Residue Findings of Diquat and Paraquat in Samples of Plant Origin Pilot Monitoring

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This document gives an overview of residue findings of the herbicides paraquat (PQ) and diquat (DQ) in some products of plant origin analyzed between 2022 and 2024. The compilation includes data from a pilot monitoring project of the EURL-SRM (2023-24) as well as data from the routine laboratory of the CVUA Stuttgart (2022-24).
The analysis of PQ and DQ is quite challenging and requires a special variation of the QuPPe method (see **QuPPe V12.3**). This methodology involves extraction with methanol/water but acidified with HCl rather than with formic acid in standard QuPPe. This stronger acidification is necessary in order to reduce the adsorption of PQ and DQ on the matrix surface thus achieving higher absolute recovery rates. As this methodology deviates from the standard QuPPe procedure already in the extraction step, laboratories need a guidance as to how this method can be used in a judicious way by primarily targeting commodities that are more likely to contain PQ and DQ residues. This ultimately translates in a more targeted and efficient use of lab resources. The aim of this project was therefore to spot relevant commodities for these two compounds.
All samples were analyzed according to the above QuPPe-variant. It should be noted, however, that the number and diversity of commodities analysed so far and presented in this report is still limited and that there are expectedly more types of products that may potentially contain PQ and DQ residues. Analyses will therefore continue and there will be periodic updates of this residue findings report, especially if additional types of commodities are found to be relevant.

Matrix Scope:

This study mainly targeted commodities known to have a certain PQ/DQ relevance, for example crops where desiccation is applied prior to harvesting, such as pulses, oily seeds, cereals, pseudocereals and potatoes. Targeted were also miscellaneous spices as well as certain tropical fruits, such as bananas, where PQ and DQ are potentially used to eliminate the weeds and facilitate accessibility, cultivation and harvest.

Analyte Scope:

Beyond PQ and DQ, some metabolites of the latter were also targeted. Table 1 gives an overview of the compounds targeted in this study and some notes regarding the legal status.

Table 1: Scope of compounds that were routinely monitored by the CVUA Stuttgart

Compound	Notes
Diquat	Total herbicide, not approved in the EU (approval expired in Dec. 2019). Specific MRLs were set for products where desiccation takes place prior to harvest (e.g. potatoes, pulses, oilseeds) and for some other products, (e.g. citrus, stone fruit, tree nuts, oats, strawberries, eggs) Where MRLs were set at the consensus LOQ they were set at 0.01 mg/kg for most fresh produce and milk, at 0.02 mg/kg for fresh herbs and cereals, and at 0.05 mg/kg for spices, teas, most herbal infusions and most food of animal origin.
Diquat dipyridone (DQ-DP)	Non-regulated metabolite of diquat
Diquat monopyridone (DQ-MP)	Non-regulated metabolite of diquat
Diquat Met. TOPPS (R032245)	Non-regulated metabolite of diquat. IUPAC: 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion
Paraquat	Total herbicide, not approved in the EU (approval expired in Dec. 2007). All MRLs are set at the consensus LOQ which is set at 0.02 or 0.05 mg/kg depending on the matrix

Residue Findings in Routine Samples:

Between 2022 and 2024, a total of 318 samples were analyzed for DQ and PQ at the CVUA Stuttgart. The main focus was on dry commodities (pulses, oilseeds, spices, cereals from third countries), bulb vegetables (potatoes and sweet potato from third countries) as well as on some tropical fruits (bananas, pineapples). Overall, approximately 10% and 4% of the samples contained quantifiable residues of PQ or DQ, respectively. In the case of PQ 2.5% of the samples numerically exceeded the allowed MRL. Tables 3 and 4 show the frequency of findings of DQ and PQ at levels equal or higher than 0.005 mg/kg. In principle, lower levels can also be quantified, but 0.005 mg/kg was set as a cutoff as PQ and DQ, showing strong affinity towards surfaces, tend to exhibit carry-over effects during measurement. To keep this effect under control the extracts injected directly after the injection of a positive sample within the measurement sequence were re-injected in case they were positive.

Table 3: Residue findings of Diquat by matrix group (CVUA Stuttgart 2022-2024, with optimized extraction conditions according to QuPPe-PO V12.3)

Commodity Group	Commodity	Farming	# samples	# pos. [1]	% pos.	Max (mg/kg)	Mean[2] (mg/kg)	Median[2] (mg/kg)	# ≥ MRL[3]	% ≥ MRL	Origins of positives
Pulses	**Beans**	conv.	20	0	-	-	-	-	-	-	
		organic	3	0	-	-	-	-	-	-	
	Chickpeas	conv.	14	**1**	**7 %**	0.027	n.c.	n.c.	-	-	LB (1x)
		organic	4	0	-	-	-	-	-	-	
	Lentils	conv.	13	0	-	-	-	-	-	-	
		organic	8	0	-	-	-	-	-	-	
	Peas	conv.	2	**2**	**100 %**	0.007	0.007	n.c.	-	-	NSp (2x)
		organic	0	0	-	-	-	-	-	-	
Oilseed (excl. Spices)	**Chia Seed** (Salvia hispanica)	conv.	13	**1**	**8 %**	0.005	n.c.	n.c.	-	-	PY (1x)
		organic	35	0	-	-	-	-	-	-	
	Linseed (Flax)	conv.	6	**3**	**50 %**	0.018	0.016	0.018	-	-	NSp (3x)
		organic	15	**1**	**7 %**	0.030		-	-	-	KZ (1x)
	Peanuts	conv.	8	0	-	-	-	-	-	-	
		organic	1	0	-	-	-	-	-	-	
	Sesame	conv.	13	**2**	**15 %**	0.033	0.032	n.c.	-	-	PY (1x), NSp (1x)
		organic	14	0	-	-	-	-	-	-	
	Sunflower seeds	conv.	4	0	-	-	-	-	-	-	
		organic	0	0	-	-	-	-	-	-	
Cereals (incl. Pseudocereals)	**Barley, buckwheat, rye, rice, millet, wheat and spelt pasta**	conv.	15	0	-	-	-	-	-	-	
		organic	11	0	-	-	-	-	-	-	
Spices	**Cumin**	conv.	15	**1**	**7 %**	0.011	n.c.	n.c.	-	-	TR (1x)
		organic	1	0	-	-	-	-	-	-	
	Gingerbread spice mix	conv.	6	**1**	**17 %**	0.041	n.c.	n.c.	-	-	NSp (1x)
		organic	1	0	-	-	-	-	-	-	
	Pepper, black	conv.	20	**1**	**5 %**	0.005	n.c.	n.c.	-	-	NSp (1x)
		organic	2	0	-	-	-	-	-	-	
	Other [4]	conv.	11	0	-	-	-	-	-	-	
		organic	11	0	-	-	-	-	-	-	
Root & tuber Vegetables	**Potatoes**	conv.	12	0	-	-	-	-	-	-	
		organic	1	0	-	-	-	-	-	-	
	Sweet Potatoes	conv.	10	0	-	-	-	-	-	-	
		organic	1	0	-	-	-	-	-	-	
Tropical fruits	**Banana**	conv.	3	0	-	-	-	-	-	-	
		organic	3	0	-	-	-	-	-	-	
	Pineapples	conv.	6	0	-	-	-	-	-	-	
		organic	0	0	-	-	-	-	-	-	
Other	**See footnote**[5]	conv.	15	0	-	-	-	-	-	-	
		organic	11	0	-	-	-	-	-	-	
Total			**318**	**13**	**4.1 %**	**0.041**	**0.019**	**0.018**	**0**	**0**	

[1] The number of positive samples refers to samples at or above the RL of 0.005 mg/kg
[2] Mean and median of positives. Mean is shown at n≥2 and median at n≥3
[3] Numerical MRL-exceedances
[4] caraway (2x), cinnamon (2x), clove (2x), coriander seed (1x), nutmeg (1x), paprika powder(1x), green pepper (1x), pimento (1x), dried turmeric powder (1x),
[5] green coffee (1x), moringa (1x), plantain (1x), psyllium husks (2x), psyllium seeds (2x), rapeseed (1x), vegan dairy substitute products (18x)

Table 4: Residue findings of Paraquat by matrix group (CVUA Stuttgart 2022-2024, according to QuPPe-PO V12.3)

Commodity Group	Commodity	Far-ming	# samples	# pos. [1]	% pos.	Max (mg/kg)	Mean[2] (mg/kg)	Median[2] (mg/kg)	# ≥ MRL[3]	% ≥ MRL	Origins of positives
Pulses	**Beans**	conv.	20	**1**	**5 %**	0.20	-	-	**1**	**5 %**	**AR (1x)**
		organic	3	0	-	-	-	-	-	-	
	Chickpeas	conv.	14	0	-	-	-	-	-	-	
		organic	4	0	-	-	-	-	-	-	
	Lentils	conv.	13	**1**	**8 %**	0.11	0.11	n.c.	**1**	**8 %**	**NSp (1x)**
		organic	8	0	-	-	-	-	-	-	
	Peas	conv.	2	0	-	-	-	-	-	-	
		organic	0	0	-	-	-	-	-	-	
Oilseed (excl. Spices)	**Chia Seed** (Salvia hispanica)	conv.	13	**5**	**39 %**	0.089	0.037	0.013	**2**	**15 %**	**PY (4x)**, NSp(1x)
		organic	35	**10**	**29 %**	0.095	0.016	0.006	**1**	**3 %**	PY (4x), BO (1x), **South America (1x)**, NSp (4x)
	Linseed (Flax)	conv.	6	0	-	-	-	-	-	-	
		organic	15	0	-	-	-	-	-	-	
	Peanuts	conv.	8	0	-	-	-	-	-	-	
		organic	1	0	-	-	-	-	-	-	
	Sesame	conv.	13	**2**	**15 %**	0.50	0.25	n.c.	**1**	**8 %**	PY (1x), **NSp(1x)**
		organic	14	0	-	-	-	-	-	-	
	Sunflower seeds	conv.	4	0	-	-	-	-	-	-	
		organic	0	0	-	-	-	-	-	-	
Cereals (incl. Pseudocereals)	**Barley, buckwheat, rye, rice, millet, wheat and spelt pasta**	conv.	15	0	-	-	-	-	-	-	
		organic	11	**1**	**9 %**	0.005	n.c.	n.c.	-	-	CN (1x)
Spices	**Cumin**	conv.	15	0	-	-	-	-	-	-	
		organic	1	0	-	-	-	-	-	-	
	Gingerbread spice mix	conv.	6	0	-	-	-	-	-	-	
		organic	1	**1**	**100 %**	0.007	n.c.	n.c.	-	-	NSp(1x)
	Pepper, black	conv.	20	**9**	**45 %**	0.092	0.032	0.015	**2**	**10 %**	NSp(9x)
		organic	2	0	-	-	-	-	-	-	
	Other [4]	conv.	11	0	-	-	-	-	-	-	
		organic	11	0	-	-	-	-	-	-	
Root & tuber Vegetables	**Potatoes**	conv.	12	0	-	-	-	-	-	-	
		organic	1	0	-	-	-	-	-	-	
	Sweet Potatoes	conv.	10	0	-	-	-	-	-	-	
		organic	1	0	-	-	-	-	-	-	
Tropical fruits	**Bananas**	conv.	3	0	-	-	-	-	-	-	
		organic	3	0	-	-	-	-	-	-	
	Pineapples	conv.	6	0	-	-	-	-	-	-	
		organic	0	0	-	-	-	-	-	-	
Other	**See footnote**[5]	conv.	15	0	-	-	-	-	-	-	
		organic	11	0	-	-	-	-	-	-	
Overall			**318**	**31**	**9.7 %**	**0.50**	**0.047**	**0.011**	**8**	**2.5 %**	

[1] The number of positive samples refers to samples at or above the RL of 0.005 mg/kg.
[2] Mean and median of positives. Mean is shown at n≥2 and median at n≥3
[3] Numerical MRL-exceedances
[4] Caraway (2x), cinnamon (2x), clove (2x), coriander seed (1x), nutmeg (1x), paprika powder(1x), green pepper (1x), pimento (1x), dried turmeric powder (1x),
[5] Green coffee (1x), moringa (1x), plantain (1x), psyllium husks (2x), psyllium seeds (2x), rapeseed (1x), vegan dairy substitute products (18x)

DQ-MP and TOPPS were encountered in a few of the samples that were found to contain DQ, But not every sample containing DQ also contained detectable levels of these metabolites. DQ-DP was not encountered in any of the samples. Some examples where DQ-MP and TOPPS were encountered are shown in Table 2.

Table 2: Residue findings of Diquat and its metabolites

Matrix	Diquat (mg/kg)	Diquat dipyridone (mg/kg)*	Diquat monopyridone (mg/kg) *	Diquat Met. TOPPS (mg/kg) *
Sesame seeds	0.031	-	0.004	-
Sesame seeds	0.033	-	0.004	0.008
Peas	0.007	-	0.004	-
Peas	0.006	-	0.005	-

*results are semi-quantitative

Following frequent and high findings in the first analyzed **chia** samples, with three exceedances of the MRL for PQ, one of them concerning an "organic"product, it was decided to intensify sampling and analysis of chia samples. Figures 1 and 2 show the distribution of PQ and DQ residues in 48 chia samples. For both compounds an MRL of 0.02 mg/kg currently applies. DQ residues were only detected in one single sample (at 0.005 mg/kg). In contrast, PQ was encountered much more frequently. Out of 13 analyzed chia seeds of conventional production 5 samples (39%) were found to contain residues above the reporting limit (RL). Two samples thereof (15% overall) numerically exceeded the MRL. Out of the 35 analyzed chia seeds labelled as organic, 10 samples (29%) entailed residues at or above the reporting limit, with one (3% overall) numerically exceeding the MRL. Overall, the MRL of PQ was exceeded in three out of the 48 analyzed chia samples (6.3 %). Interestingly, MRLs were only exceeded at early stages of the campaign (in 2022, see Figure 2). It is thus assumed that food business operators have reacted to fix the problem. The frequent detection of positive results at levels below the MRL is however remarkable in the case of organic products, suggesting accidental or intentional admixture of contaminated badges to organic material or the inadequate separation of the conventional and organic transport, storage or processing equipment.

Figure 1: Findings of Diquat and Paraquat in conventional and organic Chia Seeds (CVUA Stuttgart, 2022-2024)

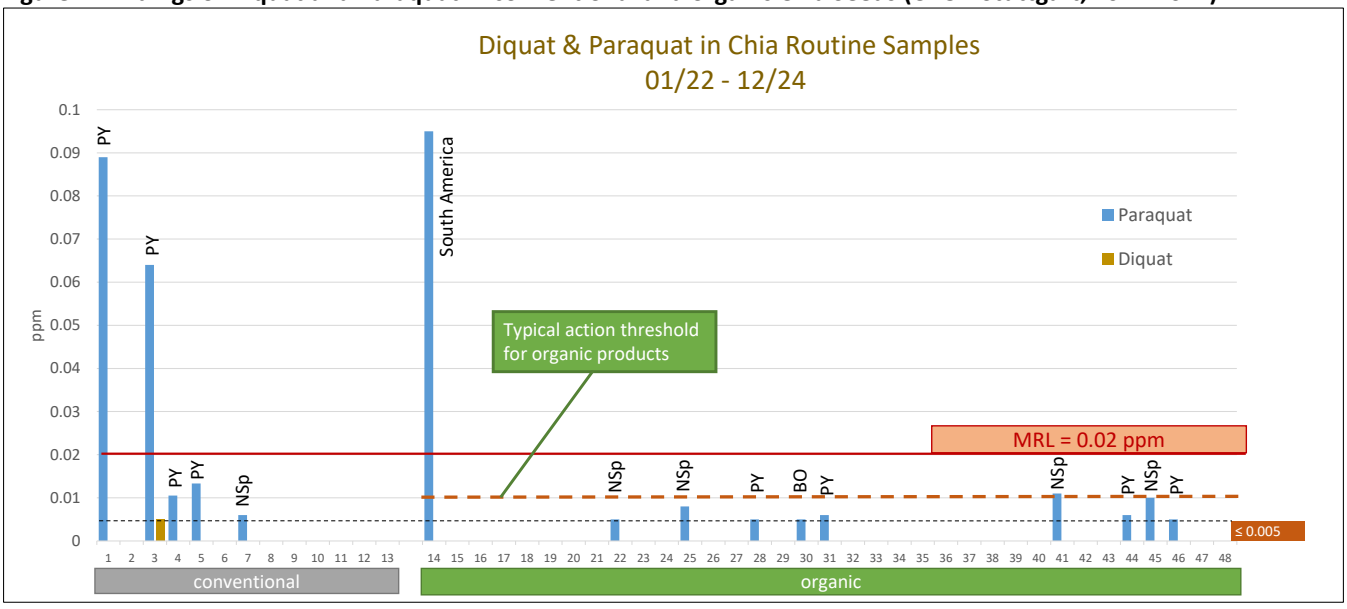
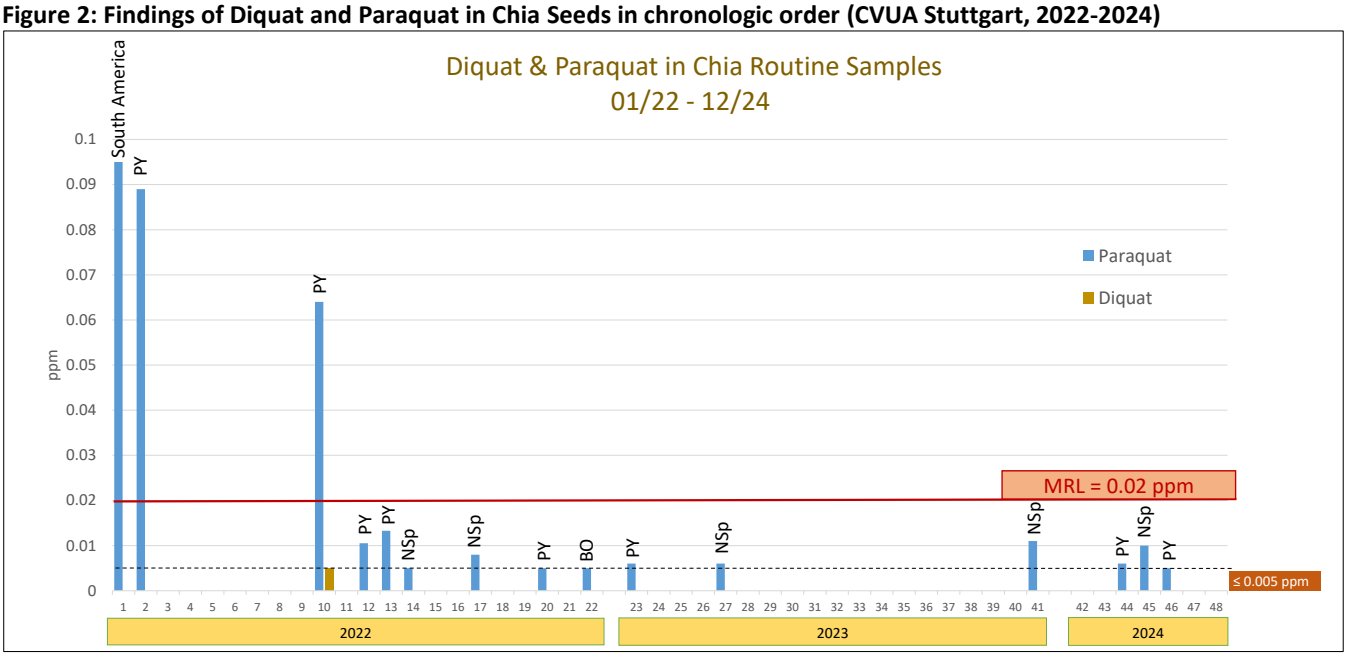
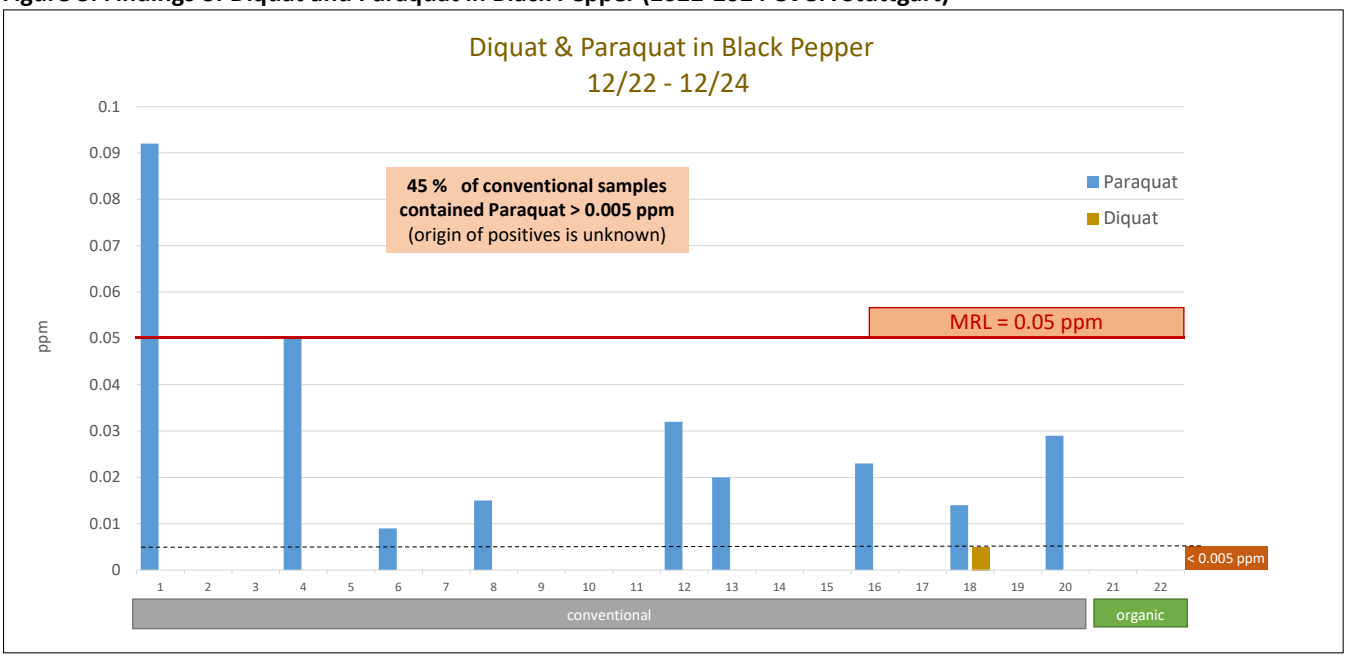


Figure 2: Findings of Diquat and Paraquat in Chia Seeds in chronologic order (CVUA Stuttgart, 2022-2024)



A commodity that surprisingly proved to be problematic is **pepper spice**. Here 9 out of 20 analyzed conventional samples (45%) were found to contain residues of paraquat at levels exceeding the reporting limit of 0.005 mg/kg. One of these samples numerically exceeded the MRL at 0.05 mg/kg, and another one was found to contain PQ at a level equal to the MRL.

Figure 3: Findings of Diquat and Paraquat in Black Pepper (2022-2024 CVUA Stuttgart)



Overview of MRL exceedances

Overall, PQ residues were found to numerically exceed the MRLs in 8 samples (2.5% overall). In 6 of these samples (1.9% overall) the MRLs were exceeded even after deducting the default measurement uncertainty (50%). One of these six samples (chia seeds from South America) was even labelled as organic.

Table 5 gives an overview of the encountered MRL-exceedances for PQ.

Table 5: Samples with residues of Paraquat exceeding existing MRLs* (CVUA Stuttgart 2022/2023)

Compound	Commodity	Country of Origin	Conc. (mg/kg)	>2x MRL**	Note
Paraquat	Chia Seed (Salvia hispanica)	„South America“	0.095	x	organic
	Chia Seed (Salvia hispanica)	Paraguay	0.089	x	
	Chia Seed (Salvia hispanica)	Paraguay	0.064	x	
	Sesame	N/A	0.50	x	
	Beans	Argentina	0.20	x	
	Lentils	N/A	0.11	x	
	Pepper, black	N/A	0.092		
	Pepper, black	N/A	0.050		

* >1xMLR

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

Residue findings in samples collected within the EURL-SRM Small-Scale-Monitoring

Within a small-scale monitoring program, a total of 87 samples originating from 22 different countries, were analyzed for DQ and PQ, This program also targeted commodities expected to be relevant for PQ and DQ, but it did not only include products marketed in the EU but also elsewhere, with aim to localize commodity/origin combinations potentially relevant for residues of these two compounds.

The 87 samples were sampled in Germany, Spain, Australia, USA and Costa Rica. In Germany, the samples were mainly sampled in shops specialized in ethnic food, e.g. Asian, Latin American, Middle Eastern. The distribution of the samples and their origin is shown in Figure 4. Pulses constituted the largest fraction of the samples and included 22 samples belonging to the genus *Phaseolus* (beans), 16 samples of the genus *Vigna* (including cowpeas, mung beans and adzuki beans), 8 samples of the genus *Lens* (lentils), 5 samples of the genus *Pisum* (peas), 4 samples of the genus *Cicer* (chickpeas), and 3 samples each of the genus *Vicia* (fava beans) and the genus *Glycine* (soybeans). Other types of commodities included 8 samples of cereals, 6 samples of chia seeds (including chan seeds), 3 samples each of linseeds and mustard seeds.

An overview of the results is shown in Table 6.

Figure 4: Types of samples analyzed within the frame work of the pilot monitoring and their origin

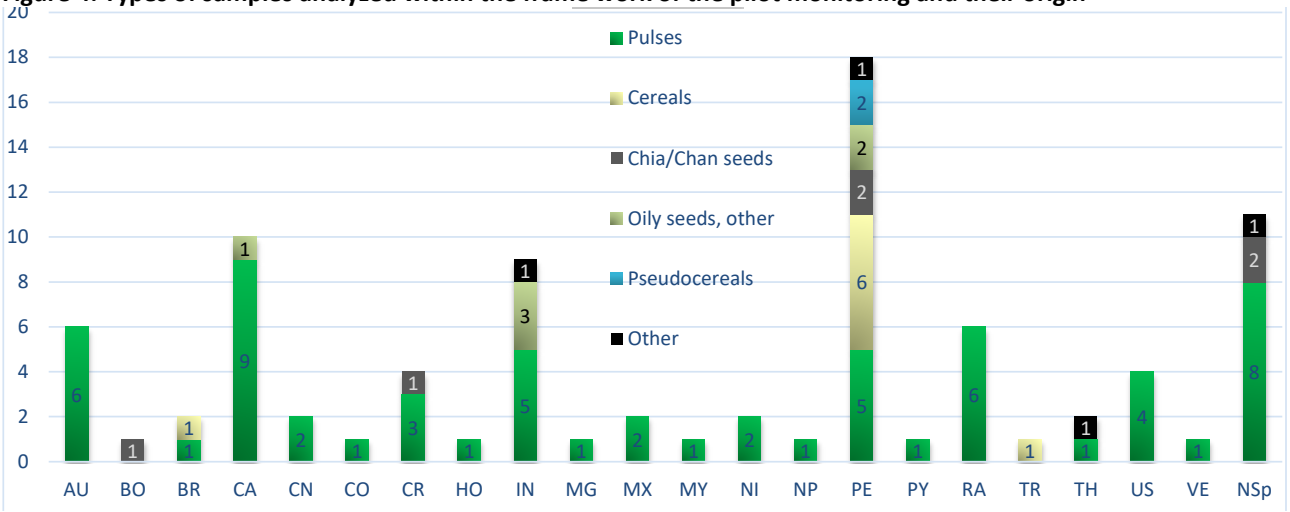


Table 6: Residue findings of Diquat and Paraquat in samples of the small-scale monitoring of the EURL-SRM

Matrix	Compound	# samples	# pos. [1]	% pos.	Max (mg/kg)	Mean [2] (mg/kg)	Median [2] (mg/kg)	# >MRL [3]	% >MRL
Pulses	DQ	61	**6**	**10 %**	0.031	0.018	0.018	0	0
	PQ	61	**15**	**25 %**	0.11	0.032	0.017	**7**	**12 %**
Chia and Chan seeds	DQ	6	**3**	**50 %**	0.53	0.22	0.11	**2**	**33 %**
	PQ	6	0	0	-	-	-	-	-
Linseed (flax)	DQ	3	0	0	-	-	-	-	-
	PQ	3	0	0	-	-	-	-	-
Mustard seeds	DQ	3	0	0	-	-	-	-	-
Cereals	DQ	8	0	0	-	-	-	-	-
	PQ	8	0	0	-	-	-	-	-
	PQ	2	0	0	-	-	-	-	-
	PQ	3	0	0	-	-	-	-	-
Other [4]	DQ	5	0	0	-	-	-	-	-
	PQ	5	0	0	-	-	-	-	-
Feed premix	DQ	1	1	100 %	0.078	-	-	-	-
	PQ	1	0	0	-	-	-	-	-

[1] The number of positive samples refers to samples exceeding the RL of 0.005 mg/kg.
[2] Mean and median of positives
[3] Numerical MRL-exceedances
[4] Chan, Tapioca, Fenugreek, Maca flour

More details about the findings can be found in Table 7, with the type of the products and their origin being highlighted.

Table 7: Findings of Paraquat and Diquat in samples from EURL small-scale monitoring

Type of sample	Matrix	Details	Origin	Paraquat (mg/kg)	Diquat (mg/kg)
Pulses **EU MRLs (mg/kg):** PQ: 0.02 DQ: 0.2 (peas 0.3)	**Beans (dried)**	**black**	RA	0.014	-
		brown	BR	-	*(0.003)**
		red	NI	0.006	-
			PY	0.017	-
		white	CR	0.045	-
			US	0.015	-
	Chickpeas (dried)		AU	0.006	-
			CA	-	0.006
			MX	0,006	-
	Lentils (dried)	**brown**	CA	-	0.031
			CA	-	0.027
			CA	0.10	-
			CR	-	0.031
			US	0.11	-
		green	AU	0.028	-
		red	CA	-	0.005
	Mung beans (dried)		RA	0.040	-
			RA	0.030	-
			VE	0.008	-
		peeled	IN	0.016	-
	Peas (dried)	**green**	CA	-	0.009
			CA	0.033	-
	Soybeans (dried)		AU	-	*(0.003)**
Pulses Overall				**N=15**	**N=6**
Chia/Chan seeds **EU MRLs (mg/kg):** PQ: 0.02; DQ: 0.02	**Chia seeds**		BO	0.005	0
			PE	0.11	0
			NSp	0.53	0
Chia/Chan Overall				**N=3**	**N=0**

*These results are to be considered semi-quantitative

PQ was encountered in 15 (25%) out of the 61 analysed samples of pulses. Two samples of lentils, one originating from CA and one from US (both sampled in CR) contained PQ levels around 0.1 mg/kg. This level exceeds the current EU-MRL of PQ in lentils of 0.02 mg/kg.
Additional cases where the EU-MRL of PQ is exceeded include the following: A sample of dried beans originating in CR (containing 0.045 mg/kg PQ), two sample of mung beans originating in RA (containing 0,040 and 0,030 mg/kg PQ), one sample of dried peas (containing 0,033 mg/kg PQ from CA) and one sample of lentils (containing 0.028 mg/kg from AU).
Among the chia/chen seeds, three out of the six analyzed samples (from BO and PE, and unspecified) were found to contain PQ residues. The sample of unspecified origin was sampled in CR and contained PQ at 0.53 mg/kg.

DQ was less frequently found compared to PQ. Remarkable findings included three findings in lentils at around 0.03 mg/kg (origins 2x CR and 1x CA). Overall, 18 (23%) out of the 78 samples analyzed within this small-scale project were found to contain PQ residues at or above the RL, and 6 samples (7.7%) were found to contain residues of DQ.