



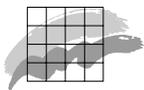
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Control of Pesticides 2002

Chemical Substances and Chemical Preparations

NERI Technical Report, No. 461

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2003

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Abstract Four different groups of products covered by the pesticide regulation have been included in the 2002 analytical chemical authority control: 1) Herbicides containing ethofumesate, phenmedipham, desmedipham, terbuthylazine and pyridate. 2) Fungicides containing tebuconazole. 3) Insecticides containing buprofezin, chlorpyrifos and dimethoate. 4) Rodenticides containing brodifacoum and difenacoum. All products were examined for the content of the respective active ingredients. Satisfactory results were found for herbicides containing pyridate, desmedipham and ethofumesate, for insecticides containing buprofezin, and for rodenticides containing difenacoum. Thus, all analysed samples of these formulations complied with the accepted tolerance limits with respect to the content of active ingredients according to Danish Statutory order on pesticides. One of the three products containing terbuthylazine, one of the four products containing dimethoate, two of the six products containing chlorpyrifos, one of the four products containing brodifacoum, two of the seven products containing phenmedipham and one of the seven products containing tebuconazole did not comply with the accepted limits of content of the respective active ingredient. On seven products, the content of active ingredient was declared only in g/L, but not in % (w/w). Declared content expressed in % (w/w) did not agree with the content expressed in g/L on two labels.

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Contents

Summary 5

Resumé 7

1 Introduction 9

2 Control Campaigns in 2002 11

2.1 Herbicides 12

2.1.1 Introduction 12

Figure 1 13

2.1.2 Samples 14

2.1.3 Results and Discussion 14

2.2 Fungicides 16

2.2.1 Introduction 16

2.2.2 Samples 16

2.2.3 Results and Discussion 16

2.3 Insecticides 18

2.3.1 Introduction 18

2.3.2 Samples 19

2.3.3 Results and Discussion 20

2.4 Rodenticides 22

2.4.1 Introduction 22

2.4.2 Samples 23

2.4.3 Results and Discussion 23

3 Conclusions 25

4 References 27

Appendix I 29

National Environmental Research Institute 31

**Faglige rapporter fra DMU/NERI Technical Reports
32**

Summary

The analytical chemical authority control of pesticide products on the Danish market performed in 2002 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.

Four different groups of products covered by the pesticide regulation were included in the 2002 analytical chemical authority control: 1) Herbicides containing ethofumesate, phenmedipham, desmedipham, terbuthylazine and pyridate. 2) Fungicides containing tebuconazole. 3) Insecticides containing buprofezin, chlorpyrifos and dimethoate. 4) Rodenticides containing brodifacoum and difenacoum.

Satisfactory results were found for herbicides containing pyridate, desmedipham and ethofumesate, for insecticides containing buprofezin, and for rodenticides containing difenacoum. Thus, the seventeen 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.

One out of the three products containing terbuthylazine did not comply with the tolerance limit for content of this active ingredient. The product had a shelf life less than 2 years, which did not appear from the label. The limited shelf life could be the reason for the low content.

The content of active ingredient in one of the four products containing dimethoate was found to be outside the tolerance limit. The product controlled was from 1994, which can be the reason.

Two of the six products containing chlorpyrifos were found to be outside the tolerance limit. The content of the active ingredient was too low compared with the declared content. One of the products was from 1998, while problems with precipitation in the other could be the reason.

One of the four products containing brodifacoum was found to be outside the tolerance limit with respect to content of active ingredient. The content was found to be just outside the tolerance limit by NERI, but just inside by the company.

Two out of the seven products containing phenmedipham and one out of the seven products containing tebuconazole did not comply with the tolerance limit for the content of the respective active ingredients. The contents of active ingredients were too low.

On seven products the content of active ingredient were declared only in g/L, but not in % (w/w) as required by the Statutory Order. Declared content expressed in % (w/w) did not agree with the content expressed in g/L on labels of two products containing chlorpyrifos.

Resumé

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked udført i 2002 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 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. Fire forskellige grupper produkter er inkluderet i den analytisk-kemiske kontrol udført af myndighederne i 2002: 1) Herbicider indeholdende ethofumesate, phenmedipham, desmedipham, terbuthylazine og pyridate. 2) Fungicider indeholdende tebuconazole. 3) Insekticider indeholdende buprofezin, chlorpyrifos og dimethoate. 4) Rodenticider indeholdende brodifacoum og difenacoum.

Der blev opnået tilfredsstillende resultater blandt herbicider indeholdende pyridat, desmedipham og ethofumesat, blandt insekticider indeholdende buprofezin og blandt rodenticider indeholdende difenacoum. Indholdet af aktivstof i alle de sytten analyserede prøver af disse bekæmpelsesmidler var indenfor den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler.

En ud af tre prøver indeholdende terbuthylazin var ikke indenfor den accepterede tolerance for indhold af aktivstof. Produktet havde begrænset holdbarhed, hvilket ikke fremgik af etiketten. Den begrænsede holdbarhed kan være årsagen til det lave indhold.

Indholdet af aktivstof i en ud af fire prøver indeholdende dimethoate var udenfor den accepterede tolerance. Det kontrollerede produkt var fra 1994, hvilket kan være årsagen.

To ud af seks prøver indeholdende chlorpyrifos var ikke indenfor den accepterede tolerance for indhold af aktivstof. Indholdet var for lavt i forhold til det deklarerede indhold. Ét af produkterne var fra 1998, mens der havde været problemer med bundfældning i det andet.

En ud af fire prøver indeholdende brodifacoum var ikke indenfor den accepterede tolerance for indhold af aktivstof. Indholdet blev af DMU fundet til at være akkurat udenfor tolerancen, mens producenten efterfølgende fandt det akkurat indenfor tolerancen.

To ud af syv produkter indeholdende phenmedipham og ét af syv produkter indeholdende tebuconazol var udenfor den accepterede tolerance for indhold af aktivstof. Indholdet var i begge tilfælde for lavt.

På syv produkter var indholdet af aktivstof kun deklareret i g/l og ikke i % som det ellers er krævet i direktivet. Deklareret indhold udtrykt i % stemte ikke overens med indholdet udtrykt i g/l på to etiketter på produkter indeholdende chlorpyrifos.

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 for the formulations are given in a Statutory Order from the Ministry of the Environment and Energy (*Miljø- og Energiministeriet, 2000*), 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 2002.

2 Control Campaigns in 2002

Control campaigns conducted in 2002 have covered active ingredients belonging to four different groups of pesticides: herbicides, fungicides, insecticides and rodenticides. 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 (*Miljø- og Energiministeriet, 2000*) specifies general tolerance of deviation from declared content. These are given in Table 2.1. Active ingredients controlled in 2002 have mainly been selected among those where products in the last decade were found not to comply with the accepted limits of content.

Samples of the various pesticide formulations covered in the 2002 control campaigns have been collected by the Chemical Inspection Service at DEPA during the months February – June 2002 from either whole sale dealers/importers or at retailer out-lets. 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. \geq 50	\pm 2.5%	(abs.)
25 < conc. \leq 50	\pm 5%	(rel.)
10 < conc. \leq 25	\pm 6%	(rel.)
2.5 < conc. \leq 10	\pm 10%	(rel.)
conc. \leq 2.5	\pm 15%	(rel.)

2.1 Herbicides

2.1.1 Introduction

Among the about 44 different active ingredients in herbicide formulations available on the Danish market (Miljøstyrelsen, 2002), products containing ethofumesate, phenmedipham, desmedipham, terbuthylazine and pyridate as active ingredients were selected for control in 2002. All products were examined for the content of active ingredient.

Ethofumesate (Figure 1,a) is a benzofuran herbicide, which in Denmark is used to control of grass and broad-leaved weeds in beets. Ethofumesate inhibits the growth of meristems, retards the cellular division, and limits formation of waxy cuticle. It is a selective systemic herbicide that is absorbed by the roots and emerging shoots (grasses). Herbicide formulations containing ethofumesate were selected for authority control in 1997, where one out of eleven products did not comply with the declared content with respect to the active ingredient.

Phenmedipham (Figure 1,b) belongs to the group of bis-carbamate herbicides. Phenmedipham is used to control a broad spectrum of broad-leaved weeds in beets and beetroots. It is a selective systemic herbicide that is absorbed through the leaves and inhibits the photosynthetic electron transport. Herbicide formulations containing phenmedipham were selected for authority control in 1997, where all thirteen products complied with the declared content with respect to the active ingredient.

Desmedipham (Figure 1,c) belongs to the group of bis-carbamate herbicides like phenmedipham. Desmedipham is used to control a broad spectrum of broad-leaved weeds in beets. It is a selective systemic herbicide which is absorbed through the leaves and inhibits the photosynthetic electron transport. Desmedipham is used only in combination with ethofumesate and phenmedipham in Denmark. Herbicide formulations containing desmedipham were selected for authority control in 1997, where all three products complied with the declared content with respect to the active ingredient.

Terbuthylazine (Figure 1,d) is a 1,3,5-triazine compound, which in Denmark is used as a broad-spectrum herbicide to control weeds in maize and forestry. Terbuthylazine is a herbicide that is mainly absorbed by the roots. It inhibits the photosynthetic electron transport. Herbicide formulations containing terbuthylazine were selected for authority control in 2000, where one out of four products did not comply with the declared content with respect to the active ingredient.

Pyridate (Figure 1,e) is a phenylpyridazine herbicide compound, which in Denmark is used to control of broad-leaved weeds in maize. Pyridate inhibits the photosynthetic electron transport. It is a selective herbicide that is mainly absorbed by the leaves. Pyridate is used only in combination with terbuthylazine in Denmark. Herbicide formulations containing pyridate has not previously been selected for authority control.

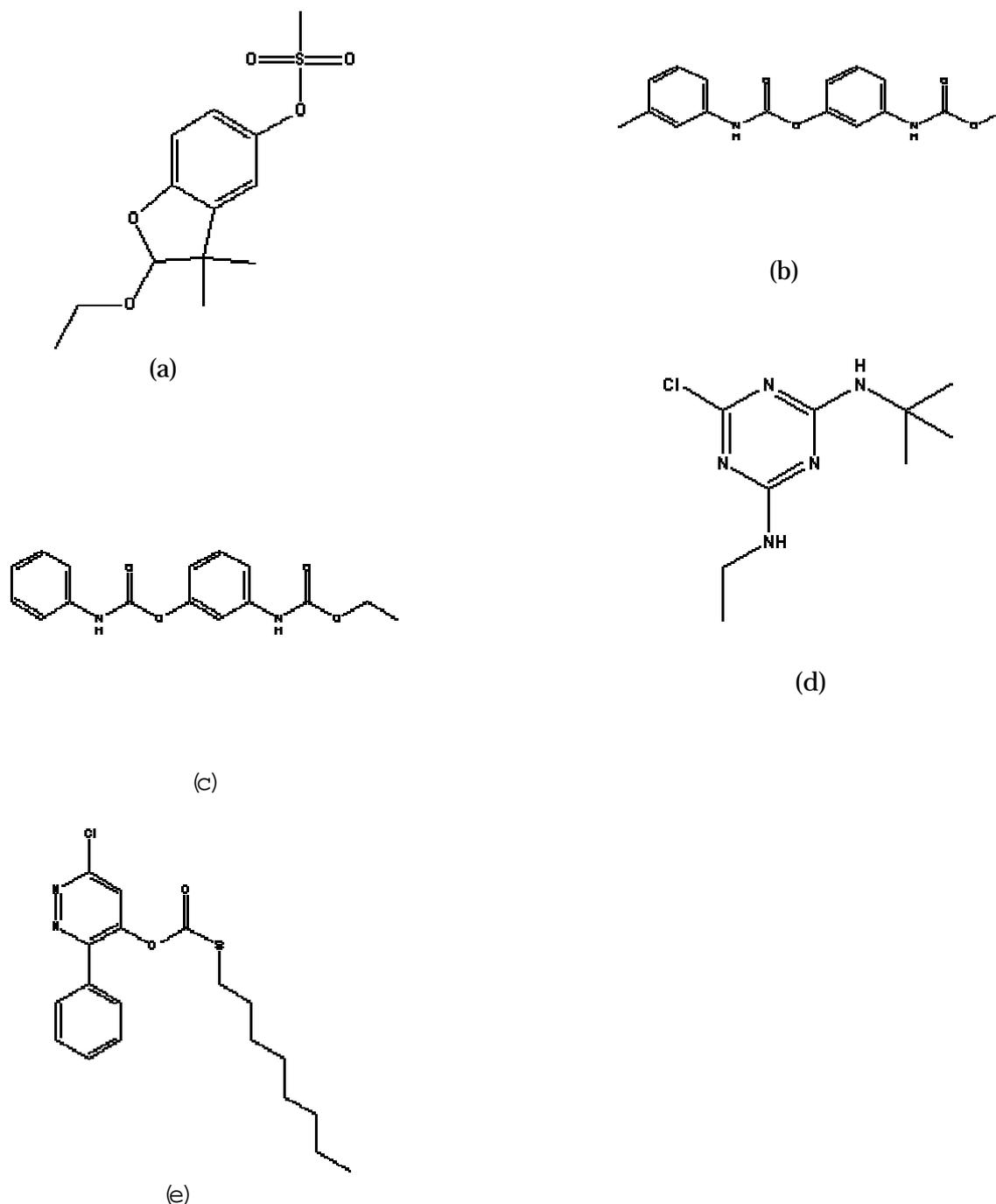


Figure 1

Chemical structures of the herbicide active ingredients: ethofumesate (a), phenmedipham (b), desmedipham (c), terbuthylazine (d) and pyridate (e).

2.1.2 Samples

At the time of sampling for the control campaign, 11 products containing ethofumesate, 8 products containing phenmedipham, and 3 products containing desmedipham were approved for use in Denmark. Only one product of each active ingredient was not available on the market during the period of the sample collection. 3 products containing terbuthylazine and 1 product containing pyridate were approved for use in Denmark. All these 4 products were available on the market during the period of the sample collection. One sample of each pesticide product was collected. The samples are listed in Appendix I.

The sample containing pyridate was analysed in May-June 2002. The samples containing terbuthylazine were analysed in August, ethofumesate containing products were analysed during the period September-December, phenmedipham was analysed in November-December, and products containing desmedipham were analysed in December.

2.1.3 Results and Discussion

The contents of ethofumesate, phenmedipham and desmedipham were determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV (*Krongaard, 2002a*). The method is with minor changes the same as the method used in the control campaign in 1997 and allows simultaneous determination of all three compounds. The method is developed on the basis of information from the manufacturer.

The contents of terbuthylazine were determined using gas chromatography and flame ionisation detection (GC-FID) (*Krongaard, 2000a*). The method is the same as the method used in the control campaign in 2000. The method is developed on the basis of two CIPAC-methods and allows simultaneous determination of terbuthylazine and simazine. Simazine was not selected for the currant authority examination.

The content of pyridate was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV (*Krongaard, 2002b*). The method is developed on the basis of information from the manufacturer.

Table 2.2 shows an agreement between declared and determined content for thirteen samples containing pyridate, desmedipham and ethofumesate. One out of the three products containing terbuthylazine and two out of the seven products containing phenmedipham did not comply with the tolerance limits for content of the respective active ingredient. The contents of active ingredient were too low. On seven products the contents of active ingredient are only declared in g/L not in % (w/w) as the Statutory Order requires. Subsequent contact to the manufacturer of the terbuthylazine product with too low content revealed that the product has limited shelf life, which did not appear from the label. The limited shelf life is maybe the reason for the low content, but not necessarily. The manufacturer has informed that the label will be corrected.

Table 2.2 Content of active ingredient in samples of herbicides.

Active ingredient	Content			NERI sample no.
	Label claim	Analysis ¹⁾	Tolerance ²⁾	
Desmedipham	1.5 % (15 g/L)	1.49 ± 0.01%	1.35 – 1.65%	02-0316
Desmedipham	- (15 g/L) ³⁾	14.9 ± 0.1 g/L	13.5 – 16.5 g/L ⁴⁾	02-0317
Ethofumesate	- (500 g/L) ³⁾	487.30 ± 1.46 g/L	475 – 525 g/L ³⁾	02-0294
Ethofumesate	45 % (500 g/L)	44.44 ± 0.13%	42.75 – 47.25%	02-0313
Ethofumesate	11.3 % (115 g/L)	11.28 ± 0.03%	10.6 – 12.0%	02-0316
Ethofumesate	- (115 g/L) ³⁾	115.5 ± 0.4 g/L	108 – 122 g/L ³⁾	02-0317
Ethofumesate	44.3 % (500 g/L)	42.00 ± 0.13%	41.1 – 46.5%	02-0323
Ethofumesate	44.3 % (500 g/L)	43.75 ± 0.13%	41.1 – 46.5%	02-0324
Ethofumesate	- (500 g/L) ³⁾	498.80 ± 1.50 g/L	475 – 525 g/L ³⁾	02-0325
Ethofumesate	44.3 % (500 g/L)	42.58 ± 0.13%	41.1 – 46.5%	02-0432
Ethofumesate	- (500 g/L) ³⁾	481.39 ± 1.44 g/L	475 – 525 g/L ³⁾	02-0433
Ethofumesate	17.5% (200 g/L)	16.53 ± 0.05%	16.4 – 18.6%	02-0435
Phenmedipham	16 % (160 g/L)	15.47 ± 0.05%	15 – 17%	02-0295
Phenmedipham	16 % (160 g/L)	15.21 ± 0.05%	15 – 17%	02-0296
Phenmedipham	15.7 % (157g/L)	14.90 ± 0.04%	14.7 – 16.7%	02-0314
Phenmedipham	16.3 % (160 g/L)	14.49 ± 0.04%	15.3 – 17.3%	02-0315*)
Phenmedipham	7.4 % (75 g/L)	6.89 ± 0.02%	6.66 – 8.14%	02-0316
Phenmedipham	- (75 g/L) ³⁾	70.24 ± 0.21%	67.5 – 82.5 g/L ⁴⁾	02-0317
Phenmedipham	28 % (320 g/L)	25.75 ± 0.08%	26.6 – 29.4%	02-0435*)
Pyridate	16.5 % (160 g/L)	17.5 ± 0.3%	15.5 – 17.5%	02-0298
Terbuthylazine	25.8 % (250 g/L)	22.41 ± 0.13%	24.5 – 27.1%	02-0298*)
Terbuthylazine	- 500 g/L ³⁾	497.5 ± 3 g/L	475 – 525 g/L ⁴⁾	02-0299
Terbuthylazine	17.4 % (200 g/L)	17.92 ± 0.11%	16.4 – 18.4%	02-0300

1) Mean ± 95% confidence limits.

2) Tolerance limits for content of active ingredients according to Danish regulations (*Miljø- og Energiministeriet, 2000*).

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 36 active ingredients in fungicide formulations were approved in Denmark in 2001 (Miljøstyrelsen, 2002). Only products containing tebuconazole, were selected for control in 2002 and examined for content of active ingredient.

Tebuconazole (Figure 2) is an azole type of fungicide, which is used only as seed dressing and wood preservatives in Denmark. Tebuconazole is a systemic fungicide used to control many fungal diseases. It inhibits steroid demethylation. Tebuconazole is a rather new active ingredient (included in the Danish register of approved pesticides in 1998). Fungicide formulations containing tebuconazole were selected for authority control in 1998, where three out of nine products did not comply with the declared content with respect to the active ingredient. The three products were all wood preservatives. This year seven wood preservatives containing tebuconazole were selected for control.

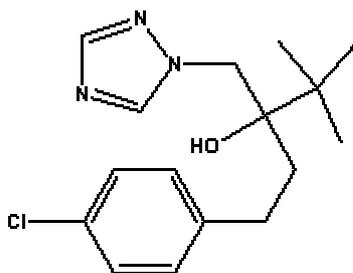


Figure 2

Chemical structure of the fungicide active ingredient tebuconazole.

2.2.2 Samples

At the time of sampling for the control campaign, six of the selected seven products containing tebuconazole were available on the market. One sample of each fungicide product was collected. The samples are listed in Appendix I.

The EW-formulation was analysed in July 2002 and the AL-formulations were analysed in September 2002.

2.2.3 Results and Discussion

The contents of tebuconazole were determined using gas chromatography and flame ionisation detection (GC-FID) (Krongaard, 1999). The method is the same as the method used in the control campaign in 1998. The method was developed on the basis of information from the manufacturer.

Table 2.3 shows an agreement between declared and determined content in five out of six samples containing tebuconazole as active ingredient. One sample contained only approx. 0.02% tebuconazole although it was declared to contain 0.93%

Table 2.3 Content of active ingredient in samples of fungicides.

Active ingredient	Content			NERI sample no.	
	Label claim		Analysis ¹⁾		Tolerance ²⁾
Tebuconazole	25 %	250 g/L	25.6 ± 0.1%	23.5 – 26.5%	02-0297
Tebuconazole	0.20 %	1.60 g/L	0.21 ± 0.001%	0.17 – 0.23 %	02-0430
Tebuconazole	0.20 %	1.60 g/L	0.19 ± 0.001%	0.17 – 0.23 %	02-0431
Tebuconazole	0.93 %	7.40 g/L	approx. 0.02%**)	0.79 – 1.07 %	02-0612*)
Tebuconazole	0.20 %	1.60 g/L	0.21 ± 0.001%	0.17 – 0.23 %	02-0717
Tebuconazole	0.93 %	7.40 g/L	0.89 ± 0.005%	0.79 – 1.07 %	02-0718

1) Mean ± 95% confidence limits.

2) Tolerated limits for content of active ingredients according to Danish regulations (*Miljø- og Energiministeriet, 2000*).

*) Found content is outside the accepted tolerance.

***) RSD not calculated. Concentration outside the validated concentration range.

2.3 Insecticides

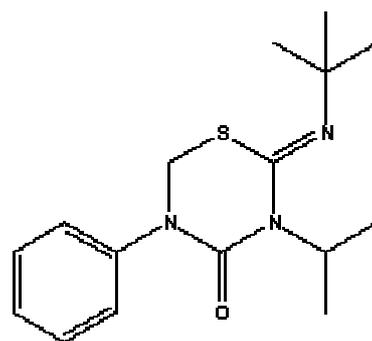
2.3.1 Introduction

Among the different insecticide formulations available on the Danish market (Miljøstyrelsen, 2002) the products containing buprofezin, chlorpyrifos and dimethoate as active ingredients were selected for control in 2002. All products were examined for content of active ingredient.

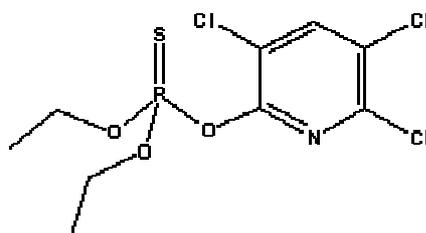
Buprofezin (Figure 3a) is used for control of green house white flies and cotton flies on ornamentals in greenhouses in Denmark. Buprofezin is a chitin synthesis and prostaglandin inhibitor with contact and stomach action. It is not translocated in the plant. Insecticide formulations containing buprofezin are rather new on the Danish market (included in the Danish register of approved pesticides in 1999) and were selected for authority control in 2000. The only product on the market in 2000 did not comply with the declared content with respect to the active ingredient.

Chlorpyrifos (Figure 3b) is an organophosphorus insecticide, which is used for control of certain insects on ornamentals in greenhouses and on household pests in Denmark. It is a cholinesterase inhibitor with contact and respiratory action. Insecticide formulations containing chlorpyrifos were selected for authority control in 1996. Three out of the five products controlled did not comply with respect to the declared content of active ingredient in 1996.

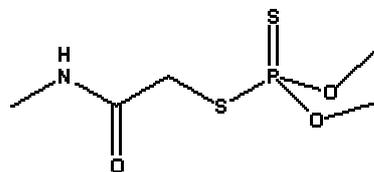
Dimethoate (Figure 3c) is an organophosphorus insecticide, which is used, for control of certain insects on plants and for control of flies in animal houses in Denmark. It is a cholinesterase inhibitor with contact and stomach action. Insecticide formulations containing dimethoate were selected for authority control in 1998. Four out of the six products controlled did not comply with respect to the declared content of active ingredient.



(a)



(b)



(c)

Figure 3

Chemical structure of the insecticide active ingredients: buprofezin (a), chlorpyrifos (b), dimethoate (c).

2.3.2 Samples

At the time of sampling, one product containing buprofezin and four products containing dimethoate as active ingredient were approved for use in Denmark. All these products were available on the market during the period of the sample collection. Only six out of the twelve products containing chlorpyrifos were available. One sample of each fungicide product was collected. The samples are listed in Appendix I

The sample containing buprofezin was analysed in June 2002, products containing dimethoate in August – September and the products containing chlorpyrifos were analysed in February 2003.

2.3.3 Results and Discussion

The content of buprofezin was determined using gas chromatography and flame ionisation detection (GC-FID) (*Krongaard, 2000b*). The method is the same as the method used in the control campaign in 2000. The method was developed in the laboratory as no CIPAC method exists and as the method provided from the manufacturer was based on packed GC-column. The method allows simultaneous determination of quinoclamin and kresoxim-methyl, but these active ingredients are not selected for authority examination this year.

The content of chlorpyrifos was determined using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV (*Krongaard, 2003a*). The method is developed based on the CIPAC method.

The content of dimethoate was determined using gas chromatography and flame ionisation detection (GC-FID) (*Krongaard, 2002c*). The method is developed based on information from the manufacturer.

Table 2.4 shows an agreement between declared and determined content made for the sample containing buprofezin, whereas the content of active ingredient in one of the products containing dimethoate and two of the products containing chlorpyrifos were found to be outside the tolerance limit. The contents in the samples were too low compared with the declared content. Declared content expressed in % (w/w) did not agree with the content expressed in g/L on labels of two products containing chlorpyrifos.

Subsequent contact to the manufacturer of the dimethoate product revealed that the product controlled was from 1994. Sample 02-0321 was from 1998. The manufacturer of 02-0719 admitted that there have been problems with precipitation, but they will investigate the problem again.

Table 2.4 Content of active ingredient in samples of insecticides.

Active ingredient	Content			NERI sample no.
	Label claim	Analysis ¹⁾	Tolerance ²⁾	
Buprofezin	0.005 % (428 g/L)	40.96 ± 0.16%	38 – 42 %	02-0611
Chlorpyrifos	0.8 % (8 g/L)	0.793 ± 0.005 %	0.68 – 0.92 %	02-0293
Chlorpyrifos	0.5 % (450 g/L)	0.247 ± 0.12 %	0.425 – 0.575 %	02-0321*)
Chlorpyrifos	2.5 % (25 g/L)	2.66 ± 0.02 %	2.13 – 2.87%	02-0322**)
Chlorpyrifos	0.8 % (8 g/L)	0.792 ± 0.005 %	0.68 – 0.92 %	02-0663
Chlorpyrifos	20 % (208 g/L)	19.24 ± 0.13 %	18.8 – 21.2 %	02-0664
Chlorpyrifos	2.5 % (36 g/L)	1.71 ± 0.01 %	2.13 – 2.87 %	02-0719*)**)
Dimethoate	38 % (400 g/L)	38.5 ± 0.3 %	36.1 – 39.9 %	02-0301
Dimethoate	38 % (400 g/L)	37.8 ± 0.3 %	36.1 – 39.9 %	02-0302
Dimethoate	45.7 % (500 g/L)	45.4 ± 0.4 %	43.4 – 48.0 %	02-0303
Dimethoate	38 % (400 g/L)	32.7 ± 0.3 %	36.1 – 39.9 %	02-0614*)

1) Mean ± 95% confidence limits.

2) Tolerance limits for content of active ingredients according to Danish regulation (*Miljø- og Energiministeriet, 2000*).

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.

***) Declared content expressed in % does not agree with the content expressed in g/L .

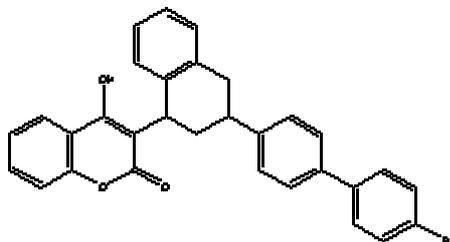
2.4 Rodenticides

2.4.1 Introduction

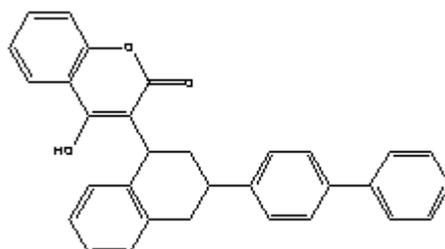
Among the seven rodenticide available on the Danish market (Miljøstyrelsen, 2002) the rodenticide formulations containing brodifacoum and difenacoum as active ingredients were selected for control in 2002, and examined for the content of respective active ingredients.

Brodifacoum (Figure 4a) is used for control of mice and rats in Denmark. Brodifacoum is an indirect anticoagulant. It inhibits the vitamin K-dependent steps in synthesis of clotting factors II, IX and X. Rodenticide formulations containing brodifacoum were selected for the authority control in 1994, where one out of the four products controlled did not comply with respect to the declared content of the active ingredient.

Difenacoum (Figure 4b) is a rodenticide, which is used for control of mice and rats in Denmark. Difenacoum is an indirect anticoagulant. It inhibits the vitamin K-dependent steps in synthesis of clotting factors II, IX and X. Rodenticide formulations containing difenacoum were selected for authority control in 1994, where the two products on the market containing difethialone did not comply with the declared content with respect to the active ingredient.



(a)



(b)

Figure 4
Chemical structure of the rodenticide active ingredients: brodifacoum (a), difenacoum (b).

2.4.2 Samples

At the time of sampling for the control campaign, five products containing brodifacoum as active ingredient were approved for use in Denmark. All these products were available on the market during the period of the sample collection. Only three out of the five products containing difenacoum were available on the market. One sample of each rodenticide product was collected. The samples are listed in Appendix I

All samples were analysed in the period March - April 2003.

2.4.3 Results and Discussion

The content of brodifacoum and difenacoum were determined by the same method using reversed phase high performance liquid chromatography and UV-detector, RP-HPLC-UV. The method used to paste and wax formulations is the same, with minor changes, as for the analysis performed in the control campaign in 1994. Pellets and seed coated with rodenticide were extracted using the CIPAC method or the method provided from the manufacturer (*Krongaard, 2003b*).

Table 2.5 Content of active ingredient in samples of insecticides.

Active ingredient	Content			NERI sample no.	
	Label claim	Analysis ¹⁾	Tolerance ²⁾		
Brodifacoum	0.005 %	-	0.00461 ± 0.00007 %	0.00425 – 0.00575 %	02-0428
Brodifacoum	0.005 %	-	0.00545 ± 0.00008 %	0.00425 – 0.00575 %	02-0604
Brodifacoum	0.005 %	-	0.00414 ± 0.00006 %	0.00425 – 0.00575 %	02-0606*)
Brodifacoum	0.005 %	-	0.00444 ± 0.00006 %	0.00425 – 0.00575 %	02-0607
Difenacoum	0.005 %	-	0.00487 ± 0.00032 %	0.00425 – 0.00575 %	02-0292
Difenacoum	0.01 %	-	0.0093 ± 0.0004 %	0.0085 – 0.0115 %	02-0427
Difenacoum	0.005 %	-	0.00484 ± 0.00031 %	0.00425 – 0.00575 %	02-0429

1) Mean ± 95% confidence limits.

2) Tolerated limits for content of active ingredients according to Danish regulations (*Miljø- og Energiministeriet, 2000*).

*) Found content is outside the accepted tolerance.

Table 2.5 shows an agreement between declared and determined content in the samples containing difenacoum, whereas the content of active ingredient in one of the four products containing brodifacoum were found to be outside the tolerance limit. The content in the sample was just too low compared with the declared content. The manufacturer received a sub-sample from the laboratory on request. The company analysed the sample to contain 0.0043 %, a content just within the tolerance limit. No further analysis has been performed.

3 Conclusions

Four different groups of products covered by the pesticide regulation were included in the 2002 analytical chemical authority control: 1) Herbicides containing ethofumesate, phenmedipham, desmedipham, terbuthylazine and pyridate. 2) Fungicides containing tebuconazole. 3) Insecticides containing buprofezin, chlorpyrifos and dimethoate. 4) Rodenticides containing brodifacoum and difenacoum. Active ingredients were mainly selected among those where products in the last decade were found not to comply with the accepted limits of content. All products were examined for the content of the active ingredients.

Satisfactory results were found among herbicides containing pyridate, desmedipham and ethofumesate, among insecticides containing buprofezin, and among rodenticides containing difenacoum. Thus, the seventeen analysed samples of these formulations complied with the accepted tolerances with respect to the content of the respective active ingredient as specified in Danish Statutory Order on pesticides.

One out of the three products containing terbuthylazine did not comply with the tolerance limit for content of this active ingredient. Subsequent contact to the manufacturer revealed that the product had limited shelf life, which did not appear from the label. The limited shelf life is maybe the reason for the low content, but not necessarily.

The content of active ingredient in one of the four products containing dimethoate was found to be outside the tolerance limit. Subsequent contact to the manufacturer revealed that the product controlled was from 1994 which can be the reason.

Two of the six products containing chlorpyrifos were found to be outside the tolerance limit. The contents in the samples were too low compared with the declared content. One product was from 1998, while the manufacturer of the other product admitted that there have been problems with precipitation in the formulation.

One of the four products containing brodifacoum was found to be outside the tolerance limit. The content in the sample was just too low compared with the declared content. Subsequently the company analysed the active ingredient to be just within the tolerance limit. No further analyses have been performed.

Two out of the seven products containing phenmedipham and one out of the seven products containing tebuconazole did not comply with the tolerance limits for content of these active ingredients. The contents of active ingredients were too low.

On seven products the contents of active ingredient were declared only in g/L, but not in w/w % as required by the Statutory Order. Declared content expressed in % (w/w) did not agree with the content expressed in g/L on labels of two products containing chlorpyrifos.

4 References

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Appendix I

Samples of pesticide formulations collected from the Danish market for authority control in 2002.

Table 1 Herbicides

1.1.1.1.1Active ingredient	1.1.1.1.2Product	Formulation type ¹⁾	1.1.1.1.3Company	NERI sample no.
Desmedipham	Betanal optima SC	SC	AgrEvo	02-0316
Desmedipham	Kemifam Pro SC	SC	AgroDan A/S	02-0317
Ethofumesate	IT-Ethofumesat	SC	Inter-Trade Aalborg A/S	02-0294
Ethofumesate	Ethosan	SC	KVK Agro A/S	02-0313
Ethofumesate	Betanal optima SC	SC	AgrEvo	02-0316
Ethofumesate	Kemifam Pro SC	SC	AgroDan A/S	02-0317
Ethofumesate	Ethofol 500 SC	SC	AgroDan A/S	02-0323
Ethofumesate	Nortron SC	SC	KVK Agro A/S	02-0324
Ethofumesate	IT-Ethofumesat	SC	Inter-Trade Aalborg A/S	02-0325
Ethofumesate	IT-Ethofumesat 50	SC	Inter-Trade Aalborg A/S	02-0432
Ethofumesate	LFS ethofumesat	SC	LFS Kemi	02-0433
Ethofumesate	Spar 2	SC	KVK Agro A/S	02-0435
Phenmedipham	Betanal Classic	SC	KVK Agro A/S	02-0295
Phenmedipham	Herbasan	SC	KVK Agro A/S	02-0296
Phenmedipham	ND Betafam	SC	NEDAB Aps	02-0314
Phenmedipham	Betasana 2000	SC	AgroDan A/S	02-0315
Phenmedipham	Betanal optima SC	SC	AgrEvo	02-0316
Phenmedipham	Kemifam Pro SC	SC	AgroDan A/S	02-0317
Phenmedipham	Spar 2	SC	KVK Agro A/S	02-0435
Pyridate	Lido 410 SC	SC	Novartis A/S	02-0298
Terbuthylazine	Lido 410 SC	SC	Novartis A/S	02-0298
Terbuthylazine	Inter-Terbuthylazin	SC	Inter-Trade Aalborg A/S	02-0299
Terbuthylazine	Laddok TE	SC	BASF A/S	02-0300

1) SC: suspension concentrate.

Table 2 Fungicides

Active ingredient	Product	Formulation type ¹⁾	Company	NERI sample no.
Tebuconazole	Folicur EW 250	EW	Bayer A/S	02-0297
Tebuconazole	Gori 22	AL	S. Dyrup & Co. A/S	02-0430
Tebuconazole	Gori 22/7	AL	S. Dyrup & Co. A/S	02-0431
Tebuconazole	Solignum Trægrender	AL	Brifa Maling A/S	02-0612
Tebuconazole	Hempitox 6722	AL	J.C.Hempel	02-0717
Tebuconazole	SECU, Type 010	AL	Larco Farve- & lakfabrik	02-0718

1) AL: any other liquid; EW: emulsion, oil in water.

Table 3 Insecticides

Active ingredient	Product	Formulation type ¹⁾	Company	NERI sample no.
Buprofezin	Applaud 40 SC	SC	Cillus A/S	02-0611
Chlorpyrifos	TanacoUniversal Insektmiddel RTU	CS	Tanaco Danmark A/S	02-0293
Chlorpyrifos	Baygon utojslokkedåse	PB	Bayer A/S	02-0321
Chlorpyrifos	Mortalin Insektlak	LA	Mortalin Produktion A/S	02-0322
Chlorpyrifos	Gett Hjem	CS	Dow Elanco	02-0663
Chlorpyrifos	Pageant M	CS	Dow Elanco	02-0664
Chlorpyrifos	Tanaco Insektlak	LA	Tanaco Danmark A/S	02-0719
Dimethoate	SweDane	EC	AgroDan A/S	02-0301
Dimethoate	Danadim	EC	Cheminova A/S	02-0302
Dimethoate	Perfektion 500S	EC	BASF A/S	02-0303
Dimethoate	Perfekthion EC	EC	BASF Danmark A/S	02-0614

1) EC: emulsifiable concentrate; CS: capsule suspension; LA: lacquer; SC: suspension concentrate; PB: plate bait.

Table 3 Rodenticides

Active ingredient	Product	Formulation type ¹⁾	Company	NERI sample no.
Brodifacoum	Brodifacoum Pasta mod mus	CL	Rentokil Initial A/S	02-0428
Brodifacoum	Klerat Voksblok	BB	Zeneca Agro A/S	02-0604
Brodifacoum	Klerat voksblok	BB	Trinol A/S	02-0606
Brodifacoum	Klerat Pellets	GB	Trinol A/S	02-0607
Difenacoum	Ridak	AB	Trinol A/S	02-0292
Difenacoum	Rentokil Difenard mod rotter	CL	Rentokil Initial A/S	02-0427
Difenacoum	Musekorn	AB	Matas	02-0429

1) CL: contact liquid or gel; BB: block bait; GB: granular bait; AB: grain bait

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