National Environmental Research Institute
Ministry of the Environment · Denmark

Control of Pesticides 2004

Chemical Substances and Chemical Preparations

NERI Technical Report, No. 559

[Tom side]

National Environmental Research Institute
Ministry of the Environment

Control of Pesticides 2004

Chemical Substances and Chemical Preparations

NERI Technical Report, No. 559
2005

Teddy Krongaard
Kitty K. Petersen
Christel Christoffersen

Data sheet

Title:	Control of Pesticides 2004
Subtitle:	Chemical Substances and Chemical Preparations
Authors:	Teddy Krongaard, Kitty K. Petersen and Christel Christoffersen
Department:	Department of Atmospheric Environment
Serial title and no.:	NERI Technical Report No. 559
Publisher:	National Environmental Research Institute © Ministry of the Environment
URL:	http://www.dmu.dk
Date of publication:	Oktober 2005
Referee:	Rossana Bossi
Financial support:	Environmental Protection Agency
Please quote:	Krongaard, T., Petersen, K.K. & Christoffersen, C. 2005: Control of Pesticides 2004. Chemical Substances and Chemical Preparations. National Environmental Research Institute, Denmark. 34pp. - NERI Technical Report No. 559. http://technical-reports.dmu.dk.

Abstract

Four different groups of products covered by the pesticide regulation were included in the 2004 analytical chemical authority control: 1) Herbicides containing bentazone, dicamba, dichlorprop-P, mecoprop-P, MCPA, foramsulfuron, iodosulfuron-methyl-sodium, rimsulfuron and triasulfuron. 2) Fungicides containing hymexazol. 3) Insecticides and molluscicides containing imidacloprid and methiocarb. 4) Rodenticides containing coumatetralyl. All samples were examined for the content of the respective active ingredients and for the content of OPEO and NPEO. All samples but two out of three contained coumatetralyl and one out of four contained dicamba 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. On three products, the content of active ingredient was declared only in g/L, but not in % (w/w) as required.

Keywords:	Control, formulations, pesticides.
Layout:	Majbritt Pedersen-Ulrich
Proof-reader:	Christel Ege-Johansen
ISBN:	87-7772-896-3
ISSN (electronic):	1600-0048
Number of pages:	34
Internet-version:	The report is available only in electronic format from NERI's homepage http://www2.dmu.dk/1_viden/2_Publikationer/3_fagrapporter/rapporter/FR559.pdf
For sale at:	Ministry of the Environment Frontlinien Rentemestervej 8 DK-2400 Copenhagen NV Denmark Tel. +45 70 12 02 11 frontlinien@frontlinien.dk

Contents

Summary

The analytical chemical authority control of pesticide products on the Danish market performed in 2004 is reported. 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 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 2004 analytical chemical authority control:

1) Herbicides containing bentazone, dicamba, dichlorprop-P, mecoprop-P, MCPA, foramsulfuron, iodosulfuron-methyl-sodium, rimsulfuron and triasulfuron.
2) Fungicides containing hymexazol.
3) Insecticides and molluscicides containing imidacloprid and methiocarb.
4) Rodenticides containing coumatetralyl.

Satisfactory results were found for herbicides containing bentazone, dichlorprop-P, mecoprop-P, MCPA, foramsulfuron, iodosulfuron-methyl-sodium, rimsulfuron and triasulfuron, for fungicides containing hymexazol, and for insecticides and molluscicides containing imidacloprid and methiocarb. 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.

Two out of three products containing coumatetralyl did not comply with the tolerance limit for content of active ingredient. The contents of coumatetralyl were too high compared with the declared content. One out of four products containing dicamba did not comply with the tolerance limit for content of active ingredient. The content of dicamba was too high compared with the declared content.

None of the examined samples contained OPEO, but one of the samples contained NPEO. The concentration of NPEO in the formulation was approximately 0.02%.

On three products the content of active ingredient were declared only in g/L, but not in % (w/w) as required by the Statutory Order.

Resumé

Rapporten indeholder resultater af analytisk kemiske kontrol af pesticidprodukter på det danske marked udført i 2004. Prøver af udvalgte grupper af bekæmpelsesmidler er indsamlet 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 af 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 myndighedskontrol i 2004:

1) Herbicider indeholdende bentazon, dicamba, dichlorprop-P, mechlorprop-P, MCPA, foramsulfuron, iodosulfuron-methyl-natrium, rimsulfuron og triasulfuron.
2) Fungicider indeholdende hymexazol.
3) Insekticider og sneglemidler indeholdende imidacloprid og methiocarb (mercaptodimethur).
4) Rodenticider indeholdende coumatetralyl.

Der blev opnået tilfredsstillende resultater blandt ukrudtsmidler indeholdende bentazon, dichlorprop-P, mechlorprop-P, MCPA, foramsulfuron, iodosulfuron-methyl-natrium, rimsulfuron og triasulfuron, og for svampemidler indeholdende hymexazol, samt for insektmidler og sneglemidler indeholdende imidacloprid og methiocarb. Indholdet af aktivstof i alle de analyserede prøver af disse bekæmpelsesmidler var indenfor den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler.

To af de tre produkter, der indeholder coumatetralyl var ikke indenfor den accepterede tolerance for indhold af aktivstof. Indholdene var for høje i forhold til de deklarerede indhold. Ét af de fire produkter, der indeholder dicamba, var ikke indenfor den accepterede tolerance for indhold af aktivstof. Indholdet var for højt i forhold til det deklarerede indhold.

Ingen af de undersøgte produkter indeholdt OPEO, men én af prøverne indeholdt NPEO. Koncentrationen af NPEO i formuleringen var cirka 0.02%.

På tre produkter var indholdet af aktivstof kun deklareret i g/l og ikke i vægt-% som det ellers er krævet i bekendtgørelsen.

1 Introduction

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

In practice 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 an assistance to DEPA. The present report describes only the part of the authority control of pesticides involving laboratory control.

Laboratory control of pesticides covers 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 content of auxiliary substances or levels of impurities.

Laboratory control work is carried out by means of 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, suspicion of a product not complying with regulations, specifications, etc.

Only the first type of laboratory control i.e. campaigns are covered by this report, which describes the laboratory control performed in 2004.

2 Control Campaigns in 2004

Control campaigns conducted in 2004 have covered active ingredients and auxiliary substances belonging to four different groups of pesticides: herbicides, fungicides, insecticides and rodenticides. All analytical chemical control was aimed at examining the content of active ingredient compared with the declared content on the label. Statutory Order in Denmark *(Miljøministeriet, 2003)* specifies 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 content of octylphenol ethoxylates and nonylphenol ethoxylates.

Samples of the various pesticide formulations covered in the 2004 control campaigns have been collected primarily by the Chemical Inspection Service at DEPA during the months March – May 2004 from either whole sale dealers/importers or at retailer out-lets. Four samples (three from the users and one from a retailer out-let) were collected by NERI in December 2004. 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 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 33 different active ingredients in herbicide formulations available on the Danish market (*Miljøstyrelsen, 2004*). Products containing bentazone, dicamba, dichlorprop-P, mecoprop-P, MCPA, foramsulfuron, iodosulfuron-methyl-sodium, rimsulfuron and triasulfuron, as active ingredients were selected for control in 2004. All products were examined for the content of active ingredient and for the content of octylphenol and nonylphenol.

Bentazone (Figure 1,a) belongs to the group of benzothiadiazinone herbicides. It is used only to control weeds in cereals, seed grasses and seed clover, maize and peas in Denmark. Bentazone is a post-emergence, selective contact herbicide, absorbed mainly by the foliage with very little translocation, but also absorbed by the roots, with translocation acropetally in the xylem. It inhibits the photosynthetic electron transport at the photosystem II receptor site. Herbicide formulations containing bentazone have not been selected for authority control for the last decade.

Dicamba (Figure 1,b) belongs to the group of benzoic acid herbicides. It is used only to control broad-leaved weeds and brush species in cereals and private lawns in Denmark. Dicamba is a selective systemic herbicide, absorbed by the leaves and roots, with ready translocation. It acts like an auxin growth regulator. Herbicide formulations containing dicamba were selected for authority control in 2000 when all examined products complied with the declared content with respect to the active ingredient.

Dichlorprop-P (Figure 1,c) is an aryloxyalkanoic acid (phenoxy acid) herbicide, which in Denmark is used as a post-emergence translocated herbicide used to control weeds in private lawns. Dichlorprop-P is a selective hormone-type herbicide absorbed through the leaves with translocation to the roots. It acts like an auxin growth regulator. Herbicide formulations containing dichlorprop-P have not been selected for authority control for the last decade.

Mecoprop-P (Figure 1,d) is an aryloxyalkanoic acid (phenoxy acid) herbicide like dichlorprop-P. It is used only to control broad-leaved weeds in lawns in Denmark. Mecoprop-P is as dichlorprop-P a selective hormone-type herbicide, which is absorbed through the leaves with translocation to the roots. It acts like an auxin growth regulator. Herbicide formulations containing mecoprop-P have not been selected for authority control for the last decade.

MCPA (Figure 1,e) is an aryloxyalkanoic acid (phenoxy acid) herbicide like dichlorprop-P and mecoprop-P. It is used only to control broad-leaved weeds in lawns in Denmark. MCPA is as dichlorprop-P and mecoprop-P a selective hormone-type herbicide. It is absorbed through the leaves and roots with translocation to the meristematic regions, where it prevents growing. Herbicide formulations contain-

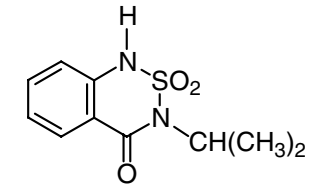
ing MCPA have not been selected for authority control during the last decade.

Foramsulfuron (Figure 1,f) belongs to the group of sulfonylurea herbicides. It is used only to control grass and broad-leaved weeds in maize in Denmark. Foramsulfuron is a post-emergence herbicide absorbed by the foliage and translocated throughout the plant, particularly to the meristematic regions. It inhibits the synthesis of the branched chain amino acids. Herbicide formulations containing foramsulfuron are rather new on the Danish market and have not previously been selected for authority control.

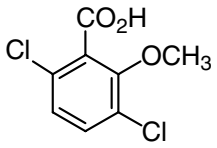
Iodosulfuron-methyl-sodium (Figure 1,g) belongs to the group of sulfonylurea herbicides. It is used only to control grass and broad-leaved weeds in cereals and maize in Denmark. Iodosulfuron-methyl-sodium is a post-emergence herbicide. It inhibits the synthesis of the branched chain amino acids valine and isoleucine. Herbicide formulations containing iodosulfuron-methyl-sodium are rather new on the Danish market and have not previously been selected for authority control.

Rimsulfuron (Figure 1,h) belongs to the group of sulfonylurea herbicides. It is used only to control grass and broad-leaved weeds in potatoes in Denmark. Rimsulfuron is a post-emergence herbicide absorbed by the foliage and the roots and translocated to the meristematic regions. It inhibits the synthesis of the branched chain amino acids valine and isoleucine. Herbicide formulations containing rimsulfuron were approved for the Danish market in 2000 and have not previously been selected for authority control.

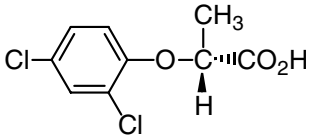
Triasulfuron (Figure 1,i) belongs to the group of sulfonylurea herbicides. It is used only to control grass and broad-leaved weeds in cereals in Denmark. Triasulfuron is a pre- and post-emergence herbicide absorbed by the foliage and the roots and translocated to the meristematic regions. It inhibits the synthesis of the branched chain amino acids valine and isoleucine. Herbicide formulations containing triasulfuron was approved for the Danish market in 1994 and was selected for authority control in 1995 when the examined product complied with the declared content with respect to the active ingredient.



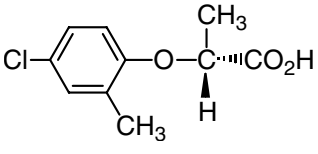
(a)



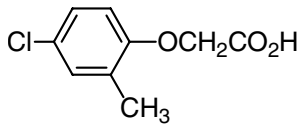
(b)



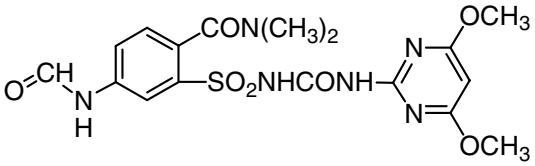
(c)



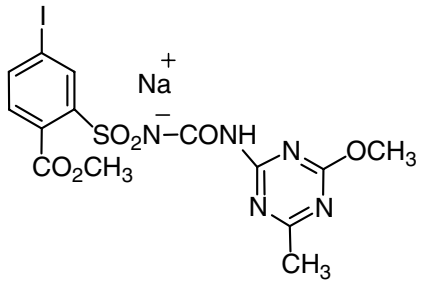
(d)



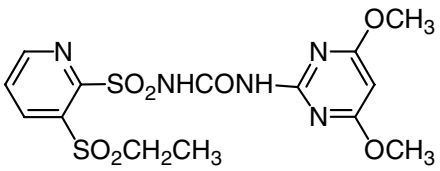
(e)



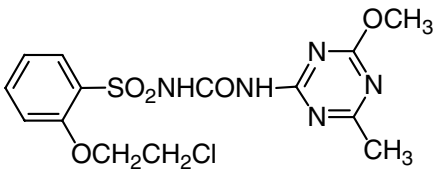
(f)



(g)



(h)



(i)

Figure 1
Chemical structure of the herbicide active ingredients: bentazone (a), dicamba (b), dichlorprop-P (c), mecoprop-P (d), MCPA (e), foramsulfuron (f), iodosulfuron-methyl-sodium (g), rimsulfuron (h) and triasulfuron (i).

2.1.2 Samples

At the time of sampling for the control campaign, one product containing mecoprop-P, one containing foramsulfuron, one containing rimsulfuron and one product containing triasulfuron were approved for use in Denmark. All these products were available on the market. Four out of five products containing bentazone as active ingredient, four out of eight products containing dicamba, three out of four products containing dichlorprop-P, nine out of thirteen products containing MCPA and one out of two products containing iodosulfuron-methyl-sodium as active ingredient 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 iodosulfuron-methyl-sodium was analysed in August 2004. The samples containing dichlorprop-P were analysed during the period September 2004 - March 2005, the foramsulfuron-containing product was analysed in October, the sample containing rimsulfuron was analysed in November and MCPA-containing products were analysed during the period November-April 2005. The products containing triasulfuron and dicamba were analysed in January-February 2005, products containing bentazone were analysed in February 2005 and the mecoprop-P-containing product was analysed in April 2005.

2.1.3 Results and Discussion

The contents of bentazone were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2005a)*. The method is developed on the basis of information from the manufacturer and the existing CIPAC method.

The contents of dicamba and triasulfuron were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2005b)*. The method is developed on the basis of information from the manufacturer and allows simultaneous determination of dicamba and triasulfuron.

The contents of dichlorprop-P and MCPA as acids were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2005c)*. The method is developed on the basis of information from the manufacturer and allows simultaneous determination of dichlorprop-P (acid) and MCPA (acid).

The contents of mecoprop-P and MCPA as esters were determined using gas chromatography and flame ionisation detection (GC-FID) *(Krongaard, 2005d)*. The method is developed on the basis of information from the manufacturer and allows simultaneous determination of dichlorprop-P (ester) and MCPA (ester) simultaneously.

The contents of foramsulfuron were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2004a)*. As no CIPAC-method on foramsul-

furon exists, the method is developed on the basis of information from the manufacturer.

The contents of iodosulfuron-methyl-sodium were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2004b)*. As no CIPAC-method on iodosulfuron-methyl-sodium exists, the method is developed on the basis of information from the manufacturer.

The contents of rimsulfuron were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2004c)*. As no CIPAC-method on rimsulfuron 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 the samples containing bentazone, dichlorprop-P, mecoprop-P, MCPA, foramsulfuron, iodosulfuron-methyl-sodium, rimsulfuron and triasulfuron, whereas the content of active ingredient in one product containing dicamba was found to be outside the tolerance limit. The content of the active ingredient in the sample was too high compared with the declared content. On three products containing MCPA, dichlorprop-P and dicamba the contents of active ingredient were only declared in g/L not in % (w/w) as the Statutory Order requires.

Table 2.2 Content of active ingredient in samples of herbicides.

Active ingredient	Content			NERI sample no.	
	Label claim	Analysis[1)]	Tolerance[2)]		
Bentazone	22.3%	-	22.0 ± 0.1%	21.2 – 23.4%	04-0116
Bentazone	17.4%	(200 g/L)	17.9 ± 0.1%	16.5 – 18.3%	04-0117
Bentazone	40%	(480 g/L)	41.4 ± 0.2%	38 – 42%	04-0118
Bentazone	40%	(480 g/L)	40.1 ± 0.2%	38 – 42%	04-0119
Dicamba	60%	-	59.1 ± 0.3%	57.5 – 62.5%	04-0113
Dicamba	0.03%	(0.32 g/L)	0.0329 ± 0.0001%	0.026 – 0.035%	04-0255
Dicamba	-[3)]	(0.32 g/L)	0.381 ± 0.001g/L	0.27 – 0.37 g/L[4)]	04-0256*)
Dicamba	0.5%	(4.5 g/L)	0.453 ± 0.001%	0.425 – 0.575%	04-0257
Dichlorprop-P	0.15%	(1.5 g/L)	0.161 ± 0.001%	0.128 – 0.173%	04-0255
Dichlorprop-P	-[3)]	(1.5 g/L)	1.63 ± 0.01 g/L	1.28 – 1.73 g/L[4)]	04-0256
Dichlorprop-P	2.2%	(23 g/L)	2.17 ± 0.07%	1.87 – 2.53%	04-0257
MCPA	63%	(750 g/L)	61.7 ± 0.3%	60.5 – 65.5%	04-0114
MCPA	18.22%	(200 g/L)	17.93 ± 0.08%	17.23 – 19.31%	04-0115
MCPA	6.7%	(75 g/L)	6.72 ± 0.03%	6.03 – 7.37%	04-0116
MCPA	63%	(750 g/L)	61.0 ± 0.3%	60.5 – 65.5%	04-0128
MCPA	0.5%	-	0.46 ± 0.02%	0.465 – 0.535%	04-0254
MCPA	0.5%	(5.2 g/L)	0.513 ± 0.002%	0.465 – 0.535%	04-0255
MCPA	-[3)]	(5.2 g/L)	5.42 ± 0.02 g/L	4.42 – 5.98 g/L[4)]	04-0256
MCPA	7.5%	(76.5 g/L)	7.22 ± 0.03%	6.75 – 8.25%	04-0257
MCPA	18.22%	(200 g/L)	18.08 ± 0.08%	17.23 – 19.31%	04-0349
Mecoprop-P	0.3%	-	0.267 ± 0.009%	0.255 – 0.345%	04-0254
Foramsulfuron	-	(300 g/kg)	292 ± 2 g/kg	285 – 315 g/kg	04-0111
Iodosulfuron-methyl-sodium	-	(10 g/Kg)	9.89 ± 0.08 g/kg	9.4 – 10.6 g/kg	04-0111
Rimsulfuron	25%	-	24.4 ± 0.2%	23.5 – 26.5%	04-0131
Triasulfuron	3%	-	2.89 ± 0.02%	2.7 – 3.3%	04-0113

1) Mean ± 95% confidence limits.
2) Tolerance limits for content of active ingredients according to Danish regulations *(Miljøministeriet, 2003)*.
3) Content (expressed as %) not declared.
4) Calculated on the basis of the declared content in g/l.
*) Found content is outside the accepted tolerance.

2.2 Fungicides

2.2.1 Introduction

About 31 active ingredients in fungicide formulations are approved in Denmark (*Miljøstyrelsen, 2004*). The product containing hymexazol was selected for control in 2004 and examined for content of active ingredient.

Hymexazol (Figure 2) is a fungicide, used in Denmark only for treatment of sugar beet seed. Hymexazol is a systemic soil and seed fungicide, which is used to control specific soil-borne fungal diseases. Hymexazol exhibits some plant growth stimulation too. Hymexazol was included in the Danish register of approved pesticides many years ago but has not previously been selected for authority control.

2.2.2 Samples

At the time of sampling for the control campaign, one product containing hymexazol was approved for use in Denmark. The product was available on the market. One sample of the fungicide product was collected. Hymexazol is only approved for industrial use. Due to the size of the container only a sub-sample and not the whole package was collected. NERI collected the sample at a seed treatment plant. The list of samples is summarised in Appendix I.

The sample containing hymexazol was analysed in January 2005.

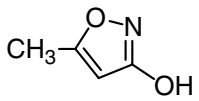


Figure 2
Chemical structure of the fungicide active ingredient: hymexazol

2.2.3 Results and Discussion

The content of hymexazol was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2005e)*. As no CIPAC-method on hymexazol exists, the method was developed on the basis of information from the manufacturer.

Table 2.3 shows agreement between declared and determined content in the sample containing hymexazol as active ingredients.

Table 2.3 Content of active ingredient in a sample of fungicides.

Active ingredient	Content			NERI sample no.
	Label claim	Analysis[1)]	Tolerance[2)]	
Hymexazol	70% -	71.0 ± 0.4%	67.5 – 73.5%	04-0674

1) Mean ± 95% confidence limits.
2) Tolerated limits for content of active ingredients according to Danish regulations *(Miljøministeriet, 2003)*.

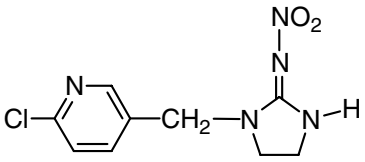
2.3 Insecticides and molluscicides

2.3.1 Introduction

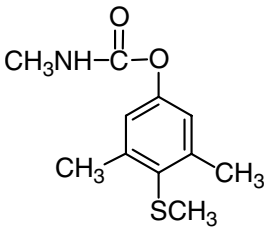
Among the different insecticide and molluscicide formulations available on the Danish market (*Miljøstyrelsen, 2004*) the products containing imidacloprid and methiocarb (mercaptodimethur) as active ingredients were selected for control in 2004. All products were examined for content of active ingredient.

Imidacloprid (Figure 3a) belongs to the group of neonicotinoids, which in Denmark is used for control of sucking insects in ornamentals, cucumber, tomato and pepper and it is used as seed treatment of beet seed in Denmark. Imidacloprid is a systemic insecticide with contact and stomach action. It acts as an antagonist by binding to postsynaptic nicotinic receptors in the insect central nervous system. Insecticide formulations containing imidacloprid were approved for the Danish market in 1998 but have not previously been selected for authority control.

Methiocarb (Figure 3b) belongs to the group of carbamates. It is used in Denmark for control of slugs and snails in ornamentals and vegetables, for control of specific thrips in ornamentals and as treatment for sugar beet seed. Methiocarb is a non-systemic cholinesterase inhibitor with contact and stomach action. Insecticide formulations containing methiocarb have been included in the Danish register of approved pesticides for many years and have not been selected for authority control in the last decade.



(a)



(b)

Figure 3
Chemical structure of the insecticide and the molluscicide active ingredients: imidacloprid (a), methiocarb (b).

2.3.2 Samples

At the time of sampling, five products containing imidacloprid and three products containing methiocarb were approved for use in Denmark. All three products containing methiocarb as active ingredient and four out of the five products containing imidacloprid were available on the market during the period of the sample collection. One sample of each insecticide product was collected. Two of the methiocarb formulations are approved to industrial use only. Due to the size of these containers only a sub-sample of each formulation and not the whole packages were collected. NERI collected these samples at a seed treatment plant. The sample list is shown in Appendix I.

The samples containing methiocarb were analysed in January 2005. The samples containing imidacloprid were analysed in the period October 2004 – February 2005.

2.3.3 Results and Discussion

The content of imidacloprid was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2005f).* The method is developed on the basis of information from the manufacturer and the existing CIPAC method.

The content of methiocarb was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2005g).* The method is developed on the basis of information from the manufacturer.

Table 2.4 shows an agreement between declared and determined content made for all seven samples containing methiocarb and imidacloprid.

Table 2.4 Content of active ingredient in samples of insecticides and molluscicides.

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
Methiocarb	1%	-	1.003 ± 0.003%	0.85 – 1.15%	04-0130
Methiocarb	43.9%	-	42.4 ± 0.1%	41.7 – 46.1%	04-0675
Methiocarb	50%	-	49.6 ± 0.1%	47.5 – 52.5%	04-0676
Imidacloprid	70%	-	69.7 ± 0.5%	67.5 – 72.5%	04-0258
Imidacloprid	2.5%	-	2.32 ± 0.06%	2.13 – 2.88%	04-0259
Imidacloprid	2.15%	-	2.188 ± 0.005%	1.82 – 2.47%	04-0467
Imidacloprid	0.025%	-	0.0245 ± 0.0005%	0.021 – 0.029%	04-0673

1) Mean ± 95% confidence limits.
2) Tolerance limits for content of active ingredients according to Danish regulation *(Miljøministeriet, 2003)*.

2.4 Rodenticides

2.4.1 Introduction

Among the eight rodenticides available on the Danish market (*Miljøstyrelsen, 2004*) the rodenticide formulations containing coumatetralyl as active ingredient were selected for control in 2004, and examined for the content of active ingredients.

Coumatetralyl (Figure 4) is used for control of rats in Denmark. Coumatetralyl acts as an anticoagulant, by blocking the formation of prothrombin in the liver. Rodenticide formulations containing coumatetralyl have been included in the Danish register of approved pesticides for many years and have not been selected for authority control in the last decade.

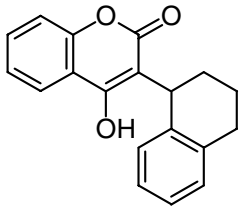


Figure 4
Chemical structure of the rodenticide coumatetralyl.

2.4.2 Samples

At the time of sampling for the control campaign, six products containing coumatetralyl as active ingredient were approved for use in Denmark. Three of these six products were available on the market during the period of the sample collection. One sample of each product was collected. The samples are listed in Appendix I

The samples were analysed in June - July 2004 and due to an inadequate analytical method again in the period August - September 2004.

2.4.3 Results and Discussion

The content of coumatetralyl was determined by using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2004d).* The method is developed on the basis of information from the manufacturer and the existing CIPAC method.

Table 2.5 shows an agreement between declared and determined content in one of the three products containing coumatetralyl, whereas the content of active ingredient of two of the products were found to be outside the tolerance limit. The content of the active ingredient in the sample was too high compared with the declared content.

Table 2.5 Content of active ingredient in samples of rodenticides

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
Coumatetralyl	0.3%	-	0.378 ± 0.003%	0.255 – 0.345%	04-0251*)
Coumatetralyl	0.3%	-	0.385 ± 0.003%	0.255 – 0.345%	04-0252*)
Coumatetralyl	0.03%	-	0.0266 ± 0.0004%	0.0255 – 0.0345%	04-0253

1) Mean ± 95% confidence limits.
2) Tolerated limits for content of active ingredients according to Danish regulations *(Miljøministeriet, 2003)*.
*) Found content is outside the accepted tolerance

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 2004. All the formulations examined for 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 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 were/are 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 exemptions given by the Danish authorities. Dealers are allowed to sell stocks after this date.

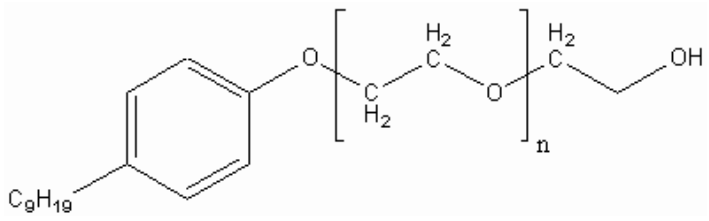


Figure 5
Chemical structure of the additive nonylphenol ethoxylate. The structure of octylphenol ethoxylate is similar, C_9H_{19} is replaced with C_8H_{17}.

2.5.2 Samples

Beside the examination of the content of active ingredient all pesticide formulations sampled in 2004 are examined for content of NPEO and OPEO. One formulated additive for manual addition is examined too. The sample list are shown in Appendix I

The samples were analysed in March 2005.

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, 2005h).* 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 2.6 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**
27	1/0	26

Table 2.6 shows that none of the 27 examined samples contain OPEO, but one of the samples contains NPEO. The concentration of NPEO in the formulation was approximately 0.02%.

3 Conclusions

Four different groups of products covered by the pesticide regulation were included in the 2004 analytical chemical authority control:

1) Herbicides containing bentazone, dicamba, dichlorprop-P, mecoprop-P, MCPA, foramsulfuron, iodosulfuron-methyl-sodium, rimsulfuron and triasulfuron.

2) Fungicides containing hymexazol.

3) Insecticides and molluscicides containing imidacloprid and methiocarb.

4) Rodenticides containing coumatetralyl.

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 herbicides containing bentazone, dichlorprop-P, mecoprop-P, MCPA, foramsulfuron, iodosulfuron-methyl-sodium, rimsulfuron and triasulfuron, for fungicides containing hymexazol, and for insecticides containing imidacloprid and methiocarb. 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.

Two out of three products containing coumatetralyl did not comply with the tolerance limit for content of active ingredient. The contents of coumatetralyl were too high compared with the declared content. One out of four products containing dicamba did not comply with the tolerance limit for content of active ingredient. The content of dicamba was too high compared with the declared content.

None of the examined samples contained OPEO, but one of the samples contained NPEO. The concentration of NPEO in the formulation was approximately 0.02%.

On three products the content of active ingredient were declared only in g/L, but not in % (w/w) as required by the Statutory Order.

4 References

Krongaard, T. (2004a): Analysemetode. Bestemmelse af foramsulfuron som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of foramsulfuron as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2004b): Analysemetode. Bestemmelse af iodosulfuron-methyl som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of iodosulfuron-methyl as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2004c): Analysemetode. Bestemmelse af rimsulfuron som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of rimsulfuron as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (2004d): Analysemetode. Bestemmelse af coumatetralyl som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of coumatetralyl as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (2005a): Analysemetode. Bestemmelse af bentazon som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of bentazone as active ingredient in pesticides. National Environmental Research Institute). 7 pp. (In Danish).

Krongaard, T. (2005b): Analysemetode. Bestemmelse af dicamba og triasulfuron som aktivstoffer i bekæmpelsesmidler. (Method of Analysis. Determination of dicamba and triasulfuron as active ingredients in pesticides. National Environmental Research Institute). 9 pp. (In Danish).

Krongaard, T. (2005c): Analysemetode. Bestemmelse af MCPA og dichlorprop-P som aktivstoffer i bekæmpelsesmidler. (Method of Analysis. Determination of MCPA and dichlorprop-P as active ingredients in pesticides. National Environmental Research Institute). 11 pp. (In Danish).

Krongaard, T. (2005d): Analysemetode. Bestemmelse af MCPA og mechlorprop-P som aktivstoffer i bekæmpelsesmidler. (Method of Analysis. Determination of MCPA and mecoprop-P as active ingredients in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2005e): Analysemetode. Bestemmelse af hymexazol som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of hymexazol as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (2005f): Analysemetode. Bestemmelse af imidacloprid som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of imidacloprid as active ingredient in pesticides. National Environmental Research Institute). 8 pp. (In Danish).

Krongaard, T. (2005g): Analysemetode. Bestemmelse af methiocarb (mercaptodimethur) som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of methiocarb (mercaptodimethur) as active ingredient in pesticides. National Environmental Research Institute). 8 pp. (In Danish).

Krongaard, T. (2005h): Analysemetode. Bestemmelse af NPEO og OPEO i bekæmpelsesmidler. (Method of Analysis. Determination of NPEO and OPEO in pesticides. National Environmental Research Institute). 9 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 (2004): Oversigt over godkendte bekæmpelsesmidler 2004.
http://mst.dk/Bekaemp/Oversigt%20over%20godkendte%20bekaempelsesmidler%202004.doc (Danish EPA, 2004: List of Approved Pesticides 2004, Danish Environmental Protection Agency). (In Danish).

Appendix I

Samples of pesticide formulations collected from the Danish market for authority control in 2004.

Table 1 Herbicides

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Bentazon	Basagran M75	SL	BASF	04-0116
Bentazon	Ladok TE	SC	BASF	04-0117
Bentazon	Basagran 480	SL	BASF	04-0118
Bentazon	IT Bentazone DK	SL	Inter-Trade	04-0119
Dicamba	Synergi 63WG	WG	Novartis	04-0113
Dicamba	Toxan plænerens Klar til brug	AL	Klarsø & Co. Aps.	04-0255
Dicamba	Material shop plæner-ens, Klar til brug	AL	Klarsø & Co. Aps.	04-0256
Dicamba	Toxan plænerens	SL	Klarsø & Co. Aps.	04-0257
Dichlorprop-P	Toxan plænerens Klar til brug	AL	Klarsø & Co. Aps.	04-0255
Dichlorprop-P	Material shop plæner-ens, Klar til brug	AL	Klarsø & Co. Aps.	04-0256
Dichlorprop-P	Toxan plænerens	SL	Klarsø & Co. Aps.	04-0257
MCPA	Metaxon	SL	BASF	04-0114
MCPA	Ariane FG	EC	Dow AgroSciences	04-0115
MCPA	Basagran M75	SL	BASF	04-0116
MCPA	NF-M 750	SL	Nordisk Alkali	04-0128
MCPA	Trim Plænerens	GR	Klarsø & Co. Aps.	04-0254
MCPA	Toxan plænerens Klar til brug	AL	Klarsø & Co. Aps.	04-0255
MCPA	Material shop plæner-ens, Klar til brug	AL	Klarsø & Co. Aps.	04-0256
MCPA	Toxan plænerens	SL	Klarsø & Co. Aps.	04-0257
MCPA	Bofix S Plænerens	EC	Tanaco	04-0349
Mecoprop-P	Trim Plænerens	GR	Klarsø & Co. Aps.	04-0254
Foramsulfuron	MaisTer	WG	Bayer A/S	04-0111
Iodosulfuron-methyl-sodium	MaisTer	WG	Bayer A/S	04-0111
Additiv to Mais Ter	MaisOil	-	Bayer A/S	04-0112

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Rimsulfuron	Titus Ukrudtsmiddel	WG	DuPont Danmark A/S	04-0131
Triasulfuron	Synergi 63WG	WG	Novartis	04-0113

1) AL: Any other liquid; EC: Emusifiable concentrate; GR: Granule; SC: Suspension concentrate; SL: Soluble concentrate; WG: Water dispersible granule.

Table 2 Fungicides

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Hymexazol	Tachigaren 70 WP	WP	DuPont Danmark A/S	04-0674

1) WP: Wettable powder.

Table 3 Insecticides and molluscicides

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Imidacloprid	Confidor WG 70	WG	Bayer A/S	04-0258
Imidacloprid	Provado insektpinde	PR	Bayer A/S	04-0259
Imidacloprid	Premise Kakelak Pasta, Premise Gel	PA	Bayer A/S	04-0467
Imidacloprid	Provado insektspray	AE	Bayer A/S	04-0672
Imidacloprid	Provado insektspray	AE	Bayer A/S	04-0673
Methiocarb	Mesurol Sneglegift 1%	GR	Bayer A/S	04-0130
Methiocarb	Mesurol SC 500	SC	Bayer A/S	04-0675
Methiocarb	Mesurol WP 50	WP	Bayer A/S	04-676

1) AE: Aerosol dispenser; GR: Granule; PA: Paste; PR: plant rodlet; SC: Suspension concentrate; WG Water dispersible granule; WP: Wettable powder.

Table 4 Rodenticides

Active ingredient	Product	Formulation type[1)]	Company	NERI sample no.
Coumatetralyl	Cuta kontaktpudder	TP	Mortalin A/S	04-0251
Coumatetralyl	Kiltin K200	TP	Kiltin A/S	04-0252
Coumatetralyl	Kiltin K100	PS	Kiltin A/S	04-0253

1) PS: seed coated with pesticide; TP: tracking powder.

National Environmental Research Institute

The National Environmental Research Institute, NERI, is a research institute of the Ministry of Environment and Energy. In Danish, NERI is called *Danmarks Miljøundersøgelser (DMU)*.
NERI's tasks are primarily to conduct research, collect data, and give advice on problems related to the environment and nature.

Addresses:

URL: http://www.dmu.dk

National Environmental Research Institute
Frederiksborgvej 399
PO Box 358
DK-4000 Roskilde
Denmark
Tel: +45 46 30 12 00
Fax: +45 46 30 11 14

Management
Personnel and Economy Secretariat
Research and Development Section
Department of Atmospheric Environment
Department of Environmental Chemistry
Department of Policy Analysis
Department of Marine Ecology
Department of Microbial Ecology and Biotechnology
Department of Arctic Environment

National Environmental Research Institute
Vejlsøvej 25
PO Box 314
DK-8600 Silkeborg
Denmark
Tel: +45 89 20 14 00
Fax: +45 89 20 14 14

Department of Lake and Estuarine Ecology
Department of Terrestrial Ecology
Department of Streams and Riparian areas

National Environmental Research Institute
Grenåvej 12-14, Kalø
DK-8410 Rønde
Denmark
Tel: +45 89 20 17 00
Fax: +45 89 20 15 15

Department of Landscape Ecology
Department of Coastal Zone Ecology

Publications:
NERI publishes professional reports, technical instructions, and the annual report. A R&D projects' catalogue is available in an electronic version on the World Wide Web.
Included in the annual report is a list of the publications from the current year.

Faglige rapporter fra DMU/NERI Technical Reports

2005

Nr. 526: Effekter af fiskeri på stenrevs algevegetation. Et pilotprojekt på Store Middelgrund i Kattegat. Af Dahl, K. 16 s. (elektronisk)
Nr. 527: The impact on skylark numbers of reductions in pesticide usage in Denmark. Predictions using a landscape-scale individual-based model. By Topping, C.J. 33 pp. (electronic)
Nr. 528: Vitamins and minerals in the traditional Greenland diet. By Andersen, S.M. 43 pp. (electronic)
Nr. 529: Mejlgrund og lillegrund. En undersøgelse af biologisk diversitet på et lavvandet område med stenrev i Samsø Bælt. Af Dahl, K., Lundsteen, S. & Tendal, O.S. 87 s. (elektronisk)
Nr. 530: Eksempler på økologisk klassificering af kystvande. Vandrammedirektiv-projekt, Fase IIIa. Af Andersen, J.H. et al. 48 s. (elektronisk)
Nr. 531: Restaurering af Skjern Å. Sammenfatning af overvågningsresultater fra 1999-2003. Af Andersen, J.M. (red.). 94 s.
Nr. 532: NOVANA. Nationwide Monitoring and Assessment Programme for the Aquatic and Terrestrial Environments. Programme Description - Part 1. By Svendsen, L.M. & Norup, B. (eds.). 53 pp., 60,00 DKK.
Nr. 533: Fate of mercury in the Arctic (FOMA). Sub-project atmosphere. By Skov, H. et al. 55 pp. (electronic)
Nr. 534: Control of pesticides 2003. Chemical Substances and Chemical Preparations. By Krongaard, T., Petersen, K.T. & Christoffersen, C. 32 pp. (electronic)
Nr. 535: Redskaber til vurdering af miljø- og naturkvalitet i de danske farvande. Typeinddeling, udvalgte indikatorer og eksempler på klassifikation. Af Dahl, K. (red.) et al. 158 s. (elektronisk)
Nr. 536: Aromatiske kulbrinter i produceret vand fra offshore olie- og gasindustrien. Test af prøvetagningsstrategi. Af Hansen, A.B. 41 s. (elektronisk)
Nr. 537: NOVANA. National Monitoring and Assessment Programme for the Aquatic and Terrestrial Environments. Programme Description - Part 2. By Svendsen, L.M., Bijl, L. van der, Boutrup, S. & Norup, B. (eds.). 137 pp., 100,00 DKK.
Nr. 538: Tungmetaller i tang og musling ved Ivituut 2004. Johansen, P. & Asmund, G. 27 s. (elektronisk)
Nr. 539: Anvendelse af molekylærgenetiske markører i naturforvaltningen. Af Andersen, L.W. et al. 70 s. (elektronisk)
Nr. 540: Cadmiumindholdet i kammusling *Chlamys islandica* ved Nuuk, Vestgrønland, 2004. Af pedersen, K.H., Jørgensen, B. & Asmund, G. 36 s. (elektronisk)
Nr. 541: Regulatory odour model development: Survey of modelling tools and datasets with focus on building effects. By Olesen, H.R. et al. 60 pp. (electronic)
Nr. 542: Jordrentetab ved arealekstensivering i landbruget. Principper og resultater. Af Schou, J.S. & Abildtrup, J. 64 s. (elektronisk)
Nr. 543: Valuation of groundwater protection versus water treatment in Denmark by Choice Experiments and Contingent Valuation. By Hasler, B. et al. 173 pp. (electronic)
Nr. 544: Air Quality Monitoring Programme. Annual Summary for 2004, Part 1 Measurements. By Kemp, K. et al. 64 pp. (electronic)
Nr. 546: Environmental monitoring at the Nalunaq Mine, South Greenland, 2004. By Glahder, C.M. & Asmund, G. 32 pp. (electronic)
Nr. 549: Kriterier for gunstig bevaringsstatus for EF-habitatdirektivets 8 marine naturtyper. Af Dahl, K. et al. 39 s. (elektronisk)
Nr. 550: Natur og Miljø 2005. Påvirkninger og tilstand. Af Bach, H. (red.) et al. 205 s., 200,00 kr.
Nr. 551: Marine områder 2004 – Tilstand og udvikling i miljø- og naturkvaliteten. NOVANA. Af Ærtebjerg, G. et al. (elektronisk)
Nr. 552: Landovervågningsoplande 2004. NOVANA. Af Grant, R. et al. (elektronisk)
Nr. 553: Søer 2004. NOVANA. Af Lauridsen, T.L. et al. (elektronisk)
Nr. 554: Vandløb 2004. NOVANA. Af Bøgestrand, J. (red.) (elektronisk)
Nr. 555: Atmosfærisk deposition 2004. NOVANA. Af Ellermann, T. et al. (elektronisk)
Nr. 557: Terrestriske naturtyper 2004. NOVANA. Af Nielsen, K.E. et al. (elektronisk)
Nr. 558: Vandmiljø og Natur 2004. Tilstand og udvikling – faglig sammenfatning. Af Andersen, J.M. et al. (elektronisk)
Nr. 560: Arter 2004. NOVANA. Af Søgaard, B. & Pihl, S. (elektronisk)

Four different groups of products covered by the pesticide regulation were included in the 2004 analytical chemical authority control:

1) Herbicides containing bentazone, dicamba, dichlorprop-P, mecoprop-P, MCPA, foramsulfuron, iodosulfuron-methyl-sodium, rimsulfuron and triasulfuron.
2) Fungicides containing hymexazol.
3) Insecticides and molluscicides containing imidacloprid and methiocarb.
4) Rodenticides containing coumatetralyl. All samples were examined for the content of the respec-tive active ingredients and for the content of OPEO and NPEO. All samples but two out of three contained coumatetralyl and one out of four contained dicamba 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. On three prod-ucts, the content of active ingredient was declared only in g/L, but not in % (w/w) as required.

National Environmental Research Institute
Ministry of the Environment

ISBN 87-7772-896-3
ISSN 1600-0048