National Environmental Research Institute
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NERI Technical Report No. 653, 2008

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Data sheet

Series title and no.:	NERI Technical Report No. 653
Title:	Control of Pesticides 2006
Subtitle:	Chemical Substances and Chemical Preparations
Authors:	Teddy Krongaard, Kitty K. Petersen and Christel Christoffersen
Department:	Department of Atmospheric Environment
Publisher:	National Environmental Research Institute © University of Aarhus - Denmark
URL:	http://www.neri.dk
Year of publication:	January 2008
Referee:	Betty Bügel Mogensen
Financial support:	Danish Environmental Protection Agency
Please cite as:	Krongaard, T., Petersen, K.K. & Christoffersen, C. 2008: Control of Pesticides 2006. Chemical Substances and Chemical Preparations. National Environmental Research Institute, University of Aarhus, Denmark. 23 pp. - NERI Technical Report No. 653. http://www.dmu.dk/Pub/FR653.pdf

Abstract: Four different groups of products covered by the pesticide regulation were included in the 2006 analytical chemical authority control: 1) Herbicides containing metamitron, propaquizafop and haloxyfop-ethoxyethyl. 2) Fungicides containing azoxystrobin, propiconazole, cyprodinil, picoxystrobin and fenpropidin. 3) Insecticides containing pirimicarb. 4) Plant growth regulators containing chlormequat chloride, mepiquat chloride and ethephon. All samples were examined for the content of active ingredients and for the content of OPEO and NPEO. All samples in this years programme complied with the accepted tolerance limits with respect to the content of the active ingredient as specified in Danish Statutory Order on pesticides. None of the examined samples contained OPEO, but one of the samples contained minor concentrations of NPEO. On the label of two products, the content of active ingredient was declared only in g/L, but not in % (w/w) as required and on one product the labelled content given in % was not in accordance with the labelled content given in g/L.

Keywords:	Control, formulations, pesticides
Layout:	Majbritt Pedersen-Ulrich
Proof-reader:	Christel Ege-Johansen
ISBN:	978-87-7073-025-9
ISSN (electronic):	1600-0048
Number of pages:	25
Internet version:	The report is available in electronic format (pdf) at NERI's website http://www.dmu.dk/Pub/FR653.pdf

Contents

National Environmental Research Institute

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Summary

The analytical chemical authority control of pesticide products on the Danish market in 2006 is described in this report. Samples of selected groups of pesticides have been collected from the market and analysed to verify whether the actual contents of the respective active ingredients in the products comply with the labelled content. The tolerance of deviation from the labelled content of active ingredient is set by the Danish Statutory Order on pesticides. In addition to the examination of the content of active ingredients, all collected samples are examined for the content of octylphenol ethoxylates (OPEO) and nonylphenol ethoxylates (NPEO). The industry and the Danish authorities have agreed on removing these compounds from all Danish-sold pesticide formulations produced after June 2000.

Four different groups of products covered by the pesticide regulation were included in the 2006 analytical chemical authority control:

1. Herbicides containing metamitron, propaquizafop and haloxyfop-ethoxyethyl.
2. Fungicides containing azoxystrobin, propiconazole, cyprodinil, picoxystrobin and fenpropidin.
3. Insecticides containing pirimicarb.
4. Plant growth regulators containing chlormequat chloride, mepiquat chloride and ethephon.

Satisfactory results were found for all examined pesticide formulations. Thus, the analysed samples of these formulations complied with the accepted tolerance limits with respect to the content of the active ingredient as specified in Danish Statutory Order on pesticides.

None of the examined samples contained OPEO, but one of the samples contained NPEO. The concentration of NPEO in the formulations was approximately 0.1 %.

On the label of two products, the content of active ingredient was declared only in g/L, but not in % (w/w) as required by the Statutory Order and on one product the labelled content given in % was not in accordance with the labelled content given in g/L.

Resumé

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked, der blev udført i 2006 af de danske myndigheder, er beskrevet i denne rapport. Prøver fra udvalgte grupper af bekæmpelsesmidler er blevet samlet fra markedet og analyseret for at verificere om det aktuelle indhold af de respektive aktivstoffer er i overensstemmelse med det deklarerede indhold. Grænsen for en accepteret afvigelse fra indholdet af aktivstof fra det deklarerede indhold er fastsat i bekendtgørelsen om bekæmpelsesmidler. Udover kontrol af indholdet af aktivstof er alle indsamlede prøver kontrolleret for indhold af octylphenolethoxylater (OPEO) og nonylphenolethoxylater (NPEO). Industrien og de danske myndigheder har indgået en frivillig aftale om at udfase disse forbindelser fra alle dansk-solgte pesticidprodukter produceret efter juni 2000.

Fire forskellige grupper af produkter er inkluderet i den analytisk-kemiske kontrol, der blev udført af myndighederne i 2006:

1. Herbicider indeholdende metamitron, propaquizafop og haloxyfop-ethoxyethyl.
2. Fungicider indeholdende azoxystrobin, propiconazol, cyprodinil, picoxystrobin og fenpropidin.
3. Insekticider indeholdende pirimicarb.
4. Vækstregulatorer indeholdende chlormequat chlorid, mepiquat chlorid og ethephon.

Der blev opnået tilfredsstillende resultater for alle undersøgte bekæmpelsesmidler. Indholdet af aktivstof i alle de analyserede prøver af disse bekæmpelsesmidler var indenfor den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler.

Ingen af de undersøgte produkter indeholdt OPEO, men én af prøverne indeholdt NPEO. Koncentrationen af NPEO i formuleringen var cirka 0,1%.

På to produkter var indholdet af aktivstof kun deklareret i g/l og ikke i % som det ellers er krævet i bekendtgørelsen og i et produkt var der ikke overensstemmelse mellem det deklarerede indhold i % og i g/L

1 Introduction

The Danish Environmental Protection Agency (DEPA) is responsible for the evaluation and the authorisation of all pesticide formulations before the introduction on the Danish market. The requirements of the formulations are given in a Statutory Order on pesticides *(Miljøministeriet, 2003)*, which also states that DEPA is responsible for control of pesticides.

In practice, the authority control activities of pesticides on the market are organised in the following way: the Chemicals Inspection Service at DEPA conducts non-laboratory control and the National Environmental Research Institute conducts the laboratory control of pesticides as assistance to DEPA. The present report describes only the part of the authority control of pesticides involving laboratory control.

Laboratory control of pesticides covers the analytical chemical examination of technical pesticides or pesticide formulations in order to verify that the products comply with the legal requirements of pesticides as well as with the specification of contents stated in the application for the pesticide product.

Analytical chemical control of pesticides may involve verification of the content of active ingredients as well as the content of auxiliary substances or levels of impurities.

Laboratory control work is carried out as two types of projects: 1) Ordinary control by way of planned campaigns, where all products with a common characteristic, e.g. the same active ingredient, are collected from the market and examined, and 2) *ad hoc* projects, which consist of laboratory control in connection with administrative work at the regulatory authorities, e.g. complaints from users concerning a specific product, the suspicion of a product not complying with regulations or specifications, etc.

Only the first type of laboratory control i.e. campaigns are covered by this report, which describes the laboratory control as performed in 2006.

2 Control Campaigns in 2006

Control campaigns conducted in 2006 have covered active ingredients and auxiliary substances belonging to four different groups of pesticides: herbicides, fungicides, insecticides and growth regulators. All analytical chemical control has aimed at examining the content of active ingredient compared with the declared content on the label. Statutory Order in Denmark *(Miljøministeriet, 2003)* specifies the general tolerance of deviation from declared content. These tolerances are given in Table 2.1. In addition to the examination of the content of active ingredients, all samples are examined for the content of octylphenol ethoxylates and nonylphenol ethoxylates.

Samples of the various pesticide formulations covered in the 2006 control campaigns have been collected by the Chemical Inspection Service at DEPA during the months May – August 2006 from either whole sale dealers/importers or at retailer outlets. One sample of each product has been collected.

Samples were stored at NERI in unopened containers until the time of analysis. The samples were stored at ambient temperature (approx. 20°C) protected from light.

Table 2.1 The tolerance of deviations from declared content of active ingredients (a.i.) in pesticides.

Declared content of a.i. %, w/w	Tolerance, %	
Conc. ≥ 50	± 2.5%	(abs.)
25 < conc. ≤ 50	± 5%	(rel.)
10 < conc. ≤ 25	± 6%	(rel.)
2.5 < conc. ≤ 10	± 10%	(rel.)
Conc. ≤ 2.5	± 15%	(rel.)

2.1 Herbicides

2.1.1 Introduction

There are 50 different active ingredients in herbicide formulations available on the Danish market (*Miljøstyrelsen, 2006*). Products containing metamitron, propaquizafop and haloxyfop-ethoxyethyl as active ingredients were selected for control in 2006. All products were examined for the content of active ingredient and for the content of octylphenol and nonylphenol.

Metamitron (Figure 1a) belongs to the group of triazinone herbicides. It is used only to control weeds in beets – and off label to few minor crops in Denmark. Metamitron is a pre- and post-emergence, selective systematic herbicide, absorbed predominantly by the roots, but also by the leaves with translocation. It inhibits the photosynthetic electron transport at the photosystem II receptor site. Herbicide formulations containing metamitron were selected for authority control in 1999.

Haloxyfop-ethoxyethyl (Figure 1b) is an aryloxyphenoxypropionate herbicide. It is used only to control annual meadow grass in grass seed and in nursery beds in Denmark. Haloxyfop-ethoxyethyl is a selective systemic herbicide, absorbed by the foliage and roots, with translocation to meristematic tissues. It inhibits the synthesis of fatty acid and inhibits the growth. Herbicide formulations containing haloxyfop-ethoxyethyl were selected for authority control in 1996.

Propaquizafop (Figure 1c) is an aryloxyphenoxypropionate herbicide. It is used only to control a broad range of annual and perennial grasses in rape, beets, potatoes and peas in Denmark. Propaquizafop is a selective systemic post-emergence herbicide, absorbed by the foliage and roots, with translocation throughout the plant. It inhibits the synthesis of fatty acid and inhibits the growth. Herbicide formulations containing propaquizafop were selected for authority control in 1997.

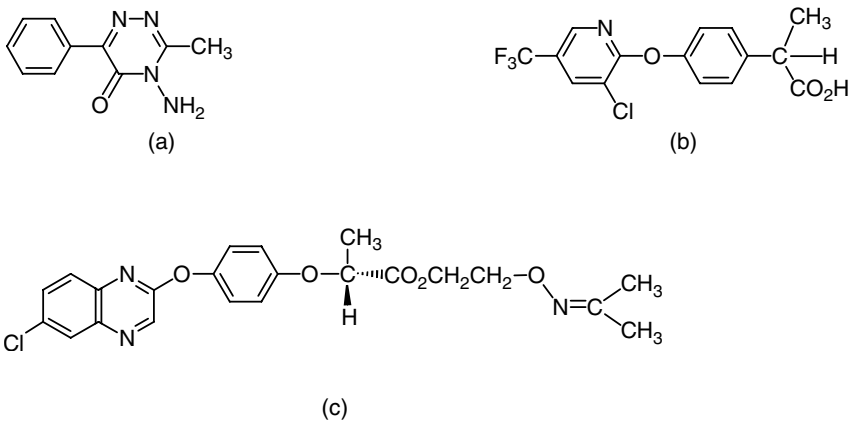

Figure 1

The chemical structure of the herbicide active ingredients: metamitron (a), haloxyfop (beware that the structure is not haloxyfop-ethoxyethyl) (b) and propaquizafop (c).

2.1.2 Samples

At the time of sampling for the control campaign, four products containing metamitron, two products containing haloxyfop-ethoxyethyl and two products containing propaquizafop were approved for use in Denmark. All products containing metamitron were available on the market and one product of each of the two active ingredients haloxyfop-ethoxyethyl and propaquizafop were available on the market during the period of the sample collection. One sample of each herbicide product was collected. The samples are listed in Appendix I.

The sample containing haloxyfop-ethoxyethyl was analysed in July 2006. The sample containing propaquizafop was analysed in October and the samples containing metamitron were analysed in November 2006.

2.1.3 Results and Discussion

The contents of metamitron were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2006a)*. The method is developed on the basis of the existing CIPAC method.

The contents of haloxyfop-ethoxyethyl were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV (*Krongaard, 2006b*). As no CIPAC-method on haloxyfop-ethoxyethyl exists, the method is developed on the basis of information from the manufacturer.

The contents of propaquizafop were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV (*Krongaard, 2006c*). As no CIPAC-method on propaquizafop exists, the method is developed on the basis of information from the manufacturer.

Table 2.2 shows agreement between declared and determined content for all six samples containing metamitron, haloxyfop-ethoxyethyl and propaquizafop as active ingredients.

Table 2.2 Content of active ingredient in samples of herbicides.

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
Metamitron	57.9 %	(700 g/L)	58.0 ± 0.5 %	55.4 – 60.4 %	ATMI 2006-165
Metamitron	57.1 %	(700 g/L)	56.5 ± 0.5 %	54.6 – 59.6 %	ATMI 2006-166
Metamitron	58.1 %	(700 g/L)	58.9 ± 0.5 %	55.6 – 60.6 %	ATMI 2006-167
Metamitron	57.9 %	(700 g/L)	58.6 ± 0.5 %	55.4 – 60.4 %	ATMI 2006-533
Haloxyfop-ethoxyethyl	12.93 %	(125 g/L)	13.1 ± 0.1 %	12.15 – 13.71 %	ATMI 2006-160
Propaquizafop	9.7 %	(100 g/L)	9.8 ± 0.1 %	8.73 – 10.67 %	ATMI 2006-165

1) Mean ± 95% confidence limits.

2) Tolerance limits for the content of active ingredients according to the Statutory Order *(Miljøministeriet, 2003)*.

2.2 Fungicides

2.2.1 Introduction

41 active ingredients in fungicide formulations are approved in Denmark (*Miljøstyrelsen, 2006*). Products containing azoxystrobin, propiconazole, cyprodinil, picoxystrobin and fenpropidin as active ingredients were selected for control in 2006. All products were examined for the content of active ingredient and for the content of octylphenol and nonylphenol.

Azoxystrobin (Figure 2a) belongs to the group of strobilurin fungicides used in Denmark for the treatment of fungal diseases in a broad range of crops (e.g. cereals, root fruits, onions, salads, cabbages, strawberry, peas and leek). Azoxystrobin affects a range of fungal enzymes by inhibiting mitochondrial respiration by blocking electron transfer. It is a systemic fungicide with protective and curative action. Fungicide formulations containing azoxystrobin were selected for authority control in 1999.

Propiconazole (Figure 2b) belongs to the group of triazole fungicides. It is used in Denmark for the treatment of fungal diseases in cereals, grass seed, beets and lawns, and off label to red- and blackcurrant, goose- and strawberry and in nurseries. Propiconazole inhibits steroid demethylation. It is a systemic foliar fungicide with protective and curative action. Fungicide formulations containing propiconazole were selected for authority control in 1992.

Cyprodinil (Figure 2c) is an anilinopyrimidine fungicide. It is used in Denmark only for the treatment of fungal diseases in wheat, rye and barley. Cyprodinil is a systemic foliar fungicide. It inhibits penetration and mycelial growth both inside and on the leaf surface. Fungicide formulations containing cyprodinil were selected for authority control in 2001.

Picoxystrobin (Figure 2d) belongs to the group of strobilurin fungicides used in Denmark only for the treatment of fungal diseases in wheat, rye and barley. Picoxystrobin affects a range of fungal enzymes by inhibiting mitochondrial respiration by blocking electron transfer. It is a systemic fungicide with protective and curative action. Fungicide formulations containing picoxystrobin were approved for the Danish market in 2005 and have not previously been selected for authority control.

Fenpropidin (Figure 2e) belongs to the group of morpholine fungicides used in Denmark only for the treatment of fungal diseases in cereals and grass seed. Fenpropidin affects powdery mildew and rust by inhibiting steroid reduction and isomerisation. It is a systemic foliar fungicide with protective, curative and eradicative action. Fungicide formulations containing fenpropidin were approved for the Danish market in 1999 and were selected for authority control in 2000.

2.2.2 Samples

At the time of sampling for the control campaign, five products containing azoxystrobin, seven containing propiconazole, six containing cyprodinil, one containing picoxystrobin and two products containing fenpropidin were approved for use in Denmark. All the products containing picoxystrobin and fenpropidin were available on the market during the period of the sample collection, while only two out of five products containing azoxystrobin, four out of seven containing propiconazole and three out of six products containing cyprodinil were available on the market during the period. One sample of each product was collected. The list of samples is summarised in Appendix I.

The samples containing cyprodinil were analysed in June 2006 and January 2007. The sample containing picoxystrobin was analysed in June 2006, samples containing azoxystrobin were analysed in September 2006, samples containing fenpropidin were analysed in January 2007 and samples containing propiconazole were analysed in February and May 2007.

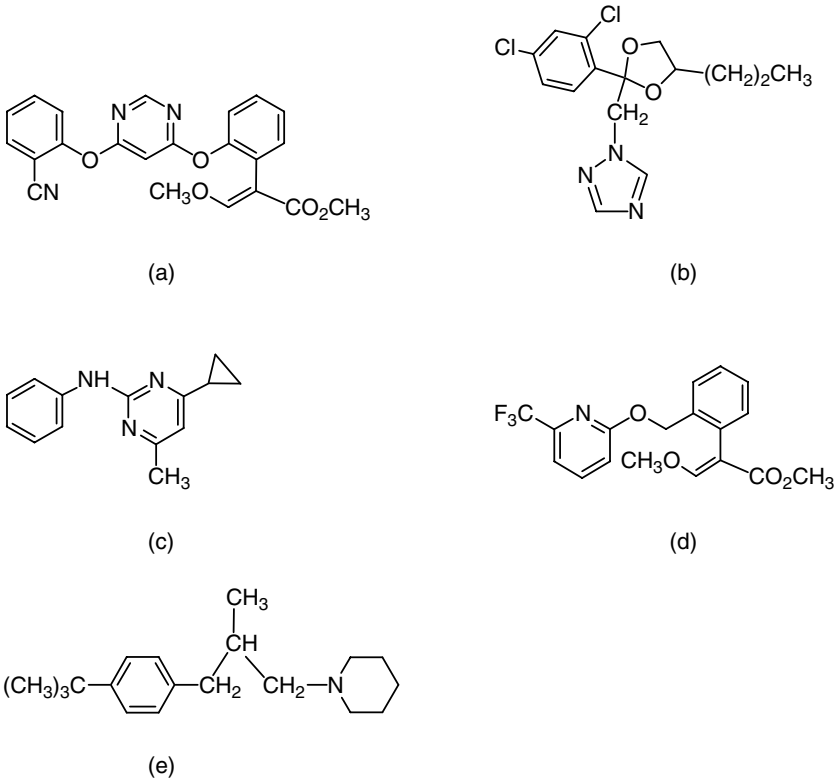

Figure 2
The chemical structure of the fungicide active ingredients: azoxystrobin (a), propiconazole (b), cyprodinil (c), picoxystrobin (d) and fenpropidin (e)

2.2.3 Results and Discussion

The content of azoxystrobin was determined using gas chromatography and flame ionization detector, FC-FID *(Krongaard, 2006d).* As no CIPAC-method on azoxystrobin exists, the method was developed on the basis of information from the manufacturer.

The content of propiconazole was determined using gas chromatography and flame ionization detector, FC-FID *(Krongaard, 2007a)*. The method is developed on the basis of information from the manufacturer. The CIPAC method is not used as it is based on packed column GC.

The content of cyprodinil and picoxystrobin was determined using gas chromatography and flame ionization detector, FC-FID *(Krongaard, 2006e)*. As no CIPAC-method on cyprodinil and picoxystrobin exists, the method was developed on the basis of information from the manufacturer. The method is able to examine formulations for content of cyprodinil and picoxystrobin simultaneously.

The content of fenpropidin was determined using gas chromatography and flame ionization detector, FC-FID *(Krongaard, 2006f).* As no CIPAC-method on fenpropidin exists, the method was developed on the basis of information from the manufacturer.

Table 2.3 shows agreement between declared and determined content for all twelve samples containing azoxystrobin, propiconazole, cyprodinil, picoxystrobin and fenpropidin as active ingredients. On one product, the content of active ingredient was declared only in g/L, but not in % (w/w) as required according to the Statutory Order *(Miljøministeriet, 2003)*.

Table 2.3 The content of active ingredient in samples of fungicides.

Active ingredient	Label claim		Content Analysis[1)]	Tolerance[2)]	NERI sample no.
Azoxystrobin	22.9 %	250g/L	21.4 ± 0.4%	21.5 – 24.3 %	ATMI 2006-164
Azoxystrobin	-[3)]	250g/L	245 ± 4 g/L	235 – 265g/L[4)]	ATMI 2006-388
Propiconazole	6 %	62.5g/L	6.27 ± 0.04%	5.4 – 6.6 %	ATMI 2006-170
Propiconazole	13 %	125g/L	12.8 ± 0.1%	12.2 – 13.8 %	ATMI 2006-171
Propiconazole	9 %	90g/L	10.0 ± 0.1%	8.1 – 9.9 %	ATMI 2006-172
Propiconazole	25 %	250g/L	25.2 ± 0.2%	23.5 – 26.5 %	ATMI 2006-173
Cyprodinil	30 %	300g/kg	29.9 ± 0.2%	28.5 – 31.5 %	ATMI 2006-168
Cyprodinil	75 %	-	73.6 ± 0.4%	72.5 – 77.5 %	ATMI 2006-169
Cyprodinil	24 %	250g/L	22.9 ± 0.2%	22.6 – 25.4 %	ATMI 2006-170
Picoxystrobin	8 %	80 g/kg	8.07 ± 0.04%	7.2 – 8.8 %	ATMI 2006-168
Fenpropidin	81.7 %	750 g/L	83.2 ± 0.9%	78.7 – 84.2 %	ATMI 2006-163
Fenpropidin	46 %	450 g/L	46.8 ± 0.5%	43.7 – 48.3 g/l	ATMI 2006-171

1) Mean ± 95% confidence limits.
2) Tolerated limits for the content of active ingredients according to the Statutory Order *(Miljøministeriet, 2003)*.
3) Content (expressed as %) not declared.
4) Calculated on the basis of the declared content in g/l.

2.3 Insecticides

2.3.1 Introduction

Among the different insecticide formulations available on the Danish market (*Miljøstyrelsen, 2006*) the products containing pirimicarb as active ingredient was selected for control in 2006. All products were examined for the content of active ingredient and for the content of octylphenol and nonylphenol.

Pirimicarb (Figure 3a) belongs to the group of carbamates. It is used in Denmark for the control of aphids on a broad range of cereals, berries, salads and herbs. Pirimicarb is a selective systemic insecticide with contact, stomach and respiratory action. It acts as a cholinesterase inhibitor. It is absorbed by the roots and translocated through the xylem. Insecticide formulations containing pirimicarb were selected for authority control in 1999.

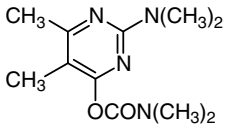

Figure 3
The chemical structure of the insecticide pirimicarb.

2.3.2 Samples

At the time of sampling, two products containing pirimicarb were approved for use in Denmark. Both products were available on the market during the period of the sample collection. One sample of each insecticide product was collected. The sample list is shown in Appendix I. The samples were analysed in June 2006.

2.3.3 Results and Discussion

The content of pirimicarb was determined using gas chromatography and flame ionization detector, FC-FID *(Krongaard, 2006g).* The method is developed on the basis of the existing CIPAC method.

Table 2.4 shows agreement between declared and determined content for both samples containing pirimicarb as active ingredients.

Table 2.4 Content of active ingredient in samples of insecticides

Active ingredient	Content		Analysis[1)]	Tolerance[2)]	NERI sample no.
	Label claim				
Pirimicarb	50%	-	51.0 ± 0.5 %	47.5 – 52.5 %	ATMI 2006-161
Pirimicarb	50%	50 g/kg	49.2 ± 0.5 %	47.5 – 52.5 %	ATMI 2006-162

[1)] Mean ± 95% confidence limits.
[2)] Tolerance limits for the content of active ingredients according to the Statutory Order (*Miljøministeriet 2003*).

2.4 Plant growth regulators

2.4.1 Introduction

Among the eleven plant growth regulators available on the Danish market (*Miljøstyrelsen, 2006*) the formulations containing chlormequat chloride, mepiquat chloride and ethephon as active ingredients were selected for control in 2006, and examined for the content of active ingredients and for the content of octylphenol and nonylphenol.

Chlormequat chloride (Figure 4a) belongs to the group of quaternary ammonium. It is used in Denmark for growth regulation of cereals, grass seed and ornamentals. Chlormequat chloride affects the growth by inhibiting cell elongation, hence shortening and strengthening the stem. Plant growth regulators containing chlormequat chloride were selected for authority control in 1994.

Mepiquat chloride (Figure 4b) belongs to the group of quaternary ammonium. It is used in Denmark for growth regulation of cereals and grass seed. Mepiquat chloride affects the growth by inhibiting cell elongation, hence shortening and strengthening the stem. Plant growth regulators containing mepiquat chloride have not previously been selected for authority control.

Ethephon (Figure 4c) belongs to the group of ethylene generators. It is used in Denmark for growth regulation of cereals and grass seed. Ethephon penetrates into the plant tissues, and is decomposed into ethylene, which affects the growth processes. Plant growth regulators containing ethephon were selected for authority control in 1996.

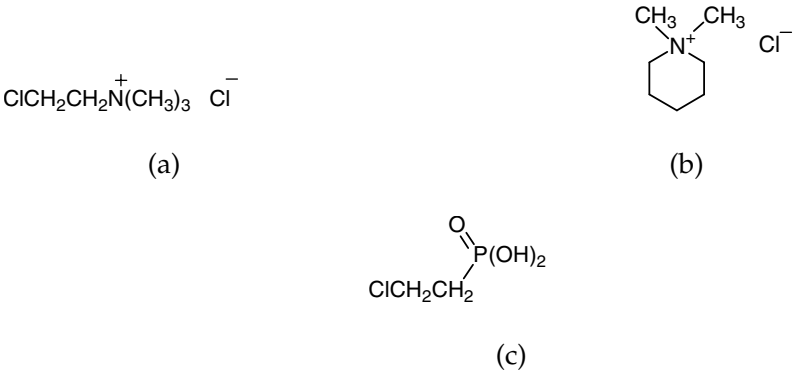

Figure 4

The chemical structure of the plant growth regulator active ingredients: chlormequat chloride (a), mepiquat chloride (b) and ethephon (c).

2.4.2 Samples

At the time of sampling for the control campaign, eleven products containing chlormequat chloride, one containing mepiquat chloride and four products containing ethephon were approved for use in Denmark. The product containing mepiquat chloride was available on the market during the period of the sample collection, while only three out of four containing ethephon and only five out of eleven products containing chlormequat chloride were available on the market during the period. One sample of each product was collected except for the products with ethephon where two samples were collected. The samples are listed in Appendix I.

The samples containing mepiquat chloride were analysed in June 2006. The sample containing ethephon was analysed in December 2006 and the samples containing chlormequat chloride were analysed in the period of September 2006 – January 2007.

2.4.3 Results and Discussion

The contents of chlormequat chloride were determined by using ion chromatography and conductivity detection *(Krongaard, 2007b).* The method is developed on the basis of information from the manufacturer and the existing CIPAC method.

The contents of mepiquat chloride were determined using reversed phase high performance liquid chromatography and MS-detector, RP-HPLC-MS (*Krongaard, 2006h*). The method is developed on the basis of the existing CIPAC method, but is transferred from ion chromatography to RP-HPLC-MS.

The contents of ethephon were determined by using potentiometric titration *(Køppen, 1996).* The method is developed on the basis of the existing CIPAC method.

Table 2.5 shows agreement between declared and determined content for all ten samples containing chlormequat chloride, mepiquat chloride and ethephon as active ingredients. On one product, the content of active ingredient was declared only in g/L, but not in % (w/w) as required according to the Statutory Order *(Miljøministeriet, 2003)*. On one label the declared content given in g/L were not in accordance with the declared content given in %. The %-content refers to chlormequat, while the g/L-content refers to chlormequat chloride

Table 2.5 The content of active ingredient in the samples of plant growth regulators

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
Chlormequat chloride	(21.7 %) 28.0 %[5)]	305 g/L	29.0 ± 0.2 %	26.6 – 29.4 %	ATMI 2006-177
Chlormequat chloride	-[3)]	460 g/L	471 ± 4 g/L	437 – 483g/L[4)]	ATMI 2006-178
Chlormequat chloride	68 %	750 g/L	68.3 ± 0.6 %	65.5 ± 70.5 %	ATMI 2006-179
Chlormequat chloride	68 %	750 g/L	69.9 ± 0.6 %	65.5 ± 70.5 %	ATMI 2006-180
Chlormequat chloride	65.9%	750 g/L	67.0 ± 0.5 %	63.4 ± 68.4 %	ATMI 2006-387
Mepiquat chloride	28 %	305 g/L	28.4 ± 0.4 %	26.6 ± 29.4 %	ATMI 2006-176
Ethephon	40 %	480 g/L	39.4 ± 0.1 %	38 - 42 %	ATMI 2006-174
Ethephon	40 %	480 g/L	40.2 ± 0.1 %	38 - 42 %	ATMI 2006-175
Ethephon	14.2 %	155 g/L	14.0 ± 0.1 %	13.4 – 15.0 %	ATMI 2006-176
Ethephon	13.8 &	155 g/L	13.5 ± 0.1 %	13.0 – 14.6 %	ATMI 2006-177

1) Mean ± 95% confidence limits.
2) Tolerated limits for the content of active ingredients according to the Statutory Order *(Miljøministeriet, 2003)*.
3) Content (expressed as %) not declared.
4) Calculated on the basis of the declared content in g/l.
5) The content is declared as 21.7% and 305 g/L. These values are not in accordance. It seems that 21.7 % refers to the content of chlormequat, while 305 g/L refer to the content of chlormequat chloride. The laboratory has recalculated the content given in percent by multiplying 21.7% with 1.2896, which is the mass ratio between chlormequat and chlormequat chloride.

2.5 Additives

2.5.1 Introduction

Among the many additives used in pesticide formulations, nonylphenol ethoxylates (NPEO) and octylphenol ethoxylates (OPEO) were selected for control in 2006. All the formulations examined for the content of active ingredient as described in the previous parts of this report have also been examined for the content of NPEO and OPEO.

NPEO and OPEO belong to the group of alkylphenol ethoxylates (APEO), a group of surface-active compounds which is widely used in the formulation of plant protection products. They are added to the formulation to change the physical properties e.g. to facilitate the transport of the active ingredient into the plants or into the insects. In the 1990's APEO was recognised to have estrogenic effects. This kind of substances is suspected to be the contributory reason for the decrease in the male reproduction ability, and to the increase in the cases of abnormality in the male sexual organs and the cases of testicle cancer. The same effects are also seen in wild living male animals. OPEO is not used as widely as NPEO in pesticide formulations, but the estrogenic effect is several times higher. The industry and the Danish authorities have agreed on removing these compounds from all Danish-sold pesticide formulations produced after June 2000 except for few exceptions given by the Danish authorities. Dealers are allowed to sell stocks after this date.

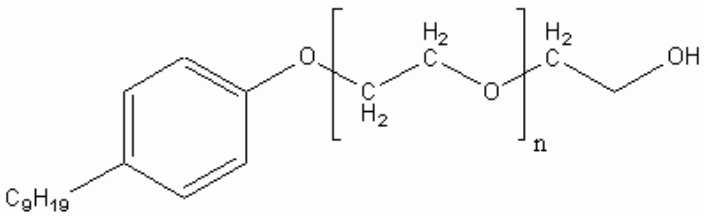

Figure 6

The chemical structure of the additive nonylphenol ethoxylate. The structure of octylphenol ethoxylate is similar, C_9H_{19} is replaced with C_8H_{17}.

2.5.2 Samples

Beside the examination of the content of active ingredient all pesticide formulations sampled in 2006 are examined for content of NPEO and OPEO. The sample list is shown in Appendix I

The samples were analysed in January- February 2007.

2.5.3 Results and Discussion

The content of NPEO and OPEO was determined by using reversed phase high performance liquid chromatography and MS-detector, RP-HPLC-MS *(Krongaard, 2006d).* As no CIPAC-method on NPEO and OPEO exists, the method was developed in the laboratory. The analytical method is capable of analysing NPEO and OPEO simultaneously.

Table 2.7 The content of NPEO and OPEO in samples of pesticide formulations.

No. of samples	No. of samples with NPEO/OPEO	No. of samples without NPEO or OPEO
25	1/0	24

Table 2.7 shows that none of the 16 examined samples contain OPEO, but one of the samples contains NPEO. The concentration of NPEO in the formulation was approximately 0.1 %.

Conclusions

Four different groups of products covered by the pesticide regulation were included in the 2006 analytical chemical authority control:

1. Herbicides containing metamitron, propaquizafop and haloxyfop-ethoxyethyl.
2. Fungicides containing azoxystrobin, propiconazole, cyprodinil, picoxystrobin and fenpropidin.
3. Insecticides containing pirimicarb.
4. Plant growth regulators containing chlormequat chloride, mepiquat chloride and ethephon.

All products were examined for the content of the active ingredients. In addition to the examination of the content of active ingredients, all collected samples were examined for content of octylphenol ethoxylates and nonylphenol ethoxylates.

Satisfactory results were found for all examined pesticide formulations. Thus, the analysed samples of these formulations complied with the accepted tolerance limits with respect to the content of the active ingredient as specified in Danish Statutory Order on pesticides.

None of the examined samples contained OPEO, but one of the samples contained NPEO. The concentration of NPEO in the formulations was approximately 0.1 %.

On the label of two products, the content of active ingredient was declared only in g/L, but not in % (w/w) as required by the Statutory Order and on one product the labelled content given in % was not in accordance with the labelled content given in g/L.

References

Krongaard, T. (2006a): Analysemetode. Bestemmelse af metamitron som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of metamitron as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2006b): Analysemetode. Bestemmelse af haloxyfop-ethoxyethyl som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of haloxyfop-ethoxyethyl as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2006c): Analysemetode. Bestemmelse af propaquizafop som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of propaquizafop as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2006d): Analysemetode. Bestemmelse af azoxystrobin som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of azoxystrobin as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2007a): Analysemetode. Bestemmelse af propiconazol som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of propiconazole as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (2006e): Analysemetode. Bestemmelse af picoxystrobin og cyprodinil som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of picoxystrobin and cyprodinil as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (2006f): Analysemetode. Bestemmelse af fenpropidin som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of fenpropidin as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (2006g): Analysemetode. Bestemmelse af pirimicarb som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of pirimicarb as active ingredient in pesticides. National Environmental Research Institute). 4 pp. (In Danish).

Krongaard, T. (2007ba): Analysemetode. Bestemmelse af chlormequat chlorid som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of diquat chlormequat chloride as active ingredient in pesticides. National Environmental Research Institute). 7 pp. (In Danish).

Krongaard, T. (2006h): Analysemetode. Bestemmelse af mepiquat chlorid som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of mepiquat chlorid as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Køppen, B. (1996): Analysemetode. Bestemmelse af ethephon som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of ethephon as active ingredient in pesticides. National Environmental Research Institute). 4 pp. (In Danish).

Krongaard, T. (2006d): Analysemetode. Bestemmelse af NPEO og OPEO i bekæmpelsesmidler. (Method of Analysis. Determination of NPEO and OPEO in pesticides. National Environmental Research Institute). 11 pp. (In Danish).

Miljøministeriet (2003): Bekendtgørelse om bekæmpelsesmidler. Miljøministeriets bekendtgørelse nr. 533 af 18. juni 2003. (Statutory Order on Pesticides. Statutory Order from the Ministry of the Environmen, No. 533 of June 18, 2003).

Miljøstyrelsen (2006): Oversigt over godkendte bekæmpelsesmidler 2006. http://www2.mst.dk/databaser/Bekaemp/2007%20Oversigt.rtf (Danish EPA, 2006: List of Approved Pesticides 2006, Danish Environmental Protection Agency). (In Danish).

Tomlin,C.D.S (2003): The Pesticide Manual. 13th Ed. British Crop Protection Council, Hampshire. United Kingdom.

Appendix I

Pesticide samples collected from the Danish market for authority control in 2006.

Table 1 Herbicides

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Haloxyfop-ethoxyethyl	Inter-Haloxyfop	EC	Inter-Trade	ATMI-2006-160
Metamitron	Goltix SC 700	SC	Makhteshim Agan	ATMI-2006-165
Metamitron	Metafol 700 SC	SC	AgroDan	ATMI-2006-166
Metamitron	ND Metamitron 700	SC	Nedab	ATMI-2006-167
Metamitron	Inter-Metamitron SC	SC	Inter-Trade	ATMI-2006-533
Propaquizafop	Goltix SC 700	SC	Makhteshim Agan	ATMI-2006-165

[1)] SC: Suspension concentrate; EC: Emusifiable concentrate.

Table 2 Fungicides

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Azoxystrobin	Amistar	SC	Syngenta	ATMI-2006-164
Azoxystrobin	LFS Azoxystrobin	SC	LFS Kemi	ATMI-2006-388
Cyprodinil	Acanto Prima	WG	Syngenta	ATMI-2006-168
Cyprodinil	Unix 75 WG	WG	Syngenta	ATMI-2006-169
Cyprodinil	Stereo 321.5 EC	EC	Novartis	ATMI-2006-170
Fenpropidin	Tern	EC	Makhteshim Agan	ATMI-2006-163
Fenpropidin	Zenith 575 EC	EC	Syngenta	ATMI-2006-171
Picoxystrobin	Acanto Prima	WG	Syngenta	ATMI-2006-168
Propiconazole	Stereo 321.5 EC	EC	Novartis	ATMI-2006-170
Propiconazole	Zenith 575 EC	EC	Syngenta	ATMI-2006-171
Propiconazole	Bumper P	EC	KFK	ATMI-2006-172
Propiconazole	Bumper 25 EC	EC	Makhteshim Agan	ATMI-2006-173

[1)] WG Water dispersible granule; EC: Emusifiable concentrate; SC: Suspension concentrate.

Table 3 Insecticides

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Pirimicarb	Pirimor G	WG	Syngenta	ATMI-2006-161
Pirimicarb	Inter-Pirimicarb	WG	Inter-Trade	ATMI-2006-162

[1)] WG Water dispersible granule.

Table 4 Plant Growth Regulators

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Chlormequat chloride	Terpal C	SE	BASF	ATMI-2006-177
Chlormequat chloride	Cycocel Extra	SE	BASF	ATMI-2006-178
Chlormequat chloride	Trece	SE	SweDane	ATMI-2006-179
Chlormequat chloride	CCC 750	SE	KemiAgro	ATMI-2006-180
Chlormequat chloride	Stabilan Extra	SE	Nufarm	ATMI-2006-387
Ethephon	IT-Ethephon	SE	Inter-Trade	ATMI-2006-174
Ethephon	IT-Ethephon	SE	Inter-Trade	ATMI-2006-175
Ethephon	Terpal	SE	BASF	ATMI-2006-176
Ethephon	Terpal C	SE	BASF	ATMI-2006-177
Mepiquat chloride	Terpal	SE	BASF	ATMI-2006-176

[1)] SE: suspo-emulsion.

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647 Criteria for favourable conservation status in Denmark. Natural habitat types and species covered by the EEC Habitats Directive and birds covered by the EEC Birds Directive. By Søgaard, b. et al. 92 pp.

646: Vandmiljø og Natur 2006. NOVANA. Tilstand og udvikling – faglig sammenfatning. Af Boutrup, S. et al. 125 s.

645 Atmosfærisk deposition 2006. NOVANA. Af Ellermann, T. et al. 62 s.

644 Arter 2006. NOVANA. Af Søgaard, B., Pihl, S. & Wind, P. 88 s.

643 Terrestriske Naturtyper 2006. NOVANA. Af Bruus, M. et al. 70 s.

642 Vandløb 2006. NOVANA. Af Bøgestrand, J. (red.). 93 s.

641 Søer 2006. NOVANA. Af Jørgensen, T.B. et al. 63 s.

640 Landovevågningsoplande 2006. NOVANA. Af Grant, R. et al. 121 s.

639 Marine områder 2005-2006. Tilstand og udvikling i miljø- og naturkvaliteten. NOVANA. Af Ærtebjerg, G. (red.). 95 s.

637 Forvaltningsmetoder i N-belastede habitatnaturtyper. Af Damgaard, C. et al. 46 s.

636 Sørestaurering i Danmark. Del 1: Tværgående analyser, Del 2: Eksempelsamling. Af Liboriussen, L., Søndergaard, M. & Jeppesen, E. (red.). 86 s. + 312 s.

635 Håndbog om dyrearter på habitatdirektivets bilag IV – til brug i administration og planlægning. Af Søgaard, B. et al. 226 s.

634 Skovenes naturtilstand. Beregningsmetoder for Habitatdirektivets skovtyper. Af Fredshavn, J.R. et al. 52 s.

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621 Evaluering af langtransportmodeller i NOVANA. Af Frohn, L.M. et al. 30 s.

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978-87-7073-025-9
ISSN 1600-0048