



Undesirable Compounds And Contaminants In Fats And Oils: Processing And Utilization

Florence LACOSTE

**ITERG, French Institute for Fats and Oils
PESSAC, France**

AOCS/IUPAC Workshop, 6-8 December 2004 - Tunis

- ⌘ **Origins of undesirable compounds**
- ⌘ **Methods and regulations**
- ⌘ **Refining efficiency**
- ⌘ **Surveillance plans**

Origins of Undesirable Compounds

Environment
contamination

Crop protection



Production process

Industrial utilisation

Transport, storage,
packaging

Environment Contamination

⌘ Metals

cadmium (ISO 15774)

lead (ISO 12193)

CE 466/2001

0,1 mg/kg

⌘ Polychloro-biphenyls

12 congeners with toxic effect (PCB)

CE 2375/2001

0,75 pgTEQ/g

⌘ Dioxins (7 PCDD, 10 PCDF)

90/642/CE
oilseeds & olive

⌘ Pesticide residues

Organochlorine residues

Organophosphorus residues

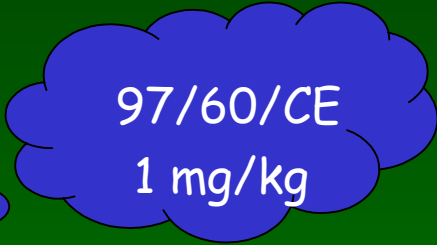
Pyrethroids,....

⌘ Hydrogenation catalysts

nickel (ISO 8294) chromium

⌘ Extraction solvent

hexane (ISO 9832)



97/60/CE
1 mg/kg

⌘ Degradation products

polycyclic aromatic hydrocarbons (ISO 15302)

trans fatty acids (ISO 15304)



EU regulation
in project

⌘ Transport & Storage, Packaging

mineral oil : n-alkanes (ISO/PWI 21034)

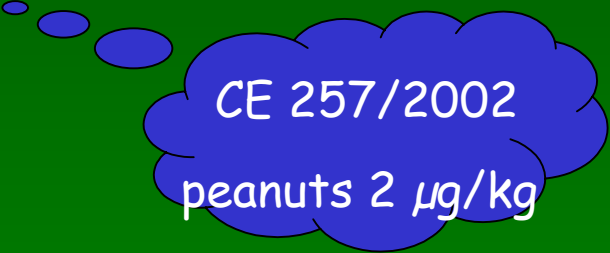
organic monomer : styrene

chlorinated solvents (ISO 1635)

mycotoxins : aflatoxin B1



CE 1989/2003
olive 0,2 mg/kg



CE 257/2002
peanuts 2 µg/kg

⌘ Industrial Utilisation

polar compounds (ISO 8420)

polymers of triglycerides (ISO 16931)

phytosterol oxidized



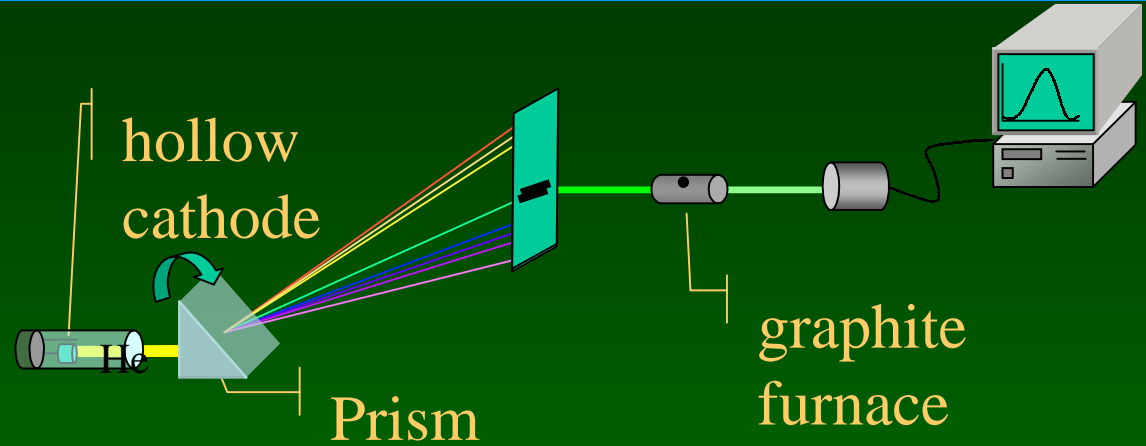
- ⌘ Origins of undesirable compounds
- ⌘ **Methods and regulations**
- ⌘ Refining efficiency
- ⌘ Surveillance plans

Metals : Cadmium, Lead, Nickel, Chromium

ISO 8294: Cu, Fe, Ni

ISO 15774: Cd

ISO 12193: Pb



➔ furnace atomic absorption

METALS	Cd	Pb	Ni	As	Cr
Determination limit (mg/kg)	0,002	0,010	0,015	0,010	0,005
Regulation limit (mg/kg)	-	0,1 EU&Codex	0,2 France	0,1 Codex	0,05 France

Solvent Analysis: Hexane, Halogenated Compounds

ISO 16035 : Volatile halogenated compounds

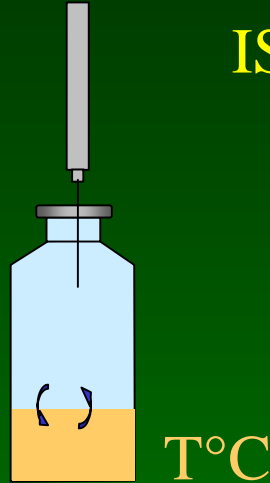
ISO 9832 : Hexane

Gaseous Phase

Équilibre



Liquid or
Solid Phase



GC/FID

Refined oil + 0,1 mg/kg



Revision of ISO 9832
to quantify 1 mg/kg (97/60/CE):

➤ Injected Volume : 2,4 ml

➤ Column Diameter : 0,53 mm

Mycotoxins: Analysis

Ochratoxin A

Extractions :

10 g of olive oil
MeOH/Water
(80:20)

LOD= 4,6 ng/kg

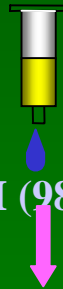


2 ml supernatant
+ 40 ml PBS

Purification :

Ochraprep column

water → event



2 ml MeOH/ CH₃COOH (98:2)

Analysis :

HPLC

Fluorescence detector

Aflatoxin B1

Extractions :

10 g of olive oil
MeOH/Water
(80:20)

LOD= 56 ng/kg



1 ml supernatant
+ 9 ml water

Purification :

Aflaprep column

2 ml ACN



Derivative:
+ CF₃COOH

Analysis :

HPLC

Fluorescence detector

Pesticide Residues: Analysis

Extractions :

200 mg of fat

ACN/CH₂Cl

(90:10 for OP)

(95:5 for OC & PYR)

Extract

Purification 1 :

Cartridge C18 (500 mg)

ACN/CH₂Cl₂ 95:5 for OC & PYR

MeOH for OP

OP

GC/NPD

hexane

Purification 2 :

Cartridge Florisil (500 mg)

hexane/CH₂Cl₂

75:25 for OC & PYR

OC +PYR

GC/ECD

EU MRLs on oilseeds and
fruits (olive) : 90/642/CE

Codex MRLs on :

- ✓ edible oil
- ✓ olive oil
- ✓ peanut oil
- ✓ cotton oil
- ✓ maize oil
- ✓ soya oil
- ✓ sunflower oil
- ✓ linseed oil



Pesticide Residues: Codex MRLs

Edible Oil Residue MRL (mg/kg)

vegetable	cypermethrine	0,5
soya	chlordan	0,02
	heptachlore	0,02
	profenofos	0,05
maize	methoprene	0,2
coton	aldicarbe	0,01
	cyhalothrine	0,02
	dicofol	0,5
	dimethipin	0,02
	fenvalerate	0,1
	flucythrinate	0,2
	glyphosate	0,05
	paraquat	0,05
	permerthrine	0,1

Edible Oil Residue MRL (mg/kg)

refined olive	dimethoate	0,05
virgin olive	fenthion	1
	methidathion	2
	parathion	2
peanut	aldicarbe	0,01
	phorate	0,05
	pyrimiphos-methyl	15
sunflower	dimethipin	0,02
	paraquat	0,05
	permethrine	1

ISO 15302 : Benzo[a]pyrene

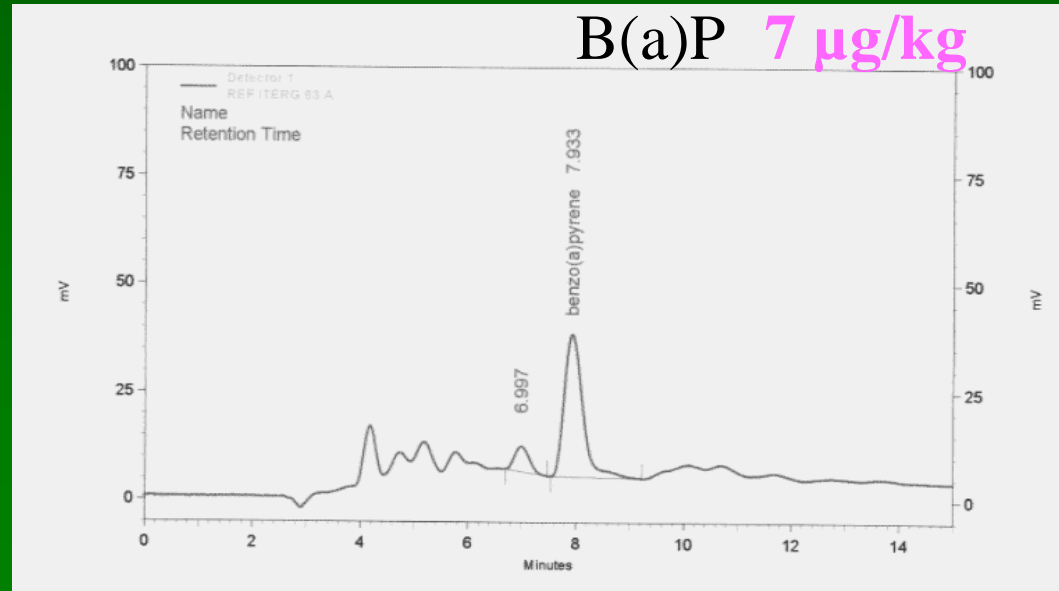
Fat
in solution
(0,4 g)

Alumina +
sodium sulfate



Evaporation &
THF addition

HPLC
Fluorescence Detection



PAHs: Recommendation

⌘ Fediol code of practice on PAHs in refined oils

total PAHs $\leq 25 \mu\text{g}/\text{kg}$ (10^{-9} g/g)
or heavy PAHs $\leq 5 \mu\text{g}/\text{kg}$

If B(a)P in crude oil $> 1 \mu\text{g}/\text{kg}$:

→ additional treatment necessary

⌘ Spain & Italy → regulation on pomace-olive oil

8 PAHs { B(a)P - B(e)P - B(a)A - B(b)F - B(k)F
DB(a,h)A - B(g,h,i)P - I(1,2,3,c-d)P

Each PAH $\leq 2 \mu\text{g}/\text{kg}$ - Sum of PAHs $\leq 5 \mu\text{g}/\text{kg}$

EPA Method 1613 : PCDDs & PCDFs

✓ **Spiking** with $^{37}\text{Cl}_4$ -2,3,7,8-TCDD (clean-up standard)

✓ **Clean-up on :**

- silica/acid silica gel (hexane)
- acid alumina (CH_2Cl_2 /hexane 20:80)
- Florisil (CH_2Cl_2)
- carbon (toluene)

✓ **HRGC/HRMS Analysis** (isotopic dilution with $^{13}\text{C}_{12}$ -PCDDs & $^{13}\text{C}_{12}$ -PCDFs solution)

Dioxins & PCBs: CE regulation

CE N° 2375/2001

Unity : pg (10-12 g) of PCCD and/or PCDF, expressed in toxic equivalent
(WHO reference) per g of fat

Animal fat

- from ruminants 3 ng WHO-PCDD/F-TEQ/kg
- from poultry 2 ng WHO-PCDD/F-TEQ/kg
- from pigs 1 ng WHO-PCDD/F-TEQ/kg
- mixed animal fat 2 ng WHO-PCDD/F-TEQ/kg

Vegetable oil 0,75 ng WHO-PCDD/F-TEQ/kg

Fish oil (human consumption) 2 ng WHO-PCDD/F-TEQ/kg



- ⌘ Origins of undesirable compounds
- ⌘ Methods and regulations
- ⌘ **Refining efficiency**
- ⌘ Surveillance plans



ITERG's Refining Pilot Plant

- Design by **CRYSTALLISATION & DEGUMMING** company
- Capacity of **300-1000 kg** per batch
- Degumming & neutralization reactor
- Bleaching & winterization reactor
- ALFA LAVAL centrifugal separator
- Automatic filter press
- High performance deodorizer (**2 x 450 kg**, up to **260 °C**)
- All stainless steel equipment

Description in INFORM, February 2004, Vol 15 (2), p. 128 -129

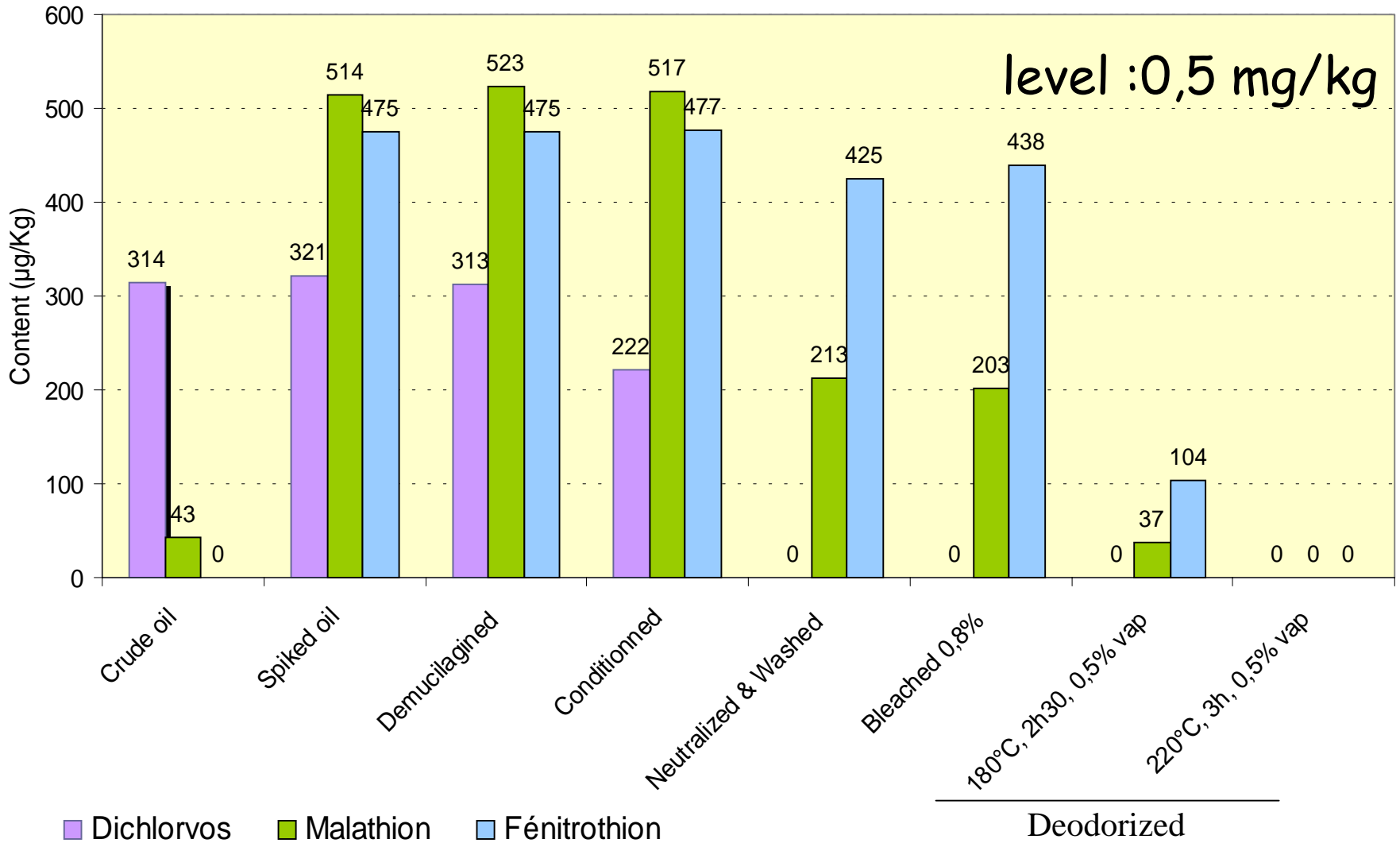


ITERG's Refining Pilot Plant





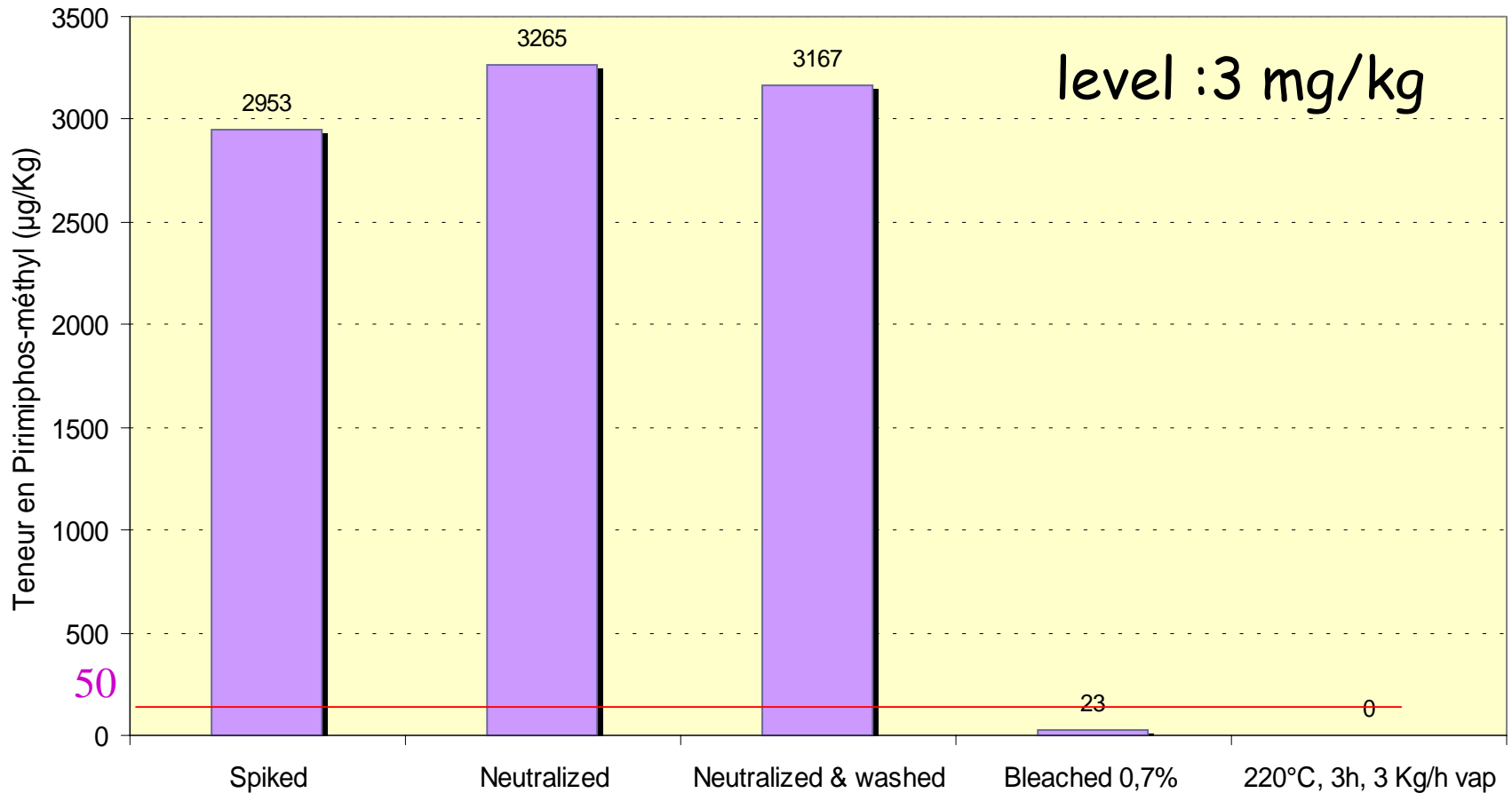
Pesticide Residue Content: Chemical Refining (1 ton)





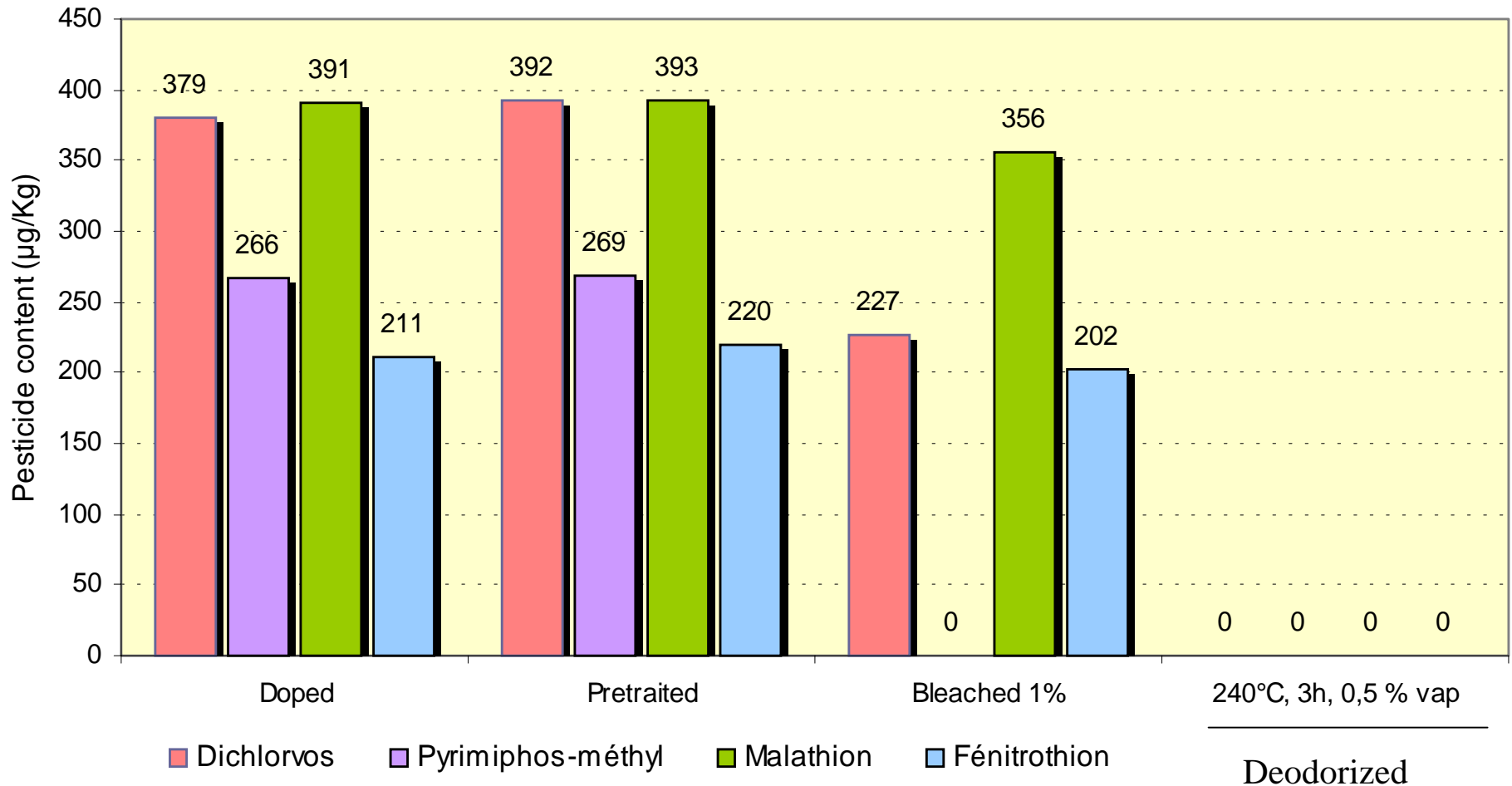
Pyrimiphos-Methyl Content: Chemical Refining (1 ton)

MRL (oleaginous seeds)
0.05 mg/kg (FR et UE)

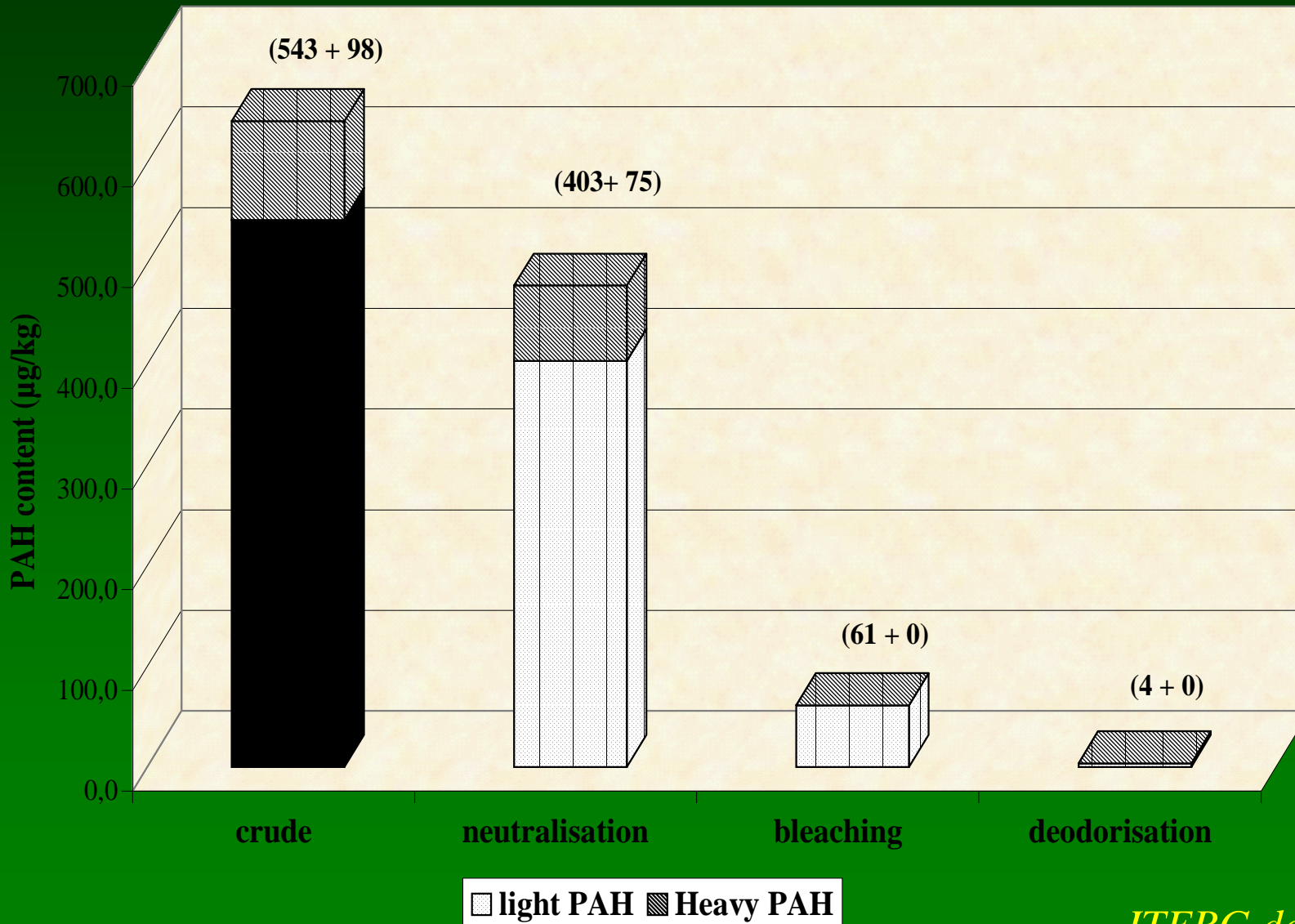




Pesticide Residue Content: Physical Refining (25 kg)



Elimination of PAHs from grapeseed oil during refining



Refining Efficiency : Lead

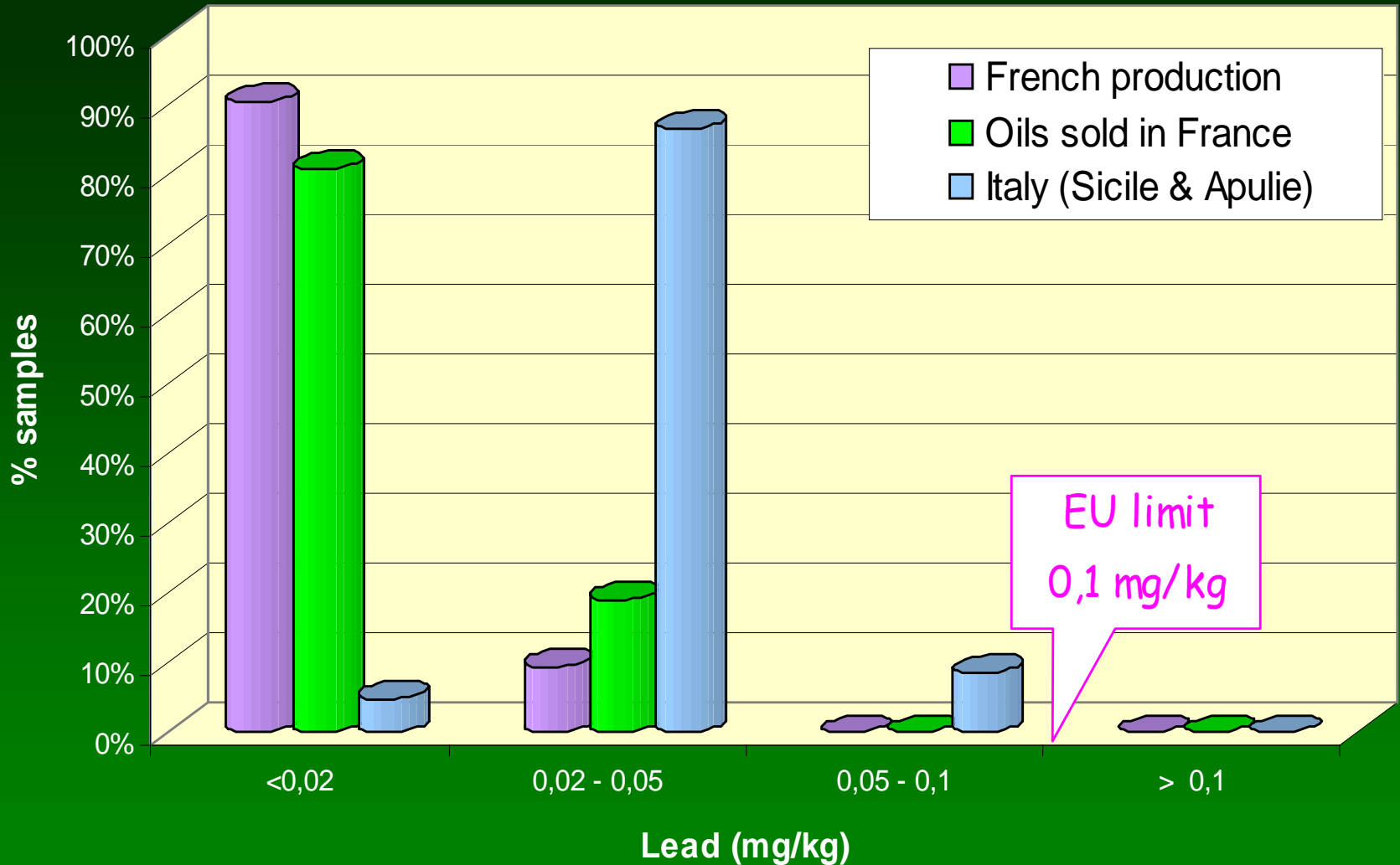
Lead (mg/kg)	Refined oils	Cold pressed oils	Animal fats
Nb samples	42	54	22
Pb ≤ 0,02	100 % samples	98 % samples	95 % samples
0,02 < Pb ≤ 0,10	-	1 sample	1 sample
Pb > 0,10	-	-	-

→ All results lower than Accepted Limit (0,1 mg/kg)

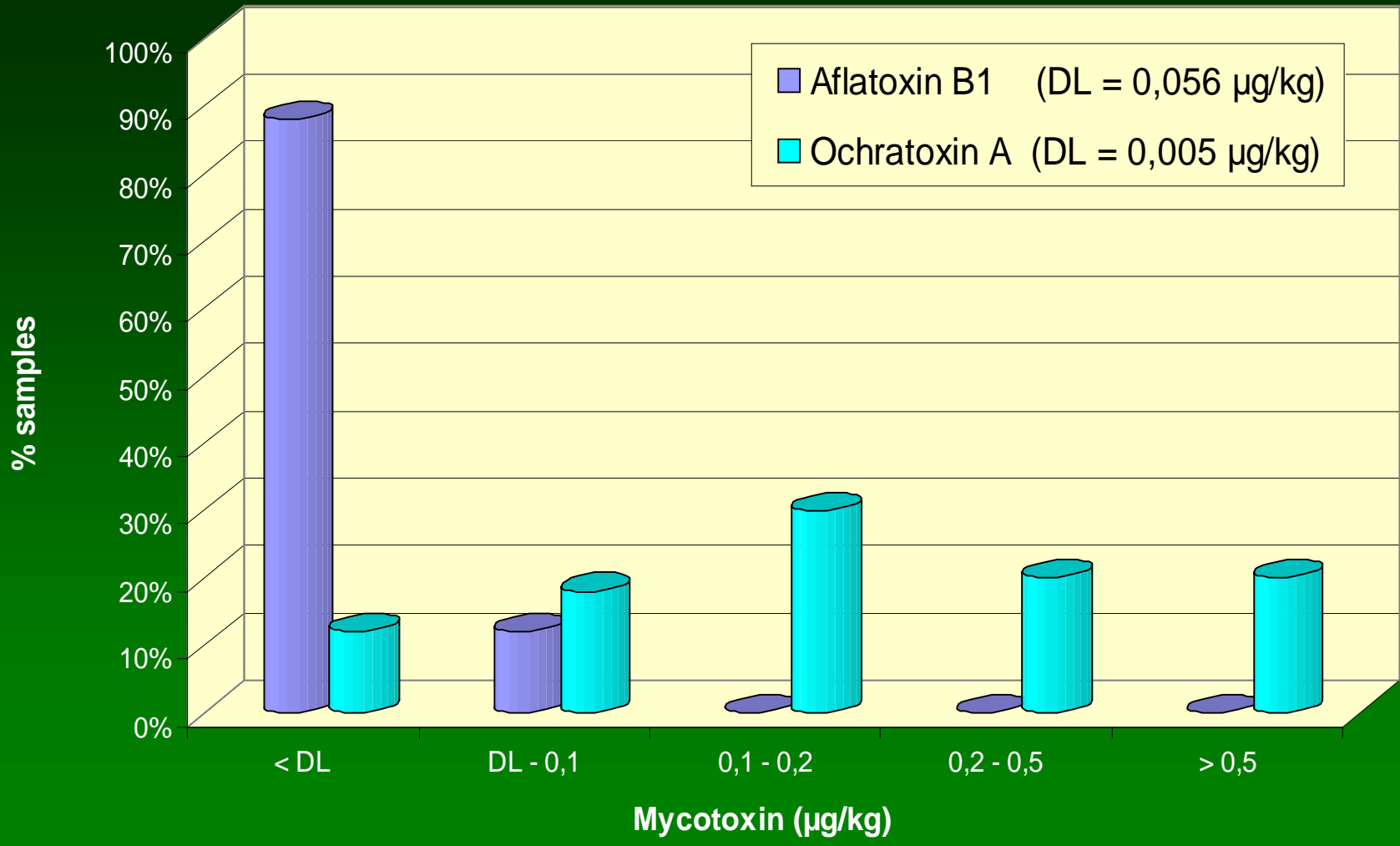


- ⌘ Origins of undesirable compounds
- ⌘ Methods and regulations
- ⌘ Refining efficiency
- ⌘ **Surveillance plans**

Virgin Olive Oils: Lead Levels

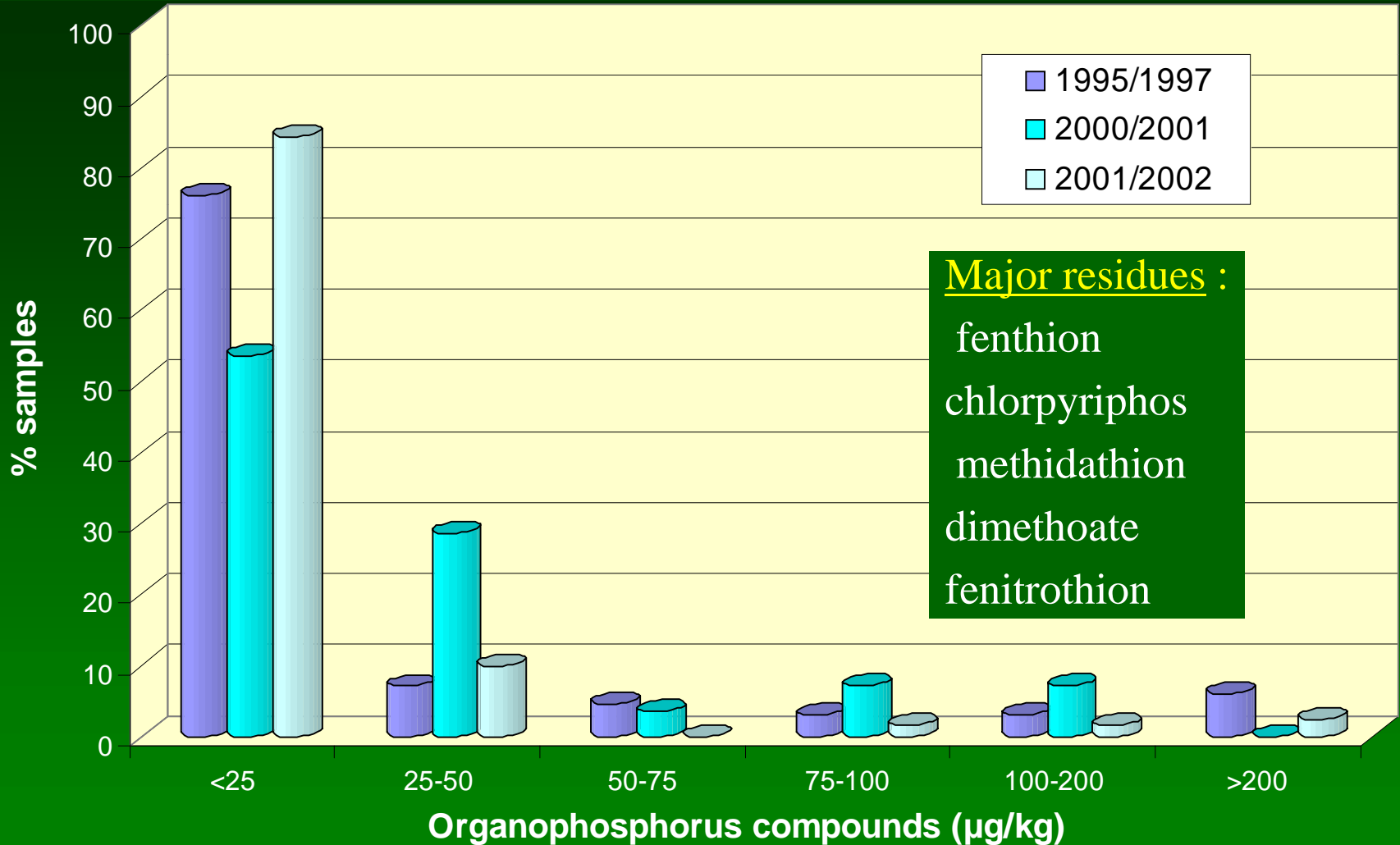


Virgin Olive Oils: Mycotoxin Levels





Virgin Olive Oils: Organophosphorus Compounds

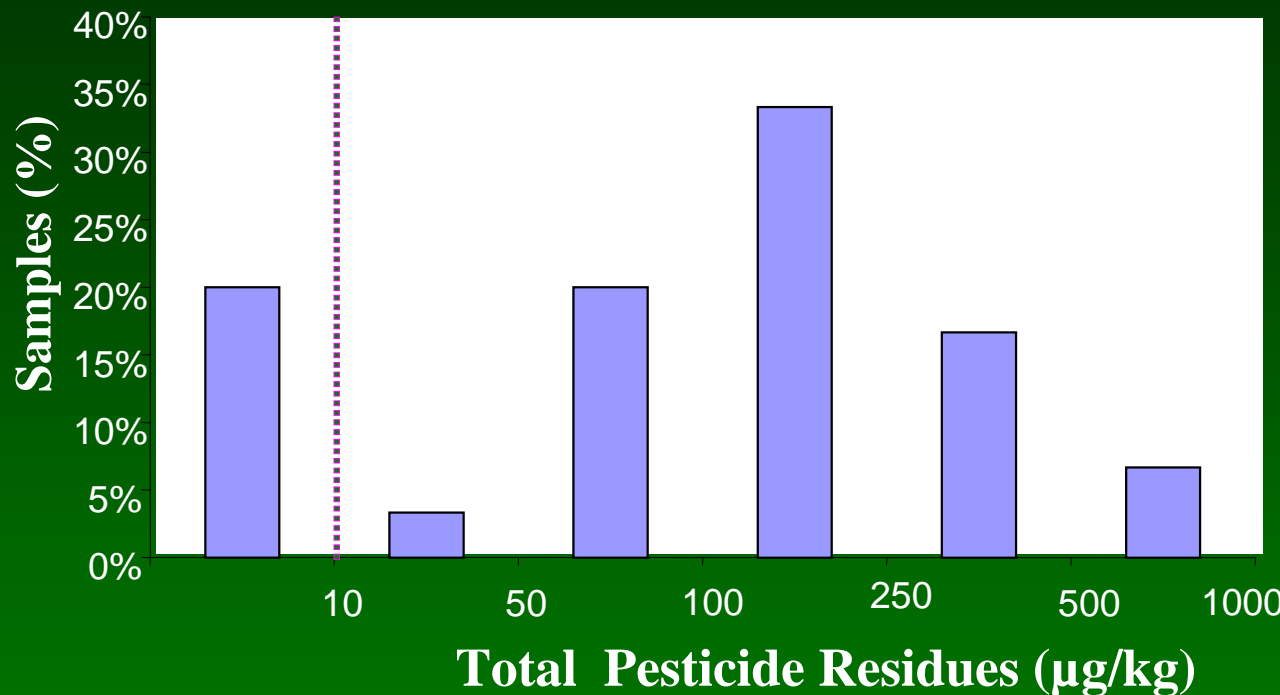


Major residues :

fenthion
chlorpyrifos
methidathion
dimethoate
fenitrothion

ITERG data (1995 to 2002)

Crude Oils (Sun, Rape): Total Pesticide Residues Levels

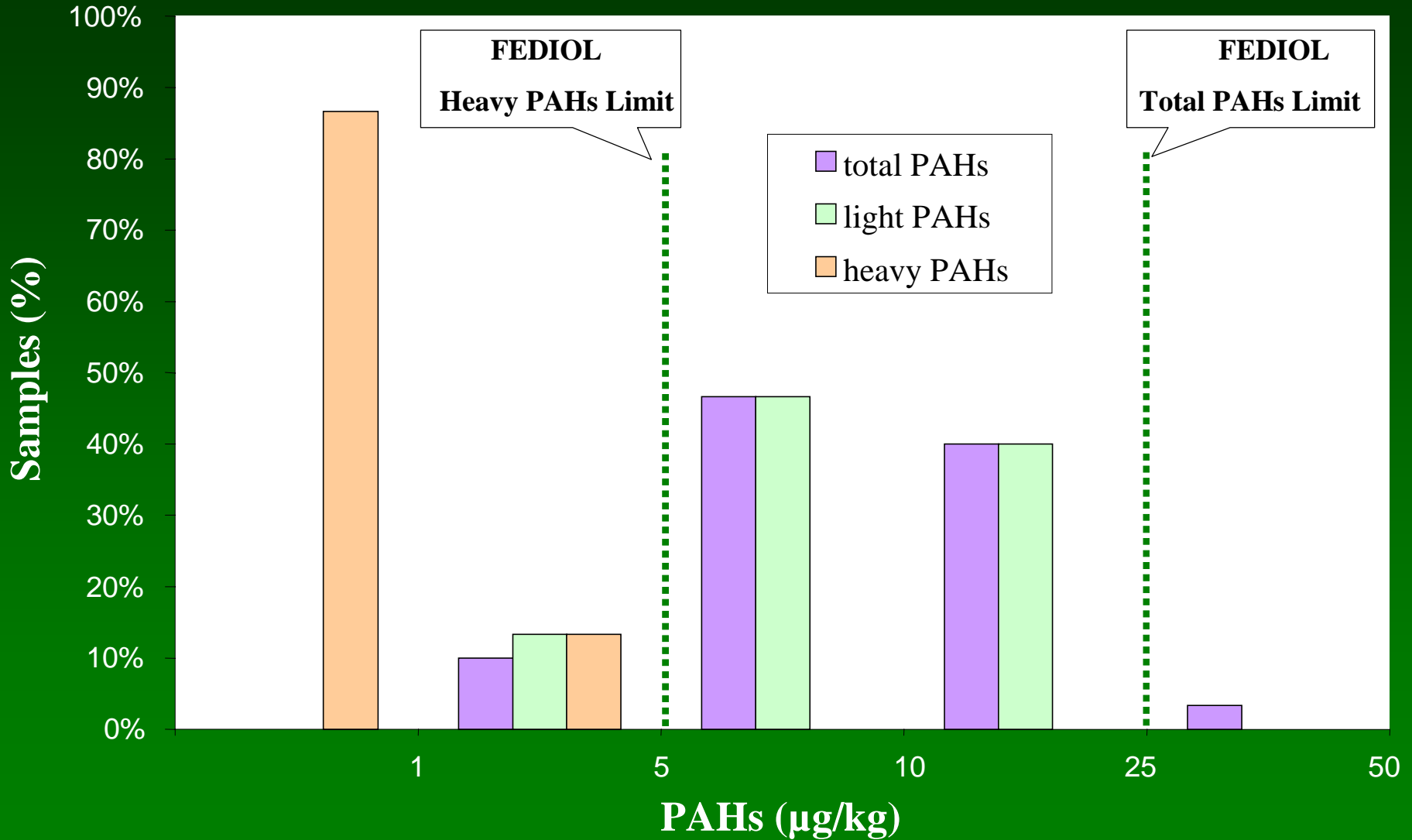


Residues	Max (µg/kg)	Frequency (%)
Pyrimiphos methyl	487	73 %
Malathion	680	67 %
Dichlorvos	106	33 %
Vinchlozolin	21	20 %
Deltaméthrin	46	13 %

30 samples (Iterg data, 2003)



Crude Oils (Sun, Rape): PAHs Levels



30 samples (Iterg data, 2003)



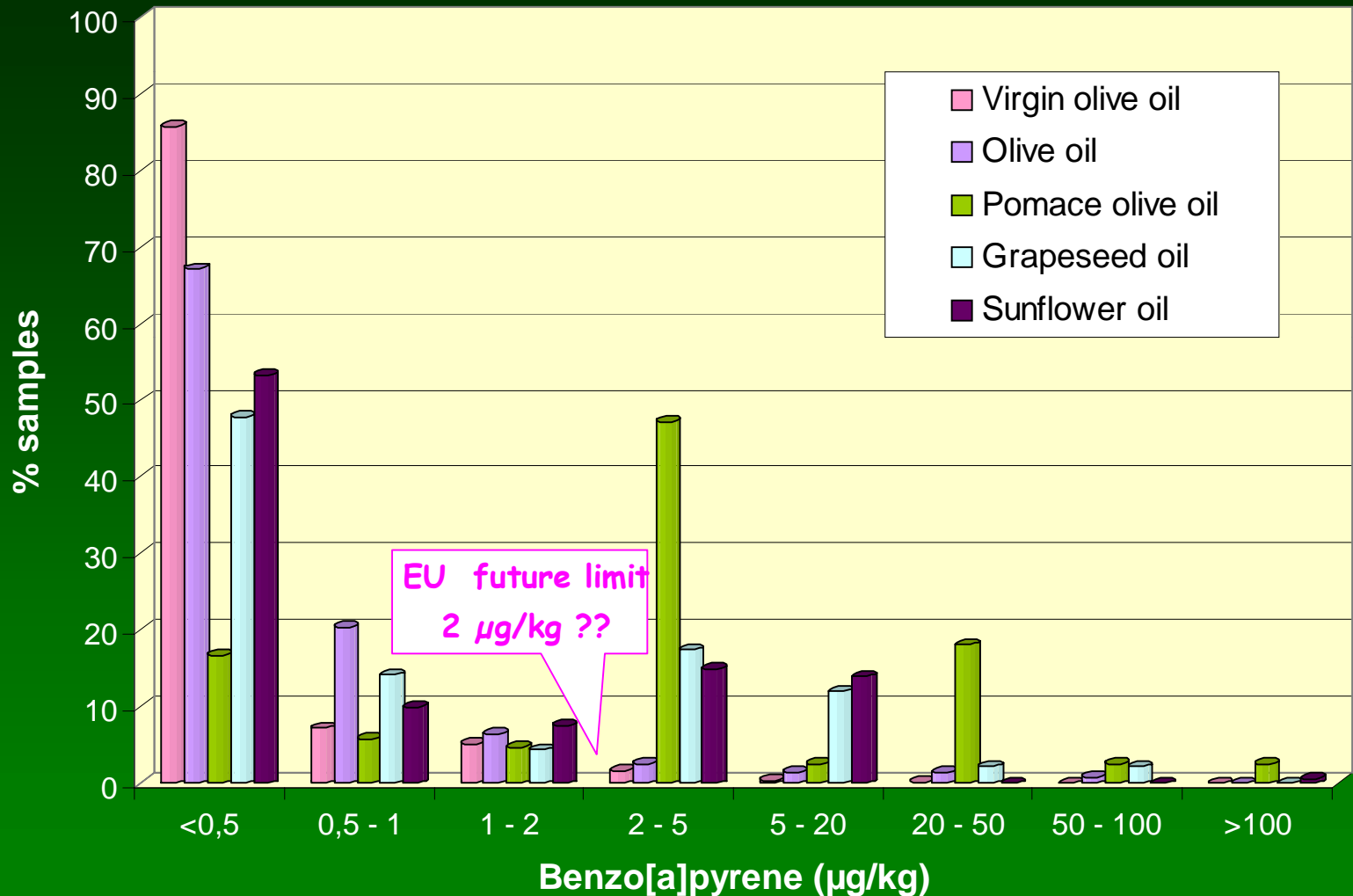
French Refined Vegetable Oils: PAHs Levels

Heavy PAH (µg/kg)	Sunflower	Rapeseed	Grapeseed	Coconut	All refined oils
Nb samples	12	7	12	5	42
Sum ≤ 5	83 % samples	100 % samples	67 % samples	3 samples	79 % of samples
Sum > 5	2 samples (5,2 – 33,6)	-	4 samples (9,3 - 14,8)	2 samples (5,3 – 19,2)	21 % of samples

→ 79 % of results lower than FEDIOL recommended value for heavy PAH (5 µg/kg)

42 samples (Iterg data, 2000)

European Vegetable Oils: Benzo[a]pyrene Levels



EU Scoop Task (Oct 2004)

European Vegetable Oils: Dioxins & PCBs Levels

Values (ng TEQ/kg)	France	Greece	Netherlands	CE 2375/2001
Type of oils	Vegetable	Olive	Vegetable	Vegetable
Dioxins	0,15 - 0,33	0,23 - 0,36	-	0,75
PCB-dioxins like	-	0,01 - 0,09	-	-
Dioxins + PCB	-	-	mean = 0,18	-

French DGCCRF (2004)

PAPADOPOULOS & col., Chemosphere (2004),57, 413-419

BAARS & col., Toxicology Letters (2004), 151, 51-61

- ✓ European and International regulations do exist for most of the undesirable compounds or contaminants that may be present in oils and fats
- ✓ For most of the undesirable compounds possibly found in oils and fats, standardised test methods do exist (or in progress)

- ✓ Oil-refining steps are efficient on contaminant elimination
- ✓ Oils and fats present low level of undesirable compounds // lead, cadmium, hexane, PAHs or pesticide residues
- ✓ Creation of survey plans warmly suggested for cold pressed oils on pesticide residues, benzo[a]pyrene, lead and ochratoxin A



Many thanks for your attention