Ministry of Environment
of Denmark
Environmental
Protection Agency

Control of Pesticides 2023

May 2024

Publisher: The Danish Environmental Protection Agency

Editors:
Maja Skou Jensen, Danish Technological Institute
Martin Karkov Kristensen, Danish Technological Institute
Sara Kobbelgaard, Danish Technological Institute

ISBN: 978-87-7038-616-6

Contents

Preface		**4**
Abbreviations		**5**
Resume		**6**
Abstract		**8**
1.	**Control campaign 2023**	**10**
1.1	Collected products	10
1.2	Tolerance of active substance	11
1.3	Analytical program and the executing party	11
1.3.1	Quantification of active substances	11
1.3.2	Physico-chemical testing	12
1.3.3	Per- and Polyfluoroalkyl Substance testing	12
2.	**Analysis of active substances**	**13**
2.1	Herbicides	13
2.1.1	Results and conclusion	13
2.2	Fungicides	17
2.2.1	Results and conclusion	17
2.3	Growth regulators	19
2.3.1	Results and conclusion	19
2.4	Insecticides	21
2.4.1	Results and conclusion	21
3.	**Physico-chemical testing**	**23**
3.1	Physico-chemical testing of selected pesticides	23
3.1.1	Appearance	23
3.1.2	Density	23
3.1.3	Persistent foaming	23
3.1.4	Emulsion stability	23
3.1.5	Suspensibility	23
3.1.6	Results	24
3.1.7	Conclusion	24
4.	**Per- and Polyfluoroalkyl Substance testing**	**25**
4.1	PFAS testing of selected pesticides	25
4.1.1	Results and conclusion	25
5.	**References**	**30**
Appendix 1		**31**

Preface

In 2023, the Danish Chemical Inspection Service of the Danish Environmental Protection Agency conducted a control of pesticide products on the Danish market. This control is in line with the " Danish National Strategy of Pesticides 2022-2026". The purpose was to analyze pesticide products available in Denmark to ensure that the active substances in the products agree with the labeled content and specifications provided by manufacturers to the Danish Environmental Protection Agency.

Furthermore, the pesticide products collected in the control campaign were tested for selected Per- and Polyfluoroalkyl Substances (PFAS).

Abbreviations

a.s.: Active substance
CIPAC: Collaborative International Pesticides Analytical Council
DANAK: Danish Accreditation and Metrology Fund
Danish EPA: The Danish Environmental Protection Agency
DTI: Danish Technological Institute
GC-FID: Gas chromatography - flame ionization detection
HPLC-DAD: High-performance liquid chromatography - diode array detection
MAM: Multi-active method
PFAS: Per- and Polyfluoroalkyl Substances
PPP, pesticides: Plant Protection Products
RSD: Relative standard deviation
STD: Standard deviation

Resume

Denne rapport beskriver den analytiske kemiske kontrol af pesticidprodukter (plantebeskyttelsesmidler) på det danske marked, der er udført af Miljøstyrelsens Kemikalieinspektion i 2023 (Ref. 1, 2).

Den planlagte kontrolkampagne dækkede over 21 aktivstoffer i forskellige kombinationer i 31 plantebeskyttelsesprodukter. Produkterne blev analyseret for at verificere, om indholdet af de respektive aktivstoffer var i overensstemmelse med produktspecifikationen og det deklarerede indhold. 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. 1278 af 06/06/2021 (gældende bekendtgørelse nr. 961 af 26/06/2023) og i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler (Ref. 3, 4).

Følgende produkter blev analyseret i den planlagte kontrolkampagne (se tabel på næste side).

- 16 herbicider indeholdende aktivstofferne Aclonifen, Clodinafop-propargyl, Diflufenican, Florasulam, Fluroxypyr-meptyl, Halauxifen-methyl, Iodosulfuron-methyl sodium, Mesosulfuron methyl, Mesotrione, Phenmedipham, Prosulfocarb, Pyroxsulam og Thifensulfuron-methyl.
- 8 fungicider indeholdende aktivstofferne Fluopyram, Prothioconazol og Tebuconazol.
- 5 vækstreguleringsmidler indeholdende aktivstofferne Prohexadione calcium, Paclobutrazol og Trinexapac-ethyl.
- 2 insekticider indeholdende aktivstofferne Abamectin og Spinosad.

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

Der blev udført fysisk-kemiske test på alle 31 pesticidprodukter.

- Udseende blev vurderet for 31 produkter.
- Densitet blev målt på 26 produkter.
- Vedvarende skumdannelse blev bestemt for 28 produkter.
- Emulsionsstabilitet blev vurderet for 12 produkter.
- Suspensibilitet blev målt for 10 produkter.

3 af produkterne, som blev testet for fysisk-kemiske parametre, var ikke i overensstemmelse med produkternes specifikationer, hvad angår udseende, 1 produkt var ikke i overensstemmelse med produktets specifikation, hvad angår skumdannelse, og 1 produkt var ikke i overensstemmelse med produktets specifikation, hvad angår suspensibilitet.

Produkterne, der blev indsamlet, blev også undersøgt for tilstedeværelsen af udvalgte PFAS-indholdsstoffer. Resultaterne viste, at der ikke blev påvist nogen PFAS-indholdsstoffer i produkterne. Analyserne af PFAS blev udført af Medico Kemiske Laboratorium ApS.

Oversigt over analyserede produkter og aktivstoffer i den planlagte kontrolkampagne.

Aktivstof	Antal analyserede produkter	Antal indenfor tolerance
Abamectin	1	1
Aclonifen	1	1
Clodinafop-propargyl	3	3
Diflufenican	3	3
Florasulam	3	3
Flropyram	1	1
Fluroxypyr-meptyl	4	4
Halauxifen-methyl	1	1
Iodosulfuron-methyl natrium	1	1
Mesosulfuron-methyl	1	1
Mesotrion	1	1
Paclobutrazol	1	1
Phenmedipham	1	1
Prohexadion calcium	1	1
Prosulforcarb	2	2
Prothioconazol	5	5
Pyroxsulam	2	2
Spinosad	1	1
Tebuconazol	3	3
Thifensulfuron-methyl	1	1
Trinexapac-ethyl	7	7
Total	44	44

Abstract

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), The Danish Chemical Inspection Service, in 2023 (Ref. 1, 2).

The planned control campaign covered 21 active substances in different combinations in 31 plant protection products (PPP, pesticides). The products were analyzed to verify whether the content of the active substances in the products in question complied with the product specification and the declared content. 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. 1278 of 06/06/2021 (applicable Danish Statutory Order 961 of 26/06/2023) as well as in Regulation 1107/2009 concerning Marketing of Plant Protection Products (Ref. 3, 4).

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

- 16 herbicides containing the active substances Aclonifen, Clodinafop-propargyl, Diflufenican, Florasulam, Fluroxypyr-meptyl, Halauxifen-methyl, Iodosulfuron-methyl sodium, Mesosulfuron methyl, Mesotrione, Phenmedipham, Prosulfocarb, Pyroxsulam and Thifensulfuron-methyl.
- 8 fungicides containing the active substances Fluopyram, Prothioconazole, and Tebuconazole.
- 5 growth regulators containing the active substances Prohexadione calcium, Paclobutrazole, and Trinexapac-ethyl.
- 2 insecticides containing the active substances Abamectin 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.

Physico-chemical tests were performed on all 31 pesticides.

- The appearance of 31 products was assessed.
- Density was measured on 26 products.
- Persistent foaming was performed on 28 products.
- The emulsion stability of 12 products was assessed.
- Suspensibility was measured on 10 products.

3 products did not comply with the specifications of the products regarding appearance, 1 product did not comply with the specifications of the product regarding persistent foaming, and 1 product did not comply with the specifications of the product regarding suspensibility.

The collected products were also examined for the presence of selected PFAS substances. The results showed that no PFAS substances were detected in the products. The PFAS analyses were conducted by Medico Kemiske Laboratorium ApS.

Overview of analyzed products and active substances in the planned control campaign.

Active substance	No. of analyzed products	No. within tolerance
Abamectin	1	1
Aclonifen	1	1
Clodinafop-propargyl	3	3
Diflufenican	3	3
Florasulam	3	3
Flropyram	1	1
Fluroxypyr-meptyl	4	4
Halauxifen-methyl	1	1
Iodosulfuron-methyl natrium	1	1
Mesosulfuron-methyl	1	1
Mesotrione	1	1
Paclobutrazole	1	1
Phenmedipham	1	1
Prohexadion calcium	1	1
Prosulforcarb	2	2
Prothioconazole	5	5
Pyroxsulam	2	2
Spinosad	1	1
Tebuconazole	3	3
Thifensulfuron-methyl	1	1
Trinexapac-ethyl	7	7
Total	44	44

1. Control campaign 2023

1.1 Collected products

The planned control campaign conducted in 2023 covered 21 active substances (a.s.) in different combinations in a total of 31 plant protection products (PPP; pesticides). The a.s. were selected according to their sales figures in the previous years, availability at retailers, and whether they had been part of previous campaigns. All products were collected by the Danish Chemical Inspection Service of the Danish Environmental Protection Agency during the period from Oktober 2022 to September 2023. The products were collected from wholesale dealers/importers or at retail outlets. An overview of the selected active substances is given in TABLE 1.

TABLE 1. Overview of selected active substances in the 2023 control campaign.

Area of application	Active substance	CAS no.
Herbicide	Aclonifen	74070-46-5
	Clodinafop-propargyl	105512-06-9
	Diflufenican	83164-33-4
	Florasulam	145701-23-1
	Fluroxypyr-meptyl	81406-37-3
	Halauxifen-methyl	943831-98-9
	Iodosulfuron-methyl sodium	144550-36-7
	Mesosulfuron methyl	208465-21-8
	Mesotrione	104206-82-8
	Phenmedipham	13684-63-4
	Prosulfocarb	52888-80-9
	Pyroxsulam	422556-08-9
	Thifensulfuron-methyl	79277-27-3
Fungicide	Fluopyram	658066-35-4
	Prothioconazole	178928-70-6
	Tebuconazole	107534-96-3
Growth regulator	Prohexadione calcium	127227-53-6
	Paclobutrazole	76738-62-0
	Trinexapac-ethyl	95266-40-3
Insecticide	Abamectin	71751-41-2
	Spinosad	168316-95-8

The collected products were stored at Chemical Characterisation and Consultancy, Danish Technological Institute (DTI) (Ref. 5), in their original packaging until the chemical analyses were initiated. The products 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 determine the content of a.s. in the products. The results of the quantitative analysis were subsequently compared to the specification of the product and the declared content on the label supplied by the authorization holder.

The Danish Statutory Order on Pesticides No. 1278 of 06/06/2021 (applicable Danish Statutory Order 961 of 26/06/2023) 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.

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

Content of active substances in g/kg or g/L at 20°C	Tolerance of deviation
Up to 25	± 15% homogeneous formulation
	± 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

1.3 Analytical program and the executing party

The analytical program was performed by Danish Technological Institute, Chemical Characterisation and Consultancy. DTI is a self-owned and not-for-profit institute (Ref. 5).

Chemical Characterisation and Consultancy is accredited by Danish Accreditation and Metrology Fund (DANAK), registration no. 90, according to DS/EN ISO/IEC 17025:2017 (Ref. 6). The Centre has a flexible accreditation for determination of a.s. in pesticide products. The methods for determination of density and persistent foaming are accredited.

1.3.1 Quantification of active substances

A total of 44 analyses for active substances were performed. Methods were adapted from existing reference methods, e.g., CIPAC.

The chemical quantification was performed on 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 five new and freshly prepared samples.

The methods used for quantification were validated based on linearity, specificity, accuracy, and by using control reference material at two levels. The validation of the implemented methods was performed on at least eight freshly prepared samples of the product. The analyses were distributed over at least two days for each product. The mean value of the analyses and the standard deviation (STD) were calculated for each day and for all eight results. The recovery percentage was determined by adding a known amount of the relevant a.s. to a minimum of five samples of each product. The mean recovery and STD were calculated.

The expanded uncertainty (k=2) of each method was calculated according to the spread of the analysis results, the recovery, and the purity of the reference standard. The expanded uncertainty is used to determine a 95% confidence interval of the result. The expanded uncertainty varies between 1.4-20% depending on the analytical method, the product formulation, and the purity of available reference material.

1.3.2 Physico-chemical testing

A total of 107 physico-chemical tests were performed on the products. The tests performed varied with the product formulation. The analytical program was carried out in accordance with the reference document presenting best practices for formulation analysis on pesticide products (Ref. 10). The results were compared to the values specified in the registration report from the authorization holder 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 a.s. in the products. Additionally, the pesticide products were submitted for evaluation of appearance (31 products), determination of persistent foaming (28 products), suspensibility (10 products), and emulsion stability (12 products).

1.3.3 Per- and Polyfluoroalkyl Substance testing

The collected products in the control campaign were tested for 33 selected Per- and Polyfluoroalkyl Substances. The content of selected PFAS was determined according to the method DS/CEN/TS 15968:2010 at Medico Kemiske Laboratorium ApS. The laboratory is accredited to perform testing under ISO 17025, but the methods and results were not accredited.

2. Analysis of active substances

In the planned Danish pesticide control campaign conducted in 2023, 31 pesticide products were selected for an analytical program. The pesticide types covered in the 2023 campaign were: Herbicides, fungicides, insecticides, and growth regulators.

2.1 Herbicides

16 herbicide products containing the a.s. Aclonifen, Clodinafop-propargyl, Diflufenican, Florasulam, Fluroxypyr-meptyl, Halauxifen-methyl, Iodosulfuron-methyl sodium, Mesosulfuron methyl, Mesotrione, Phenmedipham, Prosulfocarb, Pyroxsulam and Thifensulfuron-methyl were part of the 2023 campaign. TABLE 5 gives an overview of the analytical methods, and when the a.s. was part of a prior control campaign.

2.1.1 Results and conclusion

The results of the quantitative determination of a.s. in the herbicides are listed in TABLE 3 and TABLE 4. RSD% is the relative reproducibility percentage for the analysis of the product.

The concentration of a.s. complied with the declared content and with applicable Danish law in all 16 products.

TABLE 3. Analysis results (g/L) for herbicide products.

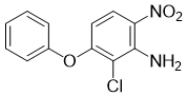
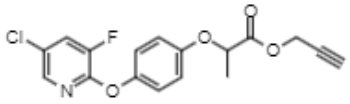
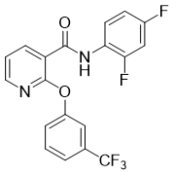
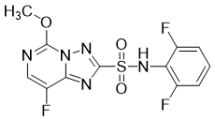
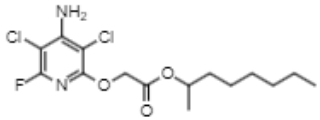
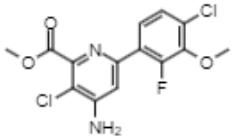
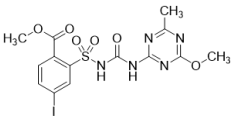
DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD%	Comply/Non-comply
133173-33	Diflufenican	500	475-525	496	1.4	Comply
133173-34	Diflufenican	500	475-525	496	0.91	Comply
133173-37	Iodosulfuron-methyl sodium	2	1.7-2.3	2.3	0.38	Comply
	Mesosulfuron-methyl	10	9-12	11	0.37	Comply
133173-38	Aclonifen	500	475-525	496	1.9	Comply
	Diflufenican	100	90-110	99	0.65	Comply
162154-4	Clodinafop-propargyl	100	90-110	97	3.3	Comply
162154-7	Prosulfucarb	800	775-825	802	0.70	Comply
162154-8	Fluroxypyr-meptyl	144	135-153	148	0.75	Comply
	Florasulam	2.5	2.1-2.9	2.5	0.52	Comply
162154-9	Phenmedipham	160	150-170	154	0.88	Comply
162154-10	Prosulfocarb	800	775-825	809	0.25	Comply
	Clodinafop-propargyl	10	9-12	10	2.0	Comply
162154-18	Fluroxypyr-meptyl	480	456-504	484	0.47	Comply
162154-19	Halauxifen-methyl	12.5	10.6-14.4	12.8	0.90	Comply

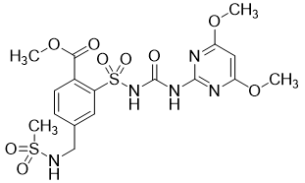
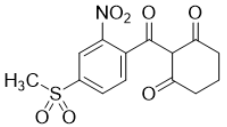
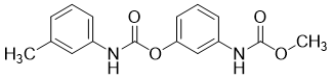
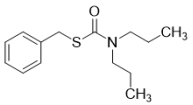
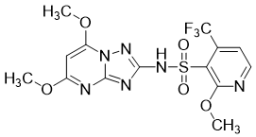
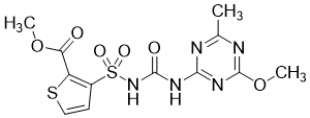
DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD%	Comply/Non-comply
	Fluroxypyr-meptyl	403.46	383.29-423.63	425.37	1.1	Comply
162154-22	Florasulam	5.0	4.3-5.8	5.0	0.55	Comply
	Fluroxypyr-meptyl	144.09	135.44-152.74	144.51	0.39	Comply

TABLE 4. Analysis results (g/kg) for herbicide products.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD%	Comply/Non-comply
133173-35	Pyroxsulam	68.3	61.5-75.1	70.2	0.28	Comply
	Florasulam	22.8	17.1-28.5	22.4	0.20	Comply
133173-36	Mesotrione	500	475-525	511	1.3	Comply
162154-11	Clodinafop-propargyl	200	188-212	201	1.3	Comply
	Pyroxsulam	75	68-83	77	1.2	Comply
162154-13	Thifensulfuron-methyl	500	475-525	492	1.1	Comply

TABLE 5. Active substances categorized as herbicides in the 2023 control campaign.

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Aclonifen	74070-46-5	2022, 2019, 2016, 2008, 2000	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 8)	
Clodinafop-propargyl	105512-06-9	2003	GC-FID, HPLC-DAD	OA-826, OA-890*	Yes	-	
Diflufenican	83164-33-4	2022, 2020, 2019, 2016, 2012, 2007	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 8)	
Florasulam	145701-23-1	2018, 2016, 2005	HPLC-DAD	OA-890 OA-880*	Yes	CIPAC MAM (Ref. 8)	
Fluroxypyr-meptyl	81406-37-3	2020, 2016, 2009, 2003	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 8)	
Halauxifen-methyl	943831-98-9	2019	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 8)	
Iodosulfuron-methyl sodium	144550-36-7	2022, 2013, 2004	HPLC-DAD	OA-911	Yes	-	

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Mesosulfuron methyl	208465-21-8	2022, 2013	HPLC-DAD	OA-911	Yes	-	
Mesotrion	104206-82-8	2022, 2017, 2008	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 8)	
Phenmedipham	13684-63-4	2011, 2002, 1997	HPLC-DAD	OA-913	Yes	-	
Prosulfocarb	52888-80-9	2022, 2017, 2016, 2009	GC-FID	OA-826	Yes	-	
Pyroxsulam	422556-08-9	2018	HPLC-DAD	OA-890	Yes	-	
Thifensulfuron-methyl	79277-27-3	2017	HPLC-DAD	OA-911	Yes	-	

*Analytical method depends on product formulation

2.2 Fungicides

Five fungicidal products containing the a.s. Fluopyram, Prothioconazole, and Tebuconazole were part of the 2023 campaign. TABLE 7 gives an overview of the analytical methods, and when the a.s. was part of a prior control campaign.

2.2.1 Results and conclusion

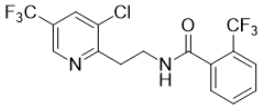
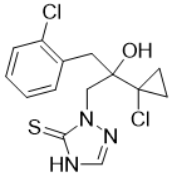
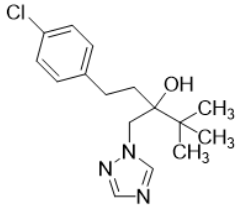
The results of the quantitative determination of a.s. in the fungicides are listed in TABLE 6. RSD% is the relative reproducibility percentage of the analysis of the product.

The concentration of a.s. complies with the declared content and with applicable Danish law in all five products.

TABLE 6. Analysis results (g/L) of fungicidal products.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD%	Comply/Non-comply
162154-1	Tebuconazole	160	150-170	158	0.95	Comply
	Prothioconazole	80	72-88	80	0.56	Comply
162154-3	Tebuconazole	80	72-88	83	0.50	Comply
	Prothioconazole	160	150-170	163	3.0	Comply
162154-5	Fluopyram	125	118-133	122	1.5	Comply
	Prothioconazole	125	118-133	121	1.1	Comply
162154-20	Prothioconazole	125	118-133	127	1.0	Comply
	Tebuconazole	125	118-133	127	0.96	Comply
162154-23	Prothioconazole	250	235-265	246	0.81	Comply

TABLE 7. Active substances categorized as fungicides in the 2023 control campaign.

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Fluopyram	658066-35-4	2021, 2020, 2018	HPLC-DAD	OA-889	Yes	-	
Prothioconazole	178928-70-6	2021, 2020, 2018, 2010, 2008	HPLC-DAD	OA-887, OA-889*	Yes	-	
Tebuconazole	107534-96-3	2022, 2018	HPLC-DAD	OA-887	Yes	-	

*Analytical method depends on product formulation.

2.3 Growth regulators

Eight growth regulators containing the a.s. Prohexadione-calcium, Paclobutrazole, and Trinexapac-ethyl were selected for the 2023 campaign. TABLE 10 states in which previous years the a.s. were selected for control and outlines the analytical method applied for each a.s.

2.3.1 Results and conclusion

The results of quantitative determinations of a.s. in the growth regulators are listed in TABLE 8 and TABLE 9. RSD% is the relative reproducibility percentage of the analysis of the product.

The concentration of a.s. complies with the declared content and with applicable Danish law in all eight products.

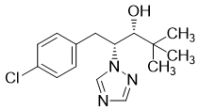
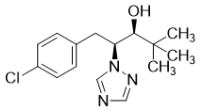
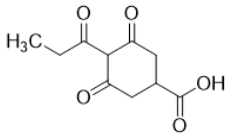
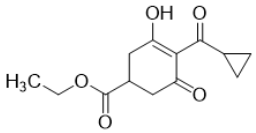
TABLE 8. Analysis results (g/L) of growth regulator products.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD%	Comply/Non-comply
162154-2	Trinexapac-ethyl	250	235-265	243	0.38	Comply
162154-15	Trinexapac-ethyl	250	235-265	246	0.18	Comply
162154-16	Trinexapac-ethyl	175	165-186	166	0.25	Comply
162154-17	Trinexapac-ethyl	250	235-265	254	1.0	Comply
162154-24	Trinexapac-ethyl	250	235-265	247	0.38	Comply
162154-25	Trinexapac-ethyl	250	235-265	248	0.32	Comply
162154-26	Paclobutrazole	4.0	3.4-4.6	4.5	0.95	Comply

TABLE 9. Analysis results (g/kg) of growth regulator products.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD%	Comply/Non-comply
162154-6	Prohexadione-calcium	50	45-55	54	0.95	Comply
	Trinexapac-ethyl	75	68-83	77	1.2	Comply

TABLE 10. Active substances categorized as growth regulators in the 2023 control campaign.

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)	
			Principle	DTI method	Accreditation	Adapted from reference method		
Paclobutrazole	76738-62-0	2021, 2018, 2008	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 8)	 (2*R*,3*R*)-	 (2*S*,3*S*)-
Prohexadione calcium	127227-53-6	2021, 2018, 2017, 2013	HPLC-DAD	OA-913	Yes			
Trinexapac-ethyl	95266-40-3	2021, 2017, 2009, 1999	HPLC-DAD	OA-880, OA-913*	Yes	CIPAC MAM (Ref. 8)		

*Analytical method depends on product formulation.

2.4 Insecticides

Two insecticides containing the a.s. Abamectin and Spinosad were selected for the 2023 campaign. TABLE 12 states in which previous years the active substances were selected for control and outlines the analytical method applied for each a.s.

2.4.1 Results and conclusion

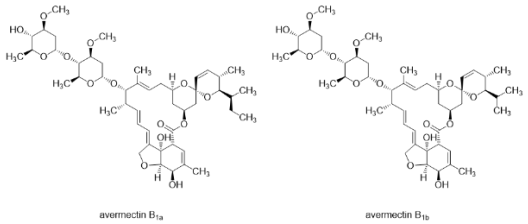
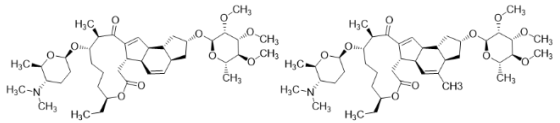
The results for quantitative determination of a.s. in the insecticides are listed in TABLE 11. RSD% is the relative reproducibility percentage for the analysis of the product.

The concentration of a.s. complies with the declared content and with applicable Danish law in both products.

TABLE 11. Analysis results (g/L) of insecticidal products.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD%	Comply/Non-comply
162154-12	Spinosad	120	113-127	121	0.29	Comply
162154-21	Abamectin	18	15-21	19	0.46	Comply

TABLE 12. Active substances categorized as insecticides in the 2023 control campaign.

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Abamectin	71751-41-2	2019	HPLC-DAD	OA-899	Yes	-	 avermectin B_{1a} avermectin B_{1b}
Spinosad	168316-95-8	2021, 2020, 2015, 2011	HPLC-DAD	OA-805	Yes	CIPAC 636 (Ref. 9)	 spinosyn A spinosyn D

3. Physico-chemical testing

The collected pesticide products were submitted to a physico-chemical testing program. A program that depends on the formulation type and is in accordance with the reference document presenting best practices for formulation analysis on pesticide products (Ref. 10). The tests included evaluation of appearance, determination of density, persistent foaming, emulsion stability, and suspensibility. The results were subsequently compared to the values specified in connection with the authorization of the product.
The physico-chemical parameters are subject to confidentiality, and only the general conclusions have been included in this report.

3.1 Physico-chemical testing of selected pesticides

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

3.1.1 Appearance

The color and physical state of the formulation were described after homogenization of the product according to DTI's method UA-407.

3.1.2 Density

The density of the formulations was determined according to DTI's analysis method UA-202 or UA-312. The methods are equivalent to CIPAC MT 3 (Ref. 11). The density of the products was determined as the average of a triple determination carried out by measuring with a Densito 30 PX densitometer or by Pycnometer. The methods are accredited.

3.1.3 Persistent foaming

The test for persistent foaming was performed in accordance with DTI's method UA-400, equivalent to CIPAC method MT 47 (Ref. 12). The highest in-use concentrations prescribed for the products were tested. Standard CIPAC water D, prepared according to CIPAC MT 18, was used unless otherwise specified for the product (Ref. 13). The amount of foam present after 1 minute was reported. The test was performed in duplicate for each pesticide product. The method is accredited.

3.1.4 Emulsion stability

The emulsion stability was determined via DTI's method UA-406 equivalent to CIPAC method MT 36 (Ref. 14). The highest in-use concentrations prescribed for the products were tested. Standard CIPAC water D, prepared according to CIPAC MT 18, was used unless otherwise specified for the product (Ref. 13). The test was performed in duplicate for each pesticide product.

3.1.5 Suspensibility

The suspensibility of the pesticidal products was determined by DTI's method UA-402. The method is equivalent to the CIPAC method MT 184 (Ref. 15). The highest in-use concentrations prescribed for the products were tested. Standard CIPAC water D, prepared according to CIPAC MT 18, was used unless otherwise specified for the product (Ref. 13).

3.1.6 Results

The tests conducted on the collected pesticides are summarized in TABLE 13.

TABLE 13. Physico-chemical tests performed on the collected pesticide products. 'X' signifies the test performed on the sample.

DTI sample no.	Appearance	Density	Persistent foaming	Emulsion stability	Suspensibility
133173-33	X	X	X		X
133173-34	X	X	X		X
133173-35	X		X		X
133173-36	X		X		X
133173-37	X	X	X		X
133173-38	X	X	X		X
162154-1	X	X	X	X	
162154-2	X	X	X	X	
162154-3	X	X	X	X	
162154-4	X	X			
162154-5	X	X	X		
162154-6	X		X		X
162154-7	X	X	X	X	
162154-8	X	X	X		
162154-9	X	X			
162154-10	X	X	X	X	
162154-11	X		X		X
162154-12	X	X	X		X
162154-13	X		X		
162154-15	X	X	X	X	
162154-16	X	X	X	X	
162154-17	X	X	X		
162154-18	X	X	X	X	
162154-19	X	X	X	X	
162154-20	X	X	X	X	
162154-21	X	X	X	X	
162154-22	X	X	X		
162154-23	X	X			
162154-24	X	X	X	X	
162154-25	X	X	X		
162154-26	X	X	X		X

3.1.7 Conclusion

Three products were non-comply for appearance, one product was non-comply for persistent foaming, and one product was non-comply for suspensibility. The test results of all other physico-chemical tests were comparable with the specified values of the product or were within the legal requirements and tolerances.

4. Per- and Polyfluoroalkyl Substance testing

The collected pesticide products were submitted to PFAS testing. The test included 33 selected PFAS substances.

4.1 PFAS testing of selected pesticides

The content of selected PFAS was determined according to the method DS/CEN/TS 15968:2010 at Medico Kemiske Laboratorium ApS. The laboratory is accredited to perform testing under ISO 17025, but the methods and results were not accredited. The samples were analyzed in duplicates and analyzed by LC-MS/MS, however, the substances 8:2 FTAC, 8:2 FTMAC and 8:2 FTOH were analyzed by GC-MS. The expanded uncertainty of the method was 30%.

4.1.1 Results and conclusion

The tests conducted on the collected pesticides are summarized in TABLE 14 and TABLE 15. The test result of the content of selected PFAS showed that none of the selected PFAS substances were detected in any of the analyzed products.

TABLE 14. Analysis results of PFAS in the collected products. ND stands for Not Detected.

Substance	CAS no.	LOD, method (µg/L)	LOQ, product (µg/kg)	Average results (µg/kg)																							
				162154-1	-2	-3	-4	-5	-6	-7	-8	-9	-10	-11	-12	-13	-15	-16	-17	-18	-19	-20	-21	-22	-23	-24	-25
PFBA	375-22-4	0.1*	1.5*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFPeA	2706-90-3	0.1*	1.5*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFHxA	307-24-4	0.1*	1.5*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFHpA	375-85-9	0.1*	1.5*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFOA	335-67-1	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFNA	375-95-1	0.1*	1.5*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFDA	335-76-2	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFUnDA	2058-94-8	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFDoDA	307-55-1	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFTrDA	376-06-7	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFOSA	754-91-6	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFBS	375-73-5	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFPeS	2706-91-4	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFHxS	355-46-4	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFHpS	375-92-8	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFOS	1763-23-1	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFNS	68259-12-1	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFDS	335-77-3	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFUnDS	749786-16-1	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFDoDS	79780-39-5	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFTrDS	791563-89-8	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4:2 FTS	757124-72-4	0.5#	7.5#	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6:2 FTS	27619-97-2	0.5#	7.5#	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8:2 FTS	39108-34-4	0.5#	7.5#	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8:2 PAP	57678-03-2	0.5	7.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8:2 diPAP	678-41-1	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
EtFOSA	4151-50-2	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Substance	CAS no.	LOD, method (µg/L)	LOQ, product (µg/kg)	Average results (µg/kg)																							
				162154-1	-2	-3	-4	-5	-6	-7	-8	-9	-10	-11	-12	-13	-15	-16	-17	-18	-19	-20	-21	-22	-23	-24	-25
EtFOSE	1691-99-2	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MeFOSA	31506-32-8	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MeFOSE	24448-09-7	0.1	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8:2 FTAC	27905-45-9	0.5	7.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8:2 FTMAC	1996-88-9	0.5	7.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8:2 FTOH	678-39-7	0.5	7.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

*The LOD of the method is 0.2 µg/L, and the LOQ of the products is 3.0 µg/kg for sample 162154-12.

#Increased 10x because of matrix effects for sample 162154-7.

TABLE 15. Analysis results of PFAS in the collected products (continued). ND stands for Not Detected.

Substance	CAS no.	LOD, method (µg/L)	LOQ, product (µg/kg)	Average results (µg/kg)					
				133173-33	133173-34	133173-35	133173-36	133173-37	133173-38
PFBA	375-22-4	0.1	1.5	ND	ND	ND	ND	ND	ND
PFPeA	2706-90-3	0.1	1.5	ND	ND	ND	ND	ND	ND
PFHxA	307-24-4	0.1	1.5	ND	ND	ND	ND	ND	ND
PFHpA	375-85-9	0.1	1.5	ND	ND	ND	ND	ND	ND
PFOA	335-67-1	0.1	1.5	ND	ND	ND	ND	ND	ND
PFNA	375-95-1	0.1	1.5	ND	ND	ND	ND	ND	ND
PFDA	335-76-2	0.1	1.5	ND	ND	ND	ND	ND	ND
PFUnDA	2058-94-8	0.1	1.5	ND	ND	ND	ND	ND	ND
PFDoDA	307-55-1	0.1	1.5	ND	ND	ND	ND	ND	ND
PFTrDA	376-06-7	0.1	1.5	ND	ND	ND	ND	ND	ND
PFOSA	754-91-6	0.1	1.5	ND	ND	ND	ND	ND	ND
PFBS	375-73-5	0.1	1.5	ND	ND	ND	ND	ND	ND
PFPeS	2706-91-4	0.1	1.5	ND	ND	ND	ND	ND	ND
PFHxS	355-46-4	0.1	1.5	ND	ND	ND	ND	ND	ND
PFHpS	375-92-8	0.1	1.5	ND	ND	ND	ND	ND	ND
PFOS	1763-23-1	0.1	1.5	ND	ND	ND	ND	ND	ND
PFNS	68259-12-1	0.1	1.5	ND	ND	ND	ND	ND	ND
PFDS	335-77-3	0.1	1.5	ND	ND	ND	ND	ND	ND
PFUnDS	749786-16-1	0.1	1.5	ND	ND	ND	ND	ND	ND
PFDoDS	79780-39-5	0.1	1.5	ND	ND	ND	ND	ND	ND
PFTrDS	791563-89-8	0.1	1.5	ND	ND	ND	ND	ND	ND
4:2 FTS	757124-72-4	0.5	7.5	ND	ND	ND	ND	ND	ND
6:2 FTS	27619-97-2	0.5	7.5	ND	ND	ND	ND	ND	ND
8:2 FTS	39108-34-4	0.5	7.5	ND	ND	ND	ND	ND	ND
8:2 PAP	57678-03-2	0.5	7.5	ND	ND	ND	ND	ND	ND
8:2 diPAP	678-41-1	0.1	1.5	ND	ND	ND	ND	ND	ND

Substance	CAS no.	LOD, method (µg/L)	LOQ, product (µg/kg)	Average results (µg/kg)					
				133173-33	133173-34	133173-35	133173-36	133173-37	133173-38
EtFOSA	4151-50-2	0.1	1.5	ND	ND	ND	ND	ND	ND
EtFOSE	1691-99-2	0.1	1.5	ND	ND	ND	ND	ND	ND
MeFOSA	31506-32-8	0.1	1.5	ND	ND	ND	ND	ND	ND
MeFOSE	24448-09-7	0.1	1.5	ND	ND	ND	ND	ND	ND
8:2 FTAC	27905-45-9	0.5	7.5	ND	ND	ND	ND	ND	ND
8:2 FTMAC	1996-88-9	0.5	7.5	ND	ND	ND	ND	ND	ND
8:2 FTOH	678-39-7	0.5	7.5	ND	ND	ND	ND	ND	ND

5. References

1. Ministry of Environment and Food of Denmark, Environmental Protection Agency (Danish EPA) site; http://eng.mst.dk/chemicals/ pesticides/ and http://mst.dk/kemi/pesticider/

2. Danish EPA, 2023, approved Pesticides 2021 http://mst.dk/kemi/database-for-bekaempelsesmidler/bmd/ (Danish)

3. Statutory Order on Pesticides No. 1278 of 06/06/2021 (applicable Danish Statutory Order 961 of 26/06/2023)

4. The regulation of the European Commission (EU) No. 546/2011 of 10 June 2011 concerning the implementation of the regulation of the European Parliament and the European Council (EF) No. 1107/2009 concerning uniform principles for evaluation and approval of crop protection agents

5. Danish Technological Institute, Kongsvang Allé 29, DK-8000 Aarhus C, Denmark, http://www.dti.dk/

6. The Danish Accreditation and Metrology Fund – DANAK, http://english.danak.dk/

7. The e-Pesticide Manual, Nineteenth Edition, online version, 2021. British Crop Protection Council, United Kingdom

8. CIPAC Multi-active method for the analysis of active substances in formulated products to support quality control, http://www.cipac.org/

9. CIPAC method 636 Spinosad. http://www.cipac.org/

10. Reference document illustrating best practices on analytical strategies and interpretation of results for the formulation analysis of plant protection products obtained during official market control. Version 1 from March 2019 - EU Working Group on Formulation Analysis.

11. CIPAC MT 3 Specific gravity, density, and weight per milliliter. http://www.cipac.org/

12. CIPAC MT 47 Persistent foaming. http://www.cipac.org/

13. CIPAC MT 18 Standard waters. http://www.cipac.org/

14. CIPAC MT 36 Emulsion characteristics of emulsifiable concentrates. http://www.cipac.org/

15. CIPAC MT 184 Suspensibility of formulations forming suspensions on dilution with water. http://www.cipac.org/

Appendix 1

Pesticide products collected for the planned control campaign 2023

TABLE 16. Herbicidal products.

DTI sample no.	Active substance	Reg. no.	Name of product	Authorization holder
133173-33	Diflufenican	501-21	Sempra 500 SC	UPL Europe Ltd.
133173-34	Diflufenican	18-416	DFF	Bayer A/S
133173-35	Pyroxsulam Florasulam	64-69	Broadway	Corteva Agriscience Denmark A/S
133173-36	Mesotrione	1-224	Tocalis	Syngenta Nordics A/S
133173-37	Iodosulfuron-methyl sodium Mesosulfuron-methyl	18-505	Atlantis OD	Bayer A/S
133173-38	Aclonifen Diflufenican	18-631	Mateno DUO SC 600	Bayer A/S
162154-4	Clodinafop-propargyl	396-74	Topik EC	ADAMA Registrations B.V.
162154-7	Prosulfucarb	1-211	Boxer	Syngenta Nordics A/S
162154-8	Fluroxypyr-meptyl Florasulam	64-68	Starane XL	Corteva Agriscience Denmark A/S
162154-9	Phenmedipham	18-528	Betanal	Bayer A/S, Bayer CropScience
162154-10	Prosulfocarb Clodinafop-propargyl	1-228	Adimax	Syngenta Nordics A/S
162154-11	Clodinafop-propargyl Pyroxsulam	1-225	Serrate	Syngenta Nordics A/S
162154-13	Thifensulfuron-methyl	11-72	Harmony 50 SX	FMC Agricultural Solutions A/S
162154-18	Fluroxypyr-meptyl	64-82	Starane 333 HL	Corteva Agriscience Denmark A/S
162154-19	Halauxifen-methyl Fluroxypyr-meptyl	64-87	Pixxaro EC	Corteva Agriscience Denmark A/S
162154-22	Florasulam Fluroxypyr-meptyl	64-78	Primus XL	Corteva Agriscience Denmark A/S

TABLE 17. Fungicidal products.

DTI sample no.	Active substance	Reg. no.	Name of product	Authorization holder
162154-1	Tebuconazole Prothioconazole	18-665	Folicur Xpert EC 240	Bayer A/S, Bayer CropScience
162154-3	Tebuconazole Prothioconazole	18-666	Proline Xpert EC 240	Bayer A/S, Bayer CropScience
162154-5	Fluopyram Prothioconazole	18-597	Propulse SE 250	Bayer A/S, Bayer CropScience
162154-20	Prothioconazole Tebuconazole	18-667	Prosaro	Bayer A/S, Bayer CropScience
162154-23	Prothioconazole	18-473	Proline EC 250	Bayer A/S, Bayer CropScience

TABLE 18. Growth regulator products.

DTI sample no.	Active substance	Reg. no.	Name of product	Authorization holder
162154-2	Trinexapac-ethyl	1-251	Sonis	Syngenta Nordics A/S
162154-6	Prohexadione calcium Trinexapac-ethyl	19-224	Medax Max	BASF A/S
162154-15	Trinexapac-ethyl	11-59	Cuadro NT	FMC Agricultural Solutions A/S
162154-16	Trinexapac-ethyl	347-41	Trimaxx M	Nufarm Deutschland GmbH
162154-17	Trinexapac-ethyl	1-249	Moddevo	Syngenta Nordics A/S
162154-24	Trinexapac-ethyl	1-154	Moddus M	Syngenta Nordics A/S
162154-25	Trinexapac-ethyl	1-223	Moddus Start	Syngenta Nordics A/S
162154-26	Paclobutrazole	544-3	Pirouette	Fine Agrochemicals Ltd.

TABLE 19. Insecticidal products.

DTI sample no.	Active substance	Reg. no.	Name of product	Authorization holder
162154-12	Spinosad	64-51	Conserve	Corteva Agriscience Denmark A/S
162154-21	Abamectin	1-192	Vertimec	Syngenta Nordics A/S

Control of Pesticides 2023

English

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), The Danish Chemical Inspection Service, in 2023.

The planned control campaign covered 21 active substances in different combinations in 31 plant protection products (PPP, pesticides). The products were analyzed to verify whether the content of the active substances in the products in question complied with the product specification and the declared content. 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. 1278 of 06/06/2021 (applicable Danish Statutory Order 961 of 26/06/2023) as well as in Regulation 1107/2009 concerning Marketing of Plant Protection Products.

Danish

Denne rapport beskriver den analytiske kemiske kontrol af pesticidprodukter (plantebeskyttelsesmidler) på det danske marked, der er udført af Miljøstyrelsens Kemikalieinspektion i 2023.

Den planlagte kontrolkampagne dækkede over 21 aktivstoffer i forskellige kombinationer i 31 plantebeskyttelsesprodukter. Produkterne blev analyseret for at verificere, om indholdet af de respektive aktivstoffer var i overensstemmelse med produktspecifikationen og det deklarerede indhold. 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. 1278 af 06/06/2021 (gældende bekendtgørelse nr. 961 af 26/06/2023) og i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler.

The Danish Environmental
Protection Agency
Tolderlundsvej 5
DK - 5000 Odense C

www.mst.dk