CONTROL OF PESTICIDES 2008

Chemical Substances and Chemical Preparations

NERI Technical Report no. 759 2009

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Data sheet

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Abstract: Four different groups of products covered by the pesticide regulation were included in the 2008 analytical chemical authority control: 1) Herbicides containing aclonifen, bromoxynil, ioxynil, fluazifop-P-butyl, fenoxaprop-P-ethyl and mesotrione. 2) Fungicides containing cyazofamid, fluazinam, pencycuron, prothioconazole, tebuconazole and terbuthylazine. 3) Insecticides containing alpha-cypermethrin and permethrin. 4) Plant growth regulators containing paclobutrazol. All samples were examined for the content of active ingredients and most of them 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 ingredients as specified in Danish Statutory Order on pesticides. None of the examined samples contained OPEO, but one contained NPEO. On five labels, the content of active ingredient was declared only in g/L, but not in % (w/w) as required and on two labels the declared content given g/L was correct, but the content given in percentage was incorrect.

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Contents

Summary

The analytical chemical authority control of pesticide products on the Danish market in 2008 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, most of the collected samples were 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 2008 analytical chemical authority control:

1. Herbicides containing aclonifen, bromoxynil, ioxynil, fluazifop-P-butyl, fenoxaprop-P-ethyl and mesotrione.
2. Fungicides containing cyazofamid, fluazinam, pencycuron, prothioconazole, tebuconazole and terbuthylazine.
3. Insecticides containing alpha-cypermethrin and permethrin.
4. Plant growth regulators containing paclobutrazol.

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 ingredients as specified in Danish Statutory Order on pesticides.

None of the examined samples contained OPEO but one contained NPEO. The manufacturer of the product informed the Danish EPA in 2005 about this specific case so no further action was taken.

On five labels, the content of active ingredient was declared only in g/L, but not in % (w/w) as required by the Statutory Order. On two labels the declared content given in g/L was correct, but the content given in percentage was incorrect.

Resumé

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked, der blev udført i 2008 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. Ud over kontrol af indholdet af aktivstof er de fleste af de 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 2008:

1. Herbicider indeholdende aclonifen, bromoxynil, ioxynil, fluazifop-P-butyl, fenoxaprop-P-ethyl og mesotrion.
2. Fungicider indeholdende cyazofamid, fluazinam, pencycuron, prothioconazol, tebuconazol og terbuthylazin.
3. Insekticider indeholdende alpha-cypermethrin og permethrin.
4. Vækstregulatorer indeholdende paclobutrazol.

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 ét produkt indeholdt NPEO. Der blev dog ikke foretaget yderligere, da producenten allerede i 2005 orienterede Miljøstyrelsen om det pågældende produkt.

På fem produkter var indholdet af aktivstof kun deklareret i g/l og ikke i % som det ellers er krævet i bekendtgørelsen. På to etiketter var indholdet angivet i procent ikke korrekt, men dog deklareret korrekt 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, Aarhus University 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 2008.

2 Control Campaigns in 2008

Control campaigns conducted in 2008 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, most samples are examined for the content of octylphenol ethoxylates and nonylphenol ethoxylates.

Samples of the various pesticide formulations covered in the 2008 control campaigns have been collected by the Chemical Inspection Service at DEPA during the months April – October 2008 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 51 different active ingredients in herbicide formulations available on the Danish market (*Miljøstyrelsen, 2009*). Products containing aclonifen, bromoxynil, ioxynil, fluazifop-P-butyl, fenoxaprop-P-ethyl and mesotrione as active ingredients were selected for control in 2008. All products were examined for the content of active ingredient and all products except from two were examined for the content of octylphenol and nonylphenol.

Aclonifen (Figure 1a) is a diphenyl ether herbicide. It is used in Denmark for pre-emergence control of grass and broad-leaved weeds in potatoes, peas, carrot and onion set. It is off-label approved to weeds in some minor root crops. Aclonifen is a systemic selective pesticide. Formulations containing aclonifen were included in the Danish register of approved pesticides in 1999 and were selected for authority control in 2000.

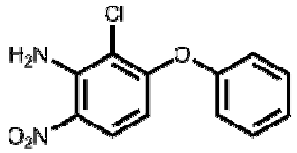
Bromoxynil (Figure 1c) is a hydroxybenzonitrile, which is used in Denmark for post-emergence control of annual broad-leaved weeds in cereals, grass seed, clover, alfalfa, medick and beet seed. It is absorbed by the foliage and inhibits the photosynthetic electron transport and uncouples oxidative phosphorylation. Herbicide formulations containing bromoxynil were selected for authority control in 2000.

Ioxynil (Figure 1d) is a hydroxybenzonitrile too, which is used in Denmark for post-emergence control of annual broad-leaved weeds in cereals, grass seed, leek, onion, clover, alfalfa, beet seed, medick etc. It is absorbed by the foliage and inhibits the photosynthetic electron transport and uncouples oxidative phosphorylation as bromoxynil does. Herbicide formulations containing ioxynil were selected for authority control in 2000.

Fluazifop-P-butyl (Figure 1e) is an 2-(4-aryloxyphenoxy)propionic acid compound, which is used for post-emergence control of weeds in meadow fescue, bush-, pome- and stone fruits, peas, root crops, rape, mustard forestry, nursery and windbreaks. It is absorbed by the foliage and inhibits the synthesis of fatty acids. Herbicide formulations containing fluazifop-P-butyl were selected for authority control in 1999.

Fenoxaprop-P-ethyl (Figure 1f) is an 2-(4-aryloxyphenoxy)propionic acid too, which is used for post-emergence control of certain annual and perennial grass in cereals, and for control of wild oat in fallow fields. It is a selective herbicide with contact and systemic action. It is absorbed by the foliage and inhibits the synthesis of fatty acids. Herbicide formulations containing fenoxaprop-P-ethyl were selected for authority control in 1999.

Mesotrione (Figure 1b) is a triketone herbicide. It is used only to control weeds in maize. It is selective to maize due to different and rapid metabolism. Mesotrione is absorbed by the foliage and inhibits the biosynthesis of carotenoid. Herbicide formulations containing mesotrione were approved for the Danish market in 2005 and have not previously been selected for authority control.



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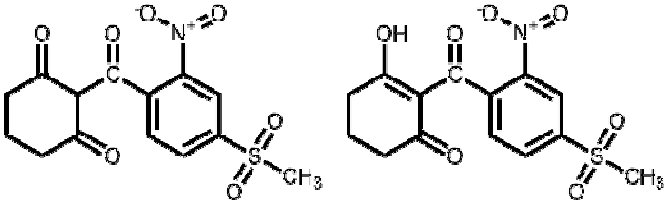

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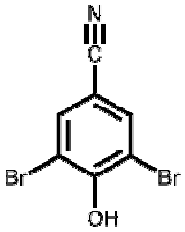

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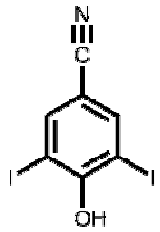

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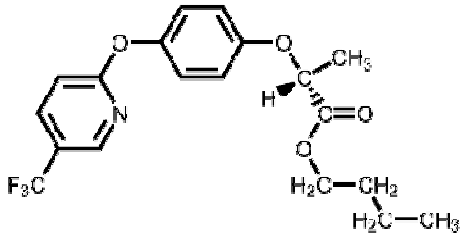

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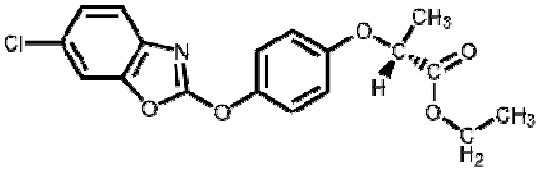


(f)

Figure 1

The chemical structure of the herbicide active ingredients: aclonifen (a), mesotrione (b) bromoxynil (c), ioxynil (d), fluazifop-P-butyl (e) and fenoxaprop-P-ethyl (f).

2.1.2 Samples

At the time of sampling for the control campaign, one product containing bromoxynil, two products containing mesotrione, fenoxaprop-P-ethyl and fluazifop-P-butyl and three products containing aclonifen and ioxynil were approved for use in Denmark. All products containing bromoxynil, mesotrione, fenoxaprop-P-ethyl and fluazifop-P-butyl were available on the market during the period of the sample collection, while two out of three products containing aclonifen and ioxynil 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 aclonifen were analysed in October 2008. The sample containing fenoxaprop-P-ethyl was analysed in December 2008. Samples containing fluazifop-P-butyl were analysed in March, samples containing ioxynil and bromoxynil were analysed in June, while samples containing mesotrione were analysed in July 2009.

2.1.3 Results and Discussion

The contents of aclonifen were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV (*Krongaard, 2008a*). As no CIPAC-method on aclonifen exists, the method is developed on the basis of information from the manufacturer.

The contents of ioxynil and bromoxynil were determined using gas chromatography and flame ionization detector, GC-FID *(Krongaard, 2009a)*. The method used is a revised CIPAC method on ioxynil. Due to chemical similarity between ioxynil and bromoxynil, the method was used for determination of bromoxynil too.

The contents of fenoxaprop-p-ethyl and the enantiomer fenoxaprop-m-ethyl were determined using normal phase high performance liquid chromatography and UV-detector (NP-HPLC-UV) (*Krongaard, 2008b*). The method is developed on the basis of the existing CIPAC method.

The contents of fluazifop-p-butyl (R-enantiomer) and the S-enantiomer were determined using normal phase high performance liquid chromatography and UV-detector (NP-HPLC-UV) (*Krongaard, 2009b*). The method is developed on the basis of the existing CIPAC method.

The contents of mesotrione were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV (*Krongaard, 2009c*). As no CIPAC-method on mesotrione exists, the method is developed on the basis of information from the manufacturer. The method is used for determination of terbuthylazine too.

Table 2.2 Content of active ingredient in samples of herbicides.

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
Aclonifen	-[3)]	600 g/L	604.4 ± 2.4 g/L	570 – 630 g/L[4)]	ATMI 2008-4308
Aclonifen	-[3)]	600 g/L	594.4 ± 2.4 g/L	570 – 630 g/L[4)]	ATMI 2008-4707
Bromoxynil	17.32 %	200 g/L	17.22 ± 0.09 %	16.28 – 18.36 %	ATMI 2008-4171
Ioxynil	17.32 %	200 g/L	17.31 ± 0.08 %	16.28 – 18.36 %	ATMI 2008-4171
Ioxynil	-[3)]	225 g/L	224.8 ± 1.1 g/L	212 – 239 g/L[4)]	ATMI 2008-4172
Fenoxprop-P-ethyl	-[3)]	69 g/L	73.2 ± 0.6 g/L	62.1 – 75.9/L[4)]	ATMI 2008-4495
Fenoxprop-P-ethyl	6.6 %	69 g/L	7.03 ± 0.06 %	5.94 – 7.26 %	ATMI 2008-4259
Fluazifop-P-butyl	13 %	125 g/L	13.26 ± 0.03 %	12.22 – 13.78 %	ATMI 2008-4173
Fluazifop-P-butyl	13.4 %*	125 g/L	13.17 ± 0.03 %	12.60 – 14.20 %	ATMI 2008-4708
Mesotrione	6.2 %	70 g/L	6.72 ± 0.01 %	5.58 – 6.82 %	ATMI 2008-4177
Mesotrione	5.83 %**	70 g/L	6.02 ± 0.01 %	5.25 – 6.41 %	ATMI 2008-4709

1) Mean ± 95% confidence limits.

2) Tolerance 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.

*) The label in Danish on the product declares 8% and 125 g/L, while the original label in German underneath declares 13.4% and 125 g/L. It can be calculated from the density of the formulation that 8% (w/w) and 125 g/L are not in accordance. The manufacturer has been informed about the incorrect content declared on the label. The tolerance is calculated on the basis of the original label.

**) The label in Danish on the product declares 7% and 70 g/L, while the original label in German declares 5.83% and 70 g/L. It can be calculated from the density of the formulation that 7% (w/w) and 70 g/L are not in accordance. The manufacturer has been informed about the incorrect content declared on the label. The tolerance is calculated on the basis of the original label.

Table 2.2 shows agreement between declared and determined content for all eleven samples containing aclonifen, bromoxynil, ioxynil, fenoxaprop-P-ethyl, fluazifop-P-butyl and mesotrione as active ingredients. On two products the contents declared in g/L and in % were not in accordance. Both products had original labels in German underneath the Danish label. The content expressed in percentage was not the same on the original label in German compared with the one in Danish. The manufacturer has been informed about the incorrect percentages on the Danish label. On four products, the content of active ingredient was declared only in g/L or in g/kg, but not in % (w/w) as required according to the Statutory Order *(Miljøministeriet, 2003)*.

2.2 Fungicides

2.2.1 Introduction

37 active ingredients in fungicide formulations are approved in Denmark (*Miljøstyrelsen, 2009*). Products containing cyazofamid, fluazinam, pencycuron, prothioconazole, tebuconazole and terbuthylazine as active ingredients were selected for control in 2008. All products were examined for the content of active ingredient and except from one formulation they were all examined for the content of octylphenol and nonylphenol.

Cyazofamid (Figure 2a) is a qil fungicide used in Denmark only for the treatment of fungal diseases in potatoes. Cyazofamid is a systemic fungicide, which inhibits complex III in the mitochondrial respiratory chain. It is a foliar and soil preventive fungicide with residual activity. Fungicide formulations containing cyazofamid were introduced on the Danish market in 2004 and have not previously been selected for authority control.

Fluazinam (Figure 2b) belongs to the group of 2,6-dinitroaniline fungicides. It is used only for the treatment of fungal diseases in potatoes and onions in Denmark. Fluazinam uncouples the mitochondrial oxidative phosphorylation inhibiting spore germination, growth etc. It is protective and has good residual effect. Fluazinam was included in the Danish register of approved pesticides in 1999 and was selected for authority control in 2000.

Pencycuron (Figure 2c) is a phenylurea fungicide used in Denmark only for the treatment of fungal diseases in potatoes. Pencycuron is a non-systemic fungicide, which inhibits the cell division. It is used as foliar or soil treatment fungicide. Fungicide formulations containing pencycuron were introduced on the Danish market in 1993 and were selected for authority control in 2003.

Prothioconazole (Figure 2d) is a fungicide, which belongs to the big group of DMI triazoles. It is used in Denmark only for the treatment of fungal diseases in cereals. Prothioconazole is a broad spectrum systemic fungicide with protective and curative action. It inhibits the steroid demethylation. Fungicide formulations containing prothioconazole were introduced to the Danish market in 2006 and have not previously been selected for authority control.

Tebuconazole (Figure 2e) is a fungicide, which belongs to the big group of DMI triazoles. It is used in Denmark for the treatment of fungal diseases in cereals, grass seed, rape, ornamentals, and off-label on golf courses and on minor crops as leek, spring onion and chives. Tebuconazole is a broad spectrum systemic fungicide with protective and curative action. It inhibits the steroid demethylation. Fungicide formulations containing tebuconazole were selected for authority control in 1998.

Terbuthylazine (Figure 2f) belongs to the group of triazine fungicides used in Denmark only for the treatment of fungal diseases in maize. Terbuthylazine affects a range of fungal enzymes by inhibiting the photosystemic electron transport at the photosystem II receptor site. It is a pre-

and post-emergence systemic fungicide which is absorbed mainly by the roots

2.2.2 Samples

At the time of sampling for the control campaign, four products containing pencycuron, three containing terbuthylazine and tebuconazole (only the products that were registered as fungicides and not formulations used as seed treatment, wood conservation etc.) and two containing prothioconazole, cyazofamid and fluazinam were approved for use in Denmark. All the products containing terbuthylazine, prothioconazole and fluazinam were available on the market during the period of the sample collection, while three out of four products containing pencycuron, two out of three products containing tebuconazole and one out of two products containing cyazofamid 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 prothioconazole were analysed in November 2008. The samples containing pencycuron and cyazofamid were analysed in March 2009, samples containing fluazinam were analysed in May 2009, while the samples containing boscalid was analysed in July 2009. Some of the samples containing tebuconazole were analysed in November 2008, while other formulations were analysed in May 2009.

2.2.3 Results and Discussion

The content of cyazofamid was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2009d).* As no CIPAC-method on cyazofamid exists the method is developed on the basis of information from the manufacturer.

The content of fluazinam was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2009e)*. As no CIPAC-method on fluazinam exists, the method is developed on the basis of information from the manufacturer.

The content of pencycuron was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2009f)*. The method is developed on the basis of information from the manufacturer. The CIPAC method is using normal phase HPLC.

The content of prothioconazole was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2009e)*. As no CIPAC-method on prothioconazole exists, the method is developed on the basis of information from the manufacturer.

The contents of terbuthylazine were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV (*Krongaard, 2009c*). As no CIPAC-method on terbuthylazine exists, the method is developed on the basis of information from the manufacturer. The method is used for determination of mesotrione too.

The content of tebuconazole was determined using gas chromatography and flame ionization detector, GC-FID *(Krongaard, 2008d)*. The method is developed on the basis of information from the manufacturer and on the basis of the existing CIPAC method.

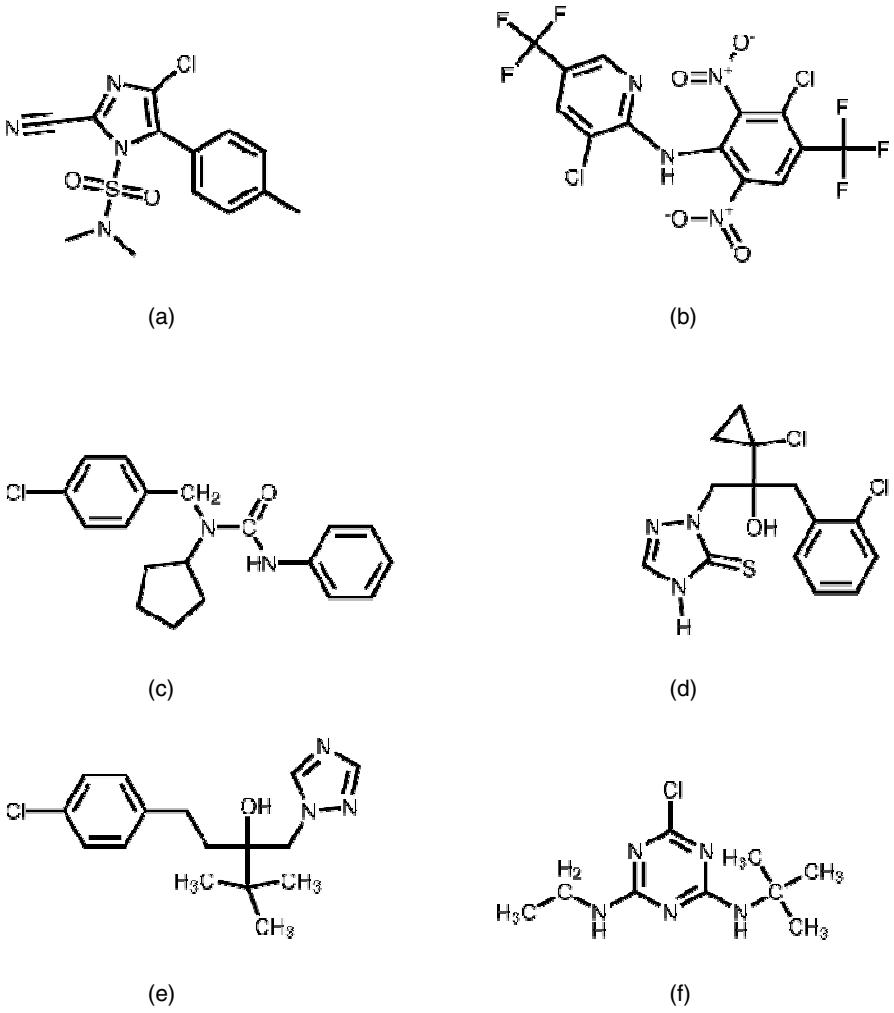


Figure 2

The chemical structure of the fungicide active ingredients: cyazofamid (a), fluazinam (b), pencycuron (c), prothioconazole (d), tebuconazole (e) and terbuthylazine (f).

Table 2.3 shows agreement between declared and determined content for all thirteen samples containing cyazofamid, fluazinam, pencycuron, prothioconazole, tebuconazole and terbuthylazine as active ingredients. On one product the content declared in g/L and in % was not in accordance. The product had an original label in German underneath a label in Danish. The content expressed in percentage is not the same on the original label in German compared with the one in Danish. The manufacturer has been informed about the incorrect content declared in percentages on the label in Danish.

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

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
Cyazofamid	35 %	400 g/L	34.9 ± 0.6%	33.25 – 36.75 %	ATMI 2008-4309
Fluazinam	38.5 %	500 g/L	39.3 ± 0.4%	36.6 – 40.4 %	ATMI 2008-4178
Fluazinam	38.5 %	500 g/L	39.4 ± 0.4%	36.6 – 40.4 %	ATMI 2008-4179
Pencycuron	22.3 %	250 g/L	21.2 ± 0.2%	21.2 – 23.4 %	ATMI 2008-4168
Pencycuron	22.8 %	250 g/L	21.9 ± 0.2%	21.7 – 23.9 %	ATMI 2008-4169
Pencycuron	12.5 %	-	12.2 ± 0.1%	11.8 – 13.3 %	ATMI 2008-4170
Prothioconazole	25 %	250 g/L	25.2 ± 0.1%	23.5 – 26.5 %	ATMI 2008-4260
Prothioconazole	25 %	250 g/L	25.3 ± 0.1%	23.5 – 26.5 %	ATMI 2008-4705
Tebuconazole	25.9 %	250 g/L	25.5 ± 0.1%	24.6 – 27.2 %	ATMI 2008-4175
Tebuconazole	0.015 %	0.15 g/kg	0.0146 ± 0.001%	0.0128 – 0.0173 %	ATMI 2008-4684
Terbuthylazine	29.3 %	330 g/L	29.0 ± 0.1%	27.8 – 30.8 %	ATMI 2008-4177
Terbuthylazine	27.5 %*	330 g/L	28.9 ± 0.1%	26.1 – 28.9 %	ATMI 2008-4709
Terbuthylazine	17.4 %	200 g/L	17.1 ± 0.1%	16.4 – 18.4 %	ATMI 2008-4174

1) Mean ± 95% confidence limits.

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

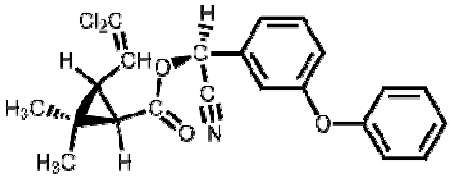
*) The label in Danish on the product declares 33% and 330 g/L, while the original label in German underneath declares 27.5% and 330 g/L. It can be calculated from the density of the formulation that 33% (w/w) and 330 g/L are not in accordance. The manufacturer has been informed about the incorrect content declared on the label. The tolerance is calculated on the basis of the original label.

2.3 Insecticides

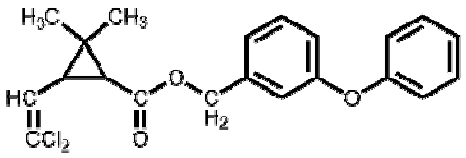
2.3.1 Introduction

Among the different insecticide formulations available on the Danish market (*Miljøstyrelsen, 2009*) the products containing alpha-cypermethrin and permethrin as active ingredients were selected for control in 2008. All products were examined for the content of the active ingredient and for the content of octylphenol and nonylphenol except for an ear-tag product, which was examined for the active ingredient only.

Alpha-cypermethrin (Figure 3a) and permethrin (Figure 3b) belong to the big group of pyrethroides. They are used in Denmark for the control of a wide range of chewing and sucking insects in an even wider range of crops and for control of insect pests in the sectors of agriculture and public health. They are non-systemic insecticides with contact and stomach action. They act by preventing transmission of impulses along the nerves by blocking for the passage of sodium ions through the sodium channels.



(a)



(f)

Figure 3

The chemical structures of the insecticides alpha-cypermethrin (a) and permethrin (b).

2.3.2 Samples

At the time of sampling, one product containing alpha-cypermethrin was approved for use in Denmark. The product was available on the market during the period of the sample collection. A broad range of products containing permethrin is present on the market. Only those with permethrin as the only active ingredient were selected. Three out of six products containing permethrin were available on the market during the period. One sample of each product were collected. The sample list is shown in Appendix I.

The sample containing alpha-cypermethrin was analysed in October 2008. The samples containing permethrin were analysed in March-May 2009.

2.3.3 Results and Discussion

The content of alpha-cypermethrin was determined using gas chromatography and flame ionization detector, GC-FID *(Krongaard, 2008e)*. The method is developed on the basis of the existing CIPAC method.

The content of permethrin was determined using gas chromatography and flame ionization detector, GC-FID *(Krongaard, 2009g)*. The method is developed on the basis of the existing CIPAC method.

Table 2.4 shows agreement between declared and determined content for all four samples containing alpha-cypermethrin and permethrin as active ingredients. On one product, the content of active ingredient was declared only in g/L or g/kg, but not in % (w/w) as required according to the Statutory Order *(Miljøministeriet, 2003)*.

Table 2.4 Content of active ingredient in samples of insecticides

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
Alpha-cypermethrin	-[3)]	50 g/L	52.5 ± 0.4 g/L	45 – 55 g/L[4)]	ATMI 2008-4176
Permethrin	4%	40 g/L	4.17 ± 0.01 %	3.6 – 4.4 %	ATMI 2008-5118
Permethrin	1%	-	1.08 ± 0.02 %	0.85 – 1.15 %	ATMI 2008-4710
Permethrin		1.2 g/tag	1.13 ± 0.02 g/tag	1.08 – 1.31 g/tag[5)]	ATMI 2008-4685

1) Mean ± 95% confidence limits.
2) Tolerance 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) Calculated on the basis of the declared content per tag and a weight of 11.55g per tag.

2.4 Plant growth regulators

2.4.1 Introduction

Among the ten plant growth regulators available on the Danish market (*Miljøstyrelsen, 2009*) the formulations containing paclobutrazol as active ingredient were selected for control in 2008, and examined for the content of active ingredients and for the content of octylphenol and nonylphenol.

Paclobutrazol (Figure 4) is absorbed by the leaves, stems or roots, and translocated to the growing sub-apical meristems to reduce vegetative growth and to improve fruit set. It is used in Denmark only for growth regulation of ornamentals in green houses. Plant growth regulators containing paclobutrazol have not previously been selected for authority control.

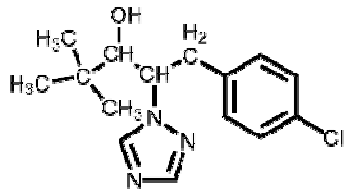


Figure 4 The chemical structure of the plant growth regulator paclobutrazol.

2.4.2 Samples

At the time of sampling for the control campaign, two products containing paclobutrazol were approved for use in Denmark. Both products were available on the market during the period of the sample collection. One sample of each product was collected. The sample list is shown in Appendix I. The samples were analysed in November 2008.

2.4.3 Results and Discussion

The content of paclobutrazol was determined using gas chromatography and flame ionization detector, GC-FID *(Krongaard, 2009h).* As no CIPAC-method on paclobutrazol exists, the method is developed on the basis of information from the manufacturer.

Table 2.5 shows agreement between declared and determined content for both samples containing paclobutrazol as active ingredient.

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)]	
Paclobutrazol	4 %	0.39%	0.44 ± 0.01 %	0.33 – 0.45 %	ATMI 2008-4706
Paclobutrazol	4 %	0.39%	0.32 ± 0.01 %	0.33 – 0.45 %	ATMI 2008-4683

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

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 2008. 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 June 2000.

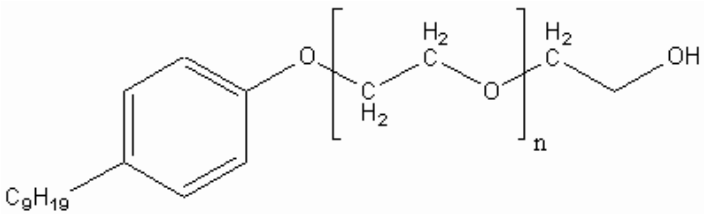


Figure 5 The chemical structure of the additive nonylphenol ethoxylate. The structure of octylphenol ethoxylate is similar, C_9H_{19} is replaced with C_8H_{17}.

2.5.2 Samples

Beside the examination of the content of active ingredient all pesticide formulations sampled in 2008 except from the ear-tag are examined for content of NPEO and OPEO. The sample list is shown in Appendix I

The samples were analysed in June 2009.

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, 2009i).* As no CIPAC-method on NPEO or OPEO exists, the method was developed in the laboratory. The analytical method is capable of analysing NPEO and OPEO simultaneously.

Table 2.6 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
24	1/0	24

Table 2.7 shows that none of the 24 examined samples contain OPEO, but one of the samples contains NPEO. The concentration of NPEO in the formulation is approximately 5.0%. Correspondence with the manufacturer revealed subsequently that the manufacturer informed the Danish EPA in 2005 about this certain case so no further action is taken.

Conclusions

Four different groups of products covered by the pesticide regulation were included in the 2008 analytical chemical authority control:

5. Herbicides containing aclonifen, bromoxynil, ioxynil, fluazifop-P-butyl, fenoxaprop-P-ethyl and mesotrione.
6. Fungicides containing cyazofamid, fluazinam, pencycuron, prothioconazole, tebuconazole and terbuthylazine.
7. Insecticides containing alpha-cypermethrin and permethrin.
8. Plant growth regulators containing paclobutrazol.

All products were examined for the content of the active ingredients. In addition to the examination of the content of active ingredients, most of the 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 ingredients as specified in Danish Statutory Order on pesticides.

None of the examined samples contained OPEO but one contained NPEO. The manufacturer of the product informed the Danish EPA in 2005 about the certain case so no further action was taken.

On five labels, the content of active ingredient was declared only in g/L, but not in % (w/w) as required by the Statutory Order. On two labels the declared content given in g/L was correct, but the content given in percentage was incorrect.

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Appendix I

Pesticide samples collected from the Danish market for authority control in 2008.

Table 1 Herbicides

Active ingredient	Product	Formulation type	Company	NERI sample no.
Aclonifen	LFS Aclonifen	SC	LFS Kemi	2008-4707
Aclonifen	Fenix	SC	Bayer	2008-4308
Bromoxonil	Oxitril CM	EC	Bayer	2008-4171
Ioxynil	Oxitril CM	EC	Bayer	2008-4171
Ioxynil	Totril	EC	Bayer	2008-4172
Mesotrion	LFS Mesotrion + Terbuthylazin	SC	LFS Kemi	2008-4709
Mesotrion	Calaris	SC	Syngenta	2008-4177
Fenoxaprop-p-ehtyl	Primera Super	EW	Bayer	2008-4259
Fluazifop-P-butyl	LFS Fluazifop-P-butyl	EC	LFS Kemi	2008-4708
Fluazifop-P-butyl	Fusilade MAX	EC	Syngenta	2008-4173
Terbuthylazin	LFS Mesotrion + Terbuthylazin	SC	LFS Kemi	2008-4709
Terbuthylazin	Calaris	SC	Syngenta	2008-4177
Terbuthylazin	Laddok TE	SC	BASF	2008-4174

SC: Suspension concentrate; EC: Emulsifiable concentrate; EW: Emulsion, oil in water.

Table 2 Fungicides

Active ingredient	Product	Formulation type	Company	NERI sample no.
Cyazafamid	Ranman	SC	Belchim	2008-4309
Fluazinam	Shirlan	SC	Zeneca	2008-4178
Fluazinam	Shirlan	SC	Syngenta	2008-4179
Pencycuron	Prestige	FS	Bayer	2008-4168
Pencycuron	Monceren FS 250	FS	Bayer	2008-4169
Pencycuron	Prestige DS 12,5	DS	Bayer	2008-4170
Prothioconazole	LFS Prothioconazol	EC	LFS Kemi	2000-4705
Prothioconazole	Proline EC 250	EC	Bayer	2008-4260
Tebuconazole	Folicur EC 250	EC	Bayer	2008-4175
Tebuconazole	Baymat Ultra Klar til brug	AE	Bayer	2008-4684

SC: Suspension concentrate; FS: Flowable concentrate for seed treatment; DS: Powder for dry seed treatment; EC: Emulsifiable concentrate; AE: Aerosol dispenser.

Table 3 Insecticides

Active ingredient	Product	Formulation type	Company	NERI sample no.
Alpha-cypermethrin	Fastac 50	EC	BASF	2008-4176
Permethrin	Pulvex	CP	Schering-Plough Animal Health	2008-4710
Permethrin	Auriplak	Ear tag	Agrolab	2008-4685
Permethrin	Flusa Extra	PO	Novartis Animal Health	2008-5118

EC: Emulsifiable concentrate; CP: contact powder; WP: wettable powder; Pour-on.

Table 4 Plant Growth Regulators

Active ingredient	Product	Formulation type	Company	NERI sample no.
Paclobutrazol	Bonzi	SC	Syngenta	2008-4706
Paclobutrazol	Pirouette	SC	Cillus	2008-4683

SC: Suspension concentrate.

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CONTROL OF PESTICIDES 2008

Chemical Substances and Chemical Preparations

Four different groups of products covered by the pesticide regulation were included in the 2008 analytical chemical authority control: 1) Herbicides containing aclonifen, bromoxynil, ioxynil, fluazifop-P-butyl, fenoxaprop-P-ethyl and mesotrione. 2) Fungicides containing cyazofamid, fluazinam, pencycuron, prothioconazole, tebuconazole and terbuthylazine. 3) Insecticides containing alpha-cypermethrin and permethrin. 4) Plant growth regulators containing paclobutrazol. All samples were examined for the content of active ingredients and most of them for the con-tent of OPEO and NPEO. All samples in this years programme complied with the accepted tolerance limits with respect to the content of the active ingredients as specified in Danish Statutory Order on pesticides. None of the examined samples contained OPEO, but one contained NPEO. On five labels, the content of active ingredient was declared only in g/L, but not in % (w/w) as required and on two labels the declared content given g/L was correct, but the content given in percentage was incorrect.

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