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Editors: Christina Østerballe Pedersen, Danish Technological Institute Eva Jacobsen, Danish Technological Institute

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Preface

This report describes the analytical chemical control of pesticides on the Danish market, which was carried out in 2020 by the Chemical Inspection Service of the Danish Environmental Protection Agency. The control is part of the Danish National Plan of Pesticides 2017-2021. Samples of selected types of pesticides on the Danish market were collected and analysed to verify whether or not the content of active substances in the pesticides complies with the product specifications, the labelled content and the information given to the Danish Environmental Protection Agency.

The Danish National Plan of Pesticides 2017-2021 is also engaged to act against illegal and counterfeit pesticides. Therefore, the objective of the analyses was also to investigate the existence of illegal or counterfeit pesticides.

Sammenfatning og konklusion

Denne rapport beskriver den analytisk kemiske kontrol af pesticidprodukter (plantebeskyttelsesmidler) på det danske marked, der er udført af Miljøstyrelsens Kemikalieinspektion i 2020 (Ref. 1, 2).

Den planlagte kontrolkampagne dækkede 23 aktivstoffer i forskellige kombinationer i 31 plantebeskyttelsesprodukter (pesticider). Produkterne blev analyseret for at verificere, om indholdet af de respektive aktivstoffer var i overensstemmelse med produktspecifikationen og det deklarerede indhold. Der blev udført i alt 43 analyser for aktivstoffer.

Grænsen for en accepteret afvigelse i indholdet af et aktivstof i forhold til det deklarerede indhold og produktspecifikationen er fastsat i bekendtgørelsen om bekæmpelsesmidler nr 910 af 15/06/2020 (dagældende bekendtgørelse nr. 815 af 18/06/2018) og i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler (Ref. 3, 4).

Følgende typer af produkter blev analyseret i den planlagte kontrolkampagne (se tabel på næste side):

- 12 fungicider indeholdende boscalid, dimethomorph, epoxiconazol, fluazinam, fluopyram, laminarin, prothioconazol, pyraclostrobin og tolclofos-methyl
- 15 herbicider indeholdende clopyralid, cyazofamid, cycloxydim, diflufenican, eddikesyre, fluroxypyr, glyphosat, MCPA, metobromuron og propyzamid
- 4 insekticider indeholdende alpha-cypermethrin, deltamethrin, flonicamid og spinosad.

Det målte indhold af aktivstoffer var i overensstemmelse med det deklarerede indhold i alle produkter, idet resultaterne er indenfor tolerancen.

Der blev udført i alt 87 fysisk-kemiske test:

- Densitet blev målt på 26 produkter
- Udseende blev vurderet for 23 produkter
- · Vedvarende skumdannelse blev bestemt for 23 produkter
- · Emulsionsstabilitet blev vurderet for 3 produkter
- Suspensibilitet blev målt for 12 produkter.

Fire produkter, som blev testet for fysisk-kemiske parametre, var ikke i overensstemmelse med produkternes specifikationer. Uoverensstemmelsen gjaldt for henholdsvis vedvarende skumdannelse og emulsionsstabilitet af de respektive produkter.

Produktlabel blev tjekket for de 31 produkter. For 6 ud af 31 produkter blev der fundet uoverensstemmelse mellem den opgivne gram pr. liter koncentration og den opgivne koncentration i vægt%.

Ud over den planlagte kontrolkampagne har Miljøstyrelsens Kemikalieinspektion udtaget 6 produkter til analyse ad hoc.

Oversigt over analyserede produkter og aktivstoffer i den planlagte kontrolkampagne.

Aktivstof	Antal analyserede produkter	Antal indenfor tolerance
alpha- Cypermethrin	1	1
Boscalid & epoxiconazol	1	1
Boscalid, epoxiconazol & pyraclostrobin	1	1
Boscalid & pyraclostrobin	3	3
Clopyralid, fluroxypyr & MCPA	1	1
Cyazofamid	1	1
Cycloxydim	1	1
Deltamethrin	1	1
Diflufenican & glyphosat	1	1
Dimethomorph & fluazinam	1	1
Eddikesyre	1	1
Flonicamid	1	1
Fluazinam	1	1
Fluopyram & prothioconazol	1	1
Glyphosat	6	6
Laminarin	1	1
MCPA	2	2
Metobromuron	1	1
Propyzamid	2	2
Spinosad	1	1
Tolclofos-methyl	2	2
TOTAL	31	31

Summary and conclusion

This report describes the analytical chemical control of plant protection products (pesticide products) on the Danish market that was carried out by the Danish Environmental Protection Agency (Danish EPA), Chemical Inspection Service, in 2020 (Ref. 1, 2).

The planned control campaign covered 23 active substances in different combinations in 31 plant protection products (PPP, pesticides). The products were analysed to verify whether the content of the active substances in the products in question complies with the product specification and the declared content. 43 analyses were carried out for active substances.

The tolerance of an accepted deviation in the content of an active substance compared to the declared content and product specification is determined in the Danish Statutory Order on Pesticides No. 910 of 15/06/2020 (applicable Danish Statutory Order 815 of 18/06/2018) as well as in Regulation 1107/2009 concerning Marketing of Plant Protection Products (Ref. 3, 4).

The following products were analysed in the planned control campaign (see table on next page):

- 12 fungicides containing boscalid, dimethomorph, epoxiconazole, fluazinam, fluopyram, laminarin, prothioconazole, pyraclostrobin, and tolclofos-methyl.
- 15 herbicides containing clopyralid, cyazofamid, cycloxydim, diflufenican, acetic acid, fluroxypyr, glyphosate, MCPA, metobromuron, and propyzamide.
- 4 insecticides containing alpha-cypermethrin, deltamethrin, flonicamid, and spinosad.

The measured content of active substances complied with the declared content in all the selected products as the results were within the range of tolerance.

In total, 87 physical-chemical tests were performed:

- Density was measured on 26 products.
- Appearance was assessed for 23 products.
- Persistent foaming was performed on 23 products.
- Emulsion stability was performed on 3 products.
- Suspensibility was performed on 12 products.

Four products that were tested for physical-chemical parameters did not comply with the specified values for persistent foaming or emulsion stability.

A label check was performed for the 31 collected products. In 6 of the 31 products, inconsistencies were found between the stated gram per litre concentration and the weight-percentage concentration.

In addition to the planned control campaign, the Danish EPA, Chemical Inspection Service, collected 6 ad hoc products for analysis.

Overview of the number of analysed products and active substances in the Planned control campaign.

Active substance	No. of analysed products	No. within tolerance
alpha- Cypermethrin	1	1
Boscalid & epoxiconazole	1	1
Boscalid, epoxiconazole & pyraclostrobin	1	1
Boscalid & pyraclostrobin	3	3
Clopyralid & fluroxypyr, MCPA	1	1
Cyazofamid	1	1
Cycloxydim	1	1
Deltamethrin	1	1
Diflufenican & glyphosate	1	1
Dimethomorph & fluazinam	1	1
Acetic acid	1	1
Flonicamid	1	1
Fluazinam	1	1
Fluopyram & prothioconazole	1	1
Glyphosate	6	6
Laminarin	1	1
MCPA	2	2
Metobromuron	1	1
Propyzamide	2	2
Spinosad	1	1
Tolclofos-methyl	2	2
TOTAL	31	31

1. Control campaign 2020

1.1 Collecting products

The Danish planned control campaign conducted in 2020 covered 23 active substances in different combinations in 31 plant protection products (PPP, pesticides). The active substances were selected according to the amount of active substance sold in previous years as well as to when the active substances recently were included in the control campaign. All products were collected by the Chemical Inspection Service of the Danish Environmental Protection Agency during the period from March to July 2020. The product samples were collected either from wholesale dealers/importers or at retailer outlets. A summary of the selected active substances is given in TABLE 1.

Area of application	Active substance	CAS no.
	Boscalid	188425-85-6
	Dimethomorph	110488-70-5
	Epoxiconazole	133855-98-8
	Fluazinam	79622-59-6
Fungicide	Fluopyram	658066-35-4
	Laminarin	9008-22-4
	Prothioconazole	178928-70-6
	Pyraclostrobin	175013-18-0
	Tolclofos-methyl	57018-04-9
	Clopyralid	1702-17-6
	Cyazofamid	120116-88-3
	Cycloxydim	101205-02-1
	Diflufenican	83164-33-4
Herbicide	Acetic acid	64-19-7
	Fluroxypyr	69377-81-7
	Glyphosate	1071-83-6
	MCPA	94-74-6
	Metobromuron	3060-89-7
	Propyzamide	23950-58-5
	alpha-Cypermethrin	67375-30-8
	Deltamethrin	52918-63-5
Insecticide	Flonicamid	158062-67-0
	Spinosad	168316-95-8

TABLE 1. Outline of selected active substances in the 2020 control campaign

The collected product samples were stored at the Laboratory for Chemistry and Microbiology, Danish Technological Institute (DTI) (Ref. 5), in their original packaging until the chemical analyses were initiated. The product samples were stored at ambient temperature and protected from light during the entire storage period.

1.2 Tolerance of active substance

The objective of the Danish EPA was to examine the content of active substances in the products. The results of the chemical analyses were subsequently compared to the specification of the product and the declared content on the label supplied by the authorisation holder.

The Danish Statutory Order on Pesticides of No. 910 of 15/06/2020 (applicable Danish Statutory Order 815 of 18/06/2018) and Regulation 1107/2009 concerning Marketing of Plant Protection Products specify the general tolerance of deviation from the declared content of active substances. (Ref. 3, 4) These tolerances are listed in TABLE 2.

Content of active substances in g/kg or g/L at 20°C	Tolerance of deviation		
	± 15% homogeneous formulation		
Up to 25	± 25% non-homogeneous formulation		
More than 25 up to 100	± 10%		
More than 100 up to 250	± 6%		
More than 250 up to 500	± 5%		
More than 500	± 25 g/kg or ± 25 g/L		

TABLE 2. The tolerance of deviation from the declared content of active substance

1.3 Analysis 2020

The analyses of the products for active substances were performed by Danish Technological Institute, Laboratory for Chemistry and Microbiology. DTI is a self-owned and not-for-profit Institute (Ref. 5).

The Laboratory for Chemistry and Microbiology is accredited by DANAK (Danish Accreditation and Metrology Fund), registration no. 90, according to DS/EN ISO/IEC 17025:2017 (Ref. 6). The laboratory has a flexible scope for determination of active substances in pesticides. In addition, the method for determination of density of pesticides by densimeter is accredited.

1.3.1 Analysing active substances

A total of 43 analyses for active substances were performed. As far as possible, the chemical analyses were performed as at least five freshly prepared samples of each product. If the average result was outside the tolerance interval, then the analysis was repeated with a minimum of three new and freshly prepared samples.

The methods were validated with regard to linearity, specificity, accuracy, and control tests at two levels. The chemical analyses for validation were performed as at least eight freshly prepared samples of the product. The analyses were distributed over at least two days for each product formulation. The mean value of the analyses and the SD (standard deviation) were calculated for each day and for all eight results. Recovery was determined by adding a known amount of the relevant active substance to a minimum of four samples of each product. The mean recovery and SD were calculated.

The expanded uncertainty UE (k=2) of each product was calculated on the basis of the spread of the analysis results, the recovery and on the purity of the reference standard. The expanded analysis uncertainty is used to determine a 95% confidence interval of the analysis result. The expanded uncertainty varies between 2-10% depending on the analytical method, the product formulation, and the available reference standards. For one product, expanded uncertainty was 18% due to the lower purity of the reference standard (87%).

1.3.2 Physical-chemical testing

A total of 87 physical-chemical tests were performed. The tests performed vary with the product formulation. The results were compared to the values specified in connection with the authorisation of the product.

The density of all liquid products (26 products) was measured, and the results were used to determine the content in g/L of the active substance in the product. Additionally, 30 pesticide products were submitted for evaluation of appearance (23 products), determination of persistent foam (23 products), suspensibility (3 products), and emulsion stability (12 products).

2. Analysis of active substances

In this report, pesticides are defined as plant protection products (PPP). In the planned Danish pesticide control campaign conducted in 2020, 31 pesticide products were selected: fungicides, herbicides, and insecticides.

2.1 Fungicides

Thirteen fungicides containing the active substances boscalid, dimethomorph, epoxiconazole, fluazinam, fluopyram, laminarin, prothioconazole, pyraclostrobin and tolclofos-methyl were selected for the 2020 campaign. TABLE 3 states the previous years the active substances were selected for control.

Name	CAS no.	Year selected for control	Molecular structure (Ref. 7)
Boscalid	188425-85-6	2016, 2008	
Dimethomorph	110488-70-5	2016, 2007	
Epoxiconazole	133855-98-8	2016, 2007	
Fluazinam	79622-59-6	2017, 2008, 2000	C_1 HN O_2N C_1 C_2 C_1 C_2 C_3
Fluopyram	658066-35-4	2018	
Laminarin	9008-22-4	2013	H OH OH OH OH
Prothioconazole	178928-70-6	2018, 2010, 2008	CI S NN HN-
Pyraclostrobin	175013-18-0	2019, 2015, 2012, 2005	$CI - (C) - N_{N}^{N} + {}^{O}_{O}_{O}_{O}_{O}_{O}_{O}_{O}_{O}_{O}_$
Tolclofos-methyl	57018-04-9	-	$\overset{H_3C}{\underset{CI}{\longrightarrow}}\overset{CI}{\underset{O'\overset{P}{\longrightarrow}}{\xrightarrow}}^{CI}\overset{CH_3}{\underset{CH_3}{\longrightarrow}}$

TABLE 3. Fungicides in the 2020 control campaign

'-' not previously selected.

*Molecular structure as given on the certificate of analysis of the reference material.

2.1.1 Analysis

Laminarin was analysed by size-exclusion chromatography coupled with refractive index detection (HPLC-RI).

The remaining fungicides were analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD).

Boscalid, epoxiconazole, and pyraclostrobin were analysed according to DTI's method OA-902. Dimethomorph and Fluazinam were analysed according to DTI's method OA-880. Fluopyram and prothioconazole were analysed by DTI's method OA-889. Depending on the product formulation, tolclofos-methyl was analysed by either DTI's method OA-887 or OA-903.

The methods for boscalid, dimethomorph, epoxiconazole, fluazinam, pyraclostrobin, and tolclofos-methyl are accredited.

2.1.2 Results

The results of the performed measurements are listed in the following tables. RSD% is the percentage relative reproducibility of the determinations of the product.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
919029-12	Tolclofos-methyl	100	90-110	105	2.2	Comply
919029-25	Boscalid	267	254-280	267	1.3	Comply
	Pyraclostrobin	67.0	60.3-73.7	68.3	2.0	Comply
0.40000.00	Boscalid	267	254-280	261	1.2	Comply
919029-26	Pyraclostrobin	67.0	60.3-73.7	69.3	0.7	Comply

TABLE 4. Analysis results (g/kg) in fungicides

TABLE 5. Analysis results	(g/L) in fungicides
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DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/kg	Analysis result g/L	RSD %	Comply/ Non-comply
919029-1	Laminarin	45.0	40.5-49.5	49.1	0.2	Comply
040000 0	Dimethomorph	200	188-212	196	2.5	Comply
919029-2	Fluazinam	200	188-212	205	1.5	Comply
040000 40	Boscalid	233	219-247	234	2.0	Comply
919029-16	Epoxiconazol	67.0	60.3-73.7	66.2	0.6	Comply
	Boscalid	140	132-148	142	0.8	Comply
919029-17	Epoxiconazole	50.0	45.0-55.0	49.3	1.1	Comply
	Pyraclostrobin	60.0	54.0-66.0	60.6	0.7	Comply
040000 40	Fluopyram	125	118-133	120	0.4	Comply
919029-18	Prothioconazole	125	118-133	118	0.5	Comply
919029-22	Cyazofamid	160	150-170	169	0.5	Comply
919029-29	Fluazinam	500	475-525	498	0.5	Comply
919029-32	Tolclofos-methyl	500	475-525	477	0.7	Comply
040000 04	Boscalid	150	141-159	145	0.9	Comply
919029-34	Pyraclostrobin	250	235-265	238	1.2	Comply

2.1.3 Conclusion

The concentration of active substances complies with the declared content and with applicable Danish law in all of the 12 products.

2.2 Herbicides

Fifteen herbicides containing the active substances clopyralid, cyazofamid, cycloxydim, diflufenican, acetic acid, fluroxypyr, glyphosate, MCPA, metobromuron, and propyzamide were selected for the 2020 campaign. TABLE 6 states the previous years the active substances were selected for control.

Name	CAS no.	Year selected for control	Molecular structure (Ref. 7)
Acetic acid	64-19-7	2015	н₃с Он
Clopyralid	1702-17-6	2016, 2014, 2009, 2000	CI N OH
Cyazofamid	120116-88-3	2008	$\underset{H_3C}{\overset{Cl}{\longrightarrow}} \overset{Cl}{\underset{O=S}{\overset{N}{\underset{N}{\overset{Cl}{\longrightarrow}}}}} \overset{N}{\underset{O=S}{\overset{Cl}{\underset{N}{\overset{N}{\underset{N}{\overset{Cl}{\longrightarrow}}}}}} } \\ \overset{Cl}{\underset{O=S}{\overset{N}{\underset{N}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{Cl}{\underset{N}{\overset{N}{\underset{N}{\overset{Cl}{\longrightarrow}}}}} } \\ \overset{Cl}{\underset{O=S}{\overset{N}{\underset{N}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{N}{\underset{N}{\overset{Cl}{\longrightarrow}}} \\ \overset{Cl}{\underset{O=S}{\overset{N}{\underset{N}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{N}{\underset{N}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{N}{\underset{N}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{N}{\underset{N}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{Cl}{\underset{N}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{Cl}{\underset{N}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{Cl}{\underset{N}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{Cl}{\underset{N}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{Cl}{\underset{N}{\overset{Cl}{\overset{Cl}{\longrightarrow}}}} \\ \overset{Cl}{\underset{O=S}{\overset{Cl}{\underset{N}{\overset{Cl}{$
Cycloxydim	101205-02-1	2007	OH N ^{CO} CH ₃
Diflufenican	83164-33-4	2016, 2012, 2007	$(\mathbf{r}_{\mathbf{r}_{1}}^{\mathbf{r}_{1}}) = (\mathbf{r}_{1}^{\mathbf{r}_{1}})$
Fluroxypyr	69377-81-7	2016, 2009, 2003	$\overset{NH_2}{\underset{F }{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{CI}{\overset{CI}{\underset{O}{\overset{\bullet}{\underset{O}{\overset{CI}{\underset{O}{\overset{CI}{\underset{O}{\overset{CI}{\underset{O}{\overset{CI}{\underset{O}{O{\\$
Glyphosate	1071-83-6	2016, 2011, 2003	HO HO HO HOH
МСРА	94-74-6	2016, 2012, 2004	сі СН3
Metobromuron	3060-89-7	-	Br O CH3
Propyzamide	23950-58-5	1999	

TABLE 6. Herbicides in the 2020 control campaign

'-' not previously selected

2.2.1 Analysis

Acetic acid was analysed by ion-exclusion chromatography combined with diode array detection (HPLC-DAD) according to DTI's method OA-901.

Glyphosate was analysed by strong anion exchange chromatography combined with diode array detection (HPLC-DAD) according to DTI's method OA-811. The method is adapted from CIPAC method 284 Glyphosate (Ref. 8).

The remaining herbicides were analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD).

Diflufenican was analysed according to DTI's method OA-873. The method is adapted from CIPAC method 462 diflufenican (Ref. 8).

Clopyralid, fluroxypyr, MCPA, and propyzamide were analysed according to DTI's method OA-880, and cycloxydim was analysed according to DTI's method OA-887. Metobromuron was analysed according to the method of the manufacturer.

The methods for analysis of acetic acid, glyphosate, diflufenican, clopyralid, fluroxypyr, MCPA, propyzamide, and cycloxydim are accredited.

2.2.2 Results

The results of the performed measurements are listed in the tables below. RSD% is the percentage relative reproducibility of the determinations of the product.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
919029-27	Glyphosate	720	695-745	731	1.0	Comply

TABLE 7. Analysis results (g/kg) in herbicides

TABLE 8. Analysis results (g/L) in herbicides

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
919029-3	Cycloxydim	100	90-110	100	1.0	Comply
919029-8	Acetic acid	240	226-254	248	1.1	Comply
919029-13	Glyphosate	480	456-504	485	1.2	Comply
919029-14	Glyphosate	490	466-515	496	0.6	Comply
919029-15	MCPA	750	725-775	761	0.7	Comply
919029-19	Glyphosate	360	342-378	356	2.2	Comply
919029-20	Glyphosate	360	342-378	370	1.6	Comply
	Fluroxypyr- meptyl	57.6	51.9-63.4	60.9	0.7	Comply
919029-21	Clopyralid	20.0	17.0-23.0	20.5	0.7	Comply
	MCPA	200	188-212	207	1.1	Comply
919029-23	Propyzamide	400	380-420	382	0.4	Comply
040000 04	Diflufenican	40.0	36.0-44.0	39.7	0.4	Comply
919029-24	Glyphosate	250	235-265	258	0.5	Comply
919029-28	MCPA	750	725-775	755	1.1	Comply
919029-30	Propyzamide	400	380-420	391	1.2	Comply
919029-31	Glyphosate	360	342-378	357	1.1	Comply
919029-35	Metobromuron	500	475-525	516	1.4	Comply

2.2.3 Conclusion

The concentration of active substances complies with the declared content and with applicable Danish law for all of the products.

2.3 Insecticides

Four insecticides containing the active substances alpha-cypermethrin, deltamethrin, flonicamid, and spinosad were selected for the 2020 campaign. TABLE 9 states the previous years the active substances were selected for control.

Name	CAS no.	Year selected for control	Molecular structure (Ref. 7)
alpha-Cypermethrin	67375-30-8	2016, 2008	$ \begin{array}{c} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \\ \mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \\ \mathbf{h} \in \mathcal{C} } \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \\ \mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \\ \mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \\ \mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \\ \mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \\ \mathbf{h} \in \mathcal{C} } \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \\ \mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \\ \mathbf{h} \in \mathcal{C} } \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\substack{\mathbf{h} \in \mathcal{C}} \\ \mathcal{C} } \bigcap_{\substack{\mathbf{h} \in \mathcal{C}} \bigcap_{\substack{\mu, \mu \in \mathcal{C}} \bigcap_{\substack{\mu, \mu, \mu \in \mathcal{C}} \bigcap_{\substack{\mu, \mu, \mu, \mu \in \mathcal{C} } \bigcap_{\mu, \mu, \mu$
Deltamethrin	52918-63-5	2016, 2007	$(h_{0}, h_{0}, h_{0},$
Flonicamid	158062-67-0	2016, 2007	
Spinosad	168316-95-8	2017, 2008, 2000	$\begin{array}{c} H_{I,C} \\ H_{I,C} \\$

TABLE 9. Insecticides in the 2020 control campaign

2.3.1 Analysis

All insecticides were analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD).

Spinosad was analysed according to DTI's method OA-805. The method is adapted from CIPAC method 636 Spinosad (Ref. 8).

Alpha-Cypermethrin and flonicamid were analysed according to DTI's method OA-887, and deltamethrin was analysed according to DIT's method OA-880.

All methods are accredited.

2.3.2 Results

The results of the performed measurements are listed in the tables below. RSD% is the percentage relative reproducibility of the determinations of the product.

TABLE 10. Analysis results (g/kg) in insecticides

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
919029-4	Flonicamid	500	475-525	504	1.4	Comply

DTI sample no	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
919029-5	Deltamethrin	25.0	21.3-28.8	24.7	1.8	Comply
919029-6	alpha- Cypermethrin	50.0	45.0-55.0	51.6	2.1	Comply
919029-10	Spinosad	120	113-127	117	0.5	Comply

TABLE 11. Analysis results (g/L) in insecticides

2.3.3 Conclusion

The concentration of active substances complies with the declared content and with applicable Danish law for all of the products.

3. Physical-chemical testing

The density of all liquid products was measured. Additionally, the 30 pesticide products were submitted to a test programme depending on the formulation type. The tests include evaluation of appearance, determination of persistent foam, emulsion stability and suspensibility. The results were subsequently compared to the values specified in connection with the authorisation of the product. In total, 87 physical-chemical tests were performed.

As the physical-chemical parameters are subject to confidentiality, only the general conclusions have been included in this report.

3.1 Physical-chemical testing of selected pesticides

Details concerning the performed physical-chemical tests are provided below.

3.1.1 Appearance

The colour and physical state of the formulation were described after homogenization of the product.

3.1.2 Density

The density of the formulations was determined according to either DTI's analysis method UA-312 or UA-202. UA-212 is based on CIPAC MT 3 (Ref. 8) and the density of the product is determined as the average of a triple determination carried out by measuring with a Densito 30 PX densimeter. UA-202 is based on CIPAC MT 3.2 (Ref. 8), and the density of the product is determined as the average of a triple determination carried out with a pycnometer.

3.1.3 Persistent foaming

The test for persistent foaming was performed with DTI's method PCA 100 according to the CIPAC method MT 47.2 (Ref. 8). The concentration tested was the maximum concentration prescribed for the product. Standard CIPAC water D, prepared according to CIPAC MT 18.1.4, was used unless otherwise specified for the product (Ref. 8). The amount of foam was reported at the time prescribed for the product. The test was performed in duplicate for each pesticide product.

3.1.4 Emulsion stability

The test for emulsion stability was performed according to DTI's method PCA 106 corresponding to the CIPAC method MT 36.3 (Ref. 8). Highest and lowest in-use concentrations prescribed for the product were tested. Standard CIPAC water A and D, prepared according to CIPAC MT 18.1.4, was used unless otherwise specified for the product (Ref. 8). The test was performed in duplicate for each pesticide product.

3.1.5 Suspensibility

The test for suspensibility was performed according to DTI's method PCA 102 corresponding to the CIPAC method MT 184 (Ref. 8). Highest and lowest in-use concentrations prescribed for the product were tested. Standard CIPAC water D, pre-pared according to CIPAC MT 18.1.4, was used unless otherwise specified for the product (Ref. 8).

3.1.6 Results

The tests performed on selected pesticides are summarized in TABLE 12.

DTI sample no.	Appearance	Density	Persistent foam	Emulsion stability	Suspensibility
919029-1	х	х	Х		
919029-2	Х	Х	Х		Х
919029-3	х	х	Х	Х	
919029-4	Х		Х		Х
919029-5		Х			
919029-6	х	Х	Х	Х	
919029-8	Х	Х	Х		
919029-10	Х	Х	Х		Х
919029-12					
919029-13		Х			
919029-14	Х	Х	Х		
919029-15		Х			
919029-16	Х	Х	Х		Х
919029-17	Х	Х	Х		
919029-18		Х			
919029-19	Х	Х	Х		
919029-20	х	Х	Х		
919029-21	х	Х	Х	Х	
919029-22	Х	Х	Х		Х
919029-23		Х			
919029-24	Х	Х	Х		Х
919029-25	Х		Х		Х
919029-26	Х		Х		Х
919029-27	Х		Х		
919029-28		Х			
919029-29	Х	Х	Х		Х
919029-30		Х			
919029-31	X	Х	Х		
919029-32	x	х	X		X
919029-34	х	Х	Х		Х
919029-35	x	x	X		X

TABLE 12. Physical-chemical tests performed on selected pesticide products. An 'X' signifies that the test was performed.

3.1.7 Conclusion

In most cases, the test results are comparable with specified values of the product or are within the legal requirements and tolerances. For four products, the results of persistent foam or emulsion stability were not comparable with the specified values, and the products do not comply with the legal requirements.

4. Control of product labels

A label check of the declared content of active substances was performed for the 31 products collected as part of the 2020 control campaign for pesticides.

4.1 Approach

The information stated on the product label concerning the active substances were compared to the information associated with the product registration.

4.2 Results

For 6 of the 31 products, inconsistencies between the stated gram per litre concentration and the weightpercentage concentration were found. The inconsistencies are listed in the table below.

DTI sample no.	Active substances	Label check		
919029-15	МСРА	The declared %w/w-concentration is not correct. The stated %w/v concentration corresponds to the concentration of MCPA- dimethylammonium.		
919029-23	Propyzamide	The declared %w/w-concentration is not correct.		
919029-24	Diflufenican & glyphosate	The declared %w/w-concentration of glyphosate is not correct. The stated %w/w-concentration correspond to the concentration of glyphosate-isopropylammonium.		
919029-26	Boscalid & pyraclostrobin	The declared %w/w-concentration of pyraclostrobin is not correct.		
919029-28	МСРА	The declared %w/w-concentration is not correct. The stated %w/w- concentration corresponds to the concentration of MCPA- dimethylammonium.		
919029-34	Boscalid & pyraclostrobin	The declared %w/w-concentration is not correct.		

TABLE 13. Label check in the 2020 control campaign

4.3 Conclusion

In most cases, the labels are comparable with the specified values of the products. However, in six cases there were inconsistencies between the stated gram per litre concentration and the weight-percentage concentration. The products do not comply with the legal requirements.

5. Ad hoc samples 2020

In addition to the planned control campaign, the Danish EPA collected a number of suspicious samples in connection with inspection of wholesale dealers/importers or at retailer outlets, garden centres or farms. These samples were analysed ad hoc.

5.1 Collected products

Six cases of ad hoc samples were processed in 2020. The collected samples and the objective of the ad hoc analysis are listed in the table below.

EPA no.	DTI sample no.	Product name on sample packaging	Expected active substance (CAS no.)	Objective of ad hoc analysis
-	919029-11/ 919029-33	Quartz	Diflufenican (83164-33-4)	Comparison of two products labeled Quartz
2020-9564	920584-1	Bonzi	Paclobutrazol (76738-62-0)	Comparison to the product Bonzi (reg. no.1-164)
2020-18749	932435-1	Revolution/ Dicotex BL	2,4-D (94-75-7), MCPA (94-74-6), mecoprop-P (16484-77-8), & dicamba (1918-00-9)	Comparison to the prohibited product Dicotex (reg no.361-7)
2020-18866	934708-1	Kompakt 5C	Chlormequat-chloride (999-81-5)	Comparison to the product Kompakt 5C (reg. no. 49-94) and comparison to the product Bonzi (reg. no.1-164)
2020-23361	934708-1	-	Glyphosate (1071-83-6)	Measure the concentration of glyphosate

TABLE 14. Samples collected for ad hoc analysis 2020

5.2 Analysis

Individual analysis programs were compounded for the collected products based on expected product properties and objective of the ad hoc analyses. If required, the analysis program was amended based on initial results. The final analysis programs for ad hoc products are listed in the table below.

DTI sample no	Analysis program	
919029-11/ 919029-33	 Determination of density Analysis of diflufenican by HPLC-DAD according to DTI's method OA-873 Screening by GC-MS, SCAN m/z 45-550, identification by NIST 17 library Screening by FTIR 	
920584-1	 Evaluation of appearance Determination of density Analysis of paclobutrazol by RP-HPLC-DAD according to DTI's method OA-880 Analysis of propylene glycol by GC-FID according to DTI's method OA-838 	
932435-1	 Determination of density Analysis of 2,4-D, MCPA, mecoprop-P and dicamba by LC-MS ad hoc method 	

TABLE 15. Analysis program for ad hoc analyses 2020

DTI sample no	Analysis program
	Evaluation of appearance
	Determination of density
004700 4	 Screening by GC-MS, SCAN m/z 45-550, identification by NIST 17 library
934708-1	 Analysis of chlormequat-Cl by LC-MS according to DTI's method OA-1200
	 Analysis of paclobutrazol by RP-HPLC-DAD according to DTI's method OA-880
	 Analysis of propylene glycol by GC-FID according to DTI's method OA-838
034708 1	Determination of density
334700-1	 Analysis of glyphosate concentration by SAX-HPLC-DAD according to DTI's method OA-811.

5.3 Results

The results of the analysis are described in the following sections

5.3.1 Comparison of products labelled Quartz

A product labelled 'Quartz' was collected (919029-11). The product label did not correspond to the authorized label of the product Quartz (reg. no. 18-514). Therefore, a copy of the product with correct labelling was collected (919029-33), and the two products were compared based on the analysis listed in TABLE 15. The two samples were equivalent for all tested parameters except for the chromatographic profile produced by GC-MS-screening. However, it was not possible to rule out that the difference could be due to decomposition of the formulation chemicals in 919029-11(TABLE 16).

Parameter	919029-11 vs. 919029-33
Appearance	Equivalent
Density	Equivalent
Active substance concentration	Both comply with tolerances of the product 'Quartz'
GC-MS-screening	Non-conclusive
FTIR-screening	Equivalent

TABLE 16. Comparison of analysis results for sample 919029-11 and 919029-33

5.3.2 Analysis of product labelled 'Bonzi'

A product labelled 'Bonzi' was collected due to suspicion that the product might not be equivalent to the authorized product 'Bonzi'. The results were compared to the registration information of the authorized product 'Bonzi' (reg. no. 1-164) and with the analysis results of a copy of the authorized product collected as part of the 2018 control campaign. The results are listed in the table below.

TABLE 17. Comparison of analysis results for sample no. 920584-1 with the authorized product 'Bonzi' (reg. no. 1-164).

Parameter	Comparison of 920584-1 with Bonzi
Appearance	Not Equivalent
Density	Equivalent (<5% difference)
Active substance concentration	Comply with tolerances of the product 'Bonzi'
Propylene glycol concentration	Equivalent (<5% difference)

5.3.3 Analysis of product labelled 'Revolution / Dicotex BL'

A product labelled 'Revolution' was collected (sample no. 932435-1). 'Dicotex BL' was written in permanent marker on the sample packaging. The product was analysed for the active substances 2,4-D, MCPA, mechlorprop-P (MCPP-P), and dicamba pertinent to the prohibited product Dicotex (reg. no. 361-7). The analysis results are given in the table below.

DTI	Active	Analysis result	RSD	
sample no.	substance	g/L	%	
932435-1	2,4-D	0.84	1.4	
	MCPA	0.75	1.4	
	MCPP-P	0.59	1.4	
	Dicamba	0.28	4.1	

TABLE 18. Analysis results (g/L) in sample 932435-1

5.3.4 Analysis of product labelled 'Kompakt 5C

A product labelled 'Kompakt 5C' was collected (sample no. 934708-1). The product was analysed for chlormequat-chloride, the active substance pertinent to the product 'Kompakt 5C' (reg. no.49-94) and screened by GC-MS (TABLE 19). Because the GC-MS screening showed the presence of the active substance paclobutrazol, the analysis program was amended to allow for a comparison with the authorized product 'Bonzi' (reg. no. 1-164). The results are given in TABLE 20.

TABLE 19. Analysis results for 934708-1

Parameter	Analysis results
Chlormequat-Cl concentration	<0.003 %w/w
GC-MS-screening	Paclobutrazol (CAS no. 76738-62-0)

TABLE 20. Comparison of analysis results for sample no. 934708-1 with the authorized product 'Bonzi' (reg. no. 1-164)

Parameter	Comparison of 934708-1 with Bonzi	
Appearance	Not Equivalent	
Density	Equivalent (<5% difference)	
Active substance concentration	Comply with tolerances of the product 'Bonzi'	
Dremulane, aluard concentration	Not equivalent	
Propylene glycol concentration	Propylene glycol < 0.005%w/w in sample 934708-1	

5.3.5 Analysis of unmarked product

A sample was collected from an intermediate bulk container (sample no. 934708-1). The concentration of glyphosate was determined. The result is listed in the table below.

TABLE 21.	Analysis r	results (g/L) in sample	934708-1.
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DTI	Active	Analysis result	RSD
sample no.	substance	g/L	%
934708-1	Glyphosate	2.9	3.7

5.4 Conclusion

The results from the ad hoc samples in 2020 were used in further investigation of dealers/importers, retailer outlets, garden centres and farmers.

References

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- 2. Danish EPA, 2020, approved Pesticides 2020 http://mst.dk/kemi/database-for-bekaempelsesmidler/bmd/ (Danish)
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- 6. The Danish Accreditation and Metrology Fund DANAK, http://english.danak.dk/
- 7. The e-Pesticide Manual, eighteenth Edition, online version, 2016. British Crop Protection Council, United Kingdom
- CIPAC method no.284, 462, 636, MT 3, MT 3.2, MT 18.1, MT 18.1.4, MT 36.3, MT 47.2 and MT 184, http://www.cipac.org/

Appendix 1

Pesticide products collected for the planned control campaign 2020.

TABLE 22. Fungicide products

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
919029-1	Laminarin	740-1	Vacciplant	Laboratoires GOËMAR SAS
919029-2	Dimethomorph & fluazinam	396-58	Banjo Forte	ADAMA Registrations B.V.
919029-12	Tolclofos-methyl	526-2	Rizolex 10 D	Sumitomo Chemical Agro Europa S.A.
919029-16	Boscalid & Epoxiconazole	19-173	Bell	BASF A/S
919029-17	Boscalid, Epoxiconazole & pyraclostrobin	19-204	Viverda	BASF A/S
919029-18	Fluopyram & Prothioconazole	18-597	Propulse SE 250	Bayer A/S, Bayer CropScience
919029-22	Cyazofamid	352-8	Ranman TOP	ISK Biosiences Europe N.V.
919029-25	Boscalid & pyraclostrobin	19-151	Signum	BASF A/S
919029-26	Boscalid & pyraclostrobin	318-116	LFS Pyraclostrobin + Boscalid	LFS Kemi A/S
919029-29	Fluazinam	352-13	Shirlan Ultra	ISK Biosiences Europe N.V.
919029-32	Tolclofos-methyl	526-3	Rizolex 50 FW	Sumitomo Chemical Agro Europe S.A.
919029-34	Boscalid & pyraclostrobin	19-228	Pictor Active	BASF A/S

TABLE 23. Herbicide products

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
919029-3	Cycloxydim	19-93	Focus Ultra	BASF A/S
919029-8	Acetic acid	18-630	Harmonix Leaf Active	Bayer A/S, Bayer CropScience
919029-13	Glyphosate	48-43	Roundup Flex	Monsanto Crop Sciences Denmark A/S, c/o Lundgrens Advokatpartnerselskab
919029-14	Glyphosate	357-3	Gallup Hi-Aktiv	Barclay Chemicals Manufacturing Ltd.
919029-15	MCPA	347-5	Metaxon	Nufarm Deutschland GmbH
919029-19	Glyphosate	357-4	Gallup Super 360	Barclay Chemicals Manufacturing Ltd
919029-20	Glyphosate	48-16	Roundup BIO	Monsanto Crop Sciences Denmark A/S, c/o Lundgrens Advokatpartnerselskab
919029-21	Clopyralid, Fluroxypyr & MCPA	64-39	Ariane FG S	Dow AgroSciences Danmark A/S
919029-23	Propyzamide	318-158	LFS Propyzamid	LFS Kemi A/S
919029-24	Diflufenican & Glyphosate	19-241	Pistol Ukrudtsmiddel	BASF A/S
919029-27	Glyphosate	48-47	Roundup Powermax	Monsanto Crop Sciences Denmark A/S, c/o Lundgrens Advokatpartnerselskab
919029-28	MCPA	347-7	U 46 M	Nufarm Deutschland GmbH
919029-30	Propyzamide	64-72	Kerb 400 SC	Corteva Agriscience Denmark A/S
919029-31	Glyphosate	396-53	Glypper	ADAMA Registrations B.V.
919029-35	Metobromuron	632-2	Proman	Belchim Crop Protection NV/SA

TABLE 24. Insecticide products

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
919029-4	Flonicamid	352-5	Teppeki	ISK Biosiences Europe N.V.
919029-5	Deltamethin	18-541	K-Obiol EC 25	Bayer A/S, Bayer CropScience
919029-6	alpha-Cypermethrin	19-139	Fastac 50	BASF A/S
919029-10	Sinosad	64-51	Conserve	Dow AgroSciences Danmark A/S

Control of Pesticides 2020

English

The analytical chemical authority control of pesticide products on the Danish market that was carried out in 2020 by the Danish Environmental Protection Agency (Danish EPA), Chemical Inspection Service, is described in this report. Samples of selected types of plant protection products (pesticides) were collected on the Danish market and analysed to verify whether the content of the active substances in the products in question complies with the product specification and the labelled content. 31 different pesticide products were analysed as part of the planned control program and an additional 6 samples were collected for ad hoc analysis.

Danish

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked, der er udført i 2020 af den danske Miljøstyrelses Kemikalieinspektion, er beskrevet i denne rapport. Prøver fra udvalgte typer af bekæmpelsesmidler (pesticider) er blevet indsamlet og analyseret for at verificere, om indholdet af de respektive aktivstoffer er i overensstemmelse med det deklarerede indhold. I alt 31 bekæmpelsesmidler (pesticider) blev undersøgt som en del af den planlagte kontrolkampagne og herudover blev 6 prøver indsamlet til ad hoc analyse.



The Danish Environmental Protection Agency Tolderlundsvej 5 5000 Odense C

www.mst.dk