CRL for cereals

Mette Erecius Poulsen,
Hanne Bjerre Christensen and Susan Herrmann
6 December 2006
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
Activities related to pesticides residues

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

Danish Institute for Food and Veterinary Research
Control and monitoring programmes for pesticides

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

Danish Institute for Food and Veterinary Research
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

Danish Institute for Food and Veterinary Research
Instrument

- 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
- Procloraz 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

Danish Institute for Food and Veterinary Research
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, Cinidion-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, Etoxyquin, Etridiazole, Famoxadone, Fenamiphos, Fenazaquin, Fentin acetat, Fentin hydroxide, Fluazifop-p-butyl, Flumioxazin, Fluoxastrobin, Flupyr-sulfuron-methyl (-Sodium), Fluroxypyr, Flusilazole, Flutolanil
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
Preparation for future method development

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

Danish Institute for Food and Veterinary Research
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
- Difenoconazole
- Fenpropidin
- Fludioxonil
- Flutriafol

- Guazatine
- Kresoxim-methyl
- Metconazole
- Prothioconazole
- Tebuconazole
- Triadimenol
- Triticonazol

Danish Institute for Food and Veterinary Research
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

Danish Institute for Food and Veterinary Research
Insecticides

- > 14 MS
- 14 > x > 9
  - Alpha-cypermethrin
  - Deltamethrin
  - Lambda-Cyhalothrin

danish institute for food and veterinary research
Plant growth regulators

- > 14 MS
  - Chlormequat

- 14<x< 9
  - Ethephon
  - Trinexapac
## Consumption of cereals

### Denmark

<table>
<thead>
<tr>
<th></th>
<th>Cereals</th>
<th>Wheat</th>
<th>Rye</th>
<th>Oat</th>
<th>Rice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adult (74 kg bw)</td>
<td>214</td>
<td>149</td>
<td>50</td>
<td>8.5</td>
<td>6.4</td>
</tr>
<tr>
<td>Children (22 kg bw)</td>
<td>229</td>
<td>121</td>
<td>97</td>
<td>8.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

### The Netherlands

<table>
<thead>
<tr>
<th></th>
<th>Cereals</th>
<th>Wheat</th>
<th>Barley</th>
<th>Rice</th>
<th>Rye</th>
<th>Oat</th>
<th>Maize</th>
</tr>
</thead>
<tbody>
<tr>
<td>General population (63 kg bw)</td>
<td>175</td>
<td>131</td>
<td>24</td>
<td>10</td>
<td>4.4</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Children 1-6 years (17 kg bw)</td>
<td>96</td>
<td>81</td>
<td>0.4</td>
<td>6.0</td>
<td>3.1</td>
<td>1.8</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Danish Institute for Food and Veterinary Research
## Consumption of cereals

### UK

<table>
<thead>
<tr>
<th>Consumption (g/person/day)</th>
<th>Cereals</th>
<th>Wheat</th>
<th>Rice</th>
<th>Oat</th>
<th>Barley</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adults (70.1 kg bw)</td>
<td>151</td>
<td>140</td>
<td>6</td>
<td>3</td>
<td>2.3</td>
</tr>
<tr>
<td>Young children (14.5 kg bw)</td>
<td>61</td>
<td>54</td>
<td>4.2</td>
<td>2.8</td>
<td></td>
</tr>
</tbody>
</table>

### Germany

<table>
<thead>
<tr>
<th>Consumption (g/person/day)</th>
<th>Cereals</th>
<th>Wheat</th>
<th>Rice</th>
<th>Oat</th>
<th>Maize</th>
<th>Barley</th>
</tr>
</thead>
<tbody>
<tr>
<td>Children Age 2-5 (16 kg bw)</td>
<td>90</td>
<td>67</td>
<td>4</td>
<td>3</td>
<td>2.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>
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, Chlorpyriphos-methyl, Chlormequat, Deltamethrin, Chlorpyriphos, Glyphosate, Bromides, Dichlorvos and Mepiquat

Danish Institute for Food and Veterinary Research
# Intake from cereals

- **Results from the Danish Monitoring program**

<table>
<thead>
<tr>
<th>Cereals</th>
<th>Intake (µg/day)</th>
<th>Sum of Hazard Quotients in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cereals</td>
<td>25</td>
<td>0.65%</td>
</tr>
<tr>
<td>Wheat bread</td>
<td>16</td>
<td>0.34%</td>
</tr>
<tr>
<td>Rye bread</td>
<td>5.2</td>
<td>0.20%</td>
</tr>
<tr>
<td>Rolled oats</td>
<td>3.0</td>
<td>0.07%</td>
</tr>
<tr>
<td>Pasta product</td>
<td>0.2</td>
<td>0.02%</td>
</tr>
<tr>
<td>Rice, white</td>
<td>0.21</td>
<td>0.01%</td>
</tr>
<tr>
<td>Wheat bran</td>
<td>0.3</td>
<td>0.01%</td>
</tr>
</tbody>
</table>

Danish Institute for Food and Veterinary Research
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

Danish Institute for Food and Veterinary Research
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
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

Danish Institute for Food and Veterinary Research