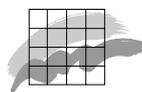


Ministry of Environment and Energy
National Environmental Research Institute

Control of Pesticides 1999

Chemical Substances and Chemical Preparations

NERI Technical Report No. 328



Miljø- og Energiministeriet
Danmarks Miljøundersøgelser

Control of Pesticides 1999

Chemical Substances and Chemical Preparations

NERI Technical Report No. 328

October 2000

Teddy Krongaard

Kitty K. Petersen

Christel Christoffersen

Department of Environmental Chemistry

Data sheet

Title: Control of Pesticides 1999
Subtitle: Chemical Substances and Chemical Preparations

Authors: Teddy Krongaard, Kitty K. Petersen and Christel Christoffersen
Department: Department of Environmental Chemistry

Serial title and no.: NERI Technical Report No. 328

Publisher: Ministry of Environment and Energy
National Environmental Research Institute ©

URL: <http://www.dmu.dk>

Date of publication: October 2000

Referee: Lars Carlsen
Layout: Majbritt Pedersen-Ulrich

Please quote: Krongaard, T., Petersen, K.K. & Christoffersen, C. (2000): Control of Pesticides 1999. Chemical Substances and Chemical Preparations. National Environmental Research Institute, Denmark. 30pp. - NERI Technical Report No. 328

Reproduction is permitted, provided the source is explicitly acknowledged.

Abstract: Four different groups of products covered by the pesticide regulation have been included in the 1999 analytical chemical authority control: 1) herbicides containing metamitron, metribuzin, propyzamide, fluazifop-p-butyl and fenoxaprop-p-ethyl, 2) plant growth regulators containing trinexapac-ethyl and flurprimidol, 3) fungicides containing imazalil, fenpropimorph, fenpiclonil and azoxystrobin, 4) insecticides containing pirimicarb as active ingredient. Furthermore a sample of technical grade chlorothalonil was analysed for impurities to see if they complied with the specifications. Satisfactory results were found among all the examined products. Thus, all the analysed samples of these pesticides complied with the accepted tolerances with respect to content of active ingredients set by the Danish regulation of pesticides. The content of different impurities in a technical material of chlorothalonil complies with the specifications too.

Keywords: Control, formulations, pesticides.

ISBN: 87-7772-565-4
ISSN (print): 0905-815X
ISSN (electronic): 1600-0048

Number of pages: 30
Circulation: 100
Price: DKK 50,- (incl. 25% VAT, excl. freight)

Internet: The report is also available as a PDF-file from NERI's homepage.

For sale at: National Environmental Research Institute
P.O. Boks 358
Frederiksborgvej 399
DK-4000 Roskilde
Denmark
Tlf.: +45 46 30 12 00
Fax: +45 46 30 11 14

Miljøbutikken
Information and Books
Læderstræde 1
DK-1201 Copenhagen K
Denmark
Tel.: +45 33 95 40 00
Fax: +45 33 92 76 90

Contents

Summary 5

Resumé 7

1 Introduction 9

2 Control Campaigns in 1999 11

2.1 Herbicides 12

2.1.1 Introduction 12

2.1.2 Samples 12

2.1.3 Results and Discussion 13

2.2 Plant growth regulators 15

2.2.1 Introduction 15

2.2.2 Samples 15

2.2.3 Results and Discussion 16

2.3 Fungicides 17

2.3.1 Introduction 17

2.3.2 Samples 18

2.3.3 Results and Discussion 19

2.4 Insecticides 21

2.4.1 Introduction 21

2.4.2 Samples 21

2.4.3 Results and Discussion 21

3 Conclusions 23

4 References 25

Appendix I 27

National Environmental Research Institute 29

NERI Technical Reports 30

Summary

The analytical chemical authority control on pesticide products on the Danish market performed in 1999 is reported. Samples of selected groups of pesticides have been collected from the market and analysed to verify whether the actual content of active ingredient agreed with the label-claimed content. Furthermore a technical grade active ingredient was analysed for impurities to see if they complied with the specifications. The tolerance of deviation of active ingredient content from label-claimed content is set by the Danish pesticide regulation.

Four different groups of products covered by the pesticide regulation have been included in the 1999 analytical chemical authority control: 1) herbicides containing met amitron, metribuzin, propyzamide, fluazifop-p-butyl and fenoxaprop-p-ethyl, 2) plant growth regulators containing trinexapac-ethyl and flurprimidol, 3) fungicides containing imazalil, fenpropimorph, fenpiclonil and azoxystrobin, 4) insecticides containing pirimicarb as active ingredient. Furthermore a sample of technical grade chlorothalonil was analysed for impurities to see if they complied with the specifications.

Satisfactory results were found among all the examined products. Thus, all the analysed samples of these pesticides complied with the accepted tolerances with respect to content of active ingredients set by the Danish regulation of pesticides. The content of different impurities in a technical material of chlorothalonil complies with the specifications too.

Resumé

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked udført i 1999 af de danske myndigheder er her afrapporteret. Prøver af udvalgte grupper af bekæmpelsesmidler er blevet samlet fra markedet og analyseret for at verificere om det aktuelle indhold af aktivstof er i overensstemmelse med det deklarerede indhold. Derudover er et teknisk aktivstof analyseret for urenheder for at se om det overholdt specifikationen. Grænsen for en accepteret afvigelse af indholdet af aktivstof fra det deklarerede indhold er fastsat i bekendtgørelsen om bekæmpelsesmidler.

Fire forskellige grupper af produkter er inkluderet i den analytisk-kemiske kontrol udført af myndighederne i 1999: 1) herbicider indeholdende metamidron, metribuzin, propyzamid, fluazifop-p-butyl og fenoxaprop-p-ethyl, 2) vækstregulerende midler indeholdende trinexapac-ethyl og flurprimidol, 3) fungicider indeholdende imazalil, fenpropimorph, fenpiclonil og azoxystrobin, 4) insekticider indeholdende pirimicarb.

Der blev opnået tilfredsstillende resultater blandt alle de undersøgte produkter. Indholdet af aktivstof i alle de analyserede prøver af disse bekæmpelsesmidler var indenfor den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler, også indholdet af forskellige urenheder i teknisk materiale af chlorothalonil var indenfor specifikationerne.

1 Introduction

In Denmark the Danish Environmental Protection Agency (DEPA) is responsible for evaluation and authorisation of all pesticides before introduction on the Danish market. Legal regulations for pesticides are given in a Statutory Order from the Ministry of the Environment and Energy (*Miljø- og Energiministeriet, 1998*), which also states that DEPA is responsible for control in relation to pesticides.

In practice authority control activities of pesticides on the market are organised in a way that 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 control whether the products comply with regulation as well as with the specification of contents stated in connection with application for approval of the pesticide product.

Analytical chemical control can involve verification of content of active ingredient as well as content of auxiliary matters or levels of impurities.

Laboratory control work covers two types of projects: 1) Ordinary control in the form 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 needed 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 control i.e., campaigns, is covered by this report, which describes the laboratory control performed in 1999.

2 Control Campaigns in 1999

Control campaigns conducted in 1999 have covered pesticides belonging to four different groups of pesticides: Herbicides, plant growth regulators, fungicides and insecticides. The analytical chemical control has aimed at examining the content of active ingredient compared to that stated on the label. In one of the campaigns a control of the level of an impurity in the pesticide active ingredient has also been included, and in two campaigns the enantiomer ratio of the active ingredients has been included too. Regulation in Denmark (*Miljø- og Energiministeriet, 1998*) specifies general tolerance of deviations from declared content. These are given in Table 2.1.

Samples of the various pesticides covered in the 1999 control campaigns have mainly been collected by the Chemical Inspection Service at DEPA primarily during the months February - November 1999 either at whole sale dealers/-importers or at retailers, only few samples have been collected by NERI.

Samples have been stored at NERI in the unopened containers until the time of analysis. The samples have been stored at ambient temperature (app. 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	
≥ 50	$\pm 2.5\%$	(abs.)
$25 < X \leq 50$	$\pm 5\%$	(rel.)
$10 < X \leq 25$	$\pm 6\%$	(rel.)
$2.5 < X \leq 10$	$\pm 10\%$	(rel.)
≤ 2.5	$\pm 15\%$	(rel.)

2.1 Herbicides

2.1.1 Introduction

Among the nearly 50 different herbicides available on the Danish market herbicides containing metamitron, metribuzin, propyzamide, fluazifop-p-butyl or fenoxaprop-p-ethyl as active ingredients were selected for control in 1999. All products were examined for content of active ingredient and the two latter also for the enantiomer content.

Metamitron (Figure 1,a) is a triazinone herbicide, which in Denmark is used only for control of grass and broad-leaved weeds in beets and root-beets. Formulations containing metamitron have not previously been selected for authority control.

Metribuzin (Figure 1,b) is a triazinone herbicide too, which is used only for control of grass and broad-leaved weeds in potatoes and alfalfa. Herbicide formulations containing metribuzin have not previously been selected for authority control.

Propyzamide (Figure 1,c) is an amide herbicide, which is used for control of seed germinated grass, volunteer cereals, chickweed and goosegrass in winter rape, alfalfa, red clover, scorzonera, bush fruit, ornamental trees and in forestry. Herbicide formulations containing propyzamide have not previously been selected for authority control.

Fluazifop-p-butyl (Figure 1,d) is an 2-(4-aryloxyphenoxy)propionic acid compound, which is used for control of wild oat, volunteer cereals, and annual and perennial grass in a range of bush-, pome- and stone fruits, root crops, rape, mustard, seed grass and forestry. Herbicide formulations containing fluazifop-p-butyl have not previously been selected for authority control.

Fenoxaprop-p-ethyl (Figure 1,e) is an 2-(4-aryloxyphenoxy)propionic acid too, which is used only for control of annual and perennial grass in spring barley, winter wheat and winter rye, and for control of wild oat in fallow fields. Fenoxaprop-p-ethyl is a new herbicide (introduced on the Danish market in 1998) and formulations have not previously been selected for authority control.

2.1.2 Samples

At the time of sampling for the control campaign (February - November 1999) one product containing fluazifop-p-butyl and two products containing fenoxaprop-p-ethyl were approved for use in Denmark. All three were available on the market during the period of the sample collection (products containing fenoxaprop-p-ethyl were collected in October 1998). One out of two approved products containing propyzamide, two out of three approved products containing metribuzin and three out of four approved products containing metamitron (*Miljøstyrelsen, 1998*) were available on the market during the period of the sampling. One sample of each pesticide product was collected. A list of the samples is given in Appendix I.

The sample containing fenoxaprop-p-ethyl was analysed at NERI during March - April 1999. The product containing propyzamide was analysed in May, metribuzin in May – June, metamitron in June and fluazifop-p-butyl in April – June 1999.

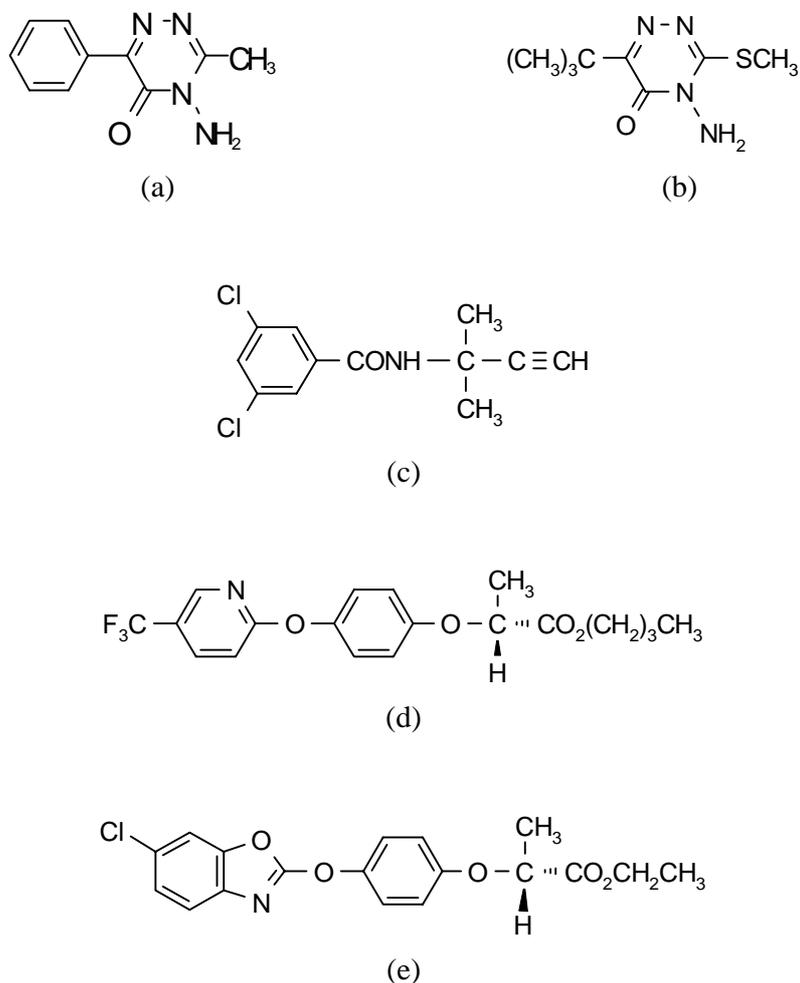


Figure 1
Chemical structures of the herbicide active ingredients: metamitron (a), metribuzin (b), propyzamide (c), fluazifop-p-butyl (d) and fenoxaprop-p-ethyl (e).

2.1.3 Results and Discussion

The contents of metribuzin were determined using gas chromatography and FID-detector (GC-FID) (Krongaard, 1999a). As no CIPAC method on metribuzin exists, the method is based on information from the manufacturer on method of analysis.

Due to similarity with metribuzin the contents of metamitron were determined using the same method as for metribuzin. A CIPAC method on metamitron doesn't exist either.

The content of propyzamide was determined using gas chromatography and FID-detector too (GC-FID) (Krongaard, 1999b). As no CIPAC method on propyzamide exists either the method is based on information from the manufacturer on method of analysis too.

The contents of the active ingredient fenoxaprop-p-ethyl and the enantiomer fenoxaprop-m-ethyl were determined using normal phase high performance liquid chromatography and UV-detector (NP-HPLC-UV). A provisional CIPAC method was used for fenoxaprop-p-ethyl, but a revised method was used for the enantiomer (*Krongaard, 1999c*).

The contents of the active ingredient fluazifop-p-butyl (R-enantiomer) and the S-enantiomer were determined using normal phase high performance liquid chromatography and UV-detector (NP-HPLC-UV). The method used for the R-isomer is close to the CIPAC method, but a revised method was used for the S-enantiomer (*Krongaard, 1999d*).

Results from the analyses are shown in Table 2.2.

Table 2.2. Content of active ingredient in samples of herbicides.

Active ingredient	Content			NERI sample no.
	Label claim	Analysis ¹⁾	Tolerance ²⁾	
metribuzin	70%	69,6 ± 0,3%	67,5 - 72,5%	9-0289
metribuzin	70%	71,7 ± 0,3%	67,5 - 72,5%	9-0290
metamitron	59,8% (700 g/l)	58,9 ± 1,1%	57,3 - 62,3%	9-0256
metamitron	70%	70,8 ± 0,2%	67,5 - 72,5%	9-0293
metamitron	58,3% (700 g/l)	57,6 ± 1,1%	55,8 - 60,8%	9-0294
propyzamide	(500 g/l) ³⁾	499,0 ± 4,8g/l	475 - 525 g/l ⁴⁾	9-0257
fluazifop-p-butyl	24,5%	23,83 ± 0,03%	23,0 - 26,0%	9-0260
fenoxaprop-p-ethyl	6,6% (69 g/l)	6,50 ± 0,04%	5,9 - 7,3%	8-0577
fenoxaprop-p-ethyl	6,6% (69 g/l)	6,65 ± 0,04%	5,9 - 7,3%	8-0578

- 1) Mean (minimum duplicate determinations) ± 95% confidence limits.
- 2) Tolerated limits for content of active ingredients according to Danish regulations (*Miljø- og Energiministeriet, 1998*).
- 3) Content (expressed as %) not declared.
- 4) Calculated on basis of declared content in g/l

As apparent from Table 2.2 good agreement between declared and determined content was found for all the samples containing metamitron, metribuzin, propyzamide, fluazifop-p-butyl and fenoxaprop-p-ethyl. Hence, all the samples complied with the tolerated limits for content of active ingredient.

In products containing fluazifop-p-butyl or fenoxaprop-p-ethyl the contents of the enantiomers form were also determined. The contents of the enantiomer forms were below the specifications for the products. The amounts of the enantiomer forms in the products are confidential information and therefore not reported here.

2.2 Plant growth regulators

2.2.1 Introduction

Among the 10 different plant growth regulators available on the Danish market in 1999 plant growth regulators containing either trinexapac-ethyl or flurprimidol as active ingredients were selected for control in 1999.

Trinexapac-ethyl (Figure 2, top) is a plant growth regulator, which in Denmark is used only in cereals. 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 is a new plant growth regulator (introduced on the Danish market in 1998). Formulations containing trinexapac-ethyl have not previously been selected for authority control.

Flurprimidol (Figure 2, bottom) is a plant growth regulator, which in Denmark is used only to reduce the growth of ornamentals in green houses. Flurprimidol is a new plant growth regulator too (also introduced on the Danish market in 1998). Formulations containing flurprimidol have not previously been selected for authority control.

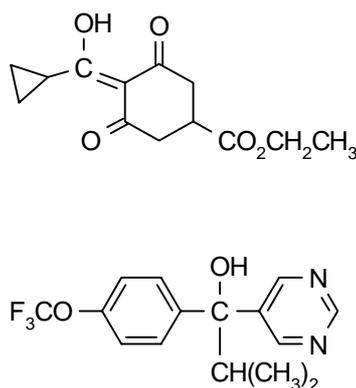


Figure 2

Chemical structure of the plant growth regulator active ingredients trinexapac-ethyl (top) and flurprimidol (bottom).

2.2.2 Samples

At the time of sampling for the control campaign (February – November 1999) only one product containing trinexapac-ethyl and one product containing flurprimidol were approved for use in Denmark. Both products were available on the market during the period of the sample collection. One sample of each pesticide product was collected. A list of the samples is given Appendix I.

The sample containing trinexapac-ethyl was analysed at NERI during May 1999. The sample containing flurprimidol was analysed at NERI in November 1999.

2.2.3 Results and Discussion

The content of trinexapac-ethyl was determined using reversed phase high performance liquid chromatography equipped with a diode array detector (RP-HPLC) (Krongaard, 1999e). As no CIPAC method on trinexapac-ethyl exists, the method is based on information from the manufacturer on method of analysis.

Similarly, content of flurprimidol was determined using reversed phase high performance liquid chromatography equipped with a diode array detector (RP-HPLC) (Krongaard, 1999f). As no CIPAC method on flurprimidol exist either, the method used is based on information from the manufacturer on method of analysis. Results from the analyses are shown in Table 2.3.

Table 2.3. Content of active ingredient in samples of plant growth regulators

Active ingredient	Content			NERI sample no.
	Label claim	Analysis ¹⁾	Tolerance ²⁾	
trinexapac-ethyl	25,2% (250 g/l)	25,7 ± 0,2%	24,4 - 26,0%	9-0261
flurprimidol	1,48% (15 g/l)	1,51 ± 0,01%	1,26 - 1,70%	9-0895

1) Mean (minimum duplicate determinations) ± 95% confidence limits.

2) Tolerated limits for content of active ingredients according to Danish regulations (*Miljø- og Energiministeriet, 1998*).

As apparent from Table 2.3 good agreement between declared and determined content was found for both samples containing trinexapac-ethyl and flurprimidol. Hence, both samples complied with the tolerated limits for content of active ingredient.

2.3 Fungicides

2.3.1 Introduction

In 1999 around 30 different fungicide active ingredients were approved in Denmark (*Miljøstyrelsen, 1998*). Among these active ingredients products containing fenpropimorph, azoxystrobin, fenpiclonil and imazalil were selected for control in 1999. In 1998 products containing chlorothalonil were selected for control of content of the active ingredient. In 1999 a technical material of chlorothalonil was selected for control of different impurities including hexachlorobenzene, which is included in the FAO-specifications.

Fenpropimorph (Figure 3,a) is a morpholine type of fungicide, which in Denmark is used for control of several fungi on cereals, seed grass, beets, beetroot, leek and chive. Formulations containing fenpropimorph have not previously been selected for authority control.

Azoxystrobin (Figure 3,b) is a strobilurin type of fungicide, which in Denmark is used only on cereals controlling fungal diseases. Azoxystrobin is a new fungicide (introduced on the Danish market in 1999) and formulations containing azoxystrobin have not previously been selected for authority control.

Fenpiclonil (Figure 3,c) is a phenylpyrrole type of fungicide that in Denmark is approved only to use on winter wheat and winter rye. Fenpiclonil is a new fungicide (introduced on the Danish market in 1998) and formulations containing fenpiclonil have not previously been selected for authority control. According to the manufacturer the product containing fenpiclonil have not yet been sold commercially in Denmark in spite of the approval.

Imazalil (Figure 3,d) is an azole type of fungicide that in Denmark is used only as seed dressing, and to control fungal diseases on tomatoes, cucumber, seed potatoes and in greenhouses on roses and ornamentals. Formulations containing imazalil have not previously been selected for authority control.

Chlorothalonil (Figure 3,e) is used for control of many fungal diseases on wheat, potatoes, peas, onions, strawberries, cucumbers, and ornamentals. Formulations containing chlorothalonil were selected for authority control in 1998. In 1999 a technical material of chlorothalonil is controlled for different impurities, such as hexachlorobenzene (Figure 3,f).

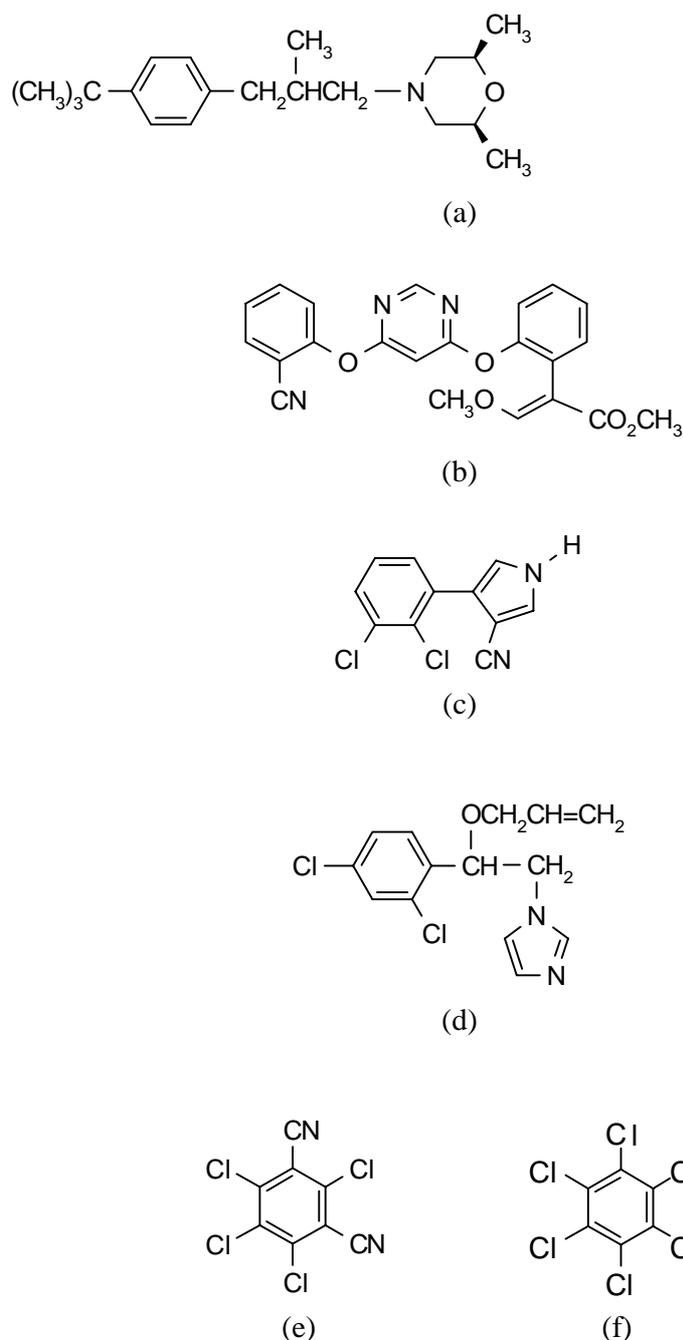


Figure 3

Chemical structure of the fungicide active ingredients fenpropimorph (a), azoxystrobin (b), fenpiclonil (c), imazalil (d), chlorothalonil (e), and hexachlorobenzene (f).

2.3.2 Samples

At the time of sampling for the control campaign (February 1999-January 2000) only one product containing fenpiclonil was approved for use in Denmark, but according to the manufacturer the product was not in retail. Three products containing azoxystrobin as active ingredient were approved for use in Denmark. Two of these were available on the market during the sampling period. Seven products containing fenpropimorph were approved, of which five were collected. Nine products containing imazalil as active ingredient were approved for use in Denmark. Six out of the nine products were available on the market during the period of the sampling, of which four were seed dressings. One sample of each fungicide product was collected. The laboratory assisted The Chemicals In-

spections Service at taking subsamples of three imazalil-containing seed dressing products (9-1254, 9-1255 and 9-1257) stored in containers, and collected the subsample of one imazalil-containing seed dressing product (0-0015). Technical grade chlorothalonil to impurity control was collected from one manufacturer. Information about the samples is given in Appendix I.

The samples containing azoxystrobin were analysed at NERI in the period July - August 1999, products containing chlorothalonil in December 1999 - January 2000, fenpropimorph products were analysed in January 2000 - February 2000, samples containing imazalil were analysed in February 2000 - March 2000.

2.3.3 Results and Discussion

The content of azoxystrobin was determined using gas chromatography with flame ionisation detector (GC-FID) (*Krongaard, 1999g*). As no CIPAC method on azoxystrobin exists, the method is based on information from the manufacturer on method of analysis.

The content of imazalil was determined using gas chromatography with flame ionisation detector (GC-FID) (*Krongaard, 2000a*). The method is based on a CIPAC method and information from the manufacturer on method of analysis.

Similarly, the content of fenpropimorph was determined using gas chromatography with flame ionisation detector (GC-FID). The method is developed in our laboratory (*Krongaard, 2000b*).

As apparent from the results in Table 2.4 good agreement between declared and determined content was found for all the samples containing fenpropimorph, azoxystrobin and imazalil. Hence, all the samples complied with the tolerated limits for content of active ingredient.

In connection with the conducted control of content of active ingredient in chlorothalonil formulations in 1998, an investigation of the level of a wide range of different impurities in technical grade chlorothalonil has further been carried out. The content of the impurities was determined using gas chromatography with mass spectrometry (GC-MS). As no CIPAC method on the impurities exist, the method is developed in our laboratory (*Krongaard, 1999h*).

There is an FAO-specification on hexachlorobenzene, one of the impurities, in technical grade chlorothalonil. The maximum content allowed is 0.3 g/kg. The content of hexachlorobenzene is below the FAO-specification and the contents of the other investigated impurities are all below the specification of the technical material. The actual natures of the impurities as well as the contents of these are confidential information and therefore not reported here.

Table 2.4. Content of active ingredient in samples of fungicides.

Active ingredient	Content			NERI sample no.
	Label claim	Analysis ¹⁾	Tolerance ²⁾	
azoxystrobin	(250 g/l) ³⁾	243,7 ± 0,8g/l	235 - 265 g/l ⁴⁾	9-0255
azoxystrobin	23,6% (250 g/l)	22,6 ± 0,1%	22,4 - 25,0%	9-0254
fenpropimorph	79,8%	79,2 ± 0,6%	82,3 - 77,3%	9-0251
fenpropimorph	38%	37,7 ± 0,3%	36,1 - 39,9%	9-0252
fenpropimorph	37,1%	36,3 ± 0,3%	35,2 - 39,0%	9-0253
fenpropimorph	80%	77,8 ± 0,6%	77,5 - 82,5%	9-0292
fenpropimorph	30%	30,5 ± 0,3%	28,5 - 31,5%	9-0295
fenpropimorph	30%	30,4 ± 0,3%	28,5 - 31,5%	9-0296
imazalil	7,26% (75 g/l)	7,22 ± 0,04%	6,53 - 7,99%	9-0316
imazalil	15%	14,74 ± 0,04%	14,1 - 15,9%	9-1215
imazalil	2%	1,99 ± 0,04%	1,7 - 2,3%	9-1216
imazalil	5,8% (50g/l)	5,73 ± 0,03%	5,2 - 6,4%	9-1254
imazalil	5,1% (50g/l)	4,80 ± 0,03%	4,6 - 5,6%	9-1255
imazalil	1,99% (20g/l)	1,90 ± 0,01%	1,69 - 2,29%	9-1256
imazalil	4,89%	4,66 ± 0,03%	4,40 - 4,98%	0-0015

1) Mean (minimum duplicate determination) ± 95% confidence limits.

2) Tolerated limits for content of active ingredients according to Danish regulations (*Miljø- og Energiministeriet, 1998*).

3) Content (expressed as %) not declared.

4) Calculated on basis of declared content in g/l.

2.4 Insecticides

2.4.1 Introduction

Among the different insecticides available on the Danish market the insecticides containing pirimicarb as active ingredient was selected for control in 1999.

Pirimicarb (Figure 4) is a carbamate insecticide that in Denmark is used for control of aphid. Formulations containing pirimicarb have not previously been selected for authority control.

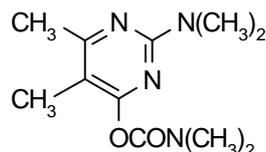


Figure 4

Chemical structure of the insecticide active ingredient pirimicarb.

2.4.2 Samples

At the time of sampling for the control campaign (February - November 1999) six products containing pirimicarb were approved for use in Denmark of which two products were available on the market during the period of the sample collection (*Miljøstyrelsen, 1998*). Normally only one sample of each product is collected, but one of the pirimicarb – products was collected in double. A list of all samples collected to the 1999-campaign is given in Appendix I.

The samples containing pirimicarb were analysed at NERI during the period November – December 1999.

2.4.3 Results and Discussion

The contents of pirimicarb were determined using gas chromatography with flame ionisation detector (GC-FID) (*Krongaard, 1999h*) based on a CIPAC method. Results from the analyses are shown in Table 2.5. As apparent from the table good agreement between declared and determined content was found for the samples containing pirimicarb. Hence, the samples comply with the tolerated limits for content of active ingredient.

Table 2.5. Content of active ingredient in samples of insecticides.

Active ingredient	Content			NERI sample no.
	Label claim	Analysis ¹⁾	Tolerance ²⁾	
pirimicarb	50%	48,3 ± 0,4%	47,5 - 52,5%	9-0263
pirimicarb	50%	49,4 ± 0,4%	47,5 - 52,5%	9-0291
pirimicarb	50%	49,9 ± 0,4%	47,5 - 52,5%	9-0315

1) Mean (minimum duplicate determinations) ± 95% confidence limits.

2) Tolerated limits for content of active ingredients according to Danish regulations (*Miljø- og Energiministeriet, 1998*).

3 Conclusions

Four different groups of products covered by the pesticide regulation have been included in the 1999 analytical chemical authority control: 1) herbicides containing metamiltron, metribuzin, propyzamide, fluzifop-p-butyl and fenoxaprop-p-ethyl, 2) plant growth regulators containing trinexapac-ethyl and flurprimidol, 3) fungicides containing imazalil, fenpropimorph, fenpiclonil and azoxystrobin, 4) insecticides containing pirimicarb as active ingredient. Furthermore a sample of technical grade chlorothalonil was analysed for impurities to see if they complied with the specifications.

Satisfactory results were found among all the examined products. Thus, all the analysed samples of these pesticides complied with the accepted tolerances with respect to content of active ingredients set by the Danish regulation of pesticides. The content of different impurities in a technical material of chlorothalonil complies with the specifications too.

4 References

Krongaard, T. (1999a): Analysemetode. Bestemmelse af met amitron og metribuzin som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of met amitron and metribuzin as active ingredient in pesticides. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (1999b): Analysemetode. Bestemmelse af propyzamid som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of propyzamide as active ingredient in pesticides. National Environmental Research Institute). 4 pp. (In Danish).

Krongaard, T. (1999c): Analysemetode. Bestemmelse af fenoxaprop-p-ethyl som aktivstof i bekæmpelsesmidler samt bestemmelse af L-isomeren fenoxaprop-m-ethyl og isomerforholdet. (Method of Analysis. Determination of fenoxaprop-p-ethyl as active ingredient in pesticide and determination of the L-isomer fenoxaprop-m-ethyl and the isomer ratio. National Environmental Research Institute). 6 pp. (In Danish).

Krongaard, T. (1999d): Analysemetode. Bestemmelse af fluazifop-p-butyl som aktivstof i bekæmpelsesmidler samt bestemmelse af S-isomeren. (Method of Analysis. Determination of fluazifop-p-butyl as active ingredient in pesticides and determination of the S-isomer. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (1999e): 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). 4 pp. (In Danish).

Krongaard, T. (1999f): Analysemetode. Bestemmelse af flurprimidol som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of flurprimidol as active ingredient in pesticides. National Environmental Research Institute). 4 pp. (In Danish).

Krongaard, T. (1999g): Analysemetode. Bestemmelse af azoxystrobin som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of azoxystrobin as active ingredient in pesticides. National Environmental Research Institute). 4 pp. (In Danish).

Krongaard, T. (1999h): Analysemetode. Bestemmelse af urenheder i tech. standard chlorothalonil (Method of Analysis. Determination of impurities in tech. standard chlorothalonil. National Environmental Research Institute). 3 pp. (In Danish).

Krongaard, T. (1999i): Analysemetode. Bestemmelse af pirimicarb som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of pirimicarb as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2000a): Analysemetode. Bestemmelse af imazail som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of imazalil as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Krongaard, T. (2000b): Analysemetode. Bestemmelse af fenpropimorph som aktivstof i bekæmpelsesmidler. (Method of Analysis. Determination of fenpropimorph as active ingredient in pesticides. National Environmental Research Institute). 5 pp. (In Danish).

Miljø- og Energiministeriet (1998): Bekendtgørelse om bekæmpelsesmidler. Miljø- og Energiministeriets bekendtgørelse nr. 241 af 27.april 1998. (Statutory Order on Pesticides. Statutory Order from the Ministry of the Environment and Energy, No. 241 of April 27, 1998).

Miljøstyrelsen (1999): Orientering fra Miljøstyrelsen, Nr. 2, 1999. Oversigt over godkendte bekæmpelsesmidler 1999. (Danish EPA Information, No. 2, 1999: List of Approved Pesticides 1999, Danish Environmental Protection Agency). (In Danish).

Appendix I

Samples of pesticides collected from the Danish market in 1999 for authority control

Table 1: Herbicides

Product	Active ingredient(s)	Formulation type ¹⁾	Company	NERI sample no.
Goltix flydende	metamitron	SC	Bayer A/S	9-0256
Kerb 500 SC	propyzamide	SC	BASF A/S	9-0257
Fusilade X-tra	fluazifop-p-butyl	EW	Zeneca Agro A/S	9-0260
Inter-Metribuzin WG	metribuzin	WG	Inter-Trade A/S	9-0289
Sencor WG	metribuzin	WG	Agro-Kemi A/S	9-0290
Goltix WG	metamitron	WG	Bayer A/S	9-0293
Goliath	metamitron	SC	KVK Agro A/S	9-0294
Primera	fenoxaprop-p-ethyl	EW	Hoechst Schering AgrEvo	8-0577
Puma Super	fenoxaprop-p-ethyl	EW	Hoechst Schering AgrEvo	8-0578

1) SC: suspension concentrate; EW: emulsion, oil in water; WG: Water dispersible granules.

Table 2: Plant growth regulators

Product	Active ingredient	Formulation type ¹⁾	Company	NERI sample no.
Moddus	trinexapac-ethyl	EC	Novartis A/S	9-0261
Topflor	flurprimidol	ME	Dow Elanco	9-0895

1) EC: emulsifiable concentrate; ME: micro-emulsion

Table 3: Fungicides

Product	Active ingredient	Formulation type¹⁾	Company	NERI sample no.
Corbel	fenpropimorph	EC	Novartis A/S	9-0251
Tilt Top	fenpropimorph	EC	Novartis A/S	9-0252
Rival	fenpropimorph	EC	Hoechst Schering AgrEvo	9-0253
Amistar	azoxystrobin	SC	Zeneca Agro A/S	9-0254
LFS Azoxystrobin	azoxystrobin	SC	LFS-Kemi	9-0255
BASF Carbol	fenpropimorph	EC	BASF A/S	9-0292
Tilt Megaturbo	fenpropimorph	EC	Novartis A/S	9-0295
Tilt Megaturbo	fenpropimorph	EC	Ciba Geigy A/S	9-0296
Fungazil 100 SL	imazalil	SL	Cillus A/S	9-0316
Fungaflor smoke	imazalil	FU	Cillus A/S	9-1215
Nectec TM Pasta	imazalil	PA	Cillus A/S	9-1216
Fungazil bejdse	imazalil	ES	Cillus A/S	9-1254
Fungazil A	imazalil	ES	Cillus A/S	9-1255
Raxil IM 035 ES	imazalil	ES	Bayer A/S	9-1256
Fungazil MLF	imazalil	ES	Agrodan	0-0015
	chlorothalonil	TC	used by Zeneca	487-7

1) EC: emulsifiable concentrate; SC: suspension concentrate; SL: soluble concentrate; FU: smoke generator; PA: Paste; ES: emulsion for seed treatment; TC: technical material.

Table 4: Insecticides

Product	Active ingredient	Formulation type¹⁾	Company	NERI sample no.
Inter-pirimicarb 50	pirimicarb	WG	Inter-Trade A/S	9-0263
Pirimor G	pirimicarb	WG	Zeneca Agro A/S	9-0291
Pirimor G	pirimicarb	WG	Zeneca Agro A/S	9-0315

1) WG: Water dispersible granules

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 Rønne
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

1999

- Nr. 297: Preservatives in Skin Creams. Analytical Chemical Control of Chemical Substances and Chemical Preparations. By Rastogi, S.C., Jensen, G.H., Petersen, M.R. & Worsøe, I.M. 70 pp., 50,00 DKK.
- Nr. 298: Methyl t-Butylether (MTBE) i drikkevand. Metodeafprøvning. Af Nyeland, B., Kvamm, B.L. 51 s., 50,00 kr.
- Nr. 299: Blykontaminering af grønlandske fugle - en undersøgelse af polarlomvie til belysning af human eksponering med bly som følge af anvendelse af blyhagl. Af Johansen, P., Asmund, G. & Riget, F.F. 27 s., 60,00 kr.
- Nr. 300: Kragefugle i et dansk kulturlandskab. Feltundersøgelser 1997-99. Af Hammershøj, M., Prang, A. & Asferg, T. 31 s., 40,00 kr.
- Nr. 301: Emissionsfaktorer for tungmetaller 1990-1996. Af Illerup, J.B., Geertinger, A., Hoffmann, L. & Christiansen, K. 66 s., 75,00 kr.
- Nr. 302: Pesticider 1 i overfladevand. Metodeafprøvning. Af Nyeland, B. & Kvamm, B.L. 322 s., 150,00 kr.
- Nr. 303: Ecological Risk Assessment of Genetically Modified Higher Plants (GMHP). Identification of Data Needs. By Kjær, C., Damgaard, C., Kjellsson, G., Strandberg, B. & Strandberg, M. 32 pp., 50,00 DKK.
- Nr. 304: Overvågning af fugle, sæler og planter 1998-99, med resultater fra feltstationerne. Af Laursen, K. (red.). 81 s., 70,00 kr.
- Nr. 305: Interkalibrering omkring bestemmelse af imposex- og interseksstadier i marine snegle. Resultat af workshop afholdt den 30.-31. marts 1999 af Det Marine Fagdatacenter. Af Strand, J. & Dahl, K. (i trykken).
- Nr. 306: Mercury in Soap in Tanzania. By Glahder, C.M., Appel, P.W.U. & Asmund, G. 19 pp., 60,00 kr.

2000

- Nr. 307: Cadmium Toxicity to Ringed Seals (*Phoca hispida*). An Epidemiological Study of possible Cadmium Induced Nephropathy and Osteodystrophy in Ringed Seals from Qaanaaq in Northwest Greenland. By Sonne-Hansen, C., Dietz, R., Leifsson, P.S., Hyldstrup, L. & Riget, F.F. (in press)
- Nr. 308: Økonomiske og miljømæssige konsekvenser af merkedordsordningerne i EU's landbrugsreform. Agenda 2000. Af Andersen, J.M., Bruun et al. 63 s., 75,00 kr.
- Nr. 309: Benzene from Traffic. Fuel Content and Air Concentrations. By Palmgren, F., Hansen, A.B., Berkowicz, R. & Skov, H. 42 pp., 60,00 DKK.
- Nr. 310: Hovedtræk af Danmarks Miljøforskning 1999. Nøgleindtryk fra Danmarks Miljøundersøgelers jubilæumskonference Dansk Miljøforskning. Af Secher, K. & Bjørnsen, P.K. 104 s., 100,00 kr.
- Nr. 311: Miljø- og naturmæssige konsekvenser af en ændret svineproduktion. Af Andersen, J.M., Asman, W.A.H., Hald, A.B., Münier, B. & Bruun, H.G. 104 s., 110,00 kr.
- Nr. 312: Effekt af døgnregulering af jagt på gæs. Af Madsen, J., Jørgensen, H.E. & Hansen, F. 64 s., 80,00 kr.
- Nr. 313: Tungmetalledfald i Danmark 1998. Af Hovmand, M. & Kemp, K. 26 s., 50,00 kr.
- Nr. 314: Virkemidler i pesticidpolitikken. Reduktion af pesticidanvendelsen på behandlede jordbrugsarealer. Af Hasler, B., Schou, J.S., Ørum, J.E. & Gårn Hansen, L. (i trykken)
- Nr. 315: Ecological Effects of Allelopathic Plants – a Review. By Kruse, M., Strandberg, M. & Strandberg, B. 64 pp., 75,00 DKK.
- Nr. 316: Overvågning af trafikens bidrag til lokal luftforurening (TOV). Målinger og analyser udført af DMU. Af Hertel, O., Berkowicz, R., Palmgren, F., Kemp, K. & Egeløv, A. 28 s. (Findes kun i elektronisk udgave)
- Nr. 317: Overvågning af bæver *Castor fiber* efter reintroduktion på Klosterheden Statsskovdistrikt 1999. Red. Berthelsen, J.P. 37 s., 40,00 kr.
- Nr. 318: Order Theoretical Tools in Environmental Sciences. Proceedings of the Second Workshop October 21st, 1999 in Roskilde, Denmark. By Sørensen, P.B. et al. 170 pp., 150,00 DKK.
- Nr. 319: Forbrug af økologiske fødevarer. Del 2: Modellering af efterspørgsel. Af Wier, M. & Smed, S. 184 s., 150,00 kr.
- Nr. 320: Transportvaner og kollektiv trafikforsyning. ALTRANS. Af Christensen, L. 154 s., 110,00 kr.
- Nr. 321: The DMU-ATMI THOR Air Pollution Forecast System. System Description. By Brandt, J., Christensen, J.H., Frohn, L.M., Berkowicz, R., Kemp, K. & Palmgren, F. 60 pp., 80,00 DKK.
- Nr. 322: Bevaringsstatus for naturtyper og arter omfattet af EF-habitatdirektivet. Af Pihl, S., Søggaard, B., Ejrnæs, R., Aude, E., Nielsen, K.E., Dahl, K. & Laursen, J.S. (i trykken)
- Nr. 323: Tests af metoder til marine vegetationsundersøgelser. Af Krause-Jensen, D., Laursen, J.S., Middelboe, A.L., Dahl, K., Hansen, J. Larsen, S.E. (in press)
- Nr. 324: Vingeindsamling fra jagtsæsonen 1999/2000 i Danmark. Wing Survey from the Huntig Season 1999/2000 in Denmark. Af Clausager, I. (in press)
- Nr. 325: Safety-Factors in Pesticide Risk Assessment. Differences in Species Sensitivity and Acute-Chronic Relations. By Elmegaard, N. & Jagers op Akkerhuis, G.A.J.M. (in press)

Four different groups of products covered by the pesticide regulation have been included in the 1999 analytical chemical authority control: 1) herbicides containing metamilon, metribuzin, propyzamide, fluazifop-p-butyl and fenoxaprop-p-ethyl, 2) plant growth regulators containing trinexapac-ethyl and flurprimidol, 3) fungicides containing imazalil, fenpropimorph, fenpiclonil and azoxystrobin, 4) insecticides containing pirimicarb as active ingredient. Furthermore a sample of technical grade chlorothalonil was analysed for impurities to see if they complied with the specifications.

Satisfactory results were found among all the examined products. Thus, all the analysed samples of these pesticides complied with the accepted tolerances with respect to content of active ingredients set by the Danish regulation of pesticides. The content of different impurities in a technical material of chlorothalonil complies with the specifications too.

Ministry of Environment and Energy
National Environmental Research Institute

ISBN: 87-7772-565-4
ISSN (print): 0905-815X
ISSN (electronic): 1600-0048