Danish Ministry of the Environment

Control of Pesticides and Biocides 2011

The analytical chemical control of Pesticides and Biocides on the Danish market

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Control of Pesticides and Biocides 2011

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Contents

Foreword

Four different types of products, covered by the pesticide and biocide regulation, were included in the 2011 analytical chemical authority control:

- Insecticides
- Fungicides
- Wood protection products
- Herbicides

All collected products were examined for content of one or more active substances according to the specification of the product given by the authorisation holder.

In this year's programme, a total of 28 samples out of the 33 tested products comply with the tolerance limits defined by the Danish Statutory Order on biocides and Regulation 1107/2009 for plant protection products.

Konklusion og sammenfatning

Den analytisk kemiske kontrol af biocid- og pesticidprodukter på det danske marked, der er udført i 2011 af den danske Miljøstyrelses Afdeling for Pesticider og Genteknologi, er beskrevet i denne rapport. Prøver fra udvalgte typer af bekæmpelsesmidler er blevet indsamlet og analyseret for at verificere, om indholdet af de respektive aktivstoffer er i overensstemmelse med produktspecifikationen og det deklarerede indhold. Grænsen for en accepteret afvigelse fra det dokumenterede indhold af aktivstof i forhold til det deklarerede indhold og produktspecifikationen er fastsat i bekendtgørelse om bekæmpelsesmidler eller i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler.

Fire forskellige typer af produkter er inkluderet i den analytisk kemiske kontrol, der blev udført af myndighederne i 2011:

- Insekticider indeholdende bifenthrin, spinosad
- Fungicider indeholdende propamocarb
- Træbeskyttelsesmidler indeholdende kobbercarbonat basisk, kobber HDO
- Herbicider indeholdende ethofumesat, phenmedipham, desmedipham, glyphosat.

Der blev undersøgt i alt 33 bekæmpelsesmidler. Indholdet af aktivstoffet i 28 af de analyserede produkter var indenfor den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler. Fem bekæmpelsesmidler havde fejl i deres angivelse af vægtprocent (w/w %) på varedeklarationen, men det analyserede indhold stemte overens med det deklarerede indhold beregnet i g/L. Disse produkter er angivet som inden for tolerancen i tabel 1, og Miljøstyrelsen har krævet, at fejlen på varedeklarationen rettes ved fremtidig salg af produkterne på det danske marked.

Aktivstof	Antal analyserede produkter	Antal inden for tolerance	Antal uden for tolerance
Bifenthrin	3	2	1
Spinosad	5	3	2
Kobbercarbonat, basisk, og kobber HDO	2	1	1
Propamocarb	3	3	0
Ethofumesat	4	4	0
Phenmedipham	4	3	1
Desmedipham og Phenmedipham	2	2	0
Glyphosat	10	10	0
Total	33	28	5

TABLE 1
OVERSIGT OVER ANTAL ANALYSEREDE PRODUKTER OG RESULTATER

Summary and conclusion

The analytical chemical authority control of pesticide and biocide products on the Danish market that was carried out in 2011 by the Danish Environmental Protection Agency (Danish EPA), Division for Pesticides and Gene Technology, is described in this report. Samples of selected types of pesticides and biocides have been collected from the Danish market and chemically analysed to verify whether or not the actual content of the respective active substances in the products comply with the labelled content. The tolerance of an accepted deviation from the documented content of the active substances compared to the declared content and product specification is determined in the Danish Statutory Order on biocides or in Regulation 1107/2009 concerning Marketing of Plant Protection Products.
Four different types of pesticides are covered by the biocide and pesticide control that was carried out by the analytical chemical authority in 2011.

- Insecticides containing Bifenthrin, Spinosad
- Fungicides containing Propamocarb
- Wood protection products containing Copper carbonate basic, Copper HDO
- Herbicides containing Ethofumesate, Phenmedipham, Desmedipham, Glyphosate.

A total of 33 different pesticide products were analysed. The content of the active substance in 28 of the analysed products were within the accepted tolerance that is determined in the Danish Statutory Order on biocides. For five products the declared content in w/w % was wrongly claimed, but the analysed content complied with the declared content in g/L. The products are therefore registered as compliant in table 2 and the Danish EPA has requested that the error on the labelling is corrected in connection with future sale of the products on the Danish market.

Active substances	Number of analysed products	Number of product comply	Number of products non-comply
Bifenthrin	3	2	1
Spinosad	5	3	2
Copper carbonate, basic, and copper HDO	2	1	1
Propamocarb	3	3	0
Ethofumesate	4	4	0
Phenmedipham	4	3	1
Desmedipham and Phenmedipham	2	2	0
Glyphosate	10	10	0
Total	33	27	6

TABLE 1
OUTLINE OF TOTAL ANALYSED PRODUCTS AND RESULTS

1. Control campaigns in 2011

1.1 Active substances

The control campaigns conducted in 2011 covered active substances belonging to four different types of biocides and pesticides – insecticides, fungicides, wood protection products and herbicides. Overall, pesticides are distinguished in two types: plant protection products and biocides (non-agricultural pesticides).

An overview of the selected active substances is given in following table:

Type	Active substances	CAS no.	Chemical Class	Area of Application
Biocides	**Bifenthrin**	82657-04-3	Pyrethroid	Insecticide
	Spinosad	131929-60-7, 168316-95-8	Macrocyclic Lactone	Insecticide
	Copper carbonate, basic	12069-69-1	Inorganic-Copper	Wood protection
	Copper HDO, Bis-(N-cyclohexyl-diazeniumdioxy)-copper	312600-89-8	Inorganic-Copper	Wood protection
Pesticides	**Ethofumesate**	26225-79-6	-	Herbicide
	Phenmedipham	13684-63-4	Bis-Carbamate	Herbicide
	Desmedipham	13684-56-5	Bis-Carbamate	Herbicide
	Glyphosate	1071-83-6	Phosphono-glycine	Herbicide
	Propamocarb	24579-73-5	Other Carbamate	Fungicide
	Spinosad	131929-60-7, 168316-95-8	Macrocyclic Lactone	Insecticide

TABLE 2
OVERVIEW OF SELECTED ACTIVE SUBSTANCES IN CONTROL CAMPAIGNS IN 2011

1.2 Tolerance

The Danish EPA aims at examining the content of active substances in the products and will compare the result of the chemical analysis with the content according to the specification of the products and declared content on the label given by the authorisation holder. The Statutory Order on biocides in Denmark and the Regulation 1107/2009 on plant protection products specify the general tolerance of deviation from the declared content[1-6]. These tolerances are listed in the following table:

Declared content (w/w %)	Tolerance	
conc. > 50	± 2.5 %	Absolute
25 < conc. ≤ 50	± 5 %	Relative
10 < conc. ≤ 25	± 6 %	Relative
2.5 < conc. ≤ 10	± 10 %	Relative
conc. ≤ 2.5	± 15 %	Relative

TABLE 3
THE TOLERANCE OF DEVIATION FROM THE DECLARED CONTENT OF ACTIVE SUBSTANCES

1.3 Collecting products and analysing for active substances

Product samples of the various pesticide and biocide formulations from different manufacturers, covered in the 2011 control campaigns, were collected by the Chemical Inspection Service from the Danish Environmental Protection Agency, Division of Pesticides and Gene Technology, during the period from March to October 2011. The product samples were bought from either wholesale dealers/importers or at retailer outlets.

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

The chemical analyses were performed as eight analyses per pesticide product. The mean value and the SD (standard deviation) were calculated and the results were compared with the tolerance of deviation from the declared content of active substances. A validation of the applied analytical method was conducted.

The analyses of the products for the active substances were performed by Danish Technological Institute, Laboratory for Chemistry and Microbiology. Danish Technological Institute (DTI) is an Approved Technology Service Institute (GTS “Godkendt Teknologisk Service” institute).

The Laboratory for Chemistry and Microbiology is accredited by DANAK (Danish Accreditation and Metrology Fund), registration no. 90, according to ISO 17025. The Laboratory complies with the GMP regulation of the Danish Medicines Agency regarding analysis of medicinal products and intermediate products (§ 39).

2. Biocides

Seven insecticides and two wood protection products were selected for the Danish Pesticide Control Campaign 2011. The selected active substances were Bifenthrin, Spinosad, Copper carbonate, basic and Copper HDO

2.1 Insecticides (Biocides)

Insecticides containing Bifenthrin and Spinosad as active substances were targeted for the control campaign for 2011. All products were examined for their content of active substances.

2.1.1 Bifenthrin

Bifenthrin is an insecticide which in Denmark is sold for ant control. Chemically, it belongs to the group of pyrethroid insecticides. Bifenthrin affects the nervous system of insects by disturbing the function of neurons through interaction with the sodium channel. Bifenthrin is active by oral and dermal exposure. Products with Bifenthrin have not previously been selected by the Danish EPA for control of content of active substances.

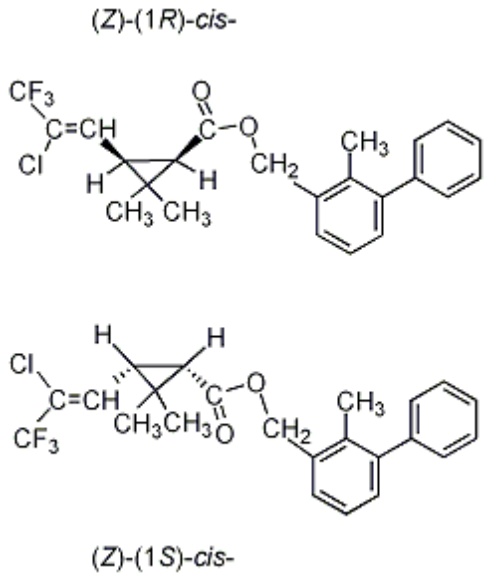
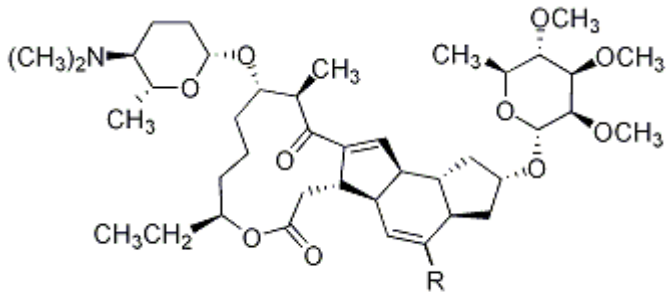


FIGURE 1 MOLECULE STRUCTURE OF BIFENTHRIN[9], CAS. NO. 82657-04-3

2.1.2 Spinosad

Spinosad is an insecticide used in Denmark for flies, larva and ant control, and it acts primarily by targeting binding sites on nicotinic acetylcholine receptors (nAChRs) of the insect nervous system. Spinosoid binding leads to disruption of acetylcholine neurotransmission, thereby killing the insects via hyperexcitation of the insect nervous system. Spinosad is active by dermal contact and ingestion. Chemically, Spinosad belongs to the group of macrocyclic lactone and is a racemic mix of two spinosoids, Spinosyn A and Spinosyn D. Products with Spinosad have not previously been selected by the Danish EPA for control of content of active substances.



spinosyn A, R = H-

spinosyn D, R = CH_3-

FIGURE 2 MOLECULE STRUCTURE OF SPINOSAD[9], CAS. NO. 131929-60-7, 168316-95-8

2.1.3 Analysis

The analysis was performed as eight freshly prepared samples of the product. The analyses were distributed on two days (four samples each day), typically within the same week. That gives a total of eight results per pesticide product. The mean value and the SD (standard deviation) were calculated.

Three selected insecticides containing Bifenthrin were analysed by reversed phase high-performance liquid chromatography combined with UV-detection, HPLC-DAD. Prior to the analyses, a validation of the applied analytical method was conducted. The method for water-soluble products containing Bifenthrin was accredited by the Danish Accreditation and Metrology Fund – DANAK, registration no. 90.

Four selected insecticides containing Spinosad were analysed by reversed phase high-performance liquid chromatography combined with UV-detection, HPLC-DAD. The method is a modified HPLC method according to CIPAC-method no. 636. A validation of the applied analytical method was conducted.

2.1.4 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following two tables:

TI sample no.	Active substances	Content in % (w/w)			Comply/ Non-comply
		Label claim	Analysis ± SD	Tolerance	
36031-2	Spinosad[1)]	1	0.727 ± 0.025	0.85 – 1.15	Non-comply
36031-3	Spinosad	0.017	0.0175 ± 0.0006	0.014 – 0.019	comply
36031-27	Spinosad	0.015	0.0171 ± 0.0006	0.013 – 0.017	Comply
36031-26	Bifenthrin[2)]	0.1	0.108 ± 0.019	0.085-0.115	Comply
36031-31	Bifenthrin[2)]	0.1	0.099 ± 0.009	0.085-0.115	Comply

TABLE 4
ANALYSIS RESULTS OF INSECTICIDES (BIOCIDES)

Comments to Table 4:
1) The guaranteed shelf life of three years was exceeded at the time of analysis
2) The method is accredited. For those two products the calculated SD is the expanded measurement uncertainty (k=2).

TI sample no.	Active substances	Content in mg/product		Comply/ Non-comply
		Label claim	Analysis ± SD	
36031-4	Spinosad	13.5	1.15 ± 0.06	Non-comply
36031-30	Bifenthrin	1	0.50 ± 0.06	Non-comply

TABLE 5
ANALYSIS RESULTS OF INSECTICIDES (BIOCIDES)

2.1.5 Conclusion

The chemical analyses of the Spinosad-containing products proved that two of the four products were below the declared content according to the product label and were therefore non-compliant. The chemical analysis for the active substance Bifenthrin resulted in one non-compliant of the three products chosen for the control campaign 2011.

2.2 Wood protection products (Biocides)

Wood protection products containing Copper carbonate, basic and Copper HDO as active substances were selected for the Danish Pesticide Control Campaign 2011. All targeted products were examined for their content of active substance and in connection with products containing two active substances, both active substances were analysed.

2.2.1 Copper carbonate, basic – CH_2Cu2O_5

Copper carbonate, basic, is an active substance in wood protection products (outdoor) in Denmark. Chemically, it belongs to the group of inorganic copper. The mechanism of Copper carbonate, basic, has not been unequivocally elucidated. Products with Copper carbonate have not previously been selected by the Danish EPA for control of content of active substances.

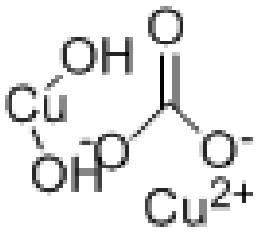


FIGURE 3 MOLECULAR STRUCTURE OF COPPER CARBONATE, BASIC[11], CAS. NO. 12069-69-1

2.2.2 Cu-HDO

Cu-HDO, Bis-(N-cyclohexyldiazeniumdioxy)-copper, is an active substance in wood protection products (outdoor) in Denmark. Chemically, it belongs to the group of inorganic copper. Cu-HDO acts by reacting with sulfhydryl groups of amino acids of fungi and causes protein denaturation. Products with Copper HDO have not previously been selected by the Danish EPA for control of content of active substances.

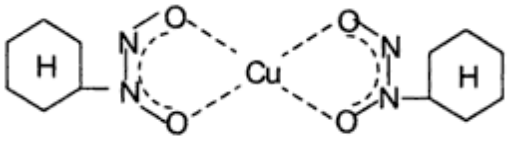


FIGURE 4 MOLECULAR STRUCTURE OF COPPER HDO[12], CAS. NO. 312600-89-8

2.2.3 Analysis

The analysis was performed as eight freshly prepared samples of the product. The analyses were distributed on two days (four samples each day), typically within the same week. That gives a total of eight results per pesticide product. The mean value and the SD (standard deviation) were calculated.

Two selected fungicides containing Copper carbonate, basic, and Copper HDO were analysed by ICP-AES according to CIPAC – MT 98.2. The method for quantifying copper was accredited by the Danish Accreditation and Metrology Fund – DANAK, registration no. 90.

2.2.4 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following table:

TI sample no.	Active substances	Content in % (w/w)			Comply/ Non-comply
		Label claim	Analysis ± SD	Tolerance	
36031-32	Copper carbonate, basic	20.5	17.9 ± 1.0	19.3 – 21.7	Non-comply
36031-33	Copper carbonate, basic	13.04	12.3 ± 0.69	12.3 – 13.8	Comply
36031-33	Cu-HDO[1)]	2.80	2.53 ± 0.027	2.52 – 3.08	Comply

TABEL 6
ANALYSIS RESULTS OF WOOD PROTECTION PRODUCTS

Comments to Tabel 6:
1) Cu-HDO is Bis-(N-cyclohexyldiazeniumdioxy)-copper

2.2.5 Conclusion

The measured content of Copper carbonate, basic, did not comply with the declared content in one product. One product containing both Copper carbonate, basic and Copper-HDO did comply with the declared content on the labelling.

3. Pesticides

Twenty herbicides, three fungicides and one insecticide were selected for the Danish Pesticide Control Campaign 2011. The selected active substances were Ethofumesate, Phenmedipham, Desmedipham, Glyphosate, Propamocarb and Spinosad.

3.1 Herbicides (Pesticides)

Herbicides containing Ethofumesate, Phenmedipham, Desmedipham and some products containing Glyphosate as active substances were selected for the control campaign for 2011. All products were examined for their content of the active substances in the products.

3.1.1 Ethofumesate

Ethofumesate is an herbicide used in Denmark against weed for example in beet fields. Ethofumesate is a selective systemic herbicide, absorbed by the emerging shoots (grasses) and roots (broad-leaved plants), with translocation to the foliage. Inhibits the growth of meristems, retards cellular division, and limits formation of waxy cuticle. Products with Ethofumesate have previously been selected by the Danish EPA in 1997 and 2002 for control of content of active substances.

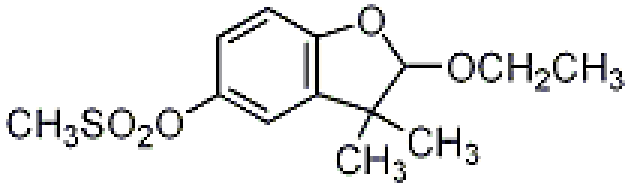


FIGURE 5 MOLECULE STRUCTURE OF ETHOFUMESATE[9], CAS. NO. 26225-79-6

3.1.2 Phenmedipham

Phenmedipham is an herbicide and is used in Denmark against weed for example in beet and strawberry fields. Chemically, it belongs to the group of bis-carbamate. Phenmedipham acts as a photosynthetic electron transport inhibitor on the photosystem II receptor site. Phenmedipham is a selective systemic herbicide, which is absorbed through the leaves with translocation primarily in the apoplast. Products with Phenmedipham have previously been selected by the Danish EPA in 1997 and 2002 for control of content of active substances.

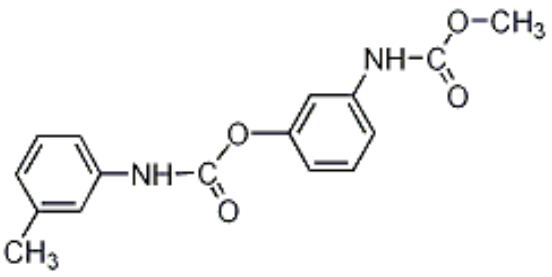


FIGURE 6 MOLECULE STRUCTURE OF PHENMEDIPHAM[9], CAS. NO. 13684-63-4

3.1.3 Desmedipham

Desmedipham is a herbicide used in Denmark against weed e.g. in beet and strawberry fields. Chemically, it belongs to the group of bis-carbamate. Desmedipham acts as a photosynthetic electron transport inhibitor on the photosystem II receptor site. Desmedipham is a selective systemic herbicide, which is absorbed through the leaves and with translocation primarily in the apoplast. Products with Desmedipham have previously been selected by the Danish EPA in 1997 and 2002 for control of content of active substances.

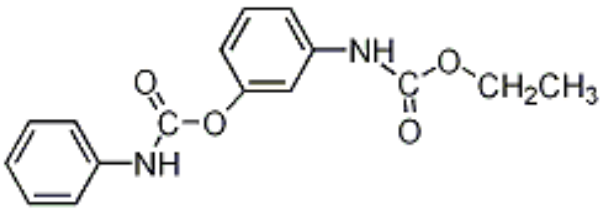


FIGURE 7 MOLECULE STRUCTURE OF DESMEDIPHAM[9], CAS. NO. 13684-56-5

3.1.4 Glyphosate

Glyphosate is a broad-spectrum herbicide used in Denmark against grasses and broadleaf weeds. Chemically, it belongs to the group of phosponoglycine. Glyphosate inhibits 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS), an enzyme of the aromatic acid biosynthetic pathway. That prevents synthesis of essential aromatic amino acids needed for protein biosynthesis. Glyphosate is a non-selective systemic herbicide, which is absorbed by the foliage with rapid translocation throughout the plant. Products with Glyphosate have previously been selected by the Danish EPA in 1996 and 2003 for control of content of active substances.

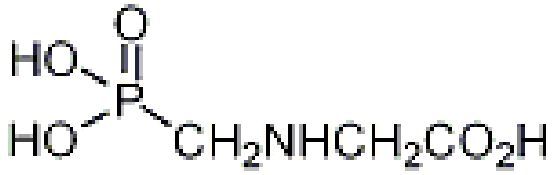


FIGURE 8 MOLECULE STRUCTURE OF GLYPHOSATE[9], CAS. NO. 1071-83-6

3.1.5 Analysis

The analysis was performed as eight freshly prepared samples of the product. The analyses were distributed on two days (four samples each day), typically within the same week. That gives a total of eight results per pesticide product. The mean value and the SD (standard deviation) were calculated.

Four selected herbicides containing Ethofumesate were analysed. The content of Ethofumesate was determined by a reversed phase high-performance liquid chromatography combined with UV-detection, HPLC-DAD. The method is a modified HPLC method according to CIPAC-method no. 233. A validation of the applied analytical method was conducted.

Four selected herbicides containing Phenmedipham and two products containing both Desmedipham and Phenmedipham were analysed. The content of Desmedipham and Phenmedipham were determined by a reversed phase high-performance liquid chromatography combined with UV-detection, HPLC-DAD. The method is a modified HPLC method according to CIPAC-method no. 77. A validation of the applied analytical method was conducted.

Ten selected herbicides containing Glyphosate were analysed by ion-exchange high-performance liquid chromatography combined with UV-detection, HPLC-DAD. The method is a modified HPLC method according to CIPAC-method no. 284. A validation of the applied analytical method was conducted.

3.1.6 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following table:

TI sample no.	Active substances	Content in % (w/w)			Comply/ Non-comply
		Label claim	Analysis ± SD	Tolerance	
36031-8	Ethofumesate	44.3	42.2 ± 0.89	42.1 – 46.5	Comply
36031-9	Ethofumesate	44.8	42.7 ± 0.96	42.6 – 47.0	Comply
36031-22	Ethofumesate	44[1)]	42.0 ± 1.2	41.8 – 46.2	Comply
36031-24	Ethofumesate	44.9	42.5 ± 1,6	42.6 – 47.1	Comply
36031-17	Phenmedipham	16.0	15.7 ± 1.4	15.0-17.0	Comply
36031-19	Phenmedipham	15.4	12.9 ± 1.2	14.5 – 16.3	Non-comply
36031-20	Phenmedipham	16.3	15.2 ± 1.5	15.3-17.3	Comply
36031-23	Phenmedipham	29.2	26.1 ± 2.2	27.7 – 30.7	Comply
36031-7	Phenmedipham	15.5	15.1 ± 1.2	14.6 – 16.4	Comply
36031-7	Desmedipham	15.5	14.9 ± 0.96	14.6 – 16.4	Comply
36031-21	Phenmedipham	15.53	14.9 ± 0.9	14.6 – 16.5	Comply
36031-21	Desmedipham	15.53	14.7 ± 0.6	14.6 – 16.5	Comply
36031-10	Glyphosate	11.3	11.6 ± 0.19	10.6-12.0	Comply
36031-11	Glyphosate	11.7	11.5 ± 0.22	11.0-12.4	Comply
36031-12	Glyphosate	0.72	0.72 ± 0.01	0.61-0.83	Comply
36031-13	Glyphosate	0.7[2)]	0.69 ± 0.01	0.60-0.81	Comply
36031-14	Glyphosate	21.4[2)]	22.1 ± 0.23	20.1-22.7	Comply
36031-15	Glyphosate	21.4[2)]	21.7 ± 1.2	20.1-22.7	Comply
36031-16	Glyphosate	0.74	0.86 ± 0.01	0.63-0.85	Comply
36031-25	Glyphosate	10.9	10.8 ± 0.17	10.2-11.6	Comply
36031-28	Glyphosate	0.7[3)]	0.69 ± 0.03	0.60-0.81	Comply
36031-29	Glyphosate	10.9	11.6 ± 0.62	10.2-11.6	Comply

TABLE 7
ANALYSIS RESULTS OF HERBICIDES

Comments to Table 7:
1) The label wrongly claims 46% by the authorisation holder and a correct label[5] is required by the Danish EPA for future sale of the product on the Danish market.
3) The label wrongly claims 28.9% by the authorisation holder and a correct label[5] is required by the Danish EPA for future sale of the product on the Danish market.
2) The label wrongly claims 1.0% by the authorisation holder and a correct label[5] is required by the Danish EPA for future sale of the product on the Danish market.

3.1.7 Conclusion

The measured content of Ethofumesate complies with the declared content of all four products. The measured content of Phenmedipham was under the declared content of one of the six examined products, whereas Desmedipham complies with the declared content of two products. Products with content of Glyphosate comply with the declared content of all ten products.

3.2 Fungicides (Pesticides)

Fungicides containing Propamocarb as active ingredient were selected for the Danish Pesticide Control Campaign 2011. All targeted products were examined for their content of active substances.

3.2.1 Propamocarb

The active substance Propamocarb is often formulated in the form of the salt Propamocarb Hydrochlorid. Propamocarb is a fungicide used in Denmark as plant protection on potatoes, lettuce, tomatoes, cucumbers and ornamental plants to control downy mildew, Phytophthora and Pythium. Chemically, it belongs to the group of carbamates. Propamocarb acts by reducing mycelial growth and development of sporangia and (zoo) spores. It is a systemic fungicide with protective action that is absorbed by the roots and leaves and transported through the plant. Products with Propamocarb have previously been selected by the Danish EPA in 2001 and 2007 for control of content of active substances.

FIGURE 9 MOLECULE STRUCTURE OF PROPAMOCARB HYDROCHLORID[9], CAS. NO. 24579-73-5

3.2.2 Analysis

The analysis was performed as eight freshly prepared samples of the product. The analyses were distributed on two days (four samples each day), typically within the same week. That gives a total of eight results per pesticide product. The mean value and the SD (standard deviation) were calculated.

Three selected fungicides containing Propamocarb were analysed by reversed phase high-performance liquid chromatography combined with UV-detection, HPLC-DAD. The method is a modified HPLC method according to CIPAC-method no. 399. A validation of the applied analytical method was conducted.

3.2.3 Results

The results from the performed measurements and the corresponding tolerance intervals are listed in the following table:

TI sample no.	Active substances	Content in % (w/w)			Comply/ Non-comply
		Label claim	Analysis ± SD	Tolerance	
36031-5	Propamocarb hydrochlorid	66.8	64.2 ± 5.6	64.3 – 69.3	Comply
36031-6	Propamocarb hydrochlorid	66.8	66.1 ± 3.5	64.3 – 69.3	Comply
36031-18	Propamocarb hydrochlorid	33.7	33.6 ± 2.3	32.0 – 35.4	Comply

TABLE 8
ANALYSIS RESULTS OF FUNGICIDES

3.2.4 Conclusion

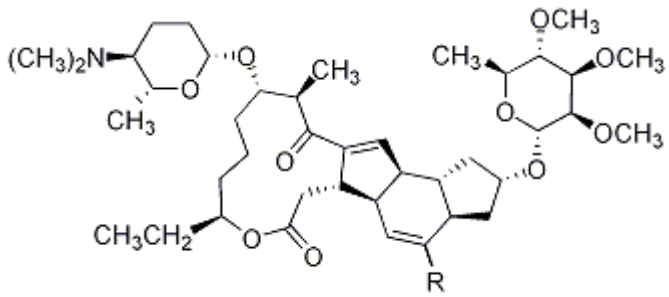
The measured content of Propamocarb complies with the declared content in all three examined fungicides.

3.3 Insecticides (Pesticides)

Insecticides containing Spinosad as active ingredient were selected for the Danish Pesticide Control Campaign 2011. All targeted products were examined for their content of active substances.

3.3.1 Spinosad

Spinosad is an insecticide used in Denmark for larva control, and it acts primarily by targeting binding sites on nicotinic acetylcholine receptors (nAChRs) of the insect nervous system. Spinosad leads to disruption of acetylcholine neurotransmission, thereby killing the insects via hyperexcitation of the insect nervous system. Spinosad is active by dermal contact and ingestion. Chemically, Spinosad belongs to the group of macrocyclic lactone and is a racemic mix of two spinosoids, Spinosyn A and Spinosyn D. Products with Spinosad have not previously been selected by the Danish EPA for control of content of active substances.



spinosyn A, R = H-

spinosyn D, R = CH_3-

FIGURE 10 MOLECULE STRUCTURE OF SPINOSAD[9], CAS. NO. 131929-60-7, 168316-95-8

3.3.2 Analysis

The analysis was performed as eight freshly prepared samples of the product. The analyses were distributed on two days (four samples each day), typically within the same week. That gives a total of eight results per pesticide product. The mean value and the SD (standard deviation) were calculated.

One selected insecticide containing Spinosad was analysed by reversed phase high-performance liquid chromatography combined with UV-detection, HPLC-DAD. The method is a modified HPLC method according to CIPAC-method no. 636. A validation of the applied analytical method was conducted.

TI sample no.	Active substances	Content in % (w/w)			Comply/ Non-comply
		Label claim	Analysis ± SD	Tolerance	
36031-1	Spinosad	11.5	11.43 ± 0.53	10.8 – 12.2	Comply

TABLE 9
ANALYSIS RESULTS OF INSECTICIDES (PESTICIDES)

3.3.3 Conclusion

The measured content of Spinosad complies with the declared content of the product.

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11. Chemical Book; http://www.chemicalbook.com/

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13. CIPAC-method no 77, no 233, no 284, no 399, no. 548, no 636, no MT 98.2; http://www.cipac.org/

Appendix 1: Pesticide and biocide samples collected from the Danish market for authority control in 2011

Pesticide and biocide samples collected from the Danish market for the authority control in 2011.

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
36031-2	Spinosad	64-66	SpY	Dow AgroSciences Danmark A/S
36031-3	Spinosad	364-28	MyreFri Loxiran Genopfyldelig lokkedåse (tidl. NEU 1262 I)	Neudorff GmbH KG
36031-4	Spinosad	364-37	MyreFri Loxiran Lokkedåse	Neudorff GmbH KG
36031-27	Spinosad	364-38	MyreFri Loxiran Lokkemiddel	Neudorff GmbH KG
36031-26	Bifenthrin	179-188	Tanaco Udvanding mod myrer	Tanaco Danmark A/S
36031-30	Bifenthrin	179-207	Myrelokkedåse	Cur Era
36031-31	Bifenthrin	179-197	Myrepulver til udvanding	Substral

TABLE 10
COLLECTED INSECTICIDES (BIOCIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
36031-32	Copper carbonate, basic	183-24	Tanalith E a	Arch Timber Protection Ltd.
36031-33	Copper carbonate, basic, Cu-HDO	660-3	Wolmanit CX-8 WB	Dr. Wolman GmbH

TABLE 11
COLLECTED WOOD PROTECTION PRODUCTS (BIOCIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
36031-8	Ethofumesate	14-178	Ethofol 500 SC	AgroDan A/S, c/o United Phosphorus
36031-9	Ethofumesate	18-451	Ethosan SC	Bayer A/S, Bayer CropScience
36031-22	Ethofumesate	242-10	ND Ethofumesat 500	Nedab ApS
36031-24	Ethofumesate	221-73	IT-Ethofumesat	Inter Trade, Aalborg A/S
36031-17	Phenmedipham	18-528	Betanal	Bayer A/S, Bayer CropScience
36031-19	Phenmedipham	242-21	ND Betafam SE	Nedab ApS
36031-20	Phenmedipham	14-216	SweDane Betasana 2000	AgroDan A/S, c/o United Phosphorus
36031-23	Phenmedipham	396-32	Kontakt 320 SC	Makhteshim Agan Holland B.V.
36031-7	Phenmedipham, Desmedipham	18-519	Betanal Power	Bayer A/S, Bayer CropScience
36031-21	Phenmedipham, Desmedipham	18-494	Kemifam Power	Bayer A/S, Bayer CropScience
36031-10	Glyphosate	48-26	Roundup Garden	Econova A/S
36031-11	Glyphosate	18-364	Keeper mod Ukrudt Koncentrat	Bayer A/S, Bayer CropScience
36031-12	Glyphosate	48-30	Roundup Spray	Monsanto Crop Sciences Denmark A/S
36031-13	Glyphosate	49-83	Rambo Spray	Trinol
36031-14	Glyphosate	18-497	Pistol	Bayer A/S, Bayer CropScience
36031-15	Glyphosate	18-498	Keeper L mod ukrudt	Bayer A/S, Bayer CropScience
36031-16	Glyphosate	18-363	Keeper Spray	Bayer A/S, Bayer CropScience
36031-25	Glyphosate	49-82	Rambo	Klarsø A/S
36031-28	Glyphosate	49-111	Combat ukrudtsmiddel, spray	Klarsø A/S
36031-29	Glyphosate	49-110	Combat ukrudtsmiddel, koncentreret	Klarsø A/S

TABLE 12
COLLECTED HERBICIDES (PESTICIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
36031-5	Propamocarb hydrochlorid	361-1	Proplant	Agriphar S.A.
36031-6	Propamocarb hydrochlorid	18-431	Previcur N	Bayer A/S, Bayer CropScience
36031-18	Propamocarb hydrochlorid	18-480	Tyfon	Bayer A/S, Bayer CropScience

TABLE 13
COLLECTED FUNGICIDES (PESTICIDES)

TI sample no.	Active substances	Reg.no	Name of product	Authorisation holder
36031-1	Spinosad	64-51	Conserve	Dow AgroSciences Danmark A/S

TABLE 14
COLLECTED INSECTICIDES (PESTICIDES)

Control of Pesticides and Biocides 2011

Summary

English

The analytical chemical authority control of pesticide and biocide products on the Danish market that was carried out in 2011 by the Danish Environmental Protection Agency (Danish EPA), Division for Pesticides and Gene Technology, is described in this report. Samples of selected types of pesticides and biocides have been collected from the Danish market and chemically analysed to verify whether or not the actual content of the respective active substances in the products comply with the labelled content. A total of 33 different pesticide products were analysed. The content of the active substance in 28 of the analysed products were within the accepted tolerance that is determined in the Danish Statutory Order on biocides.

Danish

Den analytisk kemiske kontrol af biocid- og pesticidprodukter på det danske marked, der er udført i 2011 af den danske Miljøstyrelses Afdeling for Pesticider og Genteknologi, er beskrevet i denne rapport. Prøver fra udvalgte typer af bekæmpelsesmidler er blevet indsamlet og analyseret for at verificere, om indholdet af de respektive aktivstoffer er i overensstemmelse med det deklarerede indhold. Der blev undersøgt i alt 33 bekæmpelsesmidler. Indholdet af aktivstoffet i 28 af de analyserede produkter var indenfor den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler.

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