

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

**The Food and Agricultural Organization
of the United Nations (FAO)**
Mohamed Ammati & Mark Davis

Centre National de la Lutte Antiacridienne, Nouackhot, Mauritania
Amadou Diallo

Walloon Agricultural Research Centre (CRA-W)
Agriculture and Natural Environment Department
Plant Protection Products and Biocides Physico-chemistry and Residues Unit
Olivier Pigeon, Albert Bernes, Bernard de Ryckel & Vanessa Lecocq

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

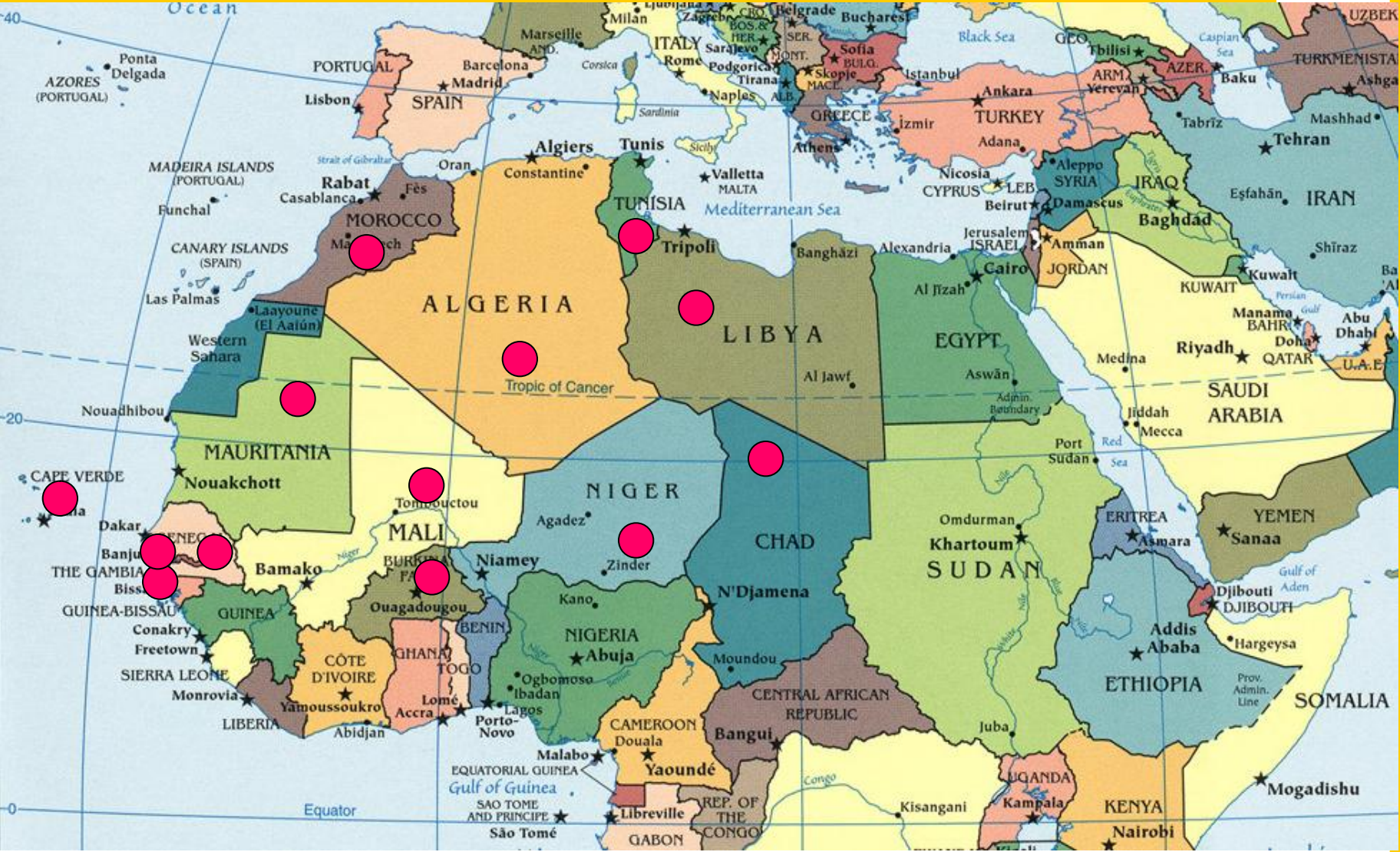
- Long experience in pesticides physico-chemistry and residues
- WHO Collaborating Centre for QC of pesticides
- Support in activities of FAO, WHO, CIPAC ...

GLP Certified

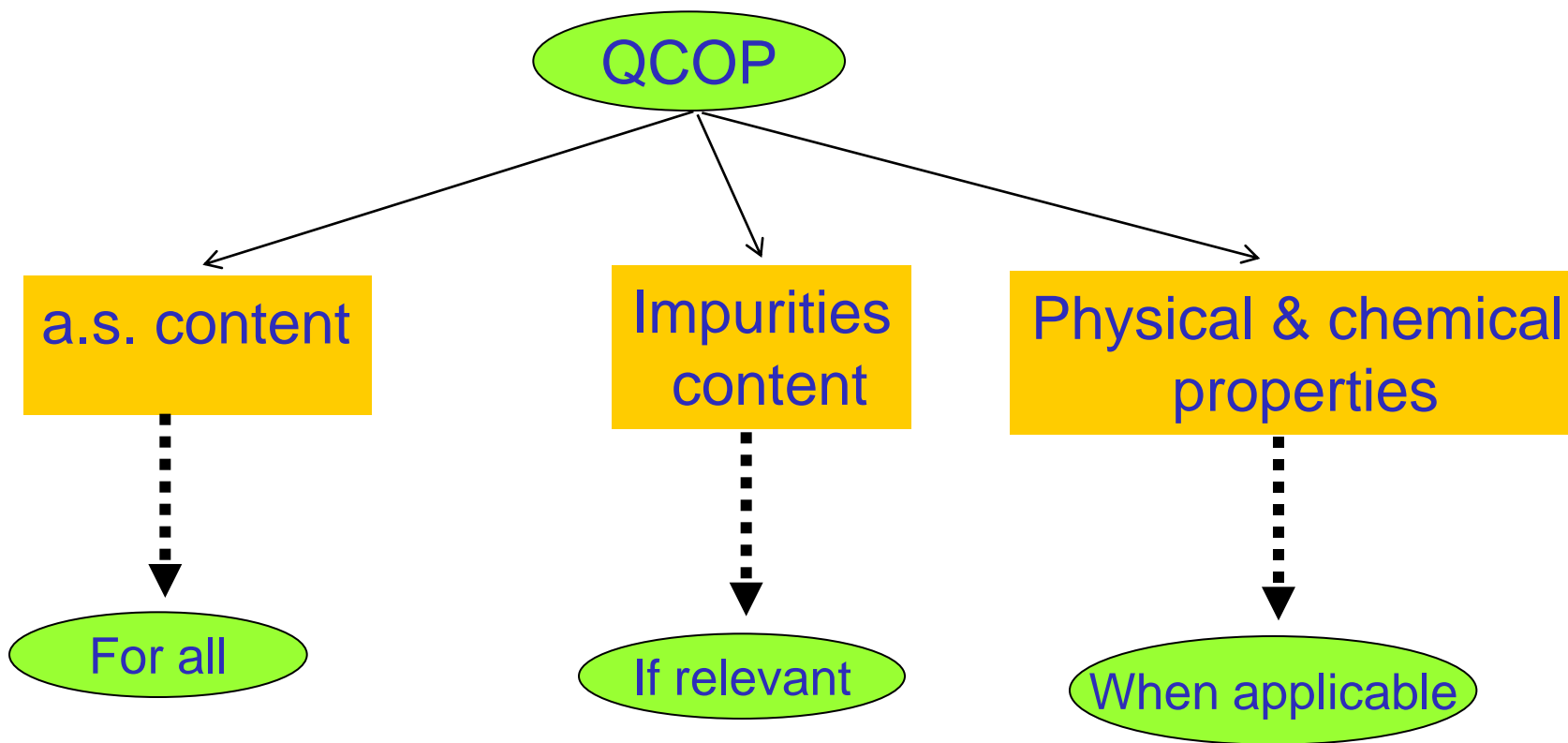
ISO 17025 Accredited

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



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

73 chlorpyrifos
03 malathion
04 fenitrothion
01 diflubenzuron

Results presented at the 2008 CIPAC Symposium

Summary of results of 2007-2008 analysis

MAURITANIA : 83 samples analyzed

Samples	According to FAO specifications		Percent of NC
	C	NC	
68 chlorpyrifos	47 C	21 NC	31%
10 malathion	0 C	10 NC	100%
4 fenitrothion	0 C	4 NC	100%
1 diflubenzuron	0 C	1 NC	100%

C : Compliant with FAO specifications

NC : Not Compliant with FAO specifications

Summary of results of 2007-2008 analysis

MAI : 89 samples analyzed

Samples	According to FAO specifications		Percent of NC
	C	NC	
45 esfenvalerate + fenitrothion	45 C	0 NC	0%
22 chlorpyrifos	14 C	8 NC	36%
12 deltamethrin	8 C	4 NC	33%
8 diflubenzuron	5 C	3 NC	38%
1 malathion	0 C	1 NC	100%
1 fenitrothion	0 C	1 NC	100%

C : Compliant with FAO specifications

NC : Not Compliant with FAO specifications

Summary of results of 2007-2008 analysis

SENEGAL : 81 samples analyzed

Samples	According to FAO specifications		Percent of NC
	C	NC	
73 chlorpyrifos	59 C	14 NC	19%
4 fenitrothion	3 C	1 NC	25%
3 malathion	0 C	3 NC	100%
1 diflubenzuron	0 C	1 NC	100%

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

Samples	According to FAO specifications		Percent of NC
163 chlorpyrifos	120 C	43 NC	26%
45 esfenvalerate + fenitrothion	45 C	0 NC	0%
14 malathion	0 C	14 NC	100%
12 deltamethrin	8 C	4 NC	33%
10 diflubenzuron	5 C	5 NC	50%
9 fenitrothion	3 C	6 NC	67%

C : Compliant with FAO specifications = 71%

NC : Not Compliant with FAO specifications = 29%

Other countries analysed in 2008

New samples analysed in 2009-2010

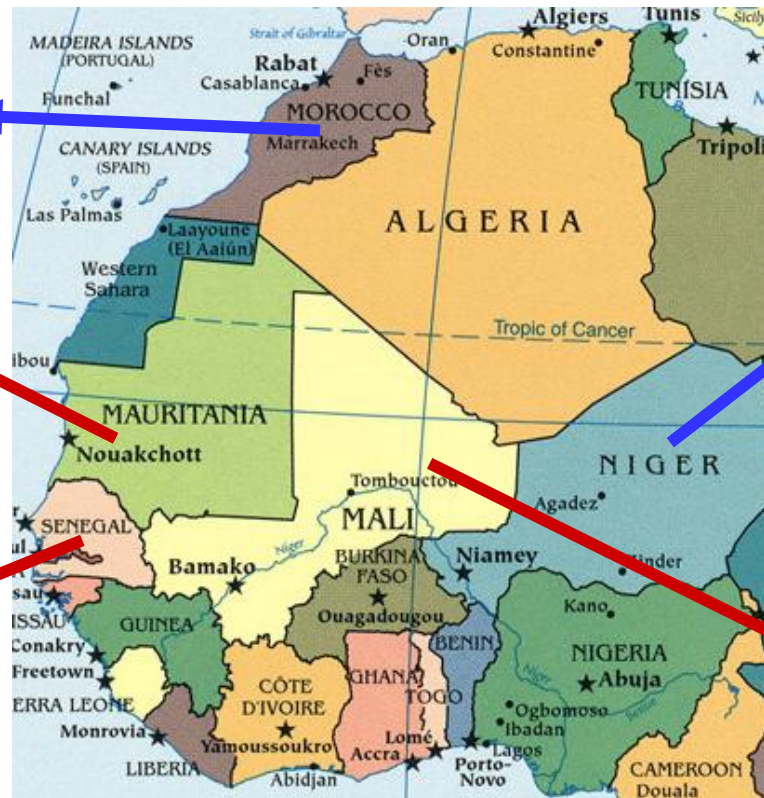
101 samples from Niger & Marocco analysed in 2008

90 samples from Mauritania, Mali & Senegal re-analysed 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, Marocco, 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

Time after dilution	Limits of stability
0 h	Initial emulsification complete
0.5 h	"Cream" , none
2.0 h	"Cream" , maximum : 1 mL "Free Oil" , none
24 h	Re-emulsification complete
24.5 h	"Cream" , none "Free Oil" , none

Lambda-cyhalothrin

FAO specification 463/EC (2003)

- **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**

Time after dilution	Limits of stability
0 h	Initial emulsification complete
0.5 h	"Cream" , maximum : 1 mL
2.0 h	"Cream" , maximum : 2 mL "Free Oil" , maximum : trace
24 h	Re-emulsification complete
24.5 h	"Cream" , maximum : 2 mL "Free Oil" , maximum : trace

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

FAO specification 35/UL (January 2010)

- **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 isooctane

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

Samples	According to FAO specifications		Percent of NC
	C	NC	
6 chlorpyrifos UL	6 C	0 NC	0%
3 deltamethrin UL	3 C	0 NC	0%
5 lambda-cyhalothrin EC	2 C	3 NC*	60%
2 tralomethrin UL	2 C	0 NC	0%

C : Compliant with FAO specifications

NC : Not Compliant with FAO specifications

*** > 1 mL of free oil after 2 hours of standing**

Summary of results of 2008 analysis

MAROCCO : 85 samples analyzed

Samples	According to FAO specifications		Percent of NC
	C	NC*	
58 chlorpyrifos UL	53 C	5 NC*	9%
5 deltamethrin UL	5 C	0 NC	0%
4 deltamethrin EC	4 C	0 NC	0%
18 malathion UL	0 C	18 NC**	100%

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

Samples	According to FAO specifications		Percent of NC
	C	NC	
3 chlorpyrifos UL	3 C	0 NC	0%
2 diflubenzuron UL	2 C	0 NC	0%
2 diflubenzuron OF	2 C	1 NC*	50%
15 fenitrothion + esfenvalerate UL	11 C	4 NC**	27%

C : Compliant with FAO specifications

NC : Not Compliant with FAO specifications

* Diflubenzuron content

** S-methyl fenitrothion content

Summary of results of 2009-2010 analysis

MAURITANIA : 37 samples analyzed

Samples	According to FAO specifications		Percent of NC
	37 chlorpyrifos UL	30 C	7 NC*

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

Samples	According to FAO specifications		Percent of NC
	31 C	0 NC	0%
31 chlorpyrifos UL			

C : Compliant with FAO specifications

NC : Not Compliant with FAO specifications

Summary of results for 2007-2008 analysis

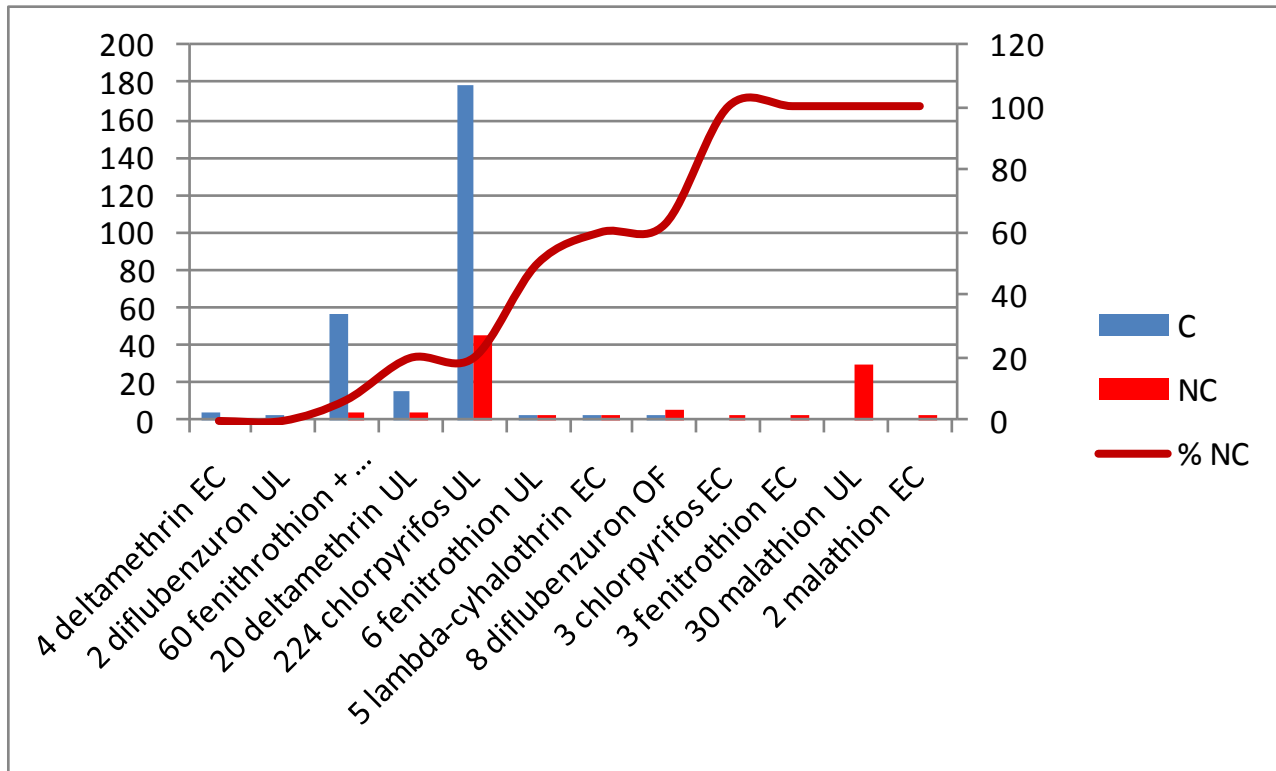
5 countries : Mali, Mauritania, Senegal, Marocco & Niger
367 samples analyzed

Test items	According to FAO specifications		Percent of NC
	224 chlorpyrifos UL	179 C	45 NC
3 chlorpyrifos EC	0 C	3 NC	100%
20 deltamethrin UL	16 C	4 NC	20%
4 deltamethrin EC	4 C	0 NC	0%
8 diflubenzuron OF	3 C	5 NC	63%
2 diflubenzuron UL	2 C	0 NC	0%

Summary of results for 2007-2008 analysis

Test items	According to FAO specifications		Percent of NC
	C	NC	
6 fenitrothion UL	3 C	3 NC	50%
3 fenitrothion EC	0 C	3 NC	100%
5 lambda-cyhalothrin EC	2 C	3 NC	60%
30 malathion UL	0 C	30 NC	100%
2 malathion EC	0 C	2 NC	100%
60 fenithrothion + esfenvalerate UL	56 C	4 NC	7%

Summary of results for 2007-2008 analysis



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

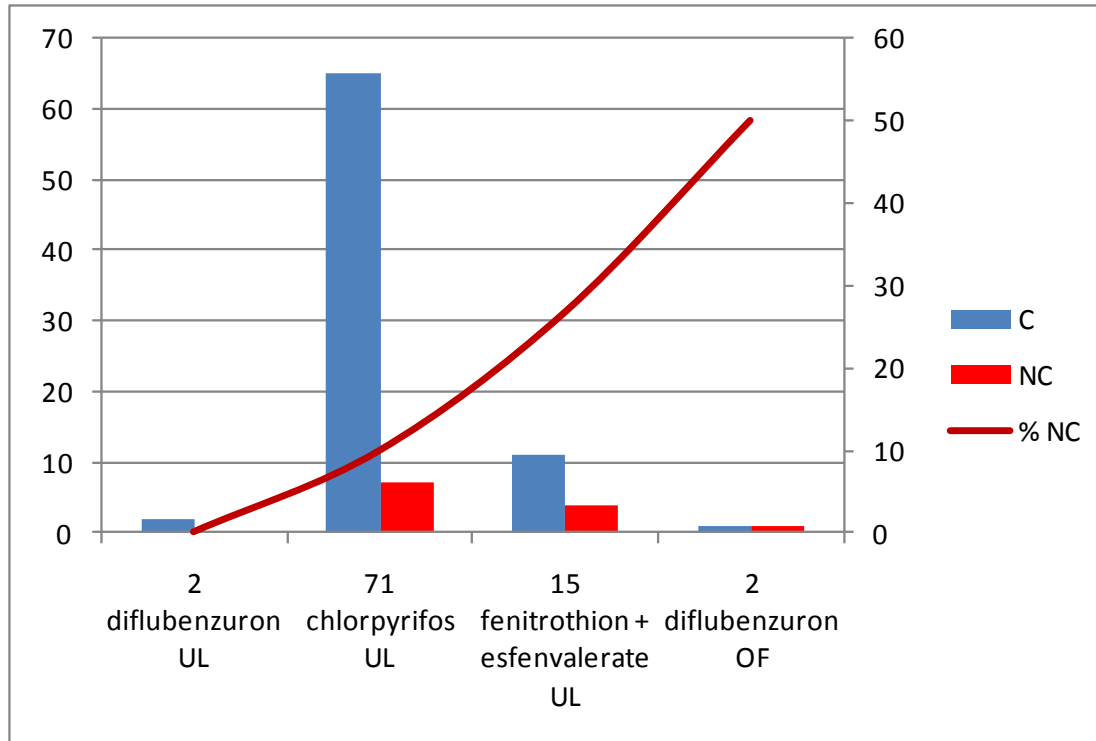
NC : Not Compliant with FAO specifications = 28 %
→ Have to be properly eliminated

Summary of results for 2009-2010 analysis

3 countries : Mali, Mauritania & Senegal
90 samples analyzed

Test items	According to FAO specifications		Percent of NC
71 chlorpyrifos UL	65 C	7 NC	10%
2 diflubenzuron OF	1 C	1 NC	50%
2 diflubenzuron UL	2 C	0 NC	0%
15 fenitrothion + esfenvalerate UL	11 C	4 NC	27%

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

