QUALITY CONTROL OF THE REMAINING STOCKS OF PESTICIDES FORMULATIONS AFTER THE 2003-2005 DESERT LOCUST UPSURGE IN NORTHERN AND WESTERN AFRICA

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Agriculture and Natural Environment Department
Plant Protection Products and Biocides Physico-chemistry and Residues Unit
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Contribution of CRA-W : Quality Control

By applying for a tender offer!

Unit 10 of CRA-W
Plant Protection Products and Biocides
Physico-chemistry and Residues Unit

- Long experience in pesticides physico-chemistry and residues
- WHO Collaborating Centre for QC of pesticides
- Support in activities of FAO, WHO, CIPAC …

GLP Certified
ISO 17025 Accredited
Origin of samples

13 Desert Locust affected Africa countries concerned
What does pesticide quality control involve?

According to FAO specifications
Contribution of CRA-W : Quality Control

Pesticide quality control : things are not easy as they seem …

Use of methods from:
- CIPAC when available…
- Agrochemical companies…

Sometimes need of optimisation of existing methods

Development of new suitable method

Can be expensive and time consuming
Samples analyzed in 2007-2008

3 countries: Mauritania, Mali & Senegal

- 68 chlorpyrifos
- 10 malathion
- 04 fenitrothion
- 01 diflubenzuron

- 73 chlorpyrifos
- 03 malathion
- 04 fenitrothion
- 01 diflubenzuron

- 22 chlorpyrifos
- 12 deltamethrin
- 08 diflubenzuron
- 01 malathion
- 01 fenitrothion
- 45 esfenvalerate + fenitrothion

Results presented at the 2008 CIPAC Symposium
# Summary of results of 2007-2008 analysis

**MAURITANIA : 83 samples analyzed**

<table>
<thead>
<tr>
<th>Samples</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>68 chlorpyrifos</td>
<td>47 C</td>
<td>21 NC</td>
</tr>
<tr>
<td>10 malathion</td>
<td>0 C</td>
<td>10 NC</td>
</tr>
<tr>
<td>4 fenitrothion</td>
<td>0 C</td>
<td>4 NC</td>
</tr>
<tr>
<td>1 diflubenzuron</td>
<td>0 C</td>
<td>1 NC</td>
</tr>
</tbody>
</table>

C : Compliant with FAO specifications

NC : Not Compliant with FAO specifications
Summary of results of 2007-2008 analysis

MALI : 89 samples analyzed

<table>
<thead>
<tr>
<th>Samples</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 esfenvalerate + fenitrothion</td>
<td>45 C</td>
<td>0 NC</td>
</tr>
<tr>
<td>22 chlorpyrifos</td>
<td>14 C</td>
<td>8 NC</td>
</tr>
<tr>
<td>12 deltamethrin</td>
<td>8 C</td>
<td>4 NC</td>
</tr>
<tr>
<td>8 diflubenzuron</td>
<td>5 C</td>
<td>3 NC</td>
</tr>
<tr>
<td>1 malathion</td>
<td>0 C</td>
<td>1 NC</td>
</tr>
<tr>
<td>1 fenitrothion</td>
<td>0 C</td>
<td>1 NC</td>
</tr>
</tbody>
</table>

C : Compliant with FAO specifications

NC : Not Compliant with FAO specifications
## Summary of results of 2007-2008 analysis

**SENEGAL : 81 samples analyzed**

<table>
<thead>
<tr>
<th>Samples</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>73 chlorpyrifos</td>
<td>59 C</td>
<td>14 NC</td>
</tr>
<tr>
<td>4 fenitrothion</td>
<td>3 C</td>
<td>1 NC</td>
</tr>
<tr>
<td>3 malathion</td>
<td>0 C</td>
<td>3 NC</td>
</tr>
<tr>
<td>1 diflubenzuron</td>
<td>0 C</td>
<td>1 NC</td>
</tr>
</tbody>
</table>

**C : Compliant with FAO specifications**

**NC : Not Compliant with FAO specifications**
### Summary of results of 2007-2008 analysis

Total for the 3 countries: 253 samples analyzed

<table>
<thead>
<tr>
<th>Samples</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>163 chlorpyrifos</td>
<td>120 C</td>
<td>26%</td>
</tr>
<tr>
<td>45 esfenvalerate + fenitrothion</td>
<td>45 C</td>
<td>0%</td>
</tr>
<tr>
<td>14 malathion</td>
<td>0 C</td>
<td>100%</td>
</tr>
<tr>
<td>12 deltamethrin</td>
<td>8 C</td>
<td>33%</td>
</tr>
<tr>
<td>10 diflubenzuron</td>
<td>5 C</td>
<td>50%</td>
</tr>
<tr>
<td>9 fenitrothion</td>
<td>3 C</td>
<td>67%</td>
</tr>
</tbody>
</table>

**C**: Compliant with FAO specifications = 71%

**NC**: Not Compliant with FAO specifications = 29%
Other countries analysed in 2008
New samples analysed in 2009-2010

101 samples from Niger & Morocco analysed in 2008
90 samples from Mauritania, Mali & Senegal reanalysed in 2009-2010

58 chlorpyrifos
09 deltamethrin
18 malathion

37 chlorpyrifos

31 chlorpyrifos

06 chlorpyrifos
03 deltamethrin
05 lambda-cyhalothrin
02 tralomethrin

03 chlorpyrifos
04 diflubenzuron
15 fenitrothion
+ esfenvalerate
Analysis of 191 samples from Niger, Morocco, Mauritania, Mali & Senegal

Quality Control according to FAO specifications
Chlorpyrifos

FAO specification 221/UL (October 2004)

- Chlorpyrifos content
  before storage
  ± 5% or 6% of the declared content
  [depending on a.i. content (450, 240 or 225 g/L)]
  after storage at 54°C for 14 days
  minimum 95% of the content before storage

- Impurity content
  before storage
  sulfotep: maximum 3 g/kg (0.3%) of the chlorpyrifos content
Deltamethrin

FAO specification 333/UL (April 2006)

- Deltamethrin content before storage
  ± 15% of the declared content (for deltamethrin 12.5 and 17.5 g/L UL)
- after storage at 54°C for 14 days
  minimum 95% of the content before storage
Deltamethrin

FAO specification 333/EC (May 2005)

- Deltamethrin content
  before storage
  ± 15% of the declared content (for deltamethrin 12.5 g/L EC)
  after storage at 54°C for 14 days
  minimum 95% of the content before storage

- Emulsion stability and re-emulsification

<table>
<thead>
<tr>
<th>Time after dilution</th>
<th>Limits of stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
<td>Initial emulsification complete</td>
</tr>
<tr>
<td>0.5 h</td>
<td>&quot;Cream&quot;, none</td>
</tr>
<tr>
<td>2.0 h</td>
<td>&quot;Cream&quot;, maximum : 1 mL &quot;Free Oil&quot;, none</td>
</tr>
<tr>
<td>24 h</td>
<td>Re-emulsification complete</td>
</tr>
<tr>
<td>24.5 h</td>
<td>&quot;Cream&quot;, none &quot;Free Oil&quot;, none</td>
</tr>
</tbody>
</table>
Lambda-cyhalothrin


- Lambda-cyhalothrin content before storage
  ± 10% of the declared content
  for lambda-cyhalothrin 50 g/L EC
  after storage at 54°C for 14 days
  minimum 95% of the content before storage

- Emulsion stability and re-emulsification

<table>
<thead>
<tr>
<th>Time after dilution</th>
<th>Limits of stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
<td>Initial emulsification complete</td>
</tr>
<tr>
<td>0.5 h</td>
<td>&quot;Cream&quot;, maximum : 1 mL</td>
</tr>
<tr>
<td>2.0 h</td>
<td>&quot;Cream&quot;, maximum : 2 mL  &quot;Free Oil&quot;, maximum : trace</td>
</tr>
<tr>
<td>24 h</td>
<td>Re-emulsification complete</td>
</tr>
<tr>
<td>24.5 h</td>
<td>&quot;Cream&quot;, maximum : 2 mL  &quot;Free Oil&quot;, maximum : trace</td>
</tr>
</tbody>
</table>
Malathion

FAO specification 12/UL (December 2004)

- Malathion content
  before storage and after storage at 54°C for 14 days
  Not less than 950 g/kg
  depending on a.i. content (450, 240 or 225 g/L)

- Impurities content
  before and after storage at 54°C for 14 days
  malaoxon: maximum 0.1% of the malathion content
  isomalathion: maximum 0.4% of the malathion content
  Me-OOSPS: maximum 1.6% of the malathion content
  Me-OOOPS: maximum 0.5% of the malathion content
Diflubenzuron

No FAO specification for UL and OF

Tralomethrin

No FAO specification

→ Use of the general specifications of the FAO/WHO Manual
Fenitrothion + esfenvalerate

No FAO specification for mai-formulations

→ Use of specification for each a.i. when existing

Fenitrothion

FAO specification 35/UL

Esfenvalerate

No FAO specification
Fenitrothion content
before storage
± 5% of the declared content
for fenitrothion 500 g/L UL
after storage at 54°C for 14 days
minimum 95% of the content before storage

Impurity content
before and after storage at 54°C for 14 days
S-methyl fenitrothion: maximum 20 g/kg (2.0%) of the fenitrothion content
TMPP: maximum 3 g/kg (0.3%) of the fenitrothion content
(not analysed)
Methods for active substances

**Chlorpyrifos**: CIPAC method 221/UL/M/3, CIPAC Handbook K, pg. 23
Reversed Phase HPLC-DAD after dissolution into acetonitrile

**Deltamethrin**: CIPAC method 333/UL/M/3, CIPAC Handbook L, pg. 45
Normal Phase HPLC-DAD after dissolution into isooctane / dioxane (80/20)

**Diflubenzuron**: CIPAC method 339/TK/M/3, CIPAC Handbook H, pg. 141
(adapted by the Unit 10 of CRA-W)
Reversed Phase HPLC-DAD after dissolution into dioxane and dilution into acetonitrile
Methods for active substances

**Fenitrothion + esfenvalerate:**
Method developed by the Unit 10 of CRA-W
Normal Phase HPLC-DAD after dissolution into isooctane / dioxane (80/20)

**Lambda-cyhalothrin:**
CIPAC method 463/EC/M/3, CIPAC Handbook K, pg. 86
GC-FID after dissolution into acetone containing dicyclohexylphthalate as internal standard

**Malathion:**
CIPAC method 12/TC/(M3)/3, CIPAC Handbook K, pg. 89
GC-FID after dissolution into tetrahydrofuran containing docosane as internal standard

**Tralomethrin:**
Method developed by the Unit 10 of CRA-W
Normal Phase HPLC-DAD after dissolution into isooctane / dioxane (80/20)
Methods for impurities

Sulfotep in chlorpyrifos: Dow AgroSciences method DAS-AM-01-058 GC-FID after adding of water and dissolution into iso-octane

S-methyl fenitrothion in fenitrothion/esfenvalerate: CIPAC method 35/EC/m3/4 Normal Phase HPLC-DAD after dissolution into dichloromethane

Malaoxon in malathion: Cheminova method VAM 008-02 Reversed phase HPLC-DAD after dissolution into acetonitrile / water (75/25)

Isomalathion in malathion: Cheminova method VAM 005-03 Reversed phase HPLC-DAD after dissolution into acetonitrile / water (75/25)

MeOOSPS-triester & MeOOOPS-triester in malathion: Cheminova method VAM 206-01 (adapted by the Unit 10 of CRA-W) GC-MS (instead of GC-FID) after dissolution into acetonitrile
Other methods

Accelerated storage stability
CIPAC method MT 46.3, CIPAC Handbook J, pg. 128
14 days at 54°C in a closed glass bottle

Density at 20°C ± 0.5°C
EEC method A.3 published in the Directive 92/69/EE
= CIPAC method MT 3.2.1, CIPAC Handbook F, pg. 13

Emulsion stability and re-emulsification (for EC)
CIPAC method MT 36.1.1, CIPAC Handbook F, pg. 108
Visual method at 5% in CIPAC water A and D at 30°C
Summary of results of 2008 analysis

NIGER : 16 samples analyzed

<table>
<thead>
<tr>
<th>Samples</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 chlorpyrifos UL</td>
<td>6 C</td>
<td>0 NC</td>
</tr>
<tr>
<td>3 deltamethrin UL</td>
<td>3 C</td>
<td>0 NC</td>
</tr>
<tr>
<td>5 lambda-cyhalothrin EC</td>
<td>2 C</td>
<td>3 NC*</td>
</tr>
<tr>
<td>2 tralomethrin UL</td>
<td>2 C</td>
<td>0 NC</td>
</tr>
</tbody>
</table>

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NC : Not Compliant with FAO specifications

* > 1 mL of free oil after 2 hours of standing
Summary of results of 2008 analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>58 chlorpyrifos UL</td>
<td>53 C</td>
<td>5 NC*</td>
</tr>
<tr>
<td>5 deltamethrin UL</td>
<td>5 C</td>
<td>0 NC</td>
</tr>
<tr>
<td>4 deltamethrin EC</td>
<td>4 C</td>
<td>0 NC</td>
</tr>
<tr>
<td>18 malathion UL</td>
<td>0 C</td>
<td>18 NC**</td>
</tr>
</tbody>
</table>

C : Compliant with FAO specifications

NC : Not Compliant with FAO specifications

* Sulfotep content

** Malaoxon content after storage (13 samples)
Isomalathion content before and after storage (18 samples)
## Summary of results of 2009-2010 analysis

**MALI : 22 samples analyzed**

<table>
<thead>
<tr>
<th>Samples</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 chlorpyrifos UL</td>
<td>3 C</td>
<td>0%</td>
</tr>
<tr>
<td>2 diflubenzuron UL</td>
<td>2 C</td>
<td>0%</td>
</tr>
<tr>
<td>2 diflubenzuron OF</td>
<td>2 C</td>
<td>50%</td>
</tr>
<tr>
<td>15 fenitrothion + esfenvalerate UL</td>
<td>11 C</td>
<td>27%</td>
</tr>
</tbody>
</table>

- C : Compliant with FAO specifications
- NC : Not Compliant with FAO specifications

* Diflubenzuron content
** S-methyl fenitrothion content
**MAURITANIA : 37 samples analyzed**

<table>
<thead>
<tr>
<th>Samples</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>37 chlorpyrifos UL</td>
<td>30 C</td>
<td>7 NC*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19%</td>
</tr>
</tbody>
</table>

**C : Compliant with FAO specifications**

**NC : Not Compliant with FAO specifications**

* Chlorpyrifos content before storage
## Summary of results of 2009-2010 analysis

**SENEGAL : 31 samples analyzed**

<table>
<thead>
<tr>
<th>Samples</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>31 chlorpyrifos UL</td>
<td>31 C</td>
<td>0 NC</td>
</tr>
</tbody>
</table>

*C : Compliant with FAO specifications  
NC : Not Compliant with FAO specifications*
5 countries: Mali, Mauritania, Senegal, Morocco & Niger
367 samples analyzed

<table>
<thead>
<tr>
<th>Test items</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>224 chlorpyrifos UL</td>
<td>179 C</td>
<td>45 NC</td>
</tr>
<tr>
<td>3 chlorpyrifos EC</td>
<td>0 C</td>
<td>3 NC</td>
</tr>
<tr>
<td>20 deltamethrin UL</td>
<td>16 C</td>
<td>4 NC</td>
</tr>
<tr>
<td>4 deltamethrin EC</td>
<td>4 C</td>
<td>0 NC</td>
</tr>
<tr>
<td>8 diflubenzuron OF</td>
<td>3 C</td>
<td>5 NC</td>
</tr>
<tr>
<td>2 diflubenzuron UL</td>
<td>2 C</td>
<td>0 NC</td>
</tr>
</tbody>
</table>
### Summary of results for 2007-2008 analysis

<table>
<thead>
<tr>
<th>Test items</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 fenitrothion UL</td>
<td>3 C</td>
<td>50%</td>
</tr>
<tr>
<td>3 fenitrothion EC</td>
<td>0 C</td>
<td>100%</td>
</tr>
<tr>
<td>5 lambda-cyhalothrin EC</td>
<td>2 C</td>
<td>60%</td>
</tr>
<tr>
<td>30 malathion UL</td>
<td>0 C</td>
<td>100%</td>
</tr>
<tr>
<td>2 malathion EC</td>
<td>0 C</td>
<td>100%</td>
</tr>
<tr>
<td>60 fenithrothion + esfenvalerate UL</td>
<td>56 C</td>
<td>7%</td>
</tr>
</tbody>
</table>
Summary of results for 2007-2008 analysis

C : Compliant with FAO specifications = 72 %  
→ Can be used until the end of 2009

NC : Not Compliant with FAO specifications = 28 %  
→ Have to be properly eliminated
Summary of results for 2009-2010 analysis

3 countries: Mali, Mauritania & Senegal
90 samples analyzed

<table>
<thead>
<tr>
<th>Test items</th>
<th>According to FAO specifications</th>
<th>Percent of NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>71 chlorpyrifos UL</td>
<td>65 C 7 NC</td>
<td>10%</td>
</tr>
<tr>
<td>2 diflubenzuron OF</td>
<td>1 C 1 NC</td>
<td>50%</td>
</tr>
<tr>
<td>2 diflubenzuron UL</td>
<td>2 C 0 NC</td>
<td>0%</td>
</tr>
<tr>
<td>15 fenitrothion + esfenvalerate UL</td>
<td>11 C 4 NC</td>
<td>27%</td>
</tr>
</tbody>
</table>
Summary of results for 2009-2010 analysis

C : Compliant with FAO specifications = 87 %
→ Can be used until January – April 2012

NC : Not Compliant with FAO specifications = 13 %
→ Have to be properly eliminated
Thank you for your attention