

CRL for cereals

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Danish Institute for Food and Veterinary Research

Danish Institute for Food and Veterinary Research

- Governmental research institute
- Danish Ministry of Family and Consumer Affairs
- Additionally 2 CRL
 - Antibiotic resistance
 - Fish diseases



Department for Food Chemistry

- Bio toxins
- Package Materials
- Environmental and Process Contaminants
- Metal and Minerals
- Nutritional factors and Vitamins
- Veterinary drugs
- Pesticides
- Aprox. 50 employees

Pesticide group



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Activities related to pesticides residues

- Scientific investigations
- Scientific and technical advisors
- Method development and validation
- National Reference Laboratory and CRL

Control and monitoring programmes for pesticides

- Drawing up annual control project plans
- Develop methods used in the monitoring program
- Reference Laboratory
- MRL setting

Scientific investigations

- Effects of exposure to specific pesticides or a combination of pesticides
 - Cooperation with toxicologists
 - Measuring feeds and residues in plasma or milk
- Intake calculations – Risk Assessment
 - Safe Foods
 - Processing factors
- ISAFRUIT
 - Pre and post harvest treatment
- External funding

Instruments

- 9 GC systems selective detectors,
- 8 GC/MS systems (iontraps, quadropols, sector)
- 9 HPLC-systems
- 11 LC/MS/MS systems
- 2 ICP/MS system
- Other mayor equipments
 - spectrophotometers, evaporating systems, freeze driers, minus 80°C freezers and one system for cryogenic homogenisation with liquid nitrogen
- Pesticide group:
 - 2 GC systems with selective detectors,
 - 2 GC/MS systems
 - 1 GC/MS/MS
 - 2 LC/MS/MS

Accredited methods

- Cereals
 - by GC with EC-, NP- and/or by MS detection and LC-MS/MS.
- Fruit and vegetables
 - by GC with EC-, NP- and /or MS detection and LC-M/MS
- Meat and fatty matrices
 - by GC with EC-, NP- and/or by MS detection
- Chlormequat and mepiquat in cereals
 - by LC-MS/MS
- Chlormequat in pears, carrots, tomato and mushrooms
 - by LC-MS/MS
- Glyphosate in cereals
 - by LC-MS/MS

Other methods

- QuEChERS
- Strobilurin fungicides in cereals and fruit
- Prochloraz in rat mothers milk
- Pesticides and degradation products in rat serum
- Chlormequat in sow milk and serum
- Imazalil in fruit and vegetables by Gas Chromatography
- Benomyl, carbendazim, thiophanat-methyl, thiabendazole, diphenyl and phenylphenol (ortho) in fruit and vegetables by HPLC
- Dithiocarbamates in fruit and vegetables

2006 – Workprogramme

- Proficiency tests – preparation for 2007
 - field spraying of wheat
 - online result submission website
- Workshop and training course for NRLs
 - Stuttgart from 6-7 December 2006
- Preparing guidelines
 - No activity
- Scientific assistance to Commission
 - Advise in relation to the Coordinated Monitoring Programme
- Technical assistance to Commission
 - Advise in relation CODEX proposal on estimation of uncertainty

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Method development 2006 (1)

- Extension of the pesticide profile for the cereal LC/MS/MS multimethod with approx. 100 pesticides
- Precursor ion and two product ions
 - 2,4-D, Acibenzolar-S-methyl, Aclonifen, Acrinathrin, Amitraz, Amitrole (Aminotriazole), Azimsulfuron, Azocyclotin, Benfuracarb, Bentazone, Binapacryl, Bitertanol, Bromoxynil, Bupirimat, Buprofenzin, Chlordane, Chlorfenapyr, 4-Chlorophenoxyacetic acid, Chlorthal-dimethyl, Cinidon-ethyl, Clethodim, Clodinafoppropargyl, Clomazone, Clopyralid, Cyazofamid, Cycloxydim, Cyhalofop-butyl, Cyhexatin, Cyromazine, Daminozide, Dementon-S-methyl sulfoxid, Demeton-S-methyl, Demeton-S-methyl sulfon, Dicamba, Dichlofenthion, Dichlorprop, Dichlorprop-P, Dicofol, Diethofencarb, Dimethomorph, Dinoterb, DNOC, Epoxiconazol, Ethofumesate, Ethoxyquin, Etridiazole, Famoxadone, Fenamiphos, Fenazaquin, Fentin acetat, Fentin hydroxide, Fluazifop-p-butyl, Flumioxazin, Fluoxastrobin, Flupyrsulfuron-methyl (-Sodium), Fluroxypyr, Flusilazole, Flutolanil.....

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Method development 2006 (2)

- Validation of QuEChERS method for cereals for approx. 85 pesticides – 4 matrices
- 85 pesticides GC/MS
- wheat, rye, rice and oats
- 0.01 – 0.2 mg/kg
- PolarisQ iontrap

GC/MS/MS

- MRM for a number of pesticides on GC/MS/MS
 - Precursor ion and two product ions

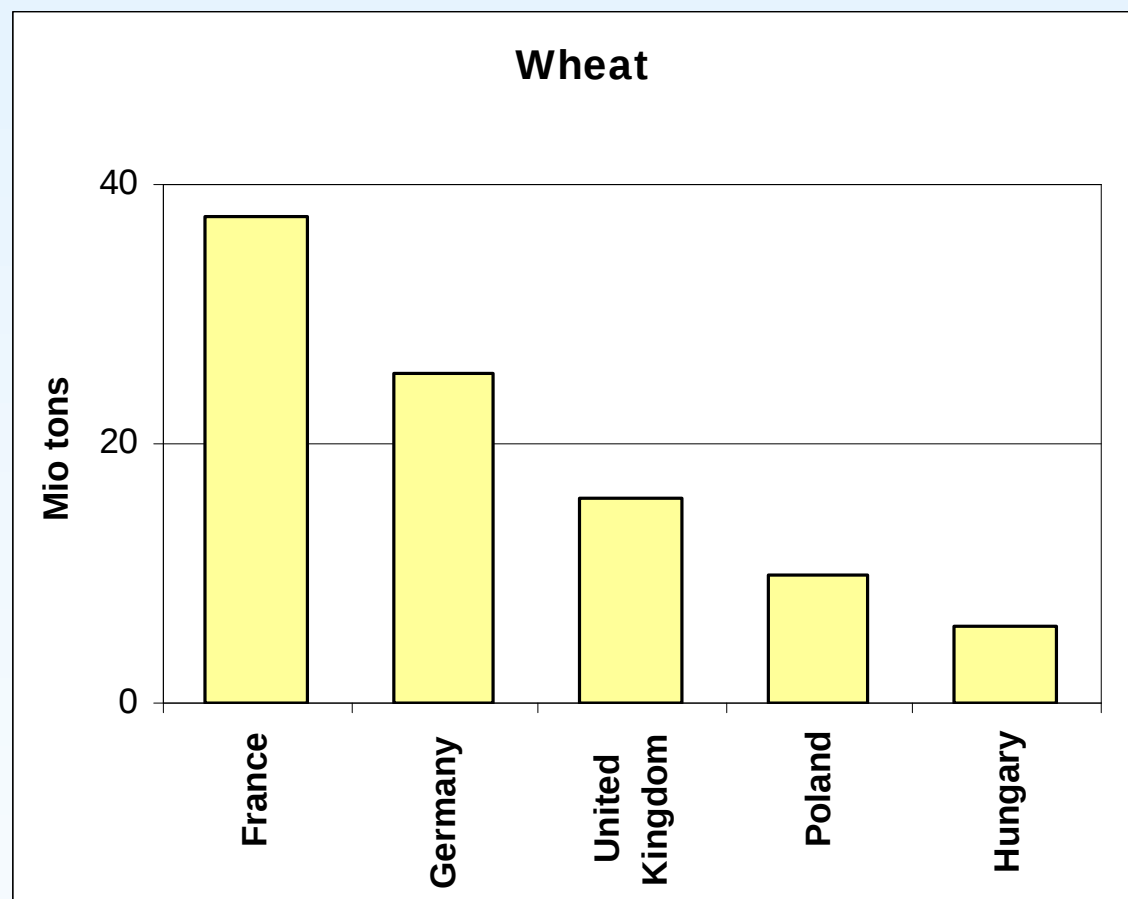


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Preparation for future method development

- Collection and evaluation of information to support the prioritization of method development projects

Production of cereals



Approved pesticides for cereal

- A list of which pesticides are authorised for use in the member states are available on circa website.
 - doesn't include information on which crops the pesticides are authorised for.
- Information collected by the Danish Institute for Agricultural Science
- Data covers only Northern and Central Europe (17 MS)
- Additionally information from France is collected from homepage of Ministry of Agriculture and Fisheries

Fungicides

- 
- > 14 MS (7)
 - Azoxystrobin
 - Epoxiconazole
 - Fenpropimorph
 - Kresoxim-methyl
 - Prochloraz
 - Propioconazole
 - Spiroxamin
 - Trifloxystrobin

Fungicides

● 14 > x > 9 (15)

- Carbendazim
- Carboxin
- Chlorothalonil
- Cyproconazole
- Difenconazole
- Fenpropidin
- Fludioxonil
- Flutriafol
- Guazatine
- Kresoxim-methyl
- Metconazole
- Prothioconazole
- Tebuconazole
- Triadimenol
- Triticonazole

Herbicide

● > 14 MS (9)

- 2,4-D
- Amidosulfuron
- Dichlorprop-P
- Fenoxaprop-P
- Florasulam
- Fluroxypyr
- Iodosulfuron-methyl-sodium
- MCPA
- Mecoprop-p
- Sulfosulfuron

● 14>x> 9 (11)

- Carfentrazone-ethyl
- Dicamba
- Diflufenican
- Flupyrsulfuron methyl
- Glyphosate
- Isoproturon
- Pendimethalin
- Propoxycarbazone
- Thifensulfuron
- Triasulfuron
- Tribenuron

Insecticides

● > 14 MS

● 14 > x > 9

- Alpha-cypermethrin
- Deltamethrin
- Lambda-Cyhalothrin

Plant growth regulators

● > 14 MS

- Chlormequat

● $14 < x < 9$

- Ethephon
- Trinexapac

Consumption of cereals

● Denmark

Consumption (g/person/day)	Cereals	Wheat	Rye	Oat	Rice
Adult (74 kg bw)	214	149	50	8.5	6.4
Children (22 kg bw)	229	121	97	8.7	2.3

● The Netherlands

Consumption (g/person/day)	Cereals	Wheat	Barley	Rice	Rye	Oat	Maize
General population (63 kg bw)	175	131	24	10	4.4	2.0	3.0
Children 1-6 years (17 kg bw)	96	81	0.4	6.0	3.1	1.8	2.5

Consumption of cereals

UK

Consumption (g/person/day)	Cereals	Wheat	Rice	Oat	Barley
Adults (70.1 kg bw)	151	140	6	3	2.3
Young children (14.5 kg bw)	61	54	4.2	2.8	

Germany

Consumption (g/person/day)	Cereals	Wheat	Rice	Oat	Maize	Barley
Children Age 2-5 (16 kg bw)	90	67	4	3	2.4	0.2

Residues in Cereals 2004

- 2719 surveillance samples were analysed
- No residues were detected in 70 %
- Residues at or below the MRL in 29 %
- Residues exceeding the MRL in 1.1 %
- 3 countries did not report any residue data
- Most frequently found pesticides were insecticides:
 - Pirimiphos-methyl, Malathion, Chlorpyrifos-methyl, Chlormequat, Deltamethrin, Chlorpyrifos, Glyphosate, Bromides, Dichlorvos and Mepiquat

Intake from cereals

- Results from the Danish Monitoring program

	Intake ($\mu\text{g/day}$)	Sum of Hazard Quotients in %
Cereals	25	0.65%
Wheat bread	16	0.34%
Rye bread	5.2	0.20%
Rolled oats	3.0	0.07%
Pasta product	0.2	0.02%
Rice, white	0.21	0.01%
Wheat bran	0.3	0.01%

Proficiency test 2007

- PLAN!
- PT-C1
 - Invitation – December 2006
 - 'possible pesticides list'
 - Approximately 45 pesticides to be sought for –
 - Approximately 10 pesticides incurred or spiked
 - 2 single residues methods
 - Sample Distribution – End of March 2007
 - Deadline for receiving results. End of April
 - Preliminary result on the Workshop in 2007
- Accreditation for providers of Proficiency Testing Schemes

Method development 2007

- Extension of the pesticide profile for the cereal multimethod on GC
- Extending of the pesticide profile of QuEChERS method for cereals
- MRM for GC/MS/MS instrument
- Interlaboratory method validation on glyphosate method
- Collection and evaluation of information to support the prioritization of method development projects

Questions from us to you

- Questionnaire for the NRL
 - Which pesticides are approved for cereals, especially MS in Southern Europe
 - Consumption of cereal
 - Scope of methods
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The Technical University of Denmark

- Merged into the Technical University of Denmark by 1 January 2007
 - 7,000 students and almost 4,000 employees.
 - A leading international university
 - Broadly founded, business-oriented technical elite university where research goes hand in hand with education, innovation and **advisory functions for government authorities**