	Unknown	0.43
	Moringa, dried	Unknown	0.36
	Rooibos tea	Unknown	0.35
	Paprika powder	Unknown	0.33
Melamine	Coriander	Germany	12.4
	Oregano	Unknown	7.7
	Potato	Germany	6.3
	Chives	Germany	2.16
	Parsley	Germany	2.0
	Wild muschrooms, dried	Unknown	1.38
	Pear	Chile	1.0
	Potato	Germany	0.95
	Beer ingredients	Germany	0.89
	Celeriac	Germany	0.81
	Parsley	Germany	0.72
	Soya, flakes	France	0.69
	Mushroom mixtures, dried	Unknown	0.6
	Potato	Germany	0.6
	Herbs, frozen	Unknown	0.48
Propamocarb	Head lettuce	Italy	3.6
	Spinach	Spain	0.9
	Leafy vegetables	Belgium	0.84
	Lollo	Germany	0.78
	Oakleafed lettuce	Italy	0.72
	Cucumber	Spain	0.71
	Tomato	Spain	0.62
	Cucumber	Spain	0.59

Compound	Commodity	Country of origin	Residue level (mg/kg)
	Cucumber	Spain	0.58
	Cucumber	Spain	0.57
	Cucumber	Turkey	0.54
	Cucumber	Spain	0.51
	Lamb's lettuce	Germany	0.45
	Cucumber	Germany	0.42
	Basil	Italy	0.38
Propamocarb-N-oxide	Cucumber	Spain	0.6
	Head lettuce	Italy	0.31
	Cucumber	Spain	0.25
	Cucumber	Turkey	0.25
	Cucumber	Spain	0.22
	Cucumber	Germany	0.21
	Cucumber	Spain	0.19
	Cucumber	Spain	0.19
	Cucumber	Germany	0.17
	Brussel's sprouts	The Netherlands	0.15
	Spinach	Spain	0.14
	Brussel's sprouts	Germany	0.11
	Cucumber	Germany	0.11
	Brussel's sprouts	The Netherlands	0.083
	Cucumber	Spain	0.078
Nicotine	Wild muschrooms, dried	Unknown	0.34
	Wild muschrooms, dried	Unknown	0.29
	Wild muschrooms, dried	China	0.25
	Moringa, dried	Unknown	0.23
	Paprika powder	Hungary	0.16
	Tea	Unknown	0.13
	Jasmine tea	Unknown	0.12
	Apricot, dried	Turkey	0.1
	Moringa, dried (food supplement)	Unknown	0.08
	Paprika powder	Unknown	0.072
	Wild muschrooms, dried	Russia	0.067
	Paprika powder	Unknown	0.065
	Moringa, dried (food supplement)	Unknown	0.062
	Paprika powder	Unknown	0.062
	Moringa, dried	Unknown	0.06
Trimesium	Rosehip tea	Unknown	1.9
	Rosehip tea	Unknown	0.55
	Paprika powder	Unknown	0.49
	Hibiscus tea	Unknown	0.43
	Black tea	Unknown	0.27
	Hibiscus tea	Unknown	0.27
	Moringa, dried (food supplement)	Unknown	0.24
	Jasmine tea	Unknown	0.16
	Moringa, dried (food supplement)	Unknown	0.15
	Paprika powder	Unknown	0.14
	Hibiscus tea	Unknown	0.14
	Paprika powder	Unknown	0.13
	Fruit tea	Unknown	0.12
	Paprika powder	Unknown	0.088
	Paprika powder	Spain	0.066
Chlormequat	Paprika powder	Unknown	4.5
	Oyster muschrooms	Poland	4.3

Compound	Commodity	Country of origin	Residue level (mg/kg)
	Paprika powder	Unknown	2.1
	Oat	Germany	1.8
	Paprika powder	Unknown	1.8
	Paprika powder	Unknown	1.6
	Paprika powder	Unknown	1.5
	Paprika powder	Unknown	1.3
	Paprika powder	Unknown	1.2
	Paprika powder	Unknown	0.95
	Paprika powder	Unknown	0.77
	Paprika powder	Unknown	0.70
	Paprika powder	Unknown	0.62
	Paprika powder	Unknown	0.58
	Paprika powder	Unknown	0.57

Table 5 Top 10 residue levels of less frequently found QuPPe-compounds (with < 50 findings in total)

Compound	Commodity	Country of origin	Residue level (mg/kg)
Propamocarb-N-desmethyl	Spinach	Spain	0.23
	Tomato	Spain	0.11
	Head lettuce	Italy	0.092
	Potato	Germany	0.048
	Oakleafed lettuce	Italy	0.046
	Cucumber	Spain	0.043
	Cucumber	Spain	0.04
	Brussel‘s sprouts	The Netherlands	0.035
	Cucumber	Spain	0.033
	Cucumber	Spain	0.03
Bromide	Chestnut	Turkey	71
	Moringa, dried (food supplement)	Unknown	55
	Tea	Tansania	55
	Moringa, dried	Unknown	49
	Moringa, dried	Unknown	49
	Lamb’s lettuce	France	43
	Coriander	Thailand	43
	Moringa, dried	Unknown	38
	Spinach	Italy	37
	Moringa, dried	Unknown	34
Ethephon	Pineapple	Costa Rica	1.3
	Pineapple	Costa Rica	1
	Paprika powder	Unknown	0.61
	Pineapple	Costa Rica	0.41
	Grapes	Egypt	0.32
	Paprika powder	Unknown	0.32
	Grapes	Namibia	0.28
	Tomato	The Netherlands	0.24
	Sour cherries, preserved	Unknown	0.22
	Paprika powder	Unknown	0.18
Mepiquat	Paprika powder	unknown	0.15
	Paprika powder	unknown	0.13
	Paprika powder	unknown	0.13

Compound	Commodity	Country of origin	Residue level (mg/kg)
	Paprika powder	unknown	0.11
	Paprika powder	unknown	0.086
	Paprika powder	unknown	0.079
	Paprika powder	Germany	0.068
	Paprika powder	unknown	0.062
	Paprika powder	unknown	0.058
	Paprika powder	Germany	0.18
Chloridazon-desphenyl	Celery	Germany	0.048
	Celery	Germany	0.018
	Chives, frozen	Germany	0.009
	Parsley	Italy	0.008
	Potato	UK	0.007
	Green beans, frozen	Germany	0.007
	Green beans	Germany	0.007
	Celeriac	Germany	0.006
	Leek	Germany	0.006
	Romaine lettuce	Germany	0.006
Maleic hydrazide	Potato	Germany	10.8
	Potato	Germany	10
	Potato	Germany	8.3
	Potato	France	8.2
	Potato	France	7.8
	Potato	Germany	7
	Onion	The Netherlands	4.1
	Onion, frozen	Germany	2.4
	Potato	Germany	1.7
	Onion	Germany	1.7
Cyromazine	Wild muschrooms, dried	unknown	0.61
	White button muschrooms	Poland	0.28
	White button muschrooms	Germany	0.22
	Mushroom mixtures, dried	unknown	0.084
	Physalis	Colomba	0.078
	Wild muschrooms, dried	Vietnam	0.041
	Melon	Brasil	0.03
	Melon	Brasil	0.02
	Melon	Brasil	0.013
	Melon	Brasil	0.009
Glyphosate	Lentils	unknown	2.2
	Paprika powder	unknown	0.9
	Barley	Poland	0.42
	Paprika powder	unknown	0.38
	Paprika powder	unknown	0.16
	Black tea	unknown	0.12
	Tea mixtures	unknown	0.1
	Barley	unknown	0.096
	Apple	Chile	0.046
	Strawberries	Germany	0.035