CONTROL OF PESTICIDES 2009

Chemical Substances and Chemical Preparations

NERI Technical Report no. 791 2010

NATIONAL ENVIRONMENTAL RESEARCH INSTITUTE
AARHUS UNIVERSITY

[Blank page]

CONTROL OF PESTICIDES 2009

Chemical Substances and Chemical Preparations

NERI Technical Report no. 791 2010

Teddy Krongaard
Kitty K. Petersen
Christel Christoffersen

NATIONAL ENVIRONMENTAL RESEARCH INSTITUTE
AARHUS UNIVERSITY

Data sheet

Series title and no.:	NERI Technical Report No. 791
Title:	Control of Pesticides 2009
Subtitle:	Chemical Substances and Chemical Preparations
Authors:	Teddy Krongaard, Kitty K. Petersen and Christel Christoffersen
Department:	Department of Atmospheric Environment
Publisher:	National Environmental Research Institute © Aarhus University - Denmark
URL:	http://www.neri.dk
Year of publication:	October 2010
Referee:	Rossana Bossi
Financial support:	Danish Environmental Protection Agency
Please cite as:	Krongaard, T., Petersen, K.K. & Christoffersen, C. 2010: Control of Pesticides 2009. Chemical Substances and Chemical Preparations. National Environmental Research Institute, Aarhus University, Denmark. 21 pp. - NERI Technical Report No. 791. http://www.dmu.dk/Pub/FR791.pdf

Abstract: Three different groups of products covered by the pesticide regulation were included in the 2009 analytical chemical authority control: 1) Herbicides containing clopyralid, fluroxypyr and prosulfocarb. 2) Fungicides containing fenamidone, mandipropamid and metalaxyl-M. 3) Plant growth regulators containing daminozide and trinexapac-ethyl. All samples were examined for the content of active ingredients and for the content of OPEO and NPEO. The content of selected impurities was examined in two active ingredients. Two samples in this year's programme did not comply 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 or NPEO. The content of impurities in the active ingredient was too high in one sample. On two labels, the content of active ingredient was declared only in g/L, but not in % (w/w) as required and on three labels the declared content given g/L was covering the acid-form of the active ingredient, while the content declared in % was covering the ester-form.

Keywords:	Control, formulations, pesticides
Layout:	Majbritt Pedersen-Ulrich
Proof-reader:	Christel Ege-Johansen
ISBN:	978-87-7073-185-0
ISSN (electronic):	1600-0048
Number of pages:	21
Internet version:	The report is available in electronic format (pdf) at NERI's website http://www.dmu.dk/Pub/FR791.pdf

Contents

Summary 5

Resumé 6

1 Introduction 7

2 Control Campaigns in 2009 8

2.1 Herbicides 9
2.1.1 Introduction 9
2.1.2 Samples 10
2.1.3 Results and Discussion 10
2.2 Fungicides 13
2.2.1 Introduction 13
2.2.2 Samples 13
2.2.3 Results and Discussion 13
2.3 Plant growth regulators 15
2.3.1 Introduction 15
2.3.2 Samples 15
2.3.3 Results and Discussion 15
2.4 Additives 17
2.4.1 Introduction 17
2.4.2 Samples 17
2.4.3 Results and Discussion 17

Conclusions 18

References 19

Appendix I Pesticide samples collected from the Danish market for authority control in 2009 21

National Environmental Research Institute

NERI technical reports

Summary

The analytical chemical authority control of pesticide products on the Danish market in 2009 is described in this report. Samples of selected groups of pesticides have been collected from the market and analysed to verify whether the actual contents of the respective active ingredients in the products comply with the labelled content. The tolerance of deviation from the labelled content of active ingredient is set by the Danish Statutory Order on pesticides. In addition to the examination of the content of active ingredients, all collected samples were examined for the content of octylphenol ethoxylates (OPEO) and nonylphenol ethoxylates (NPEO). The content of selected impurities was examined in two active ingredients.

Three different groups of products covered by the pesticide regulation were included in the 2009 analytical chemical authority control:

1. Herbicides containing clopyralid, fluroxypyr and prosulfocarb.
2. Fungicides containing fenamidone, mandipropamid and metalaxyl-M.
3. Plant growth regulators containing daminozide and trinexapac-ethyl.

Satisfactory results were found for most of the 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. The sample containing metalaxyl-M and one out of nine samples containing fluroxypyr did not comply with the tolerance limit for content of active ingredient. The content of both active ingredients were too low compared with the declared contents.

None of the examined samples contained OPEO or NPEO. One out of the eight examined samples containing clopyralid and fluroxypyr as active ingredients had too high content of the examined impurities compared with the specified maximum level.

On two labels, the content of active ingredient was declared only in g/L, but not in % (w/w) as required by the Statutory Order. On three labels the declared content given in g/L was for the acid-form, while the content given in percentage was for the ester-form.

Resumé

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked, der blev udført i 2009 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 alle de indsamlede prøver kontrolleret for indhold af octylphenolethoxylater (OPEO) og nonylphenolethoxylater (NPEO) og to aktivstoffer er undersøgt for indhold af udvalgte urenheder.

Tre forskellige grupper af produkter er inkluderet i den analytisk-kemiske kontrol, der blev udført af myndighederne i 2009:

1. Herbicider indeholdende clopyralid, fluroxypyr og prosulfocarb
2. Fungicider indeholdende fenamidon, mandipropamid og metalaxyl-M.
3. Vækstregulatorer indeholdende daminozide og trinexapac-ethyl.

Der blev opnået tilfredsstillende resultater for de fleste undersøgte bekæmpelsesmidler. Indholdet af aktivstof i de fleste analyserede prøver af disse bekæmpelsesmidler var indenfor den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler. Prøven indeholdende metalaxyl-M og en ud af ni prøver indeholdende fluroxypyr var ikke indenfor tolerancen. Indholdet af aktivstof var for lavt i begge produkter.

Ingen af de undersøgte produkter indeholdt OPEO eller NPEO. Ét af de undersøgte aktivstoffer havde for højt indhold af de kontrollerede urenheder sammenlignet med det specificerede maksimale indhold

På to produkter var indholdet af aktivstof kun deklareret i g/l og ikke i % som det ellers er krævet i bekendtgørelsen. På tre etiketter var det deklarerede indhold angivet i g/L gældende for syre-formen, mens det angivne indhold i procent var gældende for ester-formen.

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 2009.

2 Control Campaigns in 2009

Control campaigns conducted in 2009 have covered impurities, auxiliary substances and active ingredients belonging to three different groups of pesticides: herbicides, fungicides 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, the content of selected impurities in two active ingredients is examined and most samples are examined for the content of octylphenol ethoxylates and nonylphenol ethoxylates.

Samples of the various pesticide formulations covered in the 2009 control campaigns have been collected by the Chemical Inspection Service at DEPA during the months May – June 2009 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 (homogenous formulations)	± 15%	(rel.)
Conc. ≤ 2.5 (heterogeneous formulations)	± 25%	(rel.)

2.1 Herbicides

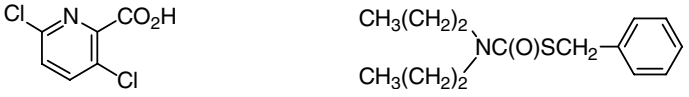
2.1.1 Introduction

There are 51 different active ingredients in herbicide formulations available on the Danish market (*Miljøstyrelsen, 2009*). Products containing clopyralid, fluroxypyr and prosulfocarb as active ingredients were selected for control in 2009. All products were examined for the content of active ingredient. The content of selected impurities was examined in samples containing clopyralid and fluroxypyr as active ingredients. All products were examined for the content of octylphenol ethoxylates and nonylphenol ethoxylates.

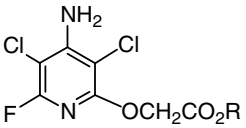
Clopyralid (Figure 1,a) is a chlorinated pyridinecarboxylic acid herbicide, which is used for control of annual and perennial broad-leaved weeds in cereals, grass seed, rape, beet, beetroot, cabbage crop, cabbage seed, potatoes, maize, caraway and strawberry, and for control of broad-leaved weeds in meadows, lawns, and other grass covered areas. Herbicide formulations containing clopyralid were selected for authority control latest in 2000.

Fluroxypyr (Figure 1,b) belongs to the group of pyridinecarboxylic acid herbicides. It is used to control a range of broad-leaved weeds in cereals, grass areas, grass seed and maize used for feed in Denmark. It is a systemic post-emergence herbicide, which is absorbed through the leaves. Herbicide formulations containing fluroxypyr were selected for authority control latest in 2003.

Prosulfocarb (Figure 1,c) belongs to the group of thiocarbamate herbicides. It is used to control a wide range of grass and broad-leaved weeds in cereals, grass areas and maize used for feed in Denmark. It is a selective systemic pre- and early post-emergence herbicide, which is absorbed through the leaves and roots. It inhibits growth of the meristematic region. Herbicide formulations containing prosulfocarb have not previously been selected for authority control.



(a) (c)



2-butoxy-1-methylethyl R = $CH_3(CH_2)_3OCH_2CH(CH_3)$-

meptyl (1-methylheptyl) R = $CH_3(CH_2)_5CH(CH_3)$-

(b)

Figure 1

The chemical structure of the herbicide active ingredients: clopyralid (a), fluroxypyr (b) and prosulfocarb (c).

2.1.2 Samples

At the time of sampling for the control campaign, fifteen products containing clopyralid, seventeen products containing fluroxypyr and five products containing prosulfocarb were approved for use in Denmark. Nine products containing clopyralid, nine products containing fluroxypyr and three products containing prosulfocarb were available on the market during the period of the sample collection. One sample of each product was collected. The list of samples is summarised in Appendix I.

The samples containing clopyralid were analysed for active ingredient in October 2009 and for impurities in November 2009. The samples containing fluroxypyr were analysed for active ingredient in November 2009 and for impurities in February 2010, while samples containing prosulfocarb were analysed in November-December 2009.

2.1.3 Results and Discussion

The contents of clopyralid were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV (*Krongaard, 2009a*). As no CIPAC-method on clopyralid exists, the method was developed on the basis of information from the manufacturer. The contents of selected impurities were determined using reversed phase high performance liquid chromatography and UV-detector. The methods were received from a manufacturer.

The contents of fluroxypyr were determined using gas chromatography and flame ionization detector, GC-FID *(Krongaard, 2009b)*. As no CIPAC-method on fluroxypyr exists, the method was developed on the basis of information from the manufacturer. The contents of selected impurities were determined using gas chromatography and MS-detector. The methods were received from a manufacturer.

The contents of prosulfocarb were determined using gas chromatography and flame ionization detector, GC-FID *(Krongaard, 2009c)*. As no CIPAC-method on prosulfocarb exists, the method was developed by NERI.

Table 2.2 Content of active ingredient in samples of herbicides.

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1]	Tolerance[2]	
Clopyralid	1.82 %	20 g/L	1.81 ± 0.01 %	1.55 – 2.09 %	ATMI 2009-6752
Clopyralid	9.56 %	100 g/L	9.35 ± 0.06 %	8.60 – 10.52 %	ATMI 2009-6753
Clopyralid	1.82 %	20 g/L	1.81 ± 0.01%	1.55 – 2.09 %	ATMI 2009-6755
Clopyralid	9.5 %	100 g/L	9.12 ± 0.06 %	8.55 – 10.45 %	ATMI 2009-6875
Clopyralid	2.87 %	30 g/L	2.66 ± 0.01 %	2.58 – 3.16 %	ATMI 2009-6911
Clopyralid	1.82 %	20 g/L	1.90 ± 0.01 %	1.55 – 2.09 %	ATMI 2009-6946
Clopyralid	1.82 %	20 g/L	1.83 ± 0.01 %	1.55 – 2.09 %	ATMI 2009-6956
Clopyralid	9.56 %	100 g/L	9.27 ± 0.06 %	8.60 – 10.52 %	ATMI 2009-6957
Clopyralid	9.5 %	100 g/L	9.33 ± 0.06 %	8.55 – 10.45 %	ATMI 2009-7432
Fluroxypyr	-[3]	180 g/L	172 ± 0.4 g/L	169.2 – 190.8 g/L[4]	ATMI 2009-6750
Fluroxypyr	25.9 %[5]				
	18.0 %[6]	180 g/L	18.8 ± 0.1 %	16.9 – 19.1 %	ATMI 2009-6751
Fluroxypyr	3.63 %	40 g/L	3.72 ± 0.01 %	3.27 – 4.00 %	ATMI 2009-6752
Fluroxypyr	14.5 %[5]				
	10.1 %[6]	100 g/L	10.2 ± 0.1 %	9.49 – 10.71 %	ATMI 2009-6754
Fluroxypyr	3.63 %	40 g/L	3.73 ± 0.01 %	3.27 – 4.00 %	ATMI 2009-6755
Fluroxypyr	18 %	180 g/L	18.2 ± 0.1 %	16.9 – 19.1 %	ATMI 2009-6873
Fluroxypyr	13.77 %[5]				
	9.56 %[6]	100 g/L	7.37 ± 0.2 %	8.60 – 10.52 %	ATMI 2009-6911*[]
Fluroxypyr	3.63 %	40 g/L	3.73 ± 0.01 %	3.27 – 4.00 %	ATMI 2009-6946
Fluroxypyr	3.63 %	40 g/L	3.72 ± 0.01 %	3.27 – 4.00 %	ATMI 2009-6956
Prosulfocarb	78.4 %	800 g/L	78.3 ± 0.9 %	75.9 – 80.9 %	ATMI 2009-6763
Prosulfocarb	-[3]	800 g/L	802 ± 9 g/L	780 – 820 g/L[4]	ATMI 2009-6764
Prosulfocarb	78.4 %	800 g/L	79.5 ± 0.9 %	75.9 – 80.9 %	ATMI 2009-6947

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) Declared content of fluroxypyr-1-meptyl ester.
6) Content of fluroxypyr calculated on the basis of the declared content of fluroxypyr-1-meptyl ester.
*) Found content is outside the accepted tolerance.

Table 2.2 shows agreement between declared and determined content for all twelve samples containing clopyralid and prosulfocarb as active ingredients. The content of active ingredient was too low in one out of nine products containing fluroxypyr. The batch number reveals that the product was produced in 2000. The content of active ingredient declared in g/L and in percentage was not in accordance on three labels. The content given in percentage was for fluroxypyr-1-meptyl ester, while the content given in g/L was for fluroxypyr. On two products, the content of active ingredient was declared only in g/L, but not in % (w/w) as required according to the Statutory Order *(Miljøministeriet, 2003)*.

Table 2.3 Content of impurities in active ingredient.

Active ingredient	Content			NERI sample no.
	Impurity	Specified max. concentration	Analysis[1)]	
Clopyralid	Imp. A	0.4%	< 0.1 %	ATMI 2009-6911
	Imp. B	4.2 %	1.5 %	
Clopyralid	Imp. A	0.4%	< 0.1 %	ATMI 2009-6753
	Imp. B	4.2 %	2.2 %	
Clopyralid	Imp. A	None (<0.1 %)	0.2 %	ATMI 2009-7432*)
	Imp. B	None (<0.1 %)	0.2 %	
Fluroxypyr	Imp. A 27	None (<0.1 %)	< 0.1 %	ATMI 2009-6911
	Imp. B 28	None (<0.1 %)	< 0.1 %	
	Naphthalene		low	
Fluroxypyr	Imp. A	None (<0.1 %)	< 0.1 %	ATMI 2009-6755
	Imp. B	None (<0.1 %)	< 0.1 %	
	Naphthalene		low	
Fluroxypyr	Imp. A	None (<0.1 %)	< 0.1 %	ATMI 2009-6752
	Imp. B	None (<0.1 %)	< 0.1 %	
	Naphthalene		low	
Fluroxypyr	Imp. A	None (<0.1 %)	< 0.1 %	ATMI 2009-6956
	Imp. B	None (<0.1 %)	< 0.1 %	
	Naphthalene		low	
Fluroxypyr	Imp. A	None (<0.1 %)	< 0.1 %	ATMI 2009-6754
	Imp. B	None (<0.1 %)	< 0.1 %	
	Naphthalene		low	

*) Found content is above the specified maximum concentration.

Table 2.3 shows agreement in all samples except one between specified and determined content of selected impurities in examined samples containing clopyralid or fluroxypyr as active ingredient. The content of the two examined impurities in the active ingredient was too high in one out of the eight examined samples. Naphthalene depleted solvents were used in all formulations as required.

2.2 Fungicides

2.2.1 Introduction

37 active ingredients in fungicide formulations are approved in Denmark (*Miljøstyrelsen, 2009*). Products containing fenamidone, mandipropamid and metalaxyl-M as active ingredients were selected for control in 2009. Only metalaxyl-M products approved for use in potatoes were selected. All products were examined for the content of active ingredient as well as for the content of octylphenol ethoxylates and nonylphenol ethoxylates.

Fenamidone (Figure 2a) is an imidazolinone fungicide used in Denmark only for the treatment of fungal diseases in potatoes. Fenamidone is a systemic fungicide, which inhibits the mitochondrial respiration. It is a foliar protective and curative fungicide. Fungicide formulations containing fenamidone were introduced to the Danish market in 2007 and have not previously been selected for authority control.

Metalaxyl-M (Figure 2b) belongs to the group of phenylamide fungicides. It is used only for the treatment of fungal diseases in potatoes and for industrial seed treatment in Denmark. Metalaxyl-M inhibits protein synthesis in fungi by interference with the synthesis of ribosomal RNA. It is a systemic fungicide with protective and curative action. Metalaxyl-M was included in the Danish register of approved pesticides in 2002 and has not previously been selected for authority control.

Mandipropamid (Figure 2c) is a mandelamide fungicide used in Denmark only for the treatment of fungal diseases in potatoes, cucumber and salad. Mandipropamid is a systemic fungicide. It is a preventive foliar fungicide with some curative action. Fungicide formulations containing mandipropamid were introduced to the Danish market in 2008 and have not previously been selected for authority control.

2.2.2 Samples

At the time of sampling for the control campaign, one product containing metalaxyl-M, two products containing fenamidone and two products containing mandipropamid were approved for use in Denmark. The metalaxyl-M and the mandipropamid containing products were available on the market during the period of the sample collection, while one out of two products containing fenamidone was available. One sample of each product was collected. The list of samples is summarised in Appendix I.

The sample containing metalaxyl-M was analysed in October 2009, the sample containing fenamidone was analysed in January 2010 and mandipropamid containing products were analysed in February 2010.

2.2.3 Results and Discussion

The content of fenamidone was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2010a).* As no CIPAC-method on fenamidone exists the method is developed on the basis of information from the manufacturer.

The content of metalaxyl-M was determined using gas chromatography and flame ionization detector, GC-FID *(Krongaard, 2009d)*. The method was not able to separate metalaxyl-M and metalaxyl-S. As no CIPAC-method on metalaxyl-M exists the method is developed on the basis of information from the manufacturer.

The content of mandipropamid was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2010b)*. As no CIPAC-method on mandipropamid exists the method is developed on the basis of information from the manufacturer.

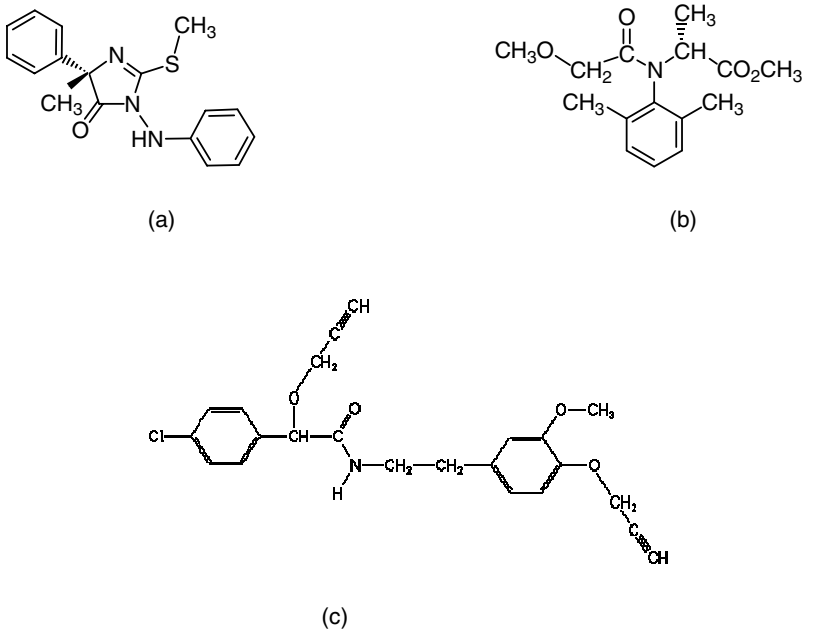


Figure 2
The chemical structure of the fungicide active ingredients: fenamidone (a), metalaxyl-M (b) and mandipropamid (c).

Table 2.4 The content of active ingredient in samples of fungicides.

Active ingredient	Content				NERI sample no.
	Label claim		Analysis[1)]	Tolerance[2)]	
Fenamidone	6.7 %	75 g/L	6.52 ± 0.04%	6.03 – 7.37 %	ATMI 2009-6762
Metalaxyl-M	4.0 %	38.8 g/kg	2.9 ± 0.1%	3.6 – 4.4 %	ATMI 2009-6761*)
Mandipropamid	23 %	250 g/L	22.3 ± 0.2%	21.6 – 24.4 %	ATMI 2009-6758
Mandipropamid	23 %	250 g/L	22.7 ± 0.2%	21.6 – 24.4 %	ATMI 2009-6759

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

Table 2.4 shows agreement between declared and determined content for the sample containing fenamidone and mandipropamid as active ingredients, while the content of active ingredient was too low in the product containing metalaxyl-M as active ingredient. The manufacturer has been informed about the low content.

2.3 Plant growth regulators

2.3.1 Introduction

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

Daminozide (Figure 3a) is absorbed by the leaves and translocated throughout the plant. It interferes with the gibberellic acid biosynthesis producing more compact plants. It is used in Denmark only for growth regulation of ornamentals in green houses. Plant growth regulators containing daminozide were selected for authority control latest in 2007.

Trinexapac-ethyl (Figure 3b) is a plant growth regulator, which is used only in cereals in Denmark. Trinexapac-ethyl reduces the stem growth by inhibition of internode elongation to prevent lodging in the cereals and to reduce the amount of straw. Trinexapac-ethyl was introduced on the Danish market in 1998. Formulations containing trinexapac-ethyl were selected for authority control latest in 1999.

(a) (b)

Figure 3 The chemical structure of the plant growth regulators daminozide (a) and trinexapac-ethyl (b).

2.3.2 Samples

At the time of sampling for the control campaign, two products containing daminozide and three products containing trinexapac-ethyl were approved for use in Denmark. One product containing daminozide and two products containing trinexapac-ethyl 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 containing trinexapac-ethyl were analysed in November 2009, and the daminozide containing product was analysed in February 2010.

2.3.3 Results and Discussion

The content of daminozide was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV *(Krongaard, 2010c).* As no CIPAC-method on daminozide exists the method is developed on the basis of information from the manufacturer.

The content of trinexapac-ethyl was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-

UV *(Krongaard, 2009e).* As no CIPAC-method on trinexapac-ethyl exists the method is developed on the basis of information from the manufacturer.

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

Active ingredient	Label claim		Content Analysis[1)]	Tolerance[2)]	NERI sample no.
Daminozide	85 %	-	85.2 ± 0.4 %	82.5 – 87.5 %	ATMI 2009-6760
Trinexapac-ethyl	25 %	250 g/L	25.3 ± 0.1 %	23.5 – 26.5	ATMI 2009-6756
Trinexapac-ethyl	25.2 %	250 g/L	25.3 ± 0.1 %	23.9 – 26.5	ATMI 2009-6757

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

Table 2.5 shows agreement between declared and determined content for all three samples containing daminozide and trinexapac-ethyl as active ingredients.

2.4 Additives

2.4.1 Introduction

Among the many additives used in pesticide formulations, nonylphenol ethoxylates (NPEO) and octylphenol ethoxylates (OPEO) were selected for control in 2009. 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.

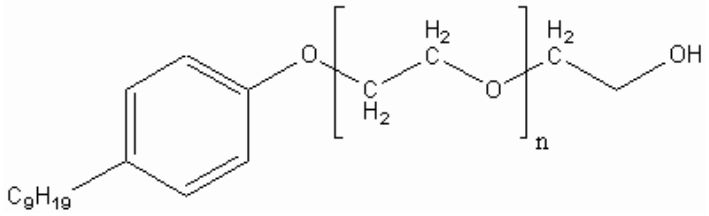


Figure 4 The chemical structure of the additive nonylphenol ethoxylate. The structure of octylphenol ethoxylate is similar, C_9H_{19} is replaced with C_8H_{17}.

2.4.2 Samples

Beside the examination of the content of active ingredient all pesticide formulations sampled in 2009 are examined for content of NPEO and OPEO. The sample list is shown in Appendix I. The samples were analysed in April 2010.

2.4.3 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, 2006).* 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
23	0/0	23

Table 2.6 shows that none of the 23 examined samples contain OPEO or NPEO.

Conclusions

Three different groups of products covered by the pesticide regulation were included in the 2009 analytical chemical authority control:

1. Herbicides containing clopyralid, fluroxypyr and prosulfocarb.
2. Fungicides containing fenamidone, mandipropamid and metalaxyl-M.
3. Plant growth regulators containing daminozide and trinexapac-ethyl.

All products were examined for the content of the active ingredients. In addition to the examination of the content of active ingredients, all the collected samples were examined for content of octylphenol ethoxylates and nonylphenol ethoxylates. The content of selected impurities was examined in samples containing clopyralid and fluroxypyr as active ingredients.

Satisfactory results were found for herbicides containing clopyralid and prosulfocarb, for fungicides containing fenamidone and mandipropamid and for plant grow regulators containing daminozide and trinexapac-ethyl. 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.

The sample containing metalaxyl-M and one out of nine samples containing fluroxypyr did not comply with the tolerance limit for content of active ingredient. The content of both active ingredients was too low compared with the declared contents.

None of the examined samples contained OPEO or NPEO.

One out of the eight examined samples containing clopyralid and fluroxypyr as active ingredients had too high content of the examined impurities compared with the specified maximum level.

On two labels, the content of active ingredient was declared only in g/L, but not in % (w/w) as required by the Statutory Order. On three labels the declared content given in g/L was for the acid-form, while the content given in percentage was for the ester-form.

References

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

Krongaard, T. (2009a): Analysemetode. Bestemmelse af clopyralid som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of clopyralid as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (2009b): Analysemetode. Bestemmelse af fluroxypyr aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of fluroxypyr as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (2009c): Analysemetode. Bestemmelse af prosulfocarb som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of prosulfocarb as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2009d): Analysemetode. Bestemmelse af metalaxyl-M som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of metalaxyl-M as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2009e): Analysemetode. Bestemmelse af trinexapac-ethyl som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of trinexapac-ethyl as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (2010a): Analysemetode. Bestemmelse af fenamidon som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of fenamidone as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (2010b): Analysemetode. Bestemmelse af mandipropamid som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of mandipropamid as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2010c): Analysemetode. Bestemmelse af daminozide som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of daminozide as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

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

Miljøstyrelsen (2009): Oversigt over godkendte bekæmpelsesmidler 2009. http://www2.mst.dk/databaser/Bekaemp/Oversigt_2009.doc (Danish EPA, 2009: List of Approved Pesticides 2009, Danish Environmental Protection Agency). (In Danish).

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

Appendix I

Pesticide samples collected from the Danish market for authority control in 2009

Table 1 Herbicides

Active ingredient	Product	Formulation type	Company	NERI sample no.
Clopyralid	Bofik S plænerens	EC	Tanaco	ATMI 2009-6752
Clopyralid	Matrigon	SL	DowAgroSciences	ATMI 2009-6753
Clopyralid	Ariane FG S	EC	DowAgroSciences	ATMI 2009-6755
Clopyralid	Cliophar	SL	DLA Agro	ATMI 2009-6875
Clopyralid	Ariane Super	EC	DowAgroSciences	ATMI 2009-6911
Clopyralid	Cab-Dan Ren plæne	EC	Cab-Dan	ATMI 2009-6946
Clopyralid	Den rigtige plænerens	EC	Tanaco	ATMI 2009-6956
Clopyralid	Glopyr 100 SL	SL	Globachem	ATMI 2009-6957
Clopyralid	Inter-Clopyralid 100	EC	InterTrade	ATMI 2009-7432
Fluroxypyr	Flurostar 180	EC	Globachem	ATMI 2009-6750
Fluroxypyr	Lodin	EC	SweDane	ATMI 2009-6751
Fluroxypyr	Bofik S plænerens	EC	Tanaco	ATMI 2009-6752
Fluroxypyr	Starane XL	SE	DowAgroSciences	ATMI 2009-6754
Fluroxypyr	Ariane FG S	EC	DowAgroSciences	ATMI 2009-6755
Fluroxypyr	Tomahawk 180 EC	EC	Makhteshim	ATMI 2009-6873
Fluroxypyr	Ariane Super	EC	DowAgroSciences	ATMI 2009-6911
Fluroxypyr	Cab-Dan Ren plæne	EC	Cab-Dan	ATMI 2009-6946
Fluroxypyr	Den rigtige plænerens	EC	Tanaco	ATMI 2009-6956
Prosulfocarb	Boxer EC	EC	Syngenta	ATMI 2009-6763
Prosulfocarb	LFS Prosulfocarb	EC	LFS Kemi	ATMI 2009-6764
Prosulfocarb	Roxy EC	EC	Globachem	ATMI 2009-6947

EC: Emulsifiable concentrate; SE: suspo-emulsion; SL:Soluble concentrate

Table 2 Fungicides

Active ingredient	Product	Formulation type	Company	NERI sample no.
Fenamidone	Tyfon	SC	Bayer	ATMI 2009-6762
Metalaxyl-M	LFS Metalaxyl-M + Mancoseb	WG	LFS Kemi	ATMI 2009-6761
Mandipropamid	Revus	SC	Syngenta	ATMI 2009-6758
Mandipropamid	LFS mandipropamid	SC	LFS Kemi	ATMI 2009-6759

SC: Suspension concentrate; WG: water dispersible granules.

Table 3 Plant Growth Regulators

Active ingredient	Product	Formulation type	Company	NERI sample no.
Daminozide	Alar SP	SP	Cillus	ATMI 2009-6760
Trinexapac-ethyl	LFS Trinexapac-ethyl	EC	LFS Kemi	ATMI 2009-6756
Trinexapac-ethyl	Moddus M	EC	Syngenta	ATMI 2009-6757

SP: water soluble powder; EC: Emulsifiable concentrate.

NERI **National Environmental Research Institute**
DMU Danmarks Miljøundersøgelser

National Environmental Research Institute, NERI, is a part of Aarhus University.

NERI undertakes research, monitoring and consultancy within environment and nature.

At NERI's website www.neri.dk you'll find information regarding ongoing research and development projects.

Furthermore the website contains a database of publications including scientific articles, reports, conference contributions etc. produced by NERI staff members.

Further information: www.neri.dk

National Environmental Research Institute
Frederiksborgvej 399
PO Box 358
DK-4000 Roskilde
Denmark
Tel: +45 4630 1200
Fax: +45 4630 1114

Management
Department of Arctic Environment
Department of Atmospheric Environment
Department of Environmental Chemistry and Microbiology
Department of Marine Ecology
Department of Policy Analysis

National Environmental Research Institute
Vejlsøvej 25
PO Box 314
DK-8600 Silkeborg
Denmark
Tel: +45 8920 1400
Fax: +45 8920 1414

Department of Freshwater Ecology
Department of Terrestrial Ecology

National Environmental Research Institute
Grenåvej 14, Kalø
DK-8410 Rønde
Denmark
Tel: +45 8920 1700
Fax: +45 8920 1514

Department of Wildlife Ecology and Biodiversity

NERI Technical Reports

NERI's website www.neri.dk contains a list of all published technical reports along with other NERI publications. All recent reports can be downloaded in electronic format (pdf) without charge. Some of the Danish reports include an English summary.

Nr./No. 2010

789 Forekomst og regulering af fritlevende mink i Danmark i jagtsæsonen 2007/08.
Af Asferg, T. 28 s.

788 Forekomst af antikoagulante rodenticider i danske rovfugle, ugler og små rovpattedyr.
En basisundersøgelse.
Af Christensen, T.K., Elmeros, M. & Lassen, P. 84 s.

787 Effekter af øgede kvælstoftilførsler på miljøet i danske fjorde.
Af Markager, S., Carstensen, J., Krause-Jensen, D., Windolf, J. & Timmermann, K. 54 s.

786 Emissions from decentralised CHP plants 2007 – Energinet.dk Environmental project no. 07/1882.
Project report 5 – Emission factors and emission inventory for decentralised CHP production.
By Nielsen, M., Nielsen, O.-K. & Thomsen, M. 113 pp.

785 Guidelines to environmental impact assessment of seismic activities in Greenland waters.
2nd edition.
By Boertmann, D., Tougaard, J., Johansen, K. & Mosbech, A. 42 pp.

784 Denmark's National Inventory Report 2010. Emission Inventories 1990-2008 – Submitted under the United Nations Framework Convention on Climate Change and the Kyoto Protocol.
By Nielsen, O.-K., Lyck, E., Mikkelsen, M.H., Hoffmann, L., Gyldenkærne, S., Winther, M., Nielsen, M., Fauser, P., Thomsen, M., Plejdrup, M.S., Albrektsen, R., Hjelgaard, K., Johannsen, V.K., Vesterdal, L., Rasmussen, E., Arfaoui, K. & Baunbæk, L. 1178 pp.

783 Miljøøkonomiske beregningspriser for emissioner.
Af Andersen, M.S. 33 s.

782 Screening for kloralkaner i sediment. Relevans for NOVANA.
Af Larsen, M.M., Hjorth, M. & Sortkjær, O. 22 s.

781 Emissionskortlægning for decentral kraftvarme 2007 – Energinet.dk miljøprojekt nr. 07/1882.
Delrapport 5 Emissionsfaktorer og emissionsopgørelse for decentral kraftvarme, 2006.
Af Nielsen, M., Nielsen, O.-K. & Thomsen, M. 105 s.

780 Heavy Metal Emissions for Danish Road Transport.
By Winther, M. & Slentø, E. 99 pp.

779 Brændefyrings bidrag til luftforurening. Nogle resultater fra projektet WOODUSE.
Af Olesen, H.R., Wåhlin, P. & Illerup, J.B. 71 s.

778 Ynglefugle i Tøndermarsken og Margrethe Kog 1975-2009. En analyse af udviklingen i fuglenes antal og fordeling med anbefalinger til forvaltningstiltag.
Af Clausen, P. & Kahlert, J. (red.) 206 s.

777 Air pollution from residential wood combustion in a Danish village.
Measuring campaign and analysis of results.
By Wåhlin, P., Olesen, H.R., Bossi, R. & Stubkjær, J. 49 pp.

776 Annual Danish Informative Inventory Report to UNECE.
Emission inventories from the base year of the protocols to year 2008.
By Nielsen, O-K., Winther, M., Mikkelsen, M.H., Hoffmann, L., Nielsen, M., Gyldenkærne, S., Fauser, P., Plejdrup, M.S., Albrektsen, R. & Hjelgaard, K. 565 pp.

775 Environmental monitoring at the former lead-zinc mine in Maarmorilik, Northwest Greenland, in 2009.
By Johansen, P., Asmund, G., Rigét, F., Johansen, K. & Schledermann, H. 32 pp.

774 Kvælstofbelastningen ved udvalgte terrestriske habitatområder i Sønderborg kommune.
Af Frohn, L. M., Skjøth, C. A., Becker, T., Geels, C. & Hertel, O. 30 s.

773 Geese, seabirds and mammals in North and Northeast Greenland.
Aerial surveys in summer 2009.
By Boertmann, D. & Nielsen, R.D. 66 pp.

772 Environmental monitoring at the Nalunaq Gold Mine, South Greenland, 2009.
By Glahder, C.M., Asmund, G. & Riget, F. 32 pp.

771 OMLHighway within the framework of SELMAGIS. Final Report.
By Jensen, S.S., Becker, T., Ketzel, M., Løfstrøm, P., Olesen, H.R. & Lorentz, H. 26 pp.

770 Road pricing, luftforurening og eksternalitetsomkostninger.
Af Jensen, S.S., Ketzel, M. & Andersen, M.S. 48 s.

CONTROL OF PESTICIDES 2009

Chemical Substances and Chemical Preparations

Three different groups of products covered by the pesticide regulation were included in the 2009 analytical chemical authority control: 1) Herbicides containing clopyralid, fluroxypyr and prosul-focarb. 2) Fungicides containing fenamidone, mandipropamid and metalaxyl-M. 3) Plant growth regulators containing daminozide and trinexapac-ethyl. All samples were examined for the content of active ingredients and for the content of OPEO and NPEO. The content of selected impurities was examined in two active ingredients. Two samples in this year's programme did not comply 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 or NPEO. The content of impurities in the active ingredient was too high in one sample. On two labels, the content of active ingredient was declared only in g/L, but not in % (w/w) as required and on three labels the declared content given g/L was covering the acid-form of the active ingredient, while the content declared in % was covering the ester-form.

ISBN: 978-87-7073-185-0
ISSN: 1600-0048